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Magnetic and
Electrochemical
Studies
of some
Encapsulated
Metal Ions

A thesis submitted for the degree of
Doctor of Philosophy
of
The Australian National University
by
Lisandra Lorraine Martin, B.Sc.(Hons),
December, 1986
The material presented in this thesis is, to the author's knowledge, my original work, except where due reference is made in the text.

[Signature]
To my mother, for her support and encouragement,

and my father, for his enthusiasm, patience and his most precious asset, time.
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ABSTRACT

The encapsulation of transition metal ions by hexadentate ligands of the macrobicyclic type involving saturated nitrogen donor atoms is the topic of this thesis. The presence of the metals V, Cr, Mn, Fe, Co, Ni and Cu in the centre of the ligand cage, has enabled the electronic structures of these cage complexes to be probed and elucidated by techniques such as magnetism, NMR, visible and ultraviolet spectroscopy in both the solid and solution states.

Magnetic susceptibilities were measured over a wide range of temperatures for the finely powdered solids. The M(II) cages were all high-spin except for Fe(II), where both high-spin \(t^4_{2g} e^2\) and low-spin \(t^6_{2g}\) configurations were observed. The M(III) cages, where \(M = Fe + Ni\), were low-spin. Non-Curie law behaviour was observed for \([Mn \text{ sar}]^{3+}\), for which the moment at 300 K apparently confirmed a high-spin, \(S = 2\) ground state but fell sharply below 150 K to values expected for an \(S = 1\) ground state. Indeed, magnetization data at high magnetic field strengths confirmed that a low-spin, \(S = 1\) ground state was in fact present. The cage complexes of V(III) and Cr(III) were magnetically dilute and uncomplicated. The magnetic data for the transition metal cages were interpreted by considering the effect of structural perturbations (e.g. trigonal and tetragonal distortions) on an octahedral ligand field ground term.

In addition, comparisons with the congeneric \([M(en)]^{n+}\) and other hexaamine complexes have been made.

Magnetic measurements in solution were obtained using the Evans NMR method, and confirmed that the magnetic moments remained unchanged in solution compared with the solid state, with the exception of the Fe(II) cages. The magnetic behaviour of the Fe(II)
The Fe(II) cages in solution were studied over the temperature range 233 + 351 K, and can be described by a model involving nearly equienergetic $^1A_{1g}$ and $^5T_{2g}$ states in spin equilibrium. The Fe(II) cages appear to be the first examples of a spin equilibrium system with pseudo-octahedral Fe(II) coordinated by saturated amine donor atoms. The presence of observable d-d bands in the electronic spectrum of these complexes provided an unusual opportunity to investigate the spin equilibrium by optical spectroscopy. Both the magnetic and optical data conform to the equilibrium model from which the relevant thermodynamic parameters were obtained.

The $^1H$ NMR of the Fe(II) cages were characterized by large isotropic paramagnetic shifts which were strongly dependent on temperature. The temperature dependence of the shifts also conformed to the spin equilibrium model, with thermodynamic parameters of a similar magnitude obtained. $^1H$ NMR studies were also performed with the contact shifted Ni(II) cages, in order to assist in the assignment of proton resonances for the Fe(II) cages.

Preliminary electrochemical studies have been used to ascertain the accessible oxidation states and to provide an indication as to the degree of reversibility and/or stability of a complex in a number of oxidation states. Measurements were performed in aqueous and non-aqueous media in order to assess the effect of solvation and/or solvent participation in the redox processes. Most complexes displayed reversible or near reversible M(II)/(III) redox processes. A correlation between the redox potential and $d^n$ electronic configuration was observed for the M(II)/(III) couples for the encapsulated metal ions, Cr + Cu. The vanadium cages, isolated in their IV oxidation state, are stabilized by deprotonation of two donor amine atoms, and show complex pH dependent equilibria which is
reflected in the observed redox properties.

The stabilization of labile transition metal ions by encapsulation within a cage, makes them ideal candidates for electron self-exchange studies. Furthermore, the cage complexes are nearly spherical with similar charges as required by the Marcus-Hush theories. Preliminary studies of self-exchange rate constants for some cage complexes by an electrochemical technique are briefly discussed.
ABBREVIATIONS

The abbreviations used in this thesis are those used commonly in the literature. Thus, acac = acetylacetone, py = pyridine, 1,4,7-triazacyclononane = tacn or [9]aneN₃, 1,2-bis(1,4,7-triaza-1-cyclononyl)ethane = dtne, dimethylformamide = DMF, dimethyl sulfoxide = DMSO, tetraethylammonium perchlorate = TEAP, tetramethylammonium trifluoromethanesulphonate = TMAT, for example. The usual abbreviations of alkyl functional groups are employed (e.g. Me = methyl and Et = ethyl). The ligands most commonly studied are referred to by an abbreviation of the trivial nomenclature that is defined in Chapter One.

Some symbols are employed for more than one parameter, although within a particular chapter a symbol will represent one parameter only.
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CHAPTER ONE

INTRODUCTION TO ENCAPSULATED COMPLEXES
1.1 GENERAL INTRODUCTION

During the past two decades considerable efforts have been made to design sexadentate macrocyclic ligands which bind strongly a variety of metal cations. Much of this activity arose from the investigation of macrocyclic polyethers\(^1\) (e.g. dibenzo[18]crown-6 \([1]\)) which are now referred to as "crown" ethers. The congeneric macrobicyclic polyethers (e.g. cryptand-[2.2.2] \([2]\)) were discovered subsequently and termed "cryptands".\(^2\) Both classes of compound were found to have a remarkable affinity for alkali and alkaline earth metal ions and to show cation selective characteristics.\(^3\)

The more recent interest in molecules of this type arose from observations with biological systems, where chelating ligands are involved in highly specific pathways. The extraordinary specificity of these ligands towards particular metals is of considerable interest and two such classes of molecules are described below.

Naturally occurring molecules called "ionophores" have been shown to exhibit a high degree of specificity and selectivity towards alkali metal ions, especially \(K^+\).\(^4\) The mode of action of these molecules, e.g. nonactin \([3]\), is to transport alkali metal ions through the lipid membranes of cells. A similar class of molecules, the "siderophores" provide a high affinity transport system for iron assimilation in aerobic organisms, e.g. enterochelin \([4]\).\(^5\) The cryptands and the macrocyclic polyethers have shown potential as model systems for "ionophore" molecules,\(^3\) and numerous synthetic analogues of the siderophores have been made in recent times.\(^3,6\)

The encapsulation of transition metal ions within a cage-like environment by such oxygen-based macrobicyclic ligands has been achieved unambiguously in only a few cases.\(^7\) However, incorporation
of nitrogen or sulphur rather than oxygen donor atoms within the ligand framework facilitates the uptake of transition metals and a number of compounds have been reported which extends significantly the field of cryptand chemistry.\(^8\)

The preparation of large ring systems like the cryptands poses a substantial synthetic challenge because the entropy effect for ring closure is unfavourable. In the case of polyether cryptands intermolecular interactions (competing with intramolecular ring closure) were minimized by carrying out the synthesis at high dilution.\(^9\) The preparation of nitrogen analogues of the macrocyclic polyethers offers an alternative strategy because the high affinity of nitrogen for many transition metal ions enables the latter to function as a "template". In other words the organic chemistry is performed about the metal centre so that the construction of the large ring can be reduced to several consecutive small ring syntheses. Thus uncoordinated nucleophiles on ligands bound to the metal ion can capture electrophilic reagents and construct the cage about the ion thereby avoiding the problem of large inhibiting entropy effects.

1.2 CLATHROCHELATES

The design\(^10\) and synthesis\(^11\) of the first examples of hexaaza macrobicycles, involved the use of a template reaction between tris-dimethyl glyoximato cobalt(III) and boron trifluoride etherate. The resulting capped complex \([\text{Co(DMG)}_3(\text{BF}_3)_2]\text{BF}_4\) \(^5\), can be reduced to the Co(II) derivative without loss of integrity of the complex. Similar reactions occur with other Lewis acids in place of BF\(_3\), for example SiCl\(_4\) and SnCl\(_4\).\(^12\)

Five capped Fe(II) complexes with the formula \([\text{Fe(DMG)}_3(\text{BOR})_2]\),
Scheme 1

Condensation reactions of formaldehyde, resulting in dioxacyclam rings.
where \( R = H, \text{CH}_3, \text{C}_2\text{H}_5, \text{i-C}_3\text{H}_7 \) and \( \text{n-C}_4\text{H}_9 \), as well as the original complex \([\text{Fe(DMG)}_3(\text{BF})_2]\) have also been prepared.\(^{13}\) Attempts to isolate the Fe(III) derivatives by either starting with \( \text{Fe}^{3+} \) salts or via oxidation of the Fe(II) clathrochelate were unsuccessful.

Holm \textit{et al.}\(^{14}\) extended the range of transition metals used as templates to prepare clathrochelates containing \( M = \text{Fe, Co, Ni, Zn,} \) [6]. These complexes are based on pyridyl-2-aldimine ligands anchored by a phosphorus atom at one apical site and then capped on the opposite trigonal face with \( \text{BF}_3\)-etherate.

The quadricyclic clathrochelate [7], synthesized about the iron(II) template proved extremely stable in acidic conditions.\(^{15}\) Both Co(II) and Ni(II) analogues have also been prepared by a similar route.

A further development in the field of clathrochelates is the "strapped" or "lacunar" complexes of Busch \textit{et al.}\(^{16}\) which contain a very small cavity around one of the metal ion axial condensation sites, [8]. Lacunar complexes of Fe(II), Co(II) and Ni(II) have been reported.

1.3 SEPULCHRATE AND SARCOPHAGINE

The work described in this thesis addresses a prominent subclass of sexadentate ligands of the macropolycyclic type involving saturated nitrogen atom donors. In particular, the two cage molecules known as sepulchrate [9] and sarcophagine [10] were first constructed by Sargeson \textit{et al.}\(^{17-19}\) by using cobalt(III) ion as a template to hold the reacting organic fragments. The possibility of achieving the synthesis of such ligands emerged from earlier observations that a variety of imines when coordinated to a cobalt(III) ion not only displayed an extraordinary stability towards
Crystal structures of [Co(III)sepulchrate]Cl, and [Co(II)sepulchrate]ZnCl, salts.
hydrolysis but were also reactive towards nucleophiles. Thus the cobalt complexes [11] and [12] could be isolated as chloride salts from concentrated HCl solutions whereas the parent imines are exceptionally sensitive to acidic conditions. On the other hand, the bound imine is readily attacked by nucleophiles such as CN⁻ and carbanions implying that it has some iminium character when coordinated to cobalt.¹⁸

Initially, the construction of ring systems utilizing both the kinetic inertness of the Co(III)-N bond and the iminium ion character was achieved by condensing formaldehyde in basic conditions with bis(1,2-diaminoethane) cobalt(III) ions to give dioxacyclam ring systems of the type shown in Scheme 1.

To quote Sargeson's words:¹⁸

"Therefore, it was a fairly short jump to the notion that the same reaction could be used to cap tris(ethane-1,2-diamine) complexes [13] along the C₃ axis of the ion, bearing in mind the symmetry and mode of synthesis of hexamethene tetramine [14]. Clearly, the trigonal symmetry about each N atom is just that required to fit on the trigonal axis of the tris(ethane-1,2-diamine) metal complex, [M(en)₃]⁺. In fact, mixing Co(en)₃³⁺ ion, NH₃ and CH₂O in aqueous solution, maintained basic with Li₂CO₃, led to the encapsulated metal ion, [15], which, in keeping with the style and humour of the cage nomenclature, we have called cobalt(III) sepulchrate, an octaaza cryptate."

1.4 SYNTHESIS OF COBALT(III) CAGES

The synthetic strategy described above depends on controlling iminium ion chemistry by using a Co³⁺ ion in place of a proton to activate an imine to nucleophilic attack. The successive steps believed to occur during the synthesis of the [CoIIIsepulchrate]³⁺ ion are detailed in Scheme 2. Formaldehyde condenses with a bound amine to give the coordinated carbinolamine which is followed by loss
Scheme 2
Mechanistic scheme for the synthesis of [Co(sep)]^{3+}.

Scheme 3
Mechanistic scheme for the synthesis of [Co(NO_2)_2sar]^{3+}.
of H₂O. The resultant imine undergoes nucleophilic attack by NH₃ to
give the gem diamine. The first six-membered ring is formed by the
addition of a second molecule of CH₂O, loss of H₂O and imine
formation which then allowed intramolecular condensation of the gem
diamine with the imine. The cap is completed by the formation of
another imine followed by intramolecular condensation with the
secondary amine.

The Co³⁺ ion becomes completely encapsulated by the same process
taking place on the opposite octahedral face of the initial
[Co(en)₃]³⁺ complex to yield the octaazacryptate,
[(1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane cobalt(III)]³⁺,
i.e., cobalt sepulchrate abbreviated as [Co sep]³⁺. It is apparent
from structure [9] that apart from the six nitrogen atoms there are
two aza caps which are not bound to the Co³⁺ ion.

A similar procedure using nitromethane in place of ammonia
yields in basic conditions an analogous complex with quaternary
carbon atoms in the form of nitro caps in the apical positions
[10]. The details of the proposed synthetic route are given in
Scheme 3. The complex has been named di-nitro-sarcophagine and is
abbreviated here as [Co(NO₂)₂sar]³⁺.²⁰

If the reaction is quenched at the appropriate times,
intermediate species can be isolated some of which have been
characterized crystallographically including substantial amounts of
the monocapped ions [16] and [17].²¹ This implies that one nitro cap
forms faster than the other as postulated in Scheme 3.

It emerges from these observations that any octahedral face
comprising three primary amine groups should be susceptible to being
capped provided the amine protons exchange relatively rapidly in the
basic conditions employed and the appropriate functional group can be
Products isolated from cage synthesis.

Scheme 4
Capping reaction on the [Co sen]^{3+} complex.
Scheme 5
Reactions yielding various substituents at the apical carbon site.
Scheme 6
Possible route to form larger cages.
oriented properly for the cyclizations. Thus, complexes of the "sen" ligand [18] can be capped either with NH$_3$ and CH$_2$O to yield [19] (methyl sep), or nitromethane and CH$_2$O to yield the nitromethyl cage [20] with C apices (Scheme 4).$^{21}$

Simple organic chemistry can be performed at the C apex to vary the substituents. Reduction of the NO$_2$ group with Zn dust gives the aminomethyl sar. Nitrosation in aqueous solution gives both the hydroxy and the chloro (chloromethylsar) derivatives in the presence of chloride ion. The chloro in turn can be substituted with a proton by catalytic hydrogenation to give the parent (methylsar) ion (Scheme 5). Similarly, reduction of the dinitro-derivative yields the diamino analogue which in turn can be converted to the dichloro cage and finally the parent cage [Co sar]$^{3+}$. Other substituents in the apical position which have been reported include -NHOH, -NO, -N(CH$_3$)$_3$+, -Br, -I, -COOH, -COOR, -NHC=OCH$_3$, -CN, -CONH$_2$, -CH$_2$OH.$^{22,23}$

In principle, it should be possible to enlarge the size of the cavity by changing the ligand from 1,2-diaminoethane to 1,3-diaminopropane. Unfortunately, attempts to cap the [Co(III)tris(1,3-diaminopropane)]$^3+$ ion, [Co(tn)$_3$]$^{3+}$, (Scheme 6) have not yet been successful.$^{24}$ The difficulty in achieving the desired product, is believed to arise from the more rapid ligand loss of the [Co(tn)$_3$]$^{3+}$ ion in the basic aqueous conditions and less favourable imine orientations for the intramolecular cyclization reactions. Some success has been achieved using [Rh(tn)$_3$]$^{3+}$ as the precursor complex when the reaction is carried out in non-aqueous media.$^{25}$ Here the larger Rh(III) ion orients the components for cyclization effectively and loses ligands less readily than the Co(III) ion.

Other polyamine complexes of cobalt(III) such as [Co(1,2-diaminocyclohexane)$_3$]$^{3+}$ $^{26}$ and [Co(1,2-diaminopropane)$_3$]$^{3+}$ $^{27}$
Scheme 7

Reactivity of the zinc-alkyl cage.
have been employed using similar synthetic strategies to form a variety of diastereoisomeric cages. In these compounds the cavity size can be modulated depending upon whether the diaminoethane moieties are oblique, "ob", or parallel, "lel", to the $C_3$ axis of the cage complex.

1.5 A ZINC-ALKYL CAGED COBALT(III) DERIVATIVE

Zinc-alkyl complexes are normally very reactive and many are pyrophoric and decompose rapidly in water or acidic solution. However, it has been found that during the dehalogenation of $[\text{Co(Cl)}_2 \text{sar}]^{3+}$ or $[\text{Co(CH}_3\text{)}_\text{Cl(sar)}]^{3+}$ with Zn dust in water, a stable product is formed involving Zn-alkyl bonds of extraordinary stability.\textsuperscript{28} The molecule is even stable in 6M HCl at 25°C. An X-ray crystal structure of one of these by-products reveals that a ZnCl\textsubscript{3} group is bound to the apical C-atom of the cap [21]. It has been suggested that the unusual stability arises from the electron-withdrawing effect of the Co(III) cage which would stabilize the Zn-C bond towards protonation and hence rupture. In addition, the three chlorine atoms attached to zinc may help to stabilize the Zn-C bond although the zinc atom is not especially hindered towards attack by a proton. The chemical reactions to the organozinc moiety are largely carbanion-like and electrophiles like Br\textsubscript{2} and I\textsubscript{2} attack the Zn-C bond to give the halo-substituted cage. Prolonged heating in either acid or base eliminates the zinc with protonation of the apical C-atom to give the sar or methylsar complex. In the presence of Na EDTA, the rate of Zn-C cleavage is significantly faster yielding $[\text{Co sar}]^{3+}$ and an olefin product (Scheme 7).

The unusual stability of the zinc-alkyl cobalt(III) derivative suggests that it may be possible to isolate relatively stable
Scheme 8
Products from the UV-photolysis of [Co(CH₃)(COOH)sar]³⁺.
analogous Mg and Cd alkyl complexes and even perhaps those of Al, Ti, Cu, Co and Ni.

1.6 COUPLING OF COBALT CAGES

The availability of a range of organic substituents at the trigonal caps (cf. Section 1.4) raises the possibility of coupling a cage to other species, for example, to other metal ions or complexes, large alkyl groups, polymer surfaces or other cages. Thus cages have been attached to polymer beads to make chiral ion exchange columns and several dimer cages have been synthesized with 1,4-diaminomethylphenyl, azo, azoxy, urea and amide linkages. The successful synthesis of dimer cages is important because it opens up the prospect of studying the electronic interaction between two encapsulated metal ions via the substituents in the apical positions.

The synthesis of these coupled cages is not a trivial exercise. One obvious route is to couple two cage radicals to form the desired dimer. The radicals can be generated photochemically by ultra-violet excitation of the ligand-to-metal charge transfer band which leads to the reduction of Co(III) to Co(II) and generation of the ligand radical. The usual decomposition of the Co(II) complex which follows this process is avoided if the metal is encapsulated and dimerization of two radicals might be expected to occur. Ultra-violet irradiation of \([\text{Co}^{III}(\text{CH}_3)(\text{COOH})\text{sar}]^{3+}\), however, yields largely \([\text{Co}^{III}(\text{CH}_3)\text{sar}]^{3+}\), together with some ring opening of the cage to give an olefin complex as shown in Scheme 8. It would appear that the carboxy-ligand radical is formed which eliminated CO$_2$ as expected. Donation of an electron from the Co(II) centre to the apical C-atom to form the carbanion, followed by capture of H$^+$ gave \([\text{Co}^{III}(\text{CH}_3)\text{sar}]^{3+}\) plus the olefin complex.
Scheme 9

Products of the UV-photolysis of the [Co(CH₃)sar(COO)Co(NH₃)₅]⁵⁺ ion.
An alternative route was devised to circumvent this decay path. The strategy was to include a second Co(III) centre attached to the carboxyl group which would be reduced preferentially. The \([\text{Co(NH}_3\text{)}_5]^{3+}\) cation was selected in the expectation that it would reduce (approx. 0 V) before the cage (approx. -0.4 V). The products isolated from the UV-photolysis of the \([\text{Co(CH}_3\text{)}\text{srar(COO)Co(NH}_3\text{)}_5]^5+\) ion (Scheme 9) revealed that this expectation was only partly successful. Only about 10-12% of the photolysis occurred by initial reduction of the \([\text{Co(NH}_3\text{)}_5]^{3+}\) moiety to yield the Co(III) cage carboxy radical which then eliminated \(\text{CO}_2\) and dimerized to give the desired head-to-head dimer. The remainder of the photolysis occurred by the initial reduction of the Co(III) cage to give \([\text{Co(CH}_3\text{)}\text{srar}]^{3+}\), the olefin complex and \([\text{Co(NH}_3\text{)}_5(\text{H}_2\text{O})]^3+\).

Detailed studies of electronic interactions between two metal ions in the coupled cages are proceeding. Both Co(III) centres appear to be reduced at the same electrochemical potential and the visible spectrum of the intermediate Co(III)/Co(II) species appears to be the mean of those of the Co(III)/Co(III) and the Co(II)/Co(II) dimers. The electron transfer rates between the dimers is not much different from the monomers. Rotatory dispersion curves provide a more sensitive probe for electronic communication between the metal ions and interestingly, these are not additive. However, to date there has been little evidence of strong coupling or intervalence behaviour from the dimers.

1.7 NITROGEN-SULPHUR LIGAND CAGES

An extension of the reaction methods outlined in Section 1.4 gives rise to a variety of new cobalt cages based either on nitrogen or a mixture of nitrogen and sulphur ligands. For example, the
Scheme 10
Synthesis and encapsulation reactions of [Co ten]³⁺.
cobalt(III) complex \([\text{Co sen}^3+]^{18}\) (cf. Scheme 4) was encapsulated by condensing formaldehyde in the presence of different nucleophiles to give access to the cages \([\text{Co(CH}_3\text{)}\text{sep}^3+]^{19}\) and \([\text{Co(CH}_3\text{)(NO}_2\text{)sar}^3+]^{20}\).

Mixed nitrogen-sulphur cages can likewise be constructed\(^{32}\) via the potentially hexadentate ligand \(4,4',4''\text{-ethylidynetris(3-thiabutan-1-amine)}\) [22], abbreviated as "ten". This was synthesized by the reaction between ethylenimine and 1,1,1-tris(mercaptomethyl)ethane whereby nucleophilic attack by sulphur on the three-membered imine ring followed by ring opening provides a facile high-yield route to the desired 2-thiaethan-1-amine linkage (Scheme 10). A mixture of the resulting hexadentate ligand "ten", with cobalt(II) acetate, when oxidized by oxygen in methanol, yields \([\text{Co ten}^3+]^{23}\).

Encapsulation of the Co(III) ion can be effected by condensing \([\text{Co ten}^3+]^{24}\) with CH\(_2\)O and NH\(_3\) to yield \([\text{Co(aza)capten}^3+]^{24}\) [24]. If nitromethane and CH\(_2\)O are employed, the analogous capping reaction results in the nitromethyl-capped complex \([\text{Co(NO}_2\text{)capten}^3+]^{25}\) [25]. The NO\(_2\) group can be reduced by Zn and HCl to yield, after reaction with O\(_2\), the protonated amino-capped complex \([\text{Co(NH}_3\text{)capten}^4+]^{26}\) [26].

An aqueous solution of the red chiral \([\text{Co(aza)capten}^3+]^{27}\) ion can be reduced with zinc amalgam under a nitrogen atmosphere to produce an extremely oxygen sensitive purple solution of the chiral cobalt(II) complex \([\text{Co(aza)capten}^2+]^{27}\) [27]. Reaction of this purple solution with oxygen yields the red cobalt(III) complex with retention of chirality. As found with the hexaamine derivatives, the stability of the \([\text{Co(aza)capten}^2+]^{28}\) complex to racemization is extraordinary and it is believed that tight packing of the ligand about the Co\(^{2+}\) ion precludes dissociation.\(^{32}\)
[Co taetacn]$^{3+}$

[Co(aza)sartacn]$^{3+}$

[Co(NO$_2$)sartacn]$^{3+}$

[Co(NH$_3$)sartacn]$^{4+}$
Scheme 11

Synthetic method for the preparation of the ligand "taetacn".
Scheme 12
Mechanism for the synthesis of [Co(aza)sartacn]$^{3+}$
1.8 MACROTRICYCLIC HEXAAMINE CAGES

The synthetic strategy of constructing a trimethylaminetriyl cap on the trigonal facial arrangement of the primary amine groups of each of the coordinated diaminoethane ligands in the precursor complex, is generally applicable for building caps on similar facial arrangements of coordinated primary amines in other metal complexes, provided their stereochemistry is not prohibitive. The synthesis, by analogous routes, of some novel macrotricyclic (hexaamine) cobalt(III) cage complexes derived from the \((1,4,7\text{-tris(2-aminoethyl)}1,4,7\text{-triazaacyclononane})\) cobalt(III) ion, \([\text{Co taetacn}]^{3+}\) [28] has been achieved.\(^{33}\) These include \([\text{Co(NO}_2\text{sartacn}]^{3+}\) [29], \([\text{Co(NH}_3\text{sartacn}]^{4+}\) [30], and \([\text{Co(aza)sartacn}]^{3+}\) [31]. The hexadentate ligand "taetacn" was synthesized by reductive alkylation of \(1,4,7\text{-triazaacyclononane} (\text{tacn})\) with phthalimidoacetaldehyde in the presence of \(\text{NaBH}_3\text{CN}\) followed by acid hydrolysis of the recovered product to remove the protecting phthaloyl groups (Scheme 11). The \([\text{Co taetacn}]^{3+}\) complex [28] was prepared by aerial oxidation of \(\text{Co}^{2+}\) ion in the presence of activated charcoal and stoichiometric amounts of \(\text{H}^+\) and crude "taetacn" in water. This treatment yields the macrotricyclic cryptates following condensation with \(\text{CH}_2\text{O}\) and either nitromethane or ammonia, as depicted in Scheme 12.

1.9 CAGE REARRANGEMENTS

Under certain conditions the macropolycyclic cages can rearrange with a concomitant change in the volume of the cavity in which the cobalt ion is accommodated. One interesting example is the cobalt(III) absar cage \([32]^{20}\) which arises from a rearrangement of a carbocation intermediate during the diazotisation of \([\text{Co(NH}_2\text{)}_2\text{sar}]^{3+}\)
Scheme 13

Reaction scheme for the rearrangement to the absar cage.
Scheme 14
Formation of \([\text{Co(CH}_3\text{(OH)absar)}^{3+}]\) from \([\text{Co(CH}_3\text{(NO}_2\text{)sar)}^{3+}]\).
with NO\(^+\) in aqueous solution (Scheme 13). The migration of the CH\(_2\) group to an exocyclic location means that the cap is now much tighter and the cage should be less able to tolerate a larger central metal ion such as Co\(^{2+}\). Not surprisingly evidence for an increase in the ligand field strength is found in the electronic spectra of the [Co(Cl)absar]\(^{3+}\) and [Co(Cl)(CH\(_3\))absar]\(^{3+}\) (\(\lambda_{\text{max}} = 458\) nm) compared with the analogous [Co(Cl)\(^{2}\)sar]\(^{3+}\) complex (\(\lambda_{\text{max}} = 474\) nm). Similarly, the redox potential of the [Co(Cl)absar]\(^{3+}\) and [Co(Cl)(CH\(_3\))absar]\(^{3+}\) are more negative by \(-0.23\) V consistent with the Co\(^{2+}\) ion being less readily accommodated in the rearranged cage.

It has been pointed out\(^{34}\) that the "absar" rearrangement (Scheme 13) is surprising since it runs counter to expectation in relation to the bridgehead organic chemistry. For example, if the rearrangement followed that observed in analogous adamantyl bridgehead chemistry, it should take place in the reverse direction, i.e.

```
       +
       /       /  \\
      N-1-3---N-1-3---N
```

It has been postulated that one reason for the observed phenomenon could be the strong repulsion between the charges when the carbocation is generated at the bridgehead close to the Co\(^{3+}\) ion. This interaction is obviously reduced by the rearrangement.

When [Co(CH\(_3\))(NO\(_2\))sar]\(^{3+}\) is treated with base, a similar rearrangement is observed to yield [Co(CH\(_3\))(OH)absar]\(^{3+}\) (Scheme 14). Firstly, a retro-aldol reaction occurs to break the cage. Then, after loss of the imine in basic conditions, a Nef reaction gives the ketone at pH \(\approx 4\). Finally, under basic conditions again, the ketone condenses with the deprotonated primary amine coordinated to the Co(III) centre to give the methylhydroxy absar complex,
Scheme 15
Reactions arising from capping [Co tame$_2$]$^{3+}$.

Figure 1.1
Cobalt(III) hexaamine complexes and their absorption maxima from the $^1T_{1g} \leftrightarrow ^1A_{1g}$ transition.
[Co(CH$_3$)(OH)absar]$^{3+}$. The tightening of the cavity size within the rearranged cage is once more reflected in the ligand field spectra ($\lambda_{\text{max}} = 458 \text{ nm vs.} 472 \text{ nm}$ for the [Co(CH$_3$)(OH)sar]$^{3+}$) and a redox potential more negative by $-0.25 \text{ V}$.

The above rearrangements imply that if the volume of the cavity is increased, larger cations and consequently lower oxidation states will be stabilized. This objective, although straightforward, is not easy to achieve experimentally (cf. Section 1.4). For example, attempts have been made to cap the [Co$^{III}$bis(1,1,1-tris(aminomethyl)ethane]$^{3+}$ ion, [Co(tame)$_2$]$^{3+}$ with CH$_2$O and nitromethane (Scheme 15) but the reaction does not occur as planned.$^{35}$ One of the faces is capped readily and the other commences on the right path but after the imino-methylene moiety is generated, an adjacent deprotonated amine attacks the imine carbon to give an extremely strained four-membered ring. This is followed by another condensation and cyclization of the same type. The net result is a very distorted cryptand which has been expanded by introducing six-membered rings on one side of the ligand and contracted with four-membered rings on the other. Not surprisingly, these factors are reflected in the variation of ligand field spectra within a series of hexaamine cobalt(III) complexes (Figure 1.1).

1.10 PROPERTIES OF COBALT(II) CAGES

Encapsulation of the cobalt(II) ion within the macropolycyclic hexadentate ligand confers unusual stability and novel properties upon the complex. In particular, the [Co sep]$^{2+}$ exhibits no exchange with $^{60}$Co$^{2+}$(aq) after 24 hours at $25^\circ$C.$^{17,18}$ This is in marked contrast to the microsecond timescale usually observed for ligand exchange rates for monodentate ligands bound to Co(II). Likewise,
the chiral [Co sep]$^{2+}$ ion showed no loss of optical activity over two
hours and was quantitatively reoxidized by peroxide to Co(III)
reducing $O_2^{2-}$ to $H_2O$. Chemistry of this type is most unusual for
cobalt amine systems which racemize rapidly and are reoxidized to
form peroxy dimers.

This kinetic inertness of the chiral species enables electron
transfer studies to be carried out by mixing the chiral form of one
oxidation state with the catoptric form of the other. For example,
in Equation 1,

\[
\Delta-[Co \text{ sep}]^{2+} + \Delta-[Co \text{ sep}]^{3+} + \Delta-[Co \text{ sep}]^{3+} + \Delta-[Co \text{ sep}]^{2+} \ldots \tag{1}
\]

the electron self-exchange rate constant, $k$, is approx. $10^5$-fold
faster$^{17,20,21}$ than that for the [Co(en)$_3$]$^{3+/2+}$ analogue, even though
the electronic configurations of the pairs of complexes are very
similar, as gauged from their ligand field spectra, magnetic
properties, and bond lengths.$^{17,20,21,36}$ The dramatic difference in
rate constant has been attributed to ligand strain effects not
present in the [Co(en)$_3$]$^{3+/2+}$ ions. This shows up in observed
distortions of bond angles and torsion angles$^{20,21}$ and in the
molecular mechanics calculations.$^{20}$ The cavity volume appears a
little too small for the Co(II) ion and a little too large for the
Co(III) ion. The strain generated in the ligand in both oxidation
states aids the stretching of the Co(III)-N bonds and compression of
the Co(II)-N bonds to achieve the transition state even though the
strain effect does not appear in the ground state metal-ligand bond
lengths.$^{17,37}$

1.11 ELECTRON TRANSFER STUDIES

The potential value of the cobalt complexes as electron transfer
agents was one of the early realizations of the cage studies. The series of apically substituted sarcophagine molecules which include the substituents $-\text{NO}_2$, $-\text{NHOH}$, $-\text{NO}$, $-\text{NH}_2$, $-\text{NH}_3^+$, $-\text{N(CH}_3)_2^+$, $-\text{OH}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{NHCOCH}_3$, $-\text{CN}$, $-\text{CONH}_2$, $-\text{CH}_2\text{OH}$ span a range of redox potentials of at least 600 mV, i.e., ten orders of magnitude in equilibrium constant and five orders of magnitude in redox reaction rate for the Co(II)/Co(III) cage systems.\textsuperscript{23} These results confirm that electronic communication between the apical substituents and the metal centre is present, a feature also observed in the NMR chemical shifts of the apical carbon atom.\textsuperscript{20} However, the ligand field spectra are apparently insensitive to variation of apical substituents.\textsuperscript{38}

A study of electron transfer reactions between pairs of cobalt caged ions\textsuperscript{36} has shown that electron transfer rates conform well to the Marcus-Hush theoretical model.\textsuperscript{36} This good agreement between theory and experiment can be attributed to the spherical nature of the ions, together with their chemically innocent interactions required by the model. In addition, the unusual inertness of the cages to ligand dissociation in both Co(II) and Co(III) oxidation states, provides for maintenance of the integrity of the components during an electron-transfer reaction.

One significant application of their redox properties occurs in the exploitation of solar energy, where the cobalt(III) cage complexes are utilized as electron-transfer agents (ETA) in the Ru(2,2'-bipyridine)$_3^{2+}$, Pt catalyst, ethylenediaminetetraacetic acid, mediated photoreduction of water. The cage complexes were found to be as efficient as methylviologen for the production of hydrogen, but they exhibited turnover numbers at least two orders of magnitude greater.\textsuperscript{40-42}
A recent advance in the search for photo-receptive molecules has included the synthesis of a cobalt(III) cage complex attached to an anthracene molecule at the apical site of the cage [33]. Coupling of the photosensitizer (anthracene) to the electron transfer agent (cobalt cage) was hoped to provide more efficient photochemical hydrogen production. However, although the intramolecular electron transfer was efficient the reverse process was also very fast and the hydrogen production decreased overall.\textsuperscript{43a}

Perhaps the major advantage of the cage complexes as electron transfer agents is their long-term stability in the photochemical cycles involved in the photoreduction of water compared to that of the electron transfer agent viologen.\textsuperscript{40-43} The desirable properties of cobalt cage complexes for use as electron transfer agents are summarized as follows:\textsuperscript{43a}

(i) very high stability in the Co(III) and Co(II) oxidation states,
(ii) Photochemical inertness to solar radiation in both oxidation states,
(iii) ready control of redox potential of the Co(III)/Co(II) couple by varying apical ligand substituents,
(iv) ready control of the rate of electron self-exchange of the Co(III)/Co(II) couple by alteration of the structure of the cage ligand.
(v) ability to control the charge of the complexes by the introduction of charged substituents, and
(vi) ability to alter steric factors.
1.12 OTHER CAGES SYNTHESIZED BY METAL TEMPLATE REACTIONS

From the preceding discussion, it is clear that any substitutionally inert metal ion should be able to function as a template to also achieve encapsulation. Therefore, in an analogous manner to that described in Section 1.4, \([M \text{ sep}]^{n+}\) and \([M \text{ sar}]^{m+}\) (M = Rh(III), Ir(III) and Pt(IV)) cages have been prepared from their \([M(\text{en})_3]^{n+}\) precursors. Attempts to synthesize Cu\(^{2+}\), Ni\(^{2+}\) and Cr\(^{3+}\) derivatives by the same capping strategy were unsuccessful. The preference of nickel(II) and copper(II) ions for the square planar configuration appears to be the salient reason preventing their encapsulation by the condensation chemistry (described in Section 1.4). However, instability of the imine 'cap precursor' prevents ready formation of the Cr\(^{3+}\) homologue. In the case of the chromium(III) cage, as soon as the imine is formed, rupture of the Cr-N bond is enhanced and in aqueous conditions this bond will not readily reform. A claim has been made for the synthesis of \([\text{Cr sep}]^{3+}\) but is is based upon only one infrared frequency and no analytical data were presented. However, \([\text{Ni sep}]^{2+}\) has been isolated as a very minor reaction product (<1% yield) and structurally characterized.

In the case of \([\text{Ru(en)}_3]^{3+}\) and \([\text{Os(en)}_3]^{3+}\), after the imines are formed on the diaminoethane moiety, the complexes disproportionate spontaneously in the basic conditions into the M(II) and M(IV) species. Of these products, the M(II) complex resists addition of a nucleophile and the M(IV) complex exhibits facile oxidation of the methylene group, originating from the diaminoethane unit, to produce Ru(II) imines.
Table 1.1

Periodic Table; with metal ions encapsulated by the ligand sar shown in bold.
1.13 SYNTHESIS OF LABILE METAL CAGES

The so-called "inert" transition metal ions, Co(III), Rh(III), Ir(III) and Pt(IV), were obvious choices for the encapsulation process to form ligands like sarcophagine and sepulchrate. It provided a more difficult synthetic challenge to effect similar encapsulation of labile transition metal ions (cf. Section 1.12).

The problem of preparation of cages with labile transition metal ions was circumvented by extruding the Co(II) ion from the cage to obtain the free ligand. This was achieved by treatment of the cobalt(II) cage with either refluxing HBr to remove the metal as CoBr$_4^{2-}$ or with cyanide anions to form the Co(CN)$_6^{3-}$ species, thus allowing isolation of the free cage in good yields.$^{47}$ Other workers have used HCl sealed in a Carius tube, also with success.$^{48}$ Once isolation of the free ligand was achieved, the range of metal ions that could be encapsulated was greatly extended. Those fully characterized complexes of sar and/or the cogeneric di-amino type complexes are shown in bold type in Table 1.1.

1.14 STRUCTURAL ASPECTS OF THE CAGE COMPLEXES

X-ray crystal structures have been determined for a series of transition metal cages.$^{49}$ The series allows an analysis of the competition between preferred metal stereochemistry and the demands of the ligand, in determining the overall geometry. The trigonal twist angles about the C$_3$ axis, $\phi$, are graphically represented together with the number of d-electrons for the metal ions in Figure 1.2; $\phi = 0^\circ$ corresponds to a trigonal prism (TP) and $\phi = 60^\circ$ to a trigonal anti-prism (TAP or Octahedron).$^{50}$ The complexes fall into two groups. The first group are characterized by $\phi = 28^\circ$, and structures similar to that of the metal-free ligand are observed.
Figure 1.2

Trigonal twist angle, $\phi$, as a function of d electron configuration for the metal cages.
All these examples have small ligand field stabilization energies (LFSE) and the ligand appears to be dictating the structures. The second group lie more towards the trigonal anti-prismatic structure in the order Ni(II) < Cr(III) < Fe(III) < Co(III). For these cage complexes the ligand field contribution is greater than the first group and the metal is directing the overall structure.

The \([\text{Co sep}]^2+\) is an exception to the classification described above. For this complex, a "flattening" at the angles around the N cap provides relief for strain about the metal centre. Cobalt(II) cages with a C atom in the same cap position are unable to relieve the strain in this manner and substantial trigonal twists are observed about the metal centres. \(^5^0\)

The Zn(II), Cd(II) and Hg(II) triad, having no LFSE exhibits trigonal twist angles similar to the diprotonated ligand. Although, the larger metal ions exhibit an increasing trend towards the trigonal prism.

1.15 THESIS OVERVIEW

This thesis describes an extension of the studies summarized in Sections 1.1 - 1.14. The program of work has been focused on the synthesis and properties of encapsulated transition metal ions. At the outset it was anticipated that some of the unusual properties observed for the prototype cobalt cages would also be observed for the other transition metals. In particular, it was hoped that complexes which are normally labile would become kinetically inert, perhaps with stable chiral forms. Since the metal cages are mononuclear, those areas of transition metal chemistry where polymerization frequently occurs can be avoided. Stabilization of unusual mononuclear oxidation states was a possibility, unfettered by
the hydrolysis problems which frequently plague the chemistry of aquated transition metal complexes. Clearly, encapsulated transition metal ions offer an unusual opportunity to study the properties of an analogous series of complexes in the same coordination environment and to compare and contrast their behaviour with congeneric $\text{M(NH}_3\text{)}^n_6^{n^+}$ and $\text{M(en)}_3^{n^+}$ complexes.

The overall synthetic strategy included the objective of isolating cages in a variety of oxidation states to widen the range of electronic configurations available for spectroscopic and magnetic studies. Such a series of transition metal complexes should be magnetically dilute and measurements of paramagnetic susceptibility over a wide range of temperature were intended to provide detailed information on electronic configuration and those parameters describing the ligand field. The magnetic moments were also measured by the Evans NMR method to determine whether the electron configuration of the complex remained unchanged in solution.

An electrochemical study was undertaken in order to determine the redox nature of the metal complexes and other parameters of thermodynamic significance; e.g. correlations between the energy of the redox orbital and the number of $d$ electrons present and chemical and electrochemical reversibility. Such a study could perhaps lead to electrochemical synthesis at controlled potentials as an alternative route to prepare some of the metal ion cages.

Several workers have discussed redox reactions in relation to the Marcus-Hush theories for outer-sphere electron transfer. The cage complexes, because of their inert nature and near spherical shape have proved especially well-suited for testing the electron-transfer theories. Self-exchange and cross-reaction rates which have been measured for the cobalt cages correlate well and conform to the
Marcus-Hush model. Electrochemical methods were explored as a possible alternative technique for following the rapid electron transfer rates anticipated for some of the other transition metal cages.

In brief, an exploration of the variation in properties of the metal ion cages with the change in electronic structure of the metal ions was undertaken. Also, the variation in properties of the cage complexes with changes in oxidation state needed examination. This thesis describes and analyses some of the effects pertaining to the magnetic properties, electronic spectra and spin states of cage complexes of the first row transition metal ions. In addition, the redox and electrochemical behaviour of these systems were examined.
CHAPTER TWO

SOLID STATE MAGNETISM
2.1 INTRODUCTION

The success achieved in encapsulating a variety of transition metals in cages of the sepulchrate and sarcophagine types, raises the question as to whether encapsulation affects the electronic structure and properties of the resulting complexes. The oxidation state and d-electron configuration of the central ion together with the dimensions and conformation of the cage would all be expected to exert an influence.

One powerful technique for studying the structure and bonding of these cage complexes in the polycrystalline state is measurement of magnetic susceptibility.\(^{52}\)

A wealth of documented examples\(^{53}\) illustrate the application of magnetic measurements to probe the electronic structures of newly synthesized complexes of transition metal ions. However, most of these measurements have been confined to room temperature studies or to a limited temperature range.

In order to maximize the information obtained from the present magnetic susceptibility measurements, it is necessary (i) to extend the temperature range from room to liquid helium temperatures for powder studies, and (ii) to use single crystal anisotropy measurements, which are extremely sensitive to geometric distortions. Ideally, integration of both methods provides the most accurate description of electronic and stereochemical structure. However, single crystal measurements require specialized equipment and knowledge and were beyond the scope of this investigation.

The measurement of powder magnetic susceptibility, \(\chi\), can provide information on spin state, magnetic exchange, spin
equilibria, stereochemistry, and can provide an insight into the
details of splitting patterns evident only at low temperatures.

In the present study, the magnetic behaviour of cage complexes
with 3d\textsuperscript{n} (n = 1-10) configurations, was determined between 4.2-300 K
using the Faraday method. These cages provided a range of metal ions
in various oxidation states, encapsulated within a ligand framework,
which should provide a magnetically dilute environment.

Analysis and interpretation of the magnetic data in this thesis
has utilized a qualitative approach based on ligand field theory and
angular overlap model (AOM) when appropriate. Theoretical aspects of
these models are described elsewhere.\textsuperscript{54-57} No attempt has been made
to rigorously determine ligand field parameters but "order of
magnitude" values are obtained where possible. The present data are
compared with the magnetic properties of unencapsulated hexaamine
complexes reported in the literature.

A parallel EPR study, performed by P. Comba\textsuperscript{58} and X-ray
structural studies performed by A.H. White \textit{et al.}, for M(II) and
M(IV) cages and by M.R. Snow \textit{et al.}, for M(III) cages also provided
valuable structural information and are considered where relevant.\textsuperscript{49}

Prior Magnetic Studies With Cages

Early examples of cage complexes centred around inert metal ions
especially cobalt(III) (\textit{cf.} Chapter One). As anticipated for both
sepulchrate and sarcophagine ligands the cobalt(III) ion is low-spin
and diamagnetic. However, the room temperature magnetic moment
measured for [Co\textsuperscript{II} sep]\textsuperscript{2+} was high-spin ($\mu_{\text{eff}} = 4.72$ B.M.),
indicating that the ligand field strength, 10 Dq was similar to the
tris(1,2-diaminoethane) complex.\textsuperscript{17} Second and third row cage
complexes of rhodium, iridium and platinum with a 4d\textsuperscript{6} and 5d\textsuperscript{6}
configuration were low-spin and diamagnetic as anticipated.\textsuperscript{44}
2.2 THEORETICAL CONSIDERATIONS

The theoretical foundations of magnetochemistry are detailed in most standard textbooks on the subject, and will only be briefly discussed.

When a substance is placed in a homogeneous magnetic field, $H$, the magnetic induction, $B$, is expressed by Equation 2,

$$B = H + 4\pi I$$

...(2)

where $I$ is the intensity of magnetization due to the substance itself becoming magnetized. The measured quantity in these measurements is the volume susceptibility, $\kappa$, which is related to $I$ by Equation 3,

$$\kappa = \frac{I}{H}$$

...(3)

However, it is usual to measure the mass rather than the volume susceptibility. The susceptibility per gram, $\chi_g$, is defined by Equation 4,

$$\chi_g = \frac{\kappa}{\rho}$$

...(4)

where $\rho$ is the density of the substance. Similarly, the molar susceptibility, $\chi_M$, is defined by Equation 5,

$$\chi_M = \chi_g \cdot MW$$

...(5)

where $MW$ is the molecular weight of the substance.

Magnetically dilute paramagnetic substances exhibit positive intensities of magnetization which are directly proportional to the applied magnetic field, $H$. Thus, for these simple substances, the susceptibility per gram is itself independent of the field, however, it varies inversely with temperature.
This behaviour is understood assuming that each atom or molecule acts like a magnetic dipole. These dipoles, when placed in a magnetic field can align, or be 'space-quantized' so that they assume one of a limited number of orientations relative to the field. This alignment is reflected in the effective magnetic moment, $\mu_{\text{eff}}$, (Equation 6) where,

$$\mu_{\text{eff}} = \left( \frac{3k}{N\beta^2} \right)^{1/2} \left( \chi_M T \right)^{1/2}$$

$$= 2.828 (\chi_M T)^{1/2}$$

This expression arises from Langevin's theory of paramagnetism, and Curie's law and describes the temperature dependence of a magnetically dilute paramagnet. The 'spin-only' expression for the magnetic moment can be calculated from Equation 7,

$$\mu_{\text{SO}} = \left[ 4S(S+1) \right]^{1/2} = \left[ n(n+2) \right]^{1/2}$$

where $S$ is the total spin angular momentum of $n$ unpaired electrons.

The tendency of the dipoles to orient with the magnetic field is counteracted by the randomizing effects produced by the thermal energy, $kT$. Paramagnets, that exhibit no interaction between dipoles are called 'magnetically dilute'. Experimentally, the randomization effect caused by the thermal energy is reflected in a decrease in susceptibility with increasing temperature, known as the Curie Law, and represented by Equation 8,

$$\chi_M = \frac{C}{T}$$

where $C$ is the Curie constant, characteristic of every substance. For ideal magnetically dilute substances this law holds well. In non-ideal situations, a more exact relationship (Equation 9),
\[ \chi_M = \frac{C}{T-\Theta} \quad \ldots(9) \]

is followed, where \( \Theta \) is the Weiss constant. A linear graph of \( 1/\chi(T) \) for a substance that obeys Equation 9, will be characterized by an intercept of \( \Theta \) on the \( T \) axis.

2.3 EXPERIMENTAL

2.3.1 Preparation of Magnetic Samples

All complexes were analyzed just prior to the magnetic measurements to determine analytical purity.

The complex ( \( \approx 20-30 \) mg) was finely ground with an agate mortar and pestle, packed tightly into a small bucket,† then weighed to five decimal places. The weight of the sample and bucket was also checked after completion of the magnetic measurements to check for any weight loss on evacuation.

Air-sensitive samples were sealed in argon filled ampoules prior to measurement. In these cases, the samples were finely ground and packed into the gold bucket inside a nitrogen filled glove bag. The sample was then checked for signs of oxidation (by checking if any colour change had occurred) before and after the measurements.

2.3.2 Magnetic Susceptibility Measurements and Treatment of Data

The average mass susceptibility, \( \chi_M \), was measured using an extensively modified Oxford Instruments Faraday magnetometer with redesigned supports for the microbalance and superconducting

† The bucket used for variable temperature measurements is made of gold, and that used for single temperature measurements of glass.
Figure 2.1
Diagram of the variable temperature susceptibility balance.
magnets. The system comprised a liquid-helium Dewar with a NbTi superconducting magnet assembly to provide the main and gradient fields, a variable-temperature insert for sample temperature control, a Sartorius microbalance (model 4104) for force measurements, and associated vacuum facilities (Figure 2.1).

The main and gradient fields were independently variable; however, usual values were 10 or 40 kG and 1000 GHz, respectively. Measurements were made manually between 4.2 and 20 K. At higher temperatures a Hewlett Packard coupler controller (2570A) and microcomputer (HP86) were used for automatic data logging.

Temperatures below 30 K were measured with a 1000 Ω carbon resistor while above 30 K a Cu/constantan thermocouple was employed. The carbon resistor was found to be slightly field dependent below ~10 K. For measurements at other than the lowest attainable temperature (4.28 K) errors of up to 0.2 K can result from this dependence. In general, the errors in temperature were found to be less than 0.1 K.

Magnetization measurements at six field strengths between 5 and 46 kG were made over the temperature range 4.2 to 220 K, for \([\text{Mn}^{\text{III\text{-sar}}}(\text{CF}_3\text{SO}_3)_3]\). In order to prevent sample alignment at high magnetic fields and low temperatures, samples were ground with

\[ \text{For Fe(II) and Co(II) cages, 5 and 10 kG main fields were employed in order to prevent sample alignment.} \]
Vaseline and a uniform mull was prepared. Measurements were made with both increasing and decreasing magnetic fields, and there was no evidence of sample orientation.

Once the data were corrected for both Vaseline and the sample holder, the mass of the sample was determined by comparing the gram susceptibility of the neat powder at 10 kG with that of the mull, over a temperature range of 30 K.

Before measuring susceptibilities over a wide temperature range, the room temperature magnetic moment of all compounds were measured on a second Faraday balance consisting of a Newport 4 inch electromagnet and a Cahn RG electrobalance. Field strengths of 5 to 6.5 kG, calibrated against Hg[Co(CNS)₄] were used to ensure no field dependent impurities were present in the sample. The results obtained with the room temperature and Oxford Faraday balances generally agreed to better than 0.05 B.M.

Some room temperature magnetic moments were measured by the Faraday method on a Newport Instruments Gouy balance with a 3/2" type C electromagnet and a Faraday kit conversion as supplied. The diamagnetic corrections for the metal-free ligands were measured using their hydrated bromide salts, i.e. sar.₄½HBr.3H₂O and (NH₂)₂sar.5HBr.3H₂O. Tabulated values of Pascal's constants were used to determine the susceptibilities of the water and HBr molecules for each compound and resulted in \( \chi_d(\text{sar}) = -300 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \) and \( \chi_d((\text{NH₂})_2\text{sar}) = -172 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1} \). Unless otherwise stated all measurements are in the unrationalized c.g.s. electromagnetic units which has been the standard practice of magnetochemists for many years. S.I. units are rationalized, and so the conversion from c.g.s. e.m.u. to S.I. magnetic units involves factors which include \( 4\pi \), since the permeability of free space is \( 4\pi \times 10^{-7} \text{ kg ms}^{-2} \text{A}^{-2} \).
in S.I., but is unity, and dimensionless, in the c.g.s. system. For convenience, the well-known c.g.s. system is retained here.†

In the forthcoming discussion of the magnetic behaviour of the cage complexes, an octahedral ligand field is assumed to be the initial perturbation of the free ion term. Other perturbations that remove orbital or spin degeneracy, i.e. spin-orbit coupling, zero-field splitting, Jahn-Teller distortions etc. are considered as subsequent perturbations where relevant.

2.3.3 Computer Assisted Calculations

Susceptibility calculations were performed with a Fortran program COM/MAG on the Monash University Burrough's 6700 computer. The indicator of "best fit" was obtained by minimization of the R factor, defined by Equation 10,

\[ R = \frac{\sum (x_{\text{obs}} - x_{\text{calc}})^2}{\sum x_{\text{obs}}^2} \times 100 \quad \ldots(10) \]

Some data were fitted using a Fortran program CAMMAG, developed at Cambridge University. The input data for this program were the molecular dimensions of the cage required for the angular overlap model (AOM) parameters. The output of the program yields spectral transition energies and assignments, magnetic susceptibilities and their orientations and molecular g-tensors. Further details of this program are provided in reference 62.

† In the c.g.s. system the Bohr magneton is \(0.92731 \times 10^{-20}\) erg gauss\(^{-1}\) and in S.I. it is \(0.92731 \times 10^{-23}\) A m molecule\(^{-1}\). Using these values, the magnetic moment, \(\mu\), is \(2.828(\chi_{\text{MT}})^{1/2}\) Bohr magnetons in S.I. units. These two expressions give the same numerical value for the magnetic moment, and are valid in either system of units.
Figure 2.2
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [V:sar-2H](PF₆)₂·5H₂O.

Figure 2.3
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [V(NH₃)₂:sar-2H]Cl₄·5H₂O.
2.4 RESULTS AND DISCUSSION

2.4.1 The 3d\(^1\) Configuration

Attempts to isolate the Ti(III) cage have so far been unsuccessful. However, success has been achieved in the isolation of what are believed to be the first hexaamine complexes of V(IV). The \([V \text{ sar-2H}]_2\text{(PF}_6\text{)}_2\cdot5\text{H}_2\text{O}\) and \([V(\text{NH}_3)_2\text{sar-2H}]\text{Cl}_4\cdot5\text{H}_2\text{O}\) complexes, (sar-2H indicates deprotonation at coordinated N-atoms), exist as doubly deprotonated salts.

The magnetic moments measured at room temperature for these complexes are \(\mu_{\text{eff}} = 1.80\) B.M. for \([V \text{ sar-2H}]^{2+}\) (\(\Theta = 3.2\) K), and \(\mu_{\text{eff}} = 1.93\) B.M. for \([V(\text{NH}_3)_2\text{sar-2H}]^{4+}\) (\(\Theta = 3.1\) K), consistent with the expected 3d\(^1\) configuration. Both complexes show little variation of their moments when cooled to liquid helium temperature (Figures 2.2 and 2.3).

The action of a cubic ligand field on the free ion \(^2\text{D}\) term lifts its degeneracy and leads to a \(^2\text{T}_{2g}\) term lying lowest. The six-fold degeneracy of this ground term may be lifted by spin-orbit coupling, as discussed by Kotani\(^{55}\) (cf. Figure 2.4); it may also be removed by a ligand field of symmetry lower than cubic. It has been shown that ligand fields of low symmetry have comparatively little effect on the effective magnetic moment unless they raise the orbital degeneracy of the \(^2\text{T}_{2g}\) term by more than ten times the spin-orbit coupling constant.\(^{57}\) However, for small splittings of the \(^2\text{T}_{2g}\) term, the moment should vary markedly with temperature.

A study of the magnetic properties of six V(IV) complexes\(^{63}\) illustrates well both mechanisms for lifting the degeneracy of the \(^2\text{T}_{2g}\) term, and provides a useful model for discussion of the magnetism of the V(IV) cages. Of the six complexes, three are
Figure 2.4
Splitting diagram for the 3d\(^1\) configuration.

Figure 2.5
Variation of the magnetic moment with temperature for an octahedrally coordinated 3d\(^1\) ion.
tetrachlorovanadyl salts, influenced by a strong axial ligand field, with the ground term split by some 1000 - 2000 cm\(^{-1}\), i.e. the ground term is effectively an orbital singlet, and should result in Curie law behaviour with \( \mu_{\text{eff}} = 1.73 \) B.M. On the other hand, the three hexachlorovanadate(IV) salts exhibit small axial fields of comparable energy to the spin-orbit coupling, which should lead to a strong temperature dependence of the magnetic moment (cf. \( \mu_{\text{eff}} \) vs. \( T \) for octahedrally coordinated 3d\(^1\) ion, Figure 2.5). The magnetic data for the six complexes over the temperature range 300 - 80 K are summarized in Table 2.1.

### TABLE 2.1

Magnetic Moments for some V(IV) complexes.\(^{63}\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \mu_{\text{eff}} ) at 300 K, B.M.</th>
<th>( \mu_{\text{eff}} ) at 80 K, B.M.</th>
<th>( \Delta \mu ), B.M.</th>
<th>( \Delta \mu ), B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cs}_2\text{VCl}_6 )</td>
<td>1.83</td>
<td>1.35</td>
<td>0.48</td>
<td>0.44</td>
</tr>
<tr>
<td>( (\text{pyH})_2\text{VCl}_6 )</td>
<td>1.76</td>
<td>1.28</td>
<td>0.48 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>( (\text{quinH})_2\text{VCl}_6 )</td>
<td>1.76</td>
<td>1.40</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>( (\text{pyH})_2\text{VOCl}_4 )</td>
<td>1.76</td>
<td>1.67</td>
<td>0.09</td>
<td>0.08 ± 0.02</td>
</tr>
<tr>
<td>( (\text{pyH})_2\text{VOCl}_4 \cdot 2\text{H}_2\text{O} )</td>
<td>1.72</td>
<td>1.66</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>( (\text{quinH})_2\text{VOCl}_4 )</td>
<td>1.75</td>
<td>1.66</td>
<td>0.09</td>
<td></td>
</tr>
</tbody>
</table>

Clearly, the vanadyl complexes in Table 2.1, exhibit a smaller range of the magnetic moments (seen in \( \Delta \mu \)) than the corresponding hexachloro-derivatives over the same temperature range. It is suggested here that this difference in behaviour can be interpreted as being directly proportional to the degree of distortion of the first coordination sphere; i.e. it proposed that \( \Delta \mu \propto \delta \), where \( \Delta \mu \)
Figure 2.6

Splitting diagram for the $3d^1$ ($t_{2g}^1$) configuration in a tetragonal (elongation) field with spin-orbit coupling.
is the change in magnetic moment over a significant temperature range and, $\delta$ cm$^{-1}$ is the extent to which the degeneracy of the $^{2}T_{2g}$ level is raised by an axial ligand field.

If this criterion is applied to the V(IV) cage complexes, $\Delta \mu = 0.19$ B.M. for $[\text{V sar-2H}]^{2+}$ and $\Delta \mu = 0.12$ B.M. for $[\text{V(NH}_3)_2\text{ar-2H}]^{4+}$, implying a significant distortion of the $\text{VN}_6$-core for both complexes.

Although, this analysis is very qualitative, the prediction of an orbital singlet as the ground term for the vanadium(IV) cage complexes based upon the average magnetic susceptibility, was later substantiated by EPR studies.$^{65}$ Furthermore, structural studies performed on the $[\text{V(NH}_3)_2\text{ar-2H}]\text{(S}_2\text{O}_5)_2\cdot\text{H}_2\text{O}$ complex revealed that the cation symmetry was approximately trigonal ($D_3$) and the coordination environment of the metal was not octahedral but close to trigonal prismatic, with a trigonal twist angle, $\phi = 18^\circ$. $^{50}$

The two sites of deprotonation reside at the secondary (donor) nitrogen atoms, although disorder about the $N_6$ donor core prevents their specific location by X-ray methods. The observed distortion can be rationalized in terms of the metal attempting to attain a pseudo-vanadyl arrangement with the deprotonated nitrogen atoms. The splitting diagram in Figure 2.6 gives an appropriate description of axial distortion together with spin orbit coupling for the two V(IV) cages.

As mentioned above, the EPR data$^{66}$ also show considerable anisotropy in the principal EPR parameters ($g$ and $A$) which are symptomatic of a distorted system and suggest that the unpaired electron resides in an orbital with mainly $d_{z^2}$ character, i.e., indicating $^2A_1$ ground state in trigonal prismatic geometry. Single crystal magnetic anisotropy studies would be a useful addition to the available data, to confirm the ground state assignment.
For the d\(^1\) configuration, there is no preference for the metal ion in terms of ligand field stabilization energy (LFSE). On this basis the ligand can be regarded as dictating the overall symmetry of the MN\(_6\)-core.\(^{50}\)

### 2.4.2 The 3d\(^2\) Configuration

The magnetic moment at room temperature has been measured for a vanadium(III) cage, which was prepared electrochemically from \([\text{VIV(NH}_3\text{)}_2\text{sar-2H}]^{4+}\). At 295 K a moment of 2.90 B.M. was obtained, which agrees with the spin-only value of 2.83 B.M., generally observed for a d\(^2\) ion in octahedral geometry (Table 2.2).

**TABLE 2.2**

Magnetic moments and Weiss constants for some V(III) complexes.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\mu_{\text{eff}}) at 300 K, B.M.</th>
<th>(\theta), K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(acac)(_3)</td>
<td>2.80</td>
<td>-2</td>
<td>67,70</td>
</tr>
<tr>
<td>(\text{K}_3\text{VF}_6)</td>
<td>2.79</td>
<td>-14</td>
<td>68</td>
</tr>
<tr>
<td>V(pn)(_3)Cl(_3)</td>
<td>2.80</td>
<td></td>
<td>69</td>
</tr>
<tr>
<td>V(en)(_3)Cl(_3)</td>
<td>2.79</td>
<td></td>
<td>69</td>
</tr>
<tr>
<td>(\text{K}_3[\text{V(C}_2\text{O}_4\text{)}_3]\cdot \text{3H}_2\text{O})</td>
<td>2.80</td>
<td>-1</td>
<td>70</td>
</tr>
<tr>
<td>(\text{K}_3[\text{V(NCS)}_6]\cdot \text{4H}_2\text{O})</td>
<td>2.66</td>
<td></td>
<td>70</td>
</tr>
<tr>
<td>V[((\text{NH}_2\text{)}_2\text{CO})_6]\text{(ClO}_4\text{)}_3)</td>
<td>2.71</td>
<td></td>
<td>70</td>
</tr>
</tbody>
</table>

The \(3\text{F}\) free ion term under the action of a cubic crystal field gives rise to the \(3\text{T}_{1g}\) ground term. As found for the d\(^1\) ion, the orbital degeneracy of the \(3\text{T}_{1g}\) can be lifted by an axial component to the ligand field, into \(3\text{A}\) and \(3\text{E}\) states. In addition, the spin
Figure 2.7

Splitting diagram for a 3d\textsuperscript{2} ion, initially in an octahedral field.
degeneracy can also be lifted by the action of spin-orbit coupling, and results in a manifold of levels accessible for thermal population at room temperature. These influences on the splitting pattern of the d^2 ion in an octahedral geometry are schematically represented in Figure 2.7.

The formulation [V(NH_3)_2sar]^5+, is consistent with the analytical data, where protonation of the ligand has occurred during the reduction of the V(IV) complex to V(III). This protonation is not unexpected as the pKa’s (for the donor amines) for the M(III) cages are of the order of 10-12 (cf. Table 6.15), whereas the fully protonated V(IV) must have a pK_a < 0.

The d^2 ion can exhibit either a high-spin or low-spin configuration depending on the symmetry of the ligand field. The preference of six coordinate complexes has been analyzed for trigonal prismatic (TP) and trigonal antiprismatic (TAP or O_h) geometries. The dependence of d-orbital energies as a function of the trigonal twist angle, \( \phi \), is schematically illustrated in Figure 2.8, where the spectroscopically labelled states translate to the following orbitals; \( a_1' = d_{z^2} \), \( e' = d_{x^2-y^2} \), \( d_{xy} \), and \( e'' = d_{xz}, d_{yz} \).

If the V(III) cage retains the observed structure of the V(IV) parent, i.e. \( \phi = 18^\circ \), then the V(III) complex is expected to be diamagnetic with an \( a_1^{12} \) ground state configuration. However, the observed \( \mu_{eff} = 2.90 \) B.M. is consistent with an increase in the trigonal twist angle towards 60\(^\circ\) corresponding to pseudo-octahedral geometry with a high-spin \( t_{2g}^2 \) ground state configuration.

Similar observations have been made for several TP dithiolato complexes of vanadium(0). In these examples a two-electron reduction was found to cause a twist about the three-fold axis towards octahedral coordination.
Figure 2.8
Variation of the energies of the d orbitals as a function of the twist angle.
Figure 2.9
Variation of the magnetic moment and the reciprocal susceptibility with temperature for \([\text{Cr(NH}_2\text{)}_2\text{sar}]\text{Cl}_3/2\text{H}_2\text{O}\).

Figure 2.10
Variation of the magnetic moment and the reciprocal susceptibility with temperature for \([\text{Cr(NH}_3\text{)}_2\text{sar}]\text{Cl}_5\).
Figure 2.11
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Cr sar](CF$_3$SO$_3$)$_3$.

Figure 2.12
Magnetic moment vs. temperature curve fitted to Equation 12, with $g = 1.928$ and $D = 0.56$ cm$^{-1}$ for [Cr sar](CF$_3$SO$_3$)$_3$. 
A variable temperature investigation of \([\text{V(NH}_3\text{)}_2\text{sar}]^{5+}\) was not attempted due to an insufficient amount of sample. However, the magnetism of this ion over a range of temperatures is of interest and will be undertaken in the near future.

2.4.3 The 3d\(^3\) Configuration

The 3d\(^3\) configuration, with a \(^4\text{A}_2\text{g}\) ground term in octahedral geometry, is not, to a first approximation, affected by the detailed nature of the ligand field. The magnetic moments for \([\text{Cr(NH}_2\text{)}_2\text{sar}]\text{Cl}_3\text{H}_2\text{O}, [\text{Cr(NH}_3\text{)}_2\text{sar}]\text{Cl}_5\text{H}_2\text{O}\) and \([\text{Cr sars}]\text{(CF}_3\text{SO}_3)_3\) at room temperature, are close to or a little reduced from the spin-only value for three unpaired spins (\(\mu_{\text{SO}} = 3.87\) B.M.) in a pseudo-octahedral environment. The magnetic moment for a \(^4\text{A}_2\text{g}\) term is expressed by Equation 11,

\[
\mu_{\text{eff}} = 3.87 \left(1 - \frac{4 \lambda}{10 \text{ Dq}}\right) \quad \text{...(11)}
\]

when considering only first order Zeeman splittings. From Equation 11, for small values of the spin-orbit coupling constant, \(\lambda (\lambda = 90\ \text{cm}^{-1} \text{ for the Cr}^{3+}\text{ion})\) together with large values of the ligand field parameter, 10 Dq (\(\approx 22,000\ \text{cm}^{-1}\) for \(\text{CrN}_6\) complexes), the difference between the experimental and spin-only values for \(\mu_{\text{eff}}\) is expected to be small.

Each complex exhibits Curie-like dependence of \(\chi\) with temperature and a small decrease is observed in \(\mu_{\text{eff}}\) below \(\approx 20\)K (Figures 2.9, 2.10 and 2.11). This small decrease in \(\mu_{\text{eff}}\) is symptomatic of a small zero-field splitting of the \(^4\text{A}_2\text{g}\) ground term into \(M_S = \pm 3/2\) and \(M_S = \pm 1/2\) levels (separated by 2D) and brought about by a combination of spin-orbit coupling and ligand field distortion effects. Analysis of the variable temperature data using
Figure 2.14
Magnetic moment vs. temperature curve fitted to Equation 12, with $g = 1.943$ and $D = 0.56 \text{ cm}^{-1}$ for [Cr(NH$_2$)$_2$sa]Cl$_3$·1/2H$_2$O.

Figure 2.13
Magnetic moment vs. temperature curve fitted to Equation 12, with $g = 1.956$ and $D = 0.71 \text{ cm}^{-1}$ for [Cr(NH$_3$)$_2$sa]Cl$_6$. 
a Hamiltonian of the type (Equation 12),

\[ \mathcal{H} = D(S_z^2 - 1/3S(S + 1)) + g \beta H.S \quad \ldots (12) \]

where \( D \) is the axial zero-field splitting in cm\(^{-1}\), and \( S \) and \( H \), are the total spin and magnetic field operators; yielded good fits (Figures 2.12, 2.13 and 2.14) with values of \( g \) and \( D \) shown in Table 2.3. The zero-field splitting of the \( ^4A_{2g} \) ground state is extremely small (\( D < 1 \) cm\(^{-1}\)) and uncertainties in \( D \) are reasonably large due to the small variation in magnetic moment with temperature. The sign of \( D \) could not be evaluated from the magnetic data alone, possibly single crystal magnetic data would provide a more sensitive method. The \( g \) values obtained are less than 2 as expected for the Cr(III) ion due to spin-orbit coupling with higher lying levels i.e.

\[ g = 2(1 - \frac{4\lambda}{10Dq}) \cdot \]

Using the visible absorption spectrum of these complexes in aqueous solution, it is possible to estimate independently a value for the axial zero-field splitting parameter, \( D \). For these calculations a splitting diagram similar to Figure 2.15, is assumed; with an essentially cubic ligand field perturbed by a small trigonal distortion. The observed splitting of the \( ^4T_{2g} \) band, \( \delta \), and the 10 \( Dq \) for the complex, together with the spin-orbit coupling constant are then related according to the relation (Equation 13),

\[ 2D = \frac{8\lambda^2 \delta}{(10Dq)^2} \quad \ldots (13) \]

where \( \lambda = 90 \) cm\(^{-1}\), \( \delta = 400 \) cm\(^{-1}\) and 10 \( Dq = 22,026 \) cm\(^{-1}\) for the \([\text{Cr(NH}_3\text{)}_2\text{sar}]^{5+} \) ion.\(^7\) Using these parameters, the \( D \) value obtained is 0.05 cm\(^{-1}\), which can be compared to that deduced from the
Figure 2.15

Splitting diagram for the $3d^3(t_{2g})^3$ configuration.
susceptibility fits discussed previously (Table 2.3). These parameters can also be compared to those obtained for the [Cr(en)$_3$]$^{3+}$ ion where $g = 1.987$, $D = 0.04$ cm$^{-1}$ and $10 Dq = 21,740$ cm$^{-1}$.$^{58}$ The effect of encapsulation upon the electronic structure of the CrN$_6$ chromophore is thus found to be quite small.

**TABLE 2.3**

Magnetic moments and Weiss constants for some Cr(III) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{\text{eff}}$ at 300 K, B.M.</th>
<th>$\mu_{\text{eff}}$ at 4.2 K, B.M.</th>
<th>$\theta$, $^a$ K</th>
<th>$D$, cm$^{-1}$</th>
<th>$g_{\text{iso}}$</th>
<th>$R$, $^b$ %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(NH$_3$)$_2$ sar] Cl$_3$ \·1/2H$_2$O</td>
<td>3.74</td>
<td>3.72</td>
<td></td>
<td>0.56</td>
<td>1.943</td>
<td>0.71</td>
<td>this work</td>
</tr>
<tr>
<td>[Cr(NH$_3$)$_2$ sar] Cl$_5$</td>
<td>3.80</td>
<td>3.73</td>
<td>0.4</td>
<td>0.71</td>
<td>1.956</td>
<td>0.69</td>
<td>this work</td>
</tr>
<tr>
<td><a href="CF$_3$SO$_3$">Cr sar</a>$_3$</td>
<td>3.75</td>
<td>3.69</td>
<td>-1.2</td>
<td>0.56</td>
<td>1.928</td>
<td>0.73</td>
<td>this work</td>
</tr>
<tr>
<td>[Cr dtne] Br$_3$.1/2H$_2$O</td>
<td>3.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>87</td>
</tr>
<tr>
<td>[Cr(NH$_3$)$_6$] Br$_3$</td>
<td>3.77</td>
<td>3.77$^c$</td>
<td>-7</td>
<td></td>
<td></td>
<td></td>
<td>74</td>
</tr>
<tr>
<td>[Cr(urea)$_6$] Cl$_3$</td>
<td>3.64</td>
<td>3.64$^c$</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td>74</td>
</tr>
<tr>
<td>[Cr(en)$_3$] Cl$_3$.3H$_2$O</td>
<td>3.83</td>
<td>3.83$^d$</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td>74</td>
</tr>
<tr>
<td>K$_3$(Cr(CNS)$_6$) ·4H$_2$O</td>
<td>3.80</td>
<td></td>
<td>0</td>
<td></td>
<td></td>
<td></td>
<td>74</td>
</tr>
</tbody>
</table>

$^a$ The Weiss constant, $\theta$, was obtained using linear least squares fit over the entire temperature range for this work.

$^b$ $R$ is defined in Equation 10.

$^c$ Measured at 90 K.

$^d$ Measured at 85 K.

Comparisons between the magnetic susceptibility of other amine complexes are also included in Table 2.3. Although, these data have been collected over a limited temperature range only, the same general features are observed for these complexes.
Figure 2.16

Splitting diagram for the 3d⁴ \((t_{2g}^{3}e_{g}^{1})\) configuration in a weak field.
EPR studies on powder and frozen glasses of the chromium(III) cage complexes have shown well-resolved lines due to transitions occurring between the various \( M_S = \pm 3/2 \) and \( M_S = \pm 1/2 \) sublevels. Spin Hamiltonian analysis of the EPR data again yielded a value for D of a similar order of magnitude to those obtained from the magnetic susceptibility data. Small rhombic splittings of the resonances were also evident.

### 2.4.4 The 3d⁴ Configuration

The published magnetic properties of pseudo-octahedral Mn(III) compounds are dominated by the high-spin, \( S=2 \) configuration with very few examples of the low-spin, \( S=1 \) ground state being authenticated. A weak or medium ligand field in octahedral symmetry splits the \( ^5D \) free ion term to give a \( ^5E_g \) ground term and a \( ^5T_{2g} \) excited term. The effect of non-cubic symmetry and/or Jahn-Teller distortions is to remove the orbital degeneracy of the \( ^5E_g \) term to give an orbital singlet lying lowest (either a \( ^5A_{1g} \) or \( ^5B_{1g} \) in \( D_{4h} \) symmetry). The spin degeneracy of the orbital singlet ground term is further removed by spin-orbit coupling giving rise to zero-field \( M_S \) sub-levels (Figure 2.16).

The exact nature of the ground state depends critically on the symmetry of the ligand field about the Mn(III) ion. If the \( d_{x^2-y^2} \) orbital is unoccupied then an 'octahedral' complex is expected to be axially elongated with the \( ^5B_{1g} \) level lying lowest. For such a ground term D will be negative. Conversely, compression of the octahedron (\( d_{z^2} \) unoccupied) results in the \( ^5A_{1g} \) lying lowest with D positive. The zero-field splitting in Mn(III) is typically of the order of a few wavenumbers, so that the magnetic properties are expected to be Curie-like and close to spin-only (\( \mu_{SO} = 4.90 \) B.M.)
Figure 2.17
Variation of the magnetic moment and the reciprocal susceptibility with temperature for \([\text{Mn sar}]([\text{CF}_3\text{SO}_3])_3\).

Figure 2.18
Splitting diagram for the $^3T_{1g}$ ground term from the $t_{2g}^4$ configuration in a strong field.
except at very low temperatures (< 15 K) where a rapid decrease in the magnetic moment occurs.

The magnetic moment for \([\text{Mn sar}] (\text{CF}_3\text{SO}_3)_3\) is plotted as a function of temperature in Figure 2.17. The moment at room temperature (\(\mu_{\text{eff}} = 4.72\) B.M.) is reduced from its spin-only value (\(\mu_{\text{SO}} = 4.90\) B.M.) even more than predicted for a high-spin \(d^4\) ion by Equation 14,

\[
\mu_{\text{eff}} = \mu_{\text{SO}} (1 - \frac{2\lambda}{10\ Dq}) \quad \cdots \ (14)
\]

where the free ion value of \(\lambda = 90\ \text{cm}^{-1}\) and \(10\ Dq = 20,000\ \text{cm}^{-1}\) for Mn(III). The moment remains virtually unchanged over the temperature range \(300 + \rightarrow 150\ K\). However, at temperatures below 150 K the moment falls steadily until the value \(\mu_{\text{eff}} = 3.67\) B.M. is reached at 4.3 K, the lowest temperature attainable in this work.

This observed temperature dependence of the moment is extremely unusual and unexpected for high-spin (pseudo-octahedral) Mn(III) compounds, which invariably are independent of temperature over a wide range of temperatures.\(^{64,76,77}\) Perhaps surprisingly, the observed \(\mu(T)\) behaviour in the temperature region below 150 K for \([\text{Mn sar}]^{3+}\) is more reminiscent of the strong dependence on temperature expected of the moment for a \(3_T^g\) ground term arising from the low-spin \((t^4_{2g})\) configuration (cf. Figure 2.18).

Low-spin magnetic behaviour has been observed for \(K_3[\text{Mn(CN)}_6]\) and \(K_3[\text{Mn(OH)}(\text{CN})_5]\) which display moments at room temperature of 3.50 B.M.\(^{78}\) and 2.92 B.M.\(^{79}\), respectively. The sole temperature study was on \(K_3[\text{Mn(CN)}_6]\) in which the moment of 3.50 B.M. at 300 K decreased to 1.00 B.M. at 4 K, the susceptibility becoming independent of temperature over the lower part of the temperature range.

The orbital degeneracy of a low-spin \(3_T^g\) \((t^4_{2g})\) ground state is
Figure 2.19
Variation of the magnetic moment with temperature for a low-spin, octahedrally coordinated $3d^4$ ion.

Figure 2.20
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Mn sar](ClO$_4$)$_3$. 
partially lifted by spin-orbit coupling as shown in Figure 2.18 and as a result, the calculated $\mu_{\text{eff}}$ is expected to be strongly dependent on temperature at lower temperatures (below $kT/|\lambda| = 1.0$ in Figure 2.19). Low-spin compounds have $\lambda = -180 \text{ cm}^{-1}$, so that the moment at 300 K should be about 3.50 B.M. and then fall rapidly to zero with decreasing temperature as shown in Figure 2.19.

The $\mu(T)$ dependence for the perchlorate salt, $\text{[Mn sar]}(\text{ClO}_4)_3$ (Figure 2.20) almost model that observed in Figure 2.17, for $\text{[Mn sar]}(\text{CF}_3\text{SO}_3)_3$, except for a reduction in moment, $\mu_{\text{eff}} = 3.09 \text{ B.M.}$ at 4.3 K. The $\mu(T)$ data for both $\text{[Mn sar]}(\text{CF}_3\text{SO}_3)_3$ and $\text{[Mn sar]}(\text{ClO}_4)_3$ at temperatures below 150 K do not conform to the above simplified model for a $^3T_{1g}$ ground state but are more like that of an orbitally non-degenerate $S=1$ ground state.

In order to establish unambiguously that the ground state at low temperatures was indeed a spin triplet, the saturation behaviour of the paramagnet was studied at low temperatures and applied magnetic fields up to 46 k Gauss. In the derivation of Curie's law, it is assumed that the term $M_{\text{gg}} H/kT \ll 1$ but at low temperature and in high fields, this inequality no longer holds. The magnetization, $M$, of the sample is then described by the expression (Equation 15),

$$M = N g \beta S \left[ \frac{2S+1}{2S} \coth \left( \frac{2S+1}{2S} x \right) - \frac{1}{2S} \coth \left( \frac{1}{2S} x \right) \right] \quad \ldots(15)$$

$$= N g S B_S(x) \quad \text{where} \quad x = \frac{\beta g \beta H}{kT}$$

The expression $B(x)$ is usually termed the Brillouin function which approaches unity as $x \to \infty$, i.e., in sufficiently large external fields, the magnetic dipoles will be directed so that the magnetization along the direction of $H$ is the maximum possible; i.e.
Figure 2.21
Magnetization of \([\text{Mn sar}](\text{CF}_2\text{SO}_3)\)_2 at 4.3 K and at field strengths between 5-46 kGauss. Included are Brillouin functions for \(S = 1\) and \(S = 2\).
Figure 2.22
Magnetization of [Mn sar](CF3SO3)3 at 5, 30 and 46 kGauss over a range of temperatures. Included is the Brillouin function for \( S=1 \).
there will be saturation.

The magnetization behaviour observed for $[\text{Mn sar}]\text{(CF}_3\text{SO}_3)_3$ at 4.3 K and fields of 5, 10, 20, 30, 40 and 46 k Gauss is plotted as a function of $H/T$ in Figure 2.21. The saturation moment $\langle \mu \rangle = \frac{xH}{N\beta}$ is compared with the calculated Brillouin functions for a spin triplet ground state and a spin quintet ground state. Although the experimental data lie slightly above the spin triplet curve, there is no doubt that the saturation moment asymptotes to the value $2$ as $H/T \to \infty$, thereby confirming that the ground state is $S = 1$.

The experimental data reveal that the sample $[\text{Mn sar}]\text{(CF}_3\text{SO}_3)_3$ appears to magnetize somewhat more easily than expected for a simple magnetically dilute $S = 1$ paramagnet. There could be several explanations for this behaviour. Although the polycrystalline material was distributed in a Vaseline mull to inhibit orientation of the crystals under the influence of the applied magnetic field, it is possible that some orientation still occurred so that saturation was observed at values of $H/T$ lower than expected. Furthermore, it has been assumed, arbitrarily that the orbital angular momentum has been fully quenched in the ground state (i.e. $L = 0$) which is unlikely to be true for a $^3T_{1g}$ ground term. Also, it is assumed in this work that magnetic exchange between discrete $[\text{Mn sar}]\text{(CF}_3\text{SO}_3)_3$ molecules is absent.

If the magnetization, $M$, of the sample, measured over a wide range of temperatures, greater than 4.3 K, is plotted against $H/T$ for each value of $H$, then it emerges that the ease of magnetization increases with the size of the applied field (Figure 2.22). This also suggests that the polycrystalline sample might be orientating to some extent in the Vaseline mull, the degree of orientation increasing with $H$. 

Figure 2.23
Variation of the magnetic moment and susceptibility with temperature for [Mn (TRP)] (ref. 81).
The magnetization data confirm that the ground state of the complex \([\text{Mn sar}]\)(\(\text{CF}_3\text{SO}_3\))\(_3\) at 4.3 K is \(3\text{Ig}\) if octahedral symmetry is assumed. However, the \(u(T)\) data suggest that at temperatures above about 150 K, the complex is predominantly high-spin arising from a \(^5\text{Eg}\) term. There are no obvious discontinuities in the \(u(T)\) curve which would be indicative of a phase transition as was observed for the complex \([\text{tris}(1-(2-\text{azolyl})-2-\text{azabuten}-4-\text{yl})\text{amine}]\) manganese(III).\(^{81}\) For this compound, at temperatures above 50 K, the moment \(\mu_{\text{eff}} = 4.9\) B.M. is that expected for a \(^5\text{Eg}\) term. However, below this temperature a phase change occurs and the magnetic moment of 3.2 B.M. is consistent with a \(3\text{Ig}\) term in a distorted octahedral symmetry (Figure 2.23).

Preliminary calculations have been performed in order to estimate the energy of the triplet level with respect to an assumed \(^5\text{Eg}\) ground state. The computer program used, CAMMAG,\(^{62}\) requires the input of structural parameters in order to determine the angular overlap parameters \(e_\sigma\) and \(e_\pi\) for the orbitals of the six donor nitrogen atoms about the metal ion. Unfortunately, the crystal structure of \([\text{Mn sar}]\)(\(\text{CF}_3\text{SO}_3\))\(_3\) is incomplete, with disordered sites for both cation and anion in the lattice, and therefore the known geometric parameters of the nickel(II) cage were used to yield an \(e_\sigma\) value of 4350. The \(e_\pi\) was set at zero. Using the Racah parameters, \(B = 760\) cm\(^{-1}\), \(C = 0\); a spin-orbit coupling parameter, \(\xi = 350\) cm\(^{-1}\); and the orbital reduction factor, \(k = 0.8\), it has been shown that the triplet state could lie within 3000 cm\(^{-1}\) above the quintet ground state. Furthermore, the five spin sub-levels which are calculated to lie lowest, corresponding to a \(^5\text{A}_{\text{lg}}\) ground state with zero-field splitting where \(M_S = 0\) lies lowest (\(D_m = 3\) cm\(^{-1}\)). Approximately 300 cm\(^{-1}\) above these zero-field split sub-levels, a further five levels
are found which can be attributed to a $^5B_{1g}$ state also with zero-field splitting.

Although, this theoretical model appears to agree with inferences from magnetic data that the $^3T_{1g}$ and $^5E_g$ states are nearly equienergetic\(^\dagger\), spin-allowed d-d bands are predicted to occur at 12,000, 12,365 and 12,785 cm\(^{-1}\) whereas the observed transitions occur at 7,370 and 23,700 cm\(^{-1}\).

Although this angular overlap model does not agree with all facets of the [Mn sar]\(^{3+}\) data, it should not be discarded without further trial using the structural parameters for the [Mn sar](CF\(_3\)SO\(_3\))\(_3\) when these are available. Certainly, Jahn-Teller effects for the Mn\(^{3+}\) ion would be expected to produce considerable geometric distortion compared with the nickel(II) structure used in the above calculations.

Golding, Healy and White\(^\text{76}\) have developed expressions for the temperature dependence of the magnetic properties for d\(^4\) ions in an intermediate field of octahedral symmetry when the $^5E$ state and the lowest lying $^3T_1$ state have comparable energies. In their model, the magnitude of the spin-orbit coupling interaction (for the Mn\(^{3+}\) ion, $\zeta = 350$ cm\(^{-1}\)) between the $^5E$ and $^3T_1$ is assumed to be comparable to the energy separation of the two states. The energy separation of the $^3T_1$ and $^5E$ states is defined as $x\zeta$; when $x$ is positive the $^5E$ is the ground state. The theoretical dependence calculated for the effective magnetic moment for various values of $x\zeta$ is shown in Figure 2.24 where $\mu_{\text{eff}}$ is plotted against $kT/\zeta$. As $x\zeta$ tends to a large positive value, $\mu_{\text{eff}} \to 4.90$ B.M. over the whole temperature range.

\(^\dagger\) That is, they lie close to a ligand field crossover.
Figure 2.24

Variation of the magnetic moment with temperature for a $^5E_g \rightarrow {}^3T_{1g}$ spin equilibrium (ref. 76). Included are experimental data for [Mn sar](ClO$_4$)$_3$ (•).
On the other hand, when $x\zeta$ tends to a large negative value, the limiting magnetic moment (dotted curve) shows the strong temperature dependence expected for a $3T_1$ state, falling to zero as $kT/\zeta \to 0$.

The experimental results for $[\text{Mn sar}](\text{CF}_3\text{SO}_3)_3$ are superimposed on Figure 2.24. Above 150 K (which corresponds to $kT/\zeta = 0.3$ if $\zeta = 350 \text{ cm}^{-1}$), the effective magnetic moment is almost independent of temperature as required by the model. The observed value $\mu_{\text{eff}} = 4.72 \text{ B.M.}$ suggests that $x\zeta = 7$ so that the $3T_1$ state should lie about 2000 cm$^{-1}$ above the $5E$ state in this temperature range. However, below 150 K although $\mu_{\text{eff}}$ decreases as $kT/\zeta$ gets smaller, the moment does not fall to zero as required by their model but appears to have reached a limiting value of about 3.0 B.M. at 4.3 K. Clearly, the triplet state of $[\text{Mn sar}]^{3+}$ does not conform in its magnetic properties to the simple octahedral model with spin-orbit coupling.

An alternative spin equilibrium model has also been considered, which assumes two non-interacting spin states, i.e. $^3A(T_1) + ^5A(E)$. The theory for such a model is treated in Chapter Four. The graph of $\log_{10}K_{\text{eq}}$ vs. $1/T$, deviated grossly from linearity suggesting a poor correlation with this model. A further difficulty that arises in that the experimentally observed value for the magnetic moment at $T > 150$ K (i.e. $\mu_{\text{eff}} = 4.7$ B.M.) is much too high, even by considering an orbital contribution to the spin-only magnetic moments.

In order to contemplate other possible origins of the anomalous magnetic behaviour of $[\text{Mn sar}]^{3+}$, it is instructive to consider the preference of hexaamine cage complexes for octahedral versus trigonal prismatic stereochemistries. The qualitative variation of the energies of the d-orbitals as a function of the twist angle, $\phi$
(cf. Section 1.14) for octahedral (trigonal antiprism, TAP) and trigonal prismatic (TP) geometries is illustrated in Figure 1.2. It should be noted that the energy span of the d-orbitals in the TP is 2/3(10 Dq), i.e. considerably less than in the TAP.71 If the [Mn sar]^{3+} cage complex in its low-spin form is distorted towards a TP geometry, then the triplet-state would arise from the electron configuration \( a_1^2 e_2^2 \) which is orbitally non-degenerate. In this event, the observed moment is expected to be close to the spin-only value of 2.83 B.M. similar to that observed at 4.3 K.

The unusual combination of a spin triplet, \( S = 1 \) state at 4.3 K (magnetization) and a relatively high and constant value of \( \mu_{\text{eff}} = 4.7 \) B.M. above 150 K, might arise from extensive mixing of several low-lying \( S = 1 \) and \( S = 2 \) spin states in the crossover region via spin-orbit coupling. This situation has been analysed in considerable detail for the \( S = 1 \) spin state of \((5,10,15,20\text{-tetraphenylporphrin})\text{iron(II)}, (\text{FeTPP})\).82 Although a detailed ligand field calculation is beyond the scope of this work, the principle features of the \( \mu(T) \) curves observed for [Mn sar](CF_{3}SO_{3})_{3} and [Mn sar](ClO_{4})_{3} can be reproduced by applying the simpler spin Hamiltonian formalism for the \( S = 1 \) ground state where zero-field splitting, \( D \), arises from mixing this state with higher but low-lying excited states. Spin-orbit coupling partly lifts the three-fold spin degeneracy into \( M_S = 0 \) and \( M_S = \pm 1 \), with a separation \( D \). The magnetization measurements establish that \( M_S = \pm 1 \) lies below \( M_S = 0 \), so that \( D \) is negative.

The expression for the calculated average magnetic susceptibility, with \( g = 3.3 \) and \( D = -50 \text{ cm}^{-1} \),

\[
\mu_{\text{eff}}^2 = g^2 \left[ \frac{2 + 32/3 \cdot T/0.261(e^{D/KT} - 1)}{e^{D/KT} + 2} \right] \quad \text{...(16)}
\]
Figure 2.25

Magnetic moment vs. temperature curve for [Mn sar](CF₃SO₃)₃ (●) and [Mn sar](ClO₄)₃ (□), compared with curves calculated using Equation 16 with a) g = 3.3 and D = -50 cm⁻¹ and b) g = 3.1 and D = -50 cm⁻¹.
is compared with the experimental data for [Mn sar](CF₃SO₃)₃ and [Mn sar](ClO₄)₃ in Figure 2.25. The high value of g (compared with
\( g = 2.94 \) in FeTPP) accounts for the high observed moment of
\( u_{\text{eff}} = 4.6 \pm 4.7 \) B.M. above 100 K, whereas, the sharp decrease in
\( u_{\text{eff}} \) below this temperature is extremely sensitive to the magnitude
of the ZFS parameter, D. Considerable elaboration of this simple
model, following the work of Boyd et al.¹ is required to describe
the detailed electronic structure and magnetic properties of the
Mn(III) cages.

2.4.5 The 3d⁵ Configuration

Interestingly, examples of both high-spin (t²⁵g e²g), and low-spin
(t²⁵g) cages have been prepared for the d⁵ ions, Mn²⁺ and Fe³⁺. Their
magnetic behaviour has been studied over the temperature range 4.2 -
300 K.

The Fe(III) cage is the first example of a low-spin cage complex
in this thesis, and warrants a brief description of the nature of the
spin state. The change in spin multiplicity is brought about by the
transfer of two electrons from the e₉ to the t₂⁵g levels, thereby
lowering the (ligand field) energy by 20 Dq. This stabilization is
offset by the increase in Coulombic repulsion between the five
electrons confined to t₂⁵g-orbitals, and the exchange energy of
electron pairing, 2\( \Pi \). The resulting spin state is now either high-
spin if 10 Dq < \( \Pi \), or low-spin if 10 Dq > \( \Pi \). If, however,
10 Dq = \( \Pi \), a spin-equilibrium or electronic crossover can occur
where both high-spin and low-spin ground terms become thermally
populated (discussed further in Chapter Four).
Figure 2.26
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Mn sar](ClO₄)₂.

Figure 2.27
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Mn(NH₃)₂sar](ClO₄)₄·2H₂O.
The high-spin Configuration

The free ion ground term, \( ^6S \), is far removed from the first excited state for the Mn\(^{2+} \) ion. The ground term in a ligand field of octahedral symmetry is \( ^6A_{1g} \) and it is not split by fields of lower symmetry. This term is an orbital singlet and consequently has no orbital angular momentum associated with it. The action of spin-orbit coupling can partially remove the six-fold degeneracy into three Kramer's doublets with \( M_S = \pm 1/2, \pm 3/2, \) and \( \pm 5/2 \). This splitting is very small and the magnetic properties are simply described using the spin-only formula (Equation 17),

\[
\mu_{\text{eff}} = [4S(S + 1)]^{1/2} = 5.92 \ \text{B.M.} \ \ \ \ ... (17)
\]

The magnetic susceptibility of the two Mn(II) complexes included in this study, has been measured over the temperature range 4.2 - 300 K. Both complexes, \([\text{Mn sar}]^{2+}\) and \([\text{Mn(NH}_3)_2\text{sar}]^{4+}\), are high-spin, i.e. \( S = 5/2 \), with \( ^6A_{1g} \) ground terms. The non-degenerate nature of the ground term results in Curie law magnetic behaviour with the magnetic moments being almost independent of temperature (Figures 2.26 and 2.27). The measured moment remains unchanged over the temperature range 300 + \( \rightarrow \) 20 K. However, at temperatures below \( \approx 20 \) K, the moment decreases from \( \approx 5.9 \) B.M. at 300 K to \( \approx 5.7 \) B.M. at 4.2 K for both complexes.

This small drop in moment at low temperatures has been attributed to the zero-field splitting effect with the Kramers doublet \( M_S = \pm 1/2 \) lying lowest in energy. The magnetic properties in this low temperature region have been modelled using a \( S = 5/2 \) Spin Hamiltonian, i.e.

\[
\mathcal{H} = D S_z^2 + E (S_x^2 + S_y^2) + g\beta H, \ \ \ \ ... (18)
\]

*together with a non-cubic ligand field
assuming \( g = 2.0 \) and varying both axial (D) and rhombic (E) zero-field splitting parameters. The values which gave the best fit for both complexes are given in Table 2.4.

\[
\text{\textbf{TABLE 2.4}}
\]

Magnetic Moments and zero-field splitting parameters for Mn(II) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \mu_{\text{eff}} ) at 300K, B.M.</th>
<th>( \mu_{\text{eff}} ) at 4.2K, B.M.</th>
<th>D, cm(^{-1})</th>
<th>E, cm(^{-1})</th>
<th>( R^a ), %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="ClO(_4)">Mn sar</a>(_2)</td>
<td>5.91</td>
<td>5.70</td>
<td>0.5( \pm )0.1</td>
<td>0.05( \pm )0.01</td>
<td>0.830</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.6</td>
<td>0</td>
<td>0.830</td>
<td>this work</td>
</tr>
<tr>
<td>[Mn(NH(_3))(_2)sar] (ClO(_4))(_4)(2)H(_2)O</td>
<td>5.85</td>
<td>5.69</td>
<td>0.5( \pm )0.1</td>
<td>0.1( \pm )0.1</td>
<td>1.383</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.6</td>
<td>0</td>
<td>1.385</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.7</td>
<td>0</td>
<td>1.396</td>
<td>this work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.4</td>
<td>0.2</td>
<td>1.404</td>
<td>this work</td>
</tr>
<tr>
<td>[Mn(NH(_3))(_6)]CrO(_4)</td>
<td>5.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>83</td>
</tr>
<tr>
<td>[Mn(en(_3)]Br(_2)</td>
<td>5.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>84</td>
</tr>
<tr>
<td><a href="PF(_6)">Mn dtne</a>(_2)</td>
<td>5.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>87</td>
</tr>
</tbody>
</table>

\( a \) R is defined by Equation 10.

The observed magnetic behaviour of the two Mn(II) cages is in good agreement with other six-coordinated Mn(II) amine complexes, which are also included in Table 2.4; even though the latter have been studied over a somewhat limited temperature range.

The low-spin \( d^5 \) Configuration

The Fe\(^{3+} \) ion with its additional nuclear charge compared to the Mn\(^{2+} \) ion, is expected to exert a greater electrostatic influence upon the attached ligands; usually, resulting in a significantly stronger
Figure 2.28
Energy level diagram for the 3d$^5$ ion.

Figure 2.29
Splitting diagram for the 3d$^5$ (t$_{2g}$ $^5$) configuration in a strong field.
ligand field. Thus the low-spin magnetic behaviour found for the [Fe sar]Cl₃·H₂O complex was not unexpected although there are very few with six saturated amine donor atoms known.⁸⁵–⁸⁷

The ground term in O₃₃ symmetry, 2T₂g, arises from a 2I free ion spectroscopic state (Figure 2.28). As with other S = 1/2 systems (cf. Section 2.4.1), the orbital degeneracy can be lifted via axial distortion or spin-orbit coupling (Figure 2.29), or by both mechanisms. However, contrary to the previous complexes, the low-spin complexes exhibit an axial ligand field component estimated to be only a few hundred reciprocal wavenumbers.⁸⁸

The magnetic moment measured at room temperature for the [Fe sar]Cl₃·H₂O complex, of μₑff = 2.55 B.M. is in accord with that expected for octahedrally coordinated low-spin Fe(III). The orbital contribution to the spin-only magnetic moment (μ_SO = 1.73 B.M.) is seen to be substantial at room temperature; however, as the temperature is lowered, the moment decreases towards the spin-only value (Figure 2.30).

The graph of reciprocal molar susceptibility versus temperature (included on Figure 2.30), obeys the Curie law below ~ 40 K but shows substantial deviation from linearity at higher temperatures. This deviation may be reflecting the presence of a low-lying high-spin state (i.e. second order Zeeman effects).

The temperature dependence of the susceptibility data for [Fe sar]Cl₃·H₂O was analyzed using a least squares minimization program (called COM/LSYM†), where the axial splitting parameter, δₐₓ, and the spin-orbit coupling constant, λ, were both

† 2T₂g strong field basis functions were used.
Figure 2.30
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Fe sar]Cl$_3$.1/2H$_2$O.
allowed to vary. The curve of best fit gave $\delta_{\text{ax}} = 400 \pm 100 \text{ cm}^{-1}$, and $\lambda = -300 \pm 50 \text{ cm}^{-1}$. These results can be compared to those obtained using powder EPR measurements at 4.2 K, where $\delta_{\text{ax}} = 126 \text{ cm}^{-1}$, and $\lambda$ was set at $-460 \text{ cm}^{-1}$. The EPR data were characterized by broad signals which revealed anisotropy in the $g$ values ($g_\parallel = 2.93$ and $g_\perp = 2.12$) but could not detect any rhombic component. This is consistent with an X-ray structure determination of the $[\text{Fe sar}]\text{(NO}_3\text{)}_3$ which showed the FeN$_6$ core to lie only 7° away from the ideal octahedral arrangement.

The susceptibility results for the $[\text{Fe sar}]^{3+}$ complex are compared to a number of Fe(III) hexaamine complexes in Table 2.5.

**TABLE 2.5**

Magnetic moments, Weiss constants and ligand field parameters for Fe(III) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{\text{eff}}$ at 300 K, B.M.</th>
<th>$\mu_{\text{eff}}$ at 80 K, B.M.</th>
<th>$\theta$, K</th>
<th>$\delta$, cm$^{-1}$</th>
<th>$\lambda$, cm$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe sar}]\text{Cl}_3\cdot\text{H}_2\text{O}$</td>
<td>2.55</td>
<td>2.08</td>
<td>400</td>
<td>-300</td>
<td>this work</td>
<td></td>
</tr>
<tr>
<td>$[\text{Fe(en)}_3]\text{Cl}_3$</td>
<td>2.45</td>
<td>2.17</td>
<td>0 or 400 or -400</td>
<td>-400</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>$[\text{Fe(phen)}_3]^{3+}$^\text{a}</td>
<td>2.40</td>
<td>2.13</td>
<td>18</td>
<td>600</td>
<td>-400</td>
<td>88</td>
</tr>
<tr>
<td>$[\text{Fe(bipy)}_3]^{3+}$^\text{a}</td>
<td>2.40</td>
<td>2.18</td>
<td>27</td>
<td>600</td>
<td>-400</td>
<td>88</td>
</tr>
<tr>
<td>$[\text{Fe([9]aneN}_3\text{)}]\text{Br}_3\cdot\text{H}_2\text{O}$</td>
<td>2.3</td>
<td></td>
<td></td>
<td></td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>$[\text{Fe(dtne)}]\text{Br}_3\cdot\text{H}_2\text{O}$</td>
<td>2.7</td>
<td></td>
<td></td>
<td></td>
<td>87</td>
<td></td>
</tr>
</tbody>
</table>

^\text{a} Complex is a (ClO$_4$)$_3\cdot$3H$_2$O salt.
Figure 2.31
Splitting diagram for the $3d^6$ ($t_{2g}^4e_g^2$) configuration in a weak field.

Figure 2.32
Variation of the magnetic moment with temperature for the $3d^6$ configuration in an octahedral ligand field (ref. 54).
2.4.6. The 3d\textsuperscript{6} Configuration

The iron(II) and cobalt(III) ions are the best known examples of the transition metal series with the 3d\textsuperscript{6} configuration. As found for all cobalt(III) hexaamine complexes, the cobalt(III) cages possess low-spin, t\textsuperscript{6}\textsubscript{2g} configurations, as deduced from their electronic and \textsuperscript{1}H NMR spectra and X-ray structural data. Accordingly, these complexes were not included in the magnetic studies.

The Fe(II) cage complexes constitute an unusual class of complexes with representatives of both high-spin and low-spin configurations being found.

The high-spin d\textsuperscript{6} Configuration

In an octahedral crystal field the free ion ground state, 5\textsuperscript{D}, gives rise to a 5\textsuperscript{T\textsubscript{2g}} term lying \textasciitilde 10,000 cm\textsuperscript{-1} below a 5\textsuperscript{Eg} term (Figure 2.31). Spin-orbit coupling between the levels is usually small and the effect of the excited 5\textsuperscript{Eg} term on the magnetic properties can be neglected. A theoretical plot of \( \mu_{\text{eff}} \) against \( kT/|\lambda| \) (Figure 2.32), illustrates the anticipated behaviour for high-spin Fe(II) compounds (\( \lambda = -100 \text{ cm}^{-1} \)) and indicates a room temperature magnetic moment of 5.64 B.M. Departure from octahedral symmetry, e.g., by axial distortion will lift the orbital degeneracy of the 5\textsuperscript{T\textsubscript{2g}} term, as shown in Figure 2.31. This lowering in symmetry will usually result in a reduction in the effective magnetic moment, towards its spin-only value (\( \mu_{\text{SO}} = 4.90 \text{ B.M.} \)).

The [Fe sar]\textsuperscript{2+} and [Fe(NH\textsubscript{3})\textsubscript{2} sar]\textsuperscript{4+} complexes are air sensitive, and are readily oxidized via a oxidative dehydrogenation mechanism\textsuperscript{89} (Scheme 16) to imines. The first magnetic measurements were made for two separate preparations of [Fe(NH\textsubscript{3})\textsubscript{2} sar]Cl\textsubscript{4} \cdot 5H\textsubscript{2}O and indicated impurities were present in the sample which led to a "hump" in the \( \mu(T) \) curve (Figure 2.33). However, the measured magnetic moments at
Scheme 16
Oxidative dehydrogenation mechanism proposed for imine formation for the Fe(II) cages.
Figure 2.33
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Fe(NH$_3$)$_2$sar]Cl$_4$·5H$_2$O.

Figure 2.34
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Fe(NH$_3$)$_2$sar]Br$_2$Cl$_2$·4H$_2$O.
Figure 2.35
Splitting diagram for the $^5T_{2g}$ term from the $3d^6$ configuration.
room temperature, $\mu_{\text{eff}} = 5.12$ and $5.23$ B.M., were as expected for a high-spin Fe(II) complex. Subsequent isolation and magnetic characterization of pure samples eliminated the anomalous "hump" and gave reproducible high-spin behaviour.

A temperature independent moment ($\mu_{\text{eff}} = 5.42 \pm 0.1$ B.M.) was observed for the $[\text{Fe(NH}_3)_2\text{sar}]\text{Br}_2\text{Cl}_2\cdot 4\text{H}_2\text{O}$ complex, over the temperature range $230^\dagger + = 40$ K. At temperatures below 40 K, the moment decreased rapidly to $\mu_{\text{eff}} = 4.44$ B.M. at 4.2 K (Figure 2.34).

In order to understand the possible origin of this magnetic behaviour, the effects of spin-orbit coupling and axial distortions must be considered. The action of spin-orbit coupling on the cubic, $^5T_{2g}$ ground term results in three levels separated by $3\lambda^\dagger\dagger$ and $2\lambda$ (Figure 2.35) with $J = 3$ lying lowest. Application of an external magnetic field removes the seven-fold spin degeneracy and results in a manifold of thermally accessible levels. This description implies a dependence of the magnetic moment on temperature as shown earlier in Figure 2.32, with the spin-only value of the moment expected at absolute zero.

The X-ray crystal structure for $[\text{Fe(NH}_3)_2\text{sar}]\text{(NO}_3)_4\cdot\text{H}_2\text{O}$ indicates low symmetry components are present with a trigonal twist angle, $\phi = 28.6^\circ$ lying midway between the trigonal prismatic ($\phi = 0^\circ$) and trigonal anti-prismatic (octahedral, $\phi = 60^\circ$) extremes. However, this distortion should have little effect on the magnetic properties of the $^5T_{2g}$ term, unless the orbital degeneracy is lifted e.g. by an

\[ \uparrow \text{Measurement of the moment above 230 K was not possible due to instrumental difficulties.} \]

\[ \dagger\dagger \text{The Fe}^{2+} \text{ free ion value for the spin-orbit coupling constant is } \lambda = -100 \text{ cm}^{-1}. \]
Figure 2.36
Splitting diagram for the $^5T_{2g}$ ground term from the 3d$^6$ configuration in a weak field.

Figure 2.37
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Fe sar](CF$_3$SO$_3$)$_2$. 
axial distortion of an amount much greater than the spin-orbit coupling constant.\textsuperscript{90}

Readdressing the case of [Fe(NH\textsubscript{3})\textsubscript{2}sar]\textsuperscript{4+}, the effective magnetic moment is insensitive to temperature from 230 K until \(\approx 40\) K (Figure 2.34). However, the moment falls by almost 1 B.M. at temperatures < 40 K, to a value below the spin-only value (i.e. \(\mu_{\text{eff}}(4.2\) K) = 4.44 B.M.). This suggests that the action of zero-field splitting is giving rise to a non-magnetic sub-level (\(M_S = 0\)) lying lowest.

This interpretation would not be unexpected for a high-spin Fe(II) complex in which there is appreciable zero-field splitting of the ground state. For example, if the axial distortion shown in Figure 2.31 is large enough to give a \(^5B_2\) state lying lowest, then zero-field splitting of the ground \(S = 2\) multiplet would be as shown in Figure 2.36.

The magnetic moment of the [Fe sar](CF\textsubscript{3}SO\textsubscript{3})\textsubscript{2} complex follows the same temperature dependence as that just described for [Fe(NH\textsubscript{3})\textsubscript{2}sar]\textsuperscript{4+} complex except that the \(\mu(T)\) curve is shifted down the moment axis (Figure 2.37). At 230 K the \(\mu_{\text{eff}} = 5.15\) B.M., and the action of zero-field splitting lowers the moment to 3.82 B.M. at 4.2 K. Although an impurity could result in a lowering of the moment, the complexity of the splitting diagram for the \(^5T_{2g}\) term and the variability in published values for high-spin Fe(II) complexes indicates caution should be observed to prevent over-interpretation of these data (cf. references 64, 74, 75). The complex is clearly high-spin and the data agree with a spin-orbit coupled \(^5T_{2g}\) ground state behaviour.

Table 2.6 illustrates well the variance in the magnetic data obtained for a series of similar high spin tris(1,2-diaminoethane)iron(II) complexes.\textsuperscript{91}
The magnetic moment of the $[\text{Fe(en)}_3]^{2+}$ chloride and bromide salts actually increases as the temperature is lowered, as predicted, whereas the moment for the iodide salt decreases at lower temperatures. The data for the chloride and bromide salts has been interpreted using a Figgis-type model which gives the moment as a function of the spin-orbit coupling constant, $\lambda = -100 \text{ cm}^{-1}$, the
delocalization parameter, $k = 0.7$, and a distortion parameter, $v$, (where $v = (\delta t_{2g}/\lambda) = 0$). The iodide salt did not fit the model, as the moment was lower than the calculated values. Some other examples of high-spin Fe(II) complexes are presented in Table 2.7, together with the Fe(II) cage data.

Finally, the complex $[\text{Fe(CH}_3\text{sar}^2]^+$ was prepared for solution studies and although not included in the solid state measurements, can qualitatively be regarded as another high-spin Fe(II) cage. This prediction is based on the lack of absorption in the visible region, as the other high-spin Fe(II) complexes exhibit electronic transitions in the range $10,000 - 12,000 \text{ cm}^{-1}$.

### Table 2.7

Magnetic moments and Weiss constants for some Fe(II) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{\text{eff}}$ at 300K, B.M.</th>
<th>$\mu_{\text{eff}}$ at 4.3K, B.M.</th>
<th>Temperature Range, K</th>
<th>$\theta$, K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe(NH}_3^2\text{sar}]\text{Br}_2\text{Cl}_2\cdot4\text{H}_2\text{O}$</td>
<td>5.42$^b$</td>
<td>4.44</td>
<td>230-4.3</td>
<td>1.5</td>
<td>this work</td>
</tr>
<tr>
<td>$<a href="%5Ctext%7BCF%7D_3%5Ctext%7BSO%7D_3">\text{Fe sar}</a>_2$</td>
<td>5.15$^b$</td>
<td>3.82</td>
<td>230-4.3</td>
<td>-</td>
<td>this work</td>
</tr>
<tr>
<td>$[\text{Fe(en)}_3][\text{Fe}_2(\text{CO})_8]^a$</td>
<td>5.36</td>
<td></td>
<td>294-90</td>
<td>-2</td>
<td>54</td>
</tr>
<tr>
<td>$[\text{Fe(NH}_3^6][\text{Fe}_2(\text{CO})_8]^a$</td>
<td>5.45</td>
<td></td>
<td>292-77</td>
<td>-5</td>
<td>54</td>
</tr>
<tr>
<td>$[\text{Fe py}_6]I_6$</td>
<td>5.51</td>
<td></td>
<td>293-77</td>
<td>-2</td>
<td>54</td>
</tr>
</tbody>
</table>

$^a$ Anion diamagnetic

$^b$ Measured at 230 K.
$[\text{Co(NO}_2\text{)}_2\text{char}]^{3+}$

[34]
The low-spin $d^6$ Configuration

The isolation of the $[\text{Fe} (\text{NH}_2)_2 \text{sar}] (\text{CF}_3 \text{SO}_3)_2$ complex as deep blue crystals indicated strong electronic transitions in the visible region and suggested the magnetic behaviour differed from that of the high-spin Fe(II) cage complexes. The susceptibility of the complex, measured at 293 K, was $\chi = -3 \times 10^{-7}$ cm$^3$ gm$^{-1}$, i.e. the six electrons are paired in the $t_{2g}$ subset.

The diamagnetic nature of the complex raises questions regarding the subtle nature of the lattice forces in the crystal, as the same nuclear charge and ligand field is present as for the two high-spin complexes. However, the measurement of magnetic moments in solution (cf. Chapters Three and Four) indicate the close proximity of the Fe(II) cages to the crossover region. Thus, small distortions in geometry or electronic delocalization could result in the $[\text{Fe} (\text{NH}_2)_2 \text{sar}]^{2+}$ complex favouring a $1_{A_{1g}}$ ground term.

It is of interest to note that the complex $[\text{Fe} ([9] \text{aneN}_3)_2] \text{Br}_2 \cdot 3 \text{H}_2 \text{O}$, containing six saturated amine donor atoms, is diamagnetic. However, removal of the water of crystallization yields a paramagnetic sample with a temperature-dependence of susceptibility which suggests a spin-crossover.

2.4.7 The 3$d^7$ Configuration

Five cage complexes with the 3$d^7$ configuration have been included in this section. The $[\text{Ni} \text{sar}]^{3+}$, $[\text{Co} \text{sar}]^{2+}$ and $[\text{Co} (\text{NH}_3)_2 \text{sar}]^{4+}$ complexes are those originally studied to define the magnetic properties of the 3$d^7$ configuration. In addition, the subsequent availability of two further examples of the cobalt(II) ion encapsulated by ligands similar to sarcophagine extended the range of $d^7$-cages studied.
Figure 2.38
Splitting diagram for the 3d⁷ (t²g⁵ e_g²) configuration in a weak field.

Figure 2.39
Splitting diagram of the ⁴T₁g term by spin-orbit coupling.
The first example is $\text{A(1e1)3-[Co(NO_2)_{2}\text{char}](ClO_4)_2\cdot2H_2O}$ [34], a complex which consists of a cage with 1,2-diaminocyclohexane units in place of the 1,2-diaminoethane of the sar-type ligand and which also contains nitro substituents at the two apical "cap" sites.

Cage complexes containing three sulphur and three nitrogen donor atoms were discussed in Section 1.7 of Chapter One and provide the second example. Although the room temperature moment of $[\text{Co(aza)capten}](\text{CF}_3\text{SO}_3)_2$ [27], has been reported, it was of interest to extend this measurement to a range of temperatures. The mixed donor atoms alter the ligand field significantly within the cage environment, and low-spin Co(II) is observed.

**The high-spin $d^7$ Configuration**

The $^4F$ free ion spectroscopic state, is split in an octahedral crystal field with a $^4T_{1g}$ ground term and excited $^4T_{2g}$ and $^4A_{2g}$ states lying in ascending order of energy. The splitting of the ground term in the presence of an axial crystal field and spin-orbit coupling is illustrated in Figure 2.38 and 2.39. The orbital angular momentum in the $^4T_{1g}$ ground term causes the effective magnetic moment to be raised considerably above the spin-only value ($\mu_{SO} = 3.87$ B.M.), and is expected to be about 5.2 B.M. at 300 K with an appreciable dependence on temperature. Room temperature moments, observed to lie below this value, are usually associated with a symmetry lower than octahedral, the most common deformation arising from axial distortions (cf. Figure 2.38). For pseudo-octahedral geometries, the moment is calculated to decrease to $\mu_{eff} = 3.8$ B.M. at 0 K, and zero-field splitting could result in a further reduction in the moment.

The air-sensitive nature of the Co(II) cage complexes provided experimental difficulties similar to those found with the Fe(II) cage.
Figure 2.40
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Co(NH$_3$)$_2$sar]Cl$_4$.5H$_2$O.

Figure 2.41
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Co(NH$_3$)$_2$sar](ZnCl$_4$)$_2$. 
complexes (cf. Section 2.4.6). Therefore, the magnetic purity of the [Co(NH\textsubscript{3})\textsubscript{2}sar]\textsuperscript{4+} complex was ascertained by checking the reproducibility of $\chi(T)$ for a number of different salts and preparations. The chloride and zinc tetrachloride salts gave similar results and both were typical for a high-spin $d^7$ system with a $^4T_{1g}$ ground term; i.e. both complexes showed an increase in the magnetic moment as the temperature was lowered below 300 K, reaching a maximum value at \(\approx 100\) K and then decreasing as the temperature is lowered further (Figures 2.40 and 2.41). The room temperature moments of ca. 4.5 B.M. lie above the spin-only value of 3.87 B.M. as anticipated, i.e. they have a significant orbital contribution to the moment. The $^4T_{1g}$ ground term and the usual value of the spin-orbit coupling constant for the Co(II) ion, $\lambda = -170$ cm\textsuperscript{-1}, is expected to result in a magnetic moment of about 5.2 B.M. (at 300 K). The somewhat reduced value can be attributed to symmetry lower than octahedral for the Co(II) cage complexes, i.e. an axial distortion could yield an orbital singlet, $^4A$ ground term (cf. Figure 2.38) and account for the observed lowering of the magnetic moment below 5.2 B.M.

The X-ray crystal structure for [(NH\textsubscript{3})\textsubscript{2}sar](NO\textsubscript{3})\textsubscript{4}\textsuperscript{2-}H\textsubscript{2}O, confirms the presence of a significant distortion from octahedral symmetry, with a trigonal twist angle, $\phi = 29^\circ$.

The magnetic moment for the nitrate salt of [Co(NH\textsubscript{3})\textsubscript{2}sar]\textsuperscript{4+}, varied in a similar manner to that of the chloride and tetrachlorozincate salts, over the same temperature range (Figure 2.42). However, the curve is displaced to higher moments with a room temperature moment of 4.95 B.M., rising to 5.21 B.M. (at 100 K), then falling to 4.69 B.M. (at 4.2 K). For a second preparation of the chloride salt, the shape of the moment versus temperature curve was
Figure 2.42
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Co(NH$_3)_2$sar](NO$_3$)$_4$.

Figure 2.43
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Co sar][ZnCl$_4$].
similar; however, at 240 K, $\mu_{\text{eff}} = 4.83$ B.M. which drops to $\mu_{\text{eff}} = 4.46$ B.M. at 4.3 K.

The magnetic behaviour of the [Co sar](ZnCl$_4$) complex agrees well with that observed for the [Co(NH$_3$)$_2$sar]$^{4+}$ complexes (chloride and tetrachlorozincate salts) with $\mu_{\text{eff}}(215 \text{ K})^\dagger = 4.42$ B.M. decreasing to $\mu_{\text{eff}} = 3.82$ B.M. at 4.2 K (Figure 2.43).

The data presented so far, indicate that although the overall shapes of the $\mu(T)$ curves are similar, significant variations in moment values do occur, which present some difficulties in the detailed interpretation. The $\Delta(1e_l)_3-[\text{Co(NO}_2)_2\text{char}](\text{ClO}_4)_2\cdot2\text{H}_2\text{O}$ complex was included in this study in an attempt to extend the range of Co(II) cages studied and also, in the hope that the variation of data obtained for the sar-type complexes could be understood better. The data obtained for this complex were viewed in light of possible differences between it and the Co(II) sar-type cages, i.e. electron withdrawing nature of the apical substituents and structural variations caused by the conformational rigidity of the cyclo-hexane rings.

At room temperature, $\Delta(1e_l)_3-[\text{Co(NO}_2)_2\text{char}]^{2+}$ exhibits a magnetic moment, $\mu_{\text{eff}} = 4.73$ B.M., which increases to 4.80 B.M. as the temperature is lowered to $\approx 140$ K and then falls to 4.16 B.M. at 4.2 K (Figure 2.44). This behaviour is similar to that observed for the sar-type cages.

The magnetic behaviour of the Co(II) cage complexes discussed so

$\dagger$ Instrumental difficulties restricted the measurement of moments above 240 K.

$\ddagger$ Instrumental difficulties restricted the measurement of moments above 215 K.
Variation of the magnetic moment and reciprocal susceptibility with temperature for $\Delta(\text{lel})_2\text{[Co(NO}_2\text{)}_2\text{char]}(\text{ClO}_4)_2\text{.2H}_2\text{O}$. 

Figure 2.44
far, are all characterized by a similar strong dependence of the moment on temperature. Unfortunately, the splitting diagrams for the \( ^4T_{1g} \) term (Figures 2.38 and 2.39) do not assist greatly in the detailed fitting of the data except to indicate that the susceptibility is anticipated to be temperature dependent.

Attempts were made to fit the data using a parametric model which included the simultaneous perturbation by spin-orbit coupling and by axial ligand field distortions. Unfortunately, it was not possible to obtain an unambiguous choice of parameters. In fact, the difficulties of interpreting the \( \chi(T) \) behaviour of the cobalt(II) ion is clearly illustrated by a review which included 32 examples of magnetically dilute complexes with formally octahedral geometry, and room temperature moments that ranged from 4.25 - 5.90 B.M. The authors attributed this "large spread" of values (in part, at least) to distortions in crystal symmetry which, should influence the magnitude of the orbital contribution and also the splitting of the \( ^4T_{1g} \) ground term (i.e. a larger splitting yielding a lower magnetic moment value).

The cobalt(II) cage data could possibly be rationalized in terms of the presence of a significant orbital quenching occurring at room temperature which appears to be gradually removed as the temperature falls to ca. 100 - 120 K. At temperatures below 100 K the moment drops towards the spin-only moment. This hypothesis is, however, in conflict with one postulated by Figgis and Nyholm where they presumed the orbital contribution is maintained unchanged by variation in temperature for several compounds studied. However, the temperature range they employed was significantly less than that used for our study and could account for this discrepancy.

In view of the variations found in the \( \mu(T) \) behaviour for the
Figure 2.45

Origin of the $^2E$ ground term for the low-spin $3d^7$ configuration.
Co(II) cages, the purity of the samples must be considered. All samples were analytically pure prior to measurement; however, the cobalt(II) complexes are sensitive to oxidation. If oxidation has occurred prior to, or during measurement of the moment, the moment is likely to be reduced with the creation of diamagnetic cobalt(III) in the lattice. The stability of the cobalt(II) complexes over a five hour period was examined using a sample of the chloride salt of the [Co(NH$_3$)$_2$sar]$^{4+}$ complex. During this period of time no change was observed in the value of the magnetic moment, nor was sample decomposition found to occur, i.e. \( \mu_{\text{eff}}(\text{ca. } 300 \text{ K}) = 4.8 \pm 0.1 \text{ B.M.} \).

Although, considerable diversity has been found in the magnetic moment values and temperature dependence for the Co(II) cages, they are compatible with the behaviour expected for a pseudo-octahedral geometry. It is useful to compare the magnetic characteristics of these ions with other hexaamine complexes with similar geometry and electronic features. For convenience, the moments of the cobalt(II) cages, included in the above discussion, are restated and tabulated with other examples in Table 2.8.

**The low-spin \( d^7 \) Configuration**

In an octahedral field, the low-spin \( d^7 \) ion with a free ion \( ^2G \) ground state gives rise to a \( ^2E_g \) term lying lowest with excited states in ascending order \( ^2T_{1g}, ^2T_{2g}, ^2A_{1g} \) and \( ^2A_{2g} \) well above the ground term. The \( ^2E \) term has no orbital angular momentum and remains unaffected by spin-orbit coupling (to first order) to give a pair Kramers' doublets (Figure 2.45).

Although cage complexes containing the \( N_3S_3 \) chromophore are not directly related to this study, the report\(^{93}\) of a low-spin cobalt(II) cage complex \( (\mu_{\text{eff}} \text{ at } 300 \text{ K} = 1.89 \text{ B.M.}) \) is of interest for this work. The occurrence of a low-spin configuration for cobalt(II) and
### TABLE 2.8

Magnetic moments and Weiss constants for Co(II) Hexaamines.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{\text{eff}}$ at 300 K, B.M.</th>
<th>$\mu_{\text{eff}}$ at 80 K, B.M.</th>
<th>$\mu_{\text{eff}}$ at 4.3 K, B.M.</th>
<th>$\theta$, K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><a href="ZnCl$_4$">Co(NH$_3$)$_2$sar</a>$_2$</td>
<td>4.47</td>
<td>4.60</td>
<td>4.11</td>
<td>-0.7</td>
<td>this work</td>
</tr>
<tr>
<td>[Co(NH$_3$)$_2$sar]Cl$_4$·5H$_2$O (#1)</td>
<td>4.47</td>
<td>4.52</td>
<td>4.05</td>
<td></td>
<td>this work</td>
</tr>
<tr>
<td>[Co(NH$_3$)$_2$sar]Cl$_4$·5H$_2$O (#2)</td>
<td>4.83$^a$</td>
<td>4.79</td>
<td>4.46</td>
<td>2.4</td>
<td>this work</td>
</tr>
<tr>
<td><a href="NO$_3$">Co(NH$_3$)$_2$sar</a>$_4$</td>
<td>4.95</td>
<td>5.17</td>
<td>4.69</td>
<td>-2.2</td>
<td>this work</td>
</tr>
<tr>
<td><a href="ZnCl$_4$">Co sar</a></td>
<td>4.42$^b$</td>
<td>4.26</td>
<td>3.82</td>
<td></td>
<td>this work</td>
</tr>
<tr>
<td>$\Delta$(lel)$_3$-<a href="ClO$_4$">Co(NO$_2$)$_2$char</a>$_2$·2H$_2$O</td>
<td>4.73</td>
<td>4.71</td>
<td>4.16</td>
<td></td>
<td>this work</td>
</tr>
<tr>
<td>[Co([9]aneN$_3$)$_2$]Cl$_2$</td>
<td>4.8</td>
<td></td>
<td></td>
<td></td>
<td>86</td>
</tr>
<tr>
<td>[Co(NH$_3$)$_6$]Cl$_2$</td>
<td>4.96</td>
<td></td>
<td></td>
<td></td>
<td>96</td>
</tr>
<tr>
<td>[Co(NH$_3$)$_6$]SO$_4$</td>
<td>5.90</td>
<td></td>
<td></td>
<td></td>
<td>27 98</td>
</tr>
<tr>
<td>[Co(en)$_3$]Cl$_2$</td>
<td>3.82</td>
<td></td>
<td></td>
<td></td>
<td>96</td>
</tr>
<tr>
<td>[Co(en)$_3$]SO$_4$</td>
<td>4.56</td>
<td></td>
<td></td>
<td></td>
<td>15 98</td>
</tr>
<tr>
<td><a href="ClO$_4$">Co(phen)$_3$</a>$_2$</td>
<td>4.7</td>
<td>5.54$^c$</td>
<td>4.25$^d$</td>
<td>3.50</td>
<td>11 95</td>
</tr>
<tr>
<td><a href="ClO$_4$">Co(bipy)$_3$</a>$_2$</td>
<td>4.83</td>
<td>4.52</td>
<td>4.47$^d$</td>
<td>3.97</td>
<td>94 97</td>
</tr>
</tbody>
</table>

a Measured at 240 K,  
b Measured at 215 K,  
c Measured at 90 K,  
d Measured at 77 K,  

with amine donor atoms is extremely rare, with those known, usually not completely characterized (cf. reference 99). In fact Ballhausen comments$^{100}$ that for octahedral coordination, a value of $10 \ Dq > 15,000 \ \text{cm}^{-1}$ is required for a low-spin divalent metal ion of the
Figure 2.46
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Co(aza)capten](CF₃SO₃)₂.
first row transition series, and predicts only the cyanide ligand would fulfill this requirement.

The magnetic moment of \([\text{Co(aza)capten}]^{2+}\) at room temperature, was re-measured and compared with the published value; \(\mu_{\text{eff}}(296 \text{ K}) = 2.04 \text{ B.M. (cf. } \mu_{\text{eff}}(298 \text{ K}) = 1.89 \text{ B.M. and in } D_2O \text{ solution}\mu_{\text{eff}}(301 \text{ K}) = 2.35 \text{ B.M.)}^{93}\). Over the temperature range 300 K to 4.2 K the moment falls linearly with temperature to the spin-only value of 1.73 B.M. (Figure 2.46). The \(S = 1/2\) spin system is expected to give moments of about 1.80 + 1.85 B.M., as found with hexanitrocobaltates(II).^{74}

The low-spin configuration observed for \([\text{Co(aza)capten}]^{2+}\), warrants some discussion of the relative strength of the ligand fields for the \(\text{Co(II)N}_3\text{S}_3\) and the high-spin \(\text{Co(II)N}_6\) type cages. The \(\text{Co(III)}\) derivatives are both low-spin; with the first ligand field transition, \( ^1T_2g + ^1A_1g\), for each occurring at similar energies.^{20,32} This indicated that,

\[
(10 \text{ Dq} - 4 \text{ B})_{\text{N}_6} = (10 \text{ Dq} - 4 \text{ B})_{\text{N}_3\text{S}_3}
\]

It is anticipated that replacement of nitrogen by sulphur should lead to a decrease in the Racah parameter, \(B\),^{122} so that, if \(B_{\text{N}_3\text{S}_3} < B_{\text{N}_6}\), the \((10 \text{ Dq})_{\text{N}_3\text{S}_3} < (10 \text{ Dq})_{\text{N}_6}\). For example, if \(4B_{\text{N}_6}\) is assumed to be 5000 cm\(^{-1}\) and \(4B_{\text{N}_3\text{S}_3} = 3000 \text{ cm}^{-1}\), then \((10 \text{ Dq})_{\text{N}_6} = 21,000 \text{ cm}^{-1}\) compared with \((10 \text{ Dq})_{\text{N}_3\text{S}_3} = 19,000 \text{ cm}^{-1}\), i.e. of significantly different ligand field strengths. Returning to the \(\text{Co(II)}\) cages, it seems likely that the low-spin configuration observed for the \(\text{Co(II)N}_3\text{S}_3\) cage may not arise from an increase in the ligand field parameter, 10 Dq, but rather from a substantial reduction \(B\), for \(\text{Co(II)N}_3\text{S}_3\) compared with \(\text{Co(II)N}_6\). Interestingly, this interpretation contrasts with that of Wieghardt et al.,^{86,92} where
$[\text{M([9]aneN}_3)_2]^{n+}$

[35]
the change from high-spin \( \mu_{\text{eff}} = 4.8 \ \text{B.M.} \) for \([\text{Co([9]aneN}_3)_2]\text{Cl}_2 \) \[35\] to the low-spin \( \mu_{\text{eff}} = 1.82 \ \text{B.M.} \) for \([\text{Co([9]aneS}_3)_2](\text{BF}_4)_2\) \( \text{Co(II)S}_6 \), was attributed solely to an increase in ligand field strength.

Encapsulation of the nickel(III) ion by the sar ligand, provided an opportunity to examine the low-spin \( d^7 \) configuration with the \( N_6 \) donor ligand.

The magnetic moment of \([\text{Ni sar}](\text{CF}_3\text{SO}_3)_3\) has only been measured at room temperature, with a value of \( \mu_{\text{eff}} = 2.36 \ \text{B.M.} \) obtained. However, some field dependence of the moment was observed with this sample, and attempts to further purify the complex have not yet been successful.

The low-spin character of the \([\text{Ni sar}]^{3+}\) ion contrasts the high-spin \([\text{Co sar}]^{2+}\) and reflects the influence on 10 \( D_q \) of the higher charge of the nickel(III) ion.

ESR measurements confirm the low-spin description for \([\text{Ni sar}]^{3+}\), and in addition indicate anisotropy in the \( g \) values. Using powder samples at 4.2 K, the values \( g_x = 2.113 \) and \( g_y = g_z = 2.04 \) with indications of a small rhombic splitting of the \( y \) and \( z \) lines were obtained. Comba suggested that the unpaired electron resides in an orbital chiefly \( d_{z^2} \) in character i.e. a \( ^2A_1 \) ground state.\[58\]

The lack of available low-spin data for comparison is not unexpected since the isolation of stable nickel(III) complexes is still rare and their magnetic characterization even more elusive. However, the report\[86\] of a hexaamine complex, \([\text{Ni([9]aneN}_3)_2](\text{ClO}_4)_3\), with a moment of 2.0 B.M. at 293 K agrees well with the observed behaviour of the nickel(III) cage.
Figure 2.47
Splitting diagram for the $3d^6 \ (t_{2g}^6 e_g^2)$ configuration in a weak ligand field.
2.4.8 The 3d$^8$ Configuration

In an octahedral field, the free Ni$^{2+}$ ion ground term, $^3F$ is split into a $^3A_{2g}$ ground term with excited $^3T_{2g}$ and $^3T_{1g}$ terms lying above it (Figure 2.47). The presence of an axial field has no effect on the $^3A_{2g}$ term but lifts the degeneracy of the excited orbital triplets into a singlet and doublet. However, spin-orbit coupling partially lifts the three-fold spin degeneracy of the ground term giving a small zero-field splitting, usually 1 - 2 cm$^{-1}$ (Figure 2.47). This has very little effect on the magnetic moment except at very low temperatures. If zero-field splitting is ignored, the effective magnetic moment is given by Equation 19,

$$\mu_{\text{eff}} = 2.83(1 - \frac{4\lambda}{10Dq}) \quad \ldots(19)$$

and is expected to remain essentially independent of temperature.

If $\lambda = -315$ cm$^{-1}$ (free ion value) and $10Dq$ ca. 8000 - 10,000 cm$^{-1}$, magnetic moments are expected to lie in the range, 3.1 - 3.4 B.M.

The cage complexes of nickel(II), i.e. [Ni(NH$_3$)$_2$sar](ClO$_4$)$_4$·2H$_2$O and [Ni sar](ClO$_4$)$_2$ each display magnetic properties expected of the $^3A_{2g}$ ground term in pseudo-octahedral geometry (cf. Table 2.10). The magnetic moments at 300 K, are raised somewhat above the $S = 1$ spin-only value, as anticipated, through spin-orbit coupling, and second-order Zeeman effects. With the decrease in temperature, the moment remains essentially unchanged except for small decreases below 50 K (Figures 2.48 and 2.49). The linear dependence of $1/\chi$ versus $T$, suggests that these Curie paramagnets would be suitable magnetochemical calibrants for temperature and susceptibility measurements.

As in the cases for the other A-ground state ions, Cr(III) and Mn(II), the susceptibility data have been fitted using the spin
Figure 2.48
Variation of the magnetic moment and the reciprocal susceptibility with temperature for \([\text{Ni(NH}_3]_2\text{sar}][\text{ClO}_4]_4\cdot2\text{H}_2\text{O}\).

Figure 2.49
Variation of the magnetic moment and the reciprocal susceptibility with temperature for \([\text{Ni sar}][\text{ClO}_4]_2\).
Figure 2.50
Splitting diagram for the $3d^8$ configuration in a weak/medium ligand field.
Figure 2.51
Magnetic moment vs. temperature for $[\text{Ni(NH}_3\text{)}_2\text{sar}]^{4+}$, fitted with a zero-field splitting, $D = 1.1$ cm$^{-1}$.
Hamiltonian formalism. In this case, the $S = 1$ ground state splits into $M_S = \pm 1$ and 0 sub-levels, separated by $D$ in zero-field through mixing by spin-orbit interaction with components of the excited $^3T_{2g}$ state, the latter is also split by axial ligand-field distortion (Figure 2.50). The data are not sensitive enough to detect any lower symmetry rhombic, $E$, component of the ligand field.

The susceptibility data for the $[\text{Ni(NH}_3\text{)}_2\text{sar}]^{4+}$ complex were fitted using the computer program COM/MAG. The spin-orbit coupling constant, $\lambda$, and orbital reduction factor, $k$, where $\lambda = -260$ cm$^{-1}$ and $k = 0.71$ gave a good fit from 300 K to 15 K (Figure 2.51) and resulted in $D = 1.1$ cm$^{-1}$ (Table 2.9).

**TABLE 2.9**

Zero-field splitting and $g$ values calculated for $[\text{Ni(NH}_3\text{)}_2\text{sar}](\text{ClO}_4)_4\cdot 2\text{H}_2\text{O}$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$g$</th>
<th>$D_{zz}$ cm$^{-1}$</th>
<th>Temperature Range of Best Fit, K</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Ni(NH}_3\text{)}_2\text{sar}]$ (ClO$_4$)$_4\cdot 2$H$_2$O</td>
<td>2.0$^a$</td>
<td>1.1</td>
<td>300 $\rightarrow$ 15</td>
<td>Magnetism</td>
</tr>
<tr>
<td></td>
<td>2.13</td>
<td>1.7</td>
<td>300 $\rightarrow$ 4.3</td>
<td>Magnetism</td>
</tr>
<tr>
<td></td>
<td>2.12</td>
<td>1.63</td>
<td>$&lt; 50$</td>
<td>Magnetism</td>
</tr>
<tr>
<td></td>
<td>2.17</td>
<td>-2.89$^b$</td>
<td>300</td>
<td>Visible Spectrum</td>
</tr>
</tbody>
</table>

  | $-1.82$ |

  $^a$ $g$ was held at this value.

  $^b$ where $\zeta = 500$ cm$^{-1}$ was used in Equation 20 for the calculation of $D$.

However, a better fit was obtained by using a spin Hamiltonian similar to that described earlier in Equation 12. Over the entire temperature range the best fit yielded values for $g = 2.13$ and $D = 1.7$ cm$^{-1}$ (Figure 2.52). As the zero-field splitting parameter is most sensitive in the low temperature region, the temperature range
Figure 2.52
Magnetic moment vs. temperature for [Ni(NH$_3$)$_2$sar]$^{4+}$, fitted to Equation 12 with $g = 2.13$ and $D = 1.7$ cm$^{-1}$.

Figure 2.53
Magnetic moment vs. temperature for [Ni(NH$_3$)$_2$sar]$^{4+}$, fitted to Equation 12 with $g = 2.12$ and $D = 1.63$ cm$^{-1}$ for $T < 50$ K.
< 50 K was fitted independently and gave values for $g = 2.12$ and $D = 1.63 \text{ cm}^{-1}$ (Figure 2.53, Table 2.9). Using the latter set of parameters the high temperature region is however, underestimated by ca. 0.02 B.M..

Using the electronic absorption spectrum for $[\text{Ni(NH}_3)_2\text{sar}]^{4+}$, it is possible to estimate a value of $D$, by applying the energies of the $^3E, ^3B_2(^3T_2g) + ^3A_{2g}$ bands (i.e. 12,420 and 11,390 cm$^{-1}$) together with the single-electron spin-orbit coupling parameter for Ni$^{2+}$, $\zeta = 630 \text{ cm}^{-1}$, to the expression$^{101}$

$$D = \zeta^2 \left( \frac{1}{E(^3E)} - \frac{1}{E(^3B_2)} \right) \quad \ldots(20)$$

The values obtained for $D$, agreed well with those obtained using the susceptibility data (cf. Table 2.9).

In addition, the $g$ values, calculated from the fitting of the susceptibility data can be compared to $g = 2.17$ calculated from

$$g = (2.0023 - \frac{8\lambda}{10 \text{ Dq}}) \quad \ldots (21)$$

where $\lambda = -\zeta/2S$ and $10 \text{ Dq} = 11,733 \text{ cm}^{-1}$ for $[\text{Ni(NH}_3)_2\text{sar}]^{4+}$ (cf. Table 2.9).

The small values for $D$ obtained in these analyses are probably due to a symmetry field lower than octahedral. Both nitrate and chloride salts of the $[\text{Ni(NH}_3)_2\text{sar}]^{4+}$ ion have been studied by X-ray crystallography.$^{49a}$ The Ni-N distances in the NiN$_6$ chromophore of the nitrate salt are essentially equal ($2.11 \pm 0.01 \text{ Å}$), whereas, the chloride salt has two Ni-N bonds shorter than the other four, ($2 \times 2.08 \pm 0.01 \text{ Å}$ and $4 \times 2.12 \pm 0.01 \text{ Å}$). These differences arise from
the different orientations of the chelate rings as the chloride salt is \((\text{lel})_2\text{(ob)}\), while the nitrate salt is \((\text{lel})_3\).^{49a} However, the trigonal twist angles for the two complex salts are identical, with \(\phi = 46 \pm 1^\circ\).

Although, no magnetic measurements have been obtained for \([\text{Ni sep}]\text{(ClO}_4\text{)}_2\), the X-ray crystal structure has been determined, together with its optical spectrum. The optical spectrum, indicates octahedral coordination, and is discussed further in Chapter Three. The structure indicates six essentially equivalent Ni-N bond lengths, \(2.10 \pm 0.01\ \text{Å}\), identical to those in \([\text{Ni(NH}_3\text{)}_2\text{sar}]\text{(NO}_3\text{)}_4\).^{46}

A wealth of magnetic data has been acquired for Ni(II) hexaamine complexes, over a wide range of temperatures. Some examples are now considered to compare their magnetic behaviour with the Ni(II) cages.

The \([\text{Ni(en)}_3]\text{(NO}_3\text{)}_2\) complex has been subject to rigorous magnetic analysis using average susceptibility magnetization and magnetic (single crystal) anisotropy measurements.\(^{60}\) The average magnetic moment, \(\mu_{\text{eff}} = 3.08 \pm 0.02\ \text{B.M.}\) is independent of temperature from 300 - 30 K then falls to ca. 2.2 B.M. from 30 - 4.2 K. Crystallographic data show the coordination geometry about the nickel(II) ion is considerably distorted from octahedral symmetry both by compression along the three fold axis and a twist towards trigonal prismatic coordination. The authors concluded that their results were however, insensitive to the trigonal distortion but calculated \(D = -0.65\ \text{cm}^{-1}\).

Crystallographic comparisons between \([\text{Ni(en)}_3]^{2+}\) and the Ni(II) cages, indicate the \([\text{Ni(en)}_3]^{2+}\) complex is significantly more distorted than the cages. This appears to be reflected in the somewhat lower magnetic moment observed for \([\text{Ni(en)}_3]^{2+}\), \(\mu_{\text{eff}} = 2.2\) B.M., than those for the cages, \([\text{Ni(NH}_3\text{)}_2\text{sar}]^{4+}\), \(\mu_{\text{eff}} = 2.88\) B.M.
Figure 2.54
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Cu(NH$_3$)$_2$sar]Cl$_4$.2H$_2$O.

Figure 2.55
Variation of the magnetic moment and the reciprocal susceptibility with temperature for [Cu sar](ClO$_4$)$_2$. 
and \([\text{Ni sar}]^{2+}\), \(\mu_{\text{eff}} = 2.95\) B.M. at 4.2 K.

The moments of some other examples of nickel(II) hexaamine complexes are tabulated (Table 2.10), together with the Ni(II) cages.

**TABLE 2.10**

Magnetic moments and Weiss constants for Ni(II) hexaamines.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\mu_{\text{eff}}) at 300 K, B.M.</th>
<th>(\theta), K</th>
<th>Temperature range, K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Ni(NH}_3)_2\text{sar}]\text{(ClO}_4\text{)}_4\cdot2\text{H}_2\text{O})</td>
<td>3.03</td>
<td>1.5</td>
<td>4.3 + 297</td>
<td>this work</td>
</tr>
<tr>
<td>([\text{Ni(sar)}]\text{(ClO}_4\text{)}_2)</td>
<td>3.06</td>
<td>1.5</td>
<td>4.3 + 297</td>
<td>this work</td>
</tr>
<tr>
<td>([\text{Ni(NH}_3)_6\text{]}\text{Cl}_2)</td>
<td>3.04</td>
<td>9</td>
<td>4 + 300</td>
<td>102</td>
</tr>
<tr>
<td>([\text{Ni(en)}_3\text{(NO}_3\text{)}_2)</td>
<td>3.03</td>
<td>1.8</td>
<td>2.01 + 300</td>
<td>60</td>
</tr>
<tr>
<td>([\text{Ni(9} \text{aneN}_3\text{)}_2\text{(ClO}_4\text{)}_2)</td>
<td>2.80</td>
<td></td>
<td>300</td>
<td>103</td>
</tr>
<tr>
<td>([\text{Ni dtne}\text{(ClO}_4\text{)}_2\cdot2\text{H}_2\text{O})</td>
<td>3.1</td>
<td></td>
<td>300</td>
<td>87</td>
</tr>
</tbody>
</table>

### 2.4.9 The 3d⁹ Configuration

Both \([\text{Cu(NH}_3)_2\text{sar}]\text{Cl}_4\cdot6\text{H}_2\text{O}\) and \([\text{Cu sar}]\text{(ClO}_4\text{)}_2\) display magnetic moments as a function of temperature which are typical of \(S = 1/2\) Curie paramagnets (Figures 2.54 and 2.55). The room temperature moment is 1.91 B.M. for the sar complex and 1.92 B.M. for the di-ammonium derivative and they decrease to 1.79 B.M. and 1.89 B.M. respectively at 4.2 K.

The energy level diagram for the \(2D\) free Cu\(^{2+}\) ion in an octahedral field is shown in Figure 2.56. The \(^2E_g\) ground term which lies about 10,000 cm\(^{-1}\) below the excited \(^2T_{2g}\) state, is split into two singlets in a ligand field of tetragonal symmetry (Figure 2.56). The degeneracy of the excited state can also partially lifted
Free Octahedral Tetragonal ion field (elongation)

Figure 2.56
Splitting diagram for the $3d^9 (t_{2g}^6e_g^3)$ configuration.
in the lower symmetry. Although, the ground state of the 3d$^9$
configuration is effectively an orbital singlet, with an expected
spin-only moment of 1.73 B.M., "mixing-in" of the upper states with
the ground term by spin-orbit coupling increases the expected moments
to about 1.9 B.M. (Equation 22) since,

$$\mu_{\text{eff}} = 1.73 \left(1 - \frac{2\lambda}{10 D}\right)$$  \quad \text{(22)}

The spin degeneracy can not be removed by a zero-field splitting
mechanism, as the Kramers doublet can only be split by application of
an external magnetic field.

It is noteworthy that the origin of the tetragonal distortion is
usually via a Jahn-Teller mechanism. Elongation along the four-fold
axis of the octahedron will result in the $^2A_1$ level lying lowest,
whereas, compression will result in the $^2B_2$ lying lowest.

The $1/\chi$ versus $T$ plots, for $[\text{Cu(NH}_3)_2\text{sar}]^{4+}$ and $[\text{Cu sar}]^{2+}$, are
nearly linear, and suggest, as for the nickel(II) cages, that they
too could be employed as magnetic calibrants. The bulk
susceptibility data of the powdered samples do not reveal structural
or electronic distortions which become apparent in crystallographic
and ESR studies. There are three different Cu-N distances (2.046,
2.160, 2.290 Å) in the CuN$_6$ chromophore of $[\text{Cu(NH}_3)_2\text{sar}]^{4+}$. It is
hard to say whether such distortions are dominated by Jahn-Teller or
ligand conformational effects, or both. A detailed ESR study has
revealed three g values for $[\text{Cu(NH}_3)_2\text{sar}]^{4+}$ and $[\text{Cu sar}]^{2+}$ arising
from rhombically distorted ligand fields, e.g. for $[\text{Cu(NH}_3)_2\text{sar}]^{4+}$,
g$_z = 2.22$, g$_x = 2.04$, g$_y = 2.069$, and $A_z = 138$ gauss, cf.
$[\text{Cu(en)}_3]^{2+}$, g$_z = 2.159$, g$_x = 2.053$, g$_y = 2.134$. The overall
electronic distortion is therefore tetragonal plus rhombic, and the
unpaired electron resides chiefly in an orbital of $d_{x^2-y^2}$ character.

There are many examples in the literature, of six-coordinate pseudo-octahedral amine complexes of copper(II) with magnetic moments which are similar to those observed in this work; some of these are listed in Table 2.11.

**TABLE 2.11**

Magnetic moments and Weiss constants for Cu(II) hexaamines.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{\text{eff}}$ at 300 K, B.M.</th>
<th>$\mu_{\text{eff}}$ at 80 K, B.M.</th>
<th>$\mu_{\text{eff}}$ at 4.3 K, B.M.</th>
<th>$\theta$, K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Cu(NH}_3)_2\text{sar}]\text{Cl}_4.6\text{H}_2\text{O}$</td>
<td>1.92</td>
<td>1.92</td>
<td>1.89</td>
<td>0.1</td>
<td>this work</td>
</tr>
<tr>
<td>$[\text{Cu sar}]\text{(ClO}_4)_2$</td>
<td>1.91</td>
<td>1.86</td>
<td>1.79</td>
<td>0.9</td>
<td>this work</td>
</tr>
<tr>
<td>$[\text{Cu dtne}]\text{(ClO}_4)_2$</td>
<td>2.2</td>
<td></td>
<td></td>
<td></td>
<td>87</td>
</tr>
<tr>
<td>$[\text{Cu([9]aneN}_3)_2\text{N}_2\text{O}_3)_2$</td>
<td>1.92</td>
<td></td>
<td></td>
<td></td>
<td>103</td>
</tr>
<tr>
<td>$[\text{Cu(NH}_3)_6]\text{Cl}_2$</td>
<td>1.87$^a$</td>
<td></td>
<td></td>
<td></td>
<td>104</td>
</tr>
<tr>
<td>$[\text{Cu(NH}_3)_6]\text{Br}_2$</td>
<td>1.85$^a$</td>
<td></td>
<td></td>
<td></td>
<td>104</td>
</tr>
<tr>
<td>$[\text{Cu(NH}_3)_6]\text{I}_2$</td>
<td>1.95</td>
<td></td>
<td></td>
<td></td>
<td>104</td>
</tr>
<tr>
<td>$[\text{Cu(phen)}_3]\text{(ClO}_4)_2$</td>
<td>1.91</td>
<td>1.96$^b$</td>
<td></td>
<td>-9</td>
<td>105</td>
</tr>
<tr>
<td>$[\text{Cu(bipy)}_3]\text{(ClO}_4)_2$</td>
<td>1.96</td>
<td>1.91$^b$</td>
<td></td>
<td>5</td>
<td>105</td>
</tr>
<tr>
<td>$[\text{Cu(en)}_3]\text{(CF}_3\text{CO}_2)_2.\text{H}_2\text{O}$</td>
<td>1.92</td>
<td></td>
<td></td>
<td></td>
<td>106</td>
</tr>
</tbody>
</table>

$^a$ Measured at 293 K.

$^b$ Measured at 90 K.

2.4.10 The $3d^{10}$ Configuration

The zinc(II) complexes, $[\text{Zn sar}](\text{CF}_3\text{SO}_3)_2$ and $[\text{Zn(NH}_3)_2\text{sar}]$ $(\text{CF}_3\text{SO}_3)_4$ were measured at room temperature to determine whether any residual magnetism could be detected. Both complexes proved
diamagnetic with uncorrected $\chi_M$ values of $-8.13 \times 10^{-5}$ and $-4.14 \times 10^{-4}$ cm$^3$ mol$^{-1}$ respectively, as expected.

2.5 CONCLUSION

It is extremely unusual to have available a series of complexes encompassing all members of the first row transition metal ions from V to Zn. The constant coordination environment has provided an opportunity to study the magnetic properties of the metal ion in a magnetically dilute situation over a range of oxidation states.

The metal(II) cage complexes of $[M \text{sar}]^{2+}$ and $[M(\text{NH}_3)_2\text{sar}]^{4+}$ all proved to be high-spin indicating the ligand can be regarded as generating a weak/medium ligand-field. However the higher metal charge for the metal(III) cage complexes, induces the low-spin configuration for Mn(III), Fe(III), Co(III) and Ni(III).

The low-spin $S = 1$ ground state for $[\text{Mn sar}]^{3+}$, established by magnetization measurements, was a surprising result in view of $\mu_{\text{eff}} = 4.7$ B.M. at 300 K. The unusual temperature dependence observed for the moment, can be reproduced by including extensive mixing of wave functions by spin-orbit coupling into the ground state from low-lying higher levels. It was encouraging to find such close agreement between the calculated and experimental data, especially in view of the simplified model utilized here.

Generally, the $\mu(T)$ behaviour observed for the cage complexes examined was consistent with pseudo-octahedral geometry and agreed with published values obtained for similar hexaamine complexes. An unusual example was however, the diamagnetic $[\text{Fe(NH}_2)_2\text{sar}]$ ($\text{CF}_3\text{SO}_3$)$_2$. It is unlikely that a change in ligand-field strength is present for this complex compared with the two high-spin Fe(II) cages. Thus, all these Fe(II) complexes must lie very close to the
spin crossover region, with lattice effects the salient factor in determining their ultimate spin state in the crystal. This observation was later borne out as the Fe(II) cages were shown to exist in a spin equilibrium while in solution (cf. Chapter Four). An obvious extension for these studies would be to explore a variety of crystal lattices, perhaps with various degrees of solvation in order to induce the Fe(II) cages into a spin equilibrium in the solid state. In addition, a more subtle choice of apical substituents on the Fe(II) cages e.g. [Fe(NH$_3$/2)sar]$^{4+/2+}$ or [Fe(CH$_3$)(NH$_3$/2)sar]$^{3+/2+}$ could enable an equilibrium situation to occur.

In conclusion it can be noted that some of the cages (in particular Ni(II) and Cu(II) complexes) demonstrated their suitability for use as magnetic calibrants, as they displayed temperature independent moments over a wide range of temperature.
CHAPTER THREE

ELECTRONIC PROPERTIES AND CHARACTERIZATION IN SOLUTION
3.1 INTRODUCTION

The measurement of magnetic susceptibility of polycrystalline samples described in the previous chapter has provided information concerning fine details of the electronic structure of encapsulated transition metal ions in the solid state. It was felt desirable also to measure magnetic properties in solution to ascertain whether intermolecular interactions were influencing the magnetism and whether alternative conformations of the cages might be adopted; i.e., whether the ligand field might be modified by relaxing distortions imposed by lattice forces. The information obtained from such magnetic studies can be reinforced by measurements of optical spectra of these cages in solution which provide complementary data on electron configuration and ligand field parameters.

In this investigation, the magnetic moments of a series of cage complexes have been measured by the Evans NMR method, in order to define the electronic configurations in aqueous solution. The absorption spectra of some of these cages have also been measured in aqueous solution. A more detailed analysis of the absorption spectra of a number of cage complexes has been undertaken and these data are discussed where appropriate.

3.2 THEORETICAL FOUNDATIONS FOR THE EVANS METHOD

The correlation between the shifts of the proton resonances for an inert reference molecule together with a paramagnetic species in solution was first described by Evans using the theoretical expression of Dickinson. The bulk magnetic susceptibilities of samples examined by NMR can also affect the magnetic fields experienced by the other nuclei. The field produced on a uniform
distribution of magnetizable material surrounding a paramagnetic species has been calculated by Dickinson and the resonance field shift, $\Delta H$ induced in the diamagnetic medium by the paramagnetic solute is given by Equation 23,

$$\frac{\Delta H}{H} = \left(\frac{4\pi}{3} - \alpha\right) \Delta \kappa$$

...(23)

where $\Delta \kappa$ is the change in volume susceptibility caused by the addition of paramagnetic solute and $\alpha$ depends upon the geometry of the magnetizing field and will be addressed further on.

The theoretical expression in terms of the mass susceptibilities is given by Equation 24,

$$\chi_g = -\frac{\Delta \nu}{\left(\frac{4\pi}{3} - \alpha\right) v m} + \chi_0 + \frac{\chi_0 (d - d_s)}{m}$$

...(24)

where $\chi_g$ is the mass susceptibility of the solute, $v_0$ in Hz is the spectrometer frequency, $\Delta \nu$ in Hz is the change in resonance frequency of the reference substance (or solvent) caused by introduction of the paramagnetic solute, $\chi_0$ is the mass susceptibility of the solvent, $m$, is the mass of solute in 1 ml of solution, and $d_0$ and $d_s$ are, respectively, densities of solvent and solution. For highly paramagnetic substances in dilute solutions the last term can often be neglected (i.e. the densities of the solvent and solution can be considered equal) without serious error.

The molar susceptibilities, $\chi_m'$, are now calculated by Equation 25,

$$\chi_m' = -\left(\frac{3}{4\pi} - \alpha\right) \frac{\Delta \nu \cdot 10^3}{v \cdot C} + MW \cdot \chi_0 - \chi_{dia}$$

...(25)

where $C$, is the concentration of solute in mole per litre and all other parameters have been defined elsewhere.
The effective magnetic moment, \( \mu_{\text{eff}} \) is then calculated as described in Section 2.2.

The constant, \( \alpha \), depends upon the sample tube geometry and the magnetizing field, \( H_0 \) (Table 3.1).

### TABLE 3.1

Variation of \( \alpha \) and \( (4\pi/3 - \alpha) \) with sample container geometry

<table>
<thead>
<tr>
<th>Sample Container Geometry</th>
<th>( \alpha )</th>
<th>( (4\pi/3 - \alpha) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sphere</td>
<td>( 4\pi/3 )</td>
<td>0</td>
</tr>
<tr>
<td>Transverse cylinder</td>
<td>( 2\pi )</td>
<td>(-2\pi/3)</td>
</tr>
<tr>
<td>Longitudinal cylinder</td>
<td>0</td>
<td>( 4\pi/3 )</td>
</tr>
</tbody>
</table>

For conventional NMR spectrometers in which the magnetizing field is provided by electromagnets or permanent magnets, the cylindrical sample tube is positioned so that its long axis is perpendicular to \( H_0 \) (the transverse cylinder). For cylindrical samples and superconducting solenoids, the long axis of the sample tube is parallel to \( H_0 \) (longitudinal cylinder geometry). Therefore, the susceptibility shift is twice as large and in the opposite direction for a coaxial, solenoidal field in comparison to the shift in a conventional magnet of equivalent field.

### 3.3 EXPERIMENTAL METHOD

#### 3.3.1 The Evans NMR Method

The procedure for magnetic susceptibility determination by NMR, requires a standard NMR sample tube, inside which fits a coaxially orientated capillary tube (Figure 3.1). The solvent and "reference
Figure 3.1
Coaxial tube arrangement used for magnetic moment measurements in solution.
"probe" are placed in the inner tube, while the outer tube contains the same ingredients together with the paramagnetic species. The "reference probe" must be inert, that is, must not interact with the solute or solvent. In aqueous solutions we utilized a 1% t-butanol solution for most measurements, although, DSS (2,2-dimethyl-2-silapentanesulphonate) was also employed in some cases. No noticeable discrepancies were observed between "reference probes" for the same sample. For t-butanol as the "reference probe", two resonance lines were observed due to the methyl protons of the t-butanol in the two solutions. The downfield resonance is due to the diamagnetic solvent contained in the inner tube and the upfield resonance due to the paramagnetically shifted species in the outer tube.

Deuterated solvents were employed throughout, unless otherwise stated. The diamagnetic corrections were calculated using the solid state values (cf. Section 2.3.2), and were assumed to be independent of medium. The mass susceptibility, $\chi_0$ of D$_2$O at 293 K is $-0.637 \times 10^{-6}$ cm$^3$g$^{-1}$. All measurements were obtained using a JEOL FX200 spectrometer.

The temperature within the sample chamber was gauged by the separation between the methyl and hydroxyl protons for a sample of pure methanol. This separation in resonances, $\Delta f$ is then related to the absolute temperature by Equation 26,

$$T(K) = 403 - 0.15 \Delta f - 0.0006 \Delta f^2 \quad \ldots(26)$$

for temperatures < 30° C, and by Equation 27,

$$T(K) = 466.5 - 0.15 \Delta f \quad \ldots(27)$$
for temperatures $> 30^\circ$ C, by the separation in resonances for ethylene glycol.

The solution to be measured was allowed 10-15 mins. to equilibrate within the sample chamber. Measurements were continued until a constant separation between the two resonances was obtained.

3.3.2 Measurement of Absorption Spectra

Absorption spectra were measured using a Hewlett-Packard UV/VIS spectrophotometer (model 8450A) interfaced with a flexible disc drive (model 82902M) and attached to a Hewlett-Packard plotter (model 7225B).

Quartz cells were used and spectra were generally recorded at frequencies between 10,000 - 50,000 cm$^{-1}$.

3.4 RESULTS OF NMR MEASUREMENTS

The magnetic moments measured using the Evans NMR method are presented in Table 3.2. The observed values for the moments are in accord with those determined for polycrystalline samples (cf. Chapter Two) with the notable exception of the Fe(II) cage complexes which appear to possess intermediate moments. These anomalous Fe(II) complexes will be addressed separately in Chapter Four.

Small differences between the moments measured in the solid and solution state are attributed to errors in concentration which arise because the volumes used were small.

The study of several cage complexes containing a N$_3$S$_3$ donor core i.e. [M(aza)capten]$^{n+}$ [24], and the related [M(NH$_3$)capten]$^{n+}$ [26], has enabled a comparison to be made between the MN$_3$S$_3$ and MN$_6$ chromophores for the cages. The results for the N$_3$S$_3$ type cage complexes are presented in Table 3.3.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solution $\mu_{\text{eff}}$ B.M.</th>
<th>Solid State $\mu_{\text{eff}}$ B.M.</th>
<th>Electronic Configuration(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[V\text{IV}(\text{NH}_3)_2\text{sar}-2\text{H}]^{4+}</td>
<td>1.80</td>
<td></td>
<td>$t_{2g}^1$</td>
</tr>
<tr>
<td>[V\text{IV}\text{sar}-2\text{H}]^{2+}</td>
<td>1.93</td>
<td></td>
<td>$t_{2g}^1$</td>
</tr>
<tr>
<td>[V\text{III}(\text{NH}_3)_2\text{sar}]^{5+}</td>
<td>2.90</td>
<td></td>
<td>$t_{2g}^2$</td>
</tr>
<tr>
<td>[Cr\text{III}(\text{NH}_3)_2\text{sar}]^{5+}</td>
<td>3.80</td>
<td></td>
<td>$t_{3g}^3$</td>
</tr>
<tr>
<td>[Cr\text{III}(\text{NH}_2)_2\text{sar}]^{3+}</td>
<td>3.61</td>
<td>3.74</td>
<td>$t_{2g}^3$</td>
</tr>
<tr>
<td>[Cr\text{III}\text{sar}]^{3+}</td>
<td>3.75</td>
<td></td>
<td>$t_{2g}^3$</td>
</tr>
<tr>
<td>[Mn\text{II}\text{sar}]^{2+}</td>
<td>4.31</td>
<td>4.74</td>
<td>$t_{2g}^3$</td>
</tr>
<tr>
<td>[Mn\text{II}(\text{NH}_3)_2\text{sar}]^{4+}</td>
<td>5.69</td>
<td>5.85</td>
<td>$t_{2g}^3 e_g^2$</td>
</tr>
<tr>
<td>[Mn\text{II}\text{sar}]^{2+}</td>
<td>5.91</td>
<td></td>
<td>$t_{2g}^3 e_g^2$</td>
</tr>
<tr>
<td>[Fe\text{III}\text{sar}]^{3+}</td>
<td>2.43, 2.51</td>
<td>2.55, 2.52</td>
<td>$t_{2g}^5$</td>
</tr>
<tr>
<td>[Fe\text{II}(\text{NH}_3)_2\text{sar}]^{4+}</td>
<td>4.45, 4.46</td>
<td>5.42</td>
<td>$t_{2g}^4 e_g^2 b$</td>
</tr>
<tr>
<td>[Fe\text{II}(\text{NH}_2)_2\text{sar}]^{2+}</td>
<td>2.24</td>
<td></td>
<td>diamag.</td>
</tr>
<tr>
<td>[Fe\text{II}\text{sar}]^{2+}</td>
<td>2.03, 2.27</td>
<td>5.15</td>
<td>$t_{2g}^4 e_g^2 b$</td>
</tr>
<tr>
<td>[Co\text{III}(\text{NH}_3)_2\text{sar}]^{5+}</td>
<td>diamag.</td>
<td>diamag.</td>
<td>$t_{2g}^6$</td>
</tr>
<tr>
<td>[Co\text{III}\text{sar}]^{3+}</td>
<td>diamag.</td>
<td>diamag.</td>
<td>$t_{2g}^6$</td>
</tr>
<tr>
<td>[Co\text{II}(\text{NH}_3)_2\text{sar}]^{4+}</td>
<td>4.54, 4.56</td>
<td>4.47</td>
<td>$t_{2g}^5 e_g^2$</td>
</tr>
<tr>
<td>[Co\text{II}\text{sar}]^{2+}</td>
<td>4.42</td>
<td></td>
<td>$t_{2g}^5 e_g^2$</td>
</tr>
<tr>
<td>[Ni\text{III}\text{sar}]^{3+}</td>
<td>2.36</td>
<td></td>
<td>$t_{2g}^5 e_g^1$</td>
</tr>
<tr>
<td>[Ni\text{II}(\text{NH}_3)_2\text{sar}]^{4+}</td>
<td>2.86</td>
<td>3.03</td>
<td>$t_{2g}^6 e_g^2$</td>
</tr>
<tr>
<td>[Ni\text{II}\text{sar}]^{2+}</td>
<td>2.84</td>
<td>3.06</td>
<td>$t_{2g}^6 e_g^2$</td>
</tr>
<tr>
<td>[Cu\text{II}(\text{NH}_3)_2\text{sar}]^{4+}</td>
<td>2.03</td>
<td>1.92</td>
<td>$t_{2g}^6 e_g^3$</td>
</tr>
<tr>
<td>[Cu\text{II}\text{sar}]^{2+}</td>
<td>1.72</td>
<td>1.91</td>
<td>$t_{2g}^6 e_g^3$</td>
</tr>
<tr>
<td>[Zn\text{II}(\text{NH}_3)_2\text{sar}]^{4+}</td>
<td>diamag.</td>
<td>diamag.</td>
<td>$t_{2g}^6 e_g^4$</td>
</tr>
<tr>
<td>[Zn\text{II}\text{sar}]^{2+}</td>
<td>diamag.</td>
<td>diamag.</td>
<td>$t_{2g}^6 e_g^4$</td>
</tr>
</tbody>
</table>

\(^a\) Assuming octahedral symmetry.
\(^b\) In solid state only.
### Magnetic moments for transition metal \( \text{N}_3\text{S}_3 \)-type cages in solution and solid states.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solution ( \mu_{\text{eff}}, \text{B.M.} )</th>
<th>Solid State ( \mu_{\text{eff}}, \text{B.M.} )</th>
<th>Electronic Configuration</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[\text{Fe}^{\text{II}}(\text{NH}_3)\text{capten}]^{3+}]</td>
<td>diamag.</td>
<td></td>
<td>( t_{2g}^{6} )</td>
<td>this work</td>
</tr>
<tr>
<td>[\text{Co}^{\text{II}}(\text{NH}_3)\text{capten}]^{3+}]</td>
<td>2.01</td>
<td></td>
<td>( t_{2g}^{6} )</td>
<td>this work</td>
</tr>
<tr>
<td>[\text{Co}^{\text{II}}(\text{aza})\text{capten}]^{2+}]</td>
<td>2.35</td>
<td>2.12, 1.89</td>
<td>( t_{2g}^{6} )</td>
<td>93</td>
</tr>
<tr>
<td>[\text{Ni}^{\text{II}}(\text{NH}_3)\text{capten}]^{3+}]</td>
<td>3.25</td>
<td></td>
<td>( t_{2g}^{6} )</td>
<td>this work</td>
</tr>
</tbody>
</table>

* a Assuming octahedral symmetry.
  * b This work.

The \( \text{Mn}(\text{III}) \) complex, \([\text{Mn}^{\text{III}}\text{sar})(\text{NO}_3)_{3}\] is unstable in neutral solutions so that the moment was determined under acidic conditions where the solution was sufficiently stable for sample preparation and the initial NMR measurement. Deuterated trifluoromethane sulphonic acid, \( \text{CF}_3\text{SO}_3\text{D} \), was chosen as both solvent and reference probe, because of its poor coordinating properties and high acidity. The magnetic susceptibility was determined in this case, by the shift in residual protonated trifluoromethane sulphonic acid, between the inner and outer tubes. Even under these acidic conditions, the value of the moment decreased slowly with time. It is possible that this decrease arises from metal extrusion from the cage or disproportion.

The cage complexes of \( \text{Fe}(\text{III}) \) and \( \text{Co}(\text{II}) \) were extremely air-sensitive in neutral pH solutions and required an argon filled glovebox for sample preparation and storage prior to NMR
measurements.

The magnetic moment of $[\text{Co}^{II}(\text{NH}_3)_2\text{sar}]\text{Cl}_4\cdot6\text{H}_2\text{O}$ was measured over a limited temperature range and the data are presented in Table 3.4. It appears that the moment is temperature dependent although the experimental scatter of the data make this conclusion tentative and a somewhat more extended temperature range is desirable. A contributing factor towards this scatter is the variation of solvent susceptibility, $\chi_0$ which will vary with temperature due to changes in viscosity.

The magnetic moment of the $[\text{Fe}^{III}\text{sar}]\text{Cl}_3\cdot\text{H}_2\text{O}$ complex has also been measured over a temperature range, and displays the temperature dependence anticipated for the low-spin $t^5_{2g}$ configuration (Table 3.5).

### Table 3.4

Temperature dependence of the magnetic moment of $[\text{Co}^{II}(\text{NH}_3)_2\text{sar}]\text{Cl}_4\cdot6\text{H}_2\text{O}$ measured in $\text{D}_2\text{O}$ solution.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>$X M_| \times 10^3$</th>
<th>$\mu_{\text{eff}}$, B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>287.2</td>
<td>8.74</td>
<td>4.48</td>
</tr>
<tr>
<td>293.8</td>
<td>8.35</td>
<td>4.43</td>
</tr>
<tr>
<td>294.7</td>
<td>8.84</td>
<td>4.56</td>
</tr>
<tr>
<td>295.6</td>
<td>8.72</td>
<td>4.54</td>
</tr>
<tr>
<td>325.8</td>
<td>8.70</td>
<td>4.76</td>
</tr>
<tr>
<td>329.7</td>
<td>8.59</td>
<td>4.76</td>
</tr>
<tr>
<td>334.4</td>
<td>8.51</td>
<td>4.77</td>
</tr>
</tbody>
</table>
Figure 3.2
Electronic absorption spectrum of \([\text{V(NH}_3\text{)}_2\text{ar-2H}]^{4+}\)-type A.

Figure 3.3
Electronic absorption spectrum of \([\text{V(NH}_3\text{)}_2\text{ar-2H}]^{4+}\)-type B.
TABLE 3.5
Temperature dependence of the magnetic moment of [Fe sar]Cl_3.H_2O measured in D_2O solution.

<table>
<thead>
<tr>
<th>Temperature, K</th>
<th>$\chi_M \times 10^3$</th>
<th>$\mu_{eff}$, B.M.</th>
</tr>
</thead>
<tbody>
<tr>
<td>287.2</td>
<td>2.59</td>
<td>2.44</td>
</tr>
<tr>
<td>293.8</td>
<td>2.51</td>
<td>2.43</td>
</tr>
<tr>
<td>295.6</td>
<td>2.66</td>
<td>2.51</td>
</tr>
<tr>
<td>325.8</td>
<td>2.42</td>
<td>2.51</td>
</tr>
<tr>
<td>329.7</td>
<td>2.41</td>
<td>2.52</td>
</tr>
<tr>
<td>334.4</td>
<td>2.40</td>
<td>2.53</td>
</tr>
</tbody>
</table>

3.5 RESULTS OF VISIBLE-UV SPECTROSCOPY

3.5.1 Vanadium Cages

Two spectroscopically distinct forms of the [V(NH_3)_2sar-2H]^4+ complex ion have been isolated and are referred to as V(IV)-type A (Figure 3.2) and V(IV)-type B (Figure 3.3). Analytical data show the two forms are of the same composition, and could therefore be considered isomers. As mentioned earlier (Section 2.3.2), the single crystal X-ray structure for V(IV)-type A revealed disorder about the VN_6 core thereby preventing location of the "deprotonation sites". Speculation as to the structural difference between the two forms is precluded by the paucity of information on vanadium(IV) amine complexes. Only V(IV)-type A will be considered in the following discussion.

A detailed ESR study of the complex also confirms a deviation from axial symmetry. In addition, it was established that the geometry remains unchanged in solution over a large range of
Figure 3.4
Electronic absorption spectrum of [V(NH₃)₂sar]⁵⁺.
The published ESR parameters are $g_x = 1.975$, $g_y = 1.970$, $g_z = 1.992$, $g_{iso} = 1.979$; $A_x = 92 \times 10^{-4}$, $A_y = 99 \times 10^{-4}$, $A_z = 16 \times 10^{-4}$, and $A_{iso} = 68 \times 10^{-4}$ cm$^{-1}$ indicating a $^2A_1$ ground state. The electronic spectrum of $[V(NH_3)_2sar-2H]Cl_4.5H_2O$ (Figure 3.2) exhibits four strong transitions (three peaks and one shoulder). These arise from charge transfer and/or ligand-to-ligand bands which unfortunately mask the expected $^2E_g + ^2T_{2g}$ band that should occur with an energy of 10 Dq.

It is interesting to note that the optical spectrum of $[V(NH_3)_2sar-2H]^4+$ is an unusual example of a cage complex in which a rich array of intense charge transfer bands are observed. Therefore it appears reasonable to speculate that these transitions might originate from the unique circumstances of having two deprotonated nitrogen donor atoms bound to the central ion in a pseudo-vanadyl arrangement. The charge transfer bands could arise from the double bond character of the deprotonated V=N linkages. The observed transitions are included in Table 3.6.

In Chapter Two, it was mentioned that the electrochemical reduction of $[V(NH_3)_2sar-2H]^4+$ resulted in the isolation of the $3d^2$ vanadium(III) cage. This electrochemical synthesis was exploited to obtain the optical spectrum of the V(III) complex in situ (Figure 3.4). Spectroelectrochemistry is a valuable technique for studying the spectra of unstable molecules or transient species in solution. An advantage in this type of optical measurement is that the redox process can be undertaken in successive stages, thereby enabling intermediates formed during the redox reaction to be identified.

The spectral transitions, $\bar{\nu}$, for $[VII(NH_3)_2sar]^5+$ are compared with some other vanadium(III) complexes in Table 3.6.
TABLE 3.6
Electronic transitions for some 3d\(^1\) and 3d\(^2\) vanadium complexes.

<table>
<thead>
<tr>
<th></th>
<th>(\tilde{v})/cm(^{-1})</th>
<th>(\varepsilon,)/cm(^{-1})</th>
<th>Assignment</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{V}^\text{IV}(\text{NH}_3)_2\text{sar}-2\text{H}]^{4+})</td>
<td>11,310</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- type A</td>
<td>20,750(sh)</td>
<td>23,670</td>
<td>30,170</td>
<td>36,300</td>
</tr>
<tr>
<td>([\text{V}^\text{IV}(\text{NH}_3)_2\text{sar}-2\text{H}]^{4+})</td>
<td>19,600(sh)</td>
<td>23,400</td>
<td>31,000</td>
<td>800</td>
</tr>
<tr>
<td>- type B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{V}^\text{III}(\text{NH}_3)_2\text{sar}]^{5+})</td>
<td>27,130</td>
<td>37,750</td>
<td>600</td>
<td>1700</td>
</tr>
<tr>
<td>([\text{V}(\text{en})_3]^{3+}) (a, b)</td>
<td>17,000(sh)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{V}(\text{pn})_3]^{3+})</td>
<td>21,000</td>
<td>(3T_2g + 3T_{1g}(F))</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>29,500</td>
<td>(3T_{1g}(P) + 3T_{1g}(F))</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>39,000</td>
<td>(3A_{2g} + 3T_{1g}(F))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{V}(\text{H}_2\text{O})_6]^{3+})</td>
<td>17,000</td>
<td>5.6</td>
<td>(3T_2g + 3T_{1g}(F))</td>
<td>110</td>
</tr>
<tr>
<td></td>
<td>25,200</td>
<td>8.3</td>
<td>(3T_{1g}(P) + 3T_{1g}(F))</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(35,700)(^c)</td>
<td></td>
<td>((-A_{2g} + 3T_{1g}(F)))</td>
<td></td>
</tr>
</tbody>
</table>

* Spectra were obtained by diffuse reflectance measurements.

b Trigonal splitting of the \(3T_2g\) level by ca. 4000 cm\(^{-1}\) was evident.

c Not observed in spectrum.
Figure 3.5
Electronic absorption spectra of some Cr(III) cages a) $[\text{Cr(NH}_3\text{)}_2\text{sar}]^{5+}$, b) $[\text{Crsar}]^{3+}$ and c) $[\text{Cr(NH}_2\text{)}_2\text{sar}]^{3+}$.
3.5.2 Chromium Cages

The chromium(III) cages have received considerable attention with respect to their spectroscopic, photochemical and photophysical properties.73,111,112

Two intense transitions are observed in the visible region (Figure 3.5), which are ascribed to the spin-allowed $^4T_{2g} + ^4A_{2g}$ and $^4T_{1g} + ^4A_{2g}$ transitions in octahedral symmetry. The transitional energies are tabulated in Table 3.7.

**TABLE 3.7**

Electronic transitions, assignments and 10 $D_q$ for Chromium(III) complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\bar{v}_{\text{cm}^{-1}}$</th>
<th>$\varepsilon_{\text{M}^{-1}\text{cm}^{-1}}$</th>
<th>Assignment of Transitions</th>
<th>$10D_q$, cm$^{-1}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(NH$_2$)$_2$sar]$^{3+}$</td>
<td>21,930 (sh)</td>
<td>203</td>
<td>$(^2T_{2g} + ^4A_{2g})^a$</td>
<td>22,350</td>
<td>73</td>
</tr>
<tr>
<td>[Cr(NH$_3$)$_2$sar]$^{5+}$</td>
<td>22,350</td>
<td>208</td>
<td>$^4T_{2g} + ^4A_{2g}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>28,940</td>
<td>109</td>
<td>$^4T_{1g} + ^4A_{2g}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cr sar]$^{3+}$</td>
<td>21,860</td>
<td>153</td>
<td>$(^2T_{2g} + ^4A_{2g})^a$</td>
<td>22,250</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>22,250</td>
<td>156</td>
<td>$^4T_{2g} + ^4A_{2g}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>28,820</td>
<td>91</td>
<td>$^4T_{1g} + ^4A_{2g}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cr sep]$^{3+}$</td>
<td>21,740</td>
<td>100</td>
<td>$^4T_{2g} + ^4A_{2g}$</td>
<td>21,740</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>28,990</td>
<td>102</td>
<td>$^4T_{1g} + ^4A_{2g}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cr(en)$_3$]$^{3+}$</td>
<td>21,930</td>
<td>72</td>
<td>$^4T_{2g} + ^4A_{2g}$</td>
<td>21,930</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>28,330</td>
<td>63</td>
<td>$^4T_{1g} + ^4A_{2g}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Cr(NH$_3$)$_6$]$^{3+}$</td>
<td>21,790</td>
<td>45</td>
<td>$^4T_{2g} + ^4A_{2g}$</td>
<td>21,790</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>28,490</td>
<td>38</td>
<td>$^4T_{1g} + ^4A_{2g}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a* Assignment of these transitions have been suggested by P. Comba and A.W.H Mau.
In the weak field limit for the d^3 configuration, 10 Dq is given simply by the interval E[^4T2g(F)−^4A2g(F)], i.e. the energy of the first spin-allowed absorption band. It is seen from Table 3.7 that 10 Dq = 22,000 cm\(^{-1}\) and that encapsulation has little influence on this parameter.

**TABLE 3.8**

Electronic transitions, assignments and 10 Dq for transition metal cages.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\bar{\nu}), cm(^{-1})</th>
<th>(\bar{E}), M(^{-1})cm(^{-1})</th>
<th>Assignment of Transition(^a)</th>
<th>10 Dq, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Mn(^{III})sar(^{3+})]</td>
<td>7,370</td>
<td></td>
<td>(^5)A + (^5)B(_1)(C(_2))</td>
<td>20,010</td>
</tr>
<tr>
<td></td>
<td>23,700</td>
<td></td>
<td>(^5)A, (^5)B, (^5)A + (^5)B(_1)(C(_2))</td>
<td></td>
</tr>
<tr>
<td>[Mn(^{II})(NH(_3))(_2)sar(^{4+})]</td>
<td>14,120 (sh)</td>
<td></td>
<td>(^4)T(_1)g(G) + (^6)A(_1)g + (^6)A(_1)g</td>
<td>11,820</td>
</tr>
<tr>
<td></td>
<td>14,784</td>
<td></td>
<td>(^4)T(_2)g(G) + (^6)A(_1)g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18,932</td>
<td></td>
<td>(^4)E(_g)(G) + (^6)A(_1)g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22,883</td>
<td></td>
<td>(^4)A(_1)g(G) + (^6)A(_1)g</td>
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</tr>
<tr>
<td></td>
<td>23,234</td>
<td></td>
<td>(^4)T(_2)g(D) + (^6)A(_1)g</td>
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</tr>
<tr>
<td></td>
<td>24,498</td>
<td></td>
<td>(^4)E(_g)(D) + (^6)A(_1)g</td>
<td></td>
</tr>
<tr>
<td></td>
<td>26,274</td>
<td></td>
<td>(^4)T(_1)g(P) + (^6)A(_1)g</td>
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</tr>
<tr>
<td></td>
<td>27,042</td>
<td></td>
<td>(^2)T(_2)g + (^2)T(_2)g + (^2)E(_g) + (^2)T(_2)g</td>
<td></td>
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<tr>
<td>[Fe(^{III})sar(^{3+})]</td>
<td>18,900 (sh)</td>
<td>108</td>
<td>(^2)T(_2)g + (^2)T(_2)g + (^2)E(_g) + (^2)T(_2)g</td>
<td>20,020</td>
</tr>
<tr>
<td></td>
<td>22,830</td>
<td>333</td>
<td>(^2)T(_2)g + (^2)E(_g) + (^2)T(_2)g</td>
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<tr>
<td></td>
<td>24,600 (sh)</td>
<td>297</td>
<td>(^2)T(_2)g + (^2)T(_1)g + (^2)T(_2)g</td>
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<tr>
<td></td>
<td>27,290</td>
<td>924</td>
<td>(^2)A(_1)g + (^2)T(_2)g</td>
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</tr>
<tr>
<td></td>
<td>31,900 (sh)</td>
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<td>(^2)E(_g) + (^2)T(_2)g</td>
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</tr>
<tr>
<td>[Co(^{III})(NH(_3))(_2)sar(^{5+})]</td>
<td>21,050</td>
<td>146</td>
<td>(^1)T(_1)g + (^1)A(_1)g</td>
<td>22,050</td>
</tr>
<tr>
<td></td>
<td>29,200</td>
<td>132</td>
<td>(^1)T(_2)g + (^1)A(_1)g</td>
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</table>

(Contd.)
<table>
<thead>
<tr>
<th>Complex</th>
<th>Assignments</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CoIIIsar]³⁺</td>
<td>1T₁g + 1A₁g</td>
<td>21,140</td>
</tr>
<tr>
<td></td>
<td>1T₂g + 1A₁g</td>
<td>29,030</td>
</tr>
<tr>
<td>[CoII(NH₃)₂sar]⁴⁺</td>
<td>4T₂g + 4T₁g</td>
<td>10,320</td>
</tr>
<tr>
<td></td>
<td>2T₂g, 2T₁g, 4A₂g + 4T₁g</td>
<td>15,700 (sh)</td>
</tr>
<tr>
<td></td>
<td>4T₁g(P) + 4T₁g</td>
<td>16,410 (sh)</td>
</tr>
<tr>
<td></td>
<td>4T₁g(P) + 4T₁g</td>
<td>17,070 (sh)</td>
</tr>
<tr>
<td></td>
<td>4T₁g(P) + 4T₁g</td>
<td>21,220</td>
</tr>
<tr>
<td></td>
<td>4T₁g(P) + 4T₁g</td>
<td>29,380 (sh)</td>
</tr>
<tr>
<td>[NiIIIsar]³⁺</td>
<td>11,390 (sh)</td>
<td>11,350 (sh)</td>
</tr>
<tr>
<td></td>
<td>11,770 (sh)</td>
<td>12,490</td>
</tr>
<tr>
<td></td>
<td>20,390 (sh)</td>
<td>13,122 (sh)</td>
</tr>
<tr>
<td></td>
<td>11,770 (sh)</td>
<td>24,541 (sh)</td>
</tr>
<tr>
<td></td>
<td>11,770 (sh)</td>
<td>31,060 (sh)</td>
</tr>
<tr>
<td>[NiII(NH₃)₂sar]⁴⁺</td>
<td>3B₂ + 3A₂g(D₄)</td>
<td>11,390 (sh)</td>
</tr>
<tr>
<td></td>
<td>3E + 3A₂g(D₄)</td>
<td>12,420</td>
</tr>
<tr>
<td></td>
<td>1A₁, 1B₁ + 3A₂g(D₄)</td>
<td>12,770 (sh)</td>
</tr>
<tr>
<td></td>
<td>3A₂ + 3A₂g(D₄)</td>
<td>19,810</td>
</tr>
<tr>
<td></td>
<td>3E + 3A₂g(D₄)</td>
<td>20,390 (sh)</td>
</tr>
<tr>
<td></td>
<td>3A₂, 3E + 3A₂g(D₄)</td>
<td>30,320</td>
</tr>
<tr>
<td>[NiIIIsar]²⁺</td>
<td>3B₂ + 3A₂g(D₄)</td>
<td>11,440 (sh)</td>
</tr>
<tr>
<td></td>
<td>3E + 3A₂g(D₄)</td>
<td>12,430</td>
</tr>
<tr>
<td></td>
<td>1A₁, 1B₁ + 3A₂g(D₄)</td>
<td>12,890</td>
</tr>
<tr>
<td></td>
<td>3A₂ + 3A₂g(D₄)</td>
<td>19,810</td>
</tr>
<tr>
<td></td>
<td>3E + 3A₂g(D₄)</td>
<td>20,390 (sh)</td>
</tr>
<tr>
<td></td>
<td>3A₂, 3E + 3A₂g(D₄)</td>
<td>30,430</td>
</tr>
<tr>
<td>[CuII(NH₃)₂sar]⁴⁺</td>
<td>2A₁ + 2B₁(C₂)</td>
<td>8,454</td>
</tr>
<tr>
<td></td>
<td>2A, 2B₁, 2A + 2B₁(C₂)</td>
<td>15,090</td>
</tr>
<tr>
<td>[CuIIIsar]²⁺</td>
<td>2A₁ + 2B₁(C₂)</td>
<td>8,409</td>
</tr>
<tr>
<td></td>
<td>2A, 2B₁, 2A + 2B₁(C₂)</td>
<td>15,310</td>
</tr>
</tbody>
</table>

a Assignments suggested by P. Comba (ref. 58).
Figure 3.8
Electronic absorption spectrum of a) [Mn(NH$_3$)$_2$sal]$^{3+}$, b) [Co(NH$_3$)$_2$sal]$^{4+}$,
c) [Ni(NH$_3$)$_2$sal]$^{2+}$ and d) [Cu(NH$_3$)$_2$sal]$^{2+}$.
3.5.3 The Other Transition Metal Cages

The visible and ultraviolet spectra for the cage complexes of Mn^{III}, Fe^{II}, Mn^{II}, Co^{III}, Co^{II}, Ni^{III}, Ni^{II} and Cu^{II}, have been measured in parallel studies by others in our laboratory and these results are summarized in Table 3.8. The main features of the spectra can be discerned in Figures 3.6 and 3.7.

3.6 DISCUSSION OF MAGNETIC AND OPTICAL PARAMETERS

The high-spin configuration, observed for the polycrystalline M(II)N_6 cages (cf. Chapter Two) is maintained in solution for the cage complexes included in this chapter (cf. Table 3.2). The magnetic moments observed in solution for the M(III)N_6 cages, are also in accord with those obtained in the solid state; with the V(III) and Cr(III) cages being high-spin while the Mn(III), Fe(III), Co(III) and Ni(III) cages are low-spin at room temperature.

The N_3S_3-chromophore cages, [M(NH_3)capten]^3+ where M = Fe^{II}, Co^{II} and Ni^{II}, were included in this study to enable a comparison of the magnetic properties for differing encapsulation environments to be made. Both solid and solution magnetic moments for [Co^{II}(aza)capten]^2+ had been measured at room temperature prior to this study. With the availability of the protonated amino-capped derivative, it was hoped that the ligand field generated by this ligand would be weaker than that of the aza-capped cage, perhaps providing a ligand field of similar strength to the sar-type ligands.

The [Fe^{II}(NH_3)capten]^3+ and [Co^{II}(NH_3)capten]^3+ cages are found to be low-spin in solution, confirming that the ratio 10 Dq/B is greater than that generated by the sar-type ligands in solution (see also the discussion in Chapters Two and Four).
Figure 3.7
Electronic absorption spectrum of a) [Mn sar]$^{2+}$, b) [Fe sar]$^{2+}$, c) [Co(NH$_3$)$_2$ sar]$^{2+}$ and d) [Ni sar]$^{2+}$. 
[Ni^{II}(NH_3)capten]^{3+} complex, however, is paramagnetic, indicating that the pseudo-octahedral geometry is maintained, rather than undergoing a distortion that would lead to the pairing of two eg electrons.

The moments of the [Fe^{III}sar]^{3+} and [Co^{II}(NH_3)_2sar]^{4+} complexes were measured in solution over a limited temperature range (Tables 3.4 and 3.5), in order to ascertain whether their susceptibility-temperature behaviour was similar to that measured in the solid state. In both cases, the moments displayed a dependence on temperature in the range 287 - 334 K; however, the experimental scatter was large and precluded a more detailed analysis. An extension of the measurements to lower temperatures might assist in identifying the origin of the \( \chi (T) \) behaviour in solution. However, the choice of solvent to provide a suitable range for measurements at lower temperatures is a more difficult problem. This study was confined to aqueous media in order to correlate later these findings with electron transfer measurements (cf. Chapter Seven).

The optical spectra obtained for the N_6-chromophore sar-type cages can be classified into three categories; (1) those with octahedral geometry; (2) those with pseudo-octahedral geometry, evident from small splittings of the optical absorption bands, and (3) those where the d-d transitions are masked by charge-transfer bands, precluding any spin-state information.

The vanadium cages appear to fall into Category 3, with intense transitions that can not easily be attributed to any d-d character. A more detailed investigation is required e.g. using magnetic circular dichroism (MCD), to identify the origin of these transitions.

However, the 10 Dq values for the vanadium cages can be
estimated from the trends observed in Table 3.9. The increased charge on the vanadium(IV) nucleus compared to the metal(III) cages should result in the ligand field transition lying at ca. 30,000 - 32,000 cm\(^{-1}\) (= 10 Dq). Similarly, the 10 Dq value for the vanadium(III) cage can be estimated to lie between 20,000 and 22,000 cm\(^{-1}\) by comparison with the values obtained for the other metal(III) cage complexes.

**TABLE 3.9**

10 Dq values for transition metal cages.

<table>
<thead>
<tr>
<th>M\text{II}</th>
<th>10 Dq, cm(^{-1})</th>
<th>M\text{III}</th>
<th>10 Dq, cm(^{-1})</th>
<th>M\text{IV}</th>
<th>10 Dq, cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn\text{II}</td>
<td>12,000</td>
<td>Mn\text{III}</td>
<td>20,000</td>
<td>Cr\text{III}</td>
<td>22,000</td>
</tr>
<tr>
<td>Co\text{II}</td>
<td>12,000</td>
<td>Fe\text{III}</td>
<td>20,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni\text{II}</td>
<td>12,000</td>
<td>Co\text{III}</td>
<td>22,000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu\text{II}</td>
<td>11,000</td>
<td>Ni\text{III}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V\text{III}</td>
<td>20,000(^a)</td>
<td></td>
<td></td>
<td>v\text{IV}</td>
<td>30,000(^a)</td>
</tr>
</tbody>
</table>

\(^a\) Values estimated by comparison with other metal cage values.

The chromium(III) cages are structurally very similar as deduced from their optical spectra. Their absorption transitions have been assigned in octahedral symmetry although other workers have suggested that D\(_3\) symmetry better describes the observed spectra.\(^{58}\) The assignment of transitions shows the expected spin allowed \(4T_{2g} + 4A_{2g}\) and \(4T_{1g} + 4A_{2g}\) bands, and in addition the weak spin forbidden \(2E_g, 2T_{1g} + 4A_{2g}\) bands. An extensive array of photochemical and
photophysical measurements have been employed for the study of these complexes, although they are not directly relevant to this study.

Comba has interpreted the spectrum of \([\text{Mn sar}]^{3+}\) in terms of \(C_2\) symmetry, and suggests that in solution a considerable trigonal field is expected with a trigonal twist angle, \(\phi \approx 40^\circ\). In solution the value of 10 \(D_q\) was calculated to be \(\approx 20,000\ \text{cm}^{-1}\) which lies far away from the estimated high-spin/low-spin crossover limit of \(28,000\ \text{cm}^{-1}\). It is interesting to note that the solid state magnetic measurements for this complex (cf. Chapter Two) indicate that the complex lies much closer to the crossover limit than anticipated by Comba. However, if the Racah parameter for interelectronic repulsion, \(B\) is considerably reduced below the value for the free \(\text{Mn}^{3+}\) ion, then the ratio \((10 \ D_q/B)\) may lie close to the crossover value.

The weak optical bands observed for both \([\text{Mn}^{2+}(\text{NH}_3)_2\text{sar}]^{4+}\) and \([\text{Mn}^{2+}\text{sar}]^{2+}\) complexes are due to the expected spin and Laporte forbidden sextet-quartet transitions. Comba has analysed the data using transitions arising from both \(D^{-}\) and \(G\)-states of the free \(\text{Mn}^{2+}\) ion. The symmetry has been assumed to be octahedral, and a 10 \(D_q\) value of \(\approx 11,000 - 11,800\ \text{cm}^{-1}\) was deduced.

The spectrum of \([\text{Fe}^{III}\text{sar}]^{3+}\), is dominated by several transitions in the visible region. The assignment of these transitions is based on the published interpretation of the spectra of \([\text{Fe}(\text{en})_3]\text{Cl}_3\) and \(K_3[\text{Fe(CN)}_6]^{4-}\) and agrees well with octahedral geometry for the \(\text{FeN}_6\) core.

The \([\text{Co sar}]^{3+}\) and \([\text{Co(NH}_3)_2\text{sar}]^{5+}\) complexes exhibit two well-resolved optical transitions expected for octahedral symmetry. These are assigned to \(1T_{1g} + 1A_{1g}\) for the lower energy transition and \(1T_{2g} + 1A_{1g}\) for the higher energy transitions. These absorption
bands are of similar energy for the other Co$^{III}\text{N}_6$-chromophore cages and are well documented.\textsuperscript{20,21} The 10 Dq value included in Table 3.9 for Co(III) is that obtained for [Co sar]$^{3+}$ and [Co(NH$_3$)$_2$sar]$^{5+}$, although it agrees well with other Co(III) cages of the sarcophagine type.

The optical spectrum of [Co(NH$_3$)$_2$sar]$^{4+}$ consists of several weak transitions in the visible region. The assignment of transitions is hampered somewhat by the poor resolution in the region 15,000 - 17,000 cm$^{-1}$ which precludes a more thorough analysis. The transitions are assigned in octahedral symmetry and no evidence is found in solution for the substantial trigonal twist observed in the X-ray crystal structure. As with the Co(III) cages, the spectra are discussed in more detail elsewhere.\textsuperscript{38}

The electronic spectrum of [Ni sar]$^{3+}$ is obscured in the visible region, by the "tail" of a charge transfer band which precludes analysis of the expected d-d transitions. It is assumed that this Jahn-Teller active $t^6_2g\, e^1_2$ configuration would result in two or three d-d transitions by splitting of the ground $^2E_g$ term into $^2B_1$ and $^2A_1$ terms. As commented earlier for the vanadium cages, the value of 10 Dq can be gauged by comparison with values obtained for other metal(III) cage complexes (Table 3.9). Thus the value should lie between 20,000 and 22,000 cm$^{-1}$ for [Ni sar]$^{3+}$.

The Ni(II) cages, [Ni(NH$_3$)$_2$sar]$^{4+}$ and [Ni sar]$^{2+}$ are characterized by essentially identical electronic spectra in the visible region. Although three bands are observed, small splittings are apparent in these bands which imply the symmetry is at best pseudo-octahedral approximating to $D_4\sigma$. The transitions have been assigned by Comba\textsuperscript{58} as shown in Table 3.8. The electronic spectrum of [Ni sep]$^{2+}$, has been reported,\textsuperscript{46} and consists of two transitions
in the visible region at 19,600 and 31,600 cm\(^{-1}\). These transitions were assigned in octahedral symmetry to \(3T_{1g}(F) + 3A_{2g}\) and \(3T_{1g}(P) + 3A_{2g}\), respectively. No reference was made to the occurrence of the lower energy \(3T_{2g}(F) + 3A_{2g}\) transition.

The azure blue colour in solution is characteristic of the \([\text{Cu sar}]^{2+}\) and \([\text{Cu(NH}_{3})_{2}\text{sar}]^{4+}\) cages arising from a strong electronic transition in the visible region. The \(\text{Cu}^{2+}\) ion in an "octahedral" environment is regarded as the classical example of Jahn-Teller distortion. As is evident from the X-ray crystal structure of \([\text{Cu(NH}_{3})_{2}\text{sar}](\text{NO}_{3})_{4}\), two trans CuN bonds are longer than the other four which indicates Jahn-Teller distortion in these compounds. The orbital degeneracy of the \(2E_g\) ground term and that of the \(2T_{2g}\) excited term will be lifted under these conditions. The assignment of optical transitions in Table 3.8 has been made assuming \(C_{2v}\) symmetry by Comba,\(^{58}\) based on the splitting diagram in Figure 2.56.

3.7 CONCLUSIONS

The salient feature most evident from this study is the similarity between the electronic behaviour of the cage complexes in both solid and solution states, i.e. the magnetic moment measurements in solution are in close agreement with those obtained for polycrystalline samples. From these measurements alone, it can be concluded that the magnetic properties of the cage complexes included in this study, are determined primarily by intramolecular and not by intermolecular interactions. That is to say, encapsulation of the metal ion provides a magnetically dilute environment, eliminating any pathways for magnetic exchange sometimes found in coordination complexes. However, although magnetic measurements at room temperature are sufficient to determine the spin-state of the cage
complexes in both solid and solution, these measurements proved rather insensitive to the presence of molecular distortions.

In the solid state, information concerning distortions from octahedral symmetry became evident in the magnetic measurements at low temperatures i.e. < 10 K, and provided detailed knowledge of the combined effects of spin-orbit coupling and lowered molecular symmetry from sub-level splittings of the order of several wavenumbers. However, in solution this extended temperature range is not accessible, restricting somewhat the comparison of data obtained in solution and solid states. However, the optical absorption spectra in solution are more sensitive to geometrical distortions and, in some cases, the splitting of ligand field bands indicates a molecular symmetry lower than octahedral.
CHAPTER FOUR

SPIN EQUILIBRIA IN IRON(II) CAGE COMPLEXES
4.1 INTRODUCTION

The anomalous magnetic behaviour of the iron(II) cages was revealed by the investigation of magnetic and optical properties of first row transition metal cages in solution (cf. Figure 4.15). The magnetic moments of these cages at room temperature lie between the values expected for high-spin and low-spin $3d^6$ configurations. On the other hand, the optical spectra were dominated by two absorptions in the visible region ascribed to the low-spin $1T_{1g} + 1A_{1g}$ and $1T_{2g} + 1A_{1g}$ transitions.

The intermediate magnetic moments of these anomalous complexes could be attributed to either,

(1) an intermediate triplet spin state (i.e. $S = 1$) as the ground state, or
(2) nearly equienergetic low-spin ($1A_{1g}$) and high-spin ($5T_{2g}$) states resulting in a spin equilibrium between these levels.

The presence of the two characteristic low-spin transitions in the absorption spectra appeared to support the spin equilibrium model. However, further more detailed investigations were warranted to establish unambiguously the origin of the magnetic anomaly for these complexes.

The existence of spin equilibria between two electronic states is well established and has been described in several reviews. However, most studies of this phenomenon have been restricted to the solid state, presumably due to either compound instability or the disappearance of the necessary equilibrium conditions in solution. Some examples of iron(II) spin equilibria that have been characterized in solution are with the ligands,
\[ \text{[Fe(HB(X,Y-pz)3)2]} \]

where \( X = \text{CH}_3, \ Y = \text{H}; \ X = Y = \text{H} \) or \( X = Y = \text{CH}_3 \).

[36]

\[ \text{[Fe(6-CH}_3\text{Py})_n(\text{Py})_m\text{tren}]^{2+} \]

where \( n + m = 3 \).

[37]
Figure 4.1
Energy level diagram for $3d^6$ ions in an octahedral ligand field.
(1) hydrotris(l-pyrazolyl)borate [36], 117-119
(2) tris[4-{(6-R)-2-pyridyl}-3-aza-3-butenyl]amine [37], R=H or CH₃, 120
(3) tris[2-(2'-pyridyl)imidazole], 121 and
(4) tris[2-(2'-pyridyl)benzimidazole], 121

Thus, affirmation of this hypothesis for the iron(II) cages would indeed provide the intriguing prospect of a new class of iron(II) complex in spin equilibrium but containing a fully saturated hexaamine ligand.

A comprehensive study in solution of the variation with temperature of the

(1) magnetic moment, measured using Evans' method;
(2) optical absorption spectrum; and
(3) isotropically shifted ¹H NMR spectrum (cf. Chapter Five);

has been undertaken. In the following text the anomalous behaviour of the iron(II) cages is discussed in terms of the theoretical model first described by A.H. Ewald, R.L. Martin, I.G. Ross and A.H. White. 122

Consideration is given to the role of inter- and intramolecular influences upon the iron cages as the magnetic behaviour observed in solid and solution states differs markedly for the iron(II) cages.

4.2 THE SPIN EQUILIBRIUM MODEL

4.2.1 General Features

Complexes whose ligand field strength, 10 Dq, lies sufficiently close to the mean pairing energy, Ω, can result in both high-spin and low-spin states coexisting. The crossover region for a d⁶ ion in an octahedral ligand field is illustrated in Figure 4.1, which is adapted from Tanabe and Sugano's classic paper. 123 Figure 4.1
Figure 4.2

Representation of the potential energy surfaces for the low-spin ($^1A_{1g}$) and high-spin ($^5T_{2g}$) terms as a function of metal-ligand bond length ($r\, (M-L)$). Illustrated is a) high-spin ground state, b) spin equilibrium and c) low-spin ground state.
reveals that the symmetry and spin of the lowest state, $^5T_{2g}$, changes to $^1A_{1g}$ when $10Dq$ passes through the value $\Pi$, i.e. the $^5T_{2g}$ term is lowest when $10Dq < \Pi$ and the $^1A_{1g}$ term lies lowest when $10Dq > \Pi$.

Diagrams of the Tanabe-Sugano type (cf. Figure 4.1) are better suited to the analysis of optical spectra than to the interpretation of physical properties involving nearly equienergetic ground states coexisting in thermal equilibrium. This limitation arises since molecular states in their equilibrium geometries do not all have the same values of $10Dq$. The transfer of electrons from the $e_g$ to the $t_{2g}$ orbital subset in changing from the high-spin, $t_{2g}^6 e_g^2$ to the low-spin, $t_{2g}^6$ configuration reduces the metal-ligand bond length, $r$, and thereby increases $10Dq$ substantially (cf. Figure 4.2(b)). It follows that Figure 4.1 can only be used to discuss term separations at constant values of $10Dq$ relevant to spectral transitions. In contrast, measurements involving equilibria between spin states provide information about energies at the equilibrium geometries and must be interpreted in terms of total molecular energies.

The essence of the spin crossover situation can be illustrated qualitatively using two schematic potential energy curves for the high-spin and low-spin states represented as a function of metal-ligand distance, $r$, in Figure 4.2. In Figure 4.2, (a) depicts the weak-field region with the high-spin $^5T_{2g}$ lying lowest. In the region of strong ligand field, the $^1A_{1g}$ term supplants the $^5T_{2g}$ as the ground state as depicted in (c). The crossover region, (b) shows the two states with equal energy. It is noteworthy, that in octahedral symmetry, the intermediate spin state, $^3T_{1g}$ is never lowest. The condition for coexistence of nearly equienergetic ground states can thus be formulated as

$$10Dq \text{ (high-spin)} < \Pi < 10Dq \text{ (low-spin)}$$

...(28)
where the 10 Dq values refer to the complex in its equilibrium geometry and \( \Pi_x \) is the value of 10 Dq at which the \( ^1\text{A}_1\text{g} \) and \( ^5\text{T}_{2\text{g}} \) terms intersect, i.e., \( \Pi_x \) must lie approximately mid-way between the two equilibrium values of 10 Dq.

The effect of temperature on the equilibrium,

\[
\text{low-spin} \leftrightarrow \text{high-spin}
\]

should depend solely on the accompanying change in free energy, \( \Delta G^\circ \), when 1 mole of low-spin species is transformed into 1 mole of high-spin species, each being in their standard states, i.e.,

\[
\{\partial(\ln K)/\partial T\}_p = \Delta G^\circ /RT^2 \quad \ldots(29)
\]

The difference in Gibbs free energy for the two spin states, \( G^\circ_{\text{hs}} - G^\circ_{\text{ls}} \), at the zero-point vibronic level, \( \Delta G(T = 0) \) is equated with \( E \), the energy difference between high-spin and low-spin states. At \( T = 0 \) K, the energy difference, \( E \), corresponds to the enthalpy difference, \( \Delta H^\circ = H^\circ_{\text{hs}} - H^\circ_{\text{ls}} > 0 \). At \( T > 0 \), the entropy contribution, \( T\Delta S \), increasingly influences the high-spin/low-spin conversion due to the greater electronic, \( S_{\text{elec}} \) and vibrational, \( S_{\text{vib}} \) contributions to the total entropy available from the high-spin state.\(^{124}\)

### 4.2.2 Treatment of Thermodynamic Data

For the spin equilibrium, \( ^1\text{A}_1\text{g} \leftrightarrow ^5\text{T}_{2\text{g}} \), the proportion of molecules in the high-spin and low-spin states can be determined at any temperature from the magnitude of any measured physical property. In the following description the magnetic moment will be used as an example, although optical density could equally well be
applied.

The mole fraction of molecules in the high-spin state, 1-θ, and the low-spin state, θ, at equilibrium is then related by

\[
K_{eq} = \frac{[^{5}T_{2g}]}{[^{1}A_{1g}]} = \frac{1-\theta}{\theta} \quad \text{(30)}
\]

If spin-only values for the magnetic moments of the two states are assumed, then

\[
\mu_{\text{expt}}^2 = (1-\theta)^2 \mu_{hs}^2 + \theta \mu_{ls}^2 = (1-\theta)24 + \theta \cdot 0 = 24 - 24\theta
\]

\[\therefore \theta = \frac{24 - \mu_{\text{expt}}^2}{24} \quad \text{(31)}\]

The free energy change for the system can be expressed as a function of temperature using Equation 32,

\[
\Delta G^o = \Delta H^o - T \Delta S^o
\]

and \(K_{eq} = e^{-\Delta G^o/RT}\)

hence \(\ln K_{eq} = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \quad \text{(32)}\)

Therefore, the calculated values of \(\log_{10} K_{eq}\) when graphed as a function of \(T^{-1}\) should be linear with a gradient

\[
\frac{d(\log_{10} K_{eq})}{d(1/T)} = -\frac{\Delta H}{2.303 R} \quad \text{(33)}
\]

† The theoretical magnetic moment for the \(^{5}T_{2g}\) state is expected to lie above the spin-only value, however, the variation in moment containing an orbital contribution is difficult to estimate over a wide range of temperatures and may also be partly quenched by symmetry lower than octahedral.
and an intercept of $\Delta S/2.303 \, R$. This value of $\Delta S$ is the total entropy contribution and can be compared with the electronic contribution calculated from the spin degeneracy for the high-spin and low-spin states, i.e.

$$\Delta S_{\text{elec}} = R \ln(2S+1)_{\text{hs}} - R \ln(2S+1)_{\text{ls}} \quad \ldots (34)$$

$$= R \ln 5 - R \ln 1$$

$$= 13.38 \, \text{J mol}^{-1} \, \text{K}^{-1}$$

($\equiv 3.20 \, \text{cal mol}^{-1} \, \text{K}^{-1}$ or $1.12 \, \text{cm}^{-1} \, \text{K}^{-1}$)

Using this simple thermodynamic model over the somewhat limited experimental temperature range, the predicted $\mu(T)$ and $\chi(T)$ behaviour over an extended range of temperatures can be calculated from Equations 35 and 36,

$$K_{\text{eq}} = \frac{\mu_{\text{expt}}^2}{24 - \mu_{\text{expt}}^2} \quad \ldots (35)$$

$$. \ln \left( \frac{\mu_{\text{expt}}^2}{24 - \mu_{\text{expt}}^2} \right) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

and

$$\chi_{\text{calc}} = \frac{K}{T} \frac{1}{[1 + K]} 24(8T)^{-1}$$

$$= \frac{3}{T} \frac{K}{[1 + K]} \quad \ldots (36)$$

### 4.2.3 The Van Vleck Theoretical Model

Van Vleck\textsuperscript{56} showed that it is possible to derive a general expression which relates the magnetic susceptibility of a compound to the manifold of energy levels which characterize the paramagnetic atom. If it is assumed that the energy of the i'th level can be expanded as a power series in the magnetic field $H$, \footnote{Conversion values used are 4.184 J/cal and 11.96 J mol$^{-1}$cm$^{-1}$.}
Figure 4.3

Energy level diagram for the low-spin ($^1A_{1g}$) and high-spin ($^5T_{2g}$) ground terms.
\[
E_I = E_1(0) + HE_1(1) + H^2E_1(2) + \ldots \quad \ldots(37)
\]

and that the component of the magnetic moment in the field direction is

\[
\mu_I = -\frac{3E_I}{3H} = -E_1(1) - 2HE_1(2) \ldots \quad \ldots(38)
\]

then it can be shown that the magnetic susceptibility per mole of the compound, \(\chi_M\), can then be calculated from Equation 39,

\[
\chi_M = N \frac{E_1[(E_1(1))^2/kT - 2E_1(2)]\exp(-E_1(0)/kT)}{E_1 \exp(-E_1(0)/kT)} \quad \ldots(39)
\]

Although the \(5T_{2g}\) term involves a number of sub-levels because the 15-fold degeneracy is partially lifted by spin-orbit coupling, it is in fact a crossover system of minimum complexity because the \(1A_{1g}\) state is without spin and orbital angular momentum.

Using the calculated energies for the full spin-orbit coupled \(5T_{2g}\) term lying below the \(1A_{1g}\) with an energy separation, \(E\), Figure 4.3, application of the Van Vleck equation (Equation 39), leads to the expression

\[
\chi_M = \frac{28}{N\beta^2} \frac{28}{(kT + 3\lambda)e^2x + (kT + 12\lambda)e^{-x} + (kT - 4\lambda)e^{-3x} + (0)e^{-5x}}
\]

\[
7e^{2x} + 5e^{-x} + 3e^{-3x} + 1e^{-5x} - 2x
\]

which reduces to Equation 40 (since \(\chi_M = \frac{N\beta^2}{3kT} \cdot \mu_{\text{eff}}^2\)),

\[
\mu_{\text{eff}}^2 = \frac{3[28x + 9.33 + (22.5x + 4.17)e^{-3x} + (24.5x - 13.5)e^{-5x}]}{x[7 + 5e^{-3x} + 3e^{-5x} + e^{-(E/\lambda + 2)x}]}
\]

\ldots(40)
Figure 4.4
Calculated variation for the magnetic moment with $kT/\lambda \lambda I$ for a spin equilibrium between $^1A_{1g} \pm ^5T_{2g}$ using a fully spin-orbit coupled model defined by Equation 40. Curves include $E/\lambda = -\infty, 2, 3, 4, 6, 8, 10$ and 15 (top to bottom).
where $x = \lambda / kT$. The variation of magnetic moment as a function of $kT/|\lambda|$ corresponding to this pattern of energy levels is shown in Figure 4.4, for different values of $E/\lambda$, including $E = \infty$, where the $^5T_{2g}$ level becomes the unique ground state (cf. Figure 4.2(a)).

Marked deviations from simple spin-only ($\mu_{SO} = 4.90$ B.M.) behaviour occurs. For $E/\lambda = -\infty$, the $\mu(T)$ curve rises to a maximum value of about 5.7 B.M. at $kT/|\lambda| = 1.2$, beyond which the moment decreases slowly to a limiting value of about 5.3 B.M. For positive values of $E/\lambda$ (i.e., $E$ is negative), the $^1A_{1g}$ state lies lowest, and the moment falls to zero as $kT/|\lambda| \to 0$ as shown in Figure 4.4. It will be noticed that since Equation 40 for $\mu_{eff}^2$ contains three disposable parameters ($g$, $E$ and $\lambda$), it should accommodate, fairly well, any susceptibility curve of the right general shape.

In Section 1.14 and Chapter Two, it was pointed out that the crystal structure determination for $[\text{Fe}^2\text{H}_{2}\text{N}_{3}\text{ars}](\text{NO}_3)_4\cdot\text{H}_2\text{O}$ indicated the presence of a trigonal twist angle, $\phi = 28.6^\circ$. Clearly, a similar departure from octahedral symmetry is possible in solution. Such large distortions can lift the orbital degeneracy of the $^5T_{2g}$ term by amounts greater than that caused by spin-orbit coupling thereby resulting in an orbital singlet high-spin ground state.

In this situation, application of Van Vleck's equation yields

$$\mu_{eff}^2 = \frac{120}{5 + e^{-(E/\lambda)x}} \ldots (41)$$

The spin-orbit coupling constant, $\lambda$ is equal to $-1/4 \xi$, where $\xi$ is the single electron spin-orbit coupling constant and $\lambda = 400$ cm$^{-1}$ for the Fe$^{2+}$ ion. Therefore, the value of $\lambda$ used in these calculations is $\lambda = -100$ cm$^{-1}$. 

---

\footnote{1 The spin-orbit coupling constant, $\lambda$ is equal to $-1/4 \xi$, where $\xi$ is the single electron spin-orbit coupling constant and $\lambda = 400$ cm$^{-1}$ for the Fe$^{2+}$ ion. Therefore, the value of $\lambda$ used in these calculations is $\lambda = -100$ cm$^{-1}$.}
Figure 4.5
Calculated variation for the magnetic moment with kT/\lambda I for a spin equilibrium between $^1A_{1g} \approx ^5T_{2g}$ using a spin-only model defined by Equation 41. Curves include $E/\lambda = -\infty, 0, 1, 2, 3, 4, 6, 8, 10$ and $15$ (top to bottom).

Figure 4.6
Calculated variation of the magnetic moment with kT/\lambda I and defined by Equation 41 together with the variation of g. Curves include (top to bottom) g = 2.8, 2.4, 2.0 and 1.6 together with $E/\lambda = -\infty$, $+1$, $+3$ and $+6$. 
where, $\mu_{\text{eff}}^2 + 24 = E + \infty$; i.e. the spin-only moment for a high-spin ground state. The variation in magnetic moment as a function of $kT/|\lambda|$ is shown in Figure 4.5 for different values of $E/\lambda$.

In the derivation of Equations 40 and 41, the $g$ value was assumed to be 2.0. However, variation of this parameter can influence the $\mu(T)$ curve quite markedly, as illustrated in Figure 4.6.

These models, as described by Equation 40 and 41, are discussed further in Section 4.4 as the basis on which the experimental data are interpreted.

### 4.2.4 Analysis of Optical Spectra

The absorption spectra were analysed using an analogous thermodynamic treatment to that described in Section 4.2.2.

In this case, the mole fraction of molecules in the high-spin and low-spin states ($1-\theta$ and $\theta$, respectively) is a function of the optical density (OD). The frequency 17,000 cm$^{-1}$ was chosen to observe the change in optical density. This wavelength corresponds to the absorption maximum for the $^1T_{lg} \rightarrow ^1A_{lg}$ transition which lies furthest from the tail of the charge transfer bands and is the least influenced by the presence of impurities of the two possible low-spin transitions.

Thus, Equation 42 describes the mole fraction of molecules in the low-spin state,

$$\theta = \frac{OD_{\text{expt}}}{OD_{ls}} \quad \text{...(42)}$$

where $OD_{ls}$ is the absorption maximum at 17,000 cm$^{-1}$ measured with all the molecules are in the low-spin state; and $OD_{\text{expt}}$ is the absorption intensity measured at 17,000 cm$^{-1}$ at constant temperature.
Figure 4.7
Calculated variation of optical density with temperature as defined by Equation 44, with solid lines indicating the variation of $\Delta H = 1500$, 1250, 1000, 800, 600, 400, 300, 200, 100 and 50 cm$^{-1}$ where $\Delta S = 1.12$ cm$^{-1}$K$^{-1}$ and the dotted lines, $\Delta S = 1.1, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0$ and 5.0 cm$^{-1}$K$^{-1}$ where $\Delta H = 800$ cm$^{-1}$ (top to bottom).
The equilibrium constant, $K_{eq}$, can therefore be expressed,

$$K_{eq} = \frac{OD_{ls}}{OD_{expt}} - 1 \quad \ldots(43)$$

Substitution of Equation 31, into Equation 43, reveals the relation

$$OD_{expt} = OD_{ls} \left( e^{\frac{AS}{R}} \cdot e^{-\frac{AH}{RT}} + 1 \right)^{-1} \quad \ldots(44)$$

Equation 44 affords a family of curves for $OD_{expt}/OD_{ls}$ versus temperature, by applying $AS_{elec} = R \ln 5$ for the entropy and varying the magnitude of $AH$ (Figure 4.7). In addition, a numerical least squares fit of Equation 44 to the experimental data provides estimates of $AH$, $AS$ and $OD_{ls}$. The results of these best fits are discussed together with the spectra measured at various temperatures in Section 4.4.2 and 4.5.

4.3 EXPERIMENTAL CONSIDERATIONS

4.3.1 Solution Magnetic Measurements

Magnetic moments for the iron(II) cages were measured in solution using the Evans method as described previously in Chapter Three. However, unlike the earlier measurements these were obtained using a Bruker CXP 200 spectrometer.

Deuterated solvents were employed throughout, and were degassed using a freeze/thaw method.

All solutions were prepared in an argon filled glovebox and were checked for signs of oxidation (by observation of any colour change) prior to measurement.

Diamagnetic corrections for the ligand and anion were assumed to be identical to the solid state values and were applied without alteration. Solvent corrections are included in Table 4.1. In some cases the correction for the deuterated compound is approximated
Flow tube assembly used for measurement of optical spectra at low temperatures (ref. 126). A is the sample rod, B are neoperene rings, C is an adjustable screw for removal of sample F, D is a borosilicate stop cock, E is a graded glass seal and G is the exhaust port with the arrows indicating the direction of helium gas flow.
by the protonated analogue.

**TABLE 4.1**

Corrections for diamagnetism of the solvent.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\chi_0 \times 10^6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_2O$</td>
<td>-0.637</td>
</tr>
<tr>
<td>$CH_3CN - d^3$</td>
<td>-0.682</td>
</tr>
<tr>
<td>$(CH_3)_2NCHO - d^7$</td>
<td>-0.524$^a$</td>
</tr>
</tbody>
</table>

$^a$ Value approximated using Pascal's constitutive corrections for atoms.

4.3.2 Optical Absorption Spectra

Spectra were obtained with a computer controlled Cary 17 Spectrometer interfaced with a Cammac Data Logger. Low temperatures were achieved using a nitrogen gas cooled flow tube (Figure 4.8). The sample temperature was determined with a thermocouple attached to the outside of the quartz cell. Variable temperature measurements, $< 273 \, K$ were carried out by controlling the rate of nitrogen "boil-off", and for temperatures $> 273 \, K$ by using a heater unit.

The solvent mixture ethanol, methanol and dimethylformamide (mixed in the ratio 4:1:1) was employed for optical measurements as it provides a good low temperature glass. The glass transition region lies at $\approx 120-130 \, K$ and was achieved in only one spectrum. Thus, quantitative measurements were possible at all temperatures above the glass transition temperature region.

Solvent contraction, due to increased viscosity at low temperatures was measured as 1.03% per 10 degrees for [Fe sar]$^{2+}$ in
EtOH/MeOH/DMF and 1.1% per 10 degrees for \([\text{Fe(NH}_3\text{)}_2\text{sar}]^{4+}\) in EtOH/MeOH/DMF/CF_3SO_3H, assuming linear contraction above the glass point. Measurement of the solvent contraction was undertaken over a minimum temperature range of 100 degrees.

Optical measurements were also undertaken using Nafion ion exchange foils. These were prepared by allowing one or two foils (≈ 0.5 × 1.0 cm) to remain overnight in a concentrated solution of the required cage complex. The foils were mounted using glue over a slit made in a piece of aluminium and sealed under a small positive pressure of helium gas in a quartz tube. The baseline was obtained using untreated Nafion foil under normal atmospheric conditions.

In a manner similar to that employed for infrared (IR) measurements, pellets or discs of powdered material were pressed for measurement of their optical spectra. The required material was ground and packed undiluted under an argon atmosphere, then pressed within an airtight device in stages of approximately 2 tonne/10 mins. to no greater than a total of 10 tonne while under vacuum. The slow rate of pressure application was necessary to achieve sufficient heat dissipation to prevent oxidation of the sample.

4.4 RESULTS

4.4.1 Solution Magnetism

It emerged from the study of the magnetic properties of the cage complexes in solution (described in Chapter Three) that the iron(II) cage complexes were characterized by anomalous magnetic moments intermediate to those observed in the solid state high-spin and low-spin compounds. The room temperature moments measured in different solvents for several of the Fe(II) cages are presented in Table 4.2.
TABLE 4.2
Magnetic moments, measured at room temperature in solution and solid states for Fe(II) cages.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\mu_{\text{eff}}$ in Solution, B.M.</th>
<th>$\mu_{\text{eff}}$ in Solid, B.M.</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe sar}]^{2+}$</td>
<td>2.03, 2.27</td>
<td>5.15$^a$</td>
<td>$D_2O$</td>
</tr>
<tr>
<td></td>
<td>2.51, 2.59</td>
<td></td>
<td>CD$_3$CN</td>
</tr>
<tr>
<td></td>
<td>2.27</td>
<td></td>
<td>DCl$^b$</td>
</tr>
<tr>
<td>$[\text{Fe(NH}_3)_2\text{sar}]^{4+}$</td>
<td>4.01, 4.45</td>
<td>5.42</td>
<td>$D_2O$</td>
</tr>
<tr>
<td></td>
<td>4.33</td>
<td></td>
<td>$d^7$-DMF</td>
</tr>
<tr>
<td>$[\text{Fe(NH}_2)_2\text{sar}]^{2+}$</td>
<td>2.23</td>
<td>diamag.</td>
<td>CD$_3$CN</td>
</tr>
<tr>
<td>$[\text{Fe(CH}_3)\text{sar}]^{2+}$</td>
<td>2.22</td>
<td>high-spin$^c$</td>
<td>$d^7$-DMF</td>
</tr>
</tbody>
</table>

a Measured at 230 K.
b 0.1M DCl in $D_2O$ with t-butanol as reference probe.
c Sample in solid state appears identical to $[\text{Fe sar}]^{2+}$ and $[\text{Fe(NH}_3)_2\text{sar}]^{4+}$ as discerned by colourless crystals rather than the more intense blue crystals of $[\text{Fe(NH}_2)_2\text{sar}]^{2+}$.

It is apparent from Table 4.2, that in solution the moments fall into two types. The magnetic moments of $[\text{Fe sar}]^{2+}$, $[\text{Fe(NH}_2)_2\text{sar}]^{2+}$ and $[\text{Fe(CH}_3)\text{sar}]^{2+}$ all lie in the range 2.0 - 2.6 B.M., while that of $[\text{Fe(NH}_3)_2\text{sar}]^{4+}$ is characterized by a higher moment of 4.0 - 4.5 B.M. at room temperature.

A study of the magnetic properties of these iron(II) cages over a more extensive range of temperatures was undertaken in order to elucidate the origin of the anomaly.

The temperature range of the measurements was extended using non-aqueous solvents; i.e. from 233 - 333 K using acetonitrile, from
Figure 4.9
Variation of magnetic moment and molar susceptibility with temperature for [Fe sar]^{2+} in CD$_3$CN.
Figure 4.10
Dependence of $\log_{10} K_{eq}$ with $1/T$ for $[\text{Fe sar}]^{2+}$ in CD$_3$CN and D$_2$O.
223 + 353 K using dimethylformamide and from 283 + 353 K in aqueous media. In each case t-butanol was used as the reference probe for the Evans moment measurements.

The observed magnetic moment and susceptibility for [Fe sar]$^{2+}$ were found to be strongly dependent upon temperature, as illustrated in Figure 4.9. These results are consistent with the behaviour expected for a low-spin $^\uparrow$ high-spin equilibrium, with the low-spin state lying lowest in energy.

Fortuitously, the temperature range accessible for acetonitrile coincides with an approximate linear dependence of the moment upon temperature. The relevant thermodynamic parameters can be evaluated from the temperature dependence of the equilibrium constant, $K_{eq} = [^5T2g]/[^1A1g]$, using a graph of log$_{10} K_{eq}$ vs. $T^{-1}$ (Figure 4.10) as described in Section 4.2.2. The estimated thermodynamic parameters are summarized in Table 4.3.

**TABLE 4.3**

Relevant thermodynamic parameters calculated for Fe(II) cages in spin equilibrium.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H$, kJ mol$^{-1}$</th>
<th>$\Delta S$, J mol$^{-1}$ K$^{-1}$</th>
<th>Temperature Range, K</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe sar]$^{2+}$</td>
<td>12.30 (1028)</td>
<td>34.08 (2.85)</td>
<td>233 - 333 K</td>
<td>CD$_3$CN</td>
</tr>
<tr>
<td>[Fe sar]$^{2+}$</td>
<td>11.76 (983)</td>
<td>29.31 (2.45)</td>
<td>306 - 353 K</td>
<td>D$_2$O</td>
</tr>
<tr>
<td>[Fe(NH$_2$)$_2$sar]$^{2+}$</td>
<td>14.23 (1190)</td>
<td>38.87 (3.25)</td>
<td>233 - 353 K</td>
<td>CD$_3$CN</td>
</tr>
<tr>
<td>[Fe(CH$_3$)sar]$^{2+}$</td>
<td>8.63 (721)</td>
<td>18.28 (1.53)</td>
<td>223 - 351 K</td>
<td>d$^7$-DMF</td>
</tr>
<tr>
<td>[Fe(CH$_3$)sar]$^{2+}$</td>
<td>10.96 (916)</td>
<td>14.75 (1.23)</td>
<td>293 - 351 K</td>
<td>d$^7$-DMF</td>
</tr>
</tbody>
</table>
Figure 4.11

Variation of magnetic moment and molar susceptibility with temperature for [Fe sar]^{2+} in D$_2$O.
Variation of magnetic moment and molar susceptibility with temperature for $[\text{Fe(NH}_2)_2\text{sar}]^{2+}$ in CD$_3$CN.
Figure 4.13
Dependence of $\log_{10} K_{eq}$ with $1/T$ for $[\text{Fe(NH}_2\text{)}_2\text{sar}]^{2+}$ in CD$_3$CN (■) and for $[\text{Fe(CH}_3\text{)}_2\text{sar}]^{2+}$ in d$_7$-DMF (○).

Figure 4.14
 Variation of magnetic moment and molar susceptibility with temperature for $[\text{Fe(CH}_3\text{)}_2\text{sar}]^{2+}$ in d$_7$-DMF.
In addition, the "higher temperature" region was investigated using water as the solvent (Figure 4.11). Similar thermodynamic parameters were obtained which are included in Table 4.3.

Similar behaviour of the magnetic moment with temperature has been observed for both [Fe(NH$_2$)$_2$sar]$^{2+}$ and [Fe(CH$_3$)sar]$^{2+}$ in a variable temperature study of these complexes in solution.

The $u(T)$ and $\chi(T)$ behaviour for [Fe(NH$_2$)$_2$sar]$^{2+}$ were studied in acetonitrile solution from 232 $>$ 351 K with a strong dependence of the moment being observed over this temperature range (Figure 4.12). Analysis of the graph of $\log_{10} K_{eq}$ vs. $T^{-1}$ (Figure 4.13) revealed similar thermodynamic parameters to those found for [Fe sar]$^{2+}$ in acetonitrile and are also presented in Table 4.3.

The measurement of the magnetic moment for [Fe(CH$_3$)sar]$^{2+}$ proved difficult in acetonitrile because the resonance position of the reference probe unfortunately coincides with the methyl resonance. Accordingly, the moment of this complex was measured in dimethylformamide which allowed a similar range of temperatures to be employed. The variation in magnetic moment and susceptibility with temperature (Figure 4.14) was linear over the temperature range studied and appeared to be consistent with the spin equilibrium model. Analysis of the data using the $\log_{10} K_{eq}$ vs. $T^{-1}$ graph (included in 4.13) indicates small deviations in the high and low temperature measurements from the line of best fit. The thermodynamic parameters calculated from the line of best fit are included in Table 4.3.

As noted earlier, the room temperature moment of [Fe(NH$_3$)$_2$sar]$^{4+}$ in aqueous solution lies below its solid state value by ca. 1 B.M., yet considerably above (by ca. 2 B.M.) the values observed in solution for [Fe sar]$^{2+}$, [Fe(NH$_2$)$_2$sar]$^{2+}$ and [Fe(CH$_3$)sar]$^{2+}$. 
The magnetic measurements for \([Fe(NH_3)_2sar]^{4+}\) were extended over a wider range of temperatures in aqueous solution in order to establish whether a spin equilibrium mechanism was also operative in this case. Surprisingly, over the temperature range 278-353 K, the magnetic moment was found to remain essentially unchanged, i.e. \(\mu_{\text{eff}} = 4.07 \pm 0.06\) B.M. (Table 4.4). The measurements were also extended to dimethylformamide solution, and over the temperature range 222-293 K, again the moment remained unchanged, \(\mu_{\text{eff}} = 4.34 \pm 0.04\) B.M. (Table 4.5).

**TABLE 4.4**
Magnetic susceptibility and moment, measured over a range of temperatures in D\(_2\)O solution.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>278</th>
<th>293</th>
<th>298</th>
<th>303</th>
<th>323</th>
<th>343</th>
<th>353</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi_M' \times 10^3)</td>
<td>7.43</td>
<td>6.87</td>
<td>6.84</td>
<td>6.69</td>
<td>6.29</td>
<td>6.10</td>
<td>6.03</td>
</tr>
<tr>
<td>(\mu_{\text{eff}}) (B.M.)</td>
<td>4.06</td>
<td>4.01</td>
<td>4.04</td>
<td>4.03</td>
<td>4.03</td>
<td>4.09</td>
<td>4.13</td>
</tr>
</tbody>
</table>

**TABLE 4.5**
Magnetic susceptibility and moment, measured over a range of temperatures in \(d^7\)-DMF solution.

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>223</th>
<th>233</th>
<th>243</th>
<th>253</th>
<th>263</th>
<th>273</th>
<th>295</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\chi_M' \times 10^3)</td>
<td>10.70</td>
<td>10.29</td>
<td>9.56</td>
<td>9.44</td>
<td>8.95</td>
<td>8.55</td>
<td>7.94</td>
</tr>
<tr>
<td>(\mu_{\text{eff}}) (B.M.)</td>
<td>4.37</td>
<td>4.38</td>
<td>4.31</td>
<td>4.37</td>
<td>4.34</td>
<td>4.32</td>
<td>4.33</td>
</tr>
</tbody>
</table>
Figure 4.15
Absorption spectrum of \([\text{Fe sar}]^{2+}\) in \(\text{D}_2\text{O}\) at 295 K.
It was immediately evident that the $\mu_{\text{eff}}(T)$ behaviour of [Fe(NH$_3$)$_2$sar]$^{4+}$ differed from that observed for the other iron(II) cage complexes. In fact, the magnetic moment is not only somewhat depressed below 4.90 B.M., but also appears to behave in a Curie-like manner with $\chi$ proportional to $T^{-1}$, rather than following the spin equilibrium behaviour, where $\chi$ is roughly proportional to $T$ in the temperature range studied.

4.4.2 Optical Spectroscopy

The colourless crystals of [Fe sar]$^{2+}$ and [Fe(NH$_3$)$_2$sar]$^{4+}$ when dissolved in solvents, give rise to coloured solutions which are pale blue. The blue crystals of [Fe(NH$_2$)$_2$sar]$^{2+}$ retained their blue colour upon dissolution.

These observations suggested that the colour change from the solid to the solution state could be investigated by the measurement of the absorption spectra of the iron(II) cages.

There were considerable difficulties in obtaining reproducible optical spectra for the iron(II) cages because of the,

(1) extremely weak d-d transitions expected for the high-spin quintet state ($\varepsilon = 5$), and the
(2) air-sensitive nature of the iron(II) complexes, in which oxidation occurs to form imines (cf. Scheme 16), which are characterized by intense absorption transitions in the visible region.

The absorption spectrum in solution of [Fe sar]$^{2+}$ measured at room temperature is presented in Figure 4.15. The two bands which dominate the visible region are assigned to the $1_{T_1g} + 1_{A_1g}$ and $1_{T_2g} + 1_{A_1g}$ electronic transitions. The solution media is D$_2$O, chosen for its wider spectral window in the near infrared (NIR) when
Figure 4.16
Absorption spectrum of $[\text{Fe sar}]^{2+}$ in D$_2$O/DMF measured at 190, 298 and 350 K (top to bottom).

Figure 4.17
Variation of the $^1T_{1g} - ^1A_{1g}$ absorption band intensity with temperature for $[\text{Fe sar}]^{2+}$ in EtOH/MeOH/DMF. Included are measurements at 130, 150, 170, 190, 210, 250, 270, 320, 340 and 360 K (top to bottom).
Figure 4.18

Calculated curves and experimental data for the variation of \( \frac{OD_{\text{exp}}}{OD_{\text{ls}}} \) with temperature for \([\text{Fe} \text{sar}]^{2+}(\triangle)\) and \([\text{Fe} \text{(NH}_3\text{)}_2\text{rar}]^{4+}(\bullet)\). Curves calculated using Equation 44 together with the "parameters of best fit" in Table 4.6.
compared with \( \text{H}_2\text{O} \). However, no high-spin transitions were observed in the expected NIR region (10,000-14,000 cm\(^{-1}\)) for the \([\text{Fe sar}]^{2+}\) complex.

The molar extinction coefficients for the two observed transitions were almost identical and were calculated using the Beer-Lambert law,\(^{110}\) to give \( \varepsilon_{\text{obs}} = 12.7 \text{ M}^{-1} \text{ cm}^{-1} \). However, this value arises from the fraction of molecules in the low-spin state, \( \theta \); therefore it is also necessary to apply Equation 42 in order to calculate \( \varepsilon_{\text{max}} \) (included later in Table 4.7) for these transitions.

The spectrum of \([\text{Fe sar}]^{2+}\), measured at 190, 298 and 350 K in \( \text{D}_2\text{O}/\text{DMF} \) solution is presented in Figure 4.16. The increase in intensity for the two low-spin transitions is apparent as the temperature is lowered, which suggests that the low-spin \( ^1\text{A}_{1g} \) state lies lowest.

A similar dependence with temperature is also observed for the \([\text{Fe sar}]^{2+}\) spectrum studied over the temperature range 130 - 350 K, in \( \text{EtOH/MeOH/DMF} \) solution. However, in both \( \text{D}_2\text{O}/\text{DMF} \) and \( \text{EtOH/MeOH/DMF} \) solutions, no bands were apparent that could be attributed to the high-spin electronic transitions.

Analysis of the low-spin absorption band at 17,000 cm\(^{-1}\) (Figure 4.17), revealed that the ratio of experimentally measured optical density to the optical density calculated when all the molecules are in the low-spin state, \( \text{i.e. } \frac{\text{OD}_{\text{expt}}}{\text{OD}_{\text{ls}}} \), is strongly dependent upon temperature (Figure 4.18). This behaviour is as expected for a spin equilibrium system and simply reflects the changing proportions of high-spin and low-spin molecules with changing temperature. It is of

\[\dagger\] The \( \theta \) value was obtained from the magnetic moment measurements.
Figure 4.19

Variation of the absorption spectrum with temperature for $[\text{Fe(NH}_3\text{)}_2\text{san}]^{2+}$ in EtOH/MeOH/DMF/CF$_3$SO$_3$H. Included are measurements at 185, 210, 240, 265 and 295 K.
interest to note that $\text{OD}_{1s}$ occurs at temperatures below 150 K when all the molecules are in the low-spin configuration.

The room temperature value for the magnetic moment of $\text{[Fe(NH}_3\text{)_2sar]}^{4+}$ lies significantly above those observed for the other iron(II) cages (cf. Tables 4.4 and 4.5). Therefore, it seemed more likely that the high-spin electronic transition(s) for the $\text{[Fe(NH}_3\text{)_2sar]}^{4+}$ complex would be observable.

Indeed, as expected, the absorption spectrum of $\text{[Fe(NH}_3\text{)_2sar]}^{4+}$ is characterized by two weak high-spin transitions in addition to the two much stronger low-spin transitions. At temperatures varying from 185 to 295 K, the intensities of the low-spin transitions decreased and a concommitant increase in the intensities of the high-spin transitions occurred (Figure 4.19).

Analysis of the low-spin band at 17,000 cm$^{-1}$ for $\text{[Fe(NH}_3\text{)_2sar]}^{4+}$, in a manner similar to that described for $\text{[Fe sar]}^{2+}$, disclosed a sigmoidal dependence of $\text{OD}_{\text{expt}}/\text{OD}_{1s}$ with temperature (included in Figure 4.18). However, in this case, the maximum value of $\text{OD}_{1s}$ lies at ca. 130 K, although this temperature was not obtained experimentally.

The $\text{OD}_{\text{expt}}/\text{OD}_{1s}$ versus temperature plots for both $\text{[Fe sar]}^{2+}$ and $\text{[Fe(NH}_3\text{)_2sar]}^{4+}$, (Figures 4.18) have been fitted using a numerical least squares fit of Equation 44 to the experimental $\text{OD}_{\text{expt}}$ curve. The parameters for best fit are included in Table 4.6.

Certainly, the most definitive optical measurement, for characterizing the spin equilibrium model, was the measurement of absorption spectra at varying pH. The optical spectrum of $\text{[Fe(NH}_2\text{)_2sar]}^{2+}$ measured in $\text{D}_2\text{O}$ (pH 8.5) alters dramatically upon the addition of one drop of pure $\text{CF}_3\text{SO}_3\text{H}$ (Figure 4.20). The resulting
Variation of the absorption spectrum with pH for $[\text{Fe(NH}_2\text{)}_2\text{sar}]^{2+}$ in D$_2$O. At pH 8.5 the species in solution is $[\text{Fe(NH}_2\text{)}_2\text{sar}]^{2+}$ (a) and at pH 4.5 is $[\text{Fe(NH}_3\text{)}_2\text{sar}]^{4+}$ (b).
solution; pH 4.5, is in fact the complex $[\text{Fe(NH}_3\text{)_2sar}]^{4+}$, and is characterized by a higher value of magnetic moment in solution than that of the original solute (cf. Table 4.2).

**TABLE 4.6**

Thermodynamic parameters for the best fit of Equation 44.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta H$, kJ mol$^{-1}$ (cm$^{-1}$)</th>
<th>$\Delta S$, J mol$^{-1}$ K$^{-1}$ (cm$^{-1}$ K$^{-1}$)</th>
<th>$OD_{18}$</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Fe sar}]^{2+}$</td>
<td>14.76 ± 0.35 (1234 ± 29)</td>
<td>39.47 ± 2.39 (3.3 ± 0.2)</td>
<td>0.122</td>
<td>EtOH, MeOH, DMF</td>
</tr>
<tr>
<td>$[\text{Fe(NH}_3\text{)_2sar}]^{4+}$</td>
<td>11.94 ± 0.32 (998 ± 27)</td>
<td>40.66 ± 2.39 (3.4 ± 0.2)</td>
<td>0.496 ± 0.005</td>
<td>EtOH, MeOH, DMF, CF$_3$SO$_3$H</td>
</tr>
</tbody>
</table>

At pH 8.5, the spectrum is dominated by two low-spin transitions at ca. 17,000 and 25,000 cm$^{-1}$ in the visible region with no high-spin transitions evident in the near infra-red region. However, at pH 4.5, the two low-spin transitions decreased to approximately one-half of their original intensity and the concomitant appearance of two weak bands attributed to the high-spin transitions at ca. 10,000 and 12,000 cm$^{-1}$ was observed.

At pH 4.5, the optical data provide unequivocal evidence for the co-existence of the high-spin and low-spin states for $[\text{Fe(NH}_3\text{)_2sar}]^{4+}$ which is also characterized by the unusual temperature independent magnetic moment in solution. Similar measurements have been undertaken with $[\text{Fe(NH}_2\text{)_2sar}]^{2+}$ dissolved in EtOH/MeOH/DMF - EtOH/MeOH/DMF/CF$_3$SO$_3$H with identical results. However, in these solutions the value of pH is not defined, although deprotonated and protonated forms of the complex can be generated.

The weak absorbance of the observed high-spin transitions precludes any accurate quantitative analysis, of the NIR region for
However, the low-spin transitions for the Fe(II) cages can be utilized to obtain approximate values for their molar extinction coefficients. The molar extinction coefficient, \( \varepsilon_{\text{max}} \), of the first ligand field band \( (^1T_{1g} + ^1A_{1g}) \) has been calculated as a function of the mole fraction of molecules in the low-spin state, \( \theta \), at room temperature (Table 4.7). These data are then extrapolated to a temperature region where all the molecules are low-spin, i.e. \( \theta = 1.0 \) and a value for \( \varepsilon_{\text{max}} \) calculated (included in Table 4.7).

**TABLE 4.7**

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \tilde{\nu} ), cm(^{-1})</th>
<th>( \varepsilon_{\text{max}} ), M(^{-1})cm(^{-1})</th>
<th>Assignment</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe sar](^{2+})</td>
<td>16,949</td>
<td>14.5</td>
<td>( ^1T_{1g} + ^1A_{1g} )</td>
<td>D(_2)O</td>
</tr>
<tr>
<td></td>
<td>25,381</td>
<td>14.5</td>
<td>( ^1T_{2g} + ^1A_{1g} )</td>
<td></td>
</tr>
<tr>
<td>[Fe(NH(_2))(_2)sar]^{2+}</td>
<td>16,985</td>
<td>19.0</td>
<td>( ^1T_{1g} + ^1A_{1g} )</td>
<td>EtOH, MeOH,</td>
</tr>
<tr>
<td></td>
<td>25,202</td>
<td>19.0</td>
<td>( ^1T_{2g} + ^1A_{1g} )</td>
<td>DMF</td>
</tr>
<tr>
<td>[Fe(NH(_3))(_2)sar]^{4+}</td>
<td>10,180</td>
<td>0.9</td>
<td>( ^5E_{g} + ^5T_{2g} )</td>
<td>EtOH, MeOH,</td>
</tr>
<tr>
<td></td>
<td>12,168</td>
<td>0.9</td>
<td></td>
<td>DMF, CF(_3)SO(_3)H</td>
</tr>
<tr>
<td></td>
<td>16,913</td>
<td>22.7</td>
<td>( ^1T_{1g} + ^1A_{1g} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>24,653</td>
<td>22.7</td>
<td>( ^1T_{1g} + ^1A_{1g} )</td>
<td></td>
</tr>
</tbody>
</table>

\( \varepsilon_{\text{max}} \) calculated for \((1-\theta) = 1\) for high-spin transitions \( (^5E_{g} + ^5T_{2g}) \) and for \( \theta = 1 \) for low-spin transitions \( (^1T_{2g} + ^1A_{1g} \) and \( ^1T_{1g} + ^1A_{1g} \)).

It must be noted that these calculated molar extinction coefficients are approximations of the true absorption intensity, which is more correctly the integrated area of the band over the full...
Figure 4.21
Absorption spectrum of $[\text{Fe(NH}_3)_2\text{sar}]^{4+}$ in Nafion foil at a) 10 K and b) 295 K.

Figure 4.22
Absorption spectrum of $[\text{Fesar}]^{2+}$ in Nafion foil at a) 10 K and b) 295 K.
Absorption spectrum of powdered $[\text{Fe(NH}_2\text{)}_2\text{sar}]^{2+}$ pressed into a transparent disc at 295 K.
Figure 4.24
Calculated curves and experimental data for the variation of magnetic moment and susceptibility with temperature for [Fe(sar)]²⁺ in CD₃CN. Calculated curves from Equation 41 using the parameters in Table 4.3.
Calculated curves and experimental data for the variation of magnetic moment and susceptibility with temperature for $[\text{Fe sar}]^{2+}$ in D$_2$O. Calculated curves from Equation 41 using the parameters in Table 4.3.
Figure 4.26

Calculated curves and experimental data for the variation of magnetic moment and susceptibility with temperature for $[\text{Fe(NH}_2)_2\text{sar}]^{2+}$ in CD$_3$CN. Calculated curves from Equation 41 using the parameters in Table 4.3.
range of wavenumbers. However, discrete bands are seldom available for such an analysis, and \( \varepsilon_{\text{max}} \), at a stated wavenumber, \( \tilde{\nu}_{\text{max}} \), corresponding to the maximum absorption is regarded here as sufficient to characterize the electronic bands.

The spectra of the iron(II) cages were also explored in Nafion foil, a spectroscopically transparent cation exchange resin. This material contains sulphonate anion residues capable of adsorbing cationic molecules in high concentration from solution. This method of study appeared to offer an attractive approach to the investigation of solution properties in the absence of solvent.

Although slightly contaminated by imine impurity, the spectra of \([\text{Fe(NH}_{3})_{2}\text{sar}^{4+}\) and \([\text{Fe sar}^{2+}\) were obtained in Nafion foil and are presented in Figures 4.21 and 4.22. As discerned in these spectra, the first low-spin ligand field bands were not significantly influenced by a temperature change from 295 K to 10 K. Also no high-spin bands are apparent in this medium, for these cages within this temperature range. It can only be concluded from Figures 4.21 and 4.22, that the spin equilibrium evident in the solution spectra is changed somewhat by the Nafion foil environment to produce low-spin behaviour at all temperatures.

Electronic spectra were also obtained in the solid state, by compressing ground crystals into a transparent disc. The spectrum of \([\text{Fe(NH}_{2})_{2}\text{sar}^{2+}\) (Figure 4.23) measured in this manner confirms the low-spin configuration established by the magnetic measurements outlined in Chapter Two. The spectra of \([\text{Fe sar}^{2+}\) and \([\text{Fe(NH}_{3})_{2}\text{sar}^{4+}\) were unsatisfactory, with oxidation products obscuring the d-d transition region.
Figure 4.27
Calculated curves and experimental data for the variation of magnetic moment and susceptibility with temperature for [Fe(CH₃)₃an]²⁺ in d⁷-DMF. Calculated curves from Equation 41 using the parameters in Table 4.3.
Calculated curves and experimental data for the variation of magnetic moment and susceptibility with temperature for [Fe(NH$_3$)$_2$sar]$^{4+}$ in D$_2$O. Calculated curves from Equation 41 using the spin-only contribution from $\Delta S$. 

Figure 4.28
Calculated curves and experimental data for the variation of magnetic moment and susceptibility with temperature for [Fe(NH$_3$)$_2$sar]$^{4+}$ in d$_7$-DMF. Calculated curves from Equation 41 using the spin-only contribution from $\Delta S$. 
Experimental magnetic susceptibility and moment data over a range of temperatures have been closely reproduced by a model involving $^{1}_{A_{1g}}$ and $^{5}_{A(5T_{2g})}$ states in thermal equilibrium. In Figures 4.24, 4.25, 4.26 and 4.27, these experimental data are compared with the $\chi(T)$ and $\mu(T)$ curves calculated using the enthalpy and entropy values listed in Table 4.3 for [Fe sar]$^{2+}$, [Fe(NH$_2$)$_2$sar]$^{2+}$ and [Fe(CH$_3$)sar]$^{2+}$.

It was not possible to estimate $\Delta H$ and $\Delta S$ values for the compound [Fe(NH$_3$)$_2$sar]$^{4+}$ from log$10^{\text{K_{eq}}}$ vs. $1/T$ plots because the magnetic moment was virtually independent of temperature (cf. Tables 4.4 and 4.5). Accordingly, $\Delta H$ and $\Delta S$ were estimated by fitting the magnetic data to Equation 41 which incorporates the simplifying assumption that only the electronic contribution of $R \ln 5$ is made to $\Delta S$. However, excellent agreement was obtained between the calculated and observed values as is observed in Figures 4.28 and 4.29.

The values obtained for the energy separation between the ground and excited state $E$ (or $\Delta H$) lie in the expected range and reveal that the $^{1}_{A_{1g}}$ state always lies lowest. These $E$ values were incorporated into a relative energy diagram for the iron(II) cages as illustrated in Figure 4.30. Although only limited significance should be attached to the magnitude of the derived values of $E$, this representation shows an interesting progression from [Fe(NH$_3$)$_2$sar]$^{4+}$ < [Fe(CH$_3$)sar]$^{2+}$ < [Fe sar]$^{2+}$ < [Fe(NH$_2$)$_2$sar]$^{2+}$. This trend suggests that electron withdrawal by the apical substituents (especially -NH$_3^+$) weakens the ligand field, and so that the $^{1}_{A_{1g}}$ and $^{5}_{A(5T_{2g})}$ states become closer in energy. It is interesting to speculate whether a further removal of charge, for example, by using -NH$_2$.BF$_3$...
Octahedral field

Lower symmetry component

- $[\text{Fe(NH}_3\text{)}_2\text{sat}]^{2+}$
- $[\text{Fe sar}]^{2+}$
- $[\text{Fe(CH}_3\text{)sar}]^{2+}$
- $[\text{Fe(NH}_3\text{)sat}]^{4+}$

Figure 4.30

Relative energies of the $^1A_{1g}$ and $^5A_1(^5T_{2g})$ levels for substituted Fe(II) cage complexes.
as an apical substituent would lead to a quintet ground state in solution.

The energy difference between the $^1A_{ig}$ and $^5A(^5T_{2g})$ levels is extremely small, i.e. of the order of $kT$ at room temperature, and the above estimates of $\Delta H$ and $\Delta S$ will also be sensitive to other parameters not included in this simple model. For example, the variation of $g$ values, distortion from octahedral symmetry, spin-orbit coupling effects, configuration interaction and molecular vibrational partition functions are all factors that should be included in more refined models.

It is interesting to note in passing that the magnitude of $\Delta H$ obtained for the iron(II) cages can be compared with corresponding values estimated from the critical temperature $T_c$ at which the maximum in their $\chi(T)$ curves, occurs using the relation,

$$E = 1.815 \kappa T_c$$

...(45)

derived by differentiation of Equation 41.

As expected, the energies calculated using this expression agree well with the previously determined values of $\Delta H$ (cf. Table 4.3) for $[\text{Fe(NH}_3)_2\text{sar}]^{4+}$. However, values of $E$ estimated from Equation 45, fall well below the $\Delta H$ values obtained for the remaining iron(II) cages. These discrepancies appear to arise from the entropy values which are greater (as determined from $\log_{10}K_{eq}$ vs. $1/T$ plots) than the $\Delta S$ (electronic) value assumed for the $[\text{Fe(NH}_3)_2\text{sar}]^{4+}$ cage.

The influence of different solvent environments on the magnetic properties was difficult to gauge as the inherent error in determining solution concentrations was considered to be the major source of experimental scatter. However, it was concluded that, if solvent interactions were influencing the position of the spin
equilibrium, this effect would be of less significance than that of the electron withdrawing/donating nature of the apical substituents.

The magnitude of the observed entropy change, $\Delta S$, includes both electronic and vibrational terms as major contributions. The electronic contribution, $\Delta S_{\text{elec}} = R \ln (2S + 1) = 13.38 \text{ J mol}^{-1} \text{ K}^{-1} (1.12 \text{ cm}^{-1} \text{ K}^{-1})$ for the quintet and singlet crossover, is compared with the values listed in Tables 4.3 and 4.6, which show that the total entropy change is larger, in each case, than the electronic term alone.\textsuperscript{††}

Investigation of the entropy contributions in some solid state spin transition systems, have demonstrated the importance of changes in the vibrational behaviour; predominantly the metal-ligand stretching and deformation vibrations with only a minor contribution to the entropy from the lattice modes.\textsuperscript{124} Using heat capacity measurements for $[\text{Fe(phen)}_2(\text{NCS})_2]$ and $[\text{Fe(phen)}_2(\text{NCS})_2]$, it was found that only one third of the total entropy change of nearly 50 J mol$^{-1}$ K$^{-1}$, on passing from low-spin to high-spin, stems from $\Delta S_{\text{elec}}$. The remaining two thirds originated from vibrational modes, with about half of the total $\Delta S_{\text{vib}}$ accounted for by changes in metal-ligand stretching frequencies.\textsuperscript{124} As lattice effects appear to be minimal in this analysis, it was assumed that a similar deployment of entropy contributions occurs for the iron(II) cages in solution.

The observation of both low-spin and high-spin absorption bands

\textsuperscript{†} No orbital contribution to the total entropy has been considered here, as lower than cubic symmetry will act to remove orbital degeneracy.\textsuperscript{127}

\textsuperscript{††} Except for $[\text{Fe(NH}_3)_2\text{sal}]$\textsuperscript{44} where the $\Delta H$ value is calculated by assuming $\Delta S = R \ln 5$. 
in the optical spectrum of \([\text{Fe(NH}_3)_2\text{sar}]^{4+}\), confirms the presence of both spin states as was deduced from magnetic behaviour. The actual appearance of discrete bands characteristic of each spin state rather than an averaged spectrum enables an upper limit for the interconversion rate to be set with respect to the time required for an electronic transition. The period for dynamic interconversion, \(\tau > 10^{-13}\) s, can be estimated since metal-ligand nuclear oscillations are of this order; thus the corresponding rate constant \(k < 10^{13}\) s\(^{-1}\). In addition, the lower limit for the rate constant can be estimated from the relaxation rate of \(\tau < 10^{-7}\) s, obtained from the averaged resonances observed in the \(^1\text{H NMR}\) spectrum. Hence, the interconversion rate constant, for the spin equilibrium should lie in the range \(10^7 < k < 10^{13}\) s\(^{-1}\).

In contrast to \([\text{Fe(NH}_3)_2\text{sar}]^{4+}\), the equilibrium is displaced in favour of the low-spin isomer for the other iron(II) cages, by an amount sufficient to prevent detection of the high-spin electronic band. However, the optical spectra of \([\text{Fe sar}]^{2+}\) and \([\text{Fe(NH}_3)_2\text{sar}]^{4+}\) show a dependence with temperature (cf. Figures 4.16, 4.17 and 4.19) which is consistent with the spin equilibrium model. The band centred at approximately 17,000 cm\(^{-1}\) (\(^1\text{T}_{1g} + ^1\text{A}_{1g}\)) was selected for quantitative analysis, as it is the least affected by imine impurities, and in addition it provided a sufficient variation in optical density with temperature to permit the independent estimation of \(\Delta H\) and \(\Delta S\) values.

The experimentally obtained ratios \(\frac{\text{OD}_{\text{expt}}}{\text{OD}_{\text{ls}}}\) versus temperature for \([\text{Fe(NH}_3)_2\text{sar}]^{4+}\) and \([\text{Fe sar}]^{2+}\) (Figure 4.18) were reproduced by a numerical least squares fitting procedure applied to Equation 44, to derive the values for \(\Delta H\) and \(\Delta S\) given in Table 4.6. These fits confirm the spin equilibrium model for both compounds,
although in both cases, the estimated values for $\Delta H$ exceed the corresponding values estimated from the magnetic measurements, especially for $[\text{Fe(NH}_3)_2\text{sar}]^{4+}$ (cf. Table 4.6). Comparison of these fits with the family of curves (Figure 4.7) calculated from Equation 44 assuming $\Delta S = R \ln 5$, reveals a much greater variation with temperature. This confirms that the entropy term for the Fe(II) cages is considerably larger than the electronic value assumed in our calculations, and is presumably due to vibrational contributions. The different solvent environments employed for the optical compared with the magnetic measurements also could be a contributing factor to this variation between the optical and magnetic $\Delta H$ values.

An unusual feature of the present iron(II) cage spectra is the absence of charge transfer bands which often obscure the d-d region of spin equilibrium complexes.$^{117,120,121}$ This has not only offered a rare opportunity to observe both the high-spin and low-spin electronic bands, but also allowed accurate determination of the 10 $Dq$ values for each spin state. At the same time, a somewhat unusual opportunity is thereby provided to estimate directly the mean pairing energy, $\Pi$.

The high-spin $^5E_g + ^5T_{2g}$ transition for $[\text{Fe(NH}_3)_2\text{sar}]^{4+}$ is split by some 2000 cm$^{-1}$, suggesting that the overall symmetry is lower than cubic. Similar 'doublet' structure has been observed for the optical transitions of $[\text{Fe(H}_2\text{O)}_6]^{2+}$ and $[\text{Co F}_6]^{3-}$, with the $^4t_{2g}^2e_{g}^2$ configuration.$^{57}$ For these examples the observed splitting of the $^5E_g + ^5T_{2g}$ transition has been attributed to the Jahn-Teller unstable excited state configuration, $^3t_{2g}^3e_{g}^3$.$^{127}$ The degeneracy of the $^5E_g$ state is lifted into two orbital singlets, resulting in the two observed optical transitions, $^5A(E) + ^5T_{2g}$ and $^5B(E) + ^5T_{2g}$ separated by ca. 2000 cm$^{-1}$.  

Octahedral field and Trigonal field and Jahn-Teller distortion

Figure 4.31
Splitting diagram for the $t_{2g}^4e_g^2$ configuration, indicating the effect of a reduction in symmetry.
A static trigonal distortion which reduces the symmetry of the ground term \( ^{5}T_{2g} \) from octahedral, together with the Jahn-Teller induced splitting of the excited state \( ^{5}E_{g} \), will give rise to a splitting diagram similar to Figure 4.31. This representation appears to be consistent with crystallographically observed trigonal twist angle, \( \phi = 28.6^\circ \) for \([Fe(NH_3)_2sar](NO_3)_4 \cdot H_2O\). In addition, an axial field will lift the degeneracy of the \( ^{5}T_{2g} \) ground term into an orbital singlet and doublet \( ^{5}B_2 \) and \( ^{5}E \) states. Therefore, in either trigonal or axial fields, an orbital singlet can lie lowest in agreement with the observed fits for the iron(II) cages.

The 10 Dq values obtained for the low- and high-spin isomers of \([Fe(NH_3)_2sar]^{4+}\), were calculated using the d-d transition energies in Table 4.7, i.e. \([10 \text{ Dq}]_l = 19,000 \text{ cm}^{-1} \) and \([10 \text{ Dq}]_h = 11,000 \text{ cm}^{-1} \).

The mean pairing energy, \( \Pi \), then can be estimated by assuming that the intersection of the high-spin and low-spin potential energy curves lies about mid-way between the two minima, i.e.

\[
\Pi = \frac{11,000 + 19,000}{2} = 15,000 \text{ cm}^{-1}
\]

The spectroscopic results for a number of Fe(II) spin equilibrium complexes and the analogous Ni(II) complexes, have been compared by several workers\(^{120,129}\) who noted that the ratio \([10 \text{ Dq}]_h(Fe^{2+})/[10 \text{ Dq}](Ni^{2+})\) was \(1.11 \pm 0.07\). The corresponding ratio for \([Fe(NH_3)_2sar]^{4+}\) of ca. 0.94 falls just outside this range. By applying the ratio 0.94 and the 10 Dq value obtained for \([Ni \text{ sar}]^{2+}\) (cf. Table 3.8), an estimate for \([10 \text{ Dq}]_h\) for \([Fe \text{ sar}]^{2+}\) can be obtained, i.e. \([10 \text{ Dq}]_h \approx 11,000 \text{ cm}^{-1}\). In a similar manner, the low-spin \([10 \text{ Dq}]_l(Fe^{2+})/[10 \text{ Dq}](Ni^{2+})\) ratio of 1.15, found for complexes of \([37]^{120}\) can be compared with that obtained for
[Fe(NH$_3$)$_2$sar]$^{4+}$, 1.62; and [Fe sar], 1.60 ([10 Dq]$_{ls}$ for [Fe sar]$^{2+}$

is 18,815 cm$^{-1}$).

It was pointed out in Section 4.2.1, that diagrams of the Tanabe-Sugano type (Figure 4.1) have the limitation that molecular states in their equilibrium geometries do not all have the same value of 10 Dq. The transfer of an electron from the t$_{2g}$ orbital subset to the e$_g$ subset increases the metal-ligand bond length and thereby decreases 10 Dq. Thus, Tanabe-Sugano diagrams which are constructed on relative energy scales can only be used to predict term separations at constant values of 10 Dq; e.g., the lowest energy electronic band $^{1}T_{1g}$ + $^{1}A_{1g}$ for [Fe sar]$^{2+}$ corresponds to a transition at a fixed value of 10 Dq (see Figure 4.32), with an energy given by $h\nu = (10 \text{ Dq})_{ls} - C$.

![Figure 4.32](image)

Absorption transitions to higher energy levels for the low-spin d$^6$ configuration.

Since the energy of the $^5T_{2g}$ term is given by $E = -4 \text{ Dq}$, it follows that the high-spin $^5T_{2g}$ term will be supplanted by the low-spin $^1A_{1g}$ term when $(20 \text{ Dq})_{\Pi} > 5B + 8C$, i.e. the fixed value of $(10 \text{ Dq})_{\Pi}$ at which the terms cross is $1/2(5B + 8C)$ and is represented by $\Pi$. If the relation between the Racah parameters for interelectronic repulsion is taken as $C = 4B$ and the value of B for the free ion as 1000 cm$^{-1}$, then the energy at the crossing point $\Pi$ in the Tanabe-Sugano diagram would be $(10 \text{ Dq})_{\Pi} = 19,600 \text{ cm}^{-1}$. 
If we now consider the total molecular energy curves of the complex in its equilibrium geometries (Figure 4.2), the values of the equilibrium parameters $10 \text{Dq}(^5T_{2g})$ and $10 \text{Dq}(^1A_{1g})$ should span that of the mean pairing energy $\Pi$, i.e., $(10 \text{Dq})_{\text{hs}} < \Pi < (10 \text{Dq})_{1s}$

The ligand field parameter $(10 \text{Dq})_{\text{hs}}$ is equal to the energy of the $^5T_{2g} + ^5E_g$ band which occurs at an energy of $11,000 \text{ cm}^{-1}$ for $[\text{Fe(NH}_3)_2\text{sar}]^{4+}$ (Table 4.7). It is seen from Figure 4.32 that the energy of $(10 \text{Dq})_{1s}$ is given by $h\nu + C = 17,000 + 4,240 \times 21,200 \text{ cm}^{-1}$ so that the above inequality is satisfied.

This analysis can be refined by recognizing that the Racah parameter for the free ion is reduced when the metal ion is complexed. The extent of the reduction can be gauged from the positions of the two low-spin bands in the optical spectra of the iron(II) cages. From Figure 4.32, the difference in energies of the $^1T_{1g} + ^1A_{1g}$ and $^1T_{2g} + ^1A_{1g}$ bands is $16 \times 128$ or $24,700 - 17,000 = 7,700 \text{ cm}^{-1}$, for $[\text{Fe(NH}_3)_2\text{sar}]^{4+}$ so that $B$ is reduced substantially from $1060 \text{ cm}^{-1}$ (free ion value) to $480 \text{ cm}^{-1}$. This leads to an amended value for $(10 \text{Dq})_{1s} = 17,000 + 1920 = 18,900 \text{ cm}^{-1}$. It was noted in Section 4.2.1, that the crossing point must lie approximately half-way between the two equilibrium values of $10 \text{Dq}$ so that $\Pi$ should be approximately $1/2(11,000 + 19,000) = 15,000 \text{ cm}^{-1}$.

An even more significant reduction in $B$ is evident for $[\text{Fe(NH}_3]\text{capten}]^{3+}$. The optical spectrum reveals two low-spin transitions of similar energy to those observed for the FeN$_6$ core cages, yet this complex remains low-spin in solution (cf. Chapter Three). Clearly the ligand field strength (gauged by $10 \text{Dq}/B$) is of comparable energy for the Fe$^{II}$N$_6$ and Fe$^{II}$N$_3$S$_3$ compounds, however $B$ is reduced even more in the latter case and the mean pairing energy becomes significantly lower, hence low-spin behaviour is observed in
both solid and solution states.

4.6 CONCLUSION

The iron(II) cages appear to be the first examples of spin equilibrium systems with pseudo-octahedral Fe(II) coordinated by saturated amine donor atoms.

In the literature, nine different spin equilibrium systems have been characterized for hexa-coordinated Fe(II); however, in each case the nitrogen donor atoms have been involved with unsaturated ring systems. The range of physico-chemical measurements that were used with these compounds have been restricted generally to magnetic and Mössbauer studies on the solid state. Optical spectroscopy has been precluded by the presence of charge transfer bands occurring in the d-d transition region.

In the case of (1) poly(1-pyrazolyl)borate-iron(II) [36], and (2) tris[4-[(6-R)-2-pyridyl]-3-aza-3-butenyl]amine-iron(II), where R = H or CH₃ [37], spin equilibrium is observed in both solid and solution states. In passing, it is noteworthy that the thermodynamic parameters obtained for these spin equilibrium complexes in solution together with those for [Fe((py)im)₃]²⁺ and [Fe((py)bim)₃]²⁺ are in good agreement with those obtained for the iron(II) cages (Table 4.8).

It is an interesting point that spin isomerism in the solid state has not been observed in this work for the iron(II) cage complexes. However, the close proximity of the iron(II) cages to the crossover region in the solid state can be deduced from the fact that both high-spin and low-spin members have been isolated and magnetically characterized (cf. Chapter Two). Thus, dissolution of diamagnetic crystals of [Fe(NH₂)₂sar]²⁺ maintains the ¹Alg ground
term in solution. However, dissolution of the high-spin paramagnetic crystals of [Fe(NH₃)₂sar]⁴⁺, [Fe(CH₃)sar]²⁺ or [Fe sar]²⁺ inverted the ¹A₁g and ⁵T₂g levels whereby the ⁵T₂g ground state becomes higher in energy and the ¹A₁g becomes the ground state in solution.

**TABLE 4.8**
Thermodynamic parameters calculated for some Fe(II) hexaamine complexes in spin equilibrium.

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH, kJ mol⁻¹</th>
<th>ΔS, J mol⁻¹ K⁻¹</th>
<th>Temperature Range, K</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>[37], R=R'=H</td>
<td>19.20</td>
<td>41.76</td>
<td>295-420</td>
<td>131</td>
</tr>
<tr>
<td>R&quot;=CH₃</td>
<td>(1605)</td>
<td>(3.49)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[37], R=H</td>
<td>11.88</td>
<td>35.56</td>
<td>184-433</td>
<td>131</td>
</tr>
<tr>
<td>R'=R&quot;=CH₃</td>
<td>(993)</td>
<td>(2.97)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[36], R=H</td>
<td>16.11</td>
<td>47.70</td>
<td></td>
<td>117</td>
</tr>
<tr>
<td>X=Y=H</td>
<td>(1347)</td>
<td>(3.99)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fe((py)imH)₃]²⁺</td>
<td>15.90</td>
<td>48.53</td>
<td></td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>(1329)</td>
<td>(4.06)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Fe((py)bimH)₃]²⁺</td>
<td>19.66</td>
<td>77.82</td>
<td></td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>(1644)</td>
<td>(6.51)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is possible that the spin equilibrium may be accompanied by a substantial trigonal twist for the iron(II) cages. The low-spin d⁶ configuration has been shown by x-ray crystallography to lie only 2° from ideal octahedral symmetry as determined for two cobalt(III) cage complexes. In contrast, the x-ray crystal structure for the high-spin d⁶ complex, [Fe(NH₃)₂sar](NO₃)₄·H₂O has a trigonal twist angle...
of $\phi = 28.6^\circ$ indicating a substantial reduction in symmetry.

The good fits provided by the calculated $\chi(T)$ and $\mu(T)$ curves for $[\text{Fe sar}]^{2+}$, $[\text{Fe(CH}_3\text{sar}]^{2+}$, $[\text{Fe(NH}_2\text{sar}]^{2+}$, and especially for the seemingly inconsistent $[\text{Fe(NH}_3\text{sar}]^{4+}$ cage whose magnetic data in solution initially appeared quite contrary to the spin equilibrium model, allow confidence in the experimental data where oddities are often accounted for by impurities and errors in the first instance. The calculated $OD_{\text{expt}}/OD_{\text{ls}}$ vs. temperature curves also provided good fits for the optical data, although the slightly differing thermodynamic parameters compared with those obtained by magnetic measurements appear to reflect the insensitivity of the optical rather than the magnetic data to the equilibrium.

Further refinement of the spin equilibrium model is currently under investigation with the complexes $[\text{Fe(CH}_3\text{(NH}_3\text{sar}]^{3+}$ and $[\text{Fe(CH}_3\text{(NH}_2\text{sar}]^{2+}$, which enable systematic changes in total charge and substituents to be made.
CHAPTER FIVE

NMR SPECTRA OF PARAMAGNETIC Fe(II) AND Ni(II) CAGES
In the standard NMR experiment with a diamagnetic substance, the applied magnetic field, \( H \), interacts with a nucleus of spin \( I \). This interaction can be represented by the spin Hamiltonian

\[ \mathcal{H} = -g_N \beta_N H \cdot I \]  

(46)

where \( g_N \) is the Landé \( g \)-factor for the nucleus, \( \beta_N \) is the nuclear Bohr magneton and \( H \) and \( I \) are the magnetic and nuclear spin vectors, respectively. The effective magnetic field experienced by the nucleus under study will be different from the applied field due to the screening effect of the electrons and may be represented by

\[ H_{\text{eff}} = H(1 - \sigma) \]  

(47)

where \( \sigma \) is termed the screening constant. Therefore, Equation 46 may be rewritten

\[ \mathcal{H} = -g_N \beta_N (1 - \sigma) H \cdot I \]  

(48)

Since it is usually difficult to calculate or determine experimentally \( \sigma \), it is customary to choose a standard reference material and define the chemical shift, \( \delta \) as

\[ \delta = \sigma - \sigma_{\text{ref}} = \frac{H - H_{\text{ref}}}{H_{\text{ref}}} \]  

(49)

In this work the cage complexes studied by NMR are paramagnetic and consequently the effect of unpaired 3d electrons must be included. The interaction of the unpaired electrons with the nucleus can be represented by an additional term in the Hamiltonian, \( A \mathbf{I} \cdot \mathbf{S} \), where \( A \) is the hyperfine interaction constant and \( \mathbf{S} \) is the electron spin vector. The spin Hamiltonian is thus expressed by,
\[ \mathcal{H} = -g_N \beta_N (1-\sigma) H I + A I S \] 

(50)

If the direction of the applied magnetic field is defined as the z-axis, the Hamiltonian can be written

\[ \mathcal{H} = -g_N \beta_N (1-\sigma) H I_z + A I_z S_z \] 

(51)

Under the usual experimental conditions only the time-averaged effect of the unpaired electron-nuclear interaction is observed and it can be shown\textsuperscript{132} that the energy of the NMR transition for a proton (\( M_I = 1 \)) is given by

\[ \Delta E = g_N \beta_N (1-\sigma) H - A \langle S_z \rangle \] 

(52)

where \( \langle S_z \rangle \) is the time-averaged value of the z-component of the electron spin. Therefore the change in the effective magnetic field, \( \Delta H \), at the nucleus due to the unpaired electrons is

\[ \Delta H = \frac{A \langle S_z \rangle}{g_N \beta_N} \] 

(53)

where \( A \) is measured in ergs\textsuperscript{†}. If, \( a \), is the hyperfine interaction constant measured in Hertz, Equation 53 becomes

\[ \Delta H = \frac{ah \langle S_z \rangle}{g_N \beta_N} \] 

(54)

The time-averaged value of the z-component of the electron spin can be determined by summing over all the states of the system assuming a Boltzmann distribution.\textsuperscript{132}

\[ \langle S_z \rangle = \frac{\sum_i E_i \langle S_z \rangle_i \exp(-E_i/kT)}{\sum_i E_i \exp(-E_i/kT)} \] 

(55)

\[ \text{† } 1 \text{ erg} = 10^{-7} \text{ Joules.} \]
Figure 5.1
Variation of the $^1$H NMR spectra of [Ni sar]$^{2+}$ with temperature.
Figure 5.2
Variation of the $^1$H NMR spectra of [Ni(NH$_3$)$_2$sar]$^{4+}$ with temperature.
where \( E_i \) is the energy of the \( i \)'th electronic level.

For the \( 2S+1A_1, 2S+1A_2 \) and \( 2S+1E \) states which may arise for a \( d^n \) transition metal ion in a ligand field of octahedral symmetry, *

\[
\langle S_z \rangle = \frac{\sum_{S_z} S_z \exp(-g B S_z/kT)}{\sum_S \exp(-g B S/kT)} \quad \cdots (56)
\]

\[
= - \frac{g B S(S+1)}{3kT} \quad \cdots (57)
\]

Hence, \( \Delta H = - \frac{a \hbar g B S(S+1)}{3g N B kT} \) \( \cdots (58) \)

so that the paramagnetic NMR field shift, \( \Delta H \), is characterized by a dependence on temperature that obeys Curie's law, \textit{i.e.} \( \Delta H \propto C/T \).

5.2 THE NI(II) CAGES

5.2.1 Results

Well-resolved \(^1H\) NMR spectra for \([\text{Ni sar}]\text{Cl}_2\) and \([\text{Ni(NH}_3)_2\text{sar}]\text{Cl}_4\), in \( D_2O \) solutions were obtained using a Brucker CXP-200 spectrometer.

Representative spectra for both complexes over the temperature range 290–368 K, are reproduced in Figures 5.1 and 5.2. A water soluble TMS\(^\dagger\) derivative, DSS\(^\dagger\dagger\), was used as the internal proton standard.

The values of \( \Delta H \) for all the protons in both molecules were calculated from the relationship

\[
\Delta H = H_{\text{expt}} - H_{\text{res}} \quad \cdots (59)
\]

\( \dagger \) TMS = tetramethylsilane.

\( \dagger\dagger \) DSS = sodium 2,2-dimethyl-2-silapentane-5-sulphonate.

* The dipolar term can be neglected in these cases.
Figure 5.3

Dependence of the chemical shift ($\delta$ in ppm or $\Delta H$ in Hz) with reciprocal temperature for [Ni sar]$^{2+}$. Solid lines calculated by applying the parameters from Table 5.1 into Equation 58.
Dependence of the chemical shift (δ in ppm or ΔH in Hz) with reciprocal temperature for [Ni(NH₃)₂sar]⁺. Solid lines calculated by applying the parameters from Table 5.2 into Equation 58.
where $H_{\text{expt}}$ is the observed chemical shift in Hertz from the reference substance (i.e. DSS), and $H_{\text{res}}$ is the collective contributions of,

(i) the unknown diamagnetic chemical shift for the proton groups in analagous diamagnetic cages, and

(ii) the unknown chemical shift from dipolar and other contributions.

The $\Delta H(1/T)$ graphs presented in Figures 5.3 and 5.4, illustrate well the linear relationship between these two parameters and confirm the Curie-like behaviour for $[\text{Ni sar}]\text{Cl}_2$ and $[\text{Ni(NH}_3)_2\text{sar}]\text{Cl}_4$ expected for a $^3\text{A}_2g$ ground state.

5.2.2 Fitting of the Experimental Data

The individual proton resonances observed for $[\text{Ni sar}]^{2+}$ and $[\text{Ni(NH}_3)_2\text{sar}]^{4+}$ (in Figures 5.1 and 5.2) have been fitted to the theoretical expression for $\Delta H$ given in Equation 58. Substitution of the relevant parameters into Equation 58 provides the expression

$$H_{\text{expt}} = -(ah) \frac{2.9252}{kT} \cdots(60)$$

where the hyperfine interaction constant, $a$, can be determined by solving a pair of simultaneous equations at the two temperatures $T_1$ and $T_2$; i.e.,

$$H_{\text{expt}(1)} - H_{\text{expt}(2)} = (ah) \left[ \frac{1}{kT_2} - \frac{1}{kT_1} \right] \cdots(61)$$

Substitution of the value of $a$ so derived, into Equation 61 then enables the residual magnetic field, $H_{\text{res}}$, to be determined. These parameters, $a$ and $H_{\text{res}}$, for both $[\text{Ni sar}]\text{Cl}_2$ and $[\text{Ni(NH}_3)_2\text{sar}]\text{Cl}_4$ are included in Tables 5.1 and 5.2. The calculated curves obtained by applying the derived values for $a$ and $H_{\text{res}}$ into Equations 59 and 60, appear as solid lines in Figures 5.3 and 5.4. These fitted curves
are in good agreement with the experimentally obtained data.

**TABLE 5.1**

Hyperfine interaction constant, and residual NMR field shift calculated for \( \text{d}^6-\text{[Ni sar]}\text{Cl}_2 \) in \( \text{D}_2\text{O} \)

<table>
<thead>
<tr>
<th>Proton(^a)</th>
<th>( \text{H}_{\text{res}} ), ( \text{Hz} )</th>
<th>( a, \text{Hz} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_A )</td>
<td>1232 Hz</td>
<td>6.16 ppm</td>
</tr>
<tr>
<td>( \text{H}_B )</td>
<td>3402 Hz</td>
<td>17.01 ppm</td>
</tr>
<tr>
<td>( \text{H}_C )</td>
<td>3029 Hz</td>
<td>15.14 ppm</td>
</tr>
<tr>
<td>( \text{H}_D )</td>
<td>4840 Hz</td>
<td>24.19 ppm</td>
</tr>
<tr>
<td>( \text{H}_{\text{apical}} )</td>
<td>(-1065) Hz</td>
<td>(-5.33) ppm</td>
</tr>
</tbody>
</table>

\(^a\) Numbering scheme for protons as defined in Figure 5.11.

**TABLE 5.2**

Hyperfine interaction constant and residual NMR field shift for \( \text{d}^6-\text{[Ni(NH}_3)_2\text{sar]}\text{Cl}_4 \) in \( \text{D}_2\text{O} \)

<table>
<thead>
<tr>
<th>Proton(^a)</th>
<th>( \text{H}_{\text{res}} ), ( \text{Hz} )</th>
<th>( a, \text{Hz} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_{A'} )</td>
<td>740 Hz</td>
<td>3.70 ppm</td>
</tr>
<tr>
<td>( \text{H}_{B'} )</td>
<td>4767 Hz</td>
<td>23.83 ppm</td>
</tr>
<tr>
<td>( \text{H}_{C'} )</td>
<td>3142 Hz</td>
<td>15.71 ppm</td>
</tr>
<tr>
<td>( \text{H}_{D'} )</td>
<td>10449 Hz</td>
<td>52.23 ppm</td>
</tr>
</tbody>
</table>

\(^a\) Numbering scheme for protons as defined in Figure 5.11.
Figure 5.5

'ob' and 'lei' configurations indicated for a) [M(en)$_3$]$^{n+}$-type complexes and for b) sar-type cage complexes.

Figure 5.6

Contacted shifts of methylene protons in a chelated 1,2-diaminoethane ring. Dotted lines are estimated chemical shifts for axial and equatorial positions in a "frozen" conformation (after ref. 134).
5.2.3 Assignment of Proton Resonances

Preliminary analysis of the proton resonances for [Ni sar]$^{2+}$ and [Ni(NH$_3$)$_2$sar]$^{4+}$ is based on comparison with published data for [Ni(en)$_3$]$^{2+}$. The [Ni(en)$_3$]$^{2+}$ ion has received considerable attention in terms of the conformational equilibrium that can exist for the chelate rings. The coordinated rings can exist in two extreme conformations, $^\dagger$ (lel)$_3$ - where the three C-C bonds are parallel to the C$_3$ axis of symmetry of the complex ion and (ob)$_3$ - where they lie oblique to the C$_3$ axis as illustrated in Figure 5.5. The two resonances observed in the H NMR spectrum for [Ni(en)$_3$]$^{2+}$ are separated by 37.1 ppm$^{134}$ (Figure 5.6) and are considered average positions for the two non-equivalent -CH$_2$- environments i.e. equatorial and axial, caused by rapid interconversion$^\dagger\dagger$ of the (ob)$_3$ and (lel)$_3$ isomers. Ho and Reilley$^{134}$ noted that the ob-lel isomerization process involves simply rotation about internal, single-bond axes of the metal-en ring. In addition, they stated that the barrier of this process is low, and should be fast on the NMR time scale at ambient temperatures. Estimates of the resonances for the equatorial and axial positions for a frozen conformation differ by 152 ppm$^{134}$ (Figure 5.6). The temperature dependence of the chemical shifts for [Ni(en)$_3$]$^{2+}$ differs markedly from Curie law behaviour as gauged from the $\Delta H \times T$ versus temperature curve.$^{134}$ This deviation from Curie law reflects the change in population of the ob and lel conformers with temperature.$^{134}$

The origin of the chemical shift difference for the methylene

$^\dagger$ (lel)$_2$(ob) and (ob)$_2$(lel) are also possible conformations.

$^\dagger\dagger$ On the NMR timescale.
Figure 5.7
Dihedral angles for the H-C-N-Ni fragment.
Figure 5.8

Dependence of the product $\delta \times T$ with temperature for [Ni sar]$^{2+}$. 
Figure 5.9

Dependence of the product $\delta \times T$ with temperature for $\text{[Ni(NH}_3\text{_2sar)]}^{4+}$. 
Figure 5.10
Energy minimized conformers of \([\text{Co sep}]^{3+}\) (after ref. 49b).
Figure 5.11

Diagramatic representations of the $^1$H NMR spectra of a) [Ni(en)$_3$]$^{2+}$, b) [Ni sar]$^{2+}$ and c) [Ni(NH$_3$)$_2$sar]$^{4+}$ at ambient temperature.
protons of \([\text{Ni}(\text{en})_3]^{2+}\), is attributed to the dihedral angle between the H-C-N and the C-N-Ni planes as shown in Figure 5.7 with a \(\cos^2 \theta\) angular dependence.\(^{133-137}\) The equatorial C-H protons have a dihedral angle approaching 180° and therefore are expected to resonate at a lower field, whereas, the axial C-H protons with a dihedral angle close to 60° would have a substantially smaller isotropic shift.

In contrast to the \(^1\text{H} \text{NMR}\) behaviour of \([\text{Ni}(\text{en})_3]^{2+}\), the cage complex \([\text{Ni sar}]^{2+}\) is characterized by a temperature independent \(\delta \times T\) versus temperature curve (Figure 5.8) while for \([\text{Ni(NH}_3)_2\text{sar}]^{4+}\), \(\delta \times T\) shows only a small dependence with temperature (Figure 5.9). If the ob-lel isomerization were observed, the chemical shift for the ring protons would be expected to be markedly dependent upon temperature. However, the cap protons would be less affected due to the smaller variation in dihedral angle associated with the conformational forms (cf. \(C_3\) and \(D_3\) symmetry isomers for \([\text{Co sep}]^{3+}\) in Figure 5.10).\(^{49b}\) We can conclude from these data, that the ring conformations of the Ni cages remain frozen on the NMR time scale.

A schematic representation of the proton resonance positions observed for \([\text{Ni}(\text{en})_3]^{2+}\), \([\text{Ni sar}]^{2+}\) and \([\text{Ni(NH}_3)_2\text{sar}]^{4+}\) is provided in Figure 5.11 to illustrate the following discussion.

It is apparent from Figure 5.11, that the calculated positions for the frozen conformation of \([\text{Ni}(\text{en})_3]^{2+}\) (suggested by Ho and Reilley\(^{134}\)) are quite similar to peaks A and D for \([\text{Ni sar}]^{2+}\) and A' and D' for \([\text{Ni(NH}_3)_2\text{sar}]^{4+}\). Such a qualitative comparison would result in the assignment for \([\text{Ni sar}]^{2+}\)(\([\text{Ni(NH}_3)_2\text{sar}]^{4+}\)) of A(A') to axial\(^{\text{ring}}\); B(B') to axial\(^{\text{cap}}\); C(C') to equatorial\(^{\text{cap}}\) and D(D') to equatorial\(^{\text{ring}}\) (axial and equatorial positions are illustrated in
Figure 5.12

Cage complex with axial, equatorial and apical protons indicated.
An alternative stratagem, in order to assign the proton resonances for the Ni(II) cages, is by the differences in their spectra. Variation of the apical substituent X (where X=H for sar and X=NH$_3$ for (NH$_3$)$_2$sar) should have a greater effect on the cap protons rather than the ring protons and any effect should be felt equally by the axial and equatorial protons on the cap. In this case a substituent effect would result in a shift of the cap proton resonances in the same direction, i.e. either both upfield or downfield. As the ring protons are not expected to be influenced to a great extent by the variation of apical substituent, then any change in resonance position between [Ni sar]$^{2+}$ and [Ni(NH$_3$)$_2$sar]$^{4+}$ spectra will result from a change in geometry as gauged by a change in dihedral angle. Such an effect will shift the axial resonance upfield and equatorial resonance downfield or vice versa.

The "differences" between the $^1$H NMR spectrum of [Ni sar]$^{2+}$ and [Ni(NH$_3$)$_2$sar]$^{4+}$ are presented in Table 5.3.$^\dagger$

Taking [Ni sar]$^{2+}$ as the point of reference, and assuming A and D are the axial and equatorial protons of the ring (therefore B and C arise from the cap) then the corresponding resonances for [Ni(NH$_3$)$_2$sar]$^{4+}$ show an increase in axial and a decrease in equatorial chemical shifts. As mentioned earlier in the discussion these shifts possibly reflect a small change in dihedral angle hence a change in geometry between the two cages. The corresponding axial and equatorial protons of the cap for [Ni sar]$^{2+}$, B and C, however, shift in the opposite sense for [Ni(NH$_3$)$_2$sar]$^{4+}$ than do A and D.

$^\dagger$ This analysis was undertaken in collaboration with R. Peachey.
These cap resonances, in fact, exhibit a decrease in axial and an increase in equatorial chemical shifts and are larger in magnitude than for the ring assignment (cf. Table 5.3). In addition, these cap assignments indicate little or no contribution by replacing X=H by X=NH₃, as the axial and equatorial resonances would be anticipated to shift in the same direction. If this assignment were correct, then

(i) a small change in geometry of the ring is accompanied by a large change in geometry of the cap between the two cages, or

(ii) the change in geometry of the ring and cap between the two cages is similar but the dihedral angle dependence of the chemical shift is markedly different.

### TABLE 5.3

Comparisons of chemical shifts for the spectra of [Ni sar]²⁺ and [Ni(NH₃)_2sar]⁴⁺ at room temperature.

<table>
<thead>
<tr>
<th>Resonance Labels from Figure 5.11 b</th>
<th>Chemical Shift Difference, a ppm [Ni sar]²⁺</th>
<th>[Ni(NH₃)_2sar]⁴⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAD</td>
<td>139.98</td>
<td>131.38</td>
</tr>
<tr>
<td>ABC</td>
<td>45.98</td>
<td>58.83</td>
</tr>
<tr>
<td>AAC</td>
<td>129.16</td>
<td>114.29</td>
</tr>
<tr>
<td>ABD</td>
<td>76.80</td>
<td>75.92</td>
</tr>
</tbody>
</table>

a Measured at 302 K for [Ni(NH₃)_2sar]⁴⁺ and 303 K for [Ni sar]²⁺

b The prime symbol, (′), used to discern [Ni sar]²⁺ resonances from [Ni(NH₃)_2sar]⁴⁺ resonances in Figure 5.11 is omitted for this table.
Similar arguments apply assuming A and C are the axial and equatorial protons of the ring for \([\text{Ni sar}]^{2+}\). The corresponding resonances for the ring protons of \([\text{Ni} (\text{NH}_3)_2 \text{sar}]^{4+}\) exhibit an increase and the cap protons, B and D, a decrease in chemical shift. This assignment appears to agree with the expected effect of a change of apical substituent upon the cap protons especially since \(X=\text{NH}_3\) will render the adjacent carbon atom more electropositive than in the case where \(X=\text{H}\). From Table 5.3 this assignment of proton resonances suggests that a difference in geometry does exist for the ring protons of \([\text{Ni sar}]^{2+}\) and \([\text{Ni} (\text{NH}_3)_2 \text{sar}]^{4+}\) but that the cap protons exist in essentially identical geometries (as gauged by the dihedral angle).

It does not appear possible that assignment of the proton resonances for \([\text{Ni sar}]^{2+}\) and \([\text{Ni} (\text{NH}_3)_2 \text{sar}]^{4+}\) can be made using the arguments in the preceding discussion. The first assignment of chemical shifts for the axial and equatorial protons of the ring are representative of shifts whose dihedral angles are vastly different and probably close to the true axial and equatorial positions of 180° and 60°, and in addition, the shifts for the cap protons are more similar in dihedral angle i.e. approaching 120°. However, the second assignment is in accord with the anticipated effect due to substitution of \(-\text{NH}_3\) in place of \(-\text{H}\) in the apical position. Therefore, valid arguments apply to both possible assignments and it is unlikely that a distinction can be made based on the available data.

5.2.4 Origins of Hyperfine Interaction Constant

The hyperfine interaction constants, \(a\), arise from two terms in the spin Hamiltonian (i) the contact term and (ii) the pseudocontact
term (the latter being related to the $g$-anisotropy). For a nickel(II) ion in a weak or medium crystal field of octahedral symmetry ($^{3}A_{2g}$) the $g$-tensor will be isotropic, and as a first approximation the pseudocontact term can be ignored. The contact contribution to $a$ may arise in two ways (i) spin polarization, (ii) delocalization of the unpaired $d$ electrons.$^{128,132,138}$ Spin polarization arising from the electron spin density, $\rho$ at a carbon (or pseudocarbon) atom $C_1$ in the fragment $C_1$-$C_n$-$H$ will yield values for proton hyperfine interaction constants of $-6.4 \times 10^7 \rho \text{ Hz}$ (for $n=0$), $-4.4 \times 10^6 \rho \text{ Hz}$ (for $n=1$) and $+1.5 \times 10^5 \rho \text{ Hz}$ (for $n=2$).$^{128,132,138}$ Delocalization of unpaired electron density from the metal, yields positive $a$ values which depend on the overlap integrals. If the hyperfine interaction constants arise entirely from spin polarization, the apical proton resonance would be expected to change sign compared with the other resonances (i.e. assuming nitrogen is a pseudocarbon atom) which is observed for $[\text{Ni sar}]^{2+}$.\textsuperscript{138}

It is not within the scope of this study to analyse in detail the origin of the observed $a$ values. However, it can be noted that extended Huckel calculations have been used in order to calculate the ratio's of spin densities at various protons for similar complexes such as $[\text{Ni(en)}_3]^{2+}$.\textsuperscript{139}

5.3 FE(II) CAGE COMPLEXES

5.3.1 Theoretical Considerations

The magnetic behaviour of the Fe(II) cages in solution has been detailed in Chapter Four. These spin equilibrium systems are characterized by non-Curie law behaviour and require further theoretical consideration to that developed in Section 5.1.
Octahedral ligand field
Spin-orbit coupling
Magnetic field

$^5T_2$ (15)

$J=3$
(7)

3$\beta$
2$\beta$
$\beta$
0
$-\beta$
$-2\beta$
$-3\beta$

$J=2$
(5)

3.5$\beta$
1.5$\beta$
0
$-1.5\beta$
$-3.5\beta$

$J=1$
(3)

3.5$\beta$
0
$-3.5\beta$

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>-16/3</td>
</tr>
<tr>
<td>15/2</td>
<td>-10/3</td>
</tr>
<tr>
<td>21/2</td>
<td>18</td>
</tr>
</tbody>
</table>

$E_3 = 1/2 \zeta$ $E_2 = -1/4 \zeta$ $E_1 = -3/4 \zeta$

Figure 5.13

Splitting diagram for the high-spin $^5T_{2g}$ ground term, where A and B are applied to Equation 62.
Figure 5.14
Calculated curves for the variation of $\Delta H$ with $kT/\zeta$ for octahedrally coordinated Fe(II) complex in spin-equilibrium. Dotted line is calculated using Equation 63 with $E/\zeta = +\infty$. Solid lines were calculated using Equation 66.
The NMR shifts of orbitally non-degenerate ions can be well represented by Equations 56-58. However, the more general case of molecules with orbitally degenerate ground states ($^{2S+1}T_1$ and $^{2S+1}T_2$) requires the value of $\langle S_z \rangle$ to be weighted over the complete manifold of levels which include the spin-orbit coupling interaction. In the present work, the paramagnetic NMR spectra of a number of cage complexes of iron(II) have been measured over a range of temperature. The behaviour of $\Delta H$ with $T$ for the high-spin ground state $^{5}T_{2g}$ which arises from the electron configuration, $t_{2g}^4 e_{g}^2$, can be calculated from the splitting diagram of the $^{5}T_{2g}$ term under the action of spin-orbit coupling and the magnetic field (Figure 5.13). For each $J$-level, the value of $\langle S_z \rangle$ can be calculated from the expression:

$$\langle S_z \rangle_J = -\frac{BH}{3kT} \left[ A + B \frac{kT}{\zeta} \right]$$

...(62)

where $\zeta$ is the single-electron spin-orbit coupling constant. The parameters $A$ and $B$ have been tabulated by Golding and are included in Figure 5.13. Summing Equation 55 over the fifteen energy levels of the $^{5}T_{2g}$ term gives

$$\langle S_z \rangle = -\frac{BH}{3kT} \left[ \frac{(56 - 112)e^{-2x/4}}{[3e^{3x/4} + 5e^{x/4} + 7e^{-2x/4}]} \right]$$

...(63)

where $x = \zeta/kT$.

The theoretical temperature dependence of the NMR spectrum expected for a high-spin octahedral iron(II) complex can be obtained by substituting this value of $\langle S_z \rangle$ into Equation 54. The resulting calculated curves are illustrated in Figure 5.14, in which, $\Delta H$ (in units of $-ah\beta N/2 g_N \beta N \zeta$ gauss) is the change in the effective
magnetic field at the nucleus due to the unpaired electrons in the paramagnetic iron molecule. The theoretical temperature dependence of the NMR spectrum (dashed line) is such that $-\Delta H$ varies approximately with the reciprocal of the absolute temperature.

It is of interest to compare this $\Delta H(T)$ curve with that calculated for a simple $^5A$(or $^5E$) term which could arise from $^5T_{2g}$ by a lowering of symmetry below octahedral (cf. Chapter Four). From Equation 58 with $S = 2$,

$$\Delta H = -\left(\frac{ah_R}{gN_r N}R\right)8x...(64)$$

and this expression is also illustrated in Figure 5.14 (solid line with $E/\zeta = +\infty$). As noted earlier for the fully spin-orbit coupled model, the expected temperature dependence of the NMR spectrum is such that $-\Delta H$ varies exactly rather than approximately with the reciprocal of the absolute temperature.

Since the low-spin $^1A_{1g}$ state arising from the electron configuration, $t_{2g}^6$ is diamagnetic, there is no additional interaction term, $A_{1g}S$ in the Hamiltonian (Equation 50). If $E$ is the energy separation of the $^5T_{2g}$ and $^1A_{1g}$ states ($E$ is positive when the ground state is $^5T_{2g}$), then for an iron(II) cage complex in spin equilibrium, the expression for $\langle S_z \rangle$ is given by

$$\langle S_z \rangle = \frac{-\frac{\Phi H}{3kT}}{[\left(\frac{63}{2} + \frac{54}{3x}\right)e^{3x/4} + \left(\frac{75}{2} - \frac{50}{3x}\right)e^{-2x/4} + \left(56 - \frac{112}{3x}\right)e^{-2x/4}]}

[3e^{3x/4} + 5e^{-2x/4} + 7e^{-2x/4} + e^{-E/kT}]}

...(65)$$

In the simpler case of a spin equilibrium between a $^5A$(or $^5E$) and the $^1A_{1g}$ states, the corresponding expression for the variation of $\Delta H$ with temperature reduces to,
Figure 5.15
Variation of the $^1$H NMR spectra with temperature for [Fe sar]$_2^+$. 
Figure 5.16
Variation of the $^1$H NMR spectra with temperature for [Fe(NH$_2$)$_2$sar]$^{2-}$. 
Figure 5.17
Variation of the $^1$H NMR spectra with temperature for $[\text{Fe}(\text{CH}_3)\text{saar}]^{2+}$. 
Figure 5.18

Variation of the $^1$H NMR spectra with temperature for $[\text{Fe(NH}_3)_2\text{sal}]^{n+}$.
When $E$ approaches infinity, this expression reduces to Equation 64.

The presence of the low-lying $^1A_{1g}$ state (i.e. where $E$ is negative) is expected to have a dramatic effect on the temperature dependence of an NMR spectrum, especially at the lower values of $kT/\zeta$. If $\alpha$ is negative, then as $kT/\zeta$ becomes smaller, $\Delta H$ at first increases, then passes through a maximum value, and finally falls to zero as $kT/\zeta$ approaches zero, the value expected if all the molecules are in the $^1A_{1g}$ ground state. Mirror image $\Delta H(T)$ curves are calculated for positive values of $\alpha$. Typical $\Delta H(T)$ curves are illustrated in Figure 5.14 for two values of the parameter $E/\zeta = -1.0$ and $-0.25$.

5.3.2 Results and Fitting the Experimental Data

The $^1H$ NMR spectra of several iron(II) cages were obtained concurrently with magnetic moment measurements as detailed in Chapter Four and are presented in Figures 5.15 to 5.18.

The values of $\Delta H$ for all the proton resonances in each molecule were calculated from the relationship in Equation 59 described for nickel(II) cages, where the parameters have been defined in Section 5.2.1.

In view of the close similarity of the $\Delta H(T)$ curves calculated for the $5T_{2g}$ and $5A$(or $5E$) states from Equations 63 and 64 (cf. Figure 5.14), the NMR spectra of the paramagnetic iron(II) cages were analysed and fitted using the simpler spin equilibrium model described by Equation 66. This reduces to

$$\Delta H = -(ah) \frac{43.878}{kT} \left[ \frac{1}{5 + e^{-E/kT}} \right] ... (67)$$
Figure 5.19
Calculated curves and experimental data for the variation of chemical shift with temperature for [Fe(sar)]²⁺ in CD₃CN. Calculated curves from Equation 66 using the parameters in Table 5.4.
Calculated curves and experimental data for the variation of chemical shift with temperature for [Fe(NH$_2$)$_2$sar]$^{2+}$ in CD$_3$CN. Calculated curves from Equation 66 using the parameters in Table 5.5.
Figure 5.21
Calculated curves and experimental data for the variation of chemical shift with temperature for [Fe(CH$_3$)$_3$ar]$_2^+$ in d$^7$-DMF. Calculated curves from Equation 66 using the parameters in Table 5.6.
where $\frac{\beta H}{3g_N\beta_N} = 0.7313 \text{ cm}^{-1}$ for the present proton magnetic resonance spectra which were recorded at a frequency of 200 MHz.

In Equation 67, the remaining unknown parameters are the hyperfine interaction constant, $a$; the energy separation between the $^1A_{1g}$ and $^5A(^5T_{2g})$ states ($E$ is negative when the ground state is $^1A_{1g}$) and the unknown residual chemical shift, $H_{\text{res}}$, in Equation 59. The experimental temperature dependent curves for each proton resonance were fitted to Equation 67 by inserting the value of $E$ estimated from the temperature dependence of the magnetic susceptibility (Chapter Four) and solving the pair of simultaneous equations obtained from measurements made at two temperatures, $T_1$ and $T_2$; i.e.

$$H_{\text{expt}(1)} - H_{\text{expt}(2)} =$$

$$= \left(\frac{43.878}{k}\right) \frac{1}{T_2} \left[5e^{-}\frac{-E}{kT_2} - 1\right] - \frac{1}{T_1} \left[5e^{-}\frac{-E}{kT_1} - 1\right]$$

$$\ldots (68)$$

Substitution of the derived value of $a$ into Equation 67 enables the residual magnetic field, $H_{\text{res}}$ to be estimated.

The hyperfine interaction constants, $a$, for the $^5A(^5T_{2g})$ state for all the protons in this series of iron(II) cages obtained by this curve fitting procedure are listed in Tables 5.4 to 5.8. The experimental points and the calculated curves are shown for all the protons in Figures 5.19 to 5.22. For some complexes, better fits to the experimental data can be obtained by employing values of $E$ which differ in magnitude but not sign from those determined from the
Figure 5.22

Calculated curves and experimental data for the variation of chemical shift with temperature for \([\text{Fe(NH}_3)_2\text{sar}]^{2+}\) in \(\text{d}_7\)-DMF. Calculated curves from Equation 66 using the parameters in Table 5.7.
magnetic data measured in solution (cf. Chapter Four). This difference was most marked in the case of \([\text{Fe}(\text{CH}_3\text{sar})]^2+\), where the NMR data are poorly reproduced by the magnetically determined value of \(E = -721 \text{ cm}^{-1}\). Even so, the value of \(E\) required to give an acceptable fit of the NMR data is only ca. 300 cm\(^{-1}\) greater, i.e. \(E = -1000 \text{ cm}^{-1}\).

The proton resonance that exhibits the greatest temperature dependence is the most sensitive to small variations of \(E\) as would be expected. The parameters \(E\), \(a\), \(\xi\) and \(H_{\text{res}}\) can all be varied to some degree without significantly upsetting the agreement between calculated and experimental data.

**TABLE 5.4**

Hyperfine interaction constant and residual NMR field shift for \([\text{Fe sar}]^2+\) in \(\text{CD}_3\text{CN}\), where \(E = -1028 \text{ cm}^{-1}\).

<table>
<thead>
<tr>
<th>Proton</th>
<th>(H_{\text{res}})</th>
<th>(a, \text{Hz})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hz</td>
<td>ppm</td>
</tr>
<tr>
<td>1</td>
<td>-196</td>
<td>-0.98</td>
</tr>
<tr>
<td>2</td>
<td>819</td>
<td>4.09</td>
</tr>
<tr>
<td>3</td>
<td>339</td>
<td>1.70</td>
</tr>
<tr>
<td>4</td>
<td>1962</td>
<td>9.80</td>
</tr>
<tr>
<td>5</td>
<td>1711</td>
<td>8.55</td>
</tr>
</tbody>
</table>
TABLE 5.5

Hyperfine interaction constant and residual NMR field shift for [Fe(NH$_2$)$_2$sar]$^{2+}$ in CD$_3$CN, where $E = -1190$ cm$^{-1}$.

<table>
<thead>
<tr>
<th>Proton</th>
<th>$H_{\text{res}}$</th>
<th>$a_{\text{Hz}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hz</td>
<td>ppm</td>
</tr>
<tr>
<td>1</td>
<td>571</td>
<td>2.86 $-4.99 \times 10^5$</td>
</tr>
<tr>
<td>2</td>
<td>414</td>
<td>2.07 $-2.08 \times 10^6$</td>
</tr>
<tr>
<td>3</td>
<td>1163</td>
<td>5.82 $-7.56 \times 10^6$</td>
</tr>
<tr>
<td>4</td>
<td>1013</td>
<td>5.06 $-8.81 \times 10^6$</td>
</tr>
</tbody>
</table>

TABLE 5.6

Hyperfine interaction constant and residual NMR field shift for [Fe(CH$_3$)sar]$^{2+}$ in d$_7$-DMF where $E = -1000$ cm$^{-1}$.

<table>
<thead>
<tr>
<th>Proton</th>
<th>$H_{\text{res}}$</th>
<th>$a_{\text{Hz}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hz</td>
<td>ppm</td>
</tr>
<tr>
<td>1</td>
<td>297</td>
<td>1.48 $4.77 \times 10^5$</td>
</tr>
<tr>
<td>2</td>
<td>-30.6</td>
<td>-0.15 $-1.21 \times 10^5$</td>
</tr>
<tr>
<td>3</td>
<td>522</td>
<td>2.61 $-2.57 \times 10^5$</td>
</tr>
<tr>
<td>4</td>
<td>81</td>
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</tr>
<tr>
<td>5 &amp; 6</td>
<td>-55</td>
<td>-0.28 $-3.17 \times 10^6$</td>
</tr>
<tr>
<td>7</td>
<td>-283</td>
<td>-1.42 $-3.49 \times 10^6$</td>
</tr>
<tr>
<td>8</td>
<td>-415</td>
<td>-2.07 $-3.62 \times 10^6$</td>
</tr>
</tbody>
</table>
TABLE 5.7

Hyperfine interaction constant and residual NMR field shift for [Fe(NH$_3$)$_2$sar]$^{4+}$ in d$_7$-DMF where $E = -54$ cm$^{-1}$

<table>
<thead>
<tr>
<th>Proton</th>
<th>$H_{\text{res}}$</th>
<th>$a_{\text{Hz}}$</th>
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</thead>
<tbody>
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</tr>
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<td>2</td>
<td>7069</td>
<td>35.33 $7.38 \times 10^4$</td>
</tr>
<tr>
<td>3</td>
<td>5227</td>
<td>26.13 $-5.99 \times 10^5$</td>
</tr>
<tr>
<td>4</td>
<td>9096</td>
<td>45.46 $-5.08 \times 10^5$</td>
</tr>
</tbody>
</table>

TABLE 5.8

Hyperfine interaction constant and residual NMR field shift for [Fe(NH$_3$)$_2$sar]$^{4+}$ in D$_2$O where $E = -179$ cm$^{-1}$

<table>
<thead>
<tr>
<th>Proton</th>
<th>$H_{\text{res}}$</th>
<th>$a_{\text{Hz}}$</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>Hz</td>
<td>ppm</td>
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<td>-30.39 $-3.43 \times 10^5$</td>
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<td>7395</td>
<td>36.96 $8.73 \times 10^4$</td>
</tr>
<tr>
<td>3</td>
<td>-4778</td>
<td>-23.88 $-1.03 \times 10^6$</td>
</tr>
<tr>
<td>4</td>
<td>1982</td>
<td>9.91 $-8.37 \times 10^5$</td>
</tr>
</tbody>
</table>

The exact assignment of proton resonances to axial, equatorial, cap and ring protons is hazardous, as was revealed earlier for the Ni(II) cages. However, it is apparent for the highly symmetrical cages: [Fe sar]$^{2+}$, [Fe(NH$_2$)$_2$sar]$^{2+}$ and [Fe(NH$_3$)$_2$sar]$^{4+}$ that the pair of downfield resonances can be attributed with some confidence to the equatorial protons of the cap and ring, whereas the pair of upfield
Figure 5.23
Diagramatic representations of the $^1$H NMR spectra of a) $[\text{Fe sar}]^{2+}$, b) $[\text{Fe(NH}_2)_2\text{sar}]^{2+}$, c) $[\text{Fe(NH}_3)_2\text{sar}]^{4+}$, d) $[\text{Fe(CH}_3)_2\text{sar}]^{2+}$, and e) $[\text{Fe(CH}_3)(\text{NH}_3)\text{sar}]^{3+}$ at ambient temperature.
resonances can be assigned to the respective axial protons by comparison with the \([\text{Ni(en)}_3]^{2+}\) spectrum. The spectra of less symmetrical cages of \([\text{Fe(CH}_3\text{sar}]^{2+}\) and \([\text{Fe(CH}_3\text{(NH}_3\text{sar)]}^{3+}\) †, are also grouped in two pairs, although further splitting within each pair occurs due to the lowered symmetry. A schematic presentation of the spectra of these iron(II) cages in Figure 5.23, illustrates well the complexity in proton assignment. It is seen that \([\text{Fe(CH}_3\text{(NH}_3\text{sar)]}^{3+}\) exhibits a "splitting" of each of the resonances observed for the parent \([\text{Fe sar}]^{2+}\), whereas \([\text{Fe(CH}_3\text{sar]}^{2+}\) exhibits "splitting" of only the two downfield resonances (compared to the parent molecule).

5.3.3 DISCUSSION

It is satisfying that the simple model described by Equation 66 reproduces so well, the observed temperature dependence of all the proton resonances in the NMR spectra of the iron(II) cages. This provides independent evidence for the co-existence of high-spin and low-spin states of the iron(II) cages in solution. Not unexpectedly, the analysis of the data confirms the conclusion from magnetic measurements that the singlet \(^1\text{Al}_{g}\) state lies lowest for each of the present compounds. However, the energy interval to the quintet \(^5\text{A}(5\text{T}_{2g})\) state is much smaller for the highly charged \([\text{Fe(NH}_2\text{sar)]}^{4+}\) cation \((E \approx 100 \text{ cm}^{-1})\) than for the divalent cations of \([\text{Fe(NH}_2\text{sar]}^{2+}, [\text{Fe sar]}^{2+}\) and \([\text{Fe(CH}_3\text{sar]}^{2+}\) \((E \approx 1100 \text{ cm}^{-1})\).

In addition, the results of \(^1\text{H}\) NMR studies together with the magnetic and optical studies are consistent with a simple model,

† K.S. Hagen, private communication.
based on orbitally non-degenerate $^1A_g$ and $^5A_1(^5T_{2g})$ levels. This suggests that in solution (i) the caged ions exist with symmetry lower than octahedral and (ii) the mechanism responsible for the paramagnetically shifted proton resonances is contact in origin as observed for the nickel(II) cage complexes. However, the residual field shift, $H_{res}$, for some protons is unexpectedly large and this could be a reflection of the presence of a pseudo-contact contribution to the NMR shifts.

The $^1H$ NMR spectra of the two nickel cages, [Ni sar]$^{2+}$ and [Ni(NH$_3$)$_2$sar]$^{4+}$, were characterized by large isotropic shifts for the proton resonances. These shifts are consistent with a contact origin, arising from the interaction term $A_{1S}$ between the unpaired electron density at the metal centre with the nuclear moments on the nearby protons.

The temperature dependence of these spectra indicates that the conformational equilibria, observed for the congeneric [Ni(en)$_3$]$^{2+}$, is not possible for the cage complexes (at least, not within the NMR time domain).

The original ambition of assigning the proton resonances for the Ni(II) cage spectra by comparison with the [Ni(en)$_3$]$^{2+}$ complex, was not achieved. However, it was possible to assign the upfield resonances to the axial protons and the downfield resonances to the equatorial protons of the ring and the cap.

Temperature dependences of the individual proton resonances observed in the Ni(II) cage spectra, were fitted using a model that provided good agreement with the experimental data. These calculated curves enabled the hyperfine interaction constant, $a$, and the residual field shift, $H_{res}$ to be estimated.
6.1 INTRODUCTION
6.1.1 General

In favourable circumstances the investigation of electrochemical properties of metal complexes in solution can provide valuable thermodynamic, structural, electronic and sometimes kinetic information. Often electrochemical methods provide the only convenient form of characterization for short-lived products formed by a redox process.\textsuperscript{141,142}

In this study, a wide range of electrochemical techniques have been employed to characterize the first row transition metal cage complexes. These investigations were usually undertaken at a mercury electrode in the first instance, generally employing the techniques of dc, ac, and differential pulse polarography (DPP) at a dropping mercury electrode (DME), cyclic voltammetry at a hanging mercury drop electrode (HMDE), and coulometry at a mercury pool electrode. Solid electrodes e.g. platinum, gold and glassy carbon were also employed in some cases because they enabled the range of positive potentials accessible in aqueous and non-aqueous media to be extended. Coulometry has also been performed with a platinum basket working electrode in a number of experiments.

Chemical redox reversibility

In order to interpret electrochemical data, it is essential to discriminate between "chemical" and "electrochemical" reversibility.

In a recent review\textsuperscript{143}, the following statement was made:

"Chemical redox reversibility pertains when two chemical species can be quantitatively changed into one another by chemical oxidants (ox) and reductants (red)".

An example which illustrates such a process is the oxidation of ferrocene, \( \text{Cp}_2\text{Fe} \), to the ferrocinium cation with ferric ions, i.e.
The redox process is "chemically reversible" if the product of oxidation reforms the original material in the presence of a mild reductant e.g. Fe$^{2+}$. The reversible chemical reaction is thus written

$$\text{Cp}_2\text{Fe} + \text{Fe}^{3+} \xrightarrow{k_1} [\text{Cp}_2\text{Fe}]^+ + \text{Fe}^{2+}$$

and is an equilibrium process described by the homogeneous second order rate constant, $k_1$ for the forward reaction and $k_{-1}$ for the reverse reaction.

**Electrochemical redox reversibility**

In contrast to the above situation, electrochemical redox processes are studied in an electric gradient field, necessary to perturb the system, i.e. a non-equilibrium situation. However, thermodynamically significant parameters can be obtained from electrochemical measurements by considering the respective time domains for a) the measuring technique, and b) the electron transfer rate. The electrochemical oxidation of Cp$_2$Fe provides a good example, i.e.

$$\text{Cp}_2\text{Fe} + [\text{Cp}_2\text{Fe}]^+ + e$$

In this case an equilibrium situation is established when the rate of the heterogeneous electron transfer, defined by $k_s$ (at a standard potential, $E^0$), is much faster than the time domain of the measurement, i.e. "electrochemical reversibility" is obtained. If the reverse situation applies, i.e. $k_s$ is relatively slow, then the process is classified as "electrochemically irreversible".
6.1.2 Prior Electrochemical Studies with Cages

Cobalt Cages

The influence of a variety of substituents at the apices of cobalt "sar-type" cages on the electrochemistry of the Co(III)/Co(II) couple has been reported. Working mainly in aqueous solution, it was found that the nature of the substituent influenced the Co(III)/Co(II) potential by some 600 mV. The most negative member of this series is [Co sar]^{3+} with \( E_{1/2} = -0.64 \) V (vs. SCE) whereas the least negative is [Co(NH_3)_2sar]^{5+} with \( E_{1/2} = -0.18 \) (vs. SCE).

The influence of the various substituents was found not to differ significantly from that observed in organic chemistry, and it has been suggested that the substantial effect which the substituent endows upon the redox couple points to a conventional Hammett-type treatment which connects \( E_{1/2} \) to a variety of physical properties.

The range of redox potentials has been further extended by utilizing cages of differing cavity sizes and attaching substituents at positions other than the apices. In addition, the mixed nitrogen-sulphur donor cage complexes of cobalt have been investigated electrochemically revealing Co(III)/(II) reduction potentials in the range -0.14 to -0.23 V (vs. SCE) in aqueous solutions. In this latter class of cage, the range of apical substituents investigated is much more limited than for the sar-type complexes.

Other Cages

Electrochemical studies have also been published for encapsulated sar-type complexes of Pt(IV), Rh(III), Ir(III) and Ag(II) ions. Electrochemical reduction of these second and third row metal ion cages proved somewhat more complicated than the Co(III) analogues; a feature attributed to the cavity size of the
ligand being too small to accommodate comfortably the metal ions of Pt(III), Rh(II), Ir(II) or Ag(I).\textsuperscript{44,145} In the reduction of the Pt(IV) cages in non-aqueous solution the Pt(III) cage was observed as a transient species, which rapidly forms a mono-deprotonated complex, i.e. $[\text{Pt}^{\text{IV}}(\text{NH}_2)\text{_2sar-H}]^{3+}$, via an intramolecular process shown below.

\[ \text{III} \rightarrow \text{IV} + \cdot \rightarrow \text{IV} \]
\[ 2\text{H}^{\text{fast}} \rightarrow \text{H}_2 \]

Although, no reduction wave was observed for cages of either Rh(III) or Ir(III) in aqueous solution, in acetone a one-electron reduction of the Rh(III) cages was observed.\textsuperscript{44a} Reduction of the stable $[\text{Ag}^{\text{II}}(\text{NH}_3)\text{_2sar}]^{4+}$ complex occurred as a two-electron process to give silver metal and free ligand.\textsuperscript{145}

6.2 THEORETICAL CONSIDERATIONS AND TREATMENT OF ELECTROCHEMICAL DATA

6.2.1 Reactions at Electrodes

The overall chemical reaction taking place in a cell is made up of two independent half-reactions, which describe the chemical changes at the two electrodes. Each half reaction responds to the interfacial potential difference at the corresponding electrode. In general, only one half reaction is of interest, that at the working electrode (WE). By standardizing or referencing the half reaction at the other half of the cell, the potential at the working electrode can be controlled. In this manner, the normal hydrogen electrode
Figure 6.1
Schematic diagram of a reduction and an oxidation process.
(NHE), with all its components at unit activity:

\[
\text{Pt/H}_2(1 \text{ atm})/\text{H}^+(a=1, \text{ aqueous})
\]

has become the internationally accepted primary reference. Unfortunately, the NHE has practical limitations for general laboratory use, and thus, a frequently employed reference is the saturated calomel electrode (SCE), i.e.

\[
\text{Hg/Hg}_2\text{Cl}_2/\text{KCl(sat'd in water})
\]

with a potential of 0.2412 V vs. NHE.

Varying the potential of the working electrode with respect to the reference electrode can be viewed as simply varying the potential energy of the electrons within the working electrode. This concept is illustrated in Figure 6.1, where driving the electrode towards negative potentials (cathodic) increases the potential energies of the electrons until they obtain sufficient energy to transfer to a vacant orbital on a species in solution thereby reducing the species. Similarly, driving the electrode towards positive potentials (anodic) lowers the potential energies of the electrons until it becomes more favourable for electrons to transfer from the occupied orbitals of some species in solution to the electrode surface, thereby oxidizing the species. The potentials at which these processes occur are related to the standard redox potentials, \(E^0\), for the specific chemical substances in solution.\(^\dagger\)

This application of a potential to the electrode in either the negative or positive direction, necessarily perturbs the system in

\[^\dagger\quad\text{Provided there is no overvoltage.}\]
response to a change in free energy (i.e. $\Delta G = -nFE$)$^\dagger$ from one condition or the other i.e. oxidation or reduction. Providing, (a) the electron transfer rate is fast or (b) the perturbation is applied slowly, the system can maintain its equilibrium state, i.e. the Nernst equation holds true. Thus for the reduction

$$O + ne \rightleftharpoons R$$

where O is the oxidized and R the reduced electroactive species in solution, the measured potential of the half-cell (vs. NHE) is related to $E^\circ$ by the Nernst Equation:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{O}{R} = E^\circ + \frac{RT}{nF} \ln \frac{\gamma_0}{\gamma_R}$$

...(70)

where $E$ is the measured potential of the cell. As activity coefficients, $\gamma$, for the oxidized and reduced species are generally unknown, the formal redox potential, $E'^{\circ}$, is often used, which incorporates the standard redox potential and the activity coefficients so that the Nernst relation becomes

$$E = E'^{\circ} + \frac{RT}{nF} \ln \frac{[O]}{[R]}$$

...(71)

where $E'^{\circ} = E^\circ + \frac{RT}{nF} \ln \frac{\gamma_0}{\gamma_R}$

$E'^{\circ}$ will vary between media, as the ionic strength will affect the corresponding activity coefficients.$^{141}$

---

$^\dagger$ Where the free energy change, $\Delta G$ is related to the number of electrons involved in the process, $n$; the Faraday, i.e., the charge on one mole of electrons in Coulombs; and $E$, the potential applied to the system.
6.2.2 Faradaic and Non-Faradaic Processes

**Faradaic Current** arises from the flow of electrons across the electrode-solution interface due to electroactive species in solution being either reduced or oxidized. The magnitude of the current is proportional to the concentration of electroactive material in solution for a diffusion controlled process.

**Non-Faradaic Current** arises due to interfacial phenomena occurring with changing potential or solution concentration but involves no electron transfer. The most significant contributions to this current originate from a) the capacitative (charging) current and, b) the migration current.

a) **Capacitative Current**

In the absence of an electroactive species in solution charge cannot cross the electrode-solution interface and the interfacial double layer behaves analogously to a capacitor. The current flow arises from the migration of ions and dipoles to charge the electrode-solution interface.

b) **Migration Current**

Most theoretical treatments of electrochemical techniques rely upon the limiting diffusion, i.e. movement of charged species under the influence of a concentration gradient. It is therefore necessary to minimize the contribution to the total current from migration, i.e. movement of charged species under the influence of an electrical potential gradient. Generally, this is achieved by the addition of a large concentration (0.1 to 1.0 M) of inert supporting electrolyte. As the concentration of electroactive material is generally $10^{-4}$ to $10^{-3}$ M, its contribution to the migration current is negligible.
Figure 6.2
Mechanism for a simple electrochemical reaction.
6.2.3 Mechanisms of Electrode Reactions

The current-voltage response for an electrochemical measurement is governed by the rate of:

(1) mass transfer - from the bulk to the electrode surface,
(2) rate of electron transfer at the electrode surface,
(3) chemical reactions preceding or following electron transfer,
(4) surface reactions e.g. absorption, desorption or crystallization.

(1) Diffusion

In an unstirred solution the mass transport of electroactive species to the electrode surface is by diffusion. Considering the electrode reaction, \( O + ne \xrightarrow{+} R \), the pathway of a general electrode reaction is schematically illustrated in Figure 6.2. The rate of diffusion is described by Fick's laws. Fick's first law describes the flux, \( J_0 \), of an electroactive species from the bulk solution to the electrode interface. This is related to its concentration gradient as functions of time and position by,

\[
-J_0(x,t) = D_0 \frac{\partial C_0(x,t)}{\partial x} \quad \text{...(72)}
\]

where \( D_0 \) and \( C_0 \) are the diffusion coefficient and concentration respectively of the oxidized species, \( O \).

Fick's second law describes the change in concentration of, \( O \), at position \( x \) with time \( t \), i.e.

\[
\frac{\partial^2 C_0(x,t)}{\partial t^2} = D_0 \frac{\partial^2 C_0(x,t)}{\partial x^2} \quad \text{...(73)}
\]

\( \uparrow \) For linear diffusion only. For the DME, it is also necessary to include a term for spherical diffusion.
Therefore at potentials in which electrolysis is occurring at the electrode-solution interface, the concentration gradient provides a constant supply of electroactive species by diffusion.

(2) Kinetics

For the cases where the rate of electron transfer, $k_\text{s}$, is slower than diffusion, the Nernst equation as presented in Equation 70, no longer describes the system accurately. It becomes necessary to include a further term (cf. Equation 78), and this will be described in Section 6.2.5.

(3) Chemical Reactions

The effect of preceding, CE or following, EC, chemical processes (i.e. C) upon the electrochemical processes (i.e. E) can be substantial as the current response becomes a function of both the kinetic and diffusion currents. These cases will not be treated here. However, treatment of these data can be obtained from references 141 and 142.

(4) Adsorption

Often the adsorption of species in solution gives rise to a separate wave (adsorption wave), or to maxima, minima and other irregularities. In addition, species adsorbed at the electrode surface can influence the position, shape or number of waves observed. The mercury electrode in particular is susceptible to this phenomenon, and examples of its effect on a number of electrochemical techniques is described in Section 6.2.5.

6.2.4 Cell Resistance

The cell described earlier with only two electrodes has somewhat limited application for current measurement as a function of the applied potential. The working electrode potential will be less than
Figure 6.3
Schematic diagram of an electrochemical cell.
the applied potential because of the iR (voltage) drop in the cell. In addition, the current passing through the reference electrode may cause its potential to deviate from its equilibrium (zero-current) value due to changes in concentration of the electroactive species at the electrode-solution interface. In order to overcome some of these errors, a three-electrode configuration is generally used (Figure 6.3). The current response to the applied potential ($E_{app}$) flows through the working and auxiliary electrodes with only a small portion of the current passing through the reference electrode. Thus, internal polarization of the reference electrode is avoided and the iR drop in the cell is largely compensated for. However, the three-electrode cell does not compensate for solution resistance between the working electrode and the tip of the reference electrode. This uncompensated resistance, $R_u$, introduces an error in the potential measurement because the true potential of the working electrode, $E_{wk}$, is given by

$$E_{wk} - E_{ref} = E_{app} - iR_u \quad \ldots(74)$$

where $i$ is the current flowing between the working and auxiliary electrode. Using positive feedback circuitry a fraction of the total current is fed-back to the current-measuring amplifier generally resulting in close to total compensation for the cell resistance.$^{141,142}$

6.2.5 Electrochemical Techniques

As mentioned earlier, the electrochemical reduction of a number of cobalt(III) cage complexes involves a one-electron reversible process.$^{23,33,144}$ These complexes are used here to illustrate the electrochemical techniques employed in this study. In addition, the
Figure 6.4

dc polarogram for the reduction of [Co sep]$^{3+}$ with parameters of interest indicated.
parameters of interest for the cobalt cages are used extensively for comparison with those obtained for the other first row transition metal cage complexes.

1. dc Polarography

The interpretation of a dc polarogram is straightforward for a diffusion controlled reversible process. By application of the appropriate Fick's laws of diffusion, the limiting or diffusion-controlled limiting current, \( i_d \), is described by the Ilkovic equation,

\[
  i_d = 0.732 \, nFCD^{1/2}m^{2/3}t^{1/6}
\]

where \( i \) is in Amperes, \( n \) is the number of electrons involved per molecule in the redox process, \( F \) is the Faraday charge on one mole of electrons, \( C \) is the concentration of electroactive species in the bulk solution in \( \text{mol cm}^{-3} \), \( D \) is the diffusion coefficient in \( \text{cm}^2 \text{s}^{-1} \), \( m \) is the flow rate of mercury in \( \text{g s}^{-1} \) and \( t \) is the drop time in seconds.\(^{141,142}\)

For a redox couple of known concentration and number of electrons involved in the process, Equation 75 provides a means for calculating the diffusion coefficient of the electroactive species. For example, reduction of a \( 5.0 \times 10^{-4} \text{M [Co sep]}^3 \) solution results in the polarogram in Figure 6.4. Application of the diffusion-controlled current, \( i_d = 0.686 \, \mu \text{A} \) into Equation 75, where \( n = 1 \), \( F = 96,487.0 \, \text{C mol}^{-1} \), \( m = 0.938 \, \text{mg s}^{-1} \) and \( t = 0.5 \, \text{s} \) then affords a value of \( 5.18 \times 10^{-6} \, \text{cm}^2 \text{s}^{-1} \) for the diffusion coefficient, \( D \). The diffusion coefficients of the oxidized and reduced halves of the redox couple are generally assumed to be equal.

For a reversible electrode process (reduction), the shape of the
Figure 6.5

An example of log$_{10} \left( \frac{i_d - i}{i} \right)$ vs. E (Volts) graphical analysis for a dc polarogram for the reduction of [Co sep]$^{3+}$. 

E$_{1/2}$ = -0.498 V
Slope = 60.9 mV
i-E curve is obtained from the combination of the Nernst and Ilkovic equations, which gives

\[ E = E^\circ + \frac{RT}{nF} \ln \left( \frac{i_d - i}{i} \right) \]  

...(76)

where \( i_d \) is the diffusion-controlled current at the end of the drop life. At \( i = i_d/2 \), i.e. \( E = E_{1/2} \) then \( E_{1/2} = E^\circ \), and Equation 76 can now be expressed

\[ E = E_{1/2} + \frac{RT}{nF} \ln \left( \frac{i_d - i}{i} \right) \]  

...(77)

and is called the Heyrovsky-Ilkovic equation.\(^{146}\) It follows, that a graphical plot of \( E \) vs. \( \log[(i_d - i)/i] \) should be linear with a slope of 2.303 RT/nF (i.e. 59/n mV at 25°C). This plot has been used extensively in this study to assess reversibility. Analysis of the polarogram for [Co sep]\(^{3+}\) (in Figure 6.4) by graphing \( \log[(i_d - i)/i] \) as a function of applied potential is illustrated in Figure 6.5. The linear relationship displays a gradient of 60.9 mV and at \( \log[(i_d - i)/i] \) equal zero (i.e. the zero intercept), the reduction potential, \( E_{1/2} = -0.496 \text{ V} \) is obtained, a value that lies within one millivolt of the published value.\(^2\) A somewhat simpler test of reversibility has also been employed in this study, that is by determination of \( E_{1/4} - E_{3/4} = 2.303 \text{ RT/nF} \log 9 = 56/n \text{ mV at 25°C.} \)

For an irreversible electrode process (reduction) the Nernst equation is no longer valid, and rate theory is used.\(^{141}\) In these cases, using the mean currents in solution;

\[ E = E^\circ + \frac{RT}{\alpha nF} \ln \left( \frac{i_d - i}{i} \right) + \frac{RT}{\alpha nF} \ln 0.886 k_s(t/D)^{1/2} \]  

...(78)

thus,

\[ E_{1/2} = E^\circ + \frac{RT}{\alpha nF} \ln 0.886 k_s(t/D)^{1/2} \]  

...(79)

where \( \alpha \) is the charge transfer coefficient and can lie between
Figure 6.6

ac polarogram for the reduction of \([\text{Co(aza)capten}]^{3+}\) with parameters of interest indicated.
0 and 1, and \( k_s \) is the heterogeneous rate constant in cm s\(^{-1}\).

2. **ac Polarography**

The superposition of a small alternating potential of fixed frequency on the dc voltage results in an ac current vs. dc potential profile\(^{147}\) of the type shown in Figure 6.6 for the reduction of [Co(aza)capten]\(^{3+}\).

For a reversible electrode process\(^{147,148}\) (reduction)

\[
I(\omega t) = \frac{n^2 F^2 A \omega D^{1/2} C \Delta E}{4RT \sin(\omega t + \frac{\pi}{4})} \quad \text{...(80)}
\]

where \( I(\omega t) \) is the fundamental harmonic alternating current, \( A \) is the electrode area in cm\(^2\), \( \omega \) is the frequency in radian s\(^{-1}\) \((\omega = 2\pi f \) where \( f \) is in Hz), \( \Delta E \) is half the peak-to-peak amplitude usually 5 mV and \( a = \frac{n F}{RT(E_{dc} - E_1^{1/2})} \).\(^{148}\) The maximum current occurs at \( a/2 = 0 \) or \( E_{dc} = E_1^{1/2} \), i.e.

\[
I_p = \frac{n^2 F^2 A \omega D^{1/2} C \Delta E}{4RT} \quad \text{...(81)}
\]

The shape of the ac reversible wave can be described by\(^{148}\)

\[
E_{dc} = E_1^{1/2} + \frac{2RT}{nF} \ln \left[ \left( \frac{I}{I_p}\right)^{1/2} + \left( \frac{I_p - I}{I_p}\right)^{1/2} \right] \quad \text{...(82)}
\]

where \( I_p \) is the peak ac current and \( I \) is the ac current at any other position on the wave. Equation 82, is the ac equivalent of the Heyrovsky-Ilkovic equation, and equates the peak potential, \( E_p \), with

\[\text{\textsuperscript{148}}\]

\[\text{\textsuperscript{149}}\]

\[\text{\textsuperscript{149}}\]

\[\text{\textsuperscript{149}}\]

\[\text{\textsuperscript{149}}\]
$E_{1/2}$ when $I = I_p$. The reversibility can be readily determined from a two-point analysis using the width at half height ($W_{1/2}$), \(^\text{148}\) i.e.

$$W_{1/2} = \frac{2RT}{nF} \ln \left( \frac{\sqrt{2+1}}{\sqrt{2-1}} \right) \quad ...(83)$$

$$= 90/n \text{ mV at } 25^\circ\text{C}.$$  

However, the most sensitive tests of reversibility for the ac wave at a particular frequency are comparisons with calculated wave shapes, \(^\text{150}\) and graphical plots with $\log[(I_p/I)^{1/2} + ((I_p - I)/I)^{1/2}]$ vs. $E$. For a reversible process, the gradient for this graph is $4.606 \frac{RT}{nF} = 118/n \text{ mV at } 25^\circ\text{C}$, and the intercept equates with $E_{1/2}$. Such analyses have been seldom used in this study, due to the complicating effects of adsorption. Reversibility over a large range of frequencies can be assessed by graphing $I_p$ vs. $\omega^{1/2}$, a linear relationship for a reversible process (cf. Equation 82).

Measurement of the heterogeneous electron transfer rate constant, $k_s$, can be obtained by the ac method, however, this technique was seldom used here. \(^\text{142}\)

Irreversible electrode processes are governed by $k_s$, which will determine the position of the peak potential on the dc potential axis, \(^\text{147,148,151,152}\) i.e.,

$$E_p = E_{1/2} + \frac{RT}{nF} \ln \left( \frac{1.349 k_s t^{1/2}}{D^{1/2}} \right) - \frac{RT}{2nF} \ln Q \quad ...(83)$$

where $Q = 1.907 (\omega t)^{1/2}$. The displacement of the $E_p$ value in the ac experiment is given by \(^\text{148}\)

$$E_p - E_{1/2} = -\frac{RT}{2nF} \ln Q \quad ...(84)$$

and the peak height approximated by \(^\text{148,151,152}\)

$$\left(I_p\right)_{\text{irrev}} = \frac{1.644 \alpha n^2 F^2 AC \omega^{1/2} D^{1/2} AE}{RT(1 + Q^{1/2})^2} \quad ...(85)$$
and substitution for $Q$ gives

$$(I_p)_{irrev} = (I_p)_{rev} \left( \frac{1.644x}{(1+Q^{1/2})^2} \right)$$

...(86)

that is $(I_p)_{irrev} < (I_p)_{rev}$.

**Phase Sensitivity**

The phase relationships of the Faradaic and capacitative currents to the input voltage provides a method of discriminating between the charging current and the Faradaic current. For a reversible process the Faradaic component lies $45^\circ$ and the charging component $90^\circ$ out-of-phase with the input voltage. Phase-sensitive detection has been found to be particularly useful in this study for detecting the presence of adsorption phenomena. Comparison of the in-phase component (Faradaic) with the quadrature (out-of-phase or capacitative) component indicates the extent to which non-Faradaic processes are contributing to the total current. The polarogram for the reduction of $[\text{Co(aza)capten}]^{3+}$, Figure 6.6, illustrates the technique of phase sensitive detection of adsorption processes well. The in-phase component appears to be an uncomplicated electron-transfer process. However, signal enhancement for the quadrature signal indicates that the cage complex is in fact strongly adsorbed.

3. **Differential Pulse Polarography**

DPP is related to the ac polarographic technique and will not be described here in detail. In this method, a periodic potential pulse of fixed amplitude, $E_p$, is applied to the dc ramp just prior to the end of the drop-life. The difference between these current values is presented to the output device resulting in a first derivative appearance of the polarogram. Reversibility is assessed by comparison of the measured half widths ($W_{1/2}$) with the theoretically
Figure 6.7
Differential pulse polarogram for the reduction of \(\text{[Co(aza)capten]}^{3+}\) with a parameter of interest indicated.

Figure 6.8
Cyclic voltammogram (dc) for the reduction of \(\text{[Co(aza)capten]}^{3+}\) with parameters of interest indicated.
obtained value, i.e. $\frac{V}{2} = 3.52 \, \text{RT/nF} = 90/n \, \text{mV at 25°C}$.

The peak potential, $E_p$, is given by

$$E_{\text{peak}} = E^{F}_{1/2} - \frac{\Delta E}{2}$$

... (87)

where $\Delta E^+$ is the pulse amplitude.

The utility of DPP for this study is due to the first derivative appearance of the wave that discriminates processes occurring just prior to the solvent limit. For example, the DPP for the reduction of $[\text{Co(aza)capten}]^{3+}$, in Figure 6.7 is characterized by $W_{1/2} = 95 \, \text{mV}$ and $E_{\text{peak}} = -0.25 \, \text{V (vs. SCE)}$ is good agreement with published values.$^{144}$

4. **dc Cyclic Voltammetry**

Perhaps the most extensively used technique for the study of the electrochemical process for metal complexes is cyclic voltammetry which offers the most convenient measurement of reversibility and kinetic parameters (cf. Chapter Seven) on a wide range of surfaces.

Application of a triangular voltage to a stationary electrode with time will result in a current response of the type pictured in Figure 6.8, for $[\text{Co(aza)capten}]^{3+}$. This technique offers the advantage of a variable time-scale and thus, is valuable for the study of electrode kinetics as well as chemical reactions coupled to charge transfer. The time-scale is altered by varying the potential sweep rate (or scan rate), thereby allowing the study of both fast and slow chemical and electrochemical reactions.$^{141,142}$

The peak current response ($i_p$, in Ampere) for a linear sweep for a reversible (Nernstian) wave is given by$^{141}$

---

$^\dagger$ $\Delta E$ is negative for a reduction process.
where \( v \) is the scan rate in Vs\(^{-1}\) and the other parameters have been defined. In addition the peak potential \( (E_p) \) and potential at half-height \( (E_p/2) \) are given by

\[
E_p = E_{1/2} - 1.11\left(\frac{RT}{nF}\right) = E_{1/2} - 28.5/n \text{ (mV)} \quad \ldots (89)
\]

and

\[
E_{p/2} = E_{1/2} + 1.09 \left(\frac{RT}{nF}\right)
\]

\[
E_p - E_{p/2} = 57/n \text{ (mV)}
\]

at 25°C. In the case of cyclic voltammetry, the separation between peak potentials (assuming initial reduction) for a cathodic \((E_p)_c\) and anodic \((E_p)_a\) scan† is

\[
(E_p)_c - (E_p)_a = 2(1.11 \frac{RT}{nF})
\]

\[
= 57/n \text{ (mV)} \text{ at 25°C}
\]

which provides a convenient test for reversibility. A further test for reversibility is the ratio of peak current \((i_p)_c/(i_p)_a\) for the forward and reverse cycle (i.e. equals unity for a reversible process).

It follows from Equations 88 and 89, that \( E_p \) should be independent of scan rate, while \( i_p \) should be proportional to the square root of the scan rate for a reversible system. The parameters of interest are noted in Figure 6.8.

† The term cathodic refers to measurement in a negative direction and anodic in a positive direction with respect to the initial potential.
For a totally irreversible reaction, i.e., $k_s$ is slow compared with the potential sweep rate,

$$0 + ne \rightarrow s R$$

the peak current is given by,\(^{141}\)

$$(i_p)_{irrev} = (2.99 \times 10^5) n (\alpha n_\alpha)^{1/2} AC_0 D_0^{1/2} v^{1/2}$$ \(\ldots(91)\)

where $\alpha$ is the charge transfer coefficient and lies between zero and one, and $n = n_\alpha = 1$ for an irreversible process and the peak potential,

$$(E_p)_{irrev} = E^\circ - \frac{RT}{\alpha n F} [0.780 + \ln \left(\frac{D_0}{k}\right) + \ln \left(\frac{\alpha n F v^{1/2}}{RT}\right)]$$ \(\ldots(92)\)

Thus, $i_p$ is proportional to $C_0$ and $v^{1/2}$, whereas, $E_p$ is a function of scan rate, shifting by an amount $1.15 RT/\alpha n F$ (or $30/\alpha n_\alpha$ mV at $25^\circ C$) for each tenfold increase in scan rate, $v$.\(^{141}\)

In the case of quasi-reversible electrode reactions, the electron transfer rate is sufficiently slow to require consideration of the reverse reaction. The peak separation $(E_p)_c - (E_p)_a$ is now a function of electron transfer rate constant, $k_s$ and the scan rate.\(^{154}\) The implications for kinetic studies will be discussed further in Chapter Seven.

**Adsorption**

Adsorption on an electrode surface can alter dramatically the information obtained from electrochemical techniques. Weakly adsorbed species may lead to enhancement of peak currents because electron transfer for the adsorbed species occurs at nearly the same potential as the 'normal' species. A strongly adsorbed species may result in an additional wave, prior to or after the 'normal' peak.\(^{155-157}\) Schematic representations of the influence of strongly
Figure 6.9

The influence of a) strongly and b) weakly adsorbed redox product with scan rate (A to D increasing scan rate)(after ref. 155).
and weakly adsorbed species upon a cyclic voltammogram are presented in Figure 6.9.\textsuperscript{141,142}

5. Cyclic ac Voltammetry

This technique allows for a second time domain to be introduced into the ac electrochemical experiment, that of the scan rate. A reversible electrode process is indicated by superposition of the forward and reverse scans of ac current vs. \(E_{dc}\), with a peak width of 90/n mV at 25°C. Chemical stability of the redox product is determined by the peak current ratio of unity.\textsuperscript{141,158}

Quasi-reversible electrode processes are characterized by a crossover potential, \(E_{co}\), in which\textsuperscript{141,158}

\[
E_{co} = E_{1/2} + \frac{RT}{nF} \ln \left( \frac{\alpha}{1-\alpha} \right) \tag{93}
\]

6. Controlled Potential Coulometry

Essentially a technique of bulk electrolysis, the total charge consumed, \(Q\) (in Coulombs) is related to the number of electrons involved in the redox process, \(n\) by

\[
Q = nF N_0 \tag{94}
\]

where \(N_0\) is the number of mole of the electroactive species initially present in the solution.

The long time domain available for this technique enables characterization of products that may have formed from an unstable redox product. For a reversible process, where the redox product is stable, an unequivocal determination of the number of electrons involved in the process can be gleaned.
6.3 EQUIPMENT AND EXPERIMENTAL METHODS

6.3.1 Procedures

Doubly distilled and deionized water was employed for aqueous measurements with either Analytical Reagent (AR) NaCF$_3$SO$_3$ or NaClO$_4$ (0.1 M) used as supporting electrolyte.

Acetonitrile (distilled over CaH$_2$) was generally employed for non-aqueous measurements although AR acetone, dimethylformamide and dimethylsulphoxide were also used. Tetraalkylammonium salts of perchlorate or trifluoromethanesulphonate were employed due to their high solubilities and low association constants in these solvents.

The solvent and supporting electrolyte was scanned to its cathodic and anodic limits prior to addition of the electroactive species to check for the presence of extraneous waves.

All solutions were degassed with argon to remove oxygen and measurements carried out under a blanket of solvent saturated argon.

No redox waves were observed for either sar or (NH$_3$)$_2$sar ligands in the typical potential range used for measurement.

6.3.2 Equipment

Measurements were performed with either a Princeton Applied Research (PAR) Model 170 electrochemical system or a PAR Model 174A polarographic analyzer interfaced to a PAR Model 122 Lock-in Amplifier via an interface accessory, PAR Model 174-50 and coupled with a Houston Instruments Ominigraphic 2000 recorder.

Rapid-scan cyclic voltammetry (>500 mV/s) was performed only with the PAR 170, together with a Tektronix 5031 dual beam storage oscilloscope and a Tektronic C-70 oscilloscope camera attachment.

Coulometry was performed using an Amel Model 551 potentiostat-galvanostat with an Amel Model 731 digital integrator.
6.3.3 Electrochemical Cell

A standard three-electrode configuration electrochemical cell was employed throughout together with positive-feedback iR compensation as illustrated in Figure 6.3. The working electrode for polarographic measurements was the dropping mercury electrode (DME). Voltammetric measurements employed either platinum or gold wires or platinum, gold or glassy carbon discs as the working electrode. The geometric areas for the disc electrodes are for platinum (33.2 mm²); gold (30.2 mm²); glassy carbon (28.3 mm²) and for a small glassy carbon electrode (6.6 mm²). Voltammetric studies, using a mercury working electrode were performed with a PAR Model 303 hanging mercury drop electrode (HMDE). A mercury pool or platinum basket were employed for coulometry.† The auxiliary electrode was a platinum wire (or gauze for coulometry) for all measurements.

For measurements in aqueous solution the calomel electrode, saturated with KCl (SCE) was employed except for those obtained using PAR Model 303, in which case Ag/AgCl/sat'd KCl(aq) was used as the reference electrode.‡ The reference electrode in non-aqueous solutions was Ag/AgCl/LiCl(sat'd in acetone). A salt bridge containing the solvent and electrolyte used in the working compartment separated the reference electrode from the solution in that compartment.

† Henceforth, coulometry refers only to controlled potential coulometric measurements.

‡‡ All potentials are vs. SCE, unless otherwise noted, for aqueous measurements.
Figure 6.10

Cyclic voltammogram of [Cu sar]^{2+} in CH_{2}CN (0.1 M TBAT) at a Pt working electrode and over a potential range 0\textendash +1.8 V at 500 mV s^{-1}.
Figure 6.11
Variation of the CV of $\text{[Cu sar]}^{2+}$ with scan rate in CH$_3$CN (0.1 M TBAT) at a Pt working electrode and over a potential range $0 \rightarrow +1.8$ V at a) 0.5 V s$^{-1}$ b) 5 V s$^{-1}$ and c) 50 V s$^{-1}$. 
6.4 RESULTS AND DISCUSSION

6.4.1 The Copper Cages

Cage complexes of the Cu$^{2+}$ ion provide an extremely interesting facet of this study because of their propensity for adopting either a square planar or distorted octahedral stereochemistry, in particular with amine ligands. The coordination geometry for crystals of $[\text{Cu(NH}_3)_2\text{sar}](\text{NO}_3)_4\cdot\text{H}_2\text{O}$, grown from neutral aqueous solutions is pseudo-octahedral, as determined by an X-ray crystal structure.

The Oxidation Process

An oxidation wave was observed for $[\text{Cu sar}]^{2+}$ at $E_{1/2} = +1.15$ V (vs. Hg/Hg$_2$Cl$_2$/sat'd LiCl in acetone)$^\dagger$ in acetonitrile solution (0.1 M TBAT as supporting electrolyte), and using a platinum working electrode by CV$^{\dagger\dagger}$ (Figure 6.10). The peak separation of 80 mV and current ratio of 3.0 suggest that the couple is quasi-reversible. A small wave is also observed, against the background current, and is visible just prior to the oxidation wave, at approx. +0.78 V. Also apparent in the cathodic sweep (reverse cycle) is a small wave which occurs at ca. +0.90 V (cf. Figure 6.10). The oxidation process was observed over a range of scan rates from 0.5 Vs$^{-1}$ to 200 Vs$^{-1}$. As revealed from Figure 6.11, the wave centred at $E_{1/2} = +1.15$ V is increasingly encroached upon by the pre-anodic and post-cathodic processes as the scan rate is increased. The forward (anodic) and reverse (cathodic) waves, centred at $E_{1/2} = +1.15$ V are attributed to the quasi-reversible metal centred oxidation, i.e.

---

$^\dagger$ FeCp$_2$/FeCp$_2^+$, $E_{1/2} = +0.415$ V vs. Hg/Hg$_2$Cl$_2$/sat'd LiCl in acetone.

$^{\dagger\dagger}$ Measured at a scan rate of 200 mVs$^{-1}$. 
Figure 6.12

dc polarogram for the reduction of [Cu sar]^{2+} in aqueous solution at a) pH 11.5, b) pH 5.0 and c) pH 1.0.
\[ [\text{Cu}^{II}_{\text{sar}}]^2+ + [\text{Cu}^{III}_{\text{sar}}]^3+ + e \quad \cdots \quad (95) \]

The usual data analyses used to assess the reversibility of the wave, i.e., \( I_p \) vs. \( v^{1/2} \) graph or by using current ratios, is complicated by the presence of the "second process", that appears to arise from strong adsorption. Thus, the oxidation reaction as observed by CV may be represented by:

\[
[\text{Cu}^{II}_{\text{sar}}]^2+ \xrightarrow{\text{adsorption}} \text{adsorption} \quad [\text{Cu}^{II}_{\text{sar}}]^2+ \xrightarrow{\text{ads}} \quad [\text{Cu}^{III}_{\text{sar}}]^3+ \xrightarrow{\text{desorption}} \text{ads}
\]

\[ \cdots \quad (96) \]

The specific, strong adsorption of an electroactive species has been described by Shain\(^{155-157}\) (cf. Section 6.2.5) and closely parallels the observed oxidative behaviour for \([\text{Cu}^{II}_{\text{sar}}]^2+\). Shain\(^{155-157}\) described the dependence of \( I_p \) with \( v \) to be linear for an adsorption wave, whereas a diffusion controlled wave exhibits a square root dependence (i.e. \( I_p \propto v^{1/2} \)). Thus, at sufficiently fast scan rates the adsorption process will dominate the electron transfer process.

It would be an interesting extension of this study to investigate the Cu(III) species further, perhaps by utilizing the spectroelectrochemical technique.

No oxidation wave was observed for \([\text{Cu(NH}_3)_2\text{sar}]^{4+}\).

**The Reduction Process**

A significant dependence of the reduction potential on pH is observed for \([\text{Cu}^{II}_{\text{sar}}]^2+\) in aqueous media (0.1 M NaCF\(_3\)SO\(_3\)) at a DME. Parameters of interest for the reduction were obtained by analysis of dc polarograms at pH's 1.5, 6.0 and 11.5 as illustrated in Figure 6.12. Graphs of \( \log[(i_d-1)/i] \) vs. \( E \) were linear for pH's 1.5 and 6.0, but deviated from linearity at potentials more negative than
$E_{1/2}$ for pH 11.5. The gradient and zero intercept values obtained from this analysis are presented in Table 6.1.

**TABLE 6.1**

Parameters of interest from $\log[1_{d-i}]/1$ vs. $E$ analysis for $[\text{Cu sar}]^{2+}$ in 0.1 M $\text{NaCF}_3\text{SO}_3$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>pH&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Gradient, mV</th>
<th>$E_{1/2}, V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Cu}^{II}\text{sar}]^{2+}$</td>
<td>1.5</td>
<td>87</td>
<td>-0.44</td>
</tr>
<tr>
<td></td>
<td>6.0</td>
<td>63</td>
<td>-0.84</td>
</tr>
<tr>
<td></td>
<td>11.5</td>
<td>43</td>
<td>-0.86</td>
</tr>
</tbody>
</table>

<sup>a</sup> pH was adjusted with HCl and NaOH.

The most interesting feature which emerges from these data is the 400 mV anodic shift in $E_{1/2}$ value in acidic solutions, i.e. a stabilization of the reduction product with respect to that observed at higher pH. In addition, it emerges from these data that the two reduction potentials at pH 1.5 and 6.0 (i.e. $E_{1/2} = -0.44$ and -0.84 V) characterize two distinct processes.

Speculation as to the nature of the reduction step at pH 1.5, was centered initially on the existence of a protonated form of the Cu(II) cage as a stable species in solution. Fortuitously, a further insight into the reduction of $[\text{Cu}^{II}\text{sar}]^{2+}$ at low pH has been forthcoming from kinetic studies.

An investigation into the mechanism of metal extrusion from the $[\text{Cu}^{II}\text{sar}]^{2+}$ cage was undertaken concurrently with the electrochemical
Figure 6.13

X-ray crystal structure of the Cu(II) macrocycle formed from [Cu sar]^{2+} in acid.
Scheme 17
Mechanism for Cu$^{2+}$ extrusion from [Cu sar]$^{2+}$ in acid medium.
studies. It was revealed that in acidic solutions (pH < 2) two macrocyclic derivatives of the Cu(II) cage existed.\textsuperscript{43a}

Over the pH range 1-2, the blue [Cu\textsuperscript{II-sar}]\textsuperscript{2+} complex undergoes a rapid colour change \( (k_1 = 7 \text{ s}^{-1} \text{ at } 25^\circ \text{ C}, \mu = 1.0 \text{ M}) \) to a purple species. However, this initial reaction is followed by a much slower \( (k_2 = 10^3 \text{ s}^{-1}) \) process which involves a change from one purple species to another. The rate law for the second step is inverse in acid concentration as well as being anion dependent. The final product is very stable and is not effected by 5 M HCl over a long period of time. However, both the initial reactant and the first intermediate decompose in 5 M HCl over a few hours \( (t_{1/2} = 4 \text{ hours}) \) to afford the CuCl\textsubscript{4}\textsuperscript{2-} ion and the protonated ligand with little or no "stable" purple product.

The X-ray crystal structure of the stable purple product has been determined\textsuperscript{49} for a crystal grown in concentrated HNO\textsubscript{3}, and is displayed in Figure 6.13. The coordination geometry is essentially planar about the Cu\textsuperscript{2+} ion with two nitrogen atoms no longer coordinated to the metal but protonated and a nitrate ion bound in a mono-dentate manner to the metal ion.

The proposed mechanism for metal extrusion from the copper cages is presented in Scheme 17, based on the kinetic, structural and stoichiometric observations.

In the light of these observations, the electrochemical reduction of [Cu\textsuperscript{II-sar}]\textsuperscript{2+} can be re-examined. It would be consistent with the kinetic study to attribute the reduction wave for [Cu\textsuperscript{II-sar}]\textsuperscript{2+} at \( E_{1/2} = -0.44 \text{ V} \) (at pH 1) to the second formed

\textsuperscript{†} I.I. Creaser, unpublished data.
Figure 6.14

CV for the reduction of $[\text{Cu(NH}_3)_2\text{sar}]^{4+}$ indicating a subsequent reoxidation process.
However, it is difficult to discern from the available data whether the reduction wave at -0.44 V is a one-electron or two-electron process. In order to assist in the identification of the number of electrons involved in the \([\text{Cu}^{II}\text{sar}]^{2+}\) reduction wave (observed at pH 1) the reduction of \([\text{Cu}^{II}(\text{NH}_3)_2\text{sar}]^{4+}\) is now considered.

Reduction of \([\text{Cu}(\text{NH}_3)_2\text{sar}]^{4+}\) at pH > 6, has been attributed to a two-electron process, as ascertained by \(i_d/C\) comparison with the one-electron reduction wave for \([\text{Co}^{III}\text{sar}]^{3+}\), and liberates copper metal and free ligand, as indicated by coulometric studies, to be described later. Detection of the \(\text{Cu}^{2+/0}\) wave by CV, a simple reversible couple in aqueous solutions, was complicated by the presence of large adsorption 'spikes' at approx. 0 V (Figure 6.14). These 'spikes' are consistent with oxidation of the mercury electrode, facilitated by the cage ligand. In DMSO media, this process has been examined, and the wave removed by titration of the ligand with \(\text{Cu}^{2+}\). The formation of a mercury(II) cage complex is postulated to be occurring in this case. A somewhat similar process is observed for reduction of \([\text{Ag}(\text{NH}_3)_2\text{sar}]^{4+}\), however the authors do not address the origin of the 'spikes'.

The reduction of the two copper cages, \([\text{Cu}^{II}(\text{NH}_3)_2\text{sar}]^{4+}\) and \([\text{Cu}^{II}\text{sar}]^{2+}\), are unique amongst the pairs of cage complexes, as they exhibit similar reduction potentials in neutral aqueous solution (cf. Tables 6.1 and 6.2).

---

† Since, solutions prepared for electrochemical studies were deoxygenated for at least 10-15 mins. prior to any measurements.
Figure 6.15

dc polarogram of [Cu(NH$_3$)$_2$sar]$^{4+}$ in aqueous solution at pH a) 1.0, b) 5.5 and c) 12.5.
Parameters of interest for log\(\frac{(i_d - i)}{i}\) vs. E analysis for \([\text{Cu(NH}_3\text{)}\text{2sar}]^{4+}\) in 0.1 M NaCF\(_3\text{SO}_3\)(aq).

<table>
<thead>
<tr>
<th>Compound</th>
<th>pH(^a)</th>
<th>Gradient, mV</th>
<th>(E_{1/2}, \text{V})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cu}^{II}\text{(NH}_3\text{)}\text{2sar}]^{4+})</td>
<td>1</td>
<td>60</td>
<td>-0.72</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>135</td>
<td>-0.85</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td></td>
<td>-0.9(^b)</td>
</tr>
</tbody>
</table>

\(^a\) pH adjusted with HC\text{ClO}_4 and NaOH.
\(^b\) Strong adsorption effects were observed.

As observed for \([\text{Cu}^{II}\text{sar}]^{2+}\) an interesting trend is observed for the reduction of \([\text{Cu}^{II}\text{(NH}_3\text{)}\text{2sar}]^{4+}\) in aqueous solutions (Table 6.2). At neutral pH and above the reduction potential remains essentially unchanged; however, in the low pH region, the reduction potential has shifted to more positive potentials (Figure 6.15), although the shift is less significant than that observed for \([\text{Cu}^{II}\text{sar}]^{2+}\). The parameter of particular interest for these measurements is the gradient of the log\(\frac{(i_d - i)}{i}\) vs. E graph (cf. Table 6.2) which suggests a reversible process at pH 1, but an irreversible process if \(n = 1\) or at best quasireversible if \(n = 2\) at pH 6.

Coulometric reduction of \([\text{Cu}^{II}\text{(NH}_3\text{)}\text{2sar}]^{4+}\), in neutral aqueous solution (0.1 M NaCF\(_3\text{SO}_3\), \(E = -1.20 \text{ V}\), mercury pool working electrode and vs. SCE) confirmed that this process is indeed a two-electron reduction. The reduced solution was evaporated to dryness and dissolved in D\(_2\text{O}\). Measurement of the \(^1\text{H}\) NMR spectrum, confirmed that only "free cage" was present, with the copper metal presumably amalgamating with the mercury pool. The reduction can thus be
Figure 6.16
ac polarogram measured at 90 Hz in aqueous solution for [Cu sar]^{2+} indicating a) quadrature and b) in phase current response and c) CV at 500 mV s^{-1}. 
\[ \text{Cu}^{II}(\text{NH}_3)_2\text{sar}]^{4+} + 2^e \rightarrow \text{Cu}^{0}(\text{NH}_3)_2\text{sar}]^{2+} + \text{Cu}^{0} + [(\text{NH}_3)_2\text{sar}]^{2+} \]

\( \ldots(97) \)

where \( E \) and \( C \) refer to electrochemical and chemical processes.

The gradient for the \( \log[(i_d - i)/i] \) vs. \( E \) graph of 135 mV cannot be related to the theoretically derived value of 58/n mV, since the process was irreversible.

At pH 1, (cf. Table 6.2), the gradient for the \( \log[(i_d - i)/i] \) vs. \( E \) graph, of 60 mV suggests that a reversible one-electron process or an irreversible two-electron process is occurring. Certainly, stabilization of Cu(I) is consistent with the known copper macrocycle chemistry.\(^5\) However, comparison of dc wave heights suggests that the reduction at pH 1 is consistent with a two-electron process.

Ac polarographic and cyclic dc voltammetric reduction parameters obtained in aqueous solution for \([\text{Cu}^{II}\text{sar}]^{2+}\) and \([\text{Cu}^{II}(\text{NH}_3)_2\text{sar}]^{4+}\) are presented in Table 6.3.

As indicated in Figure 6.16, the ac polarographic reduction wave appears "dwarfed" by a second process attributed to a post-adsorption wave. This complicating feature prevented a more detailed analysis of these data. The shape of the CV (at a HMDE, Figure 6.16) also indicates adsorption phenomena are complicating the electron transfer process, and the wave appears at more negative potentials as a result.
Figure 6.17

Reduction of [Cu(NH$_3$)$_2$sar]$^{4+}$ in aqueous solution gauged by a) ac polarography at pH 1, and by CV at pH b) 6.0, c) 1.0 and d) 12.5 with a HMDE and at a scan rate of 200 mV s$^{-1}$. 
TABLE 6.3

Electrochemical Parameters obtained at a mercury electrode.

<table>
<thead>
<tr>
<th>Compound</th>
<th>pH</th>
<th>$E_p$</th>
<th>$\Delta E_{1/2}$</th>
<th>$i_p/C$</th>
<th>$f$</th>
<th>$E_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V</td>
<td>mV</td>
<td>mAM$^{-1}$</td>
<td>Hz</td>
<td>V</td>
<td></td>
</tr>
<tr>
<td>[Cu$^{II}$sar]$^{2+}$</td>
<td>1.5</td>
<td>-0.89</td>
<td>0.63</td>
<td>100</td>
<td>-0.57$^a$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6+11</td>
<td></td>
<td></td>
<td></td>
<td>-0.92</td>
<td></td>
</tr>
<tr>
<td>[Cu$^{II}$(NH$_3$)$_2$sar]$^{4+}$</td>
<td>1</td>
<td>-0.77</td>
<td>85</td>
<td>0.98</td>
<td>100</td>
<td>-0.73$^b$</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>-0.90</td>
<td>220</td>
<td>0.44</td>
<td>100</td>
<td>-0.93$^b$</td>
</tr>
<tr>
<td></td>
<td>12.5</td>
<td>-0.98</td>
<td>100</td>
<td></td>
<td>100</td>
<td>-1.0$^c$</td>
</tr>
</tbody>
</table>

a Measured at 500 mVs$^{-1}$.
b Measured at 100 mVs$^{-1}$.
c Measured at 200 mVs$^{-1}$.

An adsorption wave is also thought to complicate the ac polarography of [Cu$^{II}$(NH$_3$)$_2$sar]$^{4+}$ in aqueous solution (cf. Figure 6.17). However, in this example, the two processes (electron transfer and adsorption) appear to be essentially coincident; although the in-phase current response appears slightly asymmetric with respect to the charging current for each growing drop from the DME. In addition, the quadrature signal is displaced towards more negative potentials compared with the dc polarographically obtained values (Figure 6.15), implying a post-reduction adsorption process. Cyclic voltammetry at pH 1 and 12.5 for [Cu$^{II}$(NH$_3$)$_2$sar]$^{4+}$ are affected by the presence of a "spike" at the maximum of the reduction wave (Figure 6.17). These "spikes" were observed for the reduction of Co(III) cages$^{23}$ and were attributed to adsorption processes. The
Figure 6.18
dc polarogram for the reduction of [Cu sar]^{2+} in CH$_3$CN (0.1 M TEAP).

Figure 6.19
CV (a), dc (b) and ac polarography (quadrature (c) and in phase (d)) for the reduction of [Cu(NH$_3$)$_2$sal]$^{2+}$ in CH$_3$CN (0.1 M TMAT).
adsorption problems are thought to account for the apparent shift in $E_p$ values for the $[\text{Cu}^{\text{II}}(\text{NH}_3)_2\text{sar}]^{4+}$ reduction at a HMDE.

In acetonitrile solution (0.1 M TEAP), reduction of $[\text{Cu}^{\text{II}}\text{Isar}]^{2+}$ at a HMDE is complicated by adsorption, however, an estimate of the half-wave potential can be obtained i.e. $E_{1/2} = -0.85$ V (Figure 6.18). The irreversibility of the reduction process is confirmed by the absence of a backwave in the CV at a gold, platinum and glassy carbon electrode with $E_p = -1.19$ V. It is of interest to note that after one reduction scan the electrode surface was visibly coated with the copper metal and required polishing and/or treatment with acid to restore the original surface.

A dc polarogram for the reduction of $[\text{Cu}^{\text{II}}(\text{NH}_3)_2\text{sar}]^{4+}$ in acetonitrile solution (0.1 M TMAT) is shown in Figure 6.19. Graphical analysis using the $\log[(i_d - i)/i]$ vs. $E$ relationship, deviates markedly from linearity at potentials more negative than $E_{1/2}$, a situation characteristic of irreversible electrode processes. The gradient of the linear region (potentials more positive than $E_{1/2}$) for this graph is 58 mV and the zero intercept is $E_{1/2} = -0.48$ V. Interestingly, the $E_{1/2}$ value has shifted towards more positive potentials in acetonitrile solution compared with that observed in aqueous solution, as anticipated by analogy with the non-aqueous reduction for cobalt(III) cages. However, the $E_{1/2}$ values observed for $[\text{Cu}^{\text{II}}\text{Isar}]^{2+}$ in acetonitrile and neutral aqueous solutions are essentially identical. Obviously, these reduction processes are somewhat more complicated than the simplistic metal-centred two-electron reduction model presented to date. Possibly, the kinetically controlled elimination of the metal from the cage or rearrangement reactions are influencing the electrode reaction, hence complicating the electron-transfer reactions at the electrode.
Figure 6.20
CV for the oxidation of [Ni sar]^{2+} at pH a) 6.0 and b) 1.0 at a gold working electrode and with a scan rate of 100 mV s^{-1}.

Figure 6.21
CV for the oxidation of [Ni sar]^{2+} at pH a) 6.0 and b) 1.0 at a platinum working
Further reduction processes were observed for \([\text{Cu}^{II}(\text{NH}_3)_2\text{sar}]^{4+}\) in acetonitrile solution at \(E > -1.6\) V (Figure 6.19). The nature of these processes are not clear, although, proton reduction is the most likely origin for one wave.

### 6.4.2 The Nickel Cages

Both \(\text{Ni}(\text{II})\) and \(\text{Ni}(\text{III})\) cages have been prepared and characterized analytically (cf. Chapter Eight) and magnetically (cf. Chapters Two and Three), and both are stable in aqueous solution for at least several hours.

#### The Oxidation Process

Oxidation of \([\text{Ni}^{II}\text{sar}]^{2+}\) has been observed at solid electrodes so that a wider positive potential range can be used compared with a HMDE or DME. In aqueous solutions (0.1 M \(\text{NaCF}_3\text{SO}_3\)), at neutral pH, a quasi-reversible redox couple is found at +0.65 V. At lower pH values, the couple becomes more reversible while at higher pH the couple is poorly defined at the solvent limit.† The parameters of interest for this process at a platinum or gold electrode, are presented in Table 6.4 and illustrated in Figures 6.20 and 6.21.

Cyclic voltammograms at a platinum electrode in acid (pH 1.0) solution are reversible as gauged from a graph of \((I_p)_{a\text{ vs. } v^{1/2}}\) for scan rates from 0.02 Vs\(^{-1}\) to 10.0 Vs\(^{-1}\). However, over this range of scan rates the peak separation, \(\Delta E\), approaches quasi-reversibility at the higher scan rates, as presented in Table 6.5.

† Re-acidification of this solution, regenerates the original couple.
TABLE 6.4
Cyclic voltammetric parameters for the oxidation of [Ni sar]\(^{2+}\) in 0.1 M NaCF\(_3\)SO\(_3\)(aq).

<table>
<thead>
<tr>
<th>Compound</th>
<th>pH</th>
<th>Electrode</th>
<th>Cyclic Voltammetry(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>((E_p)_a - \Delta E/2, \Delta E_p, (i_p)_a/(i_p)_c)</td>
</tr>
<tr>
<td>[Ni(^{II})sar](^{2+})</td>
<td>5-6</td>
<td>gold</td>
<td>+0.65, 110, 2.0</td>
</tr>
<tr>
<td></td>
<td>11.5</td>
<td>gold</td>
<td>+0.60, poorly defined</td>
</tr>
<tr>
<td></td>
<td>1(^a)</td>
<td>gold</td>
<td>+0.60, 75, 1.4</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>platinum</td>
<td>+0.66(^d), 100(^d)</td>
</tr>
<tr>
<td></td>
<td>1(^b)</td>
<td>platinum</td>
<td>+0.60, 65, 1.2</td>
</tr>
</tbody>
</table>

\(^a\) Adjusted with HClO\(_4\).
\(^b\) 0.1 M CF\(_3\)SO\(_3\)H.
\(^c\) Measured at 100 mVs\(^{-1}\).
\(^d\) Measured at 200 mVs\(^{-1}\).

TABLE 6.5
Variation in CV parameters with scan rate for [Ni sar]\(^{2+}\) in 0.1 M CF\(_3\)SO\(_3\)H\(^{aq}\) at a platinum electrode.

<table>
<thead>
<tr>
<th>Scan Rate, (Vs^{-1})</th>
<th>((E_p)_a - \Delta E/2), (\Delta E), ((i_p)_a/(i_p)_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>+0.60, 70, 1.2</td>
</tr>
<tr>
<td>0.05</td>
<td>+0.60, 75, 1.2</td>
</tr>
<tr>
<td>0.10</td>
<td>+0.60, 65, 1.0</td>
</tr>
<tr>
<td>0.20</td>
<td>+0.60, 75, 1.1</td>
</tr>
<tr>
<td>0.50</td>
<td>+0.60, 85, 1.2</td>
</tr>
<tr>
<td>1.00</td>
<td>+0.59, 70, 1.0</td>
</tr>
<tr>
<td>2.00</td>
<td>+0.59, 80, 1.0</td>
</tr>
<tr>
<td>5.00</td>
<td>+0.59, 100, 1.1</td>
</tr>
<tr>
<td>10.00</td>
<td>+0.59, 120, 1.1</td>
</tr>
</tbody>
</table>
Figure 6.22
Oxidation of \([\text{Ni-sar}]^{2+}\) in acetone (0.1 M TEAP) platinum working electrode and with a scan rate of 500 mV s\(^{-1}\).
This oxidation process for [Ni\textsuperscript{II}sar]\textsuperscript{2+} is consistent with a nearly reversible electron transfer mechanism, i.e.

\[
[Ni^{II}_{sar}]^{2+} \rightleftharpoons [Ni^{II}_{sar}]^{3+} + e \quad ...(97)
\]
in acidic solutions. Difficulties were experienced in compensating completely for the iR drop between the working and reference electrodes thereby preventing a measurement of the heterogeneous rate constant, \(k_s\).

Cyclic voltammetry in acetonitrile solutions (0.1 M TEAP) for [Ni\textsuperscript{II}sar]\textsuperscript{2+} showed that the Ni(II)/(III) redox couple was shifted by 400 mV towards more positive potentials (Figure 6.22). In this non-aqueous medium at a platinum electrode, the higher degree of reversibility was apparent over a range of scan rates and as shown in Table 6.6. In acetone, a similar shift is observed but the degree of reversibility is somewhat less (Figure 6.22).

**TABLE 6.6**

Variation in CV parameters with scan rate for [Ni\textsuperscript{I}sar]\textsuperscript{2+} in 0.1 M TEAP/acetonitrile at a platinum electrode.

<table>
<thead>
<tr>
<th>Scan Rate, (Vs^{-1})</th>
<th>((E_p)_{a} - \Delta E/2, V)</th>
<th>(\Delta E_p, mV)</th>
<th>((i_p)_a/(i_p)_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>+1.04</td>
<td>60</td>
<td>1.1</td>
</tr>
<tr>
<td>0.05</td>
<td>+1.03</td>
<td>60</td>
<td>1.1</td>
</tr>
<tr>
<td>0.10</td>
<td>+1.03</td>
<td>60</td>
<td>1.1</td>
</tr>
<tr>
<td>0.20</td>
<td>+1.03</td>
<td>60</td>
<td>1.1</td>
</tr>
<tr>
<td>0.50</td>
<td>+1.03</td>
<td>65</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Although the accessible anodic range was not sufficient to observe the oxidation of \([\text{Ni}^{II}\text{(NH}_3)_2\text{sar}]^{4+}\) in aqueous solution, a reversible CV was observed in acetonitrile. The \(E_{1/2}\) value of +1.37 V lies midway between the forward and reverse peaks which appear to be quasi-reversible at 100 mVs\(^{-1}\). The relevant parameters obtained using variable scan rates are presented in Table 6.7.

**TABLE 6.7**

Variation in CV parameters with scan rate for \([\text{Ni}(\text{NH}_3)_2\text{sar}]^{4+}\) in 0.1 M TEAP/acetonitrile at a platinum electrode.

<table>
<thead>
<tr>
<th>Scan Rate, (\text{Vs}^{-1})</th>
<th>((E_p)_a-\Delta E/2, \text{ V})</th>
<th>(\Delta E_p, \text{ mV})</th>
<th>((i_p)_a/(i_p)_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>+1.37</td>
<td>70</td>
<td>1.1</td>
</tr>
<tr>
<td>0.10</td>
<td>+1.37</td>
<td>70</td>
<td>1.0</td>
</tr>
<tr>
<td>0.20</td>
<td>+1.35</td>
<td>75</td>
<td>1.0</td>
</tr>
<tr>
<td>0.50</td>
<td>+1.35</td>
<td>80</td>
<td>1.2</td>
</tr>
</tbody>
</table>

In addition to the well-defined Ni(II)/(III) oxidation, there was some evidence of a further oxidation wave which was poorly defined at the solvent limit, i.e. \(\approx +1.7\) V. This process appeared to be irreversible on the CV timescale, and the evidence was insufficient to determine whether the oxidation was metal or ligand based.

Coulometric oxidation of a sample of \([\text{Ni}^{II}\text{sar}]^{2+}\) in neutral aqueous solution, at \(E = +0.75\) V at a platinum gauze working electrode gave a green-brown solution. Separation of the products in this solution was achieved by elution with acid employing a cation exchange resin. Three products were isolated by this technique; (1)
[Ni^{II}sar]^{2+}, the starting material; (2) [Ni^{III}sar]^{3+}, characterized by its magnetic moment (cf. Chapter Two), optical spectrum (cf. Chapter Three) and microanalytical analysis (cf. Chapter Eight); and (3) a more strongly adsorbed product. The amount of the third product was too small for further characterization. However, since the retention time on the ion exchange resin was longer than those of the Ni(II) and Ni(III) products, this product could have resulted from (1) a metal-centred oxidation to form a more highly charged species e.g. [Ni^{IV}sar]^{4+}, or (2) a ligand-based oxidation to form a species which adsorbs to the resin more strongly than the sar ligand. It seems unrealistic to assume that a Ni(IV) species is accessible at +0.75 V, however, a slow disproportionation, e.g.

$$2 \text{[Ni}^{III}\text{sar]}^{3+} \underset{\text{slow}}{\rightarrow} \text{[Ni}^{II}\text{sar]}^{2+} + \text{[Ni}^{IV}\text{sar]}^{4+} \quad \ldots(98)$$

could yield a nickel(IV) cation. Alternatively, the Ni(III) complex might undergo an intramolecular electron transfer to form a Ni^{II}-imine species. This behaviour is consistent with that observed for oxidation of Ni(II) macrocycles,\textsuperscript{162} and could be represented by:

$$\text{[Ni}^{II}\text{sar]}^{2+} + \overset{+0.65 \text{V}}{E} \text{[Ni}^{III}\text{sar]}^{3+} \overset{1}{C} \text{[Ni}^{II-\text{im-sar]}^{n+}} \quad \ldots(99)$$

where the last product in Equation 99 represents an imine species.

Further investigation of these processes, perhaps using spectroelectrochemical techniques, could assist in understanding better the oxidation processes.

**The Reduction Process**

In keeping with the reduction behaviour of Co(II)\textsuperscript{23}, Cu(II) and the other metal(II) cages (see later), both [Ni^{II}sar]^{2+} and [Ni^{II}(NH_{3})_{2}sar]^{4+} were expected to undergo a metal-centred II + 0 process.
Figure 6.23
Reduction of [Ni sar]^{2+} in CH_{3}CN at a DME using a) DPP and b) dc polarography.
The reduction of [Ni\textsuperscript{II}sar]\textsuperscript{2+} is not observed in aqueous solution and therefore must occur at potentials more negative than the solvent reduction limit, i.e. < -1.8 V. However, one unusual feature of particular interest for the reduction sweep of [Ni\textsuperscript{II}sar]\textsuperscript{2+} in aqueous solution and at a DME was noted. Although, no reduction wave is observed, a shift of the solvent reduction limit to more positive potentials occurs by some 100 mV in the presence of the [Ni\textsuperscript{II}sar]\textsuperscript{2+} cage. It is possible that this shift could be due to the catalytic reduction of protons being facilitated by the cage molecules being adsorbed at the electrode surface. Further investigation of this phenomenon is required to comprehend this process, perhaps using mixed solvent systems.

Using dc and differential pulse polarographic techniques, reduction of [Ni\textsuperscript{II}sar]\textsuperscript{2+} can be observed in acetonitrile solution (Figure 6.23). At a DME, the resulting wave has been analysed using a log[(i_d - i)/i] vs. E graph which was linear for at least 50 mV each side of E\textsubscript{1/2} and had a gradient of 79 mV. However, the E\textsubscript{1/2} value of -2.01 V, obtained from the logarithmic analysis of the dc polarogram, lies at more negative potentials than that obtained from DPP (i.e. E\textsubscript{p} = -1.84 V), and indicates an irreversible process. Comparison of the observed dc wave height with the one-electron reduction process for [Co sar]\textsuperscript{3+}/2+, confirms the two-electron nature of the [Ni\textsuperscript{II}sar]\textsuperscript{2+} reduction wave and appears to be consistent with the following mechanism,

\[
\text{[Ni\textsuperscript{II}sar]\textsuperscript{2+} + 2e} \rightarrow \text{[Ni\textsuperscript{0}sar]} + \text{Ni\textsuperscript{0} + sar} \quad \ldots(100)
\]

where both the electrochemical and chemical (complex dissociation) steps are irreversible.

The reduction of [Ni\textsuperscript{II}(NH\textsubscript{3})\textsubscript{2}sar]\textsuperscript{4+} in aqueous solution (0.1 M
Figure 6.24
Reduction of \([\text{Ni(NH}_3\text{)}_2\text{sal}]+\) in aqueous solution at a DME using a) DPP and b) dc polarography.

Figure 6.25
a) dc polarogram and b) DPP for the reduction of \([\text{Ni(NH}_3\text{)}_2\text{sal}]+\) in CH$_3$CN (0.1 M TEAP).
NaClO₄) occurs just prior to the solvent limit at a DME (Figure 6.24). A graph of log[(i_d - i)/i] vs. E for this wave has a slope of 87 mV and a zero intercept of E₁/₂ = -1.57 V. An ac polarographic sweep over the range -1.3 - -1.90 V indicates an E_p value of -1.65 V, with no adsorption phenomena being evident from the quadrature signal at f = 100 Hz. These reduction potentials can also be compared with the value obtained from DPP of E_p = -1.48 V (cf. Figure 6.24).

In acetonitrile solution, also at a DME, the reduction process occurs at more positive potentials (Figure 6.25). A graph of log[(i_d - i)/i] vs. E for this reduction step, reveals a gradient of 92 mV and a zero intercept of E₁/₂ = -1.35 V. A second reduction wave also appears in the non-aqueous medium and is attributed to an organic ligand-based reduction of the two apical ammonium groups i.e.

\[
-\text{NH}_3^{+} + \frac{1}{2} \text{H}_2 \rightarrow -\text{NH}_2 + \frac{1}{2} \text{H}_2
\]  

...(101)

This interpretation is in good agreement with the reduction behaviour of the [Co^{II}(NH₃)_2sar]^4⁺ complex in non-aqueous solution.²³

6.4.3 The Iron Cages

Both [Fe^{II}sar]^2⁺ and [Fe^{III}sar]^3⁺ have been synthesized. The greater stability of the [Fe^{III}sar]^3⁺ to aerial oxidation makes it the preferred candidate for an electrochemical investigation. However, the oxidation processes of [Fe^{II}(NH₃)_2sar]^4⁺ were examined, as this was the most synthetically stable form of the complex.

The Oxidation Process

The oxidation of [Fe^{II}(NH₃)_2sar]^4⁺ occurs just prior to the anodic limit of a DME in aqueous media. The electrochemical parameters for this process determined from dc, ac polarography (at a DME) and cyclic voltammetry (at a HMDE) are presented in Table 6.8.
Figure 6.26
Oxidation of $[\text{Fe(NH}_3)_2\text{sar}]^{4+}$ in aqueous solution using a) dc polarography, b) in phase and c) quadrature current response for ac polarography and d) CV at 500 mV s$^{-1}$. 
Evidence for adsorption processes which complicate the observed wave is detected by each of the above mentioned techniques and is illustrated in Figure 6.26.

**TABLE 6.8**

Parameters of interest for the oxidation of \([\text{Fe(NH}_3\text{)}_2\text{sar}]^{2+}\) in 0.1 M \(\text{NaClO}_4(aq)\) at a mercury electrode.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electrochemical Parameters of Interest</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Fe}^{II}(\text{NH}_2)_2\text{sar}]^{4+})</td>
<td>(E_{1/2},\text{V}) (+0.25^a)</td>
<td>dc Polarography</td>
</tr>
<tr>
<td></td>
<td>(</td>
<td>E_{1/4}-E_{3/4}</td>
</tr>
<tr>
<td></td>
<td>(i_d/C,\text{mAM}^{-1}) 1.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(E_p,\text{V}) (+0.25^b)</td>
<td>ac Polarography</td>
</tr>
<tr>
<td></td>
<td>(\Delta E_{1/2},\text{mV}) 56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(i_p/C,\text{mAM}^{-1}) 2.75</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(\Delta E_p,\text{mV}) 60</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td></td>
<td>((i_p)_a/(i_p)_c) 0.53^c</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(v,\text{mVs}^{-1}) 500</td>
<td></td>
</tr>
</tbody>
</table>

a  Adsorption pre-wave present.
b  Quadrature current is enhanced compared with in-phase current, indicative of adsorption.
c  Current ratio indicates the oxidation product is adsorbed.

Coulometry at \(+0.40\) V, for an aqueous solution of \([\text{Fe}^{II}(\text{NH}_3)_2\text{sar}]^{4+}\), (0.1 M \(\text{NaClO}_4\)) accounts for approximately seven electrons consumed per molecule. This datum is consistent with the known chemistry of the Fe(II) cages where oxidative dehydrogenation reactions to form Fe\(^{II}\)-imine products are facile (cf. Chapter Two). Mechanistically, the formation of imines occurs by initial formation of the Fe(III) species (Scheme 16). Thus, the oxidative
Figure 6.27

dc polarogram for the oxidation of $[\text{Fe}(\text{NH}_3)_2\text{sar}]^{4+}$ in acetone (0.1 M TMAT).

Figure 6.28

dc polarogram for the reduction of $[\text{Fe sar}]^{2+}$ in aqueous solution.
electrochemistry of the Fe(II) cages conforms to a mechanism whereby a chemical reaction (i.e. imine formation) follows the electrochemical oxidation of the metal ion. Electrochemical investigation of the electrolysed solution clearly identifies new species present. In particular two reduction waves, at $E = -0.17$ and $-1.46$ V are observed. Further electrolysis of this sample, until approximately fifteen electrons were consumed, resulted in only one reduction wave at a DME, at $E = -1.46$ V.

In acetone solution (0.1 M TMAT) a reversible oxidation wave at $E = +0.67$ V is observed at a DME (Figure 6.27). The reversible nature of this wave is discerned by analysis of a $\log[(i_d - i)/i]$ vs. $E$ graph, in which the gradient of 55 mV differs only slightly from the reversible value of 58/n mV for a one-electron transfer process and is consistent with the mechanism

$$[\text{Fe}^{II}(\text{NH}_3)_2\text{ar}]^{4+} \leftrightarrow [\text{Fe}^{III}(\text{NH}_3)_2\text{ar}]^{5+} + e \quad \ldots \quad (102)$$

The Reduction Process

The reduction of $[\text{Fe}^{III}\text{ar}]^{3+}$ at a DME in aqueous solution (Figure 6.28) conforms to the criterion for a reversible one-electron process as determined by $\log[(i_d - i)/i]$ vs. $E$ analysis. This yields a gradient of 56 mV$^\dagger$ (compared with 58/n mV for a theoretically reversible wave) and a zero intercept (i.e. $E_{1/2}$) of $-0.11$ V. This process is represented by Equation 103.

$$[\text{Fe}^{III}\text{ar}]^{3+} + e \leftrightarrow [\text{Fe}^{II}\text{ar}]^{2+} \quad \ldots \quad (103)$$

$^\dagger$ The deviation from theory could arise from adsorption phenomena.
Figure 6.29
dc (a) and ac voltammagram (b) quadrature c) in phase current response) for the reduction of [Fe:sar]^{2+} at a gold working electrode at pH 1.0.
At a platinum electrode the Fe(III)/(II) redox couple is reversible at slow scan rates, although at increasing scan rates the process becomes quasi-reversible. These data, obtained in neutral aqueous solution (0.1 M NaCF$_3$SO$_3$) are compared with measurements undertaken in acid solution (0.1 M CF$_3$SO$_3$H) at a gold electrode in Table 6.9 (Figure 6.29).

**TABLE 6.9**

Variation in CV parameters with scan rate, for the reduction of $\{\text{Fe sar}\}^{3+}$ in aqueous solutions, and at solid electrodes.

<table>
<thead>
<tr>
<th>Scan Rate, $v_s$ $^{-1}$</th>
<th>Au/0.1 M CF$_3$SO$_3$H(aq)</th>
<th>Pt/0.1 M NaCF$_3$SO$_3$(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$E_{1/2}, V$</td>
<td>$\Delta E_p, mV$</td>
</tr>
<tr>
<td>0.01</td>
<td>-0.17</td>
<td>60</td>
</tr>
<tr>
<td>0.02</td>
<td>-0.17</td>
<td>60</td>
</tr>
<tr>
<td>0.05</td>
<td>-0.17</td>
<td>60</td>
</tr>
<tr>
<td>0.10</td>
<td>-0.17</td>
<td>60</td>
</tr>
<tr>
<td>0.20</td>
<td>-0.17</td>
<td>60</td>
</tr>
<tr>
<td>0.50</td>
<td>-0.17</td>
<td>70</td>
</tr>
<tr>
<td>1.00</td>
<td>-0.18</td>
<td>80</td>
</tr>
<tr>
<td>2.00</td>
<td>-0.19</td>
<td>90</td>
</tr>
<tr>
<td>5.00</td>
<td>-0.20</td>
<td>120</td>
</tr>
<tr>
<td>10.00</td>
<td>-0.21</td>
<td>140</td>
</tr>
<tr>
<td>20.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

It is immediately evident from Table 6.9 that the redox couple is more stable in acidic solution as gauged by the peak separation for the forward and reverse cycles. The influence of the spin equilibrium observed for Fe(II) cage complexes in solution (cf.
Oxidation of \([\text{Mn}]^{2+}\) in aqueous solution a) dc polarogram, b) CV at HMDE (200 mV s\(^{-1}\)), c) CV at a gold working electrode and d) in phase and e) quadrature for the ac polarogram.
Chapter Four) is expected to be small in terms of the influence on electrochemical parameters.\textsuperscript{163,164} Therefore it appears that the enhanced stability of the redox species in acid solution is due to the unfavourable medium for deprotonation reactions; the precursor step necessary for the formation of imine species (cf. Scheme 16).

Ac voltammetry at a gold electrode in acid solution (0.1 M CF\textsubscript{3}SO\textsubscript{3}H) resulted in a \( E_p \) value of -0.17 V over the frequency range 20-200 Hz. The reduced intensity for the quadrature compared with the in-phase signal, indicates that adsorption is either trivially small or non-existent in this case (Figure 6.29).

No reduction waves were observed for [Fe\textsuperscript{II}(NH\textsubscript{3})\textsubscript{2}sar]\textsuperscript{4+} in aqueous solution prior to the solvent reduction limit (i.e. < -1.9 V).

6.4.4 The Manganese Cages

Synthetically, the cage complexes of Mn(II) were readily accessible. In addition, it was possible to isolate [Mn sar]\textsuperscript{3+} from acidic solutions containing the [Mn sar]\textsuperscript{2+} complex.

The Oxidation Process

[Mn\textsuperscript{II}sar]\textsuperscript{2+} exhibits an oxidation wave in aqueous solution (pH 5, 0.1 M NaClO\textsubscript{4}) at a DME (Figure 6.30). The wave appears unchanged over the pH range from 5 + 2 (adjusted using HClO\textsubscript{4}) and is characterized by a half-wave potential, \( E_{1/2} = +0.30 \) V. The ac polarogram yields a similar value for the peak potential, \( E_p = +0.31 \) V measured at 20 Hz, although the quadrature signal at the same frequency indicates that concomitant adsorption processes are occurring (cf. Figure 6.30). A graph of \( \log[(i_d - i)/i] \) vs. \( E \) reveals a small deviation from linearity with a zero intercept of +0.30 V and a slope of 36 mV which suggests that the electron
transfer departs somewhat from a reversible one-electron process indicated by,

\[ [\text{Mn}^{II}_{\text{sar}}]^2+ + e \rightarrow [\text{Mn}^{III}_{\text{sar}}]^3+ \quad \ldots (104) \]

However, the oxidation may well be reversible with adsorption at the electrode surface confusing the analysis of the polarogram. The relevant electrochemical parameters at a DME are included in Table 6.10.

Cyclic voltammetry (CV) provides a valuable technique for investigation of the oxidation process of the \([\text{Mn}^{II}_{\text{sar}}]^2+\) cage using variable time-scales. At a HMDE, the cyclic voltammogram for \([\text{Mn}^{II}_{\text{sar}}]^2+\) has been measured at scan rates from 20-500 mVs\(^{-1}\) (pH 2.5, 0.1 M NaClO\(_4\)/HClO\(_4\)) and the relevant electrochemical parameters are included in Table 6.10. It is apparent from these measurements that adsorption of the oxidation product occurs as discerned from a "spike" in the backwave (reverse cycle). The \(E^{1/2}\) values obtained by voltammetry, shown in Table 6.10, agree well with those obtained from the DME experiments, since the reference electrode (Ag/AgCl/sat'd KCl\(_{aq}\)) used for the CV measurements is -0.045 V more cathodic than the SCE.

At a stationary gold electrode, a quasi-reversible electron-transfer is observed at 200 mVs\(^{-1}\) with a \(E^{1/2} = +0.30\) V with no obvious adsorption spikes. These data are tabulated in Table 6.10 together with those obtained at pH 5 using a different gold electrode. At 200 mVs\(^{-1}\), a significant variation in both \(\Delta E\) and \((i_p)_{a}/(i_p)_{c}\) parameters is observed with the low pH measurement being more reversible (cf. Figure 6.30). This suggests that the stability of the oxidation product is enhanced in the more acidic medium.
### TABLE 6.10
Parameters of interest for the oxidation of [Mn sar]2⁺ in aqueous solution.

<table>
<thead>
<tr>
<th>dc Polarography</th>
<th>ac Polarography (^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_{1/2}) (E_{1/4} - E_{3/4}) (i_{d/C})</td>
<td>(E_p) (\Delta E_{1/2}) (i_{p/C})</td>
</tr>
<tr>
<td>V mV mAM⁻¹</td>
<td>V mV mAM⁻¹</td>
</tr>
<tr>
<td>+0.30</td>
<td>80</td>
</tr>
</tbody>
</table>

**Cyclic Voltammetry**

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Scan Rate, (mVs^{-1})</th>
<th>((E_p) - \Delta E/2) (V)</th>
<th>(\Delta E) (mV)</th>
<th>(i_p^a/(i_p)^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMDE</td>
<td>20</td>
<td>+0.26</td>
<td>60</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>+0.26</td>
<td>65</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>+0.26</td>
<td>68</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>+0.26</td>
<td>74</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>+0.26</td>
<td>75</td>
<td>1.3</td>
</tr>
<tr>
<td>gold</td>
<td>200</td>
<td>+0.30</td>
<td>90</td>
<td>1.2</td>
</tr>
</tbody>
</table>

\(^a\) Measured using an ac frequency of 20 Hz.

The number of electrons transferred per molecule was measured coulometrically as \(n = 1.0\) (platinum basket working electrode with 0.1 M NaClO\(_4\) supporting electrolyte). This coulometric information together with the quasi-reversible nature of the redox couple assessed by CV, confirms that the electrode reaction involves a simple metal centred electron transfer process.

The product of this one-electron oxidation was independently
Figure 6.31
Reduction and re-oxidation of \([\text{Mn sar}]^{2+}\) with changes measured by spectroelectrochemistry using a platinum working electrode in aqueous solution.

Figure 6.32
CV for the oxidation of \([\text{Mn(NH}_3)_2\text{sar}]^{3+}\) in CH3CN (0.1 M TEAP) and at a) gold, b) glassy carbon and c) platinum working electrode at 100 mV s\(^{-1}\).
synthesized and characterized. The room temperature magnetic moment in the solid (Chapter Two) and solution (Chapter Three) states is consistent with the formulation, \( [\text{Mn}^{\text{III}}\text{sar}]^{3+} \), with a low spin \( t_{2g}^4 \) configuration. Cyclic voltammetry, using the oxidation product as the electroactive species, reveals a quasi-reversible reduction at a gold electrode, which lies at the same potential as the oxidation of \( [\text{Mn}^{\text{II}}\text{sar}]^{2+} \). In addition, this redox couple was followed spectrophotometrically. Reduction of \( [\text{Mn}^{\text{III}}\text{sar}]^{3+} \) at \( E = 0.0 \) V results in a loss of intensity of the two characteristic absorption bands in the visible region (cf. Chapter Three). Subsequent re-oxidation of the colourless solution at \( E = +0.55 \) V restored the original absorption spectrum (Figure 6.31) in accord with:

\[
[\text{Mn}^{\text{III}}\text{sar}]^{3+} + e^- \rightarrow [\text{Mn}^{\text{II}}\text{sar}]^{2+} \quad \text{at} \quad E = 0.0 \text{ V},
\]

\[
[\text{Mn}^{\text{II}}\text{sar}]^{2+} - e^- \rightarrow [\text{Mn}^{\text{III}}\text{sar}]^{3+} \quad \text{at} \quad E = 0.55 \text{ V}.
\]

...(105)

thereby confirming the simple nature of the electron transfer.

No oxidation wave was observed for \( [\text{Mn}^{\text{II}}(\text{NH}_3)_2\text{sar}]^{4+} \) in aqueous solution at a DME. This is consistent with the substituent effect observed for the cobalt cages, where substitution of \(-\text{NH}_3^+\) groups for protons in the two apical sites, results in a positive shift of the redox potential by \( \text{ca. } 300 \text{ mV} \). Therefore the oxidation of \( [\text{Mn}^{\text{II}}(\text{NH}_3)_2\text{sar}]^{4+} \) is expected at \( \text{ca. } +0.60 \text{ V} \), a potential greater than the anodic limit of the mercury electrode in aqueous solution.

Cyclic voltammetry, undertaken in acetonitrile solution (with 0.1 M TEAP as supporting electrolyte), reveals a quasi-reversible oxidation wave for \( [\text{Mn}^{\text{II}}(\text{NH}_3)_2\text{sar}]^{4+} \) at glassy carbon, gold and platinum electrodes as observed in Figure 6.32 and Table 6.11.
TABLE 6.11

Cyclic voltammetric parameters for the oxidation of $[\text{Mn}^{II}(\text{NH}_3)_2\text{sar}]^{4+}$ in 0.1 M TEAP/CH$_3$CN

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$E_{1/2}$, V</th>
<th>$\Delta E_p$, mV</th>
<th>$(i_p)<em>{a}/(i_p)</em>{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>glassy carbon</td>
<td>+0.91</td>
<td>90</td>
<td>1.9</td>
</tr>
<tr>
<td>gold</td>
<td>+0.91</td>
<td>90</td>
<td>1.4</td>
</tr>
<tr>
<td>platinum</td>
<td>+0.91</td>
<td>100</td>
<td>1.1</td>
</tr>
</tbody>
</table>

* Measured at scan rates of 100 mVs$^{-1}$.

The half-wave potential observed for the oxidation of $[\text{Mn}^{II}(\text{NH}_3)_2\text{sar}]^{4+}$ in acetonitrile solution appears independent of the electrode surface (Table 6.11). As discussed for the aqueous measurements, comparison of these data with the comprehensive electrochemical study of cobalt cage complexes$^{23}$ indicates that the redox potential observed in non-aqueous solution lies ca. 300-400 mV more positive than that observed in aqueous media. Therefore, the experimentally observed value for the half-wave potential is in good agreement with that predicted, i.e. over the range $+0.9 \rightarrow +1.0$ V.

The reversibility of the CV's as gauged from their forward and reverse cycle peak separations ($\Delta E_p$ in Table 6.11), are at best regarded as being quasi-reversible.

At platinum, gold and glassy carbon electrodes, the surface required polishing prior to each measurement in order to remove adsorbed material. Second and subsequent scans at an untreated electrode surface resulted in the appearance of several additional waves not identified to date.
Figure 6.33
Reduction of [Mn sar]^{2+} in CH\textsubscript{3}CN and gauged by
a) dc polarography, b) DPP.

Figure 6.34
Reduction of [Mn(NH\textsubscript{3})\textsubscript{2}sar]\textsuperscript{4+} in aqueous solution using
a) CV at a glassy carbon working electrode, b) CV at a
HMDE (500 mV s\textsuperscript{-1}), c) DPP and d) dc polarography.
The Reduction Process

Reduction of \([\text{Mn}^{\text{II}}\text{sar}]^{2+}\) was not observed prior to the solvent reduction limit at a DME in neutral aqueous solutions. In acetonitrile (0.1 M TEAP), a reduction wave is evident from the dc polarogram (Figure 6.33). A graph of \(\log[(i_d - i)/i]\) vs. \(E\) for this wave, is linear with a gradient of 115 mV and a zero intercept at \(-0.98\) V (vs. Ag/AgCl(sat'd KCl)). This reduction is attributed to a metal-centred two electron process, i.e.

\[
[\text{Mn}^{\text{II}}\text{sar}]^{2+} + 2e^- \rightarrow [\text{Mn}^{\text{0}}\text{sar}] \quad (106)
\]

The gradient for the \(\log (i_d - i)/i\) vs. \(E\) graph lies far from the reversible value for a two-electron transfer but is consistent with an irreversible process. The metal in its zero oxidation state is too large to be contained within the cage cavity and the complex is expected to dissociate. This behaviour is similar to that observed for reduction of a number of other cage complexes e.g. \([\text{Cu}^{\text{II}}\text{sar}]^{2+}\), \([\text{Ni}^{\text{II}}\text{sar}]^{2+}\) and \([\text{Co}^{\text{II}}\text{sar}]^{2+}\).

A second reduction wave is observed in non-aqueous media, at more negative potentials than the first, and most likely originates from the reduction of the apical protons as described earlier (cf. Equation 101.

Some parameters of interest for the electrochemical reduction of \([\text{Mn}^{\text{II}}\text{sar}]^{2+}\) are presented in Table 6.12.

\([\text{Mn}^{\text{II}}(\text{NH}_3)_2\text{sar}]^{4+}\) exhibits a single reduction wave at a DME in aqueous media just prior to the solvent reduction limit (Figure 6.34). Analysis by \(\log[(i_d - i)/i]\) vs. \(E\) graph for this wave reveals a gradient of 109 mV and as for \([\text{Mn}^{\text{II}}\text{sar}]^{2+}\) suggests an irreversible process with a zero intercept of \(-1.65\) V.
Figure 6.35

dc polarogram for the reduction of $[\text{Mn(NH}_3\text{)}_2\text{Sar}]^{4+}$ in CH$_3$CN (0.1 M TEAP).
TABLE 6.12
Parameters of interest for the reduction of Mn(II) cages.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Electrode</th>
<th>dc Polarography</th>
<th>Differential Pulse Polarography</th>
<th>Media</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>E₁/₂, E₁/₄-E₃/₄, iₖ/C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>V</td>
<td>mV</td>
<td>mAM⁻¹</td>
</tr>
<tr>
<td>[MnII(phen)₂Cl₂]²⁺</td>
<td>DME</td>
<td>-0.98</td>
<td>180</td>
<td>2.3</td>
</tr>
<tr>
<td>[MnII(NH₃)₂sar]⁴⁺</td>
<td>DME</td>
<td>-1.65</td>
<td>200</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>HMDE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>glassy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>carbon</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>gold</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>DME</td>
<td>-1.37</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Differential Pulse Polarography (DPP), clearly discriminates the reduction wave from the solvent reduction limit with a peak potential at -1.59 V (included in Figure 6.34). Cyclic voltammetry at a glassy carbon or HMDE confirms the irreversible nature of the reduction wave (cf. Figure 6.34) which is consistent with the following mechanism:

\[
[Mn^{II}(NH₃)₂sar]^{4+} + 2e \rightarrow [Mn⁰(NH₃)₂sar]^{2+} + \text{Mn}⁰ + (NH₃)₂sar^{2+}
\]  ...(107)

No adsorption effects are observed in the ac polarogram at 400 Hz, as gauged by the reduction in the current for the quadrature signal.

Reduction of [MnII(NH₃)₂sar]⁴⁺ in acetonitrile solution occurs at a less negative potential than in aqueous solution (cf. Figure 6.35 and Table 6.12). The dc polarogram has been analyzed using a log[1000[(i_d - i)/i]] vs. E analysis which is characterized by a gradient
Figure 6.36

dc (a) and ac ((b) quadrature and (c) in phase current response at 100 Hz) togeather with d) DPP and e) CV at a HMDE (200 mV s$^{-1}$).
of 83 mV and a zero intercept of -1.37 V. Some deviation from linearity occurs for this plot, at potentials more negative than -1.4 V which is consistent with instability of the reduction product. Dissociation of the metal and the cage following two-electron reduction (as suggested earlier for [Mn$^{II}$sar]$^{2+}$) is believed to account for this deviation.

6.4.5 The Chromium Cages

The Oxidation Process

Investigation of the [Cr$^{III}$sar]$^{3+}$ ion in aqueous and non-aqueous (acetonitrile) media failed to reveal oxidation waves up to the solvent limit (~ +2V in CH$_3$CN). In addition the [Cr$^{III}$($NH_3$)$_2$sar]$^{5+}$ ion exhibits no oxidation waves at a platinum or glassy carbon electrode in either aqueous or acetonitrile solutions. Multielectron oxidation processes were however observed at a gold electrode although their origin is uncertain.

The Reduction Process

The polarographic reduction behaviour of [Cr$^{III}$sar]$^{3+}$ is greatly affected by adsorption, as gauged from both dc (including DPP) and ac techniques (Figure 6.36) in aqueous solutions (0.1 M NaCF$_3$SO$_3$). Logarithmic analysis of the dc wave is precluded due to the non-faradaic current contribution from adsorption processes; i.e.,

$$[\text{Cr}^{III}\text{sar}]^{3+} + e^- \rightarrow [\text{Cr}^{II}\text{sar}]^{2+} + [\text{Hg}] [\text{Cr}^{II}\text{sar}]^{2+}_{ads} \ldots (108)$$

Over the ac frequency range, 15-1000 Hz, the quadrature signal appears significantly enhanced, consistent with adsorption of the reduction product. The parameters of interest for this process are presented in Table 6.13.
Reduction of $[\text{Cr(NH}_3)_2\text{sar}]^{5+}$ in aqueous solution gauged by ac polarography (a) quadrature and b) in phase current response at 100 Hz), c) DPP and d) dc polarography.
The voltammetric behaviour of [CrIII{sar}]^{3+} was also effected by adsorption, with a peak separation of only 40 mV and highly distorted reverse cycle wave (Figure 6.36 and Table 6.13).

A further reduction wave is observed at \(-1.6\) V, and appears to be multi-electron process. No attempt has been made to determine the origin of this wave.

The reduction of [CrIII(NH₃)sar]^{5+} in aqueous solution (0.1 M TMAT) occurs at \(-1.04\) V as gauged by dc polarography and DPP (Figure 6.37). A graph of \(\log([i_d - i]/i)\) vs. \(E\) is linear for at least 40 mV for anodic and cathodic potentials either side of \(E_{1/2}\). The gradient of 50 mV lies just below that expected (i.e. 58/n mV) for a single electron reduction and the zero intercept (i.e. \(E_{1/2}\)) occurs at \(-1.045\) V. The one-electron nature of the Cr(III)/(II) couple was also established by dc wave-height comparison with the analogous

---

**TABLE 6.13**

Parameters of interest for the reduction of [Cr sar]^{3+} in 0.1 M NaCF₃SO₃(aq) at a mercury electrode.

<table>
<thead>
<tr>
<th>Compound</th>
<th>(E_{1/2}) or (E_p^a) V</th>
<th>Electrode</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>[CrIII{sar}]^{3+}</td>
<td>-1.45</td>
<td>DME</td>
<td>dc Polarography</td>
</tr>
<tr>
<td></td>
<td>-1.46</td>
<td>DME</td>
<td>DPP</td>
</tr>
<tr>
<td></td>
<td>-1.45</td>
<td>DME</td>
<td>ac Polarography(^b)</td>
</tr>
<tr>
<td>((E_p)_c = -1.47)</td>
<td>((E_p)_a = -1.43)</td>
<td>HMDE</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>(E_{1/2} = -1.45)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Reference electrode is SCE.

\(b\) At 100 Hz.
Figure 6.38
Reduction of $[\text{Cr(NH}_3)_2\text{sar}]^{5+}$ in aqueous solution
a) dc polarogram and b) CV at a HMDE (100 mV s$^{-1}$).
Co(III)/(II) couple (cf. Section 6.2.5). The effect of adsorption is less pronounced for \([\text{Cr}^{III} (\text{NH}_3)_2 \text{sar}]^{5+}\) than for \([\text{Cr}^{III} \text{sar}]^{3+}\); although the ac polarograms measured at frequencies in the range 10-1100 Hz show that the quadrature signal is enhanced significantly compared with the in-phase signal, i.e. indicating the presence of adsorption or a non-Faradaic process (illustrated in Figure 6.37).

Cyclic voltammetry at a HMDE for \([\text{Cr}^{III} (\text{NH}_3)_2 \text{sar}]^{5+}\), indicates the reduction couple is quasi-reversible at 100 mVs\(^{-1}\) i.e. \(\Delta E = 80\) mV (cf. Table 6.14 and Figure 6.38).

**TABLE 6.14**

<table>
<thead>
<tr>
<th>Compound</th>
<th>dc Polarography</th>
<th>ac Polarography</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(E_{1/2}), (E_{1/4}-E_{3/4}), (i_d/C), (V), mV, mAM(^{-1})</td>
<td>(E_p), (\Delta E_{1/2}), (i_p/C), (V), mV, mAM(^{-1})</td>
</tr>
<tr>
<td>([\text{Cr}^{III} (\text{NH}_3)_2 \text{sar}]^{5+})</td>
<td>-1.04 100 1.29</td>
<td>-1.05 100 2.31</td>
</tr>
<tr>
<td>([\text{Cr}^{III} (\text{NH}_2)_2 \text{sar}]^{3+})</td>
<td>-1.33(^a) 70 1.96</td>
<td>-1.34 110 1.69</td>
</tr>
</tbody>
</table>

\(a\) Pre-wave also present.

A second reduction process is also observed for \([\text{Cr}^{III} (\text{NH}_3)_2 \text{sar}]^{5+}\) in Figure 6.38. The process is multi-electron and occurs at \(-1.6\) V, although the process/es giving rise to this wave are as yet unknown. It seems unlikely that this wave originates from \(\text{Cr}(II) \rightarrow \text{Cr}(0)\), as this process is expected to occur at a potential at least one volt more negative than the M(III/II) wave (by analogy with the other transition metal cages included in this study). Also it is unlikely to arise from reduction of a proton from the apical
Spectroelectrochemistry of $[\text{Cr(NH}_3)_2\text{sar}]^{5+}$ in aqueous solution. Full line is the initial spectrum and the dashed line, after reduction at $E = -1.5 \text{ V}$ then re-oxidation at $E = 0 \text{ V}$. 

Figure 6.39
Figure 6.40
Reduction of $[\text{Cr(NH}_3\text{)}_2\text{sar}]^{5+}$ in CH$_3$CN (0.1 M TMAT)
gauged by a) dc and ac polarography b) in phase and c) quadrature current response (at 100 Hz) and d) CV at HMDE (200 mV s$^{-1}$).
substituent, i.e. $-\text{NH}_3^+ + e^- + \text{NH}_2 + 1/2 \text{H}_2$, as this is not observed in aqueous media for the cobalt analogues. The chemical instability of the Cr(II) cage has prevented its isolation to date. It is possible that, on the polarographic timescale, degradation products of the Cr(II) cage are in fact the electroactive species giving rise to the second reduction process.

Coulometry, at a mercury pool working electrode for $[\text{Cr}^{\text{III}}(\text{NH}_3)_2\text{sar}]^{3+}$, indicated near reversibility as ascertained by visible absorption spectra. A reduction potential of $E = -1.5 \text{ V}$ was applied to ensure complete reduction of the complex ion. Upon reoxidation the spectrum of $[\text{Cr}^{\text{III}}(\text{NH}_3)_2\text{sar}]^{3+}$ is regenerated albeit with a little additional impurity as observed in Figure 6.39.

In acetonitrile solution (0.1 M TMAT) three reduction waves for $[\text{Cr}^{\text{III}}(\text{NH}_3)_2\text{sar}]^{3+}$, at $E_{1/2} = -0.72, -1.07$ and $-1.38 \text{ V}$, are observed prior to the solvent reduction limit (Figure 6.40). The first reduction wave (i.e. at $E_{1/2} = -0.72 \text{ V}$) lies within the anticipated region for the Cr(III)/(II) process by comparison with cobalt cage reduction potentials in non-aqueous solutions. Ac polarography indicates that this first reduction wave embraces two processes the second involving adsorption of the product of reduction (as judged from the current increase for the quadrature signal at 100 Hz). In addition, CV at a HMDE indicates quasi-reversibility from the peak separation, $\Delta E = 100 \text{ mV}$. The nature of a second reduction process has not been discerned, although it is most likely to arise from reduction of a proton on the apical substituent, (i.e. $-\text{NH}_3^+ + e^- + \text{NH}_2 + 1/2 \text{H}_2$) by inference from cobalt cage electrochemistry. The third reduction wave observed at $E = -1.38 \text{ V}$, is thought to arise from the metal centred, Cr(II) + (0), processes for the $[\text{Cr}^{\text{II}}(\text{NH}_3)_2\text{sar}]^{4+}$ complex.
Figure 6.41

CV for the reduction of $[\text{V sar-2H}]^{2+}$ in 0.1 M $\text{HClO}_4$ (aq) at a HMDE (500 mV s$^{-1}$).
6.4.6 The Vanadium Cages

The electrochemical properties of the vanadium(IV) cages were of particular interest as they are believed to be the first examples of a non-vanadyl V(IV) complexes with saturated nitrogen donor atoms.

The aqueous electrochemistry of \([\text{V(NH}_3)_2\text{sar-2H}]^{4+}\) and \([\text{V sar-2H}]^{2+}\) is complicated by protonation equilibria, possible at both the non-donor and donor nitrogen atoms.

Interestingly, the crystallographically characterized complex, \([\text{V(NH}_3)_2\text{sar-2H}]\text{(S}_2\text{O}_6)_2\text{H}_2\text{O}]\), is insensitive to pH over the range \(1 > \text{pH} > 12\), as gauged by optical spectroscopy.

The Oxidation Process

No oxidation waves were observed for the V(IV) complexes either in aqueous media or DMSO solution, prior to the anodic limit.

The Reduction Process

Cyclic voltammetry performed at a HMDE in acid solution (0.1 M HClO\(_4\)) for \([\text{V IV sar-2H}]^{2+}\), indicates only a single reduction wave at \(E_p = -0.61\) V, and an associated re-oxidation process at \(E_p = -0.55\) V. The peak separation of \(\Delta E = 60\) mV, observed at scan rates of 100 mVs\(^{-1}\), remains essentially unchanged until much larger scan rates of 100 and 200 Vs\(^{-1}\) are employed (cf. Figure 6.41). The only feature of particular note is that the current ratio, \((i_p)_c/(i_p)_a\) is less than unity, although this ratio approaches unity at slow scan rates. Such behaviour is consistent with weak adsorption of the reduction product (cf. Figure 6.9). The expected variation of \(E_p\) with scan rate for a weakly adsorbed reduction product\(^{155-157}\) is also in accord with that observed for the \([\text{V IV sar-2H}]^{2+}\) reduction; i.e., \(E_p\) shifts towards more positive potentials with increasing scan rates. In neutral aqueous solution (0.1 M NaClO\(_4\)), similar behaviour is observed with \((E_p)_c = -0.76\) V.
Figure 6.42
CV for the reduction of $[\text{V sar-2H}]^{2+}$ in a) acetate buffer (pH 4.6) at a HMDE (500 mV s$^{-1}$) and b) TRIS buffer (pH 8.1) at a HMDE (1 V s$^{-1}$).
and \((E_p)_a = -0.70\) V.

In contrast, measurements undertaken in an acetate buffer (pH 4.6) at a HMDE, indicate two reduction waves of which the more anodic appears to be new (at \(E_p = -0.25\) V), as shown in Figure 6.42. Reduction 1, appears to be dependent upon the scan rate as confirmed by a 100 mV shift for a factor of ten \((0.5 \rightarrow 5\) V s\(^{-1}\)) in the scan rate.

At pH 8.1 (TRIS buffer), and at 1 Vs\(^{-1}\), similar behaviour is observed as at pH 4.6. However, here the first reduction wave of \([\text{VIVsar-2H}]^{2+}\) occurs at \((E_p)_1 = -0.36\) V, and the second at \((E_p)_2 = -0.88\) V (included in Figure 6.42). Reoxidation waves were observed at \(E_p = -0.82\) V and at \(E_p = -0.12\) V.

The obvious complexity of the electroreduction results for \([\text{VIVsar-2H}]^{2+}\) together with the incomplete state of this investigation limits the analysis of the redox processes described above. Qualitatively, the redox couple observed at pH 1 is likely to arise from a V(IV)/V(III) process, i.e.

\[
[V^{IV}\text{sar-2H}]^{2+} + e^{-} \rightarrow [V^{III}\text{sar-2H}]^{+} \quad \ldots (109)
\]

The shift of this couple to more negative potentials with increasing pH is consistent with further deprotonation of the complex ion or ion pairing with the buffer.

However, these reactions offer no insight into the reduction waves that appear at -0.26 V (at pH 4.6) and at -0.36 V (at pH 8.1). These waves appear to exhibit different characteristics compared with the "reversible" couples, in that repeated cyclic voltammograms indicate rapid depletion of their electrode surface concentrations. It may be that these processes are not due to metal-
centred redox processes but due to either a ligand process or even to
degradation products present in solution.

A more extended study of the behaviour of the first reduction
wave is now needed employing variable scan rates. Coulometric
studies would also provide valuable information, defining the number
of electrons involved in each reduction process.

The aqueous reduction electrochemistry of \([\text{V}^{IV}(\text{NH}_3)_2\text{sar}-2\text{H}]^{4+}\) is
even more complicated than the \([\text{V}^{IV}\text{sar}-2\text{H}]^{2+}\) congener, due to the
facile deprotonation of the two primary (apical) amines \((pK_a)_1^o = 5.47\) and \((pK_a)_2^o = 4.26\) as indicated in Table 6.15.

In this investigation measurements were performed primarily at a
mercury electrode, utilizing dc and ac polarographic and dc cyclic
voltammetric techniques at a DME or HMDE respectively. A wide range
of pH was employed in unbuffered solutions and the relevant
parameters are listed in Table 6.16.

The obvious complexities inherent within these measurements
(included in Table 6.16) can be partly understood by considering the
pK_a values for the primary (i.e. arising from the apical
substituents) and secondary (i.e. arising from the nitrogen donor
atoms) amines. The pK_a values obtained by titrametric methods for
some of the known M(II), M(III) and M(IV) cage complexes and are
collated in Table 6.15. It is interesting to note, that the primary
amines (apical substituents) for \([\text{V}^{IV}(\text{NH}_3)_2\text{sar}-2\text{H}]^{4+}\) are more basic
than those for the metal(III) cages. This effect arises from
deprotonation of the two secondary amines which render the primary
amines less acidic, i.e. the pK_a values for the primary amines of the
<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Compound</th>
<th>((pK_1)_1^a)</th>
<th>((pK_2)_1^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M(II)</td>
<td>[Mg(NH₃)₂sar]^4+</td>
<td>6.10</td>
<td>5.37</td>
</tr>
<tr>
<td></td>
<td>[Mn(NH₃)₂sar]^4+</td>
<td>6.20</td>
<td>5.37</td>
</tr>
<tr>
<td></td>
<td>[Co(NH₃)₂sar]^4+</td>
<td>6.29</td>
<td>5.40</td>
</tr>
<tr>
<td></td>
<td>[Ni(NH₃)₂sar]^4+</td>
<td>5.23</td>
<td>5.07</td>
</tr>
<tr>
<td></td>
<td>[Cu(NH₃)₂sar]^4+</td>
<td>6.03</td>
<td>5.24</td>
</tr>
<tr>
<td></td>
<td>[Zn(NH₃)₂sar]^4+</td>
<td>6.20</td>
<td>5.34</td>
</tr>
<tr>
<td></td>
<td>[Hg(NH₃)₂sar]^4+</td>
<td>6.32</td>
<td>5.44</td>
</tr>
<tr>
<td>M(III)</td>
<td>[Cr(NH₃)₂sar]^5+</td>
<td>4.48</td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td>[Co(NH₃)₂sar]^5+</td>
<td>3.31</td>
<td>2.37</td>
</tr>
<tr>
<td></td>
<td>[Ga(NH₃)₂sar]^5+</td>
<td>3.77</td>
<td>2.80</td>
</tr>
<tr>
<td></td>
<td>[In(NH₃)₂sar]^5+</td>
<td>3.90</td>
<td>3.26</td>
</tr>
<tr>
<td></td>
<td>[Co(NH₃)₂char]^5+</td>
<td>3.15</td>
<td>2.22</td>
</tr>
<tr>
<td>M(IV)</td>
<td>[V(NH₃)₂sar-2H]^4+ type A</td>
<td>5.47</td>
<td>4.26</td>
</tr>
<tr>
<td></td>
<td>[V(NH₃)₂sar-2H]^4+ type B</td>
<td>5.39</td>
<td>4.08</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>((pK_a)_2^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(NO₂)₂sar]^3+</td>
<td>8.85 ± 0.02</td>
</tr>
<tr>
<td>[Co(Cl)₂sar]^3+</td>
<td>9.85 ± 0.07</td>
</tr>
<tr>
<td>[Cr(NH₂)₂sar]^3+</td>
<td>12.9 ± 0.10</td>
</tr>
</tbody>
</table>

\(a\) \(^1\)° refers to the primary (non-coordinating) amines.  
\(b\) \(^2\)° refers to the secondary (donor) amines.

\(\dagger\) Measured by Mr. D. Bogsanni, complex and NaOH ca. 10⁻² M, \(n = 0.1\), \(pK_w = 13.75\), and at 25°C.
### TABLE 6.16

Variation of reduction parameters with pH for \([V(NH_3)_2sar-2H]^{4+}\) in aqueous solution at a mercury electrode.

<table>
<thead>
<tr>
<th>pH</th>
<th>dc Polarography</th>
<th>ac Polarography</th>
<th>Cyclic Voltammetry(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Red.1 (E_{1/2,V})</td>
<td>Red.2 (E_{1/2,V})</td>
<td>Red.3 (E_{1/2,V})</td>
</tr>
<tr>
<td>0.61</td>
<td>-0.39</td>
<td></td>
<td>-0.41</td>
</tr>
<tr>
<td>1.17</td>
<td>-0.30,(^a)-0.39</td>
<td>-0.42</td>
<td></td>
</tr>
<tr>
<td>1.99</td>
<td>-0.28, -0.46</td>
<td>-0.34, -0.46, -1.10</td>
<td>-0.42, -1.18, -0.41</td>
</tr>
<tr>
<td>3.75</td>
<td>-0.30, -0.64</td>
<td>-0.33, -0.60, -1.20</td>
<td>-0.41, (^b)-1.24, -0.54</td>
</tr>
<tr>
<td>5.09</td>
<td>-0.31, -0.75, -1.20</td>
<td>-0.37, -0.68, -1.26</td>
<td>-0.44, -1.36, -0.58</td>
</tr>
<tr>
<td>6.00</td>
<td>-0.35</td>
<td>-1.16</td>
<td>-0.44</td>
</tr>
<tr>
<td>8.22</td>
<td>-0.42</td>
<td>-1.17</td>
<td>-0.45</td>
</tr>
<tr>
<td>10.94</td>
<td>(=) 0</td>
<td>-0.47, -1.17</td>
<td>(=) 0</td>
</tr>
<tr>
<td>12.44</td>
<td>-0.14, -0.56, -1.17</td>
<td>-0.15, -0.56, -1.24</td>
<td>-0.61, -1.36, -0.77, -0.54</td>
</tr>
</tbody>
</table>

\(^a\) New wave forming as a pre-wave to the first reduction observed at pH 0.61.
\(^b\) Broad shoulder appears after this first reduction wave at \(-0.50\) V.
\(^c\) Measured at a scan rate of 50 Vs\(^{-1}\).

Protonated complex, \([V^{IV}(NH_3)_2sar]^{6+}\), are expected to be \(=0\)\(^\dagger\). This is a stark contrast to the \([Cr^{III}(NH_2)_2sar]^{3+}\) cation where \((pK_a)_{2^o} = 12.9\) (cf. Table 6.15). Thus, it is reasonable to assume that electrochemical reduction of \([V^{IV}(NH_3)_2sar-2H]^{4+}\) to the V(III) is possible.

\(^\dagger\) By analogy with the metal(II) and metal(III) complexes included in Table 6.15. In addition, \([V^{IV}(NH_3)_2sar-2H]^{4+}\) is isolated from 6M HCl (cf. Chapter Eight).
Figure 6.43
CV's for the reduction of \([\text{V(NH}_3\text{)}_2\text{sar-}2\text{H}^+]^{4+}\) at pH 6 at a HMDE (100 mV s\(^{-1}\)) showing the effect of repeat scans and increasing potential range.

Figure 6.44
Reduction of \([\text{V(NH}_3\text{)}_2\text{sar-}2\text{H}^+]^{4+}\) in acetate buffer (pH 4.05) gauged by CV at a HMDE (500 mV s\(^{-1}\)) a) single scan and b) repeat scans.
complex should be associated with a protonation of the two secondary
donor-amines to form \([\text{V}^{\text{III}}(\text{NH}_3)_2\text{sar}]^{5+}\), at pH < 2 (necessary to
maintain protonation of the primary amine groups). Therefore it
follows that:

(1) reduction of a 4+ charged \(\text{V}^{\text{IV}}\) cation leads to a 5+ charged \(\text{V}^{\text{III}}\)
cation, and

(2) in acidic solutions, \([\text{V}^{\text{III}}(\text{NH}_3)_2\text{sar}-2\text{H}]^{3+}\) should not be observed
due to facile protonation of the secondary amines.

A complementary investigation to the measurements at varying pH,
has been undertaken using cyclic voltammetry at a HMDE and differing
scan rates. This study, is however, largely incomplete with
measurements at pH 6.0 being the only ones completed. These results
are presented in Figure 6.43.

At a scan rate of 100 mVs\(^{-1}\), the first reduction (at \(E =
-0.17\) V), is reversible, although the wave shape indicates that the
electroactive species is/are adsorbed. The second reduction wave (at
\(E = -0.56\) V) appears irreversible as no backwave is observed. Two
further reduction waves occur at potentials greater than \(-0.8\) V, and
appear to be associated with two re-oxidation waves on the reverse
cycle. The first of these "more negative" reductions essentially
disappears upon repeat cycles and possibly originates from a
(subsequent) chemical process rather than an electrochemical one.

**Acetate Buffer (pH 4.05)**

Some preliminary measurements were undertaken in buffered
solutions in order to maintain the overall pH of the bulk solution
during protonation or deprotonation of the electroactive species.

Cyclic voltammetry in this media at a HMDE is characterized by
two reduction waves at \(E_p = -0.42\) and \(-0.69\) V at a scan rate of 500
mVs\(^{-1}\) (Figure 6.44). However, only one wave is seen upon re-
Figure 6.45

Reduction of $[\text{V(NH}_3\text{)}_2\text{sar-2H}]^{4+}$ in acetate buffer (pH 4.05) gauged by cyclic ac voltammetry at a) 50 Hz frequency and 10 mV s$^{-1}$ scan rate and b) 80 Hz frequency and 200 mV s$^{-1}$.

Figure 6.46

DPP for the reduction of $[\text{V(NH}_3\text{)}_2\text{sar-2H}]^{4+}$ in acetate buffer (pH 4.05)
oxidation at $E_p = -0.60$ V. Repeat cycle voltammetry over the voltage range $0.0 \pm 1.0$ V, reveals a large difference in surface concentration of the electroactive material for the first and subsequent scans of the initial reduction wave. The second reduction and re-oxidation waves are essentially unchanged by repeat scans over the same voltage range and have been attributed to a metal centred process.

The technique of cyclic ac voltammetry has been employed to assist in the analysis of these data (cf. Figure 6.45). Two features are evident for the results of various scan rates and frequencies; (1) the first and second reduction processes are of different origins which is consistent with the findings above, and (2) the second reduction wave appears to be associated with a re-oxidation wave, although, the couple is not reversible as gauged by the ratio $(i_p)_c/(i_p)_a < 1$ for scan rates less than $50$ mVs$^{-1}$. However, at scan rates of $50$, $200$ and $500$ mVs$^{-1}$, a cross-over potential, $E_{co}$, becomes increasingly significant, although the peak current ratio, $(i_p)_c/(i_p)_a$ now approximates unity for the process, as illustrated in Figure 6.45. Differential pulse polarography (DPP) also indicates the different origins for the two reduction waves (at $E_p = -0.40$ and $-0.66$ V), as they integrate for vastly different areas under their respective current-potential curves (cf. Figure 6.46).

**Acetate Buffer (pH 4.70)**

Whereas both primary (apical) amines are protonated for measurements at pH 4.05, at pH 4.70 only one of the primary amines is expected to be protonated (cf. $pK_a$ values in Table 6.15). Two reduction waves were again observed by cyclic dc voltammetry (at a HMDE), at $E_p = -0.29$ and $-0.67$ V, and one wave upon re-oxidation at
Figure 6.47
CV for the reduction of [V(NH$_3$)$_2$sar-2H]$^{4+}$ in acetate buffer (pH 4.70) at HMDE (100 mV s$^{-1}$).
At solid electrodes (Au, Pt and glassy carbon), the reduction behaviour of $[\text{V(NH}_3\text{)}_2\text{sar-2H}]^{4+}$ varied significantly for each electrode and with their pre-measurement treatment. These data are summarized in Table 6.17.

A possible origin of the pH dependence of the reduction processes in aqueous solution, could lie in an equilibrium between protonated and deprotonated (coordinated) amines of the vanadium(IV) cage which will be dependent upon pH. A scheme representing such an equilibrium together with the respective redox products is presented below:

$$
\begin{align*}
K^{1} & \quad [\text{V}^{6+}\text{(NH}_3\text{)}_2\text{sar}]^{2+} + 2\text{H}^+ \\
K^{2} & \quad [\text{V}^{5+}\text{(NH}_3\text{)}_2\text{sar}]^{3+} + 2\text{H}^+ \\
E^{(1)}_{1/2} & \quad + \text{e} \\
E^{(2)}_{1/2} & \quad + \text{e} \\
E^{(1)}_{1/2} & \quad + \text{e} \\
E^{(2)}_{1/2} & \quad + \text{e}
\end{align*}
$$

\text{Scheme 18}

Proposed scheme for protonation equilibria and redox processes for a V(IV) cage.

Although the deprotonated vanadium(IV) complex remains the dominant species in solution over the range $0 < \text{pH} < 4$, the more highly charged $[\text{V}^{6+}\text{(NH}_3\text{)}_2\text{sar}]^{6+}$ complex should exhibit more facile reduction, i.e. $E^{(1)}_{1/2}$ should lie more positive than $E^{(2)}_{1/2}$. Over the pH range, $4 < \text{pH} < 6$, the sequential deprotonation of the two primary (uncoordinated) amines of $[\text{V}^{4+}\text{(NH}_3\text{)}_2\text{sar-2H}]^{4+}$ would also exist in equilibrium (at least over a limited range of pH). These additional equilibria should shift the reduction potential (cathodically) by approximately 300 mV (as observed for the cobalt cage complexes). In a similar manner deprotonation of the primary (uncoordinated) amines for $[\text{V}^{6+}\text{(NH}_3\text{)}_2\text{sar}]^{6+}$ should also effect the reduction potential by ca. 300 mV (towards more negative potentials).
## Table 6.17

Cyclic voltammetric parameters for (initial) reduction then re-oxidation for \([\text{V(NH}_3)_2\text{ar-2H}]^{4+}\) in aqueous solution.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Scan Rate (\text{mVs}^{-1})</th>
<th>(E_p), V</th>
<th>(E_p), V</th>
<th>(E_p), V</th>
<th>(\Delta E), (i_p)_c/((i_p)_a)</th>
<th>mV</th>
</tr>
</thead>
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<tr>
<td>HMDE</td>
<td>10</td>
<td>-0.26</td>
<td>-0.67</td>
<td>-0.61</td>
<td>60</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>-0.26</td>
<td>-0.67</td>
<td>-0.61</td>
<td>60</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-0.27</td>
<td>-0.67</td>
<td>-0.61</td>
<td>60</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>-0.28</td>
<td>-0.67</td>
<td>-0.61</td>
<td>60</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>-0.29</td>
<td>-0.67</td>
<td>-0.61</td>
<td>60</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>500</td>
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<tr>
<td></td>
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<td>-1.05</td>
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<tr>
<td></td>
<td>500</td>
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<td>platinum^a</td>
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<td></td>
<td>100</td>
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<td>-0.66</td>
<td>170</td>
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<tr>
<td></td>
<td>500</td>
<td>-0.91</td>
<td></td>
<td>-0.57</td>
<td>340</td>
<td>1.6</td>
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<tr>
<td>platinum^b,e</td>
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<td>-0.85(^d)</td>
<td>-0.27(^d)</td>
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<tr>
<td></td>
<td>20</td>
<td>-0.58(-0.56)</td>
<td>-0.86(-0.88)</td>
<td>-0.25(-0.26)</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-0.62(-0.57)</td>
<td>-0.89(-0.89)</td>
<td>-0.23(-0.24)</td>
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<tr>
<td></td>
<td>100</td>
<td>-0.66(-0.58)</td>
<td>-0.91(-0.90)</td>
<td>-0.20(-0.21)</td>
<td></td>
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</tr>
<tr>
<td></td>
<td>200</td>
<td>-0.71(-0.60)</td>
<td>-0.90(-0.90)</td>
<td>-0.18(-0.18)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>-0.68(-0.56)</td>
<td>-0.90(^c)</td>
<td>-0.11(-0.14)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>glassy</td>
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<td>-0.69</td>
<td></td>
<td>-0.63</td>
<td>60</td>
<td>1.0</td>
</tr>
<tr>
<td>carbon</td>
<td>20</td>
<td>-0.70</td>
<td></td>
<td>-0.63</td>
<td>70</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>-0.71</td>
<td></td>
<td>-0.62</td>
<td>90</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>-0.72</td>
<td></td>
<td>-0.62</td>
<td>100</td>
<td>1.3</td>
</tr>
<tr>
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<td>-0.74</td>
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<td>-0.61</td>
<td>130</td>
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</tr>
<tr>
<td></td>
<td>500</td>
<td>-0.75</td>
<td></td>
<td>-0.60</td>
<td>150</td>
<td>1.2</td>
</tr>
</tbody>
</table>

- a Electrode surface cleaned prior to each run by polishing with zeolite.
- b Electrode surface cleaned prior to each run using conc. \(\text{HNO}_3\) then washing with distilled water several times.
- c After many cycles (ca. 20) the wave disappears.
- d The potential of these waves remains unchanged with number of cycles.
- e Potential for the second and subsequent cycles in brackets.
Figure 6.48
Optical spectrum of the electrochemically reduced [V(NH$_3$)$_2$sar-2H]$^{4+}$ at a platinum working electrode and where $n = 1.0$. 
The rate of equilibrium for the species in solution will govern the electrode reaction; i.e., an electroactive species which is linked to a slow equilibrium process should result in wave of variable current amplitude due to rapid depletion of its surface concentration.

The timescale of measurement appears to be particularly important for the vanadium cage electro-reduction study. Coulometry interfaced with optical absorption measurements provide a useful probe for the identification of new electro-generated species using a long timescale experiment.

Controlled potential electrolysis (CPE) of $[\text{V(NH}_3\text{)}_2\text{sar-2H}]^{4+}$ in aqueous solution ($\text{pH} = 6$, 0.1M NaCF$_3$SO$_3$) at a platinum gauze electrode and $E = -0.54$ V yielded the value $n = 1.0$. The optical spectrum generated from this reduction process is shown in Figure 6.48 together with the re-oxidation spectrum, $E = 0.0$ V and $n = 0.91$. This electrochemically prepared sample was isolated as its dithionate salt and its magnetic moment (cf. Chapter Two) is consistent with a $d^2$ ion in pseudo-octahedral geometry, i.e., a vanadium (III) species. A similar spectrum (to that in Figure 6.48) was also generated by reduction of $[\text{V}^{IV}\text{(NH}_3\text{)}_2\text{sar-2H}]^{4+}$ at a mercury pool at $E = -0.50$ V in acidic media (0.1 M CF$_3$SO$_3$H) where $n = 1.0$; and in basic media (0.01 M NaOH) where $E = -0.60$ V.

Chemical reduction of $[\text{V(NH}_3\text{)}_2\text{sar-2H}]^{4+}$ using zinc amalgam in acidic (1 M HClO$_4$) or basic (0.02 M NaOH) solutions and under a nitrogen atmosphere confirmed that the reduced species remains stable.
Figure 6.49
Optical spectra for the chemical reduction of \([\text{V(NH}_3\text{)}_2\text{sar-2H}]^{4+}\) in a) 0.1 M HClO\(_4\) where (-----) was the final spectrum and b) 0.02 M NaOH.
Figure 6.50
Optical spectra of [V(NH₃)₂sar-2H]⁴⁺ at pH 6 indicating
a) (---) initial spectrum, (---) after reduction at E = -0.6 V and
(......) after re-oxidation at E = 0.0 V; b) (---) initial spectrum,
reduction at E = -1.4 V initially forms (---) then loses intensity
(......) and finally re-oxidation at E = -0.2 V (---).
Figure 6.51

CV's for the reduction of \( [\text{V(NH}_3\text{)}_2\text{sar-2H}]^{4+} \) in DMSO (0.1 M TBAPF$_6$) at a HMDE (200 mV s$^{-1}$).
in these solutions for several hours. These spectra are included in Figure 6.49 for comparison with those of the electrochemically prepared product.

Electrochemical reduction of $[\text{V}^{IV}(\text{NH}_3)_2\text{sar-2H}]^{4+}$ at pH 6 (0.1 M NaCF$_3$SO$_3$) and at a mercury pool, indicated reversibility of the reduction at $E = -0.60$ V since re-oxidation at $-0.0$ V, generated the same spectrum as shown earlier in Figure 6.48 and is illustrated in Figure 6.50. Reduction of the same solution at more negative potentials, i.e. $E = -1.4$ V, followed by re-oxidation at $E = -0.2$ V, generated a different absorption spectrum, possibly due to a mixture of degradation products (included in Figure 6.50).

This investigation confirms the presence of a vanadium(III) cage complex after the first reduction wave, i.e. $E < -0.60$ V at mercury working electrode. However, the second reduction wave at $-1.1 < E < -1.4$ V (depending upon pH) is not well understood and requires further investigation.

A preliminary electrochemical study of the reduction of $[\text{V}^{IV}(\text{NH}_3)_2\text{sar-2H})(\text{CF}_3\text{SO}_3)^4$ in non-aqueous media (0.1 M TBAPF$_6$/DMSO) has been undertaken although the numerous reduction processes which appear are not understood to date. An example of the observed reduction waves at a HMDE are shown in Figure 6.51.

6.5 CONCLUSIONS

The electrochemical behaviour of the cage complexes of the first row transition metals described in this chapter, is dominated by metal-based redox properties. In particular the 2+ and 3+ oxidation
Figure 6.52
Variation of $M^{(III)}/M^{(II)}$ redox potentials with 3d electron configuration for $[M \text{sar}]^{3+}/2^+$ (●) and $[M(NH_3)_2\text{sar}]^{5+}/4^+$ (■) in aqueous solution.
states are common for cage complexes of the metals Cr → Cu, and are the most accessible in the both aqueous and non-aqueous media. The correlation between the 3d electronic configuration and the redox potential (for a reversible process) can provide evidence for a metal-based process. It would be expected that a stable electronic configuration i.e. a half-filled 3d shell, $(t_{2g}^6 e_g^2)$, a filled $t_{2g}$ sub-shell, $(t_{2g}^6)$ and a half-filled $t_{2g}$ sub-shell, $(t_{2g}^3)$, should be associated with an energetically difficult oxidation (or reduction) process. Conversely, oxidation (or reduction) of the other d-configurations to attain these "stable configurations" should be more facile. This predicted behaviour is observed for the $[\text{M}^{II}\text{sal}]^{2+}$ and $[\text{M}^{II}(\text{NH}_3)_2\text{sal}]^{4+}$ complexes as illustrated in Figure 6.52. The facile oxidation potentials are represented by minima in the graph of $E_{1/2}$ versus $3d^n$ and correspond to Cr(II), $(t_{2g}^3 e_g^1)$ to Cr(III), $(t_{2g}^3)$ and Co(II), $(t_{2g}^6 e_g^1)$ to Co(III), $(t_{2g}^6)$ i.e. attaining a half-filled or filled $t_{2g}$ sub-shell configuration. The maxima in Figure 6.52 are observed for oxidation of Mn(II), $(t_{2g}^3 e_g^2)$ to Mn(III), $(t_{2g}^3 e_g^1)$ and Ni(II), $(t_{2g}^6 e_g^2)$ to Ni(III), $(t_{2g}^6 e_g^1)$ i.e. loss of half-filled or filled $t_{2g}$ and $e_g$ sub-shells.

The only complexes to exhibit a stable 4+ oxidation state are the vanadium(IV) cages. It is not surprising however, that these complexes are most stable in their double deprotonated (at the coordinated amines) forms, which increases the electron density at the electron deficient metal centre (analogous to the formation of the vanadyl cation). However, sequential pH dependent equilibria result in redox properties that are complex and difficult to unravel.

† The configuration which exists immediately upon electron transfer is only considered here.
without further work.

The inability to observe the 1+ oxidation state for any of the cage complexes included in this thesis is thought to result from the restriction imposed by the limited and inflexible cavity size of the cage ligand. It is of interest to note that macrocyclic complexes generally exhibit metal-centred reduction processes of the kind \( \text{M}^{II} \text{L} \rightleftharpoons \text{M}^{I} \text{L} \rightleftharpoons \text{M}^{0} \text{L} \), where the ease of reduction is generally governed by the cavity size.\(^{165}\) The copper(II) cages in acidic media, are thought to exist as quadridentate chelates and accordingly are the most likely candidates for a 1+ reduction process to be observed. However, the investigation into the reduction behaviour for \([\text{Cu}^{II}\text{sar}]^{2+}\) and \([\text{Cu}^{II}(\text{NH}_3)_2\text{sar}]^{4+}\) is incomplete due to complicating adsorption processes together with the competitive dissociation of the complex. The reasons why the metal cages adsorb so readily on electrode surfaces is, at present, unclear. Unfortunately, it has precluded the observation of classical reversible electrochemical behaviour for the transition metal cages.

Finally, it should be noted that the electrochemical behaviour displayed by the cage complexes is determined by (1) the donor strength of the coordinating atoms, (2) the apical substituents and (3) the nature of the solvent. These points are addressed below.

In this study, the donor strength of the coordinating ligand cage is constant for all metal complexes and therefore is not considered an important parameter.

The overall change on the complex is found to have an effect on the redox potentials in the same manner as noted for the cobalt cages.\(^{23}\) It is noteworthy that protonation of the apical amine substituents was associated with a shift in reduction potential, generally by 300 mV more positive for each \([\text{M(NH}_2/3)_2\text{sar}]^{n+/n+2}\)
The range of substituents at the species of the cages included in this study, were limited to -H, -NH$_2$ and -NH$_3^+$ thus; it proved difficult to compare their influence upon the redox potential with that observed for the large number of cobalt cage complexes.$^{23}$

The nature of the solvent is an important factor in the position of the redox potential. The first row transition metal cages generally were effected by positive shifts of several hundred millivolts for measurements undertaken in non-aqueous media (compared with those undertaken in aqueous). A recent treatise addressed the importance of hydrogen-bonding by a solvent as a significant contribution to the thermodynamic redox potential$^{166}$ for a complex containing amine ligands. Such ideas, generally considered for electron transfer cross-reactions can be extended to include the free energy change associated with the solvent reorganization upon reduction or oxidation at the electrode/solution interface.

In many cases, these studies have been interpreted by comparison with parameters and redox behaviour for the cobalt cages, rather than the more usual "standard redox compounds" e.g. Cp$_2$Fe and Fe(CN)$_6^{3-}$. The redox potentials for many of the cobalt cages has been measured by a number of techniques and by a large number of different workers, reproducing the published values. In addition, the obvious comparisons possible with the other first row transition metal ion cages, makes it the preferred candidate for these studies.

An example of organic redox chemistry (observed) was discerned by comparison with known cobalt cage electrochemistry rather than independent determination. That is, the reduction of the ammonium substituent in non-aqueous media, i.e.

$$-\text{NH}_3^+ + e^- + \text{NH}_2^- + \frac{1}{2} \text{H}_2^+$$
Another organic redox process included the coulometric oxidation of \([\text{Fe(NH}_3\text{)}_2 \text{sar}^4+]\) to form imine species. However, this process is consistent with intramolecular redox chemistry to form imines via the Fe\(^{3+}\) intermediate rather than direct electrochemical oxidation of the ligand.

In conclusion, it was noted in Section 6.4.3 that the influence of the spin equilibrium on the electrochemical parameters for the Fe(II) cages was expected to be small. The findings of several workers, have indicated the insensitivity between the redox potential and the electronic configuration at the metal ion. In particular, one study examined twenty tris-dithiocarbamato iron(III) complexes where spin state equilibria exist in solution.\(^{163}\) The investigation included both theoretical and experimental analysis, concluding that the contribution of the spin equilibrium to the redox potentials was remarkably small. In addition, it was noted that the observed substituent effect was dominated by electron density at the metal centre rather than differences in electronic configuration of the metal ion.
CHAPTER SEVEN

PRELIMINARY KINETIC STUDIES
The theories of Marcus and Hush, describing outer-sphere electron transfer processes, predict a simple relationship between the rate constant for the so called "cross-reaction", $k_{12}$, the self-exchange rate constants for the individual reacting species, $k_{11}$ and $k_{22}$, and the equilibrium constant for the overall reaction, $K_{12}$. That is, for the redox reaction

$$A^{n+} + B^{m+} \xrightarrow{k_{12}} A^{(n-1)+} + B^{(m+1)+}$$

two component reactions are occurring

$$A^{n+} \xrightarrow{k_{11}} A^{(n-1)+}$$

and

$$B^{m+} \xrightarrow{k_{22}} B^{(m+1)+}$$

with their respective rate constants correlated by,

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}$$

$$f_{12} = \frac{(\log K_{12})^2}{4 \log(k_{11}k_{22}/Z^2)}$$

where $Z$ is the collision frequency (usually $Z = 10^{11} \text{ M}^{-1}\text{s}^{-1}$).

Experiments designed to test these theories have achieved limited success, generally with $(k_{12})_{\text{obs}}$ being smaller than $(k_{12})_{\text{calc}}$. However, for a series of cobalt cage complexes, their cross-reaction rate constants were found to agree remarkably well with values calculated using Equation 110, as evidenced in Table 7.1.
TABLE 7.1
Cross-reaction Rate Constants for some Cobalt Cages. 36

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Medium and Concentration, M</th>
<th>$k_{12}, \text{M}^{-1}\text{s}^{-1}$</th>
<th>$(k_{12})_{\text{calc}}, \text{M}^{-1}\text{s}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co sar]$^{2+}$ - [Co sep]$^{3+}$</td>
<td>NaCl, $[H^+] = 10^{-3}$</td>
<td>$20 \pm 1$</td>
<td>$32-46$</td>
</tr>
<tr>
<td>[Co sep]$^{2+}$ - [Co(NH$_3$)$_2$sar]$^{5+}$</td>
<td>NaClO$_4$, $[H^+] = 0.1$</td>
<td>$145 \pm 12$</td>
<td>$88-148$</td>
</tr>
<tr>
<td>[Co sar]$^{2+}$ - [Co(aza)(CH$_3$)sar]$^{3+}$</td>
<td>NaClO$_4$, $[H^+] = 10^{-3}$</td>
<td>$10 \pm 1$</td>
<td>$8-14$</td>
</tr>
<tr>
<td>[Co sar]$^{2+}$ - [Co(en)$_3$]$^{3+}$</td>
<td>NaCl, $[H^+] = 0.1$</td>
<td>$2.3 \pm 0.1$</td>
<td>$1$</td>
</tr>
<tr>
<td>[Co(NH$_3$)$_2$sar]$^{4+}$ - [Co(bpy)$_3$]$^{3+}$</td>
<td>NaClO$_4$, $[H^+] = 0.1$</td>
<td>$33 \pm 0.1$</td>
<td>$200$</td>
</tr>
<tr>
<td>Cr$_{\text{aq}}^{2+}$ - [Co sep]$^{3+}$</td>
<td>NaClO$_4$, $\mu = 0.5$, $[H^+] = 0.05-0.1$</td>
<td>$(8.7 \pm 0.1) \times 10^{-4}$</td>
<td>$&lt; 0.2$</td>
</tr>
<tr>
<td>Cr$_{\text{aq}}^{2+}$ - [Co(NH$_3$)$_2$sar]$^{5+}$</td>
<td>NaClO$_4$, $\mu = 0.5$, $[H^+] = 0.05-0.1$</td>
<td>$(8.1 \pm 0.2) \times 10^{-3}$</td>
<td>$&lt; 4$</td>
</tr>
<tr>
<td>Cr$_{\text{aq}}^{2+}$ - [Co(NH$_3$)(CH$_3$)sar]$^{4+}$</td>
<td>NaClO$_4$, $\mu = 0.5$, $[H^+] = 0.05-0.1$</td>
<td>$(4.9 \pm 0.3) \times 10^{-4}$</td>
<td>$&lt; 0.09$</td>
</tr>
<tr>
<td>Cr$_{\text{aq}}^{2+}$ - [Co(aza)(CH$_3$)sar]$^{3+}$</td>
<td>NaClO$_4$, $\mu = 0.5$, $[H^+] = 0.05-0.1$</td>
<td>$1.4 \times 10^{-4}$</td>
<td>$&lt; 0.03$</td>
</tr>
</tbody>
</table>
Good agreement was also found for cross-reactions involving cobalt cages and cobalt hexaamine complexes. However, only "order of magnitude" agreement was found for cobalt cages with the aquated ions of V$^{2+}$, Cr$^{2+}$ and Eu$^{2+}$ (included in Table 7.1).

The self-exchange rates observed for the cobalt cages are surprisingly rapid compared with those observed for the parent [Co(en)$_3$]$^{2+/3+}$ complex.\textsuperscript{17,18,36} This suggests that the self-exchange rates for other pairs of transition metal cage complexes, e.g. [Mn sar]$^{2+/3+}$, [Fe sar]$^{2+/3+}$ and [Ni sar]$^{2+/3+}$, might also be expected to be rapid. In particular, rate constants for the cage complexes of [Fe sar]$^{2+/3+}$ and [Ni sar]$^{2+/3+}$ could be much faster.
than that for \([\text{Co sar}]^{2+/3+}\) as the latter complex necessarily involves a high- to low-spin conversion upon electron transfer. In contrast to the cobalt case, the redox process for \([\text{Ni sar}]^{2+/3+}\) involves electron transfer between \(e_g\) orbital sub-sets, thus a large rate constant is expected.

The spin equilibrium observed for \([\text{Fe sar}]^{2+}\) in solution (cf. Chapters Four and Five) provides an unusual situation whereby fast electron transfer is predicted between the low-spin configurations, i.e. \(t_{2g}^6 \leftrightarrow t_{2g}^5\). However, a slow rate is expected for an electron transferred from a high-spin Fe(II) to a low-spin Fe(III) cage, as the process will be associated with large reorganizational contributions to \(\Delta G\); in particular changes in bond lengths and overall geometry. As discussed in Chapter Four, the interconversion rate for the \(^{1}A_{1g} \leftrightarrow ^5T_{2g}\) spin equilibrium observed for the Fe(II) cages, is expected to lie in the range \(10^7 < k < 10^{13}\) s\(^{-1}\). Therefore, the observable, hence rate determining electron transfer process, is expected to occur between the \(t_{2g}^4 e_g^2\) and \(t_{2g}^5\) configurations.

The self-exchange rate constant for \([\text{Mn sar}]^{2+/3+}\) is expected to be similar to that observed for the cobalt analogue. This prediction is based on the high-spin (for Mn(II)) and low-spin (for Mn(III)) ground states determined by magnetic measurements, detailed in Chapters Two and Three.

The seldom used electrochemical technique was chosen as a convenient method for examining the expected rapid electron exchanges in cage complexes, as the conventional isotope tracer and spectrophotometric techniques used for the cobalt cages were considered to be too slow. Also, the extensive paramagnetic broadening for the \(^1H\) NMR's was found for most of the complexes of
interest and precluded application of this technique.

The electrochemical determination of self-exchange rate constants derives from the theory of Marcus,\textsuperscript{39a} whereby the rate constant for a chemical (homogeneous) electron exchange, $k_{ex}$, is related to the electrochemical (heterogeneous) electron exchange rate constant, $k_\text{el}$ (measured at a standard potential, $E^\circ$) by,

$$
\frac{k_{ex}}{Z_{ex}}^{1/2} \approx \frac{k_\text{el}}{Z_{el}}
$$

...(111)

where work terms are negligible (or corrected) and $Z_{ex}$ and $Z_{el}$ are collision frequencies ($Z_{ex} = 10^{11} \text{ M}^{-1}\text{s}^{-1}$ and $Z_{el} = 10^4 \text{ cm}^{-1}\text{s}^{-1}$).\textsuperscript{39a}

The excellent agreement between the 'cross-reaction' rates observed for the cobalt cages with those calculated using the Marcus-Hush theories (Equation 110),\textsuperscript{36} suggested that the cage complexes would be ideal candidates for examining the relationship described by Equation 111.

Two cobalt cage complexes, [Co sar]\textsuperscript{3+} and [Co(aza)capten]\textsuperscript{3+} were selected for preliminary measurements to calibrate the method, as their self-exchange rates differ by several orders of magnitude. The self-exchange rate constant for [Co sar]\textsuperscript{2+/3+}, $k_{ex} = 2.1\pm0.2 \text{ M}^{-1}\text{s}^{-1}$ was measured by spectrophotometric methods\textsuperscript{167} whereas that for [Co(aza)capten]\textsuperscript{2+/3+}, $k_{ex} = 4.5\times10^3(\pm300) \text{ M}^{-1}\text{s}^{-1}$ was measured by $^1\text{H NMR}$ using a line broadening technique.\textsuperscript{93}

7.2 THEORETICAL CONSIDERATIONS

Nicholson\textsuperscript{167} has provided a theoretical foundation for the measurement of standard electron transfer rate constants, by using the electrochemical technique of cyclic voltammetry. The underlying principles stem from the observation that a reversible redox process (at a particular scan rate) may become quasi-reversible or even
Figure 7.1

Variation of $\Delta E \times n$ with $\psi$ (after ref. 167).
irreversible at increased scan rates, thus providing kinetic information. Correlation of the separation of peak-potential for the forward and reverse cycles, $\Delta E_p$, with scan rate is described by

$$\psi = \gamma^\alpha \frac{k_s}{\sqrt{\pi D_0} \sqrt{1/2} (nF/RT)^{1/2} v^{1/2}} \quad \ldots (112)$$

where $\psi$ represents a mathematical function and other parameters are defined in Chapter Six. Equation 111, has been evaluated numerically in terms of $\Delta E_p$ and $\psi$ and is represented graphically in Figure 7.1, assuming $\alpha = 0.5$. Thus, for a known scan rate, the experimental value for $\Delta E_p$ is related to the numerical function $\psi$ (in Figure 7.1), hence $k_s$ can be calculated using Equation 111. In these calculations, the simplification of $\gamma^\alpha = 1$ is used, i.e. $D_0 = D_r$, for all values of $\alpha$. In this manner the calculation of $k_s$ is possible over a range of scan rates, in going from a reversible (i.e. diffusion controlled) electron transfer, at slow scan rates, to a quasi-reversible (i.e. kinetically controlled) electron transfer, at faster scan rates.

7.3 EXPERIMENTAL

Measurements were undertaken using a standard three-electrode configuration and cell as described in Chapter Six. The concentration of cage complex employed was generally $2 \times 10^{-3}$ M; the supporting electrolyte concentration was 0.2 M NaClO$_4$ in aqueous solution.

$\dagger$ $E_p$ is approximately independent of over the range $0.3 < \alpha < 0.7$. 
The heterogeneous rate constants, \( k_s \), were calculated using Equation 112, for \([\text{Co sar}]^{3+}\) and \([\text{Co(aza)capten}]^{3+}\) are presented in Tables 7.2 and 7.3. The diffusion coefficients were obtained from the dc polarogram for the reduction of the appropriate cobalt(III) cage by applying the Ilkovic equation (Equation 75); \( D_0 = 4.5 \times 10^{-6} \text{ cm}^2\text{s}^{-1} \) for \([\text{Co sar}]^{3+}\) and \( D_0 = 1.6 \times 10^{-6} \text{ cm}^2\text{s}^{-1} \) for \([\text{Co(aza)capten}]^{3+}\).

It has been suggested by Nicholson,\textsuperscript{167} that the most accurate value for \( k_s \) is determined when \( \psi = 0.5 \).

The rate constants determined using Equation 112, are somewhat limited by the instrumental inability to select scan rates other than 2, 5, 10 and multiples of ten for these values. Therefore, \( k_s \) emerged as a range of values rather than a single value within the range of accessible scan rates. Tables 7.2 and 7.3 list the \( k_s \) values in the region of quasi-reversibility for the two couples where \( \psi = 0.5 \).

For \([\text{Co sar}]^{2+/3+}\), good agreement between the experimentally determined and calculated values of \( k_s \) is found at a HMDE and gold electrode. At the gold surface, this is a somewhat unexpected result as the \( k_s \) values for a number of cobalt cage complexes at a mercury electrode were reported to exceed those at a gold electrode by a factor of ten.\textsuperscript{23} In addition, for \([\text{Co sar}]^{2+/3+}\), the experimentally determined value \( k_s = 23 \times 10^{-3} \text{ cm s}^{-1} \) (from Table 7.2) can be compared with the published value,\textsuperscript{167} \( k_s = 1.5 \times 10^{-3} \text{ cm s}^{-1} \) where both measurements are obtained using a mercury electrode. This lack of agreement can be partly ascribed to the different diffusion coefficients used in each calculation (Bond et al.\textsuperscript{23} used \( D_0 = 1.0 \times 10^{-5} \text{ cm}^2\text{s}^{-1} \)). The slightly smaller values in \( D \) obtained in
these measurements, could be the result of adsorption processes enhancing the current response, $i_d$, hence affecting the calculated value of $D$.

### TABLE 7.2 \([Co\text{ sar}]^{2+/3+}\)

Heterogeneous rate constants calculated for \([Co\text{ sar}]^{2+/3+}\) in 0.2 M NaClO$_4$(aq).

<table>
<thead>
<tr>
<th>Working Electrode</th>
<th>Scan Rate, $Vs^{-1}$</th>
<th>$\Delta E_p$, mV</th>
<th>$\psi$</th>
<th>$k_s$, cm s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMDE</td>
<td>1.0</td>
<td>73</td>
<td>1.90</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>95</td>
<td>0.67</td>
<td>0.023</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>160</td>
<td>0.19</td>
<td>0.010</td>
</tr>
<tr>
<td>gold</td>
<td>5.0</td>
<td>77</td>
<td>1.48</td>
<td>0.078</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>95</td>
<td>0.67</td>
<td>0.050</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>109</td>
<td>0.45</td>
<td>0.048</td>
</tr>
<tr>
<td>glassy carbon #1</td>
<td>0.1</td>
<td>93</td>
<td>0.74</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>118</td>
<td>0.38</td>
<td>0.004</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>175</td>
<td>0.16</td>
<td>0.003</td>
</tr>
<tr>
<td>glassy carbon #2</td>
<td>50.0</td>
<td>80</td>
<td>1.24</td>
<td>0.208</td>
</tr>
<tr>
<td></td>
<td>100.0</td>
<td>108</td>
<td>0.46</td>
<td>0.109</td>
</tr>
<tr>
<td></td>
<td>200.0</td>
<td>204</td>
<td>0.11</td>
<td>0.038</td>
</tr>
</tbody>
</table>
TABLE 7.3 \([\text{Co(aza)capten}]^{2+/3+}\)

Heterogeneous rate constants calculated for
\([\text{Co(aza)capten}]^{2+/3+}\) in 0.2 M \(\text{NaClO}_4(\text{aq})\).

<table>
<thead>
<tr>
<th>Working Electrode</th>
<th>Scan Rate, Vs(^{-1})</th>
<th>(\Delta E), mV</th>
<th>(\psi)</th>
<th>(k_s), cm s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMDE</td>
<td>1.0</td>
<td>76</td>
<td>1.58</td>
<td>0.022</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>87</td>
<td>0.90</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>147</td>
<td>0.22</td>
<td>0.007</td>
</tr>
<tr>
<td>gold</td>
<td>2.0</td>
<td>89</td>
<td>0.84</td>
<td>0.017</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>123</td>
<td>0.33</td>
<td>0.011</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>169</td>
<td>0.17</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>200</td>
<td>0.12</td>
<td>0.008</td>
</tr>
<tr>
<td>glassy</td>
<td>0.5</td>
<td>87</td>
<td>0.90</td>
<td>0.009</td>
</tr>
<tr>
<td>carbon #1</td>
<td>1.0</td>
<td>112</td>
<td>0.42</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>166</td>
<td>0.18</td>
<td>0.004</td>
</tr>
<tr>
<td>glassy</td>
<td>50.0</td>
<td>61</td>
<td>11.0</td>
<td>1.106</td>
</tr>
<tr>
<td>carbon #2</td>
<td>100.0</td>
<td>92</td>
<td>0.74</td>
<td>0.105</td>
</tr>
<tr>
<td></td>
<td>200.0</td>
<td>111</td>
<td>0.43</td>
<td>0.086</td>
</tr>
</tbody>
</table>

A comparison of the data listed in Tables 7.2 and 7.3 reveals that only a small variation in \(k_s\) for \([\text{Co sar}]^{2+/3+}\) and \([\text{Co(aza)capten}]^{2+/3+}\) is observed at mercury and gold electrodes. However, by substituting the self-exchange rate constants into Equation 111, the calculated heterogeneous rate constants are very different; for \([\text{Co sar}]^{2+/3+}\), \(k_s\)\(_{\text{calc}}\) = 0.046 cm s\(^{-1}\) and for \([\text{Co(aza)capten}]^{2+/3+}\), \(k_s\)\(_{\text{calc}}\) = 2.121 cm s\(^{-1}\).

The disparate result for \([\text{Co(aza)capten}]^{2+/3+}\), indicates that
<table>
<thead>
<tr>
<th>Case</th>
<th>Mass</th>
<th>g</th>
<th>eV</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case 1</td>
<td>35.4</td>
<td>0.5</td>
<td>4.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Case 2</td>
<td>42.0</td>
<td>0.6</td>
<td>5.3</td>
<td>1.8</td>
</tr>
<tr>
<td>Case 3</td>
<td>38.5</td>
<td>1.0</td>
<td>6.9</td>
<td>2.6</td>
</tr>
<tr>
<td>Case 4</td>
<td>35.7</td>
<td>1.2</td>
<td>7.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Case 5</td>
<td>30.2</td>
<td>2.0</td>
<td>9.5</td>
<td>1.3</td>
</tr>
<tr>
<td>Case 6</td>
<td>35.0</td>
<td>6.0</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>Case 7</td>
<td>55.5</td>
<td>0.1</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>Case 8</td>
<td>55.5</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Case 9</td>
<td>55.5</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Case 10</td>
<td>55.5</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Case 11</td>
<td>55.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Note: The results are calculated based on the given cases and parameters.
the electrochemical equipment was setting an upper limit for the measurement of the rate constant, possibly due to a slow rise-time of the potentiostat, or slow response-time for the output signal recording device. Agreement between the calculated and experimentally obtained values of $k_s$ for $[\text{Co sar}]^{2+/3+}$ was within a factor of two indicating that the slower rate constant is more accessible using the electrochemical equipment.

Tables 7.2 and 7.3 also include measurements obtained using two glassy carbon electrodes of different diameters. Using the large diameter glassy carbon disc electrode the rate constant, $k_s$ is ten times smaller than those observed at mercury and gold electrodes. However, at the small diameter glassy carbon disc electrode an apparent increase in rate constant (approximately ten-fold), is observed for both complexes. Using the small diameter glassy carbon electrode the $k_s$ value for $[\text{Co sar}]^{2+/3+}$ still lies within a factor of two of the calculated value. Whereas, the $k_s$ value for $[\text{Co(aza)capten}]^{2+/3+}$ at the small diameter glassy carbon electrode is still an order of magnitude smaller than that calculated by Equation 111.

This apparent increase in rate constant with a small diameter electrode is indicative of incomplete iR compensation in the cell. That is, a small electrode will reduce considerably the net current flowing through the cell and therefore, the fraction of the total current necessary to "feedback" in order to compensate for iR drop in the cell will be small and more easily attainable. For a large diameter electrode, larger currents are required to "feedback" into the potentiostat in order to compensate for the iR drop in the cell. Accordingly, small errors due to incomplete iR compensation will reflect themselves as unexpectedly low $k_s$ values.142
Overall, the heterogeneous rate constants measured in this preliminary study for \([\text{Co sar}]^{2+/3+}\) appear to lie near the limit of our electrochemical equipment. Larger rate constants however, have been measured using commercial equipment which was extensively modified.\(^7\) Recent developments that include micro-electrodes, fast rise-time potentiostats, and fast \(i-V\) following equipment should permit the electrochemical measurement of \(k_s\) values for fast electron exchange systems in the near future.

The good correlation observed for the experimentally obtained \(k_s\) values with the values calculated by Equation 111, for \([\text{Co sar}]^{2+/3+}\) (at mercury and gold electrodes) confirms that this relation should be valuable for providing order-of-magnitude values for self-exchange rate constants providing the limitation of the equipment are well understood. An extension of this preliminary study to include transition metal cages other than cobalt should prove to be highly rewarding.

During the preparation of this thesis, the measurement of self-exchange rate constants for \([\text{Mn sar}]^{2+/3+}\), \([\text{Fe sar}]^{2+/3+}\) and \([\text{Ni sar}]^{2+/3+}\) was completed\(^{168}\) and the data are included in Table 7.4

A general rule applied to the interpretation of electron-transfer rates, is that, electron transfer between the \(t_{2g}\) orbital subsets of a redox couple is always very fast.\(^{169}\) This rule refers to the small geometric (e.g. bond length) changes between the oxidized and reduced forms, during electron transfer. Similarly, the electron transfer between two \(e_g\) orbital subsets is expected to be fast.

7.5 CONCLUSION

Overall, the heterogeneous rate constants measured in this preliminary study for \([\text{Co sar}]^{2+/3+}\) appear to lie near the limit of our electrochemical equipment. Larger rate constants however, have been measured using commercial equipment which was extensively modified. Recent developments that include micro-electrodes, fast rise-time potentiostats, and fast \(i-V\) following equipment should permit the electrochemical measurement of \(k_s\) values for fast electron exchange systems in the near future.

The good correlation observed for the experimentally obtained \(k_s\) values with the values calculated by Equation 111, for \([\text{Co sar}]^{2+/3+}\) (at mercury and gold electrodes) confirms that this relation should be valuable for providing order-of-magnitude values for self-exchange rate constants providing the limitation of the equipment are well understood. An extension of this preliminary study to include transition metal cages other than cobalt should prove to be highly rewarding.

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TABLE 7.4

Self-exchange rate constants for some first row transition metal cages.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$k_{11}^a$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Co sar}]^{2+/3+}$</td>
<td>2.1</td>
<td>167</td>
</tr>
<tr>
<td>$[\text{Mn sar}]^{2+/3+}$</td>
<td>10</td>
<td>169</td>
</tr>
<tr>
<td>$[\text{Fe sar}]^{2+/3+}$</td>
<td>$10^4$</td>
<td>169</td>
</tr>
<tr>
<td>$[\text{Ni sar}]^{2+/3+}$</td>
<td>$2.5 \times 10^3$</td>
<td>169</td>
</tr>
</tbody>
</table>

a Measured at 25°C.

The large rate constant observed for $[\text{Ni sar}]^{2+/3+}$ (Table 7.1), is consistent with the electron transfer being between ions with the configuration, $[\text{Ni sar}]^{2+}$, $t_{2g}^6 e_g^2$ and $[\text{Ni sar}]^{3+}$, $t_{2g}^6 e_g^1$. In addition, the large rate constant found for $[\text{Fe sar}]^{2+/3+}$ suggests that the measured process is likely to arise from the configurations $t_{2g}^6 e_t^5$, rather than $t_{2g}^6 e_g^2 e_t^4$ (cf. discussion in Section 7.1). It can be speculated that the fast interconversion rate between the high and low spin isomers of $[\text{Fe sar}]^{2+}$ aids the complex in attaining the transition-state (or activated complex); hence the overall process is characterized by the fast rate constant, $k([\text{Fe sar}]^{2+/3+}) = 10^4 \text{M}^{-1} \text{s}^{-1}$.

It was indeed pleasing to find the rate constant for $[\text{Mn sar}]^{2+/3+}$ is of a similar order of magnitude to that of $[\text{Co sar}]^{2+/3+}$ (cf. Table 7.4). The small value of $k = 10 \text{M}^{-1} \text{s}^{-1}$, provides additional and independent support for the conclusion that $[\text{Mn sar}]^{3+}$ possesses a low spin $t_{2g}^4$, $S = 1$ ground state as detailed.
in Chapter Two. In addition, the smaller rate constant observed for [Mn sar]$^{2+/3+}$ illustrates well the influence of larger geometric changes involved with electron transfer between the anti-bonding $e_g$, and the bonding $t_{2g}^*$ orbital subsets.

In conclusion, it is noted that the spherical shape of the caged ions together with the similar charges on pairs of ions, contribute significantly to the reduction of intermolecular reorganizational contributions required for a pair of ions to attain the activated complex. Therefore, the remaining "driving force" for electron transfer between pairs of cage complexes, primarily arise from intramolecular reorganization associated with different electron configurations.
8.1 INTRODUCTION

Almost a decade has passed since the preparation and characterization for the original cage complex, \([\text{Co sep}]^{3+}\) was first reported.\(^{17}\) Minor modifications of the original synthetic pathway have led to a plethora of encapsulated metal ions, with a variety of basic ligand units and substituents, as described in Chapter One.

In this work, the synthetic methods used to prepare the complexes \([\text{Co(NH}_3)_2\text{sar}]^{5+}\) and \([\text{Co sar}]^{3+}\) were those published,\(^{20}\) although modified preparative methods were often found to give better yields. \([\text{Co(NO}_2)_2\text{sar}]\text{Cl}_3\cdot\text{H}_2\text{O}\) and \([\text{Co(NH}_3)_2\text{sar}]\text{Cl}_5\cdot\text{H}_2\text{O}\) were prepared using the published syntheses\(^{20}\) and their \(^1\text{H}\) NMR spectra and analytical data were in agreement with literature values.\(^{20}\) The \([\text{Co(Cl)}_2\text{sar}]\text{Cl}_3\) and \([\text{Co sar}]\text{Cl}_3\cdot\text{H}_2\text{O}\) complexes were prepared by unpublished methods\(^{43a}\) as outlined below.

8.2 PREPARATION OF COBALT CAGES

8.2.1 The \([\text{Co(Cl)}_2\text{sar}]\text{Cl}_3\) Complex

\([\text{Co(NH}_3)_2\text{sar}]\text{Cl}_5\cdot\text{H}_2\text{O}\) (50.0 gm) was treated with concentrated nitric acid (150.0 ml) in a large vessel in a fumehood, and the mixture stirred for approximately one half hour or until the effervescence ceases. Addition of an equal volume of concentrated hydrochloric acid results in precipitation of the desired complex. The solid was collected by filtration and washed with ethanol and ether. Recrystallization from hot water and hydrochloric acid gave large needles. Yields were generally between 55-60%.

Analysis: Calculated for \(\text{C}_{14}\text{H}_{30}\text{N}_6\text{Cl}_5\text{Co}\cdot\text{H}_2\text{O}\): C, 31.33; H, 6.01; N, 15.66; Cl, 33.03; Co, 10.98.

Found: C, 31.3; H, 5.9; N, 16.3; Cl, 32.7; Co, 11.2.
8.2.2 The [Co(sar)]Cl₃·H₂O Complex

The best procedure to obtain the parent sar complex was by reductive dehalogenation of the [Co(Cl)₂sar]Cl₃ complex. Choice of the brand of zinc powder appeared to be crucial, BDH brand proving to be the most successful.

A three litre flask of distilled water (2700 ml) containing [Co(Cl)₂sar]Cl₃ (36.2 gm) was degassed while being heated on a steambath. The pH of the solution was adjusted with NaOH to 4.0-4.5. Activated zinc powder† (177.5 gm) was added in two additions to the reaction mixture over one half hour. The reaction was stirred vigorously using an overhead mechanical stirrer for three hours under slow nitrogen flow. The reaction mixture was allowed to cool, the excess zinc filtered off, and a few millilitres of glacial acetic acid added to dissolve residual Zn(OH)₂. Air was bubbled through the solution for 15-20 minutes, then the mixture was sorbed on a cation exchange column (Dowex 50W X2, H⁺ form), washed with water, 1 M HCl, and the mixture of reaction products eluted with 3 M HCl. The volume of the eluate was reduced and crystallization effected by addition of perchloric acid. This mixture of products was dissolved in distilled water and sorbed on another column (Sephadex SP C25, Na⁺ form), washed with distilled water and eluted with Na₂HPO₄ (0.2 M) to give six separate bands. Each fraction was collected, and the salt removed by sorbing the eluate on a short column (Dowex 50W X2, H⁺ form) and washing with water, 1 M HCl, and eluting the complex with 10 gms of zinc was treated with aqueous HCl solution (3 x 15 ml of 0.65 M) and washed with distilled water until acid free. The powder was dried overnight at approximately 0.01 mm Hg pressure and finely ground prior to use.

† Each 10 gms of zinc was treated with aqueous HCl solution (3 x 15 ml of 0.65 M) and washed with distilled water until acid free. The powder was dried overnight at approximately 0.01 mm Hg pressure and finely ground prior to use.
3 M HCl. All complexes were characterized and checked for purity using $^1$H NMR spectroscopy. Fraction 1 contained a small amount of unreacted $[\text{Co(Cl)}_2\text{sar}]^{3+}$, while fraction 2 contained the partially dehalogenated complex, $[\text{Co(Cl)}\text{sar}]^{3+}$. Fraction 3 was the most intense band and contained the fully dehalogenated product, $[\text{Co sar}]^{3+}$. Fractions 4 and 5 contained $[\text{Co(ClCH}_2\text{absar}]^{3+}$ and the hydroxylated product, $[\text{Co(Cl)(OH)}\text{sar}]^{3+}$, in small amounts. Fraction 6 contained a cage with a proton on one apical position and a zinc atom on the other apical position. Yields of $[\text{Co sar}]^{3+}$ were ca. 50%.

**Analysis:** Calculated for $C_{14}H_{32}N_6Cl_3Co.H_2O$: C, 35.95; H, 7.33; N, 17.97; Cl, 22.74; Co, 12.60.

Found: C, 35.8; H, 7.4; N, 17.4; Cl, 22.6; Co, 12.4.

### 8.3 PREPARATION OF CAGE LIGANDS

#### 8.3.1 The $\text{(NH}_2)_2\text{sar}$ Ligand

**A. HBr Method**

The HBr solution (48%, 300 ml) was deoxygenated with a flow of nitrogen for approximately 1 hour. $[\text{Co(NH}_3)_2\text{sar}]Cl_4$ (18.0 gm) was added to the solution which was further degassed for one half hour while the solution was heated to reflux (126°C). Reaction was allowed to continue for three hours prior to brief cooling in an ice-water bath to approximately 80°C and then carefully poured into

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†† A better yield was obtained when the HBr solution was first treated with $H_2S$ to remove any free bromine.
5 litres of deoxygenated acetone. The white solid was collected by filtration and washed with diethylether. The solid was dissolved in water, sorbed on a cation exchange column (Dowex 50W X2, H⁺ form), washed with water and the free ligand eluted with 0.2 M NaOH. Acidification of the column and elution with 3 M HCl recovered unreacted starting material. The basic liquor containing free ligand was neutralized with 1 M HCl, sorbed on another cation exchange column (Dowex 50W X2, H⁺ form), washed with distilled water, 1 M HCl, and the ligand eluted with 6 M HCl. The eluate volume was reduced under vacuum to afford the deliquescent hydrochloride salt. Addition of a few millilitres of water and a few drops of HBr solution gave the \((\text{NH}_3)_2\text{sar.5HBr}\) product upon addition of a ten-fold excess of acetone. The solid was collected by filtration, washed with diethylether and dried under vacuum. Yield \(\approx 75\%\).

Alternatively, \([\text{Co(\text{NH}_3)_2\text{sar}]Cl_5}\) (15.0 gm) was used as the starting compound being dissolved in water (30 ml) and deoxygenated for 10 minutes prior to reduction using zinc dust (1.6 gm). Addition of HBr solution (60%, 270 ml) resulted in some precipitation of the Co(II) complex. Deoxygenation for a further 30 minutes under a nitrogen stream was continued after which the solution was heated to reflux for 2 1/2 hours. The work-up procedure was then identical to that described above.

\((\text{NH}_3)_2\text{sar.5HBr}\) was converted to the free base by passage down a short anion exchange column (Dowex 1x4, HO⁻ form) followed by elution with distilled water. The eluate was collected and evaporated to

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† Alternately, the cooled reaction mixture was poured into 5 litres of distilled water containing cation exchange resin (Dowex 50W X2, H⁺ form). The solution was stirred overnight, then poured on a column as stated in the above procedure.
dryness to yield the white \((\text{NH}_3)_2\text{sar}\).

Alternatively, the acid salt was neutralized with the appropriate amount of base, dried under a high vacuum, and then extracted with acetonitrile several times. The extract was reduced in volume to afford white crystals.

Analysis: Calculated for \(\text{C}_{14}\text{H}_{34}\text{N}_8\cdot\text{H}_2\text{O}\): C, 50.57; H, 10.91; N, 33.70.

Found: C, 51.1; H, 10.7; N, 33.4.

\[\text{B. Cyanide Method 1}\]

\([\text{Co(NH}_3)_2\text{sar}]\text{Cl}_5\cdot\text{H}_2\text{O}\) (22.80 gm) was neutralized with \(\text{NaOH}\) (3.20 gm) in distilled water (100 ml) degassed for at least one half hour. Solid \(\text{CoCl}_2\cdot\text{H}_2\text{O}\) (9.52 gm) was added to the mixture. \(\text{KCN}\) (48.80 gm) dissolved in distilled water (150 ml), degassed and added dropwise to the cobalt solution at room temperature. Within a few minutes the \([\text{Co(CN)}_5]^{3-}\) had reduced the cage to give a green suspension. The solution was heated to 55\(^\circ\)C for 6-10 hours. The resulting pale solution was cooled to room temperature, evaporated to dryness, further dried by the addition of ethanol (99%, ≈ 200 ml) followed by evaporation to dryness. This procedure was repeated several times and finally the solid was dried under high vacuum for several hours prior to extraction with chlorform (5 x 100 ml). The extracts were combined and their volume reduced to approximately one half before chilling to afford crystals. Yield = 70%.

† K.S. Hagen, A. Ludi, unpublished results.
8.3.2 The sar Ligand

A. HBr Method

The procedure described in 8.3.1.A was followed. Yield = 30%.

B. Cyanide Method 1

The procedure described in 8.3.1.B was followed. However, extraction of the free base was carried out using diethylether. Yield = 40%.

C. Cyanide Method 2

[Co sar]Cl₃.H₂O (3.0 gm) was reduced with zinc powder (0.8 gm) in distilled water under a nitrogen atmosphere. Zn(CN)₂ (0.8 gm) and KCN (13.1 gm) were added to the solution which was placed under a small vacuum then refluxed using a cold finger apparatus at 80°C for approximately 3 hours. A white precipitate of [Zn sar]²⁺ formed on cooling the pale yellow reaction mixture. The solid was filtered, dissolved in water (= 50 ml), and an equal volume of concentrated HCl added. The solution was refluxed for one hour, then evaporated to dryness, dissolved in distilled water and sorbed on a cation exchange column (Dowex 50W X2, H⁺ form). The column was washed with distilled water, 1 M HCl and the complex eluted with 6 M HCl. The acid solution was evaporated to dryness, made basic with KOH solution, evaporated to dryness and dried for several hours under high vacuum. The solid was extracted with diethylether, and the volume reduced to afford white crystals. Yield = 60%.

Analysis: Calculated for C₁₄H₃₂N₆.1/3H₂O: C, 57.89; H, 11.31; N, 28.94.

Found: C, 58.7; H, 11.7; N, 28.7.
8.3.3 The (CH₃)sar Ligand

A. Cyanide Method 3†

[Co(CH₃)sar](O₂CCH₃)₃ (10.51 gm), dissolved in 50 ml of distilled water was thoroughly degassed with nitrogen. Zinc powder (1.4 gm) was added and the solution slowly reduced. The resulting cobalt(II) solution was added slowly (over 2 hours) to a refluxing solution of NaCN (34.70 gm) in distilled water (100 ml) while maintaining the nitrogen gas flow. The solution was stirred for 3 hours at 120°C. During this time white crystals form and the solution colour becomes paler. The reaction mixture was cooled and the resulting white solid was collected by filtration and dissolved in a small volume of water. In a fumehood, concentrated HCl (100-200 ml) was added and the solution heated to 120°C for at least 1 hour. The cooled solution was evaporated to dryness, triturated with water to give a highly insoluble white solid, which dissolved slowly in large volumes of boiling water. The solution was sorbed on a cation exchange column (Dowex 50W X2, H⁺ form), washed with water, 1 M HCl, and the complex eluted with 3 M HCl. The eluate was evaporated to dryness and then dried under vacuum for at least 3 hours to give an oil. Extraction with acetonitrile also gave an oily product. No further purification was attempted as complexation with ferrous ions yielded the desired product.

† A.J. Hendry, modified procedure.
8.4 PREPARATION OF TRANSITION METAL CAGES

8.4.1 Reaction of Metal Salt and Ligand

Stoichiometric amounts of the appropriate metal salt and the ligand were dissolved in distilled water, mixed and warmed gently to complete the reaction. A few drops of a concentrated solution either of NaCF\textsubscript{3}SO\textsubscript{3} or NaClO\textsubscript{4}, followed by cooling the solution in an ice bath gave crystals of the corresponding metal cage complex. In this manner the following metal complexes were isolated.

(i) \([\text{Zn sar}] (\text{CF}_3\text{SO}_3)\text{2}\)
Analysis: Calculated for C\textsubscript{16}H\textsubscript{32}N\textsubscript{6}F\textsubscript{6}O\textsubscript{6}S\textsubscript{2}Zn: C, 29.66; H, 4.98; N, 12.97; F, 17.59; S, 9.90; Zn, 10.09. Found: C, 29.8; H, 5.1; N, 12.9; F, 17.2; S, 9.9; Zn, 10.3.

(ii) \([\text{Zn(NH}_3\text{)}_2\text{sar}] (\text{CF}_3\text{SO}_3)\text{4}\)
Analysis: Calculated for C\textsubscript{18}H\textsubscript{36}N\textsubscript{8}F\textsubscript{12}O\textsubscript{12}S\textsubscript{4}Zn: C, 22.10; H, 3.71; N, 11.46; F, 23.31; Zn, 6.68. Found: C, 22.1; H, 3.6; N, 11.4; F, 23.5; Zn, 6.7.

(iii) \([\text{Cu sar}] (\text{ClO}_4)\text{2}\)
Analysis: Calculated for C\textsubscript{14}H\textsubscript{32}N\textsubscript{6}Cl\textsubscript{2}CuO\textsubscript{8}: C, 30.75; H, 5.90; N, 15.37; Cl, 12.97; Cu, 11.62. Found: C, 31.0; H, 6.2; N, 15.5; Cl, 13.2; Cu, 11.6.

(iv) \([\text{Cu(NH}_3\text{)}_2\text{sar}] (\text{ClO}_4)\text{4}.3\text{H}_2\text{O}\)
Analysis: Calculated for C\textsubscript{14}H\textsubscript{48}N\textsubscript{8}Cl\textsubscript{4}CuO\textsubscript{22}: C, 20.21; H, 5.09; N, 13.47; Cl, 17.05; Cu, 7.64. Found: C, 20.5; H, 4.8; N, 13.5; Cl, 17.4; Cu, 7.8.
(v) \([\text{Ni sar}]\)(CF₃SO₃)₂
Analysis: Calculated for C₁₆H₃₂N₆F₆NiS₂O₆: C, 29.97; H, 5.03; N, 13.11; Ni, 9.15; S, 10.00.
Found: C, 30.2; H, 5.2; N, 13.2; Ni, 9.2; S, 10.2.

(vi) \([\text{Ni(NH₃)}₂\text{sar}]\)(ClO₄)₄·2H₂O
Analysis: Calculated for C₁₄H₃₆N₈Cl₄NiO₁₆·2H₂O: C, 20.79; H, 4.98; N, 13.85; Cl, 17.3; Ni, 7.26.
Found: C, 21.1; H, 5.0; N, 13.8; Cl, 16.7; Ni, 7.3.

The anhydrous form can also be isolated by slow crystallization.
Found: C, 26.4; H, 5.9; N, 17.2; Cl, 21.5; Ni, 8.7.

(vii) \([\text{Mn(NH₃)}₂\text{sar}]\)(ClO₄)₄·2H₂O
Analysis: Calculated for C₁₄H₃₆N₈Cl₄MnO₁₆: C, 20.87; H, 5.00; N, 13.97; Cl, 17.60; Mn, 6.82.
Found: C, 20.9; H, 4.9; N, 13.8; Cl, 17.0; Mn, 6.5.

8.4.2 Preparation by Oxidation Methods

(i) \([\text{Ni sar}]\)(CF₃SO₃)₃

\([\text{Ni sar}]\)(CF₃SO₃)₂ was dissolved in 0.1 M NaCF₃SO₃ (aq) and placed in a coulometry cell containing a platinum gauze basket as the anode (working electrode), a platinum wire as the cathode (auxiliary electrode) and the calomel (Hg/HgCl₂, sat'd KCl) reference electrode. The solution was electrolysed at +0.75 V until the digital integrator reached a steady value. The solution was quickly sorbed on a cation exchange column (Dowex 50W X2, H⁺ form), washed with water, and eluted with 1 M CF₃SO₃H to give three bands of which
the middle one was the desired product. The eluate was evaporated to
dryness and then recrystallized from aqueous triflate media to yield
green needles.
Analysis: Calculated for C_{17}H_{32}N_{6}F_{9}NiO_{9}S_{3}: C, 25.82; H, 4.08;
N, 10.63.
Found: C, 26.0; H, 4.2; N, 10.6.

(ii) [Fe sar]Cl_{3}·H_{2}O ^+ 

FeCl_{2} (anhydrous) was dissolved in a minimum volume of dry
ethanol under a nitrogen stream. Some warming was required in order
to dissolve the solid in some instances. The solution was then
poured into an equivalent amount of free sar in dry ethanol also
under nitrogen. The resulting solution was acidified with a few
drops of concentrated HCl and exposed to air for a few hours
whereupon an orange precipitate formed slowly (slow oxidation gives
better yields of the complex. Fast oxidation or slow oxidation for
extended periods of time resulted in some decomposition). The
complex was recrystallized by dissolution in a minimum volume of 1 M
HCl and addition of acetone.
Analysis: Calculated for C_{14}H_{32}N_{6}FeCl_{3}·H_{2}O: C, 36.19; H, 7.37;
N, 18.09.
Found: C, 36.1; H, 7.3; N, 17.4.

(iii) [Mn sar](ClO_{4})_{3} ^+ 

[Mn sar](ClO_{4})_{2} was dissolved in distilled water and FeCl_{3}
anhydrous) added till the solution remained red. This solution was

† I.I. Creaser, unpublished results.
then diluted, sorbed on a cation exchange column (Dowex 50W X2, H\(^+\) form), washed with water, 1 M HCl, and the desired complex eluted with 3 M HCl. The eluate was evaporated to dryness, dissolved in distilled anhydrous CF\(_3\)SO\(_3\)H (≈ 0.1 gm/ml) and warmed to ≈ 50°C while on a water vacuum pump to remove HCl gas. Addition of diethyl ether (10 fold excess) to the chilled solution resulted in precipitation of the desired complex.

Analysis: Calculated for C\(_{17}\)H\(_{32}\)N\(_6\)F\(_9\)MnO\(_9\)S\(_3\).2H\(_2\)O: C, 24.82; H, 4.41; N, 10.22
Found: C, 24.3; H, 4.0; N, 9.3.

(iv) \([V(NH_3)_2sar-2H](CF_3SO_3)_4\)

(NH\(_3\))\(_2\)sar.5HBr and V(acac\(_3\)) were each dissolved in ethanol/water (1:1 mixture) in a molar ratio of 1:1. Each solution was flushed with nitrogen prior to mixing. NaOH solution was added until the solution pH was ca. 8. The solution was stirred under a blanket of nitrogen and warmed to 50°C for three days. The dark solution which resulted was diluted, sorbed on a cation exchange column (Dowex 50W X2, H\(^+\) form), and washed with water. Elution with 2 M HCl yielded a small amount (2%) of a blue band, followed by a dark red-brown band. The first band was discarded and the second eluate with 4 M HCl evaporated to dryness, redissolved in water/methanol, and chilled for several days yielded red crystals. These were converted to the triflate salt by the procedure outlined for [Mn\(^{III}\)sar](CF\(_3\)SO\(_3\))\(_3\).

Analysis: Calculated for C\(_{18}\)H\(_{34}\)N\(_6\)F\(_{12}\)O\(_{12}\)S\(_4\)V: C, 22.48; H, 3.56; N, 11.65; S, 13.34.
Found: C, 22.0; H, 3.5; N, 10.8; S, 13.3.

† Communication of general method in reference 64.
(v) \([\text{Vsar-2H}(\text{PF}_6)_2]\)

This complex was prepared by an identical synthetic procedure to that described for the \([\text{V(NH}_3)_2\text{sar-2H}]^{4+}\) complex. Crystallization was achieved by addition of an aqueous solution of NaPF\(_6\).

Analysis: Calculated for \(\text{C}_{14}\text{H}_{30}\text{N}_6\text{F}_{12}\text{P}_2\text{V}.5\text{H}_2\text{O}\): C, 23.57; H, 4.24; N, 11.78; P, 8.68.

Found: C, 23.1; H, 4.3; N, 11.1; P, 9.5.

8.4.3 Preparation by Reduction Methods

(i) \([\text{V(NH}_3)_2\text{sar}]\)(\text{S}_2\text{O}_6)_{5/2}.13/2\text{NaS}_2\text{O}_6

\([\text{V(NH}_3)_2\text{sar-2H}]\)(\text{S}_2\text{O}_6)_{2}.2\text{H}_2\text{O}\) was dissolved in 0.1 M NaCF\(_3\)SO\(_3\)(aq) and placed in a coulometry cell containing a platinum gauze basket as the cathode (working electrode), a platinum wire as the anode (auxiliary electrode) and the calomel (Hg/Hg\(_2\)Cl\(_2\), sat'd KCl) reference electrode. The solution was electrolyzed at -0.54 V until the digital integrator reached a steady value. Addition of a saturated solution of LiS\(_2\)O\(_6\) effected crystallization.

Analysis: Calculated for \(\text{C}_{14}\text{H}_{36}\text{N}_8\text{O}_{15}\text{S}_5\text{V}.13/2\text{Na}_2\text{S}_2\text{O}_6\): C, 7.98; H, 1.72; N, 5.32.

Found: C, 8.0; H, 1.8; N, 5.2.

(ii) \([\text{Cr sar}](\text{CF}_3\text{SO}_3)_3\) and \([\text{Cr(NH}_3)_2\text{sar}]\text{Cl}_5.\text{H}_2\text{O}\)

These complexes were prepared by the published method. Analytical data were in accord with the published values.
8.4.4 Preparation of Complexes under Argon

(i) \([\text{Mn sar}](\text{CF}_3\text{SO}_3)_2\]

\[
\text{Mn(O}_2\text{CCH}_3)_2\cdot 4\text{H}_2\text{O} \text{ and sar were added in a 1:1 molar ratio to}
\]

degassed distilled water. The solution was stirred for a few minutes, then a few drops of a saturated solution of aqueous NaC\(_2\text{F}_3\text{SO}_3\)

were added. Colourless crystals grew upon cooling the solution.

Analysis: Calculated for \(\text{C}_{16}\text{H}_{32}\text{N}_6\text{F}_6\text{MnO}_6\text{S}_2\):  C, 30.14; H, 5.06;

N, 13.18; F, 17.88; Mn, 8.62; S, 10.06.

Found:  C, 30.5; H, 5.2; N, 13.1; Mn, 8.4; S, 10.1.

(ii) \([\text{Fe(NH}_3)_2\text{sar}](\text{CF}_3\text{SO}_3)_4\]

\[
\text{FeCl}_2\cdot 4\text{H}_2\text{O} \text{ (0.5 gm) was treated with 2,2-methoxypropane (0.5 ml) and then diluted with dry degassed ethanol (99%, 25.0 ml) while under a flow of nitrogen at constant temperature (40°C). This solution was poured into another solution containing (NH}_3)_2\text{sar (0.79 gm) dissolved in dry, degassed ethanol (99%, 25.0 ml). The combined solutions were kept at constant temperature for approximately one hour prior to being cooled in an ice bath. A purple solid was collected by filtration, washed with ethanol, diethylether and the solid was redissolved in a few millilitres of 3 M HCl. Acetone was added until incipient precipitation of a colourless solid occurred. Cooling in an ice bath gave the desired complex in a 50% yield. The chloride salt was converted to the triflate by the procedure outlined earlier in 8.4.}
\]

Analysis: Calculated for \(\text{C}_{18}\text{H}_{36}\text{N}_8\text{F}_{12}\text{FeO}_{12}\text{S}_4\):  C, 22.32; H, 3.75;

N, 11.57; Fe, 5.77; S, 13.24.

Found:  C, 22.4; H, 3.8; N, 11.5; Fe, 5.9; S, 13.0.
(iii) \([\text{Fe sar}]\text{(CF}_3\text{SO}_3\text{)}_2\)
Sar (1.0 gm) was dissolved in distilled water (10 ml) under an argon atmosphere. Solid \(\text{Fe(O}_2\text{CCH}_3\text{)}_2\) (0.78 gm) was added giving a green solution. The solution was made acidic by addition of a few drops of anhydrous \(\text{CF}_3\text{SO}_3\text{H}\) which afforded colourless crystals. Recrystallization was achieved using an aqueous solution of \(\text{NaCF}_3\text{SO}_3\) and cooling the solution slowly. Yield = 50%.
Analysis: Calculated for \(\text{C}_16\text{H}_32\text{N}_6\text{F}_6\text{FeO}_6\text{S}_2\): C, 30.10; H, 5.05; N, 13.16; S, 10.04.
Found: C, 30.2; H, 5.0; N, 13.0; S, 8.8.

(iv) \([\text{Fe(CH}_3\text{)sar}]\text{(CF}_3\text{SO}_3\text{)}_2\)
(CH\(_3\)sar (0.13 gm) was dissolved in distilled water (3.0 ml) under an argon atmosphere to which \(\text{Fe(O}_2\text{CCH}_3\text{)}_2\) (0.10 gm) dissolved in distilled water (2.0 ml) was slowly added. The initial green solution turned blue within a few minutes and addition of a few millilitres of a \(\text{NaCF}_3\text{SO}_3\) solution resulted in a pale blue solid. The solid was collected by filtration and dried under an argon atmosphere for several hours. The solid was recrystallized by dissolution in acetonitrile and crystallization completed by the addition of diethylether. Yield = 10%. No analytical data has been obtained, however, the \(^1\text{H NMR}\) is consistent with the formulation and indicated no diamagnetic or paramagnetic impurities (cf. Chapter Five).


25. R.J. Geue and M.B. McDonald, unpublished results.


27. A.J. Hendry, unpublished results.

29. P.J. Lawson, unpublished results.
30. J.D. Lydon, unpublished results.
31. E.A. Miles, unpublished results.
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43. a) I.I. Creaser and A.M. Sargeson, unpublished results.
b) I.I. Creaser and N.F. Curtis, unpublished results.


49. a) A.H. White and L.M. Engelhardt, unpublished results.


58. P. Comba, unpublished results.


112. P. Comba and M. Maeder, unpublished results.


161. G.A. Lawrance, L.L. Martin and A.M. Sargeson, to be submitted for publication.


168. P. Bernhard and E.A. Miles, unpublished results.

1. "Paramagnetic Macrobicyclic Metal Amine Cages : Magnetic and ESR Properties",

2. "An Electrochemical Study of First Row Transition Metals Isolated in Hexaamine Cages",

3. "Magnetic Properties of Metal(III) Hexaamine Cages",

5. "Synthesis and Characterization of a Stable Hexaamine Vanadium(IV) Cage Complex",
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6. "Macrobicyclic Chromium(III) Hexaamine Complexes",
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7. "Spin Equilibrium in Ferrous Cage Complexes",
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