TRANSITION METAL COMPLEXES OF OXYGEN AND SULPHUR BASED LIGANDS

A thesis presented as partial requirement for the degree of
Doctor of Philosophy
at the
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by
Anthony Frederick Masters, B.Sc.(Hons)
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To my father

and in memory of my mother.
The material presented in this thesis is, to the author's knowledge, original work, except where due reference is made in the text.
ACKNOWLEDGEMENTS

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SUMMARY

Several new transition-metal chelates of dithio-β-diketonato ligands have been prepared and are described herein. Electrochemical, magnetochemical, infra-red, nmr, esr, electronic and mass spectral methods have been used in their characterisation. Novel compounds related to the dithioacetylacetonate anion are also described.

The mass spectrometric behaviour of a dithio-β-diketonato compound has been investigated in detail for the first time. Comparisons with the mass spectra of isostructural compounds with sulphur and oxygen donor atoms have enabled the effects on the mass spectrometric behaviour of donor atom variation in such compounds to be studied in detail. As an adjunct to these and other studies in the thesis, some substituted 1,2-dithiolium iodide compounds have been studied by mass spectrometric methods. On the basis of mass spectrometric data, evidence of the existence of a number of new compounds is presented.

Electrochemical studies have been concerned with the contributions of various structural features to the electrochemistry of transition metal chelates. Comparative studies of the effects of sulphur and oxygen as donor atoms in such compounds have been undertaken using the compounds M(acac)₃ and M(SacSac)₃ (M=Cr, Mn, Fe, Co). These studies have been extended to bis chelates, utilising the divalent nickel complexes of dipivaloylmethane and its monothio- and dithio-derivatives. Variation of the donor atom is found to influence the heterogeneous electron transfer process both kinetically and thermodynamically. The non-reversible electrochemical behaviour of a number of transition metal complexes of sulphur-based ligands has been investigated and found to be due to coupling of chemical reactions to the electrode process. Finally, a number of previously unknown redox processes of several dithio-chelate compounds are reported. The stability of a number of novel new co-ordination compounds has been demonstrated by electrochemical techniques and evidence for new classes of compounds of these sulphur-based ligands presented. Aspects of metal- as opposed to ligand-based voltammetric processes are discussed.
ABBREVIATIONS

The abbreviations used in this thesis are those used commonly in the literature. Thus, dtc = dithiocarbamate, diphos = o-phenylene-bis(dimethylphosphine), mnt = maleonitriledithiolate, xan = xanthate, for example. The usual abbreviations of alkyl and aryl functional groups are employed (e.g., Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl, Ph = phenyl, c-Hx = cyclohexyl, pyrr = pyrrolidyl). The ligands most commonly studied are those formally derived from acetylacetone (acacH) and are described by the nomenclature of references 1, 2 and 3. Some examples are given in Appendix I.

The term "charge transfer" is commonly used (and preferred by some authors) to describe the heterogeneous electron transfer in voltammetric experiments. However, its use has been restricted to the discussion of Chapter 5 and the term "electron transfer" used elsewhere to avoid any possible ambiguity with electronic spectroscopic nomenclature.

The abbreviation A ⇌ B to describe a reversible voltammetric one-electron transfer between A and B has often been used in the text (after the practice of Vlček199) rather than the more cumbersome A + ne ⇌ B.
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CHAPTER 1

INTRODUCTION
The versatility of acetylacetone as a chelating ligand is well known, and has been the subject of several reviews.\textsuperscript{4-8} This ligand possesses two very interesting capabilities which are fundamental to the study of comparative co-ordination chemistry. Thus, an extensive range of metals and metalloids can be complexed by the acetylacetonato ligand, a variety of sterochemistries being recognised. In addition to variation of the co-ordinated metal, there exists the potential for varying the donor atoms without substantially affecting the structure of the rest of the ligand system. Both of these possibilities were recognised at the turn of the century, the first being realised rapidly in the ensuing years. However, attempts to isolate dithioacetylacetone led only to the non-co-ordinating dimer I,\textsuperscript{1,9-11} a manifestation of the susceptibility of thioketo groups to polymerisation.\textsuperscript{12,13} Isolated examples of dithio-8-diketones were reported,\textsuperscript{14-17} the tendency towards polymerisation apparently being suppressed by the electron-releasing properties of the ligand substituents; however, not until the work of Martin and Stewart\textsuperscript{1} was dithioacetylacetone "isolated" in a stable form. These authors reasoned that

\[ \text{CH}_3 \quad \text{S} \quad \text{C} \quad \text{CH}_3 \\
\text{CH}_2 \quad \text{S} \quad \text{S} \quad \text{C} \quad \text{CH}_2 \\
\text{CH}_3 \quad \text{S} \quad \text{S} \quad \text{C} \quad \text{CH}_3 \\
\text{CH}_3 \quad \text{S} \quad \text{C} \quad \text{CH}_3 \]

"... Isolation of the dimer (I) establishes that both oxygen atoms of the parent diketone are, in fact, substituted by sulphur atoms in the reaction medium. Accordingly, it
seemed possible that, if the reaction were carried out in the presence of a suitable metal ion, dimer formation might be sufficiently inhibited for dithioacetylacetone to be isolated in the form of its metal complexes."

Monothio-β-diketonato complexes had been reported a few years beforehand, and so the syntheses of the $M(SacSac)_n$ complexes completed a series in which the effects of successive replacement of oxygen donor atoms by sulphur atoms could be studied.

The consequences of complete replacement of oxygen by sulphur begin to be manifest in the monothio-β-diketonato series. For example, although solid Ni(acac)$_2$ and Co(acac)$_2$ are respectively trimeric and tetrameric with octahedrally co-ordinated metal ions, Ni(Sacac)$_2$ and Co(Sacac)$_2$ are monomeric. Thus, the introduction of sulphur into the ligand stabilises the co-ordinately unsaturated monomeric forms of these complexes. However, these compounds still exhibit a tendency to expand their co-ordination spheres, as is evidenced by the varying degrees of base adduct formation. The extent to which sulphur stabilises these co-ordinately unsaturated monomers varies with metal and ligand, the manganous and ferrous derivatives of monothiodibenzoylmethane having been prepared only in the form of the dipyridinates, whilst Fe(Bu$^t$SacBu$^t$ac)$_2$ can be isolated with a simple FeO$_2$S$_2$ co-ordination sphere. It is interesting to note in passing that, in contrast to Ni(SacSac)$_2$, the nickel(II) chelate of the ligand II forms a dipyridinate, indicating the importance of contributions of other aspects of ligand structure to the stabilisation of co-ordinately unsaturated species.

A further consequence of the incorporation of sulphur into these co-ordinately unsaturated monothio-β-diketonato chelates is a
Figure 1-1. Donor atom dependence of pmr resonance positions. Values for dipivaloylmethane derivatives from this work, values of acetyl-acetone derivatives from reference 44. CDCl₃ solutions; values in ppm with tetramethylsilane as reference.
proclivity to stabilise the planar, rather than the tetrahedral stereochemistry. Consequently, although monomeric Co(acac)$_2$ and Co(Bu$^+$acBu$^+$ac)$_2$ are tetrahedral; Co(Sacac)$_2$ is tetrahedral, and Co(Bu$^+$SacBu$^+$ac)$_2$ undergoes a square planar/tetrahedral equilibrium in solution. Similarly, the nickel(II) chelates of the ligands III exhibit a square planar/tetrahedral equilibrium with the square planar form favoured when $X = S$. In some cases, the introduction of sulphur is insufficient to stabilise the planar isomer. Thus, Fe(Bu$^+$SacBu$^+$ac)$_2$ is tetrahedral, as is Zn(OEtSacSac)$_2$. The cis-configuration of cis-Fe(SacSac)$_2$(CO)$_2$ is probably better rationalised in terms of the $\pi$-backbonding properties of the carbonyl ligands, rather than by the assumption of tetrahedral Fe(SacSac)$_2$.

Introduction of sulphur into the metal co-ordination sphere also tends to favour spin pairing. It is misleading to cite the Ni(acac)$_2$/Ni(Sacac)$_2$ pair as an example here, since the diamagnetism of the latter is a consequence of the structural change. This effect is best illustrated by the octahedral ferric complexes. Whilst Fe(acac)$_3$ is high spin and Fe(SacSac)$_3$ is low spin, the ferric monothio-β-diketonates exhibit spin isomerism to an extent dependent upon the chelate ring substituents. Interestingly, although the rapidity of the spin interconversion has prevented the observation of both spin isomers at the same temperature in the Mössbauer spectra of other iron(III) "spin cross-over" systems, peaks attributed to both spin isomers have been reported in the Mössbauer and esr spectra of some iron(III) monothio-β-diketonates. A cis-meridional Fe(RCSCHCOR')$_3$ configuration was assumed in the interpretation of the esr results. However independent dipole moment and x-ray crystallographic
Figure 1-2. Reactions of Fe(SacSac)$_2$. From reference 33.
mpda = m-phenylenediamine.
studies have shown that the complexes \((R' = \text{Ph}, R = \text{Me or Ph}; \ R' = \text{CF}_3, R = \text{Me}, 2\text{-thienyl, Ph, p-MeC}_6\text{H}_4 \text{ or p-BrC}_6\text{H}_4)\) adopt a \textit{facial} rather than a \textit{meridional} configuration. A low-temperature \textit{facial-meridional} equilibrium which might be expected to occur more slowly than a spin equilibrium is a possible alternative explanation of the Mössbauer results.

A donor atom dependence is also observable in the nmr spectrum. Substitution of oxygen by sulphur causes a shift of both the methine and ring substituent proton resonances to lower fields (Fig. 1-1). The origin of this effect is unclear. Molecular orbital calculations, for example, have shown that there is less electron density at the methine proton of \(\text{Ni(SacSac)}_2\) than there is at that of \(\text{Ni(Sacac)}_2\). Contact shift nmr studies on pyridine adducts of nickel \(\beta\)-diketonates and monothio-\(\beta\)-diketonates have indicated that the sulphur donor atom facilitates delocalisation of more \(\sigma\)-, but less \(\pi\)-electron density than does oxygen.

The substitution of oxygen by sulphur is completed by the \(\text{M(SacSac)}_n\) series. All of these complexes are monomeric and low spin, and of the bis-chelated compounds, \(\text{Zn(OEtSacSac)}_2\) is the only reported tetrahedral example. \(\text{Zn(SacSac)}_2\) has been assumed to be planar, however it is more likely to be tetrahedral. Adducts of \(\text{M(SacSac)}_2\) compounds are known where \(M = \text{Fe}^{\text{II}}, \text{Co}^{\text{II}}\), or \(\text{Co}^{\text{II}}\text{Fe}^{\text{II}}\). \(\text{Fe(SacSac)}_2\) is reported to undergo the reactions opposite, whilst \(\text{Co(SacSac)}_2\) is reported to form five-co-ordinate low-spin cobalt(II) adducts with piperidine and pyridine and with \(Y(\text{C}_6\text{H}_5)_3\), where \(Y = \text{P, As, Sb and Bi}\). \(\text{Co(SacSac)}_2\) can also enlarge its co-ordination sphere in reactions involving a change in the cobalt oxidation state.

Dithioacetylacetone does not readily form as extensive a series of complexes as does acetylacetone. This is probably a consequence of the rather severe conditions necessary in the Martin-Stewart synthetic method. Early attempts to extend the range of dithio-\(\beta\)-diketonato complexes resulted instead in the isolation of compounds with the general formula \(\text{MX}_4\text{L}_2\). These compounds were observed to "decompose" on dissolution, the presence of \(\text{M}^{+2}, X^-,\) and dithiolium cations in solution being established. The formulation

\[\text{Fe(SacSac)}_2\] which has been only partially characterised.
Table 1-1. Idealised geometries of known metal dithio-β-diketonato structures.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Idealised Geometry</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(SacSac)_3</td>
<td>Octahedral</td>
<td>37, 77</td>
</tr>
<tr>
<td>Co(SacSac)_3</td>
<td>Octahedral</td>
<td>a</td>
</tr>
<tr>
<td>Rh(SacSac)_3</td>
<td>Octahedral</td>
<td>77, 79</td>
</tr>
<tr>
<td>Co(SacSac)_2</td>
<td>Square planar</td>
<td>72, 77, 78</td>
</tr>
<tr>
<td>Ni(SacSac)_2</td>
<td>Square planar</td>
<td>77, 78</td>
</tr>
<tr>
<td>Ni(NH₂SacNH₂Sac)_2</td>
<td>Square planar</td>
<td>80, present work</td>
</tr>
<tr>
<td>Zn(OEtSacSac)_2</td>
<td>Tetrahedral</td>
<td>32, 77</td>
</tr>
</tbody>
</table>

a P.M. Commons and B.F. Hoskins, unpublished results.
\[
\text{[MX}_{n}^{-2}\text{][dithiolium cation]}_{2} \text{ was specifically rejected (on the basis of the intense colour in the solid salt of two colourless ions) in favour of structures such as IV and V}^{35} \text{ or an octahedrally co-ordinated metal ion with "monodentate" sulphur bonded C}_5\text{H}_7\text{S}_2^{+} \text{ ligands, VI}.^{56,57}
\]

\[
\text{IV} \quad \text{V} \quad \text{VI}
\]

However, on the basis of chemical and spectroscopic evidence, Heath et al.\(^61\) showed the compounds MX\(_n\)(C\(_5\)H\(_7\)S\(_2\))\(_2\) to be the tetrahalometallate salts of the 3,5-dimethyl-1,2-dithiolium cation, and ascribed the intense colours of the solid compounds to charge transfer between the dithiolium cation and the tetrahalometallate anion. Crystal structure determinations\(^62-66\) subsequently confirmed this formulation, and the close Cl...S contacts observed were suggested as a pathway for the charge transfer. Additional confirmation was provided by Mössbauer spectroscopy.\(^37,67\) An extensive series of these compounds was subsequently synthesised and characterised,\(^68-71\) with a recent report providing a convenient synthetic route to the substituted-1,2-dithiolium halides.\(^72\) The 3,5-dimethyl-1,2-diselenolium cation has also been isolated.\(^73\) The range of M(SacSac)\(_n\) complexes has since been expanded by recourse to other methods of ligand generation.\(^2,35,58,74,75\) Paradoxically, the mildest and hence perhaps most promising method of SacSac generation, metathesis with Ni(SacSac)\(_2\) in refluxing alcohol,\(^76\) has received least application.

Isolation of the dithioacetylacetonates has been followed by detailed physicochemical studies. X-ray crystallographic investigations have established the structures of many of the known dithio-β-diketonates\(^32,36,37,77-80\) (Table 1-1). The divalent metal bis-chelates are square planar monomers, whilst the monomeric trivalent metal
tris-chelates are slightly but significantly distorted from an octahedral towards a trigonal prismatic stereochemistry. Two features of interest in these structures are the short S...S intraligand distances, and the localisation of ligand bonds in Fe(SacSac)₃.

Infra-red spectral assignments have been the subject of some debate since the erroneous comparison between the spectra of monomeric "square planar" Ni(SacSac)₂ and trimeric "octahedral" Ni(acac)₆. Comparative studies and normal co-ordinate analyses on the dithioacetylacetonato and related monothioacetylacetonato compounds, have established the origins of most M(SacSac)ₙ bands, although the assignment of the frequency of the C=C bond stretching mode absorption, ν(C=C), is still in dispute. Interestingly, Heath and Martin distinguish between bis- and tris-chelated complexes on the basis of the position of the ν(C=C) absorption, which is near 1490 cm⁻¹ in the former, and near 1465 cm⁻¹ in the latter compounds.

The electronic spectra are dominated by intense charge transfer transitions. Assignments of electronic spectral bands have been made on the basis of two molecular orbital calculations. These, however, differ in their choice of ground state both from each other and from that determined for Co(SacSac)₂ on the basis of single crystal magnetic anisotropy measurements. In this last study, the unpaired Co(SacSac)₂ electron was assigned to the dₓ² orbital, an assignment accepted elsewhere. Contact shift nmr studies, initially at variance with this configuration, were subsequently found to substantiate the Co(SacSac)₂ assignment.

Nmr experiments establish a marked dependence of the position of the methine proton resonance upon both the metal d-orbital population, and the chelate-ring substituents. The latter effect is rationalised readily in terms of the electron-donating capabilities of the substituents, although the reason for the metal d-orbital dependence is unclear. It should be noted, however, that changes in the metal d-orbital populations are accompanied by changes in the stereochemistry of the complexes.

Curie-Weiss behaviour has been observed for the magnetic susceptibility of paramagnetic dithio-β-diketonates. The room temperature values of µₚ for the M(SacSac)₃ complexes of the iron
Figure 1-3. Dithioacetylacetonato complexes known at the commencement of this thesis.
triad are quite low, and a number of factors, such as magnetic exchange, orbital contributions, and mixing with excited states, have been discussed in this connection.\textsuperscript{36,82} The magnetic susceptibility behaviour, and Mössbauer and esr spectra of Fe(SacSac)\textsubscript{3} are all thought to reflect the lower than octahedral symmetry of the complex.\textsuperscript{36,37,82,95,96} Even in polycrystalline form, anisotropy of the Fe(SacSac)\textsubscript{3} g-tensor is clearly evident.\textsuperscript{35,36} Only the average g-value has been measured for other dithio-β-diketonato complexes.\textsuperscript{2,36,74}

Thus, as indicated earlier, both contrasts and similarities may be found in comparing the complexes of monothio- and dithio-β-diketonato ligands. Whilst the latter compounds have been only briefly reviewed,\textsuperscript{97} the former have been the subject of several reviews,\textsuperscript{22,98-101} two of them being extremely comprehensive.

Two major objectives were apparent at the commencement of the present work. These were the development of synthetic routes to previously inaccessible and/or potentially interesting compounds, and an examination of the comparative effects of sulphur and oxygen donor atoms in electron transfer reactions. The synthetic and allied physicochemical studies are the subject of Section A.

As established when dithio-β-diketonates were first synthesised,\textsuperscript{1,81} the range of these complexes can be extended readily by varying the β-diketone in the Martin-Stewart synthesis. This modification has yielded several nickel(II) dithio-β-diketonates,\textsuperscript{1,45,81} none of which is of intrinsic interest, their properties being quite analogous to those of Ni(SacSac)\textsubscript{2}.

However, the investigations of Section A were directed towards the isolation and study of selected compounds of especial interest and potential. For example, the importance of Cr(SacSac)\textsubscript{3} and Zn(SacSac)\textsubscript{2} is twofold. Their syntheses have extended the range of SacSac compounds to metals beyond the Group VIII block (Fig. 1-3), and provide alternatives to the Martin-Stewart synthetic route. A dual purpose is similarly served by the study of the dithiomalonamidato compounds of Chapter 2. The substitution of -CH\textsubscript{3} by -NH\textsubscript{2} substituents introduces one of the most electron-donating groups into a dithio-β-diketone, and so provides an extreme case of the influence of substituents upon the behaviour of dithio-β-diketonato chelates. Additionally, these
complexes provide the only example to date in which all of the species of importance in dithio-β-diketonate chemistry (viz., protonated ligand, ligand anion, dithiolium salt and metal complexes of the first two species) may be isolated.

The second theme of this thesis is the comparative study of sulphur and oxygen as donor atoms. As indicated previously, the acac/Sacac/SacSac series of compounds provides a rare opportunity for such a comparison. Accordingly, in Section B a detailed study of the mass spectrometric behaviour of a series of nickel(II) bis-chelates differing only in the numbers of oxygen and sulphur donor atoms has been undertaken. Not only does this study establish the effect of successive replacements of oxygen donor atoms by sulphur donor atoms, but it also provides the first detailed examination of the mass spectrometric behaviour of a dithio-β-diketonato complex. To assist in the interpretation of these results and of the mass spectrometric data of Chapter 2, the electron-impact induced behaviour of a series of substituted 1,2-dithiolium iodides has been studied.

The role played by sulphur-based ligands in promoting extensive, facile electron transfer series and in the stabilisation of unusually high or low oxidation states has become increasingly apparent recently. To what extent this phenomenon is restricted to sulphur-based ligands and whether oxygen-based ligands can serve similar purposes is investigated in Section C. Additionally, the effects upon the electrochemistry (and hence upon the stabilisation of high and low oxidation states) of donor-atom variation, chelate-ring substituent variation, metal- as opposed to ligand-based electron transfer, co-ordination number and the lability of redox products are specifically investigated as part of a general discussion of the influences of several aspects of ligand design upon the electrochemistry of transition-metal chelates.
SECTION A
SYNTHETIC STUDIES
CHAPTER 2

DITHIOMALONAMIDE AND ITS Ni(II), Pd(II)
AND Pt(II) DERIVATIVES
Table 2-1. Infra-red Data (cm$^{-1}$).

<table>
<thead>
<tr>
<th>3,5-Diamino-1,2-dithiolium cation$^a$</th>
<th>Dithiomalonamide (LH) $^b$</th>
<th>NiL$_2$</th>
<th>PdL$_2$</th>
<th>PtL$_2$</th>
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</thead>
<tbody>
<tr>
<td>3315 &amp; 3270 &amp; 3140</td>
<td>$\nu$(N-H)</td>
<td>3420</td>
<td>3420</td>
<td>3410</td>
</tr>
<tr>
<td>3280</td>
<td>2940 &amp; $\nu$(C-H)</td>
<td>3398</td>
<td>3398</td>
<td>$\nu$(N-H)</td>
</tr>
<tr>
<td>3140</td>
<td>2590 &amp; $\nu$(S-H)</td>
<td>3180</td>
<td>3180</td>
<td>3180</td>
</tr>
<tr>
<td>1650</td>
<td>1622 &amp; $\delta$(NH$_2$)</td>
<td>1608</td>
<td>1608</td>
<td>1608 &amp; $\delta$(NH$_2$)</td>
</tr>
<tr>
<td>1625</td>
<td>1440 &amp; $\nu$(C-N)</td>
<td>1435</td>
<td>1430</td>
<td>1428</td>
</tr>
<tr>
<td>1515</td>
<td>1290 &amp; $\nu$(C-C)</td>
<td>1320</td>
<td>1320</td>
<td>1325</td>
</tr>
<tr>
<td>1370</td>
<td>1220 &amp; $\nu$(N-H) + $\nu_{sym}$(NCS)</td>
<td>1263</td>
<td>1130</td>
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<tr>
<td>1105</td>
<td>985 &amp; $\omega$(NH$_2$)</td>
<td>1040</td>
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<tr>
<td>965</td>
<td>800 &amp; $\nu$(C=S)</td>
<td>798</td>
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<td>720</td>
<td>740</td>
<td>740</td>
<td>740</td>
</tr>
<tr>
<td>615</td>
<td>600</td>
<td>585</td>
<td>590</td>
<td>590</td>
</tr>
<tr>
<td>530</td>
<td>460</td>
<td>450</td>
<td>450</td>
<td>450</td>
</tr>
<tr>
<td>420</td>
<td>405</td>
<td>400</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>290</td>
<td>320</td>
<td>350</td>
<td>350</td>
<td>350</td>
</tr>
</tbody>
</table>

$^a$ as the chloride salt – reference 110.

$^b$ assignments from reference 103.
Dithiomalonamide\textsuperscript{14} and N,N'-disubstituted dithiomalonamides\textsuperscript{16} can function as either neutral or anionic ligands with nitrogen and sulphur available as potential donor atoms. The small amount of data available on such complexes\textsuperscript{16,102-104} is conflicting and their interpretation is often speculative. Thus, bis(dithiomalonamidato)-nickel is claimed to be dimeric in one report,\textsuperscript{102} and monomeric in another.\textsuperscript{104} It has been inferred\textsuperscript{103} that bis(dithiomalonamide)cobaltous dichloride co-ordinates \textit{via} both sulphur atoms, whilst the co-ordination in the nickel analogue is assigned\textsuperscript{104} as being through sulphur and nitrogen. On the other hand, bis(dithiobiuret)nickel has been shown by x-ray analysis\textsuperscript{105} to involve co-ordination \textit{via} both sulphur atoms. Unfortunately, the interpretation of the infra-red data obtained for some bis(dithiobiuret)metal(II) dichlorides is not compelling.\textsuperscript{106,107} However, co-ordination \textit{via} both sulphur atoms appears to be probable in these cases.

By contrast, complexes of dithioacetylacetone and related ligands have been more extensively studied.\textsuperscript{1,3,36,44,45,52,108} Such studies have been hampered, to some extent, by the tendency of the free ligands to polymerise in the absence of a co-ordinating site. Oxidation of dithio-\(\beta\)-diketonato complexes frequently yields the corresponding 1,2-dithiolium ion.\textsuperscript{44,68,109} Dithiomalonamide offers advantages over many dithio-\(\beta\)-diketones in that it is stable in the form of free dithiomalonamide and will complex metal centres as such. Alternatively, it can lose a proton and co-ordinate metal ions as an anionic ligand, or it can readily be oxidised to the "3,5-diamino-1,2-dithiolium" ion.\textsuperscript{110} Hordvik\textsuperscript{111} has suggested that this species would be better formulated as an imine-type moiety, and this is reflected in some of its chemistry \textit{(vide infra)}. However, for purposes of reference and comparison, it will be referred to as a dithiolium ion.
Figure 2-1. Substituent dependence of $E_{1/2}$ for first reduction waves of Ni(C$_3$H$_5$S,RR')$_2$ chelates. All points from reference 2, except t-Bu/t-Bu from present work. $\alpha_m$ values from reference 145.

Figure 2-2. Substituent dependence of $E_{1/2}$ for first reduction waves of Ru(C$_5$H$_5$O$_2$RR')$_3$ chelates. $E_{1/2}$ values (at a rotating platinum electrode vs. sce in DMF) from reference 112; $\alpha_m$ values from reference 145.
The electrochemical behaviour of tris(β-diketonato)ruthenium complexes has been shown to depend upon the nature of the chelate ring substituents, and a similar effect has been observed with dithio-β-diketonates (Figs. 2-1 and 2-2). In particular, the replacement of both \( \text{CH}_3 \) groups by \( \text{NH}_2 \) groups should facilitate oxidation of the derived metal complexes.

Accordingly, complexes of both dithiomalonamide and the dithiomalonamidato anion were prepared with a view to comparing the related species: dithiolium ion, dithio-β-diketone, dithio-β-diketonate, and complexes of the latter two species. In particular, the new bis(dithiomalonamidato) complexes of palladium and platinum have been synthesised to complete the group VIII triad. Infra-red, electronic, mass and nuclear magnetic resonance spectra, and polarographic behaviour of all compounds have been reported in the hope of establishing the nature of the co-ordination and resolving anomalies in the literature.

(a) DITHIOMALONAMIDE (\( \text{NH}_2\text{SacNH}_2\text{SacH} \))

Since the initial synthesis by Lehr et al. very few references have been made to dithiomalonamide. The infra-red spectrum between 1650 \( \text{cm}^{-1} \) and 700 \( \text{cm}^{-1} \) has been assigned by Jensen and Nielsen. Table 2-1 lists those absorption bands in the range 4000 - 200 \( \text{cm}^{-1} \). The solid state infra-red spectrum (in a KBr matrix) exhibits a peak at 2590 \( \text{cm}^{-1} \) characteristic of the S-H bond stretching mode. However, no bands other than those observed in the solvent blank were observed in this region of the dimethyl sulfoxide solution spectrum, indicating that dithiomalonamide exists in the thio-enol form 1 in the solid state and probably as the dithione tautomer II in polar solvents.
Table 2-2. $^1$H NMR Spectral Details.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\delta_{\text{CH}_2}$ (ppm)</th>
<th>$\delta_{\text{CH}}$ (ppm)</th>
<th>$\delta_{\text{NH}_2}$ (ppm)</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_2\text{SacNH}_2\text{SacH}$</td>
<td>4.01(2)</td>
<td>2.68(4)</td>
<td></td>
<td>Acetone-$d_6$</td>
</tr>
<tr>
<td>$[\text{C}_3\text{H}_5\text{N}_2\text{S}_2]^+$</td>
<td>6.59</td>
<td>~ 8.9</td>
<td></td>
<td>Acetone-$d_6$</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{NH}_2\text{SacNH}_2\text{Sac})_2]$</td>
<td>5.59(1)</td>
<td>7.11(4)</td>
<td></td>
<td>DMSO-$d_6$</td>
</tr>
<tr>
<td>$[\text{Pd}(\text{NH}_2\text{SacNH}_2\text{Sac})_2]$</td>
<td>5.59(1)</td>
<td>7.22(4)</td>
<td></td>
<td>DMSO-$d_6$</td>
</tr>
<tr>
<td>$[\text{Pt}(\text{NH}_2\text{SacNH}_2\text{Sac})_2]$</td>
<td>5.55(1)</td>
<td>7.24(4)</td>
<td></td>
<td>DMSO-$d_6$</td>
</tr>
<tr>
<td>$[\text{Ni}(\text{NH}_2\text{SacNH}_2\text{SacH})_2]\text{Cl}_2$</td>
<td>4.04(2)</td>
<td>9.57(4)</td>
<td></td>
<td>DMSO-$d_6$</td>
</tr>
</tbody>
</table>

a Figures in parenthesis indicate relative integrated peak areas.

b No extra peaks were observed over the range 20 $\geq$ $\delta$ $\geq$ -10.

Figure 2-3. Schematic mass spectrum of dithiomalonamide.
This assignment is supported, in part, by nmr studies in acetone-d₆ (Table 2-2). Two peaks are observed at δ 4.01 ppm and δ 2.67 ppm (relative to TMS) with integrated areas in the ratio 1:2 respectively. Kolesova et al. reported the former peak and assigned it to the methylene protons. The other peak is assigned to NH₂ protons. Both peaks were observed to exchange with added D₂O with a resultant decrease in intensity. Dithiomalonamide may be compared with O-ethylthioacetothioacetate (OEtSacSacH) which has been shown to exist in the thio-enol form in CDCl₃ solution.

The mass spectrum of dithiomalonamide is reproduced schematically in Figure 2-3. Peaks with an intensity < 10% of the parent ion peak at m/e 134 have been omitted. The spectrum is dominated by the parent ion peak which was arbitrarily assigned an abundance of 100%. Interestingly, only a small peak was observed at m/e 133, corresponding to the 3,5-diamino-1,2-dithiolium cation, indicating very little decay via this species. In this respect, the behaviour of dithiomalonamide contrasts with that of O-ethylthioacetothioacetate, and of metal complexes of dithioacetylacetone. A peak at m/e 101, and a metastable ion at m/e ~ 76 established that the parent ion decays via loss of SH⁻.

\[
\text{NH₂SacNH₂SacH} \xrightarrow{-e} M \xrightarrow{-\text{SH}^{\cdot}} (M-33)
\]

M.W. 134 \hspace{1cm} m/e 134 \hspace{1cm} m^* 76 \hspace{1cm} m/e 101

Dithiomalonamide exhibits complicated dc polarographic behaviour at a dropping mercury electrode (dme) in acetone. Waves
Figure 2-4. Concentration dependence of $E_{1/2}$ of oxidation wave observed for dithiomalonamide.
corresponding to oxidation and reduction steps were observed; both were analysed by the standard plots of $i_d$ vs. $\sqrt{v}$ and $\log \left\{ \frac{i_d - 1}{1} \right\}$ vs. $E$, and by estimation of $E_{3/4} - E_{1/4}$ (see Chapter 5). The reduction wave at -1.90 V vs. Ag/AgCl is quite complex and appears to involve a reversible process followed by a second wave incorporating a number of non-reversible steps. The complexity of the reduction process is reflected in the asymmetry of its ac polarographic wave.

In contrast, the oxidation step is apparently reversible and diffusion controlled. However, the potential at which the oxidation wave occurs is concentration dependent over the range $1.5 \times 10^{-2} - 3.0 \times 10^{-4}$ M, yielding a value of approximately +0.32 V vs. Ag/AgCl at infinite dilution (Fig. 2-4). Further, coulometry at a mercury pool shows that the oxidation requires $1.1 \pm 0.1$ electrons/mole of dithiomalonamide. Similar behaviour has been observed in the polarography of O-ethylthioacetothioacetate, where the overall electrode process has been shown to be

$$\text{Hg} + \text{OEtSacSacH} \rightarrow [\text{Hg(OEtSacSac)}]^+ + \text{H}^+ + 2e \quad (a)$$

$$\text{OEtSacSacH} + [\text{Hg(OEtSacSac)}]^+ \Rightarrow \text{Hg(OEtSacSac)}_2 + \text{H}^+ \quad (b)$$

with reaction (b) being quite slow on the polarographic time scale; the electrode process at the dme being represented by reaction (a).

In the present case, a plot of $E_{1/2}$ vs. $\log [LH]$ (Fig. 2-4) is a straight line of gradient 31 mV (at 22°C). This result is consistent with the coulometry and is in keeping with electrode oxidation in the presence of $\text{NH}_2\text{SacNH}_2\text{SacH}$ by a mechanism similar to the above.

The gross electrochemical behaviour of dithiomalonamide, then, appears to be similar to that of O-ethylthioacetothioacetate, although the lack of information about the electrochemistry of the possible products of the dithiomalonamide oxidation precludes a more detailed analysis and comparison with O-ethylthioacetothioacetate.

The electronic spectrum of dithiomalonamide in methylcellulose has been reported previously. Again, quite analogously to O-ethylthioacetothioacetate, the spectrum has been found to be markedly solvent dependent in the present work.
Scheme 2-1

\[ [M+n(SacSac)_n] \xrightarrow{-e} C_2H_2S_2^+ \xrightarrow{-HS^*} (M-33) \]

\[ M^n = \text{Cr}^{\text{III}}, \text{Ni}^{\text{II}}, \text{Pd}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Co}^{\text{II}}, \text{Pt}^{\text{II}} \]

\[ m/e 131 \quad m^* 73.5 \quad m/e 98 \]

\[ [\text{Ni}(\text{NH}_2\text{SacNH}_2\text{Sac})_2] \xrightarrow{-e} C_3H_5N_2S_2^+ \xrightarrow{(M+1)} -\text{H}_2\text{S} \xrightarrow{(M-33)} m/e 133 \]

\[ m/e 134 \quad m/e 100 \]

\[ [\text{Ni}(\text{CF}_3\text{SacSac})_2] \xrightarrow{-e} C_5H_4F_3S_2^+ \xrightarrow{-F^*} (M-19) \]

\[ m^* 149 \quad m/e 166 \]

\[ m^* 125 \quad m/e 152 \]

\[ (M-33) \]

**Note.** The designation "M" applies only to the decay of the dithiolium ion, and not to the dithio-\(\beta\)-diketonate complex.

---

**Figure 2-5.** Schematic mass spectrum of \(\text{Ni}(\text{NH}_2\text{SacNH}_2\text{Sac})_2\).
(b) 3,5-DIAMINO-1,2-DITHIOLUM IODIDE

Hordvik's x-ray analysis\(^{111}\) suggests that the cation should be represented by resonance structures such as IV, with the positive charge on the exocyclic nitrogen atoms rather than by structures such as III which are more important for alkyl-substituted dithiolium cations.\(^{116,117}\)

\[ \text{III} \quad \text{IV} \]

Jensen\(^{110}\) has reported the infra-red spectrum over the range 4000 - 600 cm\(^{-1}\), and these results are included in Table 2-1 for comparison. Kolesova et al.\(^{114}\) have reported \(\lambda_{\text{max}}\) values in the electronic spectra of related N,N'-disubstituted 3,5-diamino-1,2-dithiolium ions in aqueous and alcoholic solutions. Their values (\(\lambda_{\text{max}} \approx 300\) nm, \(\log \varepsilon \approx 4.5\)) accord well with that (\(\lambda_{\text{max}} = 291.8\) nm, \(\log \varepsilon = 3.71\)) for 3,5-diamino-1,2-dithiolium iodide in aqueous solution.

Voltammetric studies at a platinum electrode in acetone reveal (apart from an oxidation wave, and a complex oxidation/reduction wave both attributable to the iodide ion) a non-reversible reduction at approximately -0.27 V vs. Ag/AgCl. This reduction is even more complex at the dme. The reader is referred to Chapter 6 for a discussion of the electrochemistry of some 1,2-dithiolium ions.

Chapter 4 incorporates a study of the mass spectrometric behaviour of a number of alkyl- and aryl-substituted 1,2-dithiolium cations as their iodide salts. Comparison with 3,5-diamino-1,2-dithiolium iodide establishes that its mass spectrometric behaviour is analogous to that of the other substituted 1,2-dithiolium iodides studied.

The nmr spectrum of 3,5-diamino-1,2-dithiolium iodide in acetone-\(d_6\) (Table 2-2) shows a sharp resonance at \(\delta 6.59\) ppm,
### Table 2-3. Pt-H Coupling Constants.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$J_{\text{Pt-CH}}$</th>
<th>$J_{\text{Pt-CH}_3}$</th>
<th>$J_{\text{Pt-NH}_2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pt(acac)$_2$]</td>
<td>11 $^a$</td>
<td>5 $^a$</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>10.6 $^b$</td>
<td>4.8 $^b$</td>
<td>-</td>
</tr>
<tr>
<td>[Pt(SacSac)$_2$]</td>
<td>$d$</td>
<td>$9^c$</td>
<td>-</td>
</tr>
<tr>
<td>[Pt(OEtSacSac)$_2$]</td>
<td>6.2 $^e$</td>
<td>8.6 $^e$</td>
<td>-</td>
</tr>
<tr>
<td>[Pt(NH$_2$SacNH$_2$Sac)$_2$]</td>
<td>2.3</td>
<td>-</td>
<td>6.9</td>
</tr>
</tbody>
</table>

$^a$ Ref. 119.  
$^b$ Ref. 120.  
$^c$ Ref. 82.  
$^d$ Not resolved due to limited solubility.  
$^e$ Ref. 121.
attributable to the methine proton resonance (this being in close agreement with that observed by Futterer in trifluoroacetic acid\textsuperscript{117}), and a broad resonance centred at about $\delta$ 8.95 ppm, attributable to resonance of the NH$_2$ protons. In contrast to the peak shape of the NH$_2$ proton resonance absorption in dithiomalonamide, and in complexes of dithiomalonamide and of the dithiomalonamidato anion, the $\delta$ 8.95 ppm peak in 3,5-diamino-1,2-dithiolium iodide is broad and poorly resolved.

(c) METAL DITHIOMALONAMIDATO COMPLEXES [M(NH$_2$SacNH$_2$Sac)$_2$]

The complexes with divalent nickel, palladium and platinum are diamagnetic, appear to be quite air-stable, and have melting points above 350°C, with apparent decomposition above 200°C. They are soluble in dimethyl sulfoxide, pyridine, dimethyl formamide and acetone but, unlike the corresponding M(SacSac)$_2$ compounds,\textsuperscript{1} are insoluble, or only sparingly soluble, in chloroform and benzene. Molecular weight measurements established that the nickel and palladium complexes are monomeric in pyridine. The similarity of the electronic and infra-red spectra of the three compounds, coupled with the fact that the electronic spectrum of the nickel complex is the same in the solid state and in pyridine or dimethyl sulfoxide solutions, supports a monomeric nature for the three complexes. Odnoralova and Kudryavtsev's assignment\textsuperscript{102} of the nickel compound as a dimer (on the basis of elemental analysis alone) is clearly erroneous.

(i) Mass Spectra

The dithioacetylacetonates of divalent zinc (Chapter 3), nickel, palladium, platinum and cobalt,\textsuperscript{1} all exhibit a parent ion in their mass spectra, with the most abundant peak occurring at $m/e$ 131, corresponding to the 3,5-dimethyl-1,2-dithiolium cation.\textsuperscript{1} The mass spectrometric behaviour of the present compounds, however, differs greatly from that of the dithioacetylacetonates and from each other.

Figure 2-5 shows the mass spectrum of Ni(NH$_2$SacNH$_2$Sac)$_2$. The principal differences from those of the divalent metal dithioacetyl-acetonates are the lack of a parent ion at $m/e$ 325 (in fact, a lack of any substantial peaks at $m/e$ values in excess of 136), and the lack of a
Table 2-4. Selected carbon-donor atom bond lengths.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>C-S (Å)</th>
<th>C-O (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(NH₂SacNH₂Sac)₂</td>
<td>1.734(2)</td>
<td>1.274</td>
</tr>
<tr>
<td>Zn(OEtSacSac)₂</td>
<td>1.682(4)</td>
<td>1.314(10)</td>
</tr>
<tr>
<td>Ni(SacSac)₂</td>
<td>1.685(3)</td>
<td></td>
</tr>
<tr>
<td>Zn(Bu₄acBu₄ac)₂</td>
<td>1.724(2)</td>
<td></td>
</tr>
<tr>
<td>Ni(Bu₄acBu₄ac)₂</td>
<td>1.707(4)</td>
<td></td>
</tr>
</tbody>
</table>

\[a\] See Table 2-9.

Table 2-5. Compositions of ligand N-H bond stretching modes as determined by normal co-ordinate analyses.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>(\nu(N-H)) calc.</th>
<th>% (\nu(N-H))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiocarbohydrazide</td>
<td>3326</td>
<td>100</td>
<td>132</td>
</tr>
<tr>
<td></td>
<td>3294</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3220</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Thioformamide</td>
<td>3287</td>
<td>101</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3191</td>
<td>99</td>
<td>133</td>
</tr>
</tbody>
</table>
large peak at \(m/e\) 133, corresponding to the 3,5-diamino-1,2-dithiolium cation.

A peak is observed at \(m/e\) 134, and apart from the lack of peaks corresponding to \(S_\beta\) decay, the mass spectrum of \(\text{Ni(NH}_2\text{SacNH}_2\text{Sac)}_2\) is very similar to that of the 3,5-diamino-1,2-dithiolium cation (q.v.) with peaks at \(m/e\) 134, 100, 84, 60, etc., suggesting that \(\text{Ni(NH}_2\text{SacNH}_2\text{Sac)}_2\) does, in fact, decay (perhaps thermally in the source) via the 3,5-diamino-1,2-dithiolium cation, as is observed with the divalent metal dithioacetylacetonates (Scheme 2-1). However, the 3,5-diamino-1,2-dithiolium cation peak is not the most abundant peak in the mass spectrum of \(\text{Ni(NH}_2\text{SacNH}_2\text{Sac)}_2\), whereas the 3,5-dimethyl-1,2-dithiolium cation peak is the most abundant peak in the mass spectrum of the metal dithioacetylacetonates.

Perhaps the most interesting feature of the \(\text{Ni(NH}_2\text{SacNH}_2\text{Sac)}_2\) mass spectrum, however, is a weak but well-defined cluster of peaks about \(m/e\) 402. The position of this cluster and the isotope pattern suggest that it corresponds to \([\text{Ni(NH}_2\text{SacNH}_2\text{Sac)}_2\cdot\text{(DMSO)}]^+\), i.e. that a small amount of solvated complex has been volatilised and ionised complete with dimethyl sulfoxide solvent.

The mass spectrometric behaviour of \(\text{Pd(NH}_2\text{SacNH}_2\text{Sac)}_2\) is similar to that of its nickel congener, with respect to decay via the 3,5-diamino-1,2-dithiolium cation, but additionally it exhibits peaks at \(m/e\) 338 and 274, probably corresponding to loss of \(\text{H}_2\text{S}\) from the complex, followed by loss of \(\text{S}_2\) from the species so generated.

Corresponding additional peaks are not observed for \(\text{Pt(NH}_2\text{SacNH}_2\text{Sac)}_2\), but otherwise it behaves analogously to the nickel and palladium compounds, there being no parent ion nor \([\text{M(NH}_2\text{SacNH}_2\text{Sac)}]^+\) peaks, and decay via the 3,5-diamino-1,2-dithiolium cation being evidenced by peaks at \(m/e\) 134 and 100.

(ii) Nuclear Magnetic Resonance Spectra

Table 2-2 summarises the proton nuclear magnetic resonance spectra of the three compounds in \(d_6\)-DMSO. Two peaks were observed, with integrated areas in the ratio 4:1. The resonance at \(\delta \sim 7.2\) is slightly broadened. Its intensity is decreased upon addition of \(\text{D}_2\text{O}\) and, in the
Table 2-6. Wave numbers of (N-H) bond stretching mode absorptions.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \nu(\text{N-H}) ) (cm(^{-1}))</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>thiourea (tu)</td>
<td>3365, 3258, 3156, 3097</td>
<td>140</td>
</tr>
<tr>
<td>Ni(tu)(_2)(SCN)(_2)</td>
<td>3340, 3250, 3170</td>
<td>138</td>
</tr>
<tr>
<td>Pd(tu)(_4)Cl(_2)</td>
<td>...., 3290, 3120</td>
<td>138</td>
</tr>
<tr>
<td>Pt(tu)(_4)Cl(_2)</td>
<td>3360, 3290, 3160</td>
<td>138</td>
</tr>
<tr>
<td>ethylenediamine (en)</td>
<td>3340</td>
<td>139</td>
</tr>
<tr>
<td>* Pt(en)Br(_2)</td>
<td>3270</td>
<td>139</td>
</tr>
<tr>
<td>* Co(en)(_3)Cl(_3)</td>
<td>3210</td>
<td>139</td>
</tr>
<tr>
<td>n-C(_8)H(_17)NHCH(_2)CH(_2)SH (OcLH)</td>
<td>3300</td>
<td>134</td>
</tr>
<tr>
<td>C(_6)H(_5)CH(_2)NHCH(_2)CH(_2)SH (BzLH)</td>
<td>3300</td>
<td>134</td>
</tr>
<tr>
<td>* Ni(OcL)(_2)</td>
<td>3086</td>
<td>134</td>
</tr>
<tr>
<td>* Ni(BzL)(_2)</td>
<td>3105</td>
<td>134</td>
</tr>
<tr>
<td>Ni(C(_4)H(_5)NHCH(_2)CH(_2)S)(_2)</td>
<td>3282</td>
<td>134</td>
</tr>
</tbody>
</table>

\* = ligand donor atom is nitrogen. In other cases, donor atom is sulphur.
case of the nickel complex, this resonance is shifted to higher field on addition of DCl. The $\delta \sim 5.6$ resonance is unchanged by these additions. Therefore, the former resonance is ascribed to the NH$_2$ protons and, as in dithiomalonamide, is observed despite $^{14}$N quadrupole effects, presumably because of exchange with aqueous impurities in the solvent.

The latter resonance is assigned to the methine proton. It is interesting to note that the resonances of the backbone protons are observed at progressively lower fields as the series NH$_2$SacNH$_2$Sac$^+$, M(NH$_2$SacNH$_2$Sac)$_2$, NH$_2$SacNH$_2$Sac$^+$ is traversed. This shift corresponds to decreased shielding of such protons due in part perhaps to an increase in the amount of positive charge in the resonance forms of importance (Fig. 2-6). In contrast to Pt(SacSac)$_2^+$, the splittings due to the $^{195}$Pt nucleus in Pt(NH$_2$SacNH$_2$Sac)$_2$ have been determined and are compared with those in analogous compounds in Table 2-3. Although $J_{\text{Pt-NH}_2}$ is substantially larger than $J_{\text{Pt-CH}}$ in Pt(NH$_2$SacNH$_2$Sac)$_2$, the significance of this is not clear, although it is possibly indicative of a substantial contribution to the bonding by the conjugated system V.

![Diagram of V]

Similarly, the inequality $J_{\text{Pt-NH}_2} > J_{\text{Pt-CH}_3}$ may arise because canonical structures corresponding to V cannot be written when the ring substituent is -CH$_3$ as in Pt(acac)$_2$ and Pt(SacSac)$_2$.

Should the co-ordination of the ligand be via nitrogen rather than sulphur, a value of $J_{\text{Pt-NH}_2}$ much larger than the observed value might be expected, Appleton and Hall having reported values of $J_{\text{Pt-NH}}$ of ca. 60Hz for square planar platinum(II) diamine-type complexes.

All the NH$_2$ protons of the title compounds have been found to be equivalent in the nmr experiment, such equivalence being suggestive of S,S or N,N chelation. Additionally, the NH$_2$ protons of
Table 2-7. Electronic spectra of Ni(II), Pd(II), and Pt(II) complexes of NH₂SacNH₂Sac and of related ligands.

<table>
<thead>
<tr>
<th></th>
<th>[Ni(SacSac)₂]²⁺</th>
<th>[Ni(OEtSacSac)₂]¹²⁻</th>
<th>[Ni(NH₂SacNH₂Sac)₂]⁺</th>
<th>[Pd(NH₂SacNH₂Sac)₂]⁺</th>
<th>[Pt(NH₂SacNH₂Sac)₂]⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(cm⁻¹)</td>
<td>(log ε)</td>
<td>V(cm⁻¹)</td>
<td>(log ε)</td>
<td>V(cm⁻¹)</td>
<td>(log ε)</td>
</tr>
<tr>
<td>14,890 (2.52)</td>
<td>14,700 (2.00)</td>
<td>15,620 (1.53)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17,500 (2.59)</td>
<td>20,600 (3.66)</td>
<td>24,100(sh) (3.54)</td>
<td>21,280 (2.97)</td>
<td>25,250 (3.64)</td>
<td></td>
</tr>
<tr>
<td>18,120 (3.45)</td>
<td>25,510 (3.62)</td>
<td>25,770(sh) (3.89)</td>
<td>27,470 (3.51)</td>
<td>29,760 (4.28)</td>
<td></td>
</tr>
<tr>
<td>25,670 (4.33)</td>
<td>29,600 (4.40)</td>
<td>31,250 (4.56)</td>
<td>33,080 (4.07)</td>
<td>32,470 (4.47)</td>
<td></td>
</tr>
<tr>
<td>35,460 (4.59)</td>
<td>36,500 (4.66)</td>
<td>36,600 (4.90)</td>
<td>36,100 (4.73)</td>
<td>not observed</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>36,630 (4.34)</td>
<td></td>
</tr>
<tr>
<td>41,150 (5.23)</td>
<td>42,000 (4.49)</td>
<td>38,760 (4.52)</td>
<td>not observed</td>
<td>not observed</td>
<td></td>
</tr>
</tbody>
</table>

α in DMSO solution.
[Ni(NH$_2$SacNH$_2$SacH)$_2$]Cl$_2$ have been found to be equivalent in d$_6$-DMSO, although occurring at lower field than in Ni(NH$_2$SacNH$_2$Sac)$_2$ (Table 2-2). Should the co-ordination in the chelated cation be S,N (as suggested by Peyronel et al.\textsuperscript{104} on the basis of infra-red peak splittings), then the equivalence of the amide protons would have to be ascribed to rapid exchange between the non-equivalent sites.

Accordingly, the nmr spectrum of [Ni(NH$_2$SacNH$_2$SacH)$_2$]Cl$_2$ was recorded in d$_7$-DMSO over the temperature range -80°C to +35°C. Although the spectra are extremely complex (possibly due to axial interaction of solvent with the compound leading to paramagnetism and its concomitant complexity) they are not consistent with a proton exchange mechanism. The co-ordination in [Ni(NH$_2$SacNH$_2$SacH)$_2$]Cl$_2$ would thus appear to involve either N,N or S,S symmetrical chelation.

(iii) Infra-red Spectra

Table 2-1 incorporates the infra-red spectral details of the present compounds. As a consequence of the four potential donor atoms of dithiomalonamide, there arises the possibility of S,S; N,N; or S,N chelation (although nmr spectra (\textit{vide supra}) indicate that the latter is unlikely). The gross similarity of the spectra of the three compounds suggests that the ligands have the same bonding mode in all compounds. In assigning the mode of chelation, the infra-red bands potentially of most value are those associated with metal-donor atom, C-S, C-N and NH$_2$ bond vibrations.

Absorptions in the vicinity of 300-400 cm$^{-1}$ in these compounds may reasonably be assigned to the metal-donor atom stretching mode. However, the possibility that these may be ring deformation modes cannot be ignored. Although absorptions due to M-N bond stretching modes, $\nu$(M-N), seem to occur at higher frequency than do those due to M-S bond stretching modes, $\nu$(M-S), in analogous compounds, literature values of $\nu$(M-N) and $\nu$(M-S) show that these two regions overlap.\textsuperscript{121-128} Thus, Adams\textsuperscript{126} remarks that $\nu$(M-S) bands of chelate ligands fall in the range 440-330 cm$^{-1}$, and Nakamoto\textsuperscript{128} tabulates $\nu$(Ni-S) frequencies of square planar nickel(II) bis-chelates in the range 470-330 cm$^{-1}$. Omura,\textsuperscript{129} in a series of metal-ethylene diamine complexes locates $\nu$(M-N) between 580 and 470 cm$^{-1}$. Adams\textsuperscript{125} places $\nu$(M-N) in metal amines
Table 2-8. Polarographic data.\(^a\)

<table>
<thead>
<tr>
<th>Species</th>
<th>(E_{1/2}) (V)</th>
<th>(E_{3/4} - E_{1/4}) (mV)</th>
<th>Gradient of (\log(i_d - i_1)) vs. (E) plot</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NH}_2\text{SacNH}_2\text{SacH})</td>
<td>(+0.32) (^b)</td>
<td>33 (^b)</td>
<td>59 (^c) 1 (^d)</td>
</tr>
<tr>
<td></td>
<td>-1.900</td>
<td>47</td>
<td>52</td>
</tr>
<tr>
<td>Dithiobiuret</td>
<td>+0.448</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-1.95</td>
<td>55</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Ni}(\text{NH}_2\text{SacNH}_2\text{Sac})_2])</td>
<td>(+0.6) (^e)</td>
<td>28</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-1.247</td>
<td>63</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>-1.430</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-1.760</td>
<td>46</td>
<td>42</td>
</tr>
<tr>
<td>([\text{Pd}(\text{NH}_2\text{SacNH}_2\text{Sac})_2])</td>
<td>+0.6</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-1.482</td>
<td>85</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-1.7</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>([\text{Pt}(\text{NH}_2\text{SacNH}_2\text{Sac})_2])</td>
<td>+0.640</td>
<td>63</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>-1.725</td>
<td>85</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>-1.980</td>
<td>80</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\) acetone as solvent, potentials vs. Ag/AgCl.

\(^b\) extrapolated to infinite dilution.

\(^c\) at \(1.0 \times 10^{-3}\text{M}\).

\(^d\) at 2.5 and \(3.9 \times 10^{-3}\text{M}\).
between 300 and 500 cm$^{-1}$, and Lever$^{127}$ attributes absorptions between 230 and 400 cm$^{-1}$ in the spectra of $[\text{M(diamine)}]_2X_2$ ($\text{M} = \text{Co(II)}, \text{Ni(II)}$) to $\nu(\text{M-N})$, but finds the position of this band to be dependent upon the nickel spin state in $\text{Ni}(\text{N,N-diethylethylenediamine})\text{X}_2$ ($X = \text{Cl, Br}$), these complexes being described by Lever as being octahedral and square planar respectively.

Accordingly, the position of the metal-donor atom bond stretching mode absorption cannot be used a priori for assigning the mode of co-ordination. Moreover, the coupling of the $\text{M-S}$ bond stretching mode with other modes, as evidenced by normal co-ordinate analyses$^{44,83,87}$ (in $\text{Co(SacSac)}_2$), only 57% of the intensity of the "$\nu(\text{M-S})$ band" is contributed by the absorption of the $\text{Co-S}$ bond stretching mode, and the low intensities of these absorptions, militates further against their definitive use in this regard.

The position of the $\nu(\text{C-S})$ band in the $\text{M(NH}_2\text{SacNH}_2\text{Sac)}_2$ complexes is difficult to establish. Jensen and Nielsen have assigned the dithiomalonamide C-S stretch to a band at 799 cm$^{-1}$. A shift of this band to lower frequencies on chelation would imply sulphur co-ordination.

Normal co-ordinate analyses and empirical arguments place the $\nu(\text{C-S})$ band in the divalent, square planar $\text{SacSac}$ complexes at approximately 700 cm$^{-1}$. Since the resonance structures VI and VII would be expected to make more significant contributions to the bonding in the respective $\text{ML}_2$ complexes than would VIII in $\text{M(SacSac)}_2$, it is probable that the positions of these bands (in cm$^{-1}$) will be in the order

$$\text{Ni(NH}_2\text{SacNH}_2\text{Sac)}_2 < \text{Ni(OEtSacSac)}_2 < \text{Ni(SacSac)}_2$$

In accord with this postulate, Jensen and Nielsen$^{103}$ remark that S-methylation of dithiomalonamide shifts the $\nu(\text{C-S})$ peak "possibly as low as 684 cm$^{-1}$", and Hendrickson$^2$ assigns a band at 639 cm$^{-1}$ to $\nu(\text{C-S})$ in the $\text{M(OEtSacSac)}_2$ ($\text{M} = \text{Ni, Pd, Pt}$) complexes. Peyronel et al.$^{104}$ assign a strong band at 649 cm$^{-1}$ in the spectrum of $\text{Ni(NH}_2\text{SacNH}_2\text{Sac)}_2$ to the $\nu(\text{C-S})$ absorption. Such an assignment is consistent with the foregoing remarks; however, it should be noted that the $\nu(\text{C-S})$ absorptions of $\text{M(SacSac)}_2$ ($\text{M} = \text{Co, Ni}$) and the $\nu(\text{C-Se})$ band in $\text{Ni(SeacSeac)}_2$ are weak. The C-S band lengths in $\text{Ni(NH}_2\text{SacNH}_2\text{Sac)}_2$, $\text{Zn(OEtSacSac)}_2$ and $\text{Ni(SacSac)}_2$ are consistent with the above ordering of
Figure 2-6. Variation in pmr absorption positions with amount of positive charge. δ values from Table 2-2.
\( \nu(C-S) \) stretching frequencies (Table 2-4), and thus, the \( \nu(C-S) \) band in \( \text{Ni(NH}_2\text{SacNH}_2\text{Sac)}_2 \) would be expected to be located at \( \nu \approx 639 \text{ cm}^{-1} \). (In the absence of structural data for planar \( \text{Ni(OEtSacSac)}_2 \), that of tetrahedral \( \text{Zn(OEtSacSac)}_2 \) has been included in Table 2-4. The effect of changing the chelated metal can be gauged by comparing the C-O bond lengths of planar \( \text{Ni(Bu}^t\text{acBu}^t\text{ac)}_2 \) and tetrahedral \( \text{Zn(Bu}^t\text{acBu}^t\text{ac)}_2 \).)

Assignment of \( \nu(C-S) \) is further complicated by the strong coupling between vibrational modes which occurs in such systems (for example, in \( \text{Co(SacSac)}_2 \), the 700 cm\(^{-1}\) band is calculated to contain 57% symmetric C-S stretch). Heath and Martin\(^{36}\) caution that

"... each infrared absorption may involve a substantial mixing of the normal vibrational modes and simple "assignments" should be assessed realistically. ..."

Therefore, in view of the relative complexity of the spectra in this region, the strong coupling between modes, and the uncertainty as to its position, the \( \nu(C-S) \) vibration cannot be used to diagnose the mode of co-ordination. The implicit argument of Peyronel et al. seems to be that the 649 cm\(^{-1}\) band is the \( \nu(C-S) \) band because it is lower than \( \nu(C-S) \) in the free ligand; co-ordination via sulphur would be expected to lower \( \nu(C-S) \) relative to the ligand; therefore the complexes are sulphur co-ordinated.

Jensen and Nielsen\(^{103}\) found that co-ordination via sulphur raises the frequency of the N-H bond bending mode absorption, although they quote exceptions to this generalisation, one of which is \( \text{[Co(NH}_2\text{SacNH}_2\text{SacH)}_2\text{Cl}]}_2 \), which they assumed to be sulphur chelated. A similar drop in the frequency of this absorption relative to dithiomalonamide was observed in the present compounds. However, the behaviour of this band is not altogether straightforward, as, in nickel dithiooxamide complexes,\(^{131}\) where sulphur and nitrogen co-ordination occurs, the frequency of this absorption is consistently raised above the free ligand value.

An increase in the frequency of the absorption corresponding to the C-N bond stretching mode, \( \nu(C-N) \), in the complexes relative to that in dithiomalonamide would be consistent with sulphur chelation.\(^{103}\) Such an increase is observed, but the \( \nu(C-N) \) band of dithiomalonamide has been shown\(^{103}\) to involve other coupled vibrations, although it is
regarded as predominantly $\nu(C-N)$. Again interpretations based on the position of this band should be made cautiously and in conjunction with other evidence.

The bands of most importance in ascertaining the identities of the donor atoms are those associated with $\nu(N-H)$, the $N-H$ bond stretching mode frequency (~3300 cm$^{-1}$). Normal co-ordinate analyses on ligands containing a thioamide functional group have shown these vibrations to be substantially, if not completely pure (Table 2-5). Several examples of ligands with nitrogen and sulphur as potential donors have been studied, and $\nu(N-H)$ positions have been used to establish the mode of co-ordination. Co-ordination of $-NH_2$ groups to a metal ion has been shown to result in a shift of the $N-H$ bond stretching mode absorptions to lower frequencies (Table 2-6). In the title compounds, the $N-H$ bond stretching mode absorptions are at a slightly higher frequency than in dithiomalonamide, thereby implying sulphur co-ordination.

Therefore, the compounds are believed to involve sulphur-chelated ligands, such an assignment being based primarily on the frequency of the $N-H$ bond stretching mode absorption, and supported by the shift in $\nu(C-N)$ relative to dithiomalonamide.

(iv) Electronic Spectra

The electronic spectra of Ni(NH$_2$SacNH$_2$Sac)$_2$ in dimethyl sulfoxide, in pyridine and in the solid accords well with the values given by Peyronel. Table 2-7 incorporates the electronic spectra of the present compounds. Their similarity to each other and to related compounds is apparent. As in the palladium and platinum compounds of OEtSacSac, low-energy bands corresponding to the d-d transitions of NiL$_2$ (L = SacSac, OEtSacSac, NH$_2$SacNH$_2$Sac) are not differentiated readily from the tail of the adjacent charge transfer bands in the palladium and platinum complexes of NH$_2$SacNH$_2$Sac.

The syntheses and electronic spectra in methylcellulose of the complexes Pd(NHRSacNHRSac)$_2$ ($R = H, Me, Ph$) have been reported very recently. A close correspondence exists between these spectra and that of Pd(NH$_2$SacNH$_2$Sac)$_2$ reported in the present work. Pellacani
Figure 2-7. Contents of Ni(NH₂SacNH₂Sac)₂.2DMF unit cell. Dotted lines show hydrogen bonds.
et al. assign a band at approximately 20,000 cm\(^{-1}\) to a \(x^2-y^2\rightarrow xy\) in-plane transition, and so place these ligands in the spectrochemical series of sulphur-donor ligands for planar palladium(II) complexes as follows:

\[
\text{mnt} < \text{SacSac} < \text{NHPHPhSacNHPhSac} < \text{NH}\_2\text{SacNH}\_2\text{Sac} < \text{NHMeSacNHMeSac} < \text{Et}_2\text{PS}_2 < \text{Et}_2\text{dtc} < \text{dithiooxalate}
\]

Comparison with the ordering they obtain for planar nickel(II) complexes:\(^{143}\)

\[
\text{mnt} < \text{Et}_2\text{PS}_2 < \text{SacSac} < \text{NH}\_2\text{SacNH}\_2\text{Sac} = \text{NHPHPhSacNHPhSac} = \text{NHMeSacNHMeSac} < \text{Etxan} < \text{Et}_2\text{dtc} < 2,3\text{-dimercaptopropanol} < \text{dithiomalonate} < \text{dithiooxalate}
\]

shows the influence of substituents on the nitrogen atoms in the dithiomalonamide-derived ligands to be more marked in the palladium(II) than in the nickel(II) complexes.

(v) Electrochemistry

Electrochemical studies have been performed on the complexes in acetone at a dme and at a platinum electrode (Table 2-8). The compounds undergo both cathodic and anodic behaviour at the dme.

Although, in accord with the predictions of substituent effects (Fig. 2-2, note that \(\sigma_{\text{m-x}}\text{NH}_2 = -0.16\)) that the reduction waves of the present compounds lie at far more negative potentials than those of the corresponding dithioacetylacetonates, the cathodic behaviour remains similar to that of the dithioacetylacetonates, where the formal electron transfer steps

\[
\begin{align*}
\text{M(II)} & \xrightarrow{\text{e}} \text{M(I)} & \xrightarrow{\text{e}} \text{M(O)} \\
\downarrow & & \downarrow \\
\text{[M(I)]'} & \xrightarrow{\text{e}} \text{M(O)'}
\end{align*}
\]

were observed.\(^{144}\)
Figure 2-8. Molecular structure and atomic labelling of Ni(NH$_2$SacNH$_2$Sac)$_2$ unit in Ni(NH$_2$SacNH$_2$Sac)$_2$·2DMF.
Similarly, three reduction waves were observed for Ni(NH₂SacNH₂Sac)₂, the first (most positive) of which was shown to be a one-electron process by coulometry at a mercury pool. Analyses of the usual type showed this first reduction to be diffusion controlled and reversible.

The second reduction wave (at $E_{1/2} = -1.430\text{V}$) is very much smaller than either of the other reduction waves, and its height is dependent on droptime — the wave disappearing under rapid polarographic conditions.

Under normal polarographic conditions, the third wave was shown to approach reversible behaviour, although analysis of this wave was complicated by the poor resolution of its current-voltage plateau, a consequence of the proximity of the cathodic limit of the solvent. The height of this third wave equalled that of the first wave under rapid polarographic conditions, whilst under normal conditions, the combined heights of the second and third waves nearly equalled that of the first wave.

Such behaviour is consistent with the above reduction mechanism, with the rate constant, k, for the rearrangement of the first reduction product being smaller in the present case than for Ni(SacSac)₂.

Ac polarographic studies on Ni(NH₂SacNH₂Sac)₂ confirm a complication of the reduction pathway, as a plot of the peak current of the ac wave corresponding to the first reduction, against the square root of the ac frequency ($10 < f < 1000\text{Hz}$) is non-linear.

The palladium and platinum complexes are reduced at potentials approaching the cathodic limit of the solvent, and are therefore not as readily analysed. Further, the reduction waves of these compounds are more complicated and the desired comparison with the corresponding dithioacetylacetonates is thus not possible.

Interestingly, although dithiomalonamide and dithiobiuret have similar redox potentials at the dme, reductions of bis(dithiobiureto)nickel(II) occur at more positive potentials than those of Ni(NH₂SacNH₂Sac)₂ (for bis(dithiobiureto)nickel(II)), a small prewave at $E_{1/2} = -0.96\text{ V}$, followed by two nearly overlapping waves of approximately
Table 2-9. \( \text{Ni(NH}_2\text{SacNH}_2\text{Sac)}_2 \cdot 2\text{DMF} \) interatomic distances (Å).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-S(1)</td>
<td>2.161(1)</td>
</tr>
<tr>
<td>Ni-S(2)</td>
<td>2.186(1)</td>
</tr>
<tr>
<td>S(1)-C(1)</td>
<td>1.724(2)</td>
</tr>
<tr>
<td>S(2)-C(2)</td>
<td>1.734(2)</td>
</tr>
<tr>
<td>C(1)-C(3)</td>
<td>1.384(3)</td>
</tr>
<tr>
<td>C(2)-C(3)</td>
<td>1.388(3)</td>
</tr>
<tr>
<td>C(11)-O</td>
<td>1.225(3)</td>
</tr>
<tr>
<td>C(11)-N(11)</td>
<td>1.314(3)</td>
</tr>
<tr>
<td>N(11)-C(12)</td>
<td>1.459(4)</td>
</tr>
<tr>
<td>N(11)-C(13)</td>
<td>1.443(4)</td>
</tr>
</tbody>
</table>

DMF

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(2)NiS(1)</td>
<td>96.88(2)</td>
</tr>
<tr>
<td>S(2)C(2)C(3)</td>
<td>128.6(2)</td>
</tr>
<tr>
<td>S(1)C(1)C(3)</td>
<td>128.2(2)</td>
</tr>
<tr>
<td>N(2)C(2)C(3)</td>
<td>118.9(2)</td>
</tr>
<tr>
<td>N(1)C(1)C(3)</td>
<td>118.5(2)</td>
</tr>
<tr>
<td>C(2)C(3)C(1)</td>
<td>128.2(2)</td>
</tr>
</tbody>
</table>
equal height with $E_{1/2} = -1.08$ V and $-1.17$ V were observed. A further reduction occurs at $E_{1/2} = -1.91$ V vs. Ag/AgCl. Even so, the electrochemical behaviour of bis(dithiobiureto)nickel(II) is qualitatively the same as that of Ni(SacSac)$_2$ and of Ni(NH$_2$SacNH$_2$Sac)$_2$.

It might be anticipated that protonation of the amine function(s) of Ni(NH$_2$SacNH$_2$Sac)$_2$ should shift the reduction waves anodically, due to the differing effects of $-\text{NH}_2$ and $-\text{NH}_3^+$ (for NH$_2$, $\sigma_{m-x} = -0.16$, whilst for NH$_3^+$, $\sigma_{m-x} = +0.63$, values from reference 145) upon the chelate ring. Accordingly, the titration of Ni(NH$_2$SacNH$_2$Sac)$_2$ and HBF$_4$ was followed polarographically.

A decrease in the height of the Ni(NH$_2$SacNH$_2$Sac)$_2$ reduction waves and the concomitant growth of an oxidation wave indicate that the metathetic reaction

$$\text{Ni(NH}_2\text{SacNH}_2\text{Sac})_2 + 2\text{HBF}_4 \longrightarrow 2\text{NH}_2\text{SacNH}_2\text{SacH} + \text{Ni(BF}_4)_2$$

occurs rather than protonation of the amine function of the intact complex. Confirmation of NH$_2$SacNH$_2$SacH as a reaction product was effected by performing the experiment in the presence of NH$_2$SacNH$_2$SacH and observing a growth and cathodic shift of the NH$_2$SacNH$_2$SacH oxidation wave.

All compounds exhibit an oxidation wave near +0.6V (bis(dithiobiureto)nickel(II) also exhibits an oxidation wave, the potential of which is slightly more anodic). The proximity of these waves to the anodic limit of mercury prevents detailed analyses of such waves at the dme. However, cyclic voltammetric studies reveal that the oxidation process is complex and non-reversible at a platinum electrode (even at very rapid scan rates). The shapes of the cyclic voltammograms seem to indicate coupling of the electron transfer step to one or more chemical reactions, and the non-reversibility of the oxidation process may be attributable to these reactions, rather than to the electron transfer step itself. Although oxidation of a ligand to the 3,5-diamino-1,2-dithiolium cation would explain the lack of reversibility, no evidence of this species is found on the cathodic sweep.

Further, the near equality of the dc pulse voltammetric oxidation and reduction wave heights of Ni(NH$_2$SacNH$_2$Sac)$_2$ at a platinum
Table 2-11. "Stepping" angles in Ni(NH$_2$SacNH$_2$Sac)$_2$,2DMF and related compounds (dtbH = dithiobiuret).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Stepping Angle</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(NH$_2$SacNH$_2$Sac)$_2$.2DMF</td>
<td>23.5</td>
<td>80, present work</td>
</tr>
<tr>
<td>Ni(SacSac)$_2$</td>
<td>8.6</td>
<td>77, 78</td>
</tr>
<tr>
<td>Ni(dtb)$_2$</td>
<td>11</td>
<td>105, 149</td>
</tr>
<tr>
<td>Ni(dtb)$_2$.glycol</td>
<td>31</td>
<td>150</td>
</tr>
<tr>
<td>Ni(dtbH)$_2$(ClO$_4$)$_2$.EtOH</td>
<td>21</td>
<td>151</td>
</tr>
<tr>
<td>Pd(dtb)$_2$</td>
<td>38</td>
<td>149</td>
</tr>
</tbody>
</table>
electrode suggests that both may be associated with the transfer of one electron. Formation of the 3,5-diamino-1,2-dithiolium cation would require the transfer of two electrons per $M(NH_2SacNH_2Sac)_2$ unit; i.e.

$$M^{II}(NH_2SacNH_2Sac)_2 \rightarrow M^{II}(NH_2SacNH_2Sac)^+ + C_3H_5N_2S_2^+ + 2e$$

Thus it seems more likely that the voltammetric oxidation may involve the formation of a Ni(III) species, followed by dissociation to a Ni(IV) species, as has been observed for the oxidation of bis(dithiocarbamato) complexes of the divalent nickel.146,147,148

(vi) X-ray Crystallography

Proof of the $S,S$ mode of chelation in these compounds has been obtained by x-ray crystallography on $Ni(NH_2SacNH_2Sac)_2\cdot2DMF$. This study showed the compound to consist of neutral, monomeric $Ni(NH_2SacNH_2Sac)_2$ molecules linked via hydrogen-bonding to occluded dimethyl formamide molecules, the solvent hydrogen-bonding at the amine protons (Fig. 2-7). The co-ordination of the nickel atom is approximately square planar. There are no axial interactions with the nickel atom, the nearest atom in the axial direction being a solvent carboxylic proton 3.24 Å distant. The shortest intermolecular contact in $Ni(SacSac)_2$ is the 3.68 Å separation between the nickel atoms and methine carbon atoms on adjacent molecules.78 In the present compound, the nickel atom is situated at a centre of symmetry, requiring the two ligands to be equivalent and the nickel and four sulphur atoms to be coplanar. Figure 2-8 illustrates the molecular structure and atomic labelling of $Ni(NH_2SacNH_2Sac)_2\cdot2DMF$. Interatomic distances and angles are collected in Tables 2-9 and 2-10.

The most unusual feature of the structure is that the molecule adopts a "stepped" configuration, with the normals to the mean ligand plane and the NiS₄ plane subtending an angle, $\alpha$ (Fig. 2-9), of 23.5°. This may be compared with the corresponding value of 8.6° in $Ni(SacSac)_2$, in which the "stepping" or "hinging" is not as pronounced, and with the "stepping" in complexes of dithiobiuret and of the dithiobiureto anion (Table 2-11). Perhaps significantly, the dihedral angle $\alpha$ is greater in the $Ni(dtbr)_2$ molecule when glycol is occluded in the crystal. No definite conclusions can be drawn from this however, since solvent...
<table>
<thead>
<tr>
<th>Compound</th>
<th>C-S (Å)</th>
<th>C-C (Å)</th>
<th>C-NH$_2$ (Å)</th>
<th>C-N (Å)</th>
<th>Ni-S (Å) ave.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(NH$_2$SacNH$_2$Sac)$_2$·2DMF</td>
<td>1.724(2)</td>
<td>1.384(3)</td>
<td>1.339(3)</td>
<td>-</td>
<td>2.174</td>
</tr>
<tr>
<td>Ni(SacSac)$_2$</td>
<td>1.734(2)</td>
<td>1.388(3)</td>
<td>1.388(3)</td>
<td>-</td>
<td>2.156</td>
</tr>
<tr>
<td>Ni(dtb)$_2$</td>
<td>1.685(3)</td>
<td>1.381(4)</td>
<td>-</td>
<td>1.32</td>
<td>1.32</td>
</tr>
<tr>
<td>Ni(dtb)$_2$.glycol</td>
<td>1.720(8)</td>
<td>1.34</td>
<td>1.33</td>
<td>1.33</td>
<td>2.171</td>
</tr>
<tr>
<td>Ni(dtb)$_2$.glycol</td>
<td>1.723</td>
<td>1.33</td>
<td>1.33</td>
<td>1.34</td>
<td></td>
</tr>
<tr>
<td>Ni(dtb)$_2$(ClO$_4$)$_2$.EtOH</td>
<td>1.65(2)</td>
<td>1.66(2)</td>
<td>1.38(2)</td>
<td>1.37(2)</td>
<td>1.39(2)</td>
</tr>
<tr>
<td>[Ni(n-Bu$_2$dtc)$_2$]Br</td>
<td>1.708(5)</td>
<td>-</td>
<td>-</td>
<td>1.318(8)</td>
<td>2.261(1)</td>
</tr>
<tr>
<td>dithiobiuret</td>
<td>1.673(3)</td>
<td>-</td>
<td>1.331(4)</td>
<td>1.386(4)</td>
<td>-</td>
</tr>
<tr>
<td>Co(SacSac)$_2$</td>
<td>1.716(13)</td>
<td>1.376(15)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe(pyrrdtc)$_3$ClO$_4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.32(2)</td>
<td>-</td>
</tr>
</tbody>
</table>
interaction is different in Ni(NH₂SacNH₂Sac)₂.2DMF and Ni(dtb)₂.(glycol), and since α is even greater for Pt(dtb)₂. A consequence of the "stepping" is that the nickel atom of Ni(NH₂SacNH₂Sac)₂.2DMF is displaced by 0.57 Å from the mean ligand plane (cf., 0.21 Å in Ni(SacSac)₂).

Tables 2-12 and 2-13 compare the interatomic distances of Ni(NH₂SacNH₂Sac)₂.2DMF with those of related compounds. By contrast with the equivalent C-S bond lengths in each of the divalent cobalt and nickel dithiocacetylacetonates, there are small but significant differences in the C-S bond lengths of Ni(NH₂SacNH₂Sac)₂.2DMF, both of these bonds being longer than those of Ni(SacSac)₂. A similar inequality in C-S bond lengths is observed in those of the nickel dithiobiureto complexes, these bonds being of similar length to those of Ni(NH₂SacNH₂Sac)₂.2DMF.

The ligand C-C bond lengths of Ni(NH₂SacNH₂Sac)₂.2DMF are not significantly different either from each other or from the backbone C-C bond lengths of Ni(SacSac)₂ and Co(SacSac)₂. Similarly, the backbone C-N bond lengths of the nickel dithiobiureto compounds are equal. All of these backbone bonds are of an order intermediate between double and single bonds, but have slightly more double than single bond character (cf. Table 2-14).

No significant difference exists between the C-NH₂ bond lengths of Ni(NH₂SacNH₂Sac)₂.2DMF and the C-NH₂ and C-N bond lengths of the nickel dithiobiureto compounds. These bonds, although of an order intermediate between double and single, possess a substantial amount of double bond character. Their lengths compare favourably with the C-N bond lengths in iron(IV) and nickel(IV) dithiocarbamates, where the limiting resonance form IX is expected.
Table 2-13. Selected interatomic distances ($dtbH$ = dithiobiuret).

<table>
<thead>
<tr>
<th>Compound</th>
<th>NH$_2$ - S</th>
<th>S - S intraligand</th>
<th>S - S interligand</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(NH$_2$SacNH$_2$Sac)$_2$·2DMF</td>
<td>2.65(3)</td>
<td>3.253(1)</td>
<td>2.884(1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.63(3)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(SacSac)$_2$</td>
<td></td>
<td>3.235(2)</td>
<td>2.852(2)</td>
<td>72,78</td>
</tr>
<tr>
<td>Ni(dtb)$_2$</td>
<td></td>
<td>3.220(6)</td>
<td>2.895(6)</td>
<td>105</td>
</tr>
<tr>
<td>Ni(dtb)$_2$·glycol</td>
<td>2.78(7)</td>
<td>3.200(3)</td>
<td>2.933(3)</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>2.69(7)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni(dtbH)$_2$(ClO$_4$)$_2$·EtOH</td>
<td>2.83</td>
<td>2.66</td>
<td>3.235(5)</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td>2.61</td>
<td>2.64</td>
<td>3.215(5)</td>
<td>151</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2.889(6)</td>
<td></td>
</tr>
<tr>
<td>dithiobiuret</td>
<td>2.77(4)</td>
<td></td>
<td></td>
<td>153</td>
</tr>
<tr>
<td></td>
<td>2.46(4)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(SacSac)$_2$</td>
<td></td>
<td>3.242(6)</td>
<td>2.874(6)</td>
<td>72,78</td>
</tr>
</tbody>
</table>
to make an important contribution to the bonding.

The ligand bond distances, then, indicate that the resonance structure for the ligand VI in

\[
\begin{array}{c}
\text{NH}_2 \\
\text{S} & \text{S} & \\
\text{S} & \text{C} & \text{N} \\
\text{NH}_2
\end{array}
\]

\text{VI}

Ni(NH$_2$SacNH$_2$Sac)$_2$.2DMF makes a significant contribution to the bonding in this compound. This finding substantiates the arguments above regarding the Pt-H nmr coupling constants and the frequency of the C-S bond stretching mode infra-red absorption, and challenges the assignment of Peyronel. 104

It should, however, be noted that the chelate ring and the amine substituents are not completely co-planar, the C-N bonds and the mean ligand plane subtending angles of 2.9° and 6.0° (Fig. 2-10). These angles can be attributed to intermolecular hydrogen-bonding interactions. Hydrogen-bond interactions in Ni(NH$_2$SacNH$_2$Sac)$_2$.2DMF would appear to be significant in the crystal and molecular structure. In both the intraligand N-H...S and intermolecular N-H...DMF interactions the
Table 2-14. Bond lengths for various C - X bond orders. Values from reference 155.

<table>
<thead>
<tr>
<th>Bond Lengths</th>
<th>Value (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Carbon-Carbon</strong></td>
<td></td>
</tr>
<tr>
<td>Single Bond</td>
<td></td>
</tr>
<tr>
<td>Paraffinic</td>
<td>1.541 ± 3</td>
</tr>
<tr>
<td>In Diamond</td>
<td>1.54452 ± 14</td>
</tr>
<tr>
<td>Double Bond</td>
<td>1.337 ± 6</td>
</tr>
<tr>
<td><strong>Carbon-Nitrogen</strong></td>
<td></td>
</tr>
<tr>
<td>Single Bond</td>
<td></td>
</tr>
<tr>
<td>Paraffinic</td>
<td>1.472 ± 5</td>
</tr>
<tr>
<td>Shortened (partial double bond) in N-C=0, e.g., HCO.NH₂</td>
<td>1.322 ± 3</td>
</tr>
<tr>
<td>Double Bond</td>
<td>1.252(7)</td>
</tr>
<tr>
<td><strong>Carbon-Sulphur</strong></td>
<td></td>
</tr>
<tr>
<td>Single Bond</td>
<td></td>
</tr>
<tr>
<td>Paraffinic, e.g., CH₃.SH</td>
<td>1.81(5) ± 1</td>
</tr>
<tr>
<td>Double Bond</td>
<td></td>
</tr>
<tr>
<td>Calculated value</td>
<td>1.61</td>
</tr>
</tbody>
</table>


\[ ^b \] B.F. Hoskins unpublished results.
interatomic distances are shorter than the respective sums of the van der Waals radii.\textsuperscript{156}

The presence of an inversion centre at the nickel atom requires the NiS\textsubscript{4} plane to be perfectly planar. One Ni-S bond is longer than the other, this slight inequivalence also being evident in the nickel dithiobiureto complexes. The average Ni-S bond lengths in Ni(NH\textsubscript{2}SacNH\textsubscript{2}Sac)\textsubscript{2}.2DMF and the nickel dithiobiureto complexes are approximately the same, but are all greater than those of Ni(SacSac)\textsubscript{2}. In all of these compounds, the intraligand S-Ni-S angles and the dimensions of the S\textsubscript{4} rectangles are very similar. Slightly greater non-bonded S...S distances in Ni(NH\textsubscript{2}SacNH\textsubscript{2}Sac)\textsubscript{2}.2DMF by comparison with those of Ni(SacSac)\textsubscript{2} may be interpreted in terms of higher charge density on the sulphur atoms of the former compound as a consequence of the importance of the resonance structure (VI), thereby creating slightly greater S...S separations.

The interligand S...S distances are significantly less than twice the van der Waals radius of sulphur (2 × 1.76 Å = 3.52 Å). Distances such as these have previously been interpreted as indicating some interaction between the sulphur atoms.\textsuperscript{78,105,157,158}

It might be expected that significant contributions of the resonance form VI to the bonding in Ni(NH\textsubscript{2}SacNH\textsubscript{2}Sac)\textsubscript{2}.2DMF would result in the Ni-S bond being shorter than that of Ni(SacSac)\textsubscript{2}. That this is not so is apparently a consequence of the near equality of the S...S interchelate distances and S-Ni-S angles in these compounds.

Reference to Figure 2-11 shows that the angles in the respective ligand backbones are effectively the same for Ni(SacSac)\textsubscript{2} and Ni(NH\textsubscript{2}SacNH\textsubscript{2}Sac)\textsubscript{2}.2DMF. The differences in angles between these compounds occur in the vicinity of the co-ordinating centre. The smaller C-S-Ni angle in the present compound can be attributed to the increased hinging. Similarly, the slightly smaller S-Ni-S intraligand angle is a consequence of the longer Ni-S bond in Ni(NH\textsubscript{2}SacNH\textsubscript{2}Sac)\textsubscript{2}.2DMF. Beckett and Hoskins have previously interpreted the deviations of the bond angles of the M(SacSac)\textsubscript{2} (M = Ni, Co) compounds from their expected values in terms of simple geometrical considerations. Similar arguments are expected to apply in the present case.
Figure 2-10. Schematic illustration of deviations of NH$_2$ groups from mean ligand planes in Ni(NH$_2$SacNH$_2$Sac)$_2$.2DMF. Compound viewed end on.
Thus, the x-ray crystallographic study proves the square planar NiS$_4$ co-ordination in Ni(NH$_2$SacNH$_2$Sac)$_2$.2DMF inferred above from other physical measurements, and validates interpretations of these physical measurements based on assumptions of probable ligand structure.

(d) FURTHER SYNTHETIC STUDIES

The presence of the NH$_2$ substituents on dithiomalonamide makes possible two further extensions of dithio-β-diketonate chemistry. As noted earlier, the powerful electron-donating properties of these NH$_2$ groups can be anticipated to stabilise high oxidation state compounds. Thus, it might be expected that copper would form a monomeric copper(II) complex with dithiomalonamide, rather than an analogue of the trimeric copper(I) complex formed with O-ethylthioacetothioacetate. If the stabilising influence of the NH$_2$ groups is sufficient, an electron-transfer series

$$\text{Cu(III)L}_2^+ \rightleftharpoons \text{Cu(II)L}_2 \rightleftharpoons \text{Cu(I)L}_2^-$$

could perhaps be detected, at least electrochemically.

Similarly, complexes of octahedral iron(IV), octahedral cobalt(IV) (and perhaps square planar cobalt(III) — vide infra) might be isolated by oxidation of Fe(III)L$_3$ and Co(III)L$_3$. One additional advantage provided by this system is that there would be little ambiguity in assigning the metal oxidation state, since ligand oxidation would yield the easily detectable, essentially non-co-ordinating 3,5-diamino-1,2-dithiolium cation.

Unfortunately, however, reactions of the dithiomalonamidate anion with iron, cobalt, copper and zinc cations yielded very insoluble precipitates which could not be purified by the usual methods of recrystallisation (no reaction was observed with chromium). In this regard, it is perhaps significant that the original report of Ni(NH$_2$SacNH$_2$Sac)$_2$ was part of the quest for inorganic polymers.

The second property of the NH$_2$ substituents explored in the present work is the synthetic opportunities provided by these groupings. Thus, reaction of 3,5-diamino-1,2-dithiolium iodide with acetic anhydride yields the corresponding N,N'-diacetyl salts.
Figure 2-11. Comparison of interatomic angles in Ni(SacSac)$_2$ (lower, italicised) and Ni(NH$_2$SacNH$_2$Sac)$_2$.2DMF (upper, bold).
possibility therefore arises of reacting the NH$_2$ groups of Ni(NH$_2$SacNH$_2$Sac)$_2$ to incorporate substituents with varying electron-donating capabilities in the molecule. In this way compounds of otherwise unobtainable ligands might be synthesized. A number of such reactions were attempted and the results discussed below.

(i) Reaction with Acid

As noted above, polarographic studies indicated that addition of acid to Ni(NH$_2$SacNH$_2$Sac)$_2$ results in generation of NH$_2$SacNH$_2$SacH, rather than protonation of the NH$_2$ groups.

(ii) Acetylation

Refluxing Ni(NH$_2$SacNH$_2$Sac)$_2$ in acetic anhydride failed to acetylate the NH$_2$ groups and yielded only Ni(NH$_2$SacNH$_2$Sac)$_2$.

(iii) Diazotisation

A dithio-$\beta$-diketonate complex with CN substituents can be expected to provide the greatest stabilisation of low oxidation state compounds ($\Omega_{\text{CN}} = +0.68$). Introduction of this substituent into the chelate ring was attempted via diazotisation of Ni(NH$_2$SacNH$_2$Sac)$_2$. Whilst some reaction with sodium nitrite was evident, subsequent reaction with cyanide or iodide ions was unsuccessful. Although a significant substituent effect is anticipated with N$_2^+$ as a substituent ($\Omega_{\text{N}_2^+} = +1.76^{159}$), no attempt was made to isolate this potentially highly explosive derivative.
CHAPTER 3

FURTHER DERIVATIVES OF DITHIOACETYLACETONE

The synthesis of dithioacetylacetone complexes of the Group VIII metals is not yet a reality. Extension of the range of dithioacetylacetone complexes to other metal ions requires further experimental work.

The 1,2-dimethyl-1,2-dithioacetone cation and the dithioacetylacetone anion are rotated by a two-electron reduction transfer. Reaction of the strongly reducing thiosalol(I) and with 1,2-dimethyl-1,2-dithioacetone yields a salt, that in the synthesis of dithioacetylacetone and chromous(I) chloride. Analogously, dithioacetone cannot be produced by addition of dichromate(VI) and thiosalol sources with dithioacetylacetone anions. The former reaction is apparently a result of the intimate thiosalol-dithioacetone contact or insertion by the electron transfer.
Dithioacetylacetonates are commonly prepared by the action of hydrogen sulphide on acidified acetylacetone solutions containing the appropriate metal ion. This procedure circumvents formation of the non-co-ordinating dimeric form of the ligand (I), and leads to isolation of the monomeric complexes (II). However, this method is appropriate to the syntheses of dithioacetylacetonato complexes of the Group VIII metals only. Extension of the range of dithioacetylacetonato complexes therefore requires recourse to other synthetic routes.

The 3,5-dimethyl-1,2-dithiolium cation and the dithioacetylacetonate anion are related by a two-electron electron transfer. Reaction of the strongly reducing chromium(II) ion with 3,5-dimethyl-1,2-dithiolium iodide results, then, in the synthesis of tris(dithioacetylacetonato)chromium(III), Cr(SacSac)_3. Significantly, Cr(SacSac)_3 cannot be produced by admixture of chromium(III) and solutions containing dithioacetylacetonate anions. The present synthesis is apparently a result of the intimate chromium-dithiolium contact necessitated by the electron transfer.
Table 3-1. Infra-red bands (cm⁻¹) and assignments.

<table>
<thead>
<tr>
<th>Maxima</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1465</td>
<td>C-C stretch and C-H bend</td>
</tr>
<tr>
<td>1360</td>
<td>CH₃ deformation</td>
</tr>
<tr>
<td>1327</td>
<td>C-C stretch</td>
</tr>
<tr>
<td>1305</td>
<td>C-H in-plane bend</td>
</tr>
<tr>
<td>1150</td>
<td>C-CH₃ stretch</td>
</tr>
<tr>
<td>1005</td>
<td>CH₃ rocking</td>
</tr>
<tr>
<td>842</td>
<td>C-H out-of-plane bend</td>
</tr>
<tr>
<td>738</td>
<td>C-S stretch and C-CH₃ stretch</td>
</tr>
<tr>
<td>690</td>
<td>C-S stretch</td>
</tr>
<tr>
<td>555</td>
<td>C-CH₃ stretch and ring deformation</td>
</tr>
<tr>
<td>358</td>
<td>Cr-S stretch</td>
</tr>
</tbody>
</table>
(a) TRIS(DITHIOACETYLACETONATO)CHROMIUM(III), Cr(SacSac)$_3$

Crystalline Cr(SacSac)$_3$ is a dark-green paramagnetic material which is indefinitely stable to air and moisture but decomposes at 180 °C. It dissolves in various organic solvents to give intense wine-red (transmitted light) solutions which may decompose after standing for several days. Molecular weight measurements indicate that the complex is monomeric in chloroform.

The mass spectrum is characterised by a strong molecular ion peak at $m/e$ 445, corresponding to the monomeric molecular ion [Cr(SacSac)$_3$]$^+$, and by a peak at $m/e$ 314 corresponding to [Cr(SacSac)$_2$]$^+$. As with other dithioacetylacetonato complexes, the most abundant ion in the spectrum has $m/e$ 131, and is ascribed to the resonance-stabilised 3,5-dimethyl-1,2-dithiolium cation $[CsH_7S_2]^+$, derived by two-electron loss from the ligand.

The infra-red spectrum (2000 - 300 cm$^{-1}$) of Cr(SacSac)$_3$ closely resembles those of other M(SacSac)$_3$ complexes (for example, Co(SacSac)$_3$ whose spectrum is reproduced in ref. 52). Assignments based on the normal co-ordinate analysis of Co(SacSac)$_2$ are given in Table 3-1. The strong band at 1465 cm$^{-1}$ is characteristic of the tervalent dithioacetylacetonates and distinguishes them from their divalent analogues in which this band is raised to c. 1490 cm$^{-1}$.

Results of magnetic susceptibility measurements in the range 77 - 292 K are summarised in Table 3-2. The effective magnetic moment is 3.89 B.M. at room temperature and decreases steadily at lower temperatures. A plot of $1/\chi_M'$ against temperature is linear, and the estimated value of the Weiss constant is $\theta = 20^\circ$. Recalculation according to $\mu_{\text{eff}} = 2.83[\chi_M'(T + \theta)]^{\frac{1}{2}}$ leads to a temperature-independent moment of 3.99 B.M.; however, the physical significance of $\theta$ is not clear. Similar Curie-Weiss magnetic behaviour is found in the M(SacSac)$_3$ complexes of Fe, Ru, and Os, and one possibility is that partial delocalisation of electron spin from t$_{2g}$ metal orbitals into ligand orbitals allows weak intermolecular lattice antiferromagnetism. Mössbauer spectroscopic studies have established that the magnetic moment of Fe(SacSac)$_3$ is due both to splitting of the $^5T_{2g}$ ground state as a result of the lower than octahedral symmetry of the complex, and to interaction between the ground state and excited states of suitable
Table 3-2. Magnetic properties.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$10^6\chi'_M$ (cm$^3$ mol$^{-1}$)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
<th>T (K)</th>
<th>$10^6\chi'_M$ (cm$^3$ mol$^{-1}$)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>292</td>
<td>6439</td>
<td>3.89</td>
<td>159</td>
<td>11025</td>
<td>3.76</td>
</tr>
<tr>
<td>264</td>
<td>6946</td>
<td>3.85</td>
<td>142</td>
<td>12295</td>
<td>3.75</td>
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<td>244</td>
<td>7509</td>
<td>3.84</td>
<td>123</td>
<td>14035</td>
<td>3.74</td>
</tr>
<tr>
<td>226</td>
<td>8084</td>
<td>3.84</td>
<td>103</td>
<td>16165</td>
<td>3.66</td>
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<tr>
<td>203</td>
<td>8883</td>
<td>3.81</td>
<td>77</td>
<td>20655</td>
<td>3.66</td>
</tr>
<tr>
<td>183</td>
<td>9717</td>
<td>3.78</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Diamagnetic correction for ligands = $3(85 \times 10^{-6})$ cm$^3$ mol$^{-1}$. $\mu_{\text{eff}} = 2.828 [\chi'_M T]^{1/2}$. 
symmetry. In the absence of dilution and crystallographic studies, it is not possible to determine to what extent any of these factors operates in Cr(SacSac)₃.

The magnetic moment found for Cr(SacSac)₃ is typical of octahedral chromium(III) complexes. It may be compared with the spin-only value (3.87 B.M.) and with \( \mu_{\text{eff}} \) for Cr(acac)₃ \( ^{160} \) (3.86 B.M.) and Cr(dtb)₃ (3.90 B.M.), \( ^{161} \) the latter being similar to a whole range of CrS₆ complexes.

The esr spectrum of Cr(SacSac)₃ in polycrystalline form at room temperature is characterised by a broad band centred at \( g = 1.97 \pm 0.10 \). Similar broad absorption lines have been observed for other CrS₆-type compounds. \( ^{162,163} \) It was not possible to obtain satisfactory spectra in liquid or in frozen solutions.

Initial comparisons between the metal dithioacetylacetonato and 1,2-dithiolene complexes were made between the neutral compounds. However, it was subsequently indicated \( ^{144} \) that since the dithioacetylacetonato ligand represents the most reduced member of a hypothetical ligand electron-transfer series, such comparisons should be drawn between the neutral dithioacetylacetonato complexes, and 1,2-dithiolene complexes with the ligand in the form (III). Heath \( ^{82} \) has remarked that

\[ \text{III} \]

\[ \text{S} \quad \text{S} \]

"... if any ambiguity of metal oxidation states is to be found in the dithioacetylacetonates, it seems likely to occur in the complexes of earlier transition metals, such as [Cr(SacSac)₃], where substantial \( m \)-electron depletion of the ligands could occur. ..."

In the light of the above, it is interesting to speculate on possible structures of Cr(SacSac)₃.

\( ^{\dagger} \) Where acac\(^-\) = acetylacetonate, dtb\(^-\) = dithiobenzoate.
Figure 3-1. Electronic spectrum of Cr(SacSac)$_3$. 

$10^{-3} \times \text{wavenumber (cm}^{-1})$

$10^{-3} \; \epsilon$
Neutral Cr(S_2C_2Ph_2)_3 is isomorphous with trigonal prismatic V(S_2C_2Ph_2)_3. On the basis of electrochemical and spectroscopic data, V(S_2C_2Ph_2)_3^- has also been assigned a trigonal prismatic structure. However, V(mnt)_3^-2, with which Cr(mnt)_3^-2 is isomorphous, does not adopt a trigonal prismatic geometry, but rather one described as a "trigonally distorted octahedron." Cr(mnt)_3^-3 has been inferred to be more nearly octahedral than trigonal prismatic, and its optical spectrum has been interpreted as that of a high spin octahedral complex. The geometries of Cr(O_2C_2O_2)_3^-3 and Cr(acac)_3 may be described as octahedral.

Thus, Cr(SacSac)_3 may be expected to possess an octahedral CrS_6 core, although in keeping with the above, and by comparison with Fe(SacSac)_3, some distortion from an octahedral geometry would not be surprising.

In acetone, Cr(SacSac)_3 undergoes a reversible one-electron reduction at -0.493 V against Ag/AgCl. At more negative potential (-1.28 V against Ag/AgCl) a non-reversible reduction occurs. These processes are discussed in Chapter 7.

The reversibility of the first step is consistent with an electrode reaction in which molecular structure remains intact, i.e.

\[ \text{[Cr(SacSac)_3] + e}^- \rightleftharpoons \text{[Cr(SacSac)_3]}^- \]

A similar reversible one-electron reduction occurs at less negative potentials (c. 0 V against Ag/AgCl) for the t_2^5 complexes Fe(SacSac)_3, Ru(SacSac)_3, and Os(SacSac)_3.

The electronic spectrum of Cr(SacSac)_3 in the region 10000 - 45000 cm\(^{-1}\) reveals a series of intense bands (see Fig. 3-1) and has a marked resemblance to the spectra of the tris(dithioacetylacetonates) of iron(III) and cobalt(III). The principal spectral features of these three complexes are collected in Table 3-3. Their similarity suggests that the spectra are dominated by ligand-ligand and charge-transfer transitions and that the d-d transitions of the central ion are concealed. Electronic absorption bands corresponding to bands 1, 2, 3, and 4 are found likewise in the 3d\(^{10}\) complex Zn(SacSac)_2 (vide infra).
### Table 3-3

**A. Electronic spectra of M(SacSac)₃ complexes**

<table>
<thead>
<tr>
<th>Band</th>
<th>Cr(SacSac)₃</th>
<th>Fe(SacSac)₃</th>
<th>Co(SacSac)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42910(36100)</td>
<td>not measured</td>
<td>42000(40000)</td>
</tr>
<tr>
<td>2</td>
<td>34480(25000)</td>
<td>33000(41000)</td>
<td>33000(38000)</td>
</tr>
<tr>
<td>3</td>
<td>28580</td>
<td>29000(Ru, Os)</td>
<td>29000</td>
</tr>
<tr>
<td>4</td>
<td>22620(6650)</td>
<td>22600(6000)</td>
<td>22000</td>
</tr>
<tr>
<td>5</td>
<td>17500(2875)</td>
<td>18000(3500)</td>
<td>18500(3000), 17500(3000)</td>
</tr>
<tr>
<td>6</td>
<td>13150</td>
<td>13000(790)</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>10900(710)</td>
<td>-</td>
</tr>
</tbody>
</table>

In benzene (10000 - 30000 cm⁻¹) and cyclohexane (30000 - 45000 cm⁻¹) (ν in cm⁻¹, ε (L cm⁻¹ mol⁻¹) in parenthesis, shoulders in *italics*).

**B. Electronic spectra of M(SacSac)₂ (M = Ni, Zn) complexes.**

<table>
<thead>
<tr>
<th>Ni(SacSac)₂</th>
<th>Zn(SacSac)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>41150(169800)</td>
<td>43300(30200)</td>
</tr>
<tr>
<td>36500(45700)</td>
<td></td>
</tr>
<tr>
<td>35460(38900)</td>
<td>35000(13100)</td>
</tr>
<tr>
<td>31800(4700)</td>
<td></td>
</tr>
<tr>
<td>29670(21400)</td>
<td>29200(2800)</td>
</tr>
<tr>
<td>25510(4200)</td>
<td>22600(19800)</td>
</tr>
<tr>
<td>20600(8000)</td>
<td></td>
</tr>
<tr>
<td>18120(2800)</td>
<td></td>
</tr>
<tr>
<td>14890(3200)</td>
<td></td>
</tr>
</tbody>
</table>

*a* From reference 82.

*b* In cyclohexane solution.
The band near 11000 cm$^{-1}$ in the $t_{2g}$ complexes, which is absent in the $e_g$ complexes, has been assigned as an unusually low-energy $\pi \rightarrow t_{2g}$ charge-transfer transition. This charge transfer apparently moves to higher energy in Cr(SacSac)$_3$ ($t_{2g}^3$), which is consistent with the more negative potential required for one-electron reduction of Cr(SacSac)$_3$ compared with Fe(SacSac)$_3$. Both these observations reflect the special stability assigned to half-filled and filled states of the ligand-field stabilised $t_{2g}$ electronic level.

The relatively positive $E_{1/2}$ value and the high degree of reversibility associated with the reduction of Cr(SacSac)$_3$ suggest that the formally chromium(II) species, Cr(SacSac)$_3^-$ might be isolated. Accordingly, the electrochemical reduction of Cr(SacSac)$_3$ at a platinum electrode was monitored spectrophotometrically over the region 30000 - 14000 cm$^{-1}$ in acetone/0.1 M TEAP. An increase in intensity of the absorption band 4 of Cr(SacSac)$_3$ and the appearance of several new absorption bands is apparent from Figure 3-2. These bands appear to be due to Cr(SacSac)$_3^-$, however, this formally chromium(II) complex has not yet been isolated. It is possible that Cr(SacSac)$_3^-$ could undergo slow follow-up chemical reactions which would render the Cr(SacSac)$_3^+$ Cr(SacSac)$_3^-$ reduction non-reversible on the coulometric time-scale. Cr(acac)$_3$ is shown in Chapter 7 to undergo some chemical reaction which affects only the longer time-scale electrochemical experiments.

The obvious extension of the Cr(SacSac)$_3$ synthesis is application to other strongly reducing metals with readily accessible, easily oxidised oxidation states. A seemingly suitable reductant is vanadium(II), which may be generated via a zinc/mercury amalgam in a manner analogous to chromium(II). Accordingly, the synthesis of V(SacSac)$_3$ was attempted under a nitrogen atmosphere. Reaction appeared to proceed and a small amount of product was isolated. The presence of an infra-red absorption at 1490 rather than 1460 cm$^{-1}$ indicated a bis- rather than a tris-chelate (vide supra). Comparison with the infra-red spectrum of Zn(SacSac)$_2$ showed the product of the reduction of 3,5-dimethyl-1,2-dithiolium iodide with vanadium(II) to be Zn(SacSac)$_2$, Zn$^{+2}$ ions coming from the Zn/Hg amalgam. An attempt to synthesise V(SacSac)$_3$ using an electrolytically generated vanadium(II) solution was also unsuccessful. It would therefore appear that vanadium(II) is...
Figure 3-2. Electronic spectrum of Cr(SacSac)$_3$ before (lower) and after (upper) coulometry at -0.8 V.
capable of reducing the 3,5-dimethyl-1,2-dithiolium cation, but that complexation of vanadium(III) does not occur. Isolation of V(SacSac)$_3$ may be possible at lower temperatures.

These observations indicate the possibility of producing solutions of the dithioacetylacetone anion in which the only contaminants are vanadium(III) ions (or higher oxidation state vanadium species) and the dithiolium counter-anion. Physicochemical data on the dithioacetylacetone anion can then, in theory, be collected. Such simply constituted solutions should also find convenient synthetic applications.

(b) BIS(DITHIOACETYLACETONATO)ZINC(II), Zn(SacSac)$_2$

Reduction of the 3,5-dimethyl-1,2-dithiolium cation can also be effected by sodium borohydride as indicated earlier. This method leads to Zn(SacSac)$_2$.$^+$ Attempts to complete the d$^{10}$ triand were unsuccessful. Although its synthesis was indicated by the infra-red spectrum of the crude product, Cd(SacSac)$_2$ decomposed during purification procedures. Attempts to prepare the compound in the absence of oxygen or at lower temperatures were of no avail. Unlike Fe(SacSac)$_3$, which also decomposes in solution,$^{36}$ Cd(SacSac)$_2$ could not be synthesised in a pure form, and was also unstable in the solid state. A yellow precipitate was fleetingly observed when the borohydride reduction method was extended to mercury(II).$^{170}$

The relative stabilities of the d$^{10}$ metal M(SacSac)$_2$ compounds (Hg $<$ Cd $<$ Zn) therefore parallels that of the analogous M(OEtSacSac)$_2$ compounds, although the latter are more stable than the former, and can all be isolated and characterised.$^2,^3$

Table 3-3 includes the electronic spectrum of Zn(SacSac)$_2$. Ligand to metal charge transfer excitations in Zn(SacSac)$_2$ are precluded by the d$^{10}$ configuration of zinc(II). Thus, the absorptions in Table 3-3 clearly support the assignments of Heath and Martin.

$^+$ This work was performed in collaboration with Dr. A.R. Hendrickson. Other properties of Zn(SacSac)$_2$ appear in reference 2. The following is the work of the present author, except where that of Dr. Hendrickson is acknowledged.
The mass spectrum of Zn(SacSac)\textsubscript{2} is quite similar to those of other M(SacSac)\textsubscript{2} complexes. Thus, a low intensity molecular ion is observed, with the most intense peak in the spectrum being at \( m/e \) 131, attributable to the 3,5-dimethyl-1,2-dithiolium ion. A ZnL\textsuperscript{+} peak is observed in the mass spectrum of Zn(OEtSacSac)\textsubscript{2}, but a corresponding peak cannot be established for Zn(SacSac)\textsubscript{2} without high resolution data since a large peak at \( m/e \) 196 (which is also observed in the mass spectra of Cr(SacSac)\textsubscript{3} and of \( C_{16}H_{14}S_{4} \)) overlaps with the Zn-2S isotope pattern region (\( m/e \) for Zn\textsuperscript{64}(SacSac)\textsuperscript{+} is 195).

(c) 1,2-DITHIOLIUM IODIDE, \( C_{3}H_{3}S_{2}I \)

Prior to the present work, the unsubstituted 1,2-dithiolium cation \( C_{3}H_{3}S_{2}^{+} \) was obtained either as its perchlorate, or as its iodide salt. Both syntheses are quite involved, the former yielding an unsatisfactory counter-anion, and the latter requiring the initial step of boiling diethyl fumarate in sulphur! A more convenient synthesis has been developed in the course of this work. This method involves reaction of malondialdehyde tetraethylacetal with hydrogen sulphide in the presence of hydrogen chloride and iodine, which is somewhat analogous to the preparation of other substituted-1,2-dithiolium iodides by Martin and co-workers,\textsuperscript{68,72} and affords 1,2-dithiolium iodide in good yield; its synthesis being established by elemental analyses and comparisons with published properties.
(d) BIS(1,3-DITHIOPROPANEDIALATO)NICKEL(II), Ni(HSacHSac)$_2$

The isolation of 1,2-dithiolium iodide combined with the known reducibility of substituted-1,2-dithiolium cations, raises the interesting possibility of synthesising $M(HSacHSac)_2$ complexes (IV).

\[
\text{IV}
\]

Such compounds, apart from being of intrinsic interest as the "parent" metal dithio-β-diketonato complexes, are of fundamental importance for the comparative study of the $M(SacSac)_n$ and related compounds. They provide convenient reference points for the study of substituent effects, and also systems in which physical data uncomplicated by substituent behaviour may be obtained. Obvious examples of this latter application are in the mass, infra-red and pmr spectra. Whilst the corresponding monothio-analogue, Ni(HSacHac)$_2$ (V)

\[
\text{V}
\]

has been isolated, it has not been extensively studied. Cr(HacHac)$_3$ is also known.

Reduction of 1,2-dithiolium iodide by sodium borohydride in the presence of nickel chloride yields a black or dark green product tentatively identified as Ni(HSacHSac)$_2$. Completely satisfactory
Table 3-4. pmr absorptions of dithiolium salts (A) and related nickel bis(dithio-β-diketonato) compounds (B) (δ-values ppm vs. TMS as reference).

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ_R</th>
<th>δ_H</th>
<th>Solvent</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>R = Me</td>
<td>3.12</td>
<td>8.21</td>
<td>Trifluoroacetic acid</td>
<td>72</td>
</tr>
<tr>
<td>B</td>
<td>2.31</td>
<td>7.06</td>
<td>CDCl₃</td>
<td>44</td>
</tr>
<tr>
<td>R = NH₂</td>
<td>8.9</td>
<td>6.59</td>
<td>Acetone-d₆</td>
<td>this work</td>
</tr>
<tr>
<td>B</td>
<td>7.11</td>
<td>5.59</td>
<td>DMSO-d₆</td>
<td>this work</td>
</tr>
<tr>
<td>R = H</td>
<td>10.57</td>
<td>8.88</td>
<td>Trifluoroacetic acid</td>
<td>117</td>
</tr>
<tr>
<td>B</td>
<td>3.46</td>
<td>1.52</td>
<td>CDCl₃</td>
<td>this work</td>
</tr>
</tbody>
</table>

![Chemical structures](image)

A

B
elemental analyses could not be obtained, possibly as a result of decomposition during recrystallisation. This instability is confirmed by a slow change in the pmr spectrum of the crude material with time. The compound appears more stable in the solid state, since samples prepared some time apart showed similar mass spectra. Beyer and Schöne remark that Ni(HSacSac)₂ is stable for only a short time in air and is then converted to a presumably polymeric product, which is insoluble in the customary solvents. It would appear that somewhat similar behaviour is exhibited by Ni(HSacHSac)₂ and that this mild sensitivity to air is responsible for the unsatisfactory analyses.

Mass spectrometric measurements clearly established the presence of some unreached 1,2-dithiolium iodide in the solid. Because of this impurity, no detailed analysis of the mass spectrum can be attempted here. Significantly, the mass spectrum of 1,2-dithiolium iodide shows no substantial peaks at m/e > 103, other than those of Sₓ (Chapter 4). Most importantly, however, a cluster of peaks corresponding to a NiS₄ isotope pattern is observed around m/e 264, a value corresponding to Ni(HSacHSac)²⁺. A cluster of peaks is also observed around m/e 161, which would correspond to Ni(HSacHSac)⁺, although no definite assignment can be made because of interference from S₅ (m/e 160) peaks.

The mass spectrum, then, is entirely consistent with the formulation of the product as monomeric Ni(HSacHSac)₂.

A pmr spectrum was obtained from a filtered solution of the crude material. The peaks observed are tabulated in Table 3-4, those of the 1,2-dithiolium cation, Ni(SacSac)₂, and the 3,5-dimethyl-1,2-dithiolium cation being provided for comparison.

On the basis of integrated peak areas, the pmr spectrum of "Ni(HSacHSac)₂" is assigned as in Table 3-4. This assignment is at first surprising, inasmuch as the methine proton resonance absorptions in M(SacSac)ₙ compounds have always been observed at lower field than the methyl resonance absorptions. However, the relative positions of the resonances of the protons ortho and meta to the sulphur atoms completely parallel the ordering of these absorptions in the 1,2-dithiolium cation. This phenomenon is observed in other metal dithio-β-diketonato compounds (Table 3-4). Thus, the assignments of
Figure 3-3. Infra-red spectrum of "Ni(HSacHSac)₂" (lower). The infra-red spectrum of 1,2-dithiolium iodide is included for comparison. Spectra of solid samples suspended in KBr discs.
Table 3-4 are in complete accord with the nmr behaviour of M(SacSac)$_2$ compounds with regard to the relative positions of the peaks. Unfortunately no splitting of the peaks which might further substantiate their assignment could be resolved.

Whilst the relative positions of the H$_1$ and H$_2$ peaks in the Ni(HSacHSac)$_2$ pmr spectrum are readily explained, their absolute positions are, however, surprising. Although no comparison can be made between the position of the peak due to H$_1$ and H$_3$ resonances and the positions of peaks due to substituents on carbon atoms 1 and 3 in other metal dithio-$\beta$-diketonato complexes, H$_2$ is by far the most shielded proton yet observed on carbon atom 2. Similarly, the shift in resonance positions of the protons of the 1,2-dithiolium cation upon reduction and complexation is far greater than the corresponding shift in the resonance positions of the 3,5-dimethyl-1,2-dithiolium cation protons.

The infra-red spectrum of the crude material is displayed in Figure 3-3. Whilst no definite assignments are possible at this stage, the spectrum is not inconsistent with the formulation Ni(HSacHSac)$_2$.

The demonstration that the 3,5-dimethyl-1,2-dithiolium cation can be reduced by borohydride to give solutions of the dithioacetylacetonate anion opens the way to incorporation of this method into other synthetic routes to complexes of dithiochelates.

(e) BIS(T-CYCLOPENTADIENYL)(DITHIOACETYLACETANATO)VANADIUM(IV) TETRAFLUOROBORATE, [cp$_2$V(SacSac)][BF$_4$]

Casey and Thackeray$^{173-176}$ have prepared an extensive series of vanadium(IV) compounds of the type [cp$_2$L]$^z$ (z = +1 for L = uninegative ligand, z = 0 for L = dinegative ligand) where L is a bidentate sulphur-donor ligand. Combination of their synthetic method and the borohydride reduction of the 3,5-dimethyl-1,2-dithiolium cation$^+$ yields dark green crystals of [cp$_2$V(SacSac)][BF$_4$]. The electronic, infra-red and esr spectra of this compound$^{177}$ are typical of those reported for this series of compounds.

$^+$ The synthetic work was performed in collaboration with Dr. J.R. Thackeray.
Figure 3-4. Rapid scan rate cyclic voltammograms of $[\text{cp}_2\text{V}(\text{SacSac})]^{+/-0}$ couple. Scan rate 5 V sec$^{-1}$. A, mercury electrode (0 V to -0.6 V); B, platinum electrode (+0.1 V to -0.7 V).
[cp₂V(SacSac)][BF₄] is reduced (E₁/₂ = -0.368 V) in a reversible one-electron process at both platinum and mercury electrodes (Table 3-5). Additional non-reversible reductions occur at more negative potentials. The reversibility of these non-reversible steps did not improve under very rapid scan rate cyclic voltammetric experiments and they were not characterised further. No oxidation processes were observed.

Rapid scan rate cyclic voltammograms at both platinum and mercury electrodes (Fig. 3-4) establish that the rate of heterogeneous charge transfer k_s is extremely large (see Chapter 5 for a discussion of the evaluation of kinetic parameters). A k_s value of 5 x 10⁻² cm sec⁻¹ can be calculated from the cyclic voltammogram of Figure 3-4, assuming a diffusion coefficient of 1 x 10⁻⁵ cm² sec⁻¹. The rapidity of this process is confirmed by a linear I_p vs. ω¹/₂ plot of the ac polarographic data.

In the presence of oxygen, the first reduction becomes quite non-reversible, only a very small peak being observed on the anodic cyclic voltammetric sweep. The non-reversible behaviour persists even with very rapid scan rate cyclic voltammetric sweeps. However, the reduction again becomes reversible if the oxygen is removed by degassing.

Similar behaviour has been reported for other members of this class of compounds having various dithio-ligands, and the generalised E C E mechanism below has been established.¹⁷⁸-¹⁸⁰

\[
[cp₂VL]^{z-1} + e \rightleftharpoons [cp₂VL]^{z-1} \quad (E)
\]

\[
[cp₂VL]^{z-1} \xrightarrow{k_f / k_b} [cp₂V]^{"z-2"} + L^{z-2} \quad (C)
\]

\[
L^{z-2} + Hg^0 \rightleftharpoons \text{mercury dithio chelates} \quad (E)
\]

The extent to which the various reactions proceed is dependent upon the particular dithio-chelate.

In the present case, the electrochemical behaviour is consistent with the first reduction being assigned to the process

\[
[cp₂V(IV)(SacSac)]^+ + e \rightleftharpoons [cp₂V(SacSac)]^0
\]
Table 3-5. Voltammetric data for $\text{cp}_2\text{V(SacSac)}^{1+/0}$ couple at a platinum electrode.

<table>
<thead>
<tr>
<th>$v$ (V sec$^{-1}$)</th>
<th>$i_f/i_b$</th>
<th>$\Delta E_p$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.020</td>
<td>1.36</td>
<td>65</td>
</tr>
<tr>
<td>0.100</td>
<td>0.99</td>
<td>60</td>
</tr>
<tr>
<td>0.200</td>
<td>0.97</td>
<td>63</td>
</tr>
</tbody>
</table>

$E_{1/2} = -0.368$ V

gradient of $E/\log\left(\frac{i_d}{i}\right)$ plot from polarographic data = 61.6 mV (dme)
The cyclic voltammetric data indicate that the follow-up dissociation of the formally vanadium(III) species is at best very slow in the absence of oxygen. A first-order rate constant of $6.5 \times 10^{-2}$ sec$^{-1}$ can be calculated from the ratio of the cyclic voltammetric peak heights at 20 mV sec$^{-1}$ (this value is probably an overestimate and presupposes that the rate-determining step in the dissociation is first-order). The very small cyclic voltammetric anodic peak in the presence of oxygen, even at very rapid scan rates, indicates marked acceleration of the dissociation by oxygen.

The reduction of \([\text{cp}_2\text{V(OEtSacSac)}]^+\) proceeds via the same mechanism.\(^{179}\) Whereas this mechanism has been confirmed by free ligand addition experiments for many other dithiochelates,\(^{173,178,179,181,182}\) such a test is unfortunately not possible in the present case. However, in view of the generality of the mechanism, it seems likely to pertain also for \([\text{cp}_2\text{V(SacSac)}][\text{BF}_4]^{-}\).

Bond et al. report\(^{179}\) that esr studies indicate that the first reduction step is metal- rather than ligand-based, that is, that \([\text{cp}_2\text{VL}]^2^{-1}\) contains vanadium(III). In this regard, it is interesting to note that in \([\text{cp}_2\text{V(mnt)}]\), the ligand is assigned\(^{176}\) as being in the dithiolate form (VI) which would be expected to favour a metal-based reduction (\textit{vide infra}), rather than the dithiodiketone form (VII) which would be expected to favour a ligand-based reduction. (Conversely, it is possible that a ligand-based oxidation to \([\text{cp}_2\text{V(mnt)}]^+\) might be observed at a platinum or a glassy carbon electrode.)

In some cases where dissociation of \([\text{cp}_2\text{VL}]^2^{-1}\) does not occur, reductions of \([\text{cp}_2\text{VL}]^Z\) with a sodium-mercury amalgam have been shown\(^{179}\) to result in stable vanadium(III) species in the absence of oxygen.
Thus, the interesting possibility arises from the present work of synthesising a stable (in the absence of oxygen) vanadium(III)-dithioacetylacetonato derivative.

Perhaps the greatest obstacle to the extension of the range of M(SacSac)$_n$ complexes is the unavailability of the free ligand. The rather rigorous conditions necessary in those synthetic routes developed to date have restricted the number of dithioacetylacetonato compounds. Following the development of the borohydride reduction of the 3,5-dimethyl-1,2-dithiolium cation, it became apparent that the dithioacetylacetonate anion was stable for a short time at 0 °C in the absence of a metal centre. Accordingly, the precipitation of this anion was attempted.

(f) TETRAPHENYLARSONIUM DITHIOACETYLACETONATE, (Ph$_4$As)$^+$(SacSac)$^-$$^-$

Addition of tetraphenylarsonium chloride solution to a solution of dithioacetylacetonate anions resulted in the precipitation of red crystals presumed to be (Ph$_4$As)$^+$(SacSac)$^-$. These crystals are quite soluble and cannot be recrystallised. They decompose on standing and (save for a correct As:S ratio) a satisfactory analysis could not be obtained. If, however, the crystals are collected, dissolved in methanol and added to a methanolic zinc chloride solution, Zn(SacSac)$_2$ is precipitated. It seems very likely then that the formulation (Ph$_4$As)$^+$(SacSac)$^-$$^-$ is correct. Irrespective of the precise formulation of the crystals, however, this method provides a convenient synthesis of dithioacetylacetonato complexes possessing obvious advantages over present methods. The instability of (Ph$_4$As)$^+$(SacSac)$^-$$^-$ precluded detailed physicochemical studies.

(g) C$_{10}$H$_{14}$S$_4$

In an alternative attempt to precipitate the dithioacetylacetionate anion, this time as a salt of the 3,5-dimethyl-1,2-dithiolium cation, a solution of these cations was added to a solution of dithioacetylacetionate anions. It was hoped that the anion would be stabilised to a greater degree in such a species than is the case with the tetraphenylarsenion cation. White crystals which decompose slowly in air
Figure 3-5. Nmr spectrum and tentative structure of $\text{C}_{18}\text{H}_{14}\text{S}_4$. $\delta$ values (ppm) vs. TMS as reference.
were precipitated from the above solution. Elemental analyses and a molecular weight determination (osmometry in chloroform) establish that the white crystals are monomeric $C_{10}H_{14}S_4^-$, this formulation being substantiated by the mass spectrum (molecular ion at $m/e$ 262). The substance is a non-electrolyte in acetone and in the light of these data, the simple ionic formulation (3,5-dimethyl-1,2-dithiolium)(dithioacetylacetate) was discarded.

Comparison of the infra-red spectrum of the solid with those of the dimer(I) and the 3,5-dimethyl-1,2-dithiolium cation readily established that the compound was comprised of neither entity. A sharp absorption was observed at 2520 cm$^{-1}$ and is tentatively assigned as a S-H bond stretching absorption (a peak at 2340 cm$^{-1}$ in the OEtSacSacH infra-red spectrum being similarly assigned$^2$).

The nmr spectrum in degassed (the compound reacts rapidly in the presence of oxygen) CDCl$_3$ is shown in Figure 3-5. On the basis of this spectrum, the compound is tentatively assigned the structure shown.

Although the initial aim of this synthesis was not realised, the compound obtained provides a potentially new and interesting uninegative chelating ligand. Depending upon the mode of chelation, the possibilities arise of forming mixed metal ion complexes or of gauging the carbon-bonding capabilities of various metal ions in varying oxidation states.

Although no mechanistic or kinetic data is available, it seems likely that formation of $C_{10}H_{14}S_2$ proceeds via nucleophilic attack (to which dithiolium cations are known to be susceptible$^{117}$). Reaction of $NH_2SacNH_2Sac^-$ with the 3,5-diamino-1,2-dithiolium cation might on this basis be expected to yield an analogous derivative – the $NH^+$ group acting as a powerful nucleophile. Such a reaction yielded white crystals which have yet to be characterised, but which, however, afforded a blue solution in DMF.

It can be seen from the above that several new syntheses of dithioacetylacetionato compounds have been developed in this work, and a number of interesting dithioacetylacetone derivatives synthesised and characterised for the first time. The way is now open to convenient
extensions of the range of dithioacetylacetonato complexes and the study of other novel related species.
SECTION B

MASS SPECTROMETRY
CHAPTER 4

LIGAND DONOR ATOM EFFECTS

IN MASS SPECTROMETRY
Table 4-1. Mass spectral peaks for dithioacetylacetonato complexes.  
(M = molecular ion, L = ligand)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Peaks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(SacSac)_3</td>
<td>M (M - L)</td>
<td>Chap. 3</td>
</tr>
<tr>
<td>Fe(SacSac)_3</td>
<td>(M - L)</td>
<td>36</td>
</tr>
<tr>
<td>Ru(SacSac)_3</td>
<td>no spectrum observed due to thermal decomposition</td>
<td>36</td>
</tr>
<tr>
<td>Os(SacSac)_3</td>
<td>M (M - L)</td>
<td>36</td>
</tr>
<tr>
<td>Co(SacSac)_3</td>
<td>(M - L)</td>
<td>52</td>
</tr>
<tr>
<td>Rh(SacSac)_3</td>
<td>M (M - L)</td>
<td>52</td>
</tr>
<tr>
<td>Ir(SacSac)_3</td>
<td>M (M - L)</td>
<td>52</td>
</tr>
<tr>
<td>Co(SacSac)₂</td>
<td>M</td>
<td>1</td>
</tr>
<tr>
<td>Ni(SacSac)₂</td>
<td>M</td>
<td>1</td>
</tr>
<tr>
<td>Pd(SacSac)₂</td>
<td>M</td>
<td>1</td>
</tr>
<tr>
<td>Pt(SacSac)₂</td>
<td>M</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 4-2. Intensities of major ions in the mass spectra of tBu'acBu'acH and tBu'SacBu'acH.

<table>
<thead>
<tr>
<th></th>
<th>LH = Bu'acBu'acH</th>
<th></th>
<th>LH = Bu'SacBu'acH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% TIC</td>
<td></td>
<td>% TIC</td>
</tr>
<tr>
<td>LH''</td>
<td>4</td>
<td>10</td>
<td>7</td>
</tr>
<tr>
<td>(LH-CMe₃)'</td>
<td>41</td>
<td>100</td>
<td>24</td>
</tr>
<tr>
<td>[(LH-CMe₃)-H₂O]'</td>
<td>1</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>[(LH-CMe₃)-H₂S]'</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>[(LH-CMe₃)-CO]'</td>
<td>0.5</td>
<td>1</td>
<td>0.4</td>
</tr>
<tr>
<td>CMe₃CO'</td>
<td>2</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>[(LH-CMe₃-H₂O)-CO]'</td>
<td>2</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>[(LH-CMe₃-H₂S)-CO]'</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>C₅H₁₀O'</td>
<td>0.5</td>
<td>1</td>
<td>0.3</td>
</tr>
<tr>
<td>CMe₃'</td>
<td>10</td>
<td>25</td>
<td>20</td>
</tr>
<tr>
<td>CH₃CO'</td>
<td>16</td>
<td>38</td>
<td>2</td>
</tr>
<tr>
<td>C₃H₅'</td>
<td>6</td>
<td>15</td>
<td>8</td>
</tr>
<tr>
<td>C₃H₄'</td>
<td>2</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>
The mass spectrometric behaviour of metal complexes of β-diketonates has been extensively studied. These spectra often exhibit many metal-containing ion peaks, and the fragmentation behaviour has been shown to be strongly influenced by the ability of the metal atom to undergo valence changes. Recently, the mass spectra of complexes of several monothio-β-diketonato ligands with various metal ions have been reported, and it has been concluded that the type of fragmentation is likewise dependent upon the metal ion. The mass spectra of metal dithioacetylacetonato complexes have been used primarily as an aid for their characterisation, and have been reported only briefly. The available data are summarised in Table 4-1, the spectra of all compounds being dominated by a peak at m/e 131, attributed to the 3,5-dimethyl-1,2-dithiolium cation.

The work of this Chapter was undertaken to study in detail the fragmentation of a typical metal dithio-β-diketonate, and to compare its mass spectrum with those of the corresponding monothio-β-diketonato and β-diketonato complexes. Divalent nickel complexes of the dipivaloylmethanato ligand (ButacButac) and its monothio-(ButSacButac) and dithio-analogues (BuSacBuSac) were chosen, since all are believed to be monomeric and square planar, thereby providing a rare opportunity to compare the relative effects of oxygen and sulphur donor atoms in a series of isostructural complexes. In addition, the fragmentation behaviour of the protonated ligands, ButacBuacH and ButSacBuacH can be studied. The mass spectrum of the presumably octahedral tris-complex Co(BuSacBuac)₃ has also been studied so as to extend the donor-atom comparison to tris-species, and a further study of the donor-atom effect

† For convenience, these nickel complexes will be identified in the text by their respective nickel-donor atom cores. Thus Ni(BuSacBuac)₂ ≡ NiO₂, Ni(BuSacBuac)₂ ≡ NiO₂S₂, and Ni(BuSacBuSac)₂ ≡ NiS₄.
Mass spectrometric behaviour of some substituted 1,2-dithiolium salts
has been made by comparing the mass spectrum of Ni(CF₃SacSac)₂ with that reported¹⁸⁸ for its monothio-analogue, Ni(CF₃acSac)₂.

To aid both in this study and the mass spectrometric study in Chapter 2, the mass spectrometric behaviour of several substituted-1,2-dithiolium iodides has also been investigated and these results are reported below.

RESULTS AND DISCUSSION

(a) 1,2-DITHIOLIUM IODIDES

The 1,2-dithiolium iodides used in this study were the 3,5-dimethyl-; 3-methyl-5-phenyl-; 3,4,5-trimethyl-; 3,5-diamino-1,2-dithiolium iodides, and the "parent" 1,2-dithiolium iodide ([C₃H₃S₂⁺]⁻I⁻).

These dithiolium iodides characteristically exhibit peaks at m/e 254, 128, 127, and 63.5 corresponding to I₂⁺, HI⁺, I⁺, and I²⁺, respectively. No molecular ion is observed, but the spectra show strong (M-1) peaks. These (M-1) species then lose HS⁻ to yield (M-34) species, such loss generally being confirmed by the corresponding metastable ion peak.

These observations are consistent with pyrolysis of the dithiolium iodide in the mass spectrometer (this pyrolysis being accompanied by violent fluctuations of the ion currents) to yield neutral HI and (M-1) species which then undergo electron-impact reactions as shown. A subsequent report has confirmed this mechanism.¹⁹³ Specific examples of this mechanism are included in Scheme 4-1.

The parent 1,2-dithiolium iodide ([C₃H₃S₂⁺]⁻I⁻) was the only exception to the above mechanism found in the present study. This salt yields the customary peaks due to the iodide ion and a molecular ion peak. In this case, it is not unexpected that the salt sublimes (rather than pyrolysing with loss of HI) to yield a complex activated species which then undergoes fragmentation to give the parent dithiolium cation and an iodine atom, this latter then undergoing the customary iodide reactions.

3,5-Diamino-1,2-dithiolium iodide would seem, at first sight, to disobey the above mechanism, there being only a small (M-1) peak.
Figure 4-1. Schematic mass spectra of ligands ($\Sigma_{m/e}$ = TIC for all ions $m/e > 40$).
However, it can still be thought to obey the general mechanism if it is assumed that the neutral (M-1) species, if formed, rapidly loses sulphur to give a neutral (M-33) species and that it is this (M-33) species which undergoes the electron impact reaction giving rise to the peak at m/e 100. Low-intensity peaks due to formation of decay of S₈ are also observed in the 3,5-diamino-1,2-dithiolium iodide mass spectrum.

A possible driving force for the reactions of Scheme 4-1 is the presumed stability of the six-membered aromatic species postulated.

(b) LIGANDS

The major peaks in the spectra of the ligands are shown in Figure 4-1 and Table 4-2. Those pathways which can be identified both by observation of metastable ions, and by precise mass measurement, are shown in Schemes 4-2 and 4-3. Although a peak of low intensity is found at m/e 199 (C₁₁H₁₉O₅⁻) in the Bu₄SacBu₄acH spectrum, this ligand appears to fragment quite analogously to Bu₄acBu₄acH, rather than via an "oxathiolium" ion species.

(c) METAL COMPLEXES OF DIPIVALOYLMETHANE AND ITS DERIVATIVES

Table 4-3 summarises the most important peaks in the spectra of these complexes. The spectrum of Ni₄ (Fig. 4-2) is dominated by peaks due to ions containing nickel, notably M⁺⁺, (M-C₄H₉)⁺ and (M-C₇H₁₀O₂)⁺⁺ (Scheme 4-4). This last may have the structure (L-NiC₆H₉)⁺⁺ which presupposes a butyl-to-nickel migration, analogous to migrations of phenyl, 185,187,194 methyl¹⁸⁵ and (C₇H₇)¹⁹⁵ groups reported for other β-diketonato complexes. Small peaks of approximately equal intensity corresponding to LNi⁺ and (LNiH)⁺⁺ have been shown by metastable peaks to be formed predominantly by stepwise processes rather than directly from the molecular ion. As the major metastable precursor of (LNiH)⁺⁺ is (LNiC₆H₉)⁺⁺, it is probable that at least some of the hydrogen which migrates is derived from butyl groups. No L⁺ peaks could be detected; high resolution measurement showed that a peak at m/e 183 is due predominantly to C₇H₉O₅Ni⁺ with which L⁺ is closely isobaric (Figure 4-3). Peaks due to LH⁺⁺ and its fragments were found, but the
Scheme 4-2

\[
\begin{align*}
C_4H_9 & \quad \text{+} \quad C_4H_9 \quad \text{+} \quad C_4H_9 \\
\text{m/e} & \quad 184 \\
\text{m/e} & \quad 127 \\
\text{m/e} & \quad 99 \\
\text{H}_2O & \quad \text{+} \quad C_6H_9 \quad \text{+} \quad C_6H_9 \\
\text{m/e} & \quad 109 \\
\text{m/e} & \quad 81 \\
\end{align*}
\]

Scheme 4-3

\[
\begin{align*}
C_4H_9 & \quad \text{+} \quad C_4H_9 \quad \text{+} \quad C_4H_9 \\
\text{m/e} & \quad 200 \\
\text{m/e} & \quad 143 \\
\text{m/e} & \quad 115 \\
\text{H}_2S & \quad \text{+} \quad C_6H_9 \quad \text{+} \quad C_6H_9 \\
\text{m/e} & \quad 109 \\
\text{m/e} & \quad 81 \\
\end{align*}
\]
ratios of their intensities to those of other peaks in the spectrum varied with time, indicating that they were due to ionisation of thermally generated LH, analogous behaviour having been observed in the spectra of metal acetylacetonates.

Similarly to the SacSac complexes, the spectrum of NiS₆ (Fig. 4-2) is dominated by the L⁺ ion which may have the highly stable aromatic dithiolium structure I.

\[
\begin{array}{c}
\text{C}_4\text{H}_9 \quad + \quad + \quad + \quad + \quad \text{C}_4\text{H}_9 \\
\text{S} \quad \text{S} \\
\text{I}
\end{array}
\]

This L⁺ peak is by far the most intense in the spectrum, whilst the most intense nickel-containing peak is due to the molecular ion, which is shown by metastable ion peaks to be the parent of at least some of the L⁺ ions. The spectrum is similar to that obtained from 3,5-di(t-butyl)-1,2-dithiolium perchlorate. Successive losses of neutral \(\text{C}_4\text{H}_8\) from L⁺ generate ions of compositions \(\text{C}_7\text{H}_{11}\text{S}_2^+\) and \(\text{C}_3\text{H}_3\text{S}_2^+\), probably corresponding to the 3-(t-butyl)-1,2-dithiolium, and 1,2-dithiolium cations. A major reaction of the even-electron L⁺ ion (I) is loss of a methyl radical to form an odd-electron daughter ion, the stability of which is consistent with the mass spectrometric behaviour of the substituted 1,2-dithiolium iodides discussed above. Rationalisation of this and other reactions of I are shown in Scheme 4-5.

The possibility that a low-intensity NiL⁺ peak in the NiS₆ spectrum arises from a small amount of Ni(Bu'SacBu'Sac)(Bu'SacBu'ac) impurity cannot be discounted. However, the observation of NiL⁺ peaks in the mass spectra of nickel bis(dithio-β-diketonato) chelates prepared via syntheses not involving the intermediacy of monothio-β-diketonato ligands (a reaction scheme for the Martin-Stewart synthetic route proposes that formation of nickel bis(dithio-β-diketonato) compounds proceeds via formation of nickel bis(monothio-β-diketonato) compounds)
Figure 4-2. Schematic mass spectra of the complexes NiO₄, NiO₂S₂ and NiS₄ (Σ₄₀ = TIC for all ions m/e > 40).
is consistent with the NiL⁺ peaks in the spectra of the present nickel bis(dithio-β-diketonato) compounds being derived from the molecular ions of the bis-dithio chelates.

Metal-containing fragments comprise 65% of the NiO₂S₂ total ion current (TIC), the spectrum of this compound having characteristics intermediate between those of NiO₄ and NiS₄ (Fig. 4-2 and Scheme 4-6). Thus, the nickel-containing fragment ion peaks of NiO₂S₂ are analogous to, but less intense than (as a percentage of the relative TIC's) those in the spectrum of NiO₄, and the NiO₂S₂ spectrum L⁺ peak accounts for a smaller proportion of the TIC than does the dithiolium ion peak in the spectrum of NiS₄. In contrast to both NiO₄ and NiS₄, the molecular ion is responsible for the base peak, and metastable ion peaks establish that at least some of the L⁺ ions are derived therefrom. The L⁺ ion fragments with successive losses of C₄H₈⁺, H₂S and CO, of which only the first reaction is strongly represented in the spectrum of the dithiolium ion. Daughter ions generated via these reactions (C₇H₁₁O⁺, C₇H₉O⁺ and C₆H₉⁺ respectively) are also responsible for major peaks in the spectrum of Bu'SacBu'acH.

The decrease in the proportions of the TIC carried by L⁺ as sulphur is replaced by oxygen in the series NiS₄ (66%), NiO₂S₂ (9%), NiO₄ (nil) may be due to the higher ionisation potential of oxygen relative to sulphur, to a reduction of opportunities for stabilisation of the L⁺ ions via bonding involving sulphur d-orbitals and to a less even distribution of the positive charge in II relative to I because of the higher electronegativity of oxygen relative to sulphur and carbon.

Further evidence for the lower stability of the oxathiolium ion (II) is provided by the rarity or absence of published reports of the
Figure 4.3. High resolution mass spectrum of NiO₄ in the m/e 183 region.

Scheme 4-4

\[
\begin{align*}
\text{NiO}_4^+ &\xrightarrow{-C_6H_6O} L-Ni-C_6H_{11}O^+ \\
+C_4H_9 &\xrightarrow{m/e 424} C_7H_{10}O_2^+ \xrightarrow{m/e 340} Bu-Ni-L^+ \\
O=C-CH=C(Bu)-O-Ni-L &\xrightarrow{m/e 367} \text{weak FFI metastable ion} \\
-C_7H_{10}O_2 &\xrightarrow{m/e 298} H-Ni-L^+ \\
+C_4H_9 &\xrightarrow{m/e 241} Ni-L^+ \\
-C_4H_8 &\xrightarrow{m/e 242} \text{H-Ni-L}^+ \\
\text{Ni}^1-0-C(Bu)-CH-C\equivO &\xrightarrow{m/e 184}
\end{align*}
\]
characterisation of oxathiolioum salts, while dithiolium salts have been extensively studied. The stability of catenated sulphur is well known, and in fact several synthetic routes to 1,2-dithiolium salts use such sources of sulphur as H₂S₂ and elemental sulphur.

Metastable ion data establish that some of the 3,5-di(t-butyl)-1,2-dithiolium ion (I) in the NiS₄ spectrum is derived from a parent of m/e 456, corresponding to the molecular ion of a mixed ligand variation of NiO₂S₂, Ni(Bu₄acBu₄ac)(Bu₄SacBu₄Sac), this species apparently being generated either in the mass spectrometer or as a side-product of the NiS₄ synthesis. Simultaneous introduction of NiO₄ and Ni(Bu₄SacBu₄ac)₂ into the mass spectrometer yielded a spectrum showing molecular ion peaks of the species NiO₂S₂, NiO₃S and NiO₄, and (M-57)+ peaks from NiO₂S²⁺ and NiO₄²⁺. Although these mixed ligand NiO₂S₂ and NiO₃S species are at present unknown, these mass spectrometric data offer tangible evidence of the possibility of their syntheses. The physicochemical properties of such compounds would be of great interest. As one example, the relative $E_{1/2}$ values for the reductions of the NiO₂S₂ species III and IV would be of particular relevance to the donor-atom variation electrochemical studies of Section C.

(d) BIS(TRIFLUOROMETHYL-DITHIOACETYLACETONATO)NICKEL(II), Ni(CF₃SacSac)₂

The main features of the spectrum (Fig. 4-4) are a small molecular ion peak and a large peak due to the 3-trifluoromethyl-5-methyl-1,2-dithiolium cation. Peaks typical of the fragmentation products of 1,2-dithiolium ions generated in the mass spectra of dithio-β-diketonato complexes are also observed (e.g., C₃H₃⁺, HCS⁺, CH₃CS⁺, etc.).
Table 4-3. Most intense peaks in the spectra of NiO₄, NiO₂S₂ and NiS₄.

<table>
<thead>
<tr>
<th></th>
<th>NiO₄ (%)</th>
<th>NiO₂S₂ (%)</th>
<th>NiS₄ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>28</td>
<td>55</td>
<td>7</td>
</tr>
<tr>
<td>M-C₄H₉</td>
<td>35</td>
<td>0.5</td>
<td>1</td>
</tr>
<tr>
<td>M-L</td>
<td>2</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>M-L-C₄H₉</td>
<td>1</td>
<td>0.6</td>
<td>1</td>
</tr>
<tr>
<td>C₄H₉Ni</td>
<td>2</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>LH</td>
<td>0.3</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>L</td>
<td></td>
<td>9</td>
<td>16</td>
</tr>
<tr>
<td>L-C₄H₉</td>
<td>3</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>L-Me</td>
<td></td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>L-2Me</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>C₄H₉</td>
<td>12</td>
<td>10</td>
<td>17</td>
</tr>
<tr>
<td>S</td>
<td>10</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

Scheme 4-5

\[
\text{NiS}_4^+ \rightarrow m/e 488 \\
\text{NiL}^- \rightarrow m/e 215 \\
\text{Bu-C}_4H_8 \rightarrow m/e 159 \\
\text{Bu-C}_4H_8 \rightarrow m/e 200 \\
\text{S-S} \rightarrow m/e 103 \\
\text{S-S} \rightarrow m/e 185
\]
as well as variations induced by the introduction of the trifluoromethyl group (e.g., FCS\(^+\), (L-HF\(^+\), (L-CF\(_3\))\(^+\)). Similarly to Ni(Bu\(^t\)SacBu\(^t\)Sac)\(_2\), only a small percentage (7\%) of the TIC of the Ni(CF\(_3\)SacSac)\(_2\) spectrum is due to nickel-containing ions.

(e) CONCLUSIONS

Inasmuch as all chelates exhibit peaks due to NiL\(_2\)\(^+\) and NiL\(^+\), irrespective of the donor atom set, the fragmentations of the present complexes are similar. In favourable cases, a parent ion can undergo loss of all or part of a particular ligand substituent. Thus, the highly branched t-butyl group is readily lost from the dipivalolymethane derivatives, whereas F\(^+\) and CF\(_3\)\(^+\) are lost from the trifluoro compounds. The appropriate metastable ion peaks establish that L\(^+\) ions are generated from the molecular ions and the L\(^+\) fragmentation products are found in the spectra of all the sulphur-containing compounds.

A significant difference in the spectra of the monothio- and dithio-complexes from that of the \(\beta\)-diketonato complex is that the ligand is lost from the former pair in its oxidised form L\(^+\), whereas no such peak is observed for NiO\(_4\). The presence of an intense L\(^+\) peak from NiS\(_4\) compared with the absence of a L\(^+\) peak from NiO\(_4\) is consistent with the low stability of SacSac\(^+\) and the greater stability of \(1,2\)-dithiolium ions.

Concomitant with an increase in the contribution to the TIC of L\(^+\) on going from NiO\(_4\) to NiS\(_4\), is a decrease in that of the molecular ion peaks. This is part of a general observation that the percentage of the TIC due to metal-containing peaks decreases in the order NiO\(_4\) > NiO\(_2\)S\(_2\) > NiS\(_4\). That is, the character of the spectrum changes from one dominated by the fragmentation of the complexed ligands in NiO\(_4\) to one dominated by the fragmentation of the uncomplexed, oxidised ligands in NiS\(_4\). The behaviour of the NiO\(_2\)S\(_2\) complex is intermediate between these two extremes, being similar to NiO\(_4\) with respect to the percentage of the TIC due to metal-containing ions, but similar to NiS\(_4\) in the generation and fragmentation of a strong L\(^+\) peak. Comparison between Ni(CF\(_3\)acSac)\(_2\) and Ni(CF\(_3\)SacSac)\(_2\) spectra (Table 4-4) establishes that this trend is paralleled in these complexes.
The trends discussed above are not confined to complexes of nickel. \( \text{CoO}_3\text{S}_3 \) exhibits many peaks (Fig. 4-5 and Scheme 4-7) quite analogous to those of \( \text{Co(acac)}_3 \), \( \text{Co(dibenzoylethanato)}_3 \) and \( \text{CoO}_6 \), but additionally, the spectrum is dominated by the \( L^+ \) peak at \( m/e \) 199 and its fragmentation products. Significantly, in contrast to \( \text{Co(SacSac)}_3 \) and some other tris(monothio-\( \beta \)-diketonato)cobalt(III) complexes, a molecular ion is observed for \( \text{CoO}_3\text{S}_3 \). The failure to observe a molecular ion in the complexes \( \text{M(acac)}_3 \) (\( \text{M = Cr, Fe, Co} \)) was subsequently shown to be a consequence of the method of introduction of the samples into the mass spectrometer. It may be, therefore, that some of these other cobalt-sulphur compounds will exhibit a molecular ion under favourable conditions.

![Figure 4-4. Schematic mass spectrum of Ni(CF₃SacSac)₂ (\( \chi_{4,0} = \text{TIC for all ions } m/e > 40 \)).](image)
Table 4-4. Comparison between mass spectra of Ni(CF₃acSac)₂ and Ni(CF₃SacSac)₂.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Ni(CF₃acSac)₂</th>
<th>Ni(CF₃SacSac)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Relative Intensity (%)</td>
<td>Relative Intensity (%)</td>
</tr>
<tr>
<td>M</td>
<td>70</td>
<td>12</td>
</tr>
<tr>
<td>M-F</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>M-CF₃</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>M-F-H₂S</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M-COCP₃</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>M-(L-S)</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>M-L</td>
<td>23</td>
<td>1</td>
</tr>
<tr>
<td>M-L-CF₃</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>M-2L</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>L</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>L-H</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>Other L⁺ derived peaks (see text)</td>
<td>not noted</td>
<td>35</td>
</tr>
</tbody>
</table>

From reference 188.

Figure 4-5. Schematic mass spectrum of Co(Bu⁺SacBu⁺ac)₃ (Σ₄₀ = TIC for all ions m/z > 40. Left hand scale is relative abundance (%)).
Scheme 4-7

\[
\begin{align*}
L^+ & \rightleftharpoons \text{CoL}_2 \quad \text{CoO}_3\text{S}_3^+ \\
&m/e 199 \\
&\quad \downarrow - L' \\
\text{Co}^\pi\text{L}_2^+ & \rightarrow \text{Co}^\pi\text{L}_2^+ - \text{C}_4\text{H}_6^- \\
&m/e 457 \\
&\quad \downarrow - L' \\
\text{Co}^\pi\text{L}_2^+ + - \text{C}_4\text{H}_6^- & \rightarrow \text{L-Co}^\pi\text{-(C}_7\text{H}_{10}\text{O}_5)_2^+ \\
&m/e 400 \\
\text{Co}^\pi\text{-(C}_7\text{H}_{10}\text{O}_5)_2^+ & \rightarrow - \text{C}_4\text{H}_6^- \quad \text{Co}^\pi\text{L}_2^+ \\
&m/e 201 \\
&\quad \downarrow - \text{C}_7\text{H}_{10}\text{O}_5 \\
\text{Co}^\pi\text{L}_2^+ & \rightarrow \text{Co}^+ \\
&m/e 258 \\
\text{Co}^+ & \rightarrow m/e 59
\end{align*}
\]
SECTION C

ELECTROCHEMICAL STUDIES
CHAPTER 5

TREATMENT OF ELECTROCHEMICAL DATA
The utility of electrochemical techniques in investigating mechanistic, electronic, synthetic and structural aspects of co-ordination compounds has been amply illustrated in recent years. Perhaps the most widely used of the voltammetric techniques has been dc polarography, but cyclic voltammetry and ac polarography are finding increasing favour, particularly since theoretical analyses of electrode responses have become available. Other techniques, such as pulse polarography in its several forms, high frequency methods, and techniques with time as a variable have also been employed. The coupling of the electrochemical cell to computer-based data acquisition and analysis has allowed a further degree of sophistication.

In the present work, dc and ac polarography, cyclic voltammetry and coulometry have been utilised. Theoretical concepts associated with the interpretation of the data obtained are discussed below. The discussion is divided according to technique and further subdivided according to the degree of reversibility of the charge transfer process.

In the interpretation of electrochemical measurements, perhaps the most immediate problem is to establish the degree of reversibility of the electrode process. Two useful definitions of the concept of reversibility are those provided by Brown and Large and by Delahay. According to Brown and Large

"... If a charge transfer process is said to be "reversible", one is in reality only stating that the process occurs at a significantly more rapid rate than the rate of diffusion. A charge transfer process governed by both diffusion and charge transfer kinetics is termed "quasi-reversible". A reaction in which the charge transfer process is much slower than the diffusion rate is termed "irreversible". ..."

Delahay has quantified the concept of reversibility in terms of the magnitude of the rate constant of the heterogeneous charge
Figure 5-1. dc polarogram showing parameters of interest.
transfer \( (k_s) \). At "normal" drop times (3-8 sec) the degree of reversibility of the dc polarographic charge transfer is given by the inequalities \( (k_s \text{ in cm sec}^{-1}) \)

\[
\begin{align*}
    k_s &> 2 \times 10^{-2} & \text{reversible} \\
    2 \times 10^{-2} &> k_s > 2 \times 10^{-5} & \text{quasi-reversible} \\
    k_s &< 2 \times 10^{-5} & \text{irreversible}
\end{align*}
\]

An important distinction to be made in the discussion of electrochemical reversibility is that between the reversibility of the electrode process as a whole and the reversibility of the charge transfer. Thus, the combination of an irreversible chemical reaction coupled to a reversible charge transfer results in the overall electrode process being non-reversible. In the ensuing discussion, therefore, the effects of charge transfer and coupled chemical reactions are treated separately.

(a) dc POLAROGRAPHY

Figure 5-1 shows a typical reversible dc polarographic wave and illustrates the parameters under discussion.

Interpretation of the dc polarographic response is greatly simplified if it can be established that the electrode process is diffusion controlled and reversible. The assumption of Fickian diffusion of the depolarisor to the electrode leads to the Ilkovic equation

\[
i_n = 0.732 n F C D^{1/2} m^{2/3} t^{1/6}.
\]

Since the drop time is inversely, and the mercury flow rate directly proportional to the mercury column height,

\[
i_n \propto h^{1/2}.
\]

Plots of \( i_n \) vs. \( h^{1/2} \) are therefore straight lines through the origin if the limiting current is diffusion controlled.

Diffusion coefficients may be calculated from equation (5-1). The diffusion coefficients of the oxidised and reduced halves of a redox couple are generally assumed to be equal. Although Lingane has found
the diffusion coefficients of \( \text{Ni(mnt)}_2^- \) and \( \text{Ni(mnt)}_2^{-2} \) to differ, the difference can be shown in that case to have a negligible effect upon the polarographic parameters. In the following discussion the simplifying assumption of equal diffusion coefficients will be made.

The general solution of the diffusion problem for the reduction

\[
A + ne \xrightleftharpoons[k_e^{-1}]{k_e} B
\]

has been shown to be

\[
\frac{i - i_d}{i} = \exp \left( \frac{nF(E - E^0)}{RT} \right) + \frac{1.14}{k_e} \sqrt{D_i/t} \exp \left( \frac{\alpha nF(E - E^0)}{RT} \right),
\]

where \( \alpha \) is the charge transfer coefficient \(^{220,221}\) and \( k_e^{-1} = k_e = k_s \) at \( E^0 \).

Two limiting solutions of equation (5-3) pertain. Either (a) the overall rate of the electrode process is governed by the diffusion of \( A \) and \( B \) to and from the electrode, or (b) the overall rate of the electrode process is governed by the rate of the heterogeneous charge transfer.

In the reversible case (a), equation (5-3) reduces to

\[
E = E^0 + \frac{RT}{nF} \ln \left( \frac{i - i_d}{i} \right)
\]

and, at \( i = \frac{i_d}{2} \),

\[
E_{1/2} = E^0.
\]

Note that when cognizance is taken of the difference in diffusion coefficients, equation (5-5) becomes

\[
E_{1/2} = E^0 - \frac{RT}{2nF} \ln \left( \frac{D_{ox}}{D_{red}} \right).
\]

Substitution of Lingane's values for the diffusion coefficients into equation (5-6) shows a displacement of \( E_{1/2} \) from \( E^0 \) by 3 mV for the \( \text{Ni(mnt)}_2^- \) reduction.

For the irreversible case (b)

\[
E_{1/2} = E^0 + \frac{RT}{\alpha nF} \ln \left[ 0.87 k_s \sqrt{C/D} \right].
\]
Figure 5-2. Reversible ac polarogram, showing parameters of interest.
Thus, for a reversible charge transfer, $E_{1/2}$ is a thermodynamically significant parameter, whereas in the irreversible case the thermodynamics of the system are not fully characterised by $E_{1/2}$.

A simple test of the reversibility of an electrode process is provided by assessing $E_{1/4} - E_{3/4}$. From equation (5-4),

$$E_{1/4} - E_{3/4} = \frac{RT}{nF} \ln 9$$

which at 22 °C equals $\frac{56}{n}$ mV. Similarly, in the irreversible case (b) at 22 °C,

$$E_{1/4} - E_{3/4} = \frac{56}{an} \text{ mV}.$$  

(5-9)

The above is, however, only a two-point analysis of reversibility. A more complete analysis is obtained by plotting $E$ as the ordinate and $\log \left( \frac{i_d - i}{i} \right)$ as the abscissa. For a reversible charge transfer this yields a straight line of gradient $\frac{2.303 RT}{nF} \left( \frac{58}{n} \text{ mV at 22 °C} \right)$ and vertical intercept $E_{1/2}$. Comparison of measured with calculated wave shapes can also be used to test reversibility.

(b) ac POLAROGRAPHY

Alternating current polarography essentially involves the superposition of a small alternating potential $\Delta E \approx \frac{16}{n}$ mV peak to peak upon the scanning dc potential, and measurement of the resultant alternating current as a function of the dc potential. Figure 5-2 illustrates a typical reversible ac polarogram. To date, the fundamental harmonic alternating current has most often been used, but second-harmonic experiments are finding increasing favour. Little advantage is gained by use of harmonics higher than the second, and only the fundamental harmonic has been used in the present work. Analogously to dc polarography, the ac polarographic response is influenced predominantly by the degree of reversibility of the heterogeneous charge transfer, and by the coupling of chemical reactions to the charge transfer step.
Table 5-1. Characteristics of ac wave (at 22 °C) for reversible charge transfer A + ne → B.

- $[E_{dc}]_p$ is independent of frequency
- $[E_{dc}]_p$ is independent of drop time
- $[E_{dc}]_p = E_{1/2} = E_1^R$
- $\omega_{1/2} \approx \frac{90}{n} \text{ mV}$

Plot of $I_p$ vs. $\omega^{1/2}$ is a straight line through the origin

Plot of $\log \left( \frac{\left( \frac{I_p}{I} \right)^{1/2} + \left( \frac{I_p - I}{I} \right)^{1/2} \right)$ vs. $E_{dc}$ is a straight line of gradient $\frac{117}{n} \text{ mV}$ and intercept $E_{1/2}^R$ on the potential axis
(i) Reversible Charge Transfer\textsuperscript{204,223}

For the reversible reduction,

\[ A + \text{n}e \rightleftharpoons B, \]

where \( A \) is the only species initially present in solution, the ac current is given by

\[ I(\omega t) = \frac{n^2F^2AC(\omega D)^{1/2}AE}{4RT \cosh^2(j/2)} \sin \left( \omega t + \frac{\pi}{4} \right), \]

(5-10)

where

\[ j = \frac{nF}{RT} \left( E_{dc} - E_r \right) \]

(5-11)

and the drop area \( A \), is customarily evaluated via

\[ A = 0.85(mt)^{2/3}. \]

(5-12)

Differentiation of equation (5-10) shows it to have a maximum at \( E_{dc} = [E_{dc}]_p = E_{1/2}^r \). The ac equivalent of the Heyrovsky-Ilkovic equation (5-4) can be shown to be

\[ E_{dc} = E_{1/2}^r + \frac{2RT}{nF} \ln \left( \frac{I_p}{I} \right) \]

(5-13)

and again, when \( I = I_p \), \( [E_{dc}]_p = E_{1/2}^r \).

A two point analysis of the reversibility of the ac charge transfer is provided by the width of the ac polarographic wave at half its height \( (W_{1/2}) \), since

\[ W_{1/2} = \frac{2RT}{nF} \ln \left( \frac{\sqrt{2} + 1}{\sqrt{2} - 1} \right) \]

(5-14)

which at 22 °C equals \( \frac{90}{n} \) mV. However, the most sensitive tests of the reversibility of the ac wave at a particular frequency are comparisons with calculated wave shapes,\textsuperscript{205} and graphical plots with \( \log \left( \frac{I_p}{I} \right)^{1/2} + \left( \frac{I_p - I}{I} \right)^{1/2} \) as abscissa and \( E_{dc} \) as ordinate. If the charge transfer is reversible, a straight line of gradient \( 4.606 \frac{RT}{nF} \left( \frac{117}{n} \right) \) mV at 22 °C and vertical intercept \( E_{1/2}^r \) is obtained. The reversibility over a large frequency range can be tested readily by plotting \( I_p \) against \( \omega^{1/2} \); such a plot yielding a straight line through the origin for the reversible case (equation (5-10)). Table 5-1 summarises the characteristics of a reversible ac wave.
Table 5-2. Characteristics of ac wave (at 22 °C) for irreversible charge transfer $A + ne \rightarrow B$

$[E_{dc}]_p$ shifts cathodically with increasing frequency

$[E_{dc}]_p$ shifts anodically with increasing drop time

$[E_{dc}]_p$ is displaced cathodically from $E_{1/2}$

$[E_{dc}]_p \neq E_{1/2}$

$W_{1/2} > \frac{90}{n} \text{ mV}$

$I_p$ is not a linear function of $\omega^{1/2}$

$I_{p \text{irrev.}} < I_{p \text{rev.}}$

$I_p$ is drop time dependent
(ii) Irreversible Charge Transfer

Although the polarographic response for an irreversible charge transfer was initially thought to be vanishingly small, it has since emerged that ac polarographic waves are to be expected in this case. A good approximation to the peak height of the irreversible ac wave is

\[ I_{\text{irrev}} \approx \frac{1.644 \alpha n^2 \Gamma^2 \Delta \varepsilon}{RT(1 + Q^{1/2})}, \]  

where

\[ Q = 1.907(wt)^{1/2}. \]

That is

\[ I_{\text{irrev}} \approx I_{\text{rev}} \left( \frac{1.644 \alpha}{(1 + Q^{1/2})^2} \right) \]

and therefore \( I_{\text{irrev}} < I_{\text{rev}} \).

The peak potential is given by

\[ [E_{\text{dc}}]_p = E_{1/2} + \frac{RT}{2nF} \ln \left( \frac{1.349 k t^{1/2}}{s} \right) - \frac{RT}{2nF} \ln Q \]

and is both drop-time and frequency dependent. Equation (5-18) also establishes that \([E_{\text{dc}}]_p \neq E_{1/2}^r\). It can further be shown that the peak potential of the ac wave is displaced from the dc polarographic half-wave potential according to

\[ [E_{\text{dc}}]_p - E_{1/2} = - \frac{RT}{2nF} \ln Q. \]

The characteristics of the irreversible ac wave are summarised in Table 5-2.

(iii) Quasi-reversible Charge Transfer

In the case of a Nernstian dc response and a quasi-reversible ac response, \( I_p \) is a linear function of \( \omega^{1/2} \) only at low frequencies. At high frequencies, \( I_p \) approaches a limiting, \( \omega \)-independent value given by

\[ I_p = \frac{n^2 \Gamma^2 \Delta \varepsilon k_s^\beta \alpha}{RT}. \]  

In this high-frequency limit
Table 5-3. Characteristics of ac wave (at 22 °C)

for quasi-reversible charge transfer \( A + ne = B \)

\[
\begin{align*}
&[E_{dc}]_p = E_{1/2} \quad \text{at low frequencies} \quad (k_s \gg \sqrt{2\omega D}) \\
&[E_{dc}]_p - E_{1/2} = \frac{RT}{nF} \ln \left( \frac{b}{a} \right) \quad \text{at large frequencies} \quad (k_s \ll \sqrt{2\omega D}) \\
&W_{1/2} = \frac{89}{n} \text{mV at low frequencies} \\
&W_{1/2} = \frac{143}{n} \text{mV at large frequencies}
\end{align*}
\]

\( \alpha = 0.5 \)

Plot of \( I_p \) vs. \( \omega^{1/2} \) is a straight line through the origin at low frequencies

At large frequencies, and for \( \alpha = 0.5 \), \( I_p = \frac{n^2F^2ACAE k_s}{2RT} \)
\[
[E]_{dc} = E^R_{1/2} + \frac{RT}{nF} \ln \frac{E}{E_0}.
\]

(5.21)

Since \(E^R_{1/2}\) can be determined from the dc polarogram, \(a\) can be determined. If \(a \approx 0.5\), equation (5-20) reduces to

\[
I_p = \frac{n^2F^2AC\Delta E_k}{2RT_S}
\]

(5-22)

At \(22^\circ\text{C}\), \(W_{1/2}\) varies between 89 mV at low frequencies and 143 mV at high frequencies if \(a \approx 0.5\).

Should the conditions of reversible dc charge transfer pertain, then the quasi-reversible ac polarographic wave height and shape will be independent of the mercury column height. However, if the electrode process is also quasi-reversible in the dc sense, then a drop-time dependence of the ac wave is predicted.\(^{227,228}\) Table 5-3 summarises the characteristics of quasi-reversible ac charge transfer.

(c) CYCLIC VOLTAMMETRY

Linear sweep cyclic stationary electrode polarography or voltammetry involves measurement of the current resultant upon the application of a cyclic linearly-varying dc potential scan (Fig. 5-3) to a stationary electrode. A typical reversible cyclic voltammogram is reproduced in Figure 5-4. As the behaviour of the products of electrode processes can be investigated, cyclic voltammetry has proven to be of immense value in the study of the kinetics of electrode processes, and of chemical reactions coupled to the charge transfer. The time scale of the experiment can be altered by varying the potential sweep rate, thereby allowing the study of both very fast and very slow reactions. A very recent development, cyclic ac voltammetry,\(^{229,230}\) permits further control of the time scale as a consequence of the frequency-dependence of the ac response.

(i) Reversible Charge Transfer\(^{202}\)

For the reversible reduction of \(A\) at \(22^\circ\text{C}\),

\[
A + ne \rightleftharpoons B
\]
Figure 5-3. Wave form for cyclic triangular wave voltammetry.
the peak potential of the cyclic voltammogram is related to \( E_{1/2}^r \) by

\[
E_{1/2}^r - E_p = 28.1 \text{ mV} \quad (5-23)
\]

or, in terms of the half-peak potential, \( E_{p/2} \)

\[
E_{p/2} - E_{1/2}^r = 27.7 \text{ mV} \quad (5-24)
\]

The \( E_{1/2}^r \) value can also be determined by noting that \( E = E_{1/2}^r \) when \( i = 0.8517 \). Since the \( E_{1/2}^r \) values of the two halves of a redox couple are equal if the charge transfer is reversible, it follows from equation (5-23) that the separation between the cathodic and anodic peak potentials is

\[
\Delta E_p = 56.2 \text{ mV} \quad (5-25)
\]

The peak current of the forward potential scan is given by the Randles-Sevcik equation

\[
i_p = 2.69 \times 10^5 n^{3/2} A D^{1/2} C v^{1/2} \quad (5-26)
\]

from which it follows that a plot of \( i_p \) against \( v^{1/2} \) should be a straight line through the origin. A further criterion of reversibility is that

\[
i_{cp} = i_{ap} \quad (5-27)
\]

A useful equation for the application of equation (5-27) is

\[
\frac{i_{ap}}{i_{cp}} = \frac{(i_{ap})_0}{(i_{cp})_0} + 0.485 \frac{(i_{cp})_0}{(i_{ap})_0} + 0.086 \quad (5-28)
\]

An important limitation on the use of equation (5-28) is that the switching potential \( (E_\lambda) \) be such that

\[
|E_{cp} - E_\lambda| > \frac{60}{n} \text{ mV} \quad (5-29)
\]

The characteristics of the reversible cyclic voltammogram are summarised in Table 5-4.
Figure 5-4. Reversible cyclic voltammogram, showing parameters of interest.
(ii) Irreversible Charge Transfer

In the case of an irreversible charge transfer

\[ A + ne \xrightarrow{k_s} B \]

there is no current on the reverse scan. At 22 °C, the peak potential is related to \( E^0 \) via

\[ E_p = E^0 - \frac{0.0664}{\alpha n} - \frac{0.0292}{\alpha n} \log \frac{D_a v}{k_s^2} \]

and

\[ E_{p/2} - E_p = \frac{47.1}{\alpha n} \text{ mV} \]

\( k_s \) and \( \alpha \) may be evaluated from the relation

\[ i = nFAC k_s \exp \left( -\frac{anF}{RT} (E - E_{\text{init}}) \right) \]

which is valid only for \( i < 0.1 i_p \). Table 5-5 summarises the characteristics of the irreversible cyclic voltammogram.

(iii) Quasi-reversible Charge Transfer

For the quasi-reversible reduction

\[ A + ne \xrightarrow{k_e, k_{-e}} B \]

Nicholson \(^{232}\) has related the peak potential to a parameter \( \psi \), where

\[ \psi = \left[ \frac{D_A}{D_B} \right]^2 \frac{\pi nFvD_A}{k_s \left( \frac{RT}{\alpha} \right)} \]

The solution of the boundary value problem is presented in terms of a working curve enabling \( k_s \) to be determined from \( \Delta E_p \), provided \( D_A \) is known (in the absence of a value for \( D_B \), it is assumed that \( D_A = D_B \)). Both the symmetry and peak potentials of the cyclic voltammetric waves are affected by the charge transfer coefficient \( \alpha \), however, in the range \( 0.3 < \alpha < 0.7 \), the values of \( \Delta E_p \) are nearly independent of \( \alpha \), especially for large values of \( \psi \). The problem reduces to a reversible charge transfer for \( \psi \geq 7 \), whilst for \( \psi < 0.001 \), the solution is the same as for
Table 5-4. Characteristics of cyclic voltammogram (at 22 °C) for reversible charge transfer \( A + ne = B \)

<table>
<thead>
<tr>
<th>Expression</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(</td>
<td>E_p - E_{1/2}^r</td>
</tr>
<tr>
<td>(E = E_{1/2}^r) when (i = 0.85 i_p)</td>
<td></td>
</tr>
<tr>
<td>(\Delta E_p = \frac{56}{n}) mV</td>
<td></td>
</tr>
<tr>
<td>(E_p) is independent of (v)</td>
<td></td>
</tr>
<tr>
<td>(\Delta E_p) is independent of (v)</td>
<td></td>
</tr>
<tr>
<td>(i_p) varies linearly with (v^{1/2})</td>
<td></td>
</tr>
<tr>
<td>(\frac{(i_p)_f}{(i_p)_b} = 1)</td>
<td></td>
</tr>
</tbody>
</table>

Note: The values given are for a particular reaction at 22 °C.
the irreversible case. As in the case of reversible charge transfer, it is important that the switching potential is sufficiently displaced from the forward peak. Nicholson has assumed \( E^{\alpha}_{\lambda} - E^{r}_{1/2} = \frac{141}{n} \) mV for his calculations.

Table 5-6 summarises the characteristics of the quasi-reversible cyclic voltammogram, although the assignment of quasi-reversibility to an electrode process on the basis of these criteria alone is complicated by the fact that the effects of uncompensated resistance upon the reversible cyclic voltammogram are qualitatively very similar to those of quasi-reversible charge transfer.\(^{232,233}\)

(d) COUPLED CHEMICAL REACTIONS

As mentioned earlier, polarographic and voltammetric waves can also be perturbed by the coupling of chemical reactions to the charge transfer process. For example, it can be shown readily\(^{234}\) that the effect of a chemical reaction following the charge transfer step

\[
A + ne \rightleftharpoons B \rightarrow C
\]

is to shift the dc polarographic half wave potential from \( E^{r}_{1/2} \) according to

\[
E^{\alpha}_{1/2} = E^{r}_{1/2} + \frac{0.059}{n} \log 1.349 k^{1/2} \tau^{1/2}
\]

a result analogous to the influence of a slow charge transfer upon the dc polarogram.\(^{234,225}\)

This reaction scheme also affects the ratio of the cyclic voltammetric peak heights \( \frac{IP_{\text{(anodic)}}}{IP_{\text{(cathodic)}}} \). The rate constant, \( k_{f} \), can be evaluated from cyclic voltammetric data \( \nu \alpha \) recourse to a working curve presented by Nicholson and Shain\(^{202}\) in which this ratio is plotted as a function of \( \log(k_{f} \tau) \), where

\[
\tau = \frac{|E^{\alpha}_{1/2} - E^{r}_{\lambda}|}{\nu} \text{ seconds}.
\]

This procedure was employed in the calculation of the \( k_{f} \)-value for the \([cp_{2}V(SacSac)][BF_{4}]\) reduction.
Table 5-5. Characteristics of cyclic voltammogram (at 22 °C) for irreversible charge transfer $A + ne \rightarrow B$

- $E_p$ shifts cathodically with increasing $v$
- $E_p$ is dependent upon $k_s$
- There is no faradaic current on the reverse scan
- $\frac{i_p}{v^{1/2}}$ is independent of $v$
Similarly, if a chemical equilibrium precedes a nernstian charge transfer:

$$\frac{k_1}{k_2} A + n e \rightleftharpoons B \quad K = \frac{k_1}{k_2}$$

then an ac polarographic wave of diffusion-controlled character will be observed, with its peak potential displaced from \(E_{1/2}\) by \(\frac{RT}{nF} \ln \left( \frac{K}{1 + K} \right)\).

Just as a given \(k_s\)-value will affect the various electrochemical techniques differently, a particular \(k_f\) will have differing effects on the parameters of the various time-scale experiments. Thus, \(k_f\)-induced complications evident in the dc polarographic experiment might be "outrun" by recourse to high scan-rate cyclic-voltammetric or high-frequency ac polarographic techniques.

Several discussions on the effects of coupled chemical reactions upon the observables of the various electrochemical techniques are available. Because of the many possible reaction types and experimental conditions, no attempt will be made here to summarise all the expected results. Rather, those examples of coupled chemical reactions encountered in this study will be discussed as they occur in the general text.

(e) CYCLIC VOLTAMMETRY AT A dme

Using the relationship for the area of a mercury drop

$$A = 0.85(mt)^{2/3}$$ (5-12)

at time \(t_0\) after the previous drop has been dislodged,

$$A_0 = \kappa t_0^{2/3},$$

where \(\kappa = 0.85 \ m^{2/3}\). Similarly, at a time \(t_0 + \Delta t\),

$$A_f = \kappa (t_0 + \Delta t)^{2/3}.$$

Thus

$$\Delta A = A_f - A_0 = \kappa ((t_0 + \Delta t)^{2/3} - t_0^{2/3})$$

and
Table 5-6. Characteristics of cyclic voltammogram (at 22 °C)

$k_s$ for quasi-reversible charge transfer $A + ne \rightleftharpoons B$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_p$</td>
<td>dependent on $v$</td>
</tr>
<tr>
<td>$\Delta E_p$</td>
<td>dependent on $v$</td>
</tr>
<tr>
<td>$\Delta E_p$</td>
<td>dependent on $k_s$</td>
</tr>
<tr>
<td>$\frac{i_p}{v^{1/2}}$</td>
<td>virtually independent of $v$</td>
</tr>
<tr>
<td>$\frac{(i_p)<em>{f}}{(i_p)</em>{b}}$</td>
<td>= 1 if $\alpha = 0.5$</td>
</tr>
</tbody>
</table>
\[ \Delta A = \left( 1 + \frac{\Delta t}{t_0} \right)^{2/3} - 1. \]  

That is, the percentage change in the drop area (\(\Delta A\)) during a time interval \(\Delta t\), commencing at time \(t_0\) after the previous drop has been dislodged is given by

\[ \Delta A\% = 100 \left( \left( 1 + \frac{\Delta t}{t_0} \right)^{2/3} - 1 \right) \% . \]  

It follows that in the limit as \(\frac{\Delta t}{t_0} \to 0\), then \(\Delta A\% \to 0\). Alternatively, provided that \(\Delta t < 0.08t_0\), then \(\Delta A\% < 5\%\).

Qualitatively, then, it can be seen that for sufficiently long drop times, the change in the drop area with time is slight for small time intervals near the end of the drop life. Thus, it is possible to obtain cyclic voltammograms of qualitative utility at a dme with a sufficiently long drop life. Provided the scans can be triggered at a known interval after the commencement of drop growth, it is possible to obtain successive cyclic voltammograms at freshly cleaned electrodes of known and reproducible area. Manual triggering was used in this work to initiate cyclic voltammetric scans at a dme, these having been utilised as an aid in the qualitative evaluation of the nature of electrode processes.

Figure 5-5, which shows two successive scans on the same drop at a dme, illustrates that although the current increases with drop size, the peak potentials, and therefore, peak separations do not. A quantitative theory describing this technique has been described recently.\(^{230}\)

(f) POLAROGRAPHIC DROP TIME

Perhaps the most obvious control over the time scale of polarographic experiments is provided by variation of the drop time. Drop time control in classical polarography was achieved by variation of the mercury column height, i.e., the so-called "natural drop". However, it is now possible to obtain very short drop times by mechanically dislodging drops, and this technique has been employed in the present work. The "rapid drop" technique has been shown to possess a number of
Figure 5-5. Successive cyclic voltammograms on the same drop at a DME. First scan, full curve; second scan, dashed curve.
advantages over the use of natural drops, and does not invalidate polarographic theory.
Figure 6-1. Electron transfer series of metal dithioacetylacetonates (after reference 144, a = present work), \( \rightarrow \rightarrow \) = reversible process, \(-\rightarrow\) = nonreversible process. Note that products are represented by their formal oxidation states for convenience. The electrode processes may not be metal-based.
6-1. ELECTROCHEMISTRY OF DITHIO-β-DIKETONATES AND RELATED SPECIES

Subsequent to the observations that the complexes \( M(S_2C_2R_2)_{2n}^2 \) were linked by well-defined electron-transfer series, conflicting views were expressed as to the possibility that the \( M(SacSac)_{n} \) compounds would exhibit reversible redox behaviour.\(^{243,244}\) Accordingly, polarographic studies of the latter were initiated in which the existence of reversible redox processes was established.\(^{144,169}\) Presumed solvolysis problems had beset a previous study\(^{245}\) in which non-reversible waves were observed.

The polarographic behaviour of the known \( M(SacSac)_{n} \) complexes is summarised in Figure 6-1.\(^{74,144,169}\) No oxidation waves had been observed, and all reductions, with the exceptions of those of \( \text{Co(SacSac)}_3 \) and \( \text{Rh(SacSac)}_3 \), are at least quasi-reversible. \( E_{1/2} \)-values have been correlated with the known chemistry and spectroscopic behaviour of the compounds, and the high degree of reversibility exhibited in most reductions has been interpreted as indicating that the complexes and their stereochemistries remain intact upon reduction.

The products of the first \( M(SacSac)_{2} (M=\text{Ni, Pd}) \) reductions are thought to rearrange to give two formally \( M(\text{I}) \) complexes, each of which is then reduced to a dinegative species.

\[
\text{M(II)} \overset{+e}{\underset{=}\rightarrow} \text{M(I)} \overset{+e}{\underset{=}\rightarrow} \text{M(0)}
\]

\[
\text{M(I)'} \overset{+e}{\underset{=}\rightarrow} \text{M(0)'}
\]

This rearrangement becomes less important for the heavier members of the group, the reduction of \( \text{Pt(SacSac)}_2 \) being uncomplicated (i.e. \( k \rightarrow 0 \)). Reduction of a series of bis(dithio-β-diketonato)nickel(II) complexes has revealed a marked dependence of \( E_{1/2} \) upon the ligand substituents.\(^2\)
Co(SacSac)\textsubscript{3} and Rh(SacSac)\textsubscript{3} are reduced \textit{via} a two-electron step accompanied by apparent loss of a ligand
\[ M(\text{SacSac})\textsubscript{3} + 2e^{-} \rightarrow M(\text{SacSac})_{2}^{-} + \text{SacSac}^{-} \quad M = \text{Co, Rh} \]

By contrast, Ir(SacSac)\textsubscript{3} undergoes two reversible one-electron reductions, although the potential separation between the \( E_{1/2} \)-values is small.

A number of other dithio-\( \beta \)-diketonato complexes have also been studied polarographically.\textsuperscript{2} The reductions of these compounds generally differ from those of their \( M(\text{SacSac})_{n} \) analogues to an extent entirely consistent with the variation of the ring substituents (and kinetic parameters, where applicable). Isolation of \( M(\text{OEtSacSac})_{2} \) (\( M = \text{Zn, Cd, Hg} \)) complexes\textsuperscript{3} enabled the polarography of the nd\textsuperscript{10} systems to be studied.\textsuperscript{109} Oxidation waves were observed for all complexes, these being assigned to the processes
\[ M(\text{OEtSacSac})_{2} \rightarrow M(\text{II}) + 2\text{OEtSacSac}^{+} + 4e^{-} \quad M = \text{Zn, Cd} \]
\[ \text{Hg}(\text{OEtSacSac})_{2} + \text{Hg} \rightarrow 2\text{Hg}(\text{OEtSacSac})^{+} + 2e^{-} \]

Two one-electron reductions are observed for \( \text{Zn}(\text{OEtSacSac})_{2} \), the electrode processes being postulated as\textsuperscript{109,222}
\[ \text{Zn}(\text{OEtSacSac})_{2} \xrightarrow{k} \text{Zn}(\text{OEtSacSac})_{2}^{-} \xrightarrow{k} \text{Zn}(\text{OEtSacSac})_{2}^{-2} \]

kinetically controlled
"rearrangement"

"Zn(\text{OEtSacSac})_{2}^{-2}"

Cd(\text{OEtSacSac})\textsubscript{2} also exhibits two one-electron reduction waves, however, these are irreversible and exhibit maxima. The reduction of \( \text{Hg}(\text{OEtSacSac})_{2} \) proceeds \textit{via} an irreversible two-electron step.

Prior to the present work, the only oxidative process observed polarographically for a non-d\textsuperscript{10} dithio-\( \beta \)-diketonate was that reported for Os(\text{OEtSacSac})\textsubscript{3}. Unfortunately, the proximity of the oxidation wave to the polarographic anodic limit (\textit{i.e.}, +0.8 V), precluded its characterisation, although the available data are not inconsistent with the formation of a formally Os(IV) species.\textsuperscript{2}
Several recent studies on transition metal chelates have exemplified the advantages provided by a knowledge of the redox processes of the chelating ligands.\textsuperscript{178-180,199,246} Because of the instability of most dithio-\(\beta\)-diketones, the only ligands of this class to have received study are \(\text{OEtSacSacH}\)\textsuperscript{115} and \(\text{NH}_2\text{SacNH}_2\text{SacH}\). Both compounds are reduced, presumably with the evolution of hydrogen, in a process somewhat analogous to the reduction of acetylacetone. The \(\text{OEtSacSacH}\) polarographic oxidation wave has been shown to involve electrode oxidation.

\[
\text{Hg} + \text{OEtSacSacH} \rightarrow \text{Hg(OEtSacSac)}^+ + \text{H}^+ + 2\text{e}^-
\]

Since \(\text{Hg(OEtSacSac)}^+\) slowly reacts with excess ligand, the coulometric oxidation process has been shown to be

\[
\text{Hg} + 2\text{OEtSacSacH} \rightarrow \text{Hg(OEtSacSac)}_2 + 2\text{H}^+ + 2\text{e}^-
\]

Although the products of the electrode process have not yet been synthesised, and so could not be used in the characterisation of the polarographic oxidation wave observed for solutions of \(\text{NH}_2\text{SacNH}_2\text{SacH}\); polarographic oxidation in such solutions is believed to proceed analogously to that in solutions of \(\text{OEtSacSacH}\).

\(\beta\)-Diketones exhibit both reductive and oxidative behaviour. The reduction of acetylacetone in acetonitrile has been shown to yield the acetylacetonate anion.\textsuperscript{247} This process is complicated by the preceding keto-enol tautomerism of acetylacetone, reduction being presumed to occur \textit{via} the enol form.

\[
\text{keto-acacH} \Rightarrow \text{enol-acacH} \xrightarrow{\text{e}^-} \frac{1}{2}\text{H}_2 + \text{acac}^-
\]

Further complications arise from the base-catalysis of the pre-reduction equilibrium by acac\(^-\) generated \textit{via} the reduction. \(\beta\)-Diketonate anions can be further reduced (either electrochemically, chemically or both) to dianion radicals and trianions.\textsuperscript{248-250}

Oxidation of the dibenzoylmethanate anion at a platinum electrode produces the corresponding radical which may either abstract a proton to form dibenzoylmethane or dimerise. Further products are of importance in longer time scale experiments.\textsuperscript{251} At the dme however, a
J. "iy ur e

6 - 2 . Subst ituent dependence of the reduction po tenti als of aryl­
substituted 1,2-dithiolium cations, and of the oxidation po tenti als
of aryl-substituted dithio-β-diketone anions. \( \Delta E_p = E_{1/2} \) referred
to that of phenyl-substituted derivative \( \text{X} = \text{X'} = \text{H} \) as zero, \( \sigma_p \)
substituent coefficient from reference 145. \( \Delta E_p \) values calculated
from data in reference 257.
"somewhat irreversible" anodic wave in the case of the acetylacetonate anion has been attributed to electrode oxidation.\cite{252,253} This

\[ \text{Hg} + 2\text{acac}^- \rightleftharpoons \text{Hg(acac)}_2 + 2e^- \]

wave is, of course, not observed at a platinum electrode.\cite{253}

Not unexpectedly, no anodic behaviour has been observed for substituted 1,2-dithiolium cations. However, their cathodic behaviour at a platinum electrode has been extensively studied in dichloromethane and acetonitrile solutions.\cite{254-257}

1,2-Dithiolium cations undergo three successive reductions, the first of which produces a radical species (II). The stability of this radical had been predicted on theoretical grounds,\cite{258} and its existence has been verified by esr spectroscopy. Reaction (1) is at least quasi-reversible with respect to the rate of the heterogeneous charge transfer, and has a substituent dependent $E_{1/2}$ (Fig. 6-2). Coulometric analysis established that one electron is transferred per dithiolium cation.

Radical II undergoes a monomer/dimer equilibrium (2), the magnitude of K being dependent on both the temperature and the nature of the substituent $R_3$. Thus, when $R_1 = R_2 = \text{Ph}$, and $R_3 = \text{H}$ (IIa), K is very large, IIIa may be isolated at room temperature, and the reduction of Ia is chemically non-reversible. However, when $R_1 = R_3 = \text{Ph}$, and $R_2 = \text{H}$ (IIb), K is small, the reduction of Ib is reversible, and the reduction product (IIb) gives a room temperature esr signal. This signal disappears at $-80^\circ$ and reappears on warming, indicating complete, reversible conversion to the dimer at low temperature.
Spectrophotometric studies establish that only 40% of the reduced species IIb is in the form of the radical at 25°. The reversibility of the reduction of Ib at 25° indicates that dissociation of the dimer IIIb must be very rapid. Although electronic effects are important, the position of the equilibrium (2) is primarily dependent upon steric factors. Thus, Id (R₁ = Ph, R₂ = H, R₃ = Me) and Ie (R₁ = R₃ = Me, R₂ = H) give only very short-lived radicals.

The reduction of the radicals II is chemically non-reversible. This non-reversibility has been accounted for in terms of initial formation of the anion IV followed by rearrangement to the dithio-β-diketonate anion V, the existence of which was postulated as a consequence of the similarity of the visible spectrum of Vb (λ_max 483 nm, log ε ~ 4.4) with those of the nickel and zinc chelates of dithio-dibenzoylmethane. The dithio-β-diketonate anions V undergo reversible one-electron reductions to the dianion radicals VI and oxidation to the radicals II. Although reduction of the dithio-β-diketonate anion is
electrochemically reversible, the product radical dianions could not be isolated.

6-2. EFFECTS OF STRUCTURAL AND RELATED VARIABLES ON THE ELECTROCHEMISTRY OF TRANSITION METAL COMPOUNDS

In the study of transition metal chelates, it is apparent that many modifications of the compounds affect the electrochemical response. Thus the redox process (i.e., combinations of $k_s$, $E_{1/2}^r$, $D_0$, $D_r$, etc.) of a transition metal chelate can be expected to be influenced by

(a) whether the redox process is metal- or ligand-based.
(b) the nature of the metal ion (e.g., electronic configuration, oxidation state, etc.),
(c) ligand isomerism.
(d) the geometry about the metal ion.
(e) substituents on the chelate ring.
(f) the size of the chelate ring.
(g) the amount of unsaturation within the ligand.
(h) the chelate ring donor atoms.
(i) the lability of members of the redox couple.

Any weighted combination of these factors may contribute to the electrochemical behaviour. A choice of a suitable series of closely related compounds often enables the effect of any of the above variables to be gauged while the other factors are kept constant, and in favourable cases the $E_{1/2}$ value of a particular compound may be
predicted.\textsuperscript{260} Since the magnitude of $E^0$ is clearly of fundamental importance in any redox-based applications of such compounds (e.g., stability of unusual oxidation states, use as a reductant or oxidant, oxygen transport and other biochemical properties), a knowledge of the effect of the structural and constituent variables upon $E^0$ is germane to the problem of designing a compound with predictable properties to fill such needs.

(a) METAL- AND LIGAND-BASED PROCESSES

Perhaps the most basic differentiation to be made in any discussion of the electrochemistry of ligated metal ions is whether the metal or the ligand undergoes the redox process. This is emphasised by the current interest in compounds with chelated metal ions in unusual formal oxidation states.\textsuperscript{154,260-264}

The extreme cases of a purely metal-based or purely ligand-based oxidation or reduction are often an oversimplification, since the molecular orbitals of a chelate compound will have both metal and ligand parentage. Whether a redox process is metal- or ligand-based cannot be established from isolated electrochemical measurements. Certainly, the observation of reversibility is no criterion. Comparative electrochemical studies can sometimes be useful, although care is needed in their interpretation. For example, a chelate ring substituent-dependent $E_{1/2}$ is not necessarily indicative of a ligand-based redox process, as has sometimes been implied. The most critical approaches to establishing the amount of metal character of the redox orbital are structural and, in particular, esr investigations of the redox product. In some circumstances, an esr signal may be broadened, or even not observed, so that such studies should always be augmented by magnetic susceptibility measurements.\textsuperscript{265}

The need to assign the redox process as metal- or ligand-based is best illustrated by the familiar example of the planar bis(dithiolene) complexes, \textit{[M(S\textsubscript{2}C\textsubscript{2}R\textsubscript{2})\textsubscript{2}]}\textsuperscript{z} (z = 0, -1, -2). These compounds are related by well-defined one-electron transfers. With some ligands of this type, the series has been extended to the $z = 1$ and $z = 2$ derivatives.\textsuperscript{165,244,266,267} Early descriptions of these compounds
included dinegative ligands with the metal in oxidation states IV (z = 0), III (z = -1) and II (z = -2), or two radical anion ligands with a univalent metal for z = -1. It is now generally accepted from structural and esr data that the electron transfer series are based predominantly on the ligand, the metal retaining a formal oxidation state of II.

Interestingly, recent reports establish the existence of [Ni(S₂C₂(CN)₂)₂]⁻³ in which the nickel is assigned an oxidation state of I on the basis of esr data. The z = -2 to z = -3 reduction is thus metal-based, in contrast to the other ligand-based couples.

Other examples of electron-transfer series incorporating both ligand- and metal-based processes are provided by metalloporphyrins. Thus, nickel(II) (Tetraphenylporphyrin) undergoes a metal-based, followed by two successive ligand-based oxidations:

\[ [\text{Ni(II)TPP}] \rightarrow [\text{Ni(III)TPP}] \rightarrow [\text{Ni(III)TPP}]^{2+} \rightarrow [\text{Ni(III)TPP}]^{3+} \]

Similar series exist for [Co(II)TPP] and [Fe(II)TPP], the metal- or ligand-based characters of the redox processes being established by esr and spectra data.

Establishing the ligand- or metal-based character of a redox process is obviously of fundamental importance in the discussion of the electrochemistry of metal complexes. Interestingly, the criteria of (1) a high concentration of charge on the donor atom and (2) the ability to delocalise the positive charge associated with the electron removal from the complex were recently suggested as being important in the stabilisation of high metal oxidation states, and thus, presumably, in promoting metal-based oxidations (although this is complicated by the paradox that highly negative ligands are susceptible to oxidation).

† The notation of ref. 265 has been adopted. Thus, in this example, [M(A)TPP]⁺ⁿ⁺ designates a tetraphenylporphyrin derivative of the metal M in oxidation state A, the complex having an overall charge of +n and with m unpaired electrons on the ligand.
(b) THE METAL ION

If it can be established that the electron-transfer is metal-based, then the nature of the metal ion is clearly important; relative \( E^0 \) values often being rationalised in terms of the number and distribution of d-electrons. A simple example is provided by consideration of high spin octahedral complexes of trivalent chromium and manganese. Reducing \( \text{Cr(III)} \) (\( t^3_{2g} \)) would be expected to be more difficult than reducing \( \text{Mn(III)} \) (\( t^3_{2g}eg^1 \)) to high spin \( \text{Mn(II)} \) (\( t^3_{2g}eg^2 \)), since \( \text{Cr(II)} \) will be destabilised with respect to \( \text{Cr(III)} \) as a consequence of either the energy difference between the \( t^2_{2g} \) and \( eg \) orbitals (\( \text{Cr(III)} t^3_{2g} \rightarrow \text{high spin Cr(II)} t^3_{2g}eg^1 \)) or the pairing energy of the d-electrons (\( \text{Cr(III)} \rightarrow \text{low spin Cr(II)} t^2_{2g}eg^1 \)), with contributions such as the exchange energy of the lone \( eg \) electron in high spin \( \text{Cr(II)} \), and the loss of the stability due to a half-filled subshell in \( \text{Cr(III)} \) providing further complications. Accordingly, it has been found that for the redox behaviour of the octahedral \( M(\text{dtc})_3 \) chelates with the same substituents.

"... The observed resistance of \( \text{Co(III)}[t^5_{2g}] \) and \( \text{Cr(III)}[t^3_{2g}] \) compared with \( \text{Mn(III)}[d^5] \) and \( \text{Fe(III)}[d^5] \) to both oxidation and reduction correlates well with the marked stability associated with the filled and half-filled \( t^2_{2g} \) subshell. ..."^272

Similarly, the observation of a single facile reduction of the \( M(\text{SacSac})_3 \) (\( M=\text{Fe, Ru, Os} \)) chelates has been correlated with the completion of the stabilised metal \( t^2_{2g} \) subshell.^169

Allied to the effects on \( E_{1/2} \) due to the distribution of d-electrons occasioned by the ligand-field splitting, are those due to the number of d-electrons and the metal oxidation state. Vasilevskis and Olson^273 have collected data on the oxidation of a number of metal complexes of the \( \text{Me}_6[14]\text{aneN}_4 \) macrocyclic ligand, and argue that an increase in the number of d-electrons makes the oxidation of \( M(\text{II})L \) more difficult (Table 6-1) and that the ease of oxidation of complexes with the same number of d-electrons decreases as the oxidation state increases (Table 6-1). They comment further that a change in oxidation state has a greater effect on \( E_{1/2} \) than does a charge of the same magnitude in the number of d-electrons. Unfortunately, the data are not extensive enough to yield general conclusions about the effects of these
Table 6-1. Variation of $E_{1/2}$ with oxidation state and metal d-orbital population for metal-Me$_6^{14}$aneN$_4$ complexes (after ref. 273).

<table>
<thead>
<tr>
<th>Electrode Reaction</th>
<th>$E_{1/2}$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) d-electron effect</td>
<td></td>
</tr>
<tr>
<td>$d^7$ Co(II) → Co(III) + e</td>
<td>+0.08</td>
</tr>
<tr>
<td>$d^8$ Ni(II) → Ni(III) + e</td>
<td>+0.88</td>
</tr>
<tr>
<td>$d^9$ Cu(II) → Cu(III) + e</td>
<td>+1.22</td>
</tr>
<tr>
<td>(b) oxidation-state effect</td>
<td></td>
</tr>
<tr>
<td>$d^9$ Cu(II) → Cu(III) + e</td>
<td>+1.22</td>
</tr>
<tr>
<td>$d^9$ Ni(I) → Ni(II) + e</td>
<td>-1.57</td>
</tr>
<tr>
<td>$d^8$ Ni(II) → Ni(III) + e</td>
<td>+0.88</td>
</tr>
<tr>
<td>$d^8$ Co(I) → Co(II) + e</td>
<td>-2.03</td>
</tr>
</tbody>
</table>
variables (for example, the obviously important effect of varying the
charge on the compound is not considered. The ordering of the
reductions of a series of metalloporphyrins has, for example, been
attributed to increasing charge on the ligands.\(^{274}\)); however, both
effects can be rationalised simply on electrostatic grounds.

The presence of a high spin ≠ low spin equilibrium in either
member of a redox pair will further complicate the electrochemistry.
This effect is manifest by the octahedral Fe(dtc)\(_3\)\(^n\) complexes. For
example, it has been established that \([\text{Fe}^{3+2}(\text{Et}_2\text{dtc})_3]^z\) changes from low
spin (d\(^4\)), through a mixture of high and low spin (d\(^5\)), to high spin
(d\(^6\)) as \(z=+1,0,-1\) respectively.\(^{275}\) Such behaviour might conceivably
yield separate polarographic waves for the reduction or oxidation of the
high- and low-spin isomers of an intermediate spin complex. In fact,
the trend in oxidation and reduction potentials of Fe(dtc)\(_3\) complexes is
simply that predicted on the basis of alteration of the substituents\(^{276}\)
indicating that the redox potential is independent of the metal spin
state. A theoretical treatment of the reversible polarographic
oxidation of Fe(dtc)\(_3\) undergoing a very rapid spin interconversion with
an equilibrium constant \(K\) predicts only one \(\text{Fe}^{\text{III}} \rightleftharpoons \text{Fe}^{\text{IV}}\) (or \(\text{Fe}^{\text{III}} \rightleftharpoons \text{Fe}^{\text{II}}\)
reduction wave) oxidation wave, with

\[
E_{1/2}^{\text{meas}} = E_0^{\text{Fe(IV)/h.s. Fe(III)}} + \frac{RT}{F} \ln \left( \frac{K}{1 + K} \right)
\]

and that

\[
E_{1/2}^{\text{meas}} - E_0^{\text{Fe(IV)/h.s. Fe(III)}} \leq 17.8 \text{ mV},
\]

the measured potential therefore being a good approximation to \(E_0^{\text{}}\).\(^{276}\)

A metal-based redox process will effect a change in the size
of the chelated metal. If the donor atom set is constrained relatively
rigidly about the metal atom, as in the case of some macrocyclic
ligands, then the change in size of the metal upon reduction or
oxidation may make the redox process unfavourable, if the metal-donor
atom distances cannot adjust accordingly. Thus, the reduction of
\(\text{Ni(Me}_6[14]\text{aneN}_4)\) is favoured over the reduction of \(\text{Ni(Me}_6[16]\text{aneN}_4)\),
whilst the reverse order holds for the ease of oxidation.\(^{260}\) In this
case, the redox processes are reversible. However, if, for example,
significant structural changes were necessary to accommodate a metal ion
Figure 6-3. Orbital level splitting scheme for trans- and cis-
M(CO)\textsubscript{2}(DPE)\textsubscript{2} complexes. From reference 279.
in a macrocyclic ligand "hole" after reduction or oxidation, then the redox process may be rendered non-reversible. The electrochemical behaviour of Pb(II) and Sn(II) porphyrins has been interpreted in terms of a decrease in metal ionic radii accompanying metal oxidation.\textsuperscript{277,278}

(c) LIGAND ISOMERISM

An interesting corollary to the effect of the metal ion upon the redox process is that perturbations of metal ion orbital energies can be reflected in metal-based electron transfers. Thus the observation of separate oxidation and reduction potentials for the cis- and trans-isomers of \([\text{M(CO)}_2(\text{DPE})_2]^{+n}\) \((n = 0, 1, 2, \text{DPE} = \text{bisdiphenyl-phosphinoethane})\) has been attributed to changes in the splitting of the d-orbitals in the isomers (Fig. 6-3).\textsuperscript{279} These splittings derive from the differing steric and electronic effects of the ligands in the two geometries, and result in the cis-configuration being favoured for the low metal oxidation states, and the trans-configuration being favoured for higher oxidation states. The cis-M(0) compounds, then, are invariably harder to oxidise than the trans-M(0) species, and although the product of the cis-M(0) oxidation is initially cis-M(I), this rapidly isomerises to trans-M(I). A particularly elegant example of this phenomenon is provided by cyclic ac voltammetric studies\textsuperscript{229} on cis\{Mo(CO)\_2(DPE)\_2\}.

Obviously, geometric isomerism originating at a site sufficiently distant from the metal ion to preclude isomer-induced variations in the d-orbital splitting will not be reflected in the electrochemistry. Thus, no difference is apparent in the reduction potentials of cis- and trans-M(OEtSacSac)\_2 \((M = \text{Pd, Pt})^2\) VII and VIII.

However, should geometric isomerism in complexes undergoing metal-based electron transfers lead to d-orbital splittings of different types or magnitudes, then the cis- and trans-isomers are expected to undergo redox processes at different potentials, similarly to the \([\text{M(CO)}_2(\text{DPE})_2]^{+n}\) complexes above. This effect should be observed, for example, in possible cis- and trans-isomers of M(diars)Cl\_2 complexes which are of current interest\textsuperscript{280} and which have similar symmetry properties to those of M(CO)\_2(DPE)\_2 compounds.
A similar effect to that discussed above is provided by compounds which undergo square planar ⇄ tetrahedral isomerism. On the basis of the different d-orbital splittings, separate $E_{1/2}$-values are expected for metal-based redox processes of each isomer if the interconversion rate is slow. The electrochemistry may, of course, be complicated by the kinetics of the interconversion, \textsuperscript{202,236} and the possible similar equilibria of the redox products. In the limit of slow interconversion between isomers, two waves (or sets of waves for consecutive electron transfers) are expected.

Square planar ⇄ tetrahedral equilibria are well established for many divalent metal bis(chelate) compounds.\textsuperscript{25,31,281} Two examples allied to the compounds of the present work are provided by Ni(NRacSac)$_2$ complexes (IX) and by Co(Bu$^t$SacBu$^t$ac)$_2$ (X).

\textbf{(d) METAL-ION GEOMETRY}

\begin{align*}
\text{IX} & \quad \text{Co} & \quad \text{Ni} \\
\text{X} & \quad \text{C}_4\text{H}_9 & \quad \text{C}_4\text{H}_9
\end{align*}
Table 6-2. Variation of mole fraction of $\text{Ni}(R-S\text{PhHH})_2$ in tetrahedral form ($N_t$) with R (after ref. 31).

<table>
<thead>
<tr>
<th>R</th>
<th>t-Bu</th>
<th>i-Pr</th>
<th>Et₂CH</th>
<th>Ph</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_t$</td>
<td>1.0</td>
<td>0.43</td>
<td>0.31</td>
<td>0.02</td>
</tr>
</tbody>
</table>
Complexes of type IX have been extensively studied by nmr and magnetic susceptibility measurements, and their equilibria are well characterised. The data of Table 6-2 indicate that the tetrahedral geometry is favoured by complexes with bulky R-groups. Accordingly, electrochemical investigations of a series of compounds I, with R-groups chosen so as to provide examples of "pure" tetrahedral, "pure" square planar and mixed geometries can be envisaged.

The compound X is of especial interest, as it is the intermediate member of the series CoO₄ (XI), CoO₂S₂ (X) and CoS₄ (XII).

\[
\begin{align*}
\text{X} & \quad \text{XI} \\
\text{X} & \quad \text{XII}
\end{align*}
\]

CoO₄ is known to be a tetrahedral monomer and CoS₄ is expected to be a square planar monomer analogous to Co(SacSac)₂. Nmr and magnetic susceptibility studies establish that CoO₂S₂ undergoes a temperature-dependent square planar ⇌ tetrahedral interconversion, with the tetrahedral form being favoured at high temperatures. Donor atom effects on the electrochemistry have been established by the present work, and so the series, X, XI, XII, should provide a particularly useful example of the influence on the electrochemistry of changes in the metal geometry induced by alteration of the donor atom.

(e) SUBSTITUENT VARIATION

The effect of substituents upon \(E_{1/2}\) essentially arises from the ability of substituent variation to stabilise the compounds undergoing the redox process. Irrespective of whether the electron transfer of a metal chelate is ligand- or metal-based, the chelate ring substituents exert an often profound influence upon the \(E_{1/2}\)-values. If the redox process is ligand-based, then the substituents can be
Table 6-3. Half-wave potentials for reductions of $cp_2V_L^+$ compounds (after ref. 179).

<table>
<thead>
<tr>
<th>L</th>
<th>$E_{1/2}$, V vs. Ag-AgCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-methyl xanthate</td>
<td>-0.243</td>
</tr>
<tr>
<td>O-ethyl xanthate</td>
<td>-0.254</td>
</tr>
<tr>
<td>O-isopropyl xanthate</td>
<td>-0.274</td>
</tr>
<tr>
<td>O-(n-butyl) xanthate</td>
<td>-0.288</td>
</tr>
<tr>
<td>O-cyclohexylxanthate</td>
<td>-0.300</td>
</tr>
<tr>
<td>N-methyldithiocarbamate</td>
<td>-0.418</td>
</tr>
<tr>
<td>N,N-dimethyldithiocarbamate</td>
<td>-0.416</td>
</tr>
<tr>
<td>N,N-diethylidithiocarbamate</td>
<td>-0.415</td>
</tr>
<tr>
<td>N,N-diisopropylidithiocarbamate</td>
<td>-0.428</td>
</tr>
<tr>
<td>N,N-di(n-butyl)dithiocarbamate</td>
<td>-0.422</td>
</tr>
</tbody>
</table>
anticipated to effect $E_{1/2}$ in a manner analogous to that observed in organic molecules. Thus, a plot of the sum of the Hammett substituent coefficients ($\xi_0$) against $E_{1/2}$ for the $z=-1$ to $z=-2$ reductions of nickel bis(dithiolene) complexes is a straight line described by

$$E_{1/2} = 0.74 \xi_p - 0.90$$

illustrating that the presence of electron withdrawing substituents facilitates the reduction.

It might be argued that a metal-based electron transfer will be unaffected by substituent variation, and the substituent-dependence of $E_{1/2}$ has (incorrectly) been used as a criterion of a ligand-based redox process. However, in simple valence bond terms, or on the basis of electrostatic arguments, if the inductive effect of the substituents can be transmitted through the ligand and thereby influence the amount of electron density on the metal, then substituent variation will affect $E_{1/2}$.

The influence of 1,2-dithio-chelate ring substituents upon metal-based processes is quite marked. Thus, a comparison of the effects of xanthates (XIII) and dithiocarbamates (XV) as $L$ on the $V^{IV}/V^{II}$ couple of $[\text{cp}_2VL]^+$ compounds (Table 6-3) shows that those compounds with xanthate ligands are easier to reduce than those with dithiocarbamate ligands. This effect can be rationalised in terms of the greater contribution of canonical structure XVI to the electronic structure of the dithiocarbamates, compared with the contribution of XIV to the xanthate structure, resulting in more negative charge in the vicinity of the metal centre when $L=$ dithiocarbamate. Then,

$$\text{XIII} \quad \text{XIV}$$
Table 6-4. Half-wave potentials for oxidations of ferric and cupric complexes of the 1,1-dicarboethoxy-2,2-ethylenedithiolate dianion (ded).

<table>
<thead>
<tr>
<th>Electrode Reaction</th>
<th>$E_{1/2}$, V</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{III}$ (ded)$_3$ $\rightarrow$ Fe$^{IV}$ (ded)$_3$ + e</td>
<td>-1.20</td>
<td>261</td>
</tr>
<tr>
<td>Cu$^{II}$ (ded)$_2$ $\rightarrow$ Cu$^{III}$ (ded)$_2$ + e</td>
<td>-0.50</td>
<td>262</td>
</tr>
</tbody>
</table>
"... If the electron-donor capacities of the various chelates are important, a larger ligand to metal charge donation should stabilize the more electropositive vanadium(IV) system \((\text{d}^1)\) in preference to the vanadium(III) system \((\text{d}^2)\). Such an effect should lead to \(E_{1/2}\) values generally occurring at more negative potentials, and in fact the ease of reduction correlates quite well with the amount of charge donated. ..."[179]

Certainly, the amount of charge donated is of importance, as the most difficult of these compounds to reduce are those with the dianionic ligands, mnt (XVII) and cdtc (XVIII).

An extreme example of the ability of ligand negative charge to stabilise products of electron transfer is provided by the extraordinarily easy oxidations of Cu(II) and Fe(III) complexes of ded (XIX) \(^{261,262}\). This influence of ligand negative charge on the stabilities of products of metal-based electron transfer is confirmed by the isolation and characterisation of high metal oxidation state compounds of ded and
dtc, where ligand structures such as XVI and XIX are of importance. 154,261,262

More subtle inductive effects upon redox behaviour are revealed upon variation of the xanthate-R group in the \([\text{cp}_2\text{V(xan)}]^{+}\) and \(\text{Fe(xan)}_3\) series. In the former, 179,180 the order of ease of reduction

\[
\text{Me} > \text{Et} > \text{Pr} > \text{Bu} > \text{cyclohexyl}
\]

was observed, this being paralleled by the order

\[
\text{Me} > \text{Et} > \text{i-Pr}
\]

in the latter. 276

In the dithiocarbamates, the substituent effect is still more complex; the detailed nature of the R,R' substituents becoming important. Thus, dithiocarbamate substituents may be ordered on the basis of their inductive capabilities, and via the series (for decreasing ease of reduction) 276

\[
\{\text{aryl substituents}\} > \{\text{saturated chains}\} > \{\text{\(\alpha\)-branched, saturated chains}\}
\]

\[
\begin{align*}
\text{Ph}_2 & > \text{Ph, Me} \\
\text{Me}_2 & > \text{Et}_2 \\
i-\text{Pr}_2 & > \text{c-Hx}_2
\end{align*}
\]

A steric effect of the estimated RNR angle was also noted; reduction becoming more difficult as this angle increases.

ease of reduction azetidine > pyrrolidine > Et~piperidine > (cyclohexyl)$_2$

no. of ring atoms 4 5 open 6 open
Figure 6-4. Substituent dependence of \( E_{1/2} \) for ruthenium tris(\( \delta \)-diketonato) complexes. \( \sigma_m \) values from reference 145. \( E_{1/2} \) values from reference 112.
The substituent effect has been observed in the reductions of β-diketonato complexes. In Figure 6-4, $E_0$ is plotted against $E_{1/2}$ for the reductions of a series of trivalent ruthenium tris(β-diketonato) complexes and the linear relationships

$$E_{1/2}(V) = 0.381 \Sigma_\sigma - 0.448$$

$$E_{1/2}(V) = 0.548 \Sigma_\sigma - 0.605$$

have been obtained. Although the substituent dependence of the oxidations of dtc complexes parallels that of their reductions, no substantial substituent effect was observed for the quasi-reversible one-electron oxidations of the ruthenium(III) β-diketonates. Holm has suggested that this behaviour indicates that uncomplicated chemical oxidation to ruthenium(IV) complexes might be difficult to achieve. However, the results of the present work (vide infra) indicate that the quasi-reversibility may be a function of the slow charge transfers expected for oxygen chelates at a platinum electrode and that therefore, stable ruthenium(IV) β-diketonates may be synthetically accessible.

Successive one-electron reductions of tris(β-diketonato)-chromium(III) chelates have also been shown to be subject to the influence of the electron-releasing powers of the substituents. The results suffer somewhat from the lack of complete reversibility of the reductions, however, the dependence of $E_{1/2}$ upon substituent is clear, the straight line dependences of the first and second reduction potentials upon $\Sigma_\sigma$ being described by the equations

first reduction $E_{1/2} = 1.33 \Sigma_\sigma - 1.45$ or $0.94 \Sigma_\sigma - 1.37$

second reduction $E_{1/2} = 1.22 \Sigma_\sigma - 1.91$ or $0.90 \Sigma_\sigma - 1.83$

The effect of substituents on the $E_{1/2}$ of $M(acac)_n$ complexes is quite marked, the reported range of $E_{1/2}$ values being 1.76 V when $M =$ chromium, 1.84 V when $M =$ ruthenium, and 0.73 V when $M =$ copper.

Substituent effects have also been observed for the reductions of divalent nickel dithio-β-diketonates. The relationship

$$E_{1/2} = 1.229 \Sigma_\sigma - 0.784$$
Figure 6-5. "... Schematic molecular orbital energy level diagrams for "even" and "odd" unsaturated ligand systems (X = \(=0\), \(=\text{HR}\), or \(=5\)). "Odd" or "even" are ligands containing an odd or even number of vertical \(\pi\)-orbitals. ..." Taken from reference 165.
has been found to describe the substituent dependence of the first reduction steps.

The effect of substituents on the $E_{1/2}$-values of metal-based redox processes is then primarily dependent upon the extent to which the redox products can be stabilised by the donation or withdrawal of negative charge to or from the metal. Steric effects are also clearly of importance and may be a result of the requirements of certain substituent orientations for the transmission of inductive effects.

(f) RING SIZE

Reductions of macrocyclic complexes of nickel are favoured by larger ring sizes, an effect attributed to the increase in size of the nickel ion on reduction. The converse applies to oxidations. This comparison cannot be extended easily to bidentate chelates which lack the more rigid structural constraints of tetradienate macrocycles.

Variation in the ring size of bidentate chelates is usually accompanied by other structural changes, thereby confusing the determination of ring size variation effects. A very simple approach would be to calculate $E_{1/2}$ when $E_0 = 0$ for the various ring sizes from substituent data. However, insufficient data are available for such a correlation.

The most significant differentiation between ring sizes is provided by Schrauzer's "odd" (i.e., ligands with an odd number of ring atoms) and "even" ligand classification.

"... Every "odd" unsaturated ligand system will tend to exist as a monoanion owing to the presence of the non-bonding singly occupied πMO in its energy level scheme." (Fig. 6-5) "Since no other low-lying π molecular orbitals are present, the "odd" ligands usually do not accept additional electrons and hence behave "normally". In the four-atom "even" ligands the lowest unoccupied πMO is only weakly antibonding if the two atoms at positions 1 and 4 of the butadiene framework are sulfur. Hence, this system may exist as the neutral ligand, the monoanion, or the dianion ..."165

and thus,

"... In contrast to the dithiene ligands ... "1,1- and 1,3-dithio ligands" ... are odd π-electron systems in the
neutral state and therefore will tend to form stable, diamagnetic monoanions. Their transition metal derivatives should of course also be delocalized, but these complexes are distinctly different from the dithienes. In particular, they will not possess the unusually high electron affinity of the dithienes since the ligands have no tendency to form dianions... It thus follows that the complexes of the 1,2-bidentate sulfur ligands form a very distinct group of compounds whose properties and usual structures are not likely to be duplicated by other ligand systems. ..."^243

Unfortunately, Schrauzer's classification has led to the misconceptions that "odd" ligand complexes would not undergo ready electron transfers, and that the observation of non-reversible waves from complexes with "odd" ligands, or reversible waves from complexes with "even" ligands support the ideas of Schrauzer, or that the converse invalidates them. ^244,285-288

The ability of both 1,1-dithio, 1,3-dithio, and β-diketonato chelates to undergo reversible electron transfers and to stabilise a variety of metal oxidation states has been convincingly established. ^2,74,82,144,146,154,169,261,262,272,276,289,290 Thus, any implied inability of "odd" ligand systems to undergo ready electron transfers is clearly erroneous. Similarly, the degree of reversibility of an electron transfer cannot be used to test Schrauzer's classification, as non-reversibility is not necessarily indicative of a small k_s value. Furthermore, if a redox process is reversible, then the final location of the electron is immaterial.

The fundamental difference in behaviour between "even" and "odd" unsaturated ligand chelates, and one not inconsistent with the conclusions of Schrauzer, is that "odd" ligand complexes favour metal-based, and "even" ligand complexes favour ligand-based redox processes. In the framework of Schrauzer's proposals, this is a consequence of low-lying \( \pi^* \) molecular orbitals of predominantly ligand character in the compounds of the "even" ligands.

(g) LIGAND UNSATURATION

The consequences of increasing the amount of unsaturation in the ligand are difficult to gauge. Few compounds provide data for such a study, since a change in the amount of ligand unsaturation often
accompanies other structural variations. However, the $E^0$ values of a series of ruthenium complexes with varying amounts of unsaturation in the ligands have been correlated with the π-accepting ability of the ligands.\textsuperscript{291} Interelectron repulsion in the metal ion is reduced by an increase in the amount of metal to ligand π-backbonding; ligands with the greatest π-acceptor ability thereby stabilising Ru(II) relative to Ru(III). This argument has been used by Beattie\textsuperscript{292} in comparing the Ru\textsuperscript{II}/Ru\textsuperscript{III} couples of Ru(en)$_3$\textsuperscript{+n} and Ru(en)$_2$(di-imine)$\textsuperscript{+n}$ (XX).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{ruen2.png}
\caption{Structure of Ru(en)$_2$}
\end{figure}

Similar results are obtained by successive substitutions of Ru(en)$_3$\textsuperscript{+n} by 1,10-phenanthroline ligands,\textsuperscript{292} the -N-C-C-N- backbone being common to both ligands; and by comparisons between oxidations of (NH$_3$)$_6$Ru$^{+2}$ and (NH$_3$)$_4$Ru(di-imine)$^{+2}$ (XXI).\textsuperscript{293}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{rueh4.png}
\caption{Structure of (NH$_3$)$_4$Ru}
\end{figure}

However, it should be reemphasised that in all of these cases, structural changes in the ligand backbone accompany the changes in the degree of ligand unsaturation.

Half-wave potentials of nickel macrocycles can also reflect the effect of ligand unsaturation.\textsuperscript{260} An increase in the amount of
Figure 6-6. Ligands L in the complexes NiL\textsuperscript{7} of reference 260. The reduction (R) and oxidation (O) products of NiL\textsuperscript{7} are represented by R/O, where R = Ni\textsuperscript{I} signifies reduction to Ni\textsuperscript{I}, R = L\textsuperscript{7} signifies reduction to a ligand radical stabilised by Ni\textsuperscript{II}, and O = Ni\textsuperscript{III} signifies oxidation to Ni\textsuperscript{III}L\textsuperscript{7}.
unsaturation is accompanied by a positive shift in the $E_{1/2}^{II/III}$ value. The stability of Ni$^{II}$ relative to Ni$^{III}$ as a consequence of increased ligand unsaturation has been attributed to an "... increasing degree of polarizability of the metal-ligand bond in the more unsaturated derivatives."

The position of ligand unsaturation in this series is also important. Significantly, in every case in which an $\alpha$-diimine function (XXII) occurs in a neutral macrocycle, reduction of the nickel chelate

\[ \text{XXII} \]

yielded a ligand radical stabilised by Ni$^{II}$, rather than a Ni$^{I}$ species (Fig. 6-6). Those Ni$^+$ compounds with neutral macrocyclic ligands containing the $\alpha$-diimine function (Class A ligands) are structurally analogous to the most highly oxidised member of the nickel bis(diimine) series of complexes XXIII which have "even" ligands by Schrauzer's classification, and which undergo ligand-based reductions. Thus, the ligand-based character of the Ni$^{I}$ compounds with Class A ligands is not surprising. An interesting corollary follows. Since Ni$^+$ compounds with Class A ligands are oxidised to yield Ni$^{III}$ compounds, a further, as yet unobserved, metal-based oxidation of complexes of the type XXIII
to yield Ni\textsuperscript{III} bis chelates is expected. (The analogy between iso electronic Ni(mnt\textsubscript{2})\textsuperscript{2-} and Ni(SacSac\textsubscript{2})\textsuperscript{2-} led to the observation of a metal-based Ni(mnt\textsubscript{2})\textsuperscript{2-} reduction.\textsuperscript{2,271}) Further, it is interesting to note that the metal- or ligand-based character of the reductions of some complexes containing 1,10-phenanthroline and 2,2'-bipyridyl ligands is still debated.\textsuperscript{294-297} Both of these ligands formally contain the di-imine function. However, in neither of these ligands is an analogue of the most reduced form of the di-imine ligand (XXIV) favoured.

![XXIV](image)

(h) DONOR ATOMS

Although the electrochemistry (either metal- or ligand-based) of transition-metal chelates can be expected to be intimately associated with the nature of the chelate ring donor atoms, few studies have been concerned with their role.\textsuperscript{2,179,298} The major reason for this is probably the lack of a suitable series of compounds in which the requirements of donor atoms as the only variable, and reversible redox processes are met. One of the few systems in which systematic variation of the donor atom can be studied is provided by the β-diketonate, monothio-β-diketonate and dithio-β-diketonate series of compounds. Such studies were undertaken in the present work and are reported in detail of Chapters 7 and 8.

(i) LABILITY OF MEMBERS OF THE REDOX COUPLE

Redox-based applications of transition metal chelates can often be facilitated or precluded by the lability of either member of
the redox pair. A simple example is provided by cis- and trans-M(CO)$_2$(DPE)$_2$ compounds. It was established that whilst the previously unknown trans-Mo(CO)$_2$(DPE)$_2$ should be isolable,

$$\text{trans-}[\text{Mo(CO)}_2(\text{DPE})_2]^+ \quad \overset{e}{\rightarrow} \quad \text{trans-}[\text{Mo(CO)}_2(\text{DPE})_2]$$

-0.04 V

attempts to oxidise zero-valent cis-compounds to their monovalent analogues would yield only the trans-product at room temperature as a consequence of the rapid isomerism

$$\text{cis-M(0)} \quad \overset{k}{\rightarrow} \quad \text{cis-M(I)} \quad \overset{k}{\rightarrow} \quad \text{trans-M(I)}$$

The existence of mixed-ligand ferric dithiocarbamates FeL$_x$L'$_y$ (x + y = 3) can be detected voltammetrically in mixtures of FeL$_3$ and FeL'. However, these mixed-ligand complexes could not be isolated by chromatography because of rapid ligand exchange. In contrast, non-labile Co$_x$III L'$_y$ (x + y = 3) dithiocarbamates have been isolated and characterised, and their redox potentials have been found to be linearly dependent upon successive ligand replacement.

The ability of Li$^+$ ions to induce co-ordinative relaxation of Fe(acac)$_3$' in acetonitrile

$$\text{Fe(acac)}_3 \quad \overset{\text{Li}^+}{\rightarrow} \quad \text{Fe(acac)}_3^- + 2\text{Li}^+ \quad \overset{\text{Li}_2(\text{acac})^+ + \text{Fe(acac)}_2}{\rightarrow}$$

has allowed the "unknown" complexes Fe(acac)$_2^+$, Fe(acac)$^{+2}$, Fe(acac)$_3^-$, Fe(acac)$_2$ and Fe(acac)$^-$ to be studied electrochemically and spectrophotometrically.

In an extended series of cp$_2^2$V$^IV$L$^+$ chelates (where L is a ligand with a sulphur donor atom), several V$^IV$V$^III$ reductions have been shown to be followed by loss of a ligand which then oxidises mercury.

$$[\text{cp}_2^2\text{V}^IV\text{L}]^+ + e \quad \overset{k_f}{\rightarrow} \quad [\text{cp}_2^2\text{V}^III\text{L}]^0$$

$$[\text{cp}_2^2\text{V}^III\text{L}]^0 \quad \overset{k_l}{\rightarrow} \quad "\text{cp}_2^2\text{V}^III^- + \text{L}^-"$$

$$\text{L}^- + \text{Hg}^0 \quad \overset{\text{mercury complexes}}{\rightarrow}$$
The lability of $\text{cp}_2\text{V}^{\text{III}}L$ was dependent on the chelate, $k_f$ being significant when $L=$ dithiophosphate, and very small when $L=$ xanthate. In most cases, however, $k_f$ was small enough that meaningful comparisons could be made between $E_{1/2}$-values. The synthesis of $\text{cp}_2\text{V}(\text{SacSac})\text{BF}_4$ in the course of the present work presents the interesting possibility of studying the hitherto unobtainable free SacSac$^-$ ligand. A further possible route to SacSac$^-$, also a consequence of the lability of a redox product, is provided by $\text{Co(SacSac)}_3$, which is thought to be reduced via the mechanism

$$\text{Co(SacSac)}_3 + 2e \rightarrow \text{Co(SacSac)}_2^- + \text{SacSac}^-$$

The substitution-inert behaviour of $\text{Co}^{\text{III}}$ and the lability of $\text{Co}^{\text{II}}$ are well known, and a further example of a non-labile $\text{Co}^{\text{III}}$ compound being reduced to a labile $\text{Co}^{\text{II}}$ product is provided by [Co(dipy)$_3$]$^{+3}$, the electrochemistry of which has been described by

$$\begin{align*}
\text{Co(dipy)}_3^{+3} & \longleftrightarrow E_1^0 \rightarrow \text{Co(dipy)}_3^{+2} \longleftrightarrow E_2^0 \rightarrow \text{Co(dipy)}_3^+ \\
& \downarrow \quad \downarrow \\
\text{Co(dipy)}_2^{+2} & \quad \text{Co(dipy)}_2^+ \quad \text{Co(dipy)}^+ \\
& \quad E_3 \rightarrow \text{Co(m)}
\end{align*}$$

Thus the possibility that members of the redox pair may be labile is an important factor in the interpretation and application of electrochemical data. The particular case of labile redox products producing redoxactive compounds is discussed in Chapter 9.
CHAPTER 7

INFLUENCE OF OXYGEN AND SULPHUR DONOR ATOMS ON THE ELECTROCHEMISTRY OF TRANSITION METAL TRIS CHELATES
Following the original synthesis of group 8 divalent metal dithioacetylacetonato (C_5H_7S_2 = SacSac) complexes, the range of complexes of dithio-β-diketonato ligands has been extended to include the electron configurations \(d^3, d^5, d^6, d^7, d^8, \) and \(d^{10}\). These and the cogeneric acetylacetonato compounds provide an unusual opportunity to compare directly the relative effects of oxygen and sulphur in electron-transfer processes.

Replacement of oxygen by sulphur usually results in spin pairing of metal 3d electrons and a tendency to suppress oligomer formation by complexes with co-ordinately unsaturated metal centres. Although empirical molecular orbital calculations and electronic spectral assignments have been attempted for dithio-acetylacetonato complexes, intense charge-transfer bands obscure most of the visible region precluding comparisons with the d-d transitions of the corresponding acetylacetonato complexes.

Electrochemical studies have been reported for all of the SacSac complexes. Most of them, in common with metal complexes of other bidentate sulphur ligands, undergo one or more reversible one-electron reductions. Donor atom effects in the series \([M-O]_4\), \([M-O_2S_2]\), \([M-S]_4\), \([M-O]_2\), \([M-O_2S]_2\) (\(z = 2+ \rightarrow 2-\)), similar to that of the 1,2-dithiolenes, occurs. Such studies have been restricted to bis-chelated complexes and have often been beset by problems of non-reversibility and low chemical stability of the oxygen-substituted systems. Whether the lack of reversibility is a function of the structure of the oxygen chelates or simply the inability of oxygen to facilitate fast electron-transfer steps is unknown.
Figure 7-1. Ac frequency dependence of the ac polarographic peak heights of the first reduction waves of the chelates. •, Cr(SacSac)₃; ■, Fe(acac)₃; ◆, Mn(acac)₃; ▲, Cr(acac)₃. The height of the plateaux are linearly related to $k_v$ values.
In the present Chapter, the redox properties of a selection of acetylacetonates and dithioacetylacetonates of the transition metals Cr(III), Mn(III), Fe(III), and Co(III) are compared in an attempt to evaluate the kinetic and thermodynamic consequences of substituting oxygen by sulphur in a series of closely related complexes.

(a) CHROMIUM

Both Cr(SacSac)_3 and Cr(acac)_3 exhibit two one-electron reductions at a dme. No oxidation of either compound is observed at mercury or platinum electrodes. The first reduction of Cr(SacSac)_3 has been shown (Chapter 3) to be diffusion controlled and reversible in the dc sense, and is affected neither by changes in drop time nor electrode material (Tables 7-1 and 7-2). It is also essentially reversible in ac polarography over a wide frequency range. At high frequencies, the slight difference between the ac peak potential, \( E^{P}_{dc} \), and \( E^{F}_{1/2} \) yields \( \alpha = 0.46 \); a value close to 0.5 being consistent with the polarographic behaviour of all the present compounds. A value of \( \alpha = 0.5 \) is assumed in calculations of \( k_s \) for compounds where \( \alpha \) could not be evaluated. Although a plot of \( [I(\omega t)]_P \omega^{1/2} \) begins to deviate from linearity at very high frequencies (Fig. 7-1), this departure is insufficient to permit the unambiguous calculation of \( k_s \), since small terms due to uncompensated resistance could well explain the slight non-linearity. However, it is possible to assign a lower limit to \( k_s \) (Table 7-3).

The second Cr(SacSac)_3 reduction was reported in Chapter 3 to be irreversible and assumed to be associated with product degradation. This postulate is now confirmed. Only in the limit of short controlled drop times (~ 0.1 sec) are the heights of the two Cr(SacSac)_3 waves equal. Cyclic voltammetry at a dme shows the second wave to be more nearly reversible than the corresponding Cr(acac)_3 reduction (Fig. 7-2) and at a platinum electrode establishes that the first electron transfer step of Cr(SacSac)_3 is also very fast at this electrode surface (Table 7-3).

Both Cr(acac)_3 reduction waves are extremely drop time dependent. Only at very short drop times (0.05 sec) are the wave heights approximately equal. Cyclic voltammetry at a dme establishes
Figure 7-2. Cyclic voltammetric behaviour of the chromium chelates at a dme (conc. $3 \times 10^{-3} \text{ M}$, scan rate $500 \text{ mV sec}^{-1}$). Only the second Cr(SacSac)$_3$ wave is shown. Initial potentials: Cr(acac)$_3$ -1.4 V; Cr(SacSac)$_3$ -1.1 V.
the chemical non-reversibility of the electrode processes of Cr(acac)₃.

In ac polarography $E_{1/2}^{dc}$ of the first step, although not markedly frequency dependent, is slightly more negative than $E_{1/2}$ at the same drop time. A plot of $[I(\omega t)]$ vs. $f^{1/2}$ for the first reduction is non-linear up to about 100 Hz (influence of chemical reaction). From 100-500 Hz, a linear plot characteristic of a reversible response is obtained. At higher frequencies, curvature consistent with quasi-reversibility is observed. The calculated value of $k_s$, assuming $\alpha=0.5$, is given in Table 7-3.

These data establish that Cr(acac)₃ and Cr(SacSac)₃ undergo successive reductions via the generalised mechanism:

$$\text{Cr}^{\text{III}}L_3 \xrightleftharpoons{\text{ks}} \text{Cr}^{\text{II}}L_3^- \xrightleftharpoons{\text{ks'}} \text{Cr}^{\text{I}}L_3^{-2}$$

The rate constant, $k_1$, is important only for Cr(acac)₃, which probably reflects the very negative potential at which Cr(acac)₃⁻ is generated, rather than any basic mechanistic difference between acac and SacSac complexes. At the shorter time scale of rapid drop, or high frequency ac experiments, this $k_1$ step is no longer observed. Plots of $E_{1/2}$ vs. $E_0$ (sum of Taft substituent coefficients) for both reductions of a series of tris-β-diketonato chromium(III) complexes are approximately parallel, implying that the overall stereochemistry of the complexes is retained upon successive reductions.

Substitution of sulphur for oxygen shifts both reductions to more positive potentials, and enhances the rate of electron transfer. In the absence of double layer corrections, the large difference in $E_{1/2}$ produced by altering the donor atom precludes quantitative comparisons of $k_s$ values. Even so, the present trend $k_s(O) < k_s(S)$ is also observed with the analogous divalent nickel complexes where the change in $E_{1/2}$ upon altering the donor atom is much smaller (Chapter 8).

(b) MANGANESE

For Mn(acac)₃ both oxidation (complex wave, centred at ~ +0.6 V) and reduction waves were observed at a DME, the $E_{1/2}$ of the
Table 7-1. Dependence of $E_{1/2}$ on drop time.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$4.93^b$</th>
<th>1.98$^b$</th>
<th>1.0$^b$</th>
<th>0.5$^b$</th>
<th>0.17$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mn(acac)}_3$</td>
<td>+0.028</td>
<td>+0.027</td>
<td>+0.027</td>
<td>+0.025</td>
<td>+0.024</td>
</tr>
<tr>
<td>$\text{Fe(acac)}_3$</td>
<td>-0.576</td>
<td>-0.575</td>
<td>-0.578</td>
<td>-0.578</td>
<td>-0.576</td>
</tr>
<tr>
<td>$\text{Co(acac)}_3$</td>
<td>-0.250</td>
<td>-0.270</td>
<td>-0.293</td>
<td>-0.298</td>
<td>-</td>
</tr>
<tr>
<td>$\text{Cr(SacSac)}_3$</td>
<td>-0.493</td>
<td>-0.493</td>
<td>-0.492</td>
<td>-0.493</td>
<td>-0.492</td>
</tr>
</tbody>
</table>

\(a\) The merging of the two waves of $\text{Cr(acac)}_3$ at long drop times precluded such studies on this compound, as $E_{1/2}$ could be calculated only at short drop times.

\(b\) Drop time (sec).
latter wave being drop time dependent (Table 7-1). A lack of any major asymmetry in the ac reduction wave, and the relative invariance of $[E_{dc}]_p$ with frequency are consistent with the charge transfer coefficient close to 0.5 assumed in the calculation of $k_s$ (Table 7-3).

The reduction process was sensitive to traces of oxygen, and to the working electrode material, as evidenced by cyclic voltammetry at mercury, platinum and silver electrodes. Differing $\Delta E_p$ values were observed at the same scan rate at these electrodes, indicating the different $k_s$ values at the various electrodes. No oxidation wave was observed at a platinum electrode, this being consistent with a very slow charge transfer step, which would shift the wave to considerably more positive potentials than $E^0$ and outside the solvent range. The more negative $E_{1/2}$ observed for the reduction process at platinum compared with mercury can be attributed directly to the relatively small $k_s$ value at this electrode surface (Table 7-3).

Due to the proximity of the oxidation wave to the anodic limit at a dme, it could not be fully characterised; however, the Mn(acac)$_3$ electrode behaviour is consistent with the electron transfer series

$$[\text{Mn}^{IV}(\text{acac})_3]^+ \xrightarrow{k_s} [\text{Mn}^{III}(\text{acac})_3] \xrightarrow{k_s'} [\text{Mn}^{II}(\text{acac})_3]^-$$

Certainly the lack of evidence for disproportionation of the reduced species is consistent with the chemical isolation of Na[Mn(acac)$_3$]$_3$, and, in contrast to the chromium chelates, the lack of reversibility seems to be a function only of the small $k_s$. Unfortunately, attempts to synthesise Mn(SacSac)$_3$ have, so far, proved to be unsuccessful, and, in view of the shift of $E_{1/2}$ to more positive values upon substituting oxygen by sulphur in chromium(III) $\beta$-diketonates, the manganese(II) complex Mn(SacSac)$_3$ may offer a better prospect for isolation by synthetic procedures.

(c) IRON

Fe(acac)$_3$ undergoes a single, one-electron reduction at a dme, some departure from reversibility being evident. A plot of $\left[I(\omega t)\right]_p$ vs. $f^{1/2}$ deviates from linearity at high frequencies at a dme
Table 7-2. Voltammetric behaviour of the first reduction waves of the complexes: dc polarographic data at controlled drop time of 4.93 sec. (Cr(acac)₃ value from ac polarography.)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cr(acac)₃</th>
<th>Mn(acac)₃</th>
<th>Fe(acac)₃</th>
<th>Co(acac)₃</th>
<th>Cr(SacSac)₃</th>
<th>Fe(SacSac)₃</th>
<th>Co(SacSac)₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_{1/2} ) (Hg) (V)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 mV sec⁻¹</td>
<td>-0.27</td>
<td>-0.590</td>
<td>-0.81</td>
<td>-0.487</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100 mV sec⁻¹</td>
<td>-0.30</td>
<td>-0.600</td>
<td>-0.92</td>
<td>-0.492</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(</td>
<td>E - E_a</td>
<td>) (Pt) (mV)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20 mV sec⁻¹</td>
<td>240</td>
<td>85</td>
<td></td>
<td>70</td>
<td></td>
<td></td>
<td>56.5</td>
</tr>
<tr>
<td>100 mV sec⁻¹</td>
<td>465</td>
<td>135</td>
<td></td>
<td>75</td>
<td></td>
<td></td>
<td>78</td>
</tr>
</tbody>
</table>

\( a \) \( E_{1/2} \) (Hg) determined over the concentration range \( 4.62 \times 10^{-5} \) to \( 9.23 \times 10^{-4} \) M.

\( b \) From reference 169, corrected by comparison with shift in Cr(SacSac)₃ value.

\( c \) From reference 144.

\( d \) S.V. Evans, A.R. Hendrickson, and R.L. Martin, unpublished results.
(Fig. 7-1), enabling \( k_s \) to be calculated using \( \alpha \approx 0.5 \). This value of \( \alpha \) is consistent with the polarographic data, and is confirmed by the very small drop time dependence of \( \left[ E_{dc} \right]_{P} \).

Cyclic voltammetry at a platinum electrode at scan rates between 0.02 and 5 V sec\(^{-1}\) substantiates the lack of complete reversibility at a platinum surface (Table 7-3). The \( E_{1/2} \) value is also dependent upon the electrode material (Tables 7-2 and 7-3), reflecting the different \( k_s \) values at the different electrode surfaces.

Dissociation of \( \text{Fe(acac)}_3^- \) has been demonstrated to be quite slow,\(^{299,300}\) and does not influence electrochemical experiments performed on a rapid time scale. Thus, the redox processes of the two compounds may be represented by

\[
\begin{align*}
\text{Fe(SacSac)}_3 & \rightleftharpoons \text{Fe(SacSac)}_3^- & \text{(Ref. 169)} \\
\text{Fe(acac)}_3 & \rightleftharpoons \text{Fe(acac)}_3^- \rightarrow \text{Fe(acac)}_2 + \text{acac}^- \\
\end{align*}
\]

where \( k_{s_1} > k_{s_2} \).

(d) COBALT

Two \( \text{Co(acac)}_3 \) reduction waves are observed at a dme at low concentrations (\( 5 \times 10^{-5} \) to \( 9 \times 10^{-4} \) M), the first wave having a concentration independent \( E_{1/2} \), and a limiting current varying linearly with concentration. The second wave (\( E_{1/2} \approx -1.77 \) V) is almost equal in height to the first (controlled drop 4.93 sec) and is found at approximately the potential reported for the first reduction wave of \( \text{Co(acac)}_3 \cdot \text{H}_2\text{O} \) in acetonitrile.\(^{299}\) These data yield the diffusion coefficient of Table 7-3. At higher concentrations, the \( E_{1/2} \) of the first wave is dependent upon concentration and drop time (Table 7-1). Some perturbation in the current/voltage plateau region is evident in the first wave at high concentrations, but at short drop times one wave only is observed in the region of the first reduction. The shape of the dc polarographic wave is consistent with \( \alpha \approx 0.5 \) and a slow electron transfer, the assumption of slow electron transfer being validated by ac polarography, where only a small current per unit concentration response is observed, the wave height being essentially frequency independent.
Table 7-3. Parameters calculated for the complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$D$ (cm$^2$ sec$^{-1}$)</th>
<th>$\alpha$</th>
<th>$k_S^a$ (Hg) $\times 10^2$ (cm sec$^{-1}$)</th>
<th>$k_S^b$ (Pt) $\times 10^3$ (cm sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(SacSac)$_3$</td>
<td>$2.4 \times 10^{-5}$</td>
<td>0.46</td>
<td>&gt; 100</td>
<td>19</td>
</tr>
<tr>
<td>Cr(acac)$_3$</td>
<td>-</td>
<td>0.5$^c$</td>
<td>6.8</td>
<td>&lt; 0.9</td>
</tr>
<tr>
<td>Mn(acac)$_3$</td>
<td>$2.6 \times 10^{-5}$</td>
<td>0.5$^c$</td>
<td>13</td>
<td>7.2</td>
</tr>
<tr>
<td>Fe(acac)$_3$</td>
<td>$2.6 \times 10^{-5}$</td>
<td>0.5$^c$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co(acac)$_3$</td>
<td>$2.0 \times 10^{-5}$</td>
<td>0.5$^c$</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ $k_S$ (Hg) determined by ac polarography at a controlled drop time of 4.93 sec.

$^b$ $k_S$ (Pt) determined by cyclic voltammetry at a scan rate of 20 mV sec$^{-1}$.

$^c$ Assumed (see text).
In addition to slow electron transfer, chemical non-reversibility of this electrode process would also seem to arise from loss of acac\(^{-}\). Cyclic voltammograms at a dme show an anodic wave at \(E_P \approx +0.05\) V, the potential of which is concentration dependent and which has been shown to be due to acac\(^{-}\) by addition experiments. Murray\(^{299}\) has demonstrated the possibility of acac loss following Co(acac)\(_3\) reduction. For the following mechanism,

\[
ML_3 + e^{-} \rightleftharpoons ML_3^{-} \rightleftharpoons ML_2 + L^{-}
\]

an analysis similar to that of Murray, with the assumptions of Nernstian electron transfer and complete dissociation of ML\(_3^{-}\) to ML\(_2^{-}\), yields the relationship \(E_{1/2} \propto -\log[L^{-}]\). Although the electron transfer of the Co(acac)\(_3\) reduction has been shown to be irreversible, the qualitative effect of added acac\(^{-}\) is likely to be the same as for Nernstian electron transfer. Thus, the predicted negative shift in \(E_{1/2}\) of the Co(acac)\(_3\) reduction with increasing concentration of added Na(acac) is observed (a shift to \(E_{1/2} \approx -0.42\) V being observed at a drop time of 0.5 sec, with the Co(acac)\(_3\) solution saturated with Na(acac)), and provides further confirmation that acac\(^{-}\) is a product of the reduction.

This first reduction wave is markedly electrode dependent, being shifted cathodically by 600 mV on changing from a mercury to a platinum electrode (Table 7-2). The only other electrode process in the range \(+1.3\) V to \(-1.2\) V on platinum is a small oxidation peak observed in cyclic voltammograms at \(E_P = +0.44\) V, this being close to the polarographic \(E_{1/2}\) value reported for the oxidation of Co(acac)\(_2\)\(\cdot\)H\(_2\)O (+0.32 V).\(^{299}\) This wave may not be correlated directly with the value at platinum; however, the shift in \(E_{1/2}\) on changing electrodes is in the expected direction. The anodic wave of acac\(^{-}\) observed at a dme involves mercury compound formation; no corresponding anodic wave is observed at a platinum electrode.\(^{253}\)

These observations are consistent with Co(acac)\(_3\) being reduced by the mechanism below, and lend support to the mechanism tentatively proposed for the reduction of Co(SacSac)\(_3\).\(^{144}\) Further evidence for this mechanism is presented in Chapter 9. That both Co(acac)\(_3^{-}\) and Co(SacSac)\(_3^{-}\) readily dissociate to Co(acac)\(_2\) and Co(SacSac)\(_2\) is consistent with the lability frequently observed for \([\text{Co}^{II}(\text{chelate})_3]^{+x}\).
complexes. The complexity of the Co(acac)$_3$ reduction is perhaps increased by polymerisation of the reduction product to form oligomers of the type [Co(acac)$_2$]$_n$. In the absence of a complete thermodynamic and kinetic description of the redox and associated reactions, meaningful comparisons of observed $E_{1/2}$ values cannot be made.

**SUMMARY AND CONCLUSIONS**

The substitution of oxygen for sulphur produces a negative shift in the reduction potential, $E_{1/2}^x$, which is consistent with corresponding trends observed for other metals and ligand atoms. A consequence of the more negative $E_{1/2}^x$ values of the oxygen chelates is that the products of these reductions are thermodynamically more reactive than those of their sulphur analogues and are therefore more likely to undergo follow-up chemical reactions. Despite the marked differences in $E_{1/2}^x$ values, the overall mechanisms of the electrode processes appear to differ little for corresponding oxygen and sulphur chelates. Thus, under favourable conditions, the oxygen chelates are capable of supporting electron-transfer series similar to those of their sulphur analogues.

A further consequence of the change of donor atom is an increase in the rate of the heterogeneous charge transfer such that $k_s(S) > k_s(O)$. Additionally, the rate constant is larger at a mercury than at a platinum working electrode, i.e. $k_s(Hg) > k_s(Pt)$. Although the
rate constants are not corrected for double layer effects, these trends seem to be general (see Chapter 8) and not influenced by the magnitude of the potential difference $E_{1/2}^{(S)} - E_{1/2}^{(0)}$ or by the value of the absolute potential, implying that the observed trends are real.

The $k_S$ dependence upon the donor atom and electrode material is consistent with the electron transfer step occurring via a bridging mechanism involving the electrode and the donor atom, the inequality $k_S^{(S)} > k_S^{(0)}$ reflecting the thiophilic natures of mercury and platinum. That the $E_{1/2}$ values of the sulphur chelates are independent of the electrode surface is a consequence of the large $k_S$ values. Even though $k_S^{(S)}$ may depend on the electrode material, the electron transfer is sufficiently fast for $E_{1/2}$ to remain unaltered.
CHAPTER 8

DONOR ATOM VARIATION IN TRANSITION METAL

BIS CHELATES OF NICKEL(II)
In the previous Chapter, it was demonstrated that substitution of sulphur for oxygen in some trivalent transition metal complexes of acetylacetone influences their electrochemical reduction both kinetically and thermodynamically. Thus, the first reduction steps of the compounds with sulphur donor atoms not only appear to involve a faster electron transfer, but also occur at more positive potentials. However, the above study was complicated frequently by the large difference between the reduction potential of an oxygen chelate and that of its sulphur congener. This, in the absence of data for double layer corrections, made comparisons of the $k_s$ values of the chelates somewhat uncertain.

In addition, the direct effect of the donor atoms upon the electrochemistry could not be discriminated from any additional effects due to differing electronic configurations of the chelated metal ion induced by altering the donor atom. For example, $\text{Fe(acac)}_3\ (t^{2\text{g}}_{3\text{e}}, e^2_{\text{g}})^4$ could be expected to be reduced at a potential different to that of $\text{Fe(SacSac)}_3\ (t_{\text{g}}^{5})^{36}$ on the basis of the change in electronic ground state alone.

In order to avoid these complications, these studies have been extended to the divalent nickel complexes of the dipivaloylmethanato anion ($\text{Bu'acBu'}_{\text{ac}}$), and its monothio- ($\text{Bu'SacBu'}_{\text{ac}}$) and dithio- ($\text{Bu'SacBu'Sac}$) derivatives. $^{\dagger}$ $\text{NiO}_4$ has been shown to be planar, $^{130}$ and, on the basis of their diamagnetism and the close analogy with $\text{Ni(SacSac)}_2$, $^{78} \text{NiO}_2\text{S}_2$ and $\text{NiS}_4$ are also expected to be planar. Additionally, preliminary results showed that the $E_{1/2}$ values of the first reduction steps for the three compounds span less than three hundred millivolts, so that uncertainties arising from the lack of double layer corrections are much reduced.

$^\dagger$ Nomenclature of nickel complexes as in Chapter 4.
Table 8-1. Characteristics of the reduction waves.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{1/2}$ (V)</th>
<th>grad $\alpha$ (mV)</th>
<th>$[E_{dc}]_{P}$ (V)</th>
<th>$W_{1/2}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO$_4$</td>
<td>-1.327</td>
<td>67</td>
<td>-1.318</td>
<td>117</td>
</tr>
<tr>
<td>NiO$_2$S$_2$</td>
<td>-1.190</td>
<td>59</td>
<td>-1.187</td>
<td>90</td>
</tr>
<tr>
<td>NiS$_4$</td>
<td>-1.058</td>
<td>61</td>
<td>-1.054</td>
<td>90</td>
</tr>
<tr>
<td>NiO$_2$S$_2$</td>
<td>-1.84</td>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiS$_4$</td>
<td>-1.308</td>
<td>73</td>
<td>-1.303</td>
<td>105</td>
</tr>
</tbody>
</table>

$\alpha$: gradient of $E$/log$\{\frac{i_d-i}{i}\}$ plot.
RESULTS AND DISCUSSION

Three reduction waves were observed in the dc polarography of NiS₄. The proximity of the third (most negative) wave to the cathodic limit (-2.25 V) precluded its characterisation, but parameters evaluated for the other waves are given in Table 8-1. The first wave can be assigned to the process

\[ [\text{Ni}^{t}\text{Bu}^{t}\text{SacBu}^{t}\text{Sac}]_{2} + e \rightleftharpoons [\text{Ni}^{t}\text{Bu}^{t}\text{SacBu}^{t}\text{Sac}]_{2}^{-} \]

and the second to

\[ [\text{Ni}^{t}\text{Bu}^{t}\text{SacBu}^{t}\text{Sac}]_{2}^{-} + e \rightleftharpoons [\text{Ni}^{t}\text{Bu}^{t}\text{SacBu}^{t}\text{Sac}]_{2}^{-2} \]

by analogy with the behaviour of Ni(SacSac)₂.¹⁴⁴

Neither the shapes nor positions of the first two waves are significantly affected by drop time in the range 0.2 < t < 2 sec. Analysis of the first wave showed this reduction to be reversible in the dc sense. Ni(SacSac)₂⁻ has been shown to undergo a slow but significant chemical "rearrangement".¹¹⁴ In terms of the mechanism of the Ni(SacSac)₂ reduction then, any chemical reaction of Ni(Bu'°SacBu°Sac)° occurs very slowly, if at all. The rate of this follow-up chemical reaction has been observed to depend upon the nature of the substituents on the chelate ring.³⁰⁹

At high frequencies, \( E_{dc} \) differs slightly from \( E_{1/2} \), this difference establishing that \( a \), the charge transfer coefficient, is equal to 0.46 (Table 8-2), a value according well with that determined previously for Cr(SacSac)₃. Evaluation of the diffusion coefficient by dc polarography was complicated by the proximity of the two waves, but the calculated diffusion coefficients of NiS₄ and NiO₂S₂ are almost identical, as expected for two isostructural complexes. Furthermore, the similarity of the gradients of the \( [I(\omega t)]_p / CA vs. f^{1/2} \) plots of the two species (Fig. 8-1) confirms the equivalence of the diffusion coefficients.

The ac wave shape of the first NiS₄ reduction is in excellent agreement with that expected for a reversible, one-electron reduction (Table 8-1 and Fig. 8-1), and the \( [I(\omega t)]_p / CA vs. f^{1/2} \) plot illustrates
Figure 8-1. Calculated (full lines) and experimental (points) wave shapes for the nickel chelates. Wave shapes calculated from reference 205.
that the heterogeneous electron transfer is extremely rapid. As in the case of Cr(SacSac)$_3$, small terms due to uncompensated resistance and/or inability to correct for the charging current may explain the slight departure of this plot from linearity at high frequencies, rather than departure from reversibility, and only a lower limit can be set for $k_s$ (Table 8-2). The relative effects of platinum and mercury electrodes upon the electrochemistry of the present chelates could not be determined, as all reductions occurred in the vicinity of the cathodic limit for platinum ($\sim -1.3$ V).

Analysis of data for the second and more negative NiS$_4$ reduction wave shows that this wave is very close to reversible in the dc sense. However, a plot of the ac data (Fig. 8-2) reveals that this wave is significantly less reversible than the first. The rate constant for heterogeneous electron transfer was determined from this graph.

The dc polarography of NiO$_2$S$_2$ consists of two reduction waves, the limiting currents of which are equal. Analysis of the first (more positive) wave shows it to correspond to a reversible, one-electron step (Table 8-1), and yields the diffusion coefficient of Table 8-2. Both reductions are shifted cathodically with respect to those of NiS$_4$, and the difference in $E_{1/2}$ values between the two waves is much larger than that of NiS$_4$.

That the first NiO$_2$S$_2$ reduction is reversible to ac polarography over a wide frequency range is illustrated by the linearity of the $[I(\omega t)]_p/C_{Avs. \omega^{1/2}}$ plot (Fig. 8-2), and by the agreement between the gradient of this plot and that calculated from the diffusion coefficient. As in the NiS$_4$ case, only a lower limit could be assigned to $k_s$ (Table 8-2). Comparison of the theoretical and observed wave shapes for this process (Fig. 8-1 and Table 8-1) further establishes the reversibility of the electron transfer.

One reduction wave only was observed in the dc polarography of NiO$_4$, this wave being at a more negative potential than the first reduction waves of both NiS$_4$ and NiO$_2$S$_2$ (Table 8-1). Although analysis of this wave shows it to undergo the greatest deviation from the theoretical value of $\frac{58}{n}$ mV for the slope of the $\log\left(\frac{i_2-i_1}{i_1}\right)$ vs. $E$ plot, the departure is small and this, and the wave shape (Fig. 8-1) are
Figure 8-2. Ac frequency dependence of the ac polarographic peak heights of the couples: ■, NiO$_2$S$_2$ $^{0/-1}$; ●, NiS$_4$ $^{0/-1}$; ▲, NiS$_6$ $^{-1/-2}$; ○, NiO$_4$ $^{0/-1}$.
consistent with a one-electron, almost reversible, electron transfer step in the dc sense.

However, wave shape analyses (Table 8-1 and Fig. 8-1) and the 
[I(\omega t)]_p/CA vs. \sqrt{f} behaviour of the NiO_4 reduction (Fig. 8-2), establish that this process is only quasi-reversible under ac polarographic conditions and the k_s value can be calculated (Table 8-2).

The heterogeneous electron transfers corresponding to the first reduction waves of NiO_2S_2 and NiS_4 are extremely rapid, whilst that of NiO_4 is sufficiently slow for its k_s value to be calculated. However, all three electron transfers are fast enough to be considered reversible under dc polarographic conditions. Thus, the E_{1/2} values of the first reduction waves of the present compounds have thermodynamic significance and can be used for comparative purposes. Further, as a consequence of the small potential range within which these reductions occur, the magnitudes of the differences in the k_s values are likely to be substantially unaltered upon application of double layer corrections, and trends in k_s values can be discussed with confidence.

The present study confirms that substitution of oxygen by sulphur has both thermodynamic and kinetic consequences. Thus, the greater the number of sulphur atoms about nickel, the easier is the reduction (more positive E_{1/2}) and the faster the electron transfer step. This trend parallels that for the ML_3 complexes of acetylacetone and dithioacetylacetone and the NiLL' complexes of monothio- and dithioacetylacetone (Table 8-3), although no kinetic data are available in the latter case. In the present complexes, the following ordering of the ease of reduction is established:

\[(\text{easier to reduce}) \quad \text{NiS}_4 > \text{NiO}_2\text{S}_2 > \text{NiO}_4 \quad (\text{harder to reduce})\]

Similarly, for the rate of the electron transfer, NiS_4, NiO_2S_2 > NiO_4, any difference in the k_s values of NiS_4 and NiO_2S_2 being beyond the limits of detection. The lower limit ascribed to k_s for the NiS_4 and NiO_2S_2 complexes compares well with the value of k_s > 1 cm sec^{-1} obtained for the couple^{218} (see also Chapter 10).

\[\text{Ni(mnt)}_2^- + e \rightarrow \text{Ni(mnt)}_2^{-2}\]

Interestingly, despite the ligand-based character of the redox processes
Table 8-2. Parameters calculated for the complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$10^5 D$ (cm$^2$ sec$^{-1}$)</th>
<th>$\alpha$</th>
<th>$10^2 k$ (Hg) (cm sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO$_4$</td>
<td>-</td>
<td>0.41</td>
<td>1.6</td>
</tr>
<tr>
<td>NiO$_2$S$_2$</td>
<td>1.8</td>
<td>0.47</td>
<td>&gt;100</td>
</tr>
<tr>
<td>NiS$_4$</td>
<td>1.8</td>
<td>0.46</td>
<td>&gt;100</td>
</tr>
<tr>
<td>NiS$_4^-$</td>
<td>1.8</td>
<td>0.45</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Table 8-3. Polarographic data on NiLL' complexes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nickel-donor atom set</th>
<th>$E_{1/2}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(SacSac)$_2$</td>
<td>NiS$_4$</td>
<td>-0.960 ± 0.001</td>
</tr>
<tr>
<td>Ni(SacSac)(Sacac)</td>
<td>NiS$_3$O</td>
<td>-0.979 ± 0.002</td>
</tr>
<tr>
<td>Ni(Sacac)$_2$</td>
<td>NiO$_2$S$_2$</td>
<td>-1.074 ± 0.001</td>
</tr>
</tbody>
</table>
(in contrast to the presumed metal-based character of the present processes), the ordering of the ease of the \( z = -2 \) to \( z = -1 \) couples of complexes of catechol and its monothio- and dithio-derivatives is also 

\[
\text{(easiest to oxidise) } \text{"NiS}_2^+ > "\text{NiO}_2 S^2_2 > "\text{NiO}_4^- \quad (\text{hardest to oxidise})
\]

However, some caution is attached to this comparison as not all the redox processes are fully reversible.

The apparently generally faster electron transfers of the sulphur-containing ligands implies some involvement of the donor atom in the process of electron transfer. This is consistent with the evidence of Chapter 7 which showed a dependence of the redox process upon the electrode material. Thus the electron transfer would seem to occur via a bridging mechanism. In the case of halides, it is well known that participation of the ligand in bridging and/or adsorption increases in the order \( F < Cl < Br < I \). In group VI it would also appear that the involvement of the ligand with the electron transfer step increases down the group. On this basis, it would be predicted that \( \text{k}_s \) values for the selenium analogs of \( \text{Ni(SacSac)}_2 \) and \( \text{Ni(acac)}_2 \) would be even larger; however, no data appears to be available. Significantly, larger \( \text{k}_s \) values are associated with the present square planar complexes than with the \( \text{M(chelate)}_3 \) series. Obviously, a planar structure is better suited to form a bridged complex with the electrode.

In comparing \( \text{E}_{1/2} \) values, it is essential to recognise that they reflect the relative stabilisation of one half of the redox couple with respect to the other. Thus oxygen and sulphur influence the free energies of either or both halves of the redox pair differently. It has been previously shown \(^{179}\) that an increase in ligand negative charge for a related series of dithio-chelates results in a shift to more negative potentials of the reduction wave. A simple correlation between the position of the reduction wave and the amount of ligand negative charge cannot be made in the present case because of the change in the donor atoms. However, it is perhaps significant that the \( \text{k}_s \) for the second \( \text{NiS}_4^- \) reduction is less than that for the first. Since the first reduction is highly reversible, \( \text{NiS}_4^- \) and \( \text{NiS}_4^- \) are presumed to be isostructural and \( \text{NiS}_4^- \) is expected to differ from \( \text{NiS}_4^- \) only in the
Figure 8-3. Ac frequency dependence of the ac polarographic peak height of the reduction wave for the Ni(Sac(NMe)ac)$_2$ couple.
electronic configuration and charge. Interestingly, then, the change in behaviour on going from NiS$_4$ to NiO$_4$ is qualitatively similar to that on going from NiS$_4$ to NiS$_4^-$.

"Donor atom" effects have been extended to a comparison of the reduction of Ni(Sac(NMe)ac)$_2$ (I) with those of the Ni/SacSac/Sacac compounds of Table 8-3. Ni(Sac(NMe)ac)$_2$ is a member of a series of complexes exhibiting square planar/tetrahedral equilibrium in solution. The mole fraction in the tetrahedral form has been shown to be 0.04 in CDCl$_3$. A one-electron reduction, reversible on the dc polarographic time scale (grad. of $E/log(\frac{1}{i}-\frac{1}{i})$) plot is 59.4 mV at 22 °C) was observed at -1.373 V. Ac polarographic data (Fig. 8-3) establishes the rapidity of the heterogeneous electron transfer.

Thus, although introduction of a NMe donor group into the SacSac chelate ring shifts the $E_{1/2}$-value to more negative potentials than does introduction of an oxygen donor atom, the effect of the NMe donor group upon $k_s$ does not appear to be as marked as that of oxygen donor atoms. That is, the reduction becomes more negative, but retains the high degree of reversibility associated with the sulphur-based chelates. Further comparative studies on the N/S/O donor system are needed, but the possibility arises that whilst oxidation processes of the neutral N/S-based chelates will occur at relatively negative potentials (as might also be expected for the O/S-based chelates), a higher degree of reversibility could be expected for the N/S-based chelates than for the O/S-based chelates. Thus, the synthesis of high oxidation state chelates might be better effected with N/S-based chelates than with O/S- or O-based chelates.
CHAPTER 9

THE ELECTROCHEMICAL NON-REVERSIBILITY OF SULPHUR-CHELATES
The electrochemistry of sulphur-based chelates of the transition metals has been extensively studied in the last decade. Particular emphasis has been placed on the reversible ligand-based one-electron transfers observed in the 1,2-dithiolene and related series of complexes, and, more recently, upon the isolation and characterisation of compounds with unusual metal oxidation states. Most of the comparative studies necessitate the observation of reversible electrode processes; the examples of non-reversible behaviour have, with few exceptions, been noted briefly but not interpreted. This neglect has resulted in some interesting chemistry being overlooked. Alternatively, the $E_{1/2}$ values of non-reversible processes have often and incorrectly been associated with $E^0$ in comparisons which demand thermodynamically significant parameters. Obviously, the cause and influence of non-reversibility in inorganic redox processes needs to be better understood.

Previous studies have allied redox processes of sulphur-based chelates with very rapid electron transfers. Accordingly, it seems likely that non-reversible behaviour in such systems is attributable to factors other than the rate of heterogeneous electron transfer. This postulate finds substance in those few examples where the origins of non-reversibility have been elucidated. Additionally, non-reversible redox processes of sulphur-chelates in the present work are ascribed in all cases to factors other than slow heterogeneous electron transfer. The lability of members of the redox couple is found to affect the redox process dramatically and these effects are discussed below. The lability of cobalt compounds is known to be dependent upon the metal oxidation state and so the reduction of kinetically inert Co$^{III}$ compounds to labile Co$^{II}$ compounds leads to the expectation of complex redox processes. Reductions of several cobalt(III) compounds
Figure 9-1. DC (A) and AC (B) polarographic behaviour of Co(Bu-SacButac),. Potential range +0.75 V to -1.95 V. Scan rates, 20 mV sec⁻¹. AC frequency is 400 Hz.
have been investigated and the results used as a model in the interpretations of other cases.

(a) $\text{Co(Bu}'\text{SacBu}'\text{ac})_3$

Figure 9-1 illustrates the complex redox processes with respect to the dc and ac polarographic behaviour observed for this compound. Comparisons of the limiting dc currents per unit concentration of each of these waves with that of the reversible (see Chapters 3 and 7) one-electron Cr(SacSac)$_3$ reduction establish that these $\text{Co(Bu}'\text{SacBu}'\text{ac})_3$ waves correspond to three successive one-electron steps. The electron transfer of wave 2 has a $k_1$ value of $> 0.9 \text{ cm sec}^{-1}$. This wave corresponds to a reversible one-electron reduction on the dc polarographic time-scale. The behaviour of waves 1 and 3 are consistent with coupling of chemical reactions to the electron transfer. Waves 1 and 2 merge and become one two-electron step at low temperatures ($-30^\circ \text{C}$). Similarly, the merging of these waves can be observed as the frequency of the ac polarographic experiment is increased (Figs. 9-2 and 9-3).

The three reduction waves are observed at the same at slow cyclic voltammetric scan rates (Fig. 9-4). In agreement with the polarographic behaviour, wave 2 is reversible and waves 1 and 3 are non-reversible at these slow scan rates. Those waves on the reverse scan with no cathodic counterpart on the initial scan will be discussed below. Increasing the scan rate results in waves 1 and merging to become a single two-electron step (Fig. 9-5). Under steady state conditions at very rapid scan rates, the cyclic voltammogram in the region of waves 1 and 2 simplifies to the two chemically reversible couples of Figure 9-5c. The first reduction of Figure 9-5c is not observed on the first cyclic voltammetric scan (Fig. 9-4).

These data are consistent with wave 1 corresponding to the reduction of $\text{CoL}_3$ to $\text{CoL}_3^-$ ($L = \text{Bu}'\text{SacBu}'\text{ac}^-$) followed by ligand loss from this latter species:

$$
\text{Co}^\text{III} \text{L}_3 \leftrightarrow \text{Co}^\text{II} \text{L}_3^- \xrightarrow{k} \text{Co}^\text{II} \text{L}_2 + \text{L}^-
$$

(9-1)
Figure 9-2. Frequency dependence of ac polarogram of Co(Bu\textsuperscript{+}SacBu\textsuperscript{+}ac\textsubscript{3}).
The most positive oxidation of Figure 9-5a is attributed to the oxidation of mercury in the presence of ligand generated at the electrode via equation (9-1). Mercury is known to be oxidised in the presence of the related ligands OEtSacSacH\textsuperscript{115} and NH\textsubscript{2}SacNH\textsubscript{2}SacH (Chapter 2) at a potential dependent upon the ligand concentration. In the present context, generation of ligand at the electrode is proven by the addition experiments discussed below for the cobalt dithiocarbamates, and reported for Co(acac)\textsubscript{3} in Chapter 7.

The E\textsubscript{1/2}-value observed for wave 1 is related to E\textsuperscript{0} for the redox process

\[ \text{Co}^{\text{III}}L_3 \rightleftharpoons (E_1)\text{A} \text{Co}^{\text{II}}L_3 \]

by a function of k. This function may be derived theoretically.\textsuperscript{239-241} E\textsubscript{1/2} for equation (9-1) is always more positive than E\textsubscript{1/2} for equation (9-2). However, as the time scale of the experiment is decreased (e.g., faster scan rates), or the rate constant k is lowered (lower temperatures) E\textsubscript{1/2} of equation (9-1) shifts to more negative potentials, approaching a limiting value of (E\textsubscript{1/2})\textsuperscript{A}. The k-value of equation (9-1) is sufficiently large that even at a scan rate of 100 V sec\textsuperscript{-1} its effect is still manifest (Fig. 9-5).

Wave 2 can be assigned readily to the reversible process

\[ \text{CoL}_2 \rightleftharpoons (E_1/2)\text{B} \text{CoL}_2^- \]

As discussed above, the kinetic step in equation (9-1) results in (E\textsubscript{1/2})\textsubscript{A} approaching a limiting value of (E\textsubscript{1/2})\textsuperscript{B} as the experimental time scale decreases. The merging of waves 1 and 2 in fast scan rate cyclic voltammograms therefore indicates that E\textsuperscript{r} of equation (9-3) is more positive than that of equation (9-2). That is,

\[ (E_{1/2})_B > (E_{1/2})_A \]

This conclusion, that the reversible one-electron reduction of a M\textsuperscript{II} (chelate)\textsubscript{2} species is thermodynamically favoured over that of the corresponding M\textsuperscript{III} (chelate)\textsubscript{3} species is shown below to often result in
Figure 9-3. Ratio of peak heights of first and second ac polarographic reduction waves of Co(Bu⁺SacBu⁺ac)₃ as a function of ac frequency. Value (0.226) for $f^{1/2} = 3.16$ is not shown.
complication of redox processes of sulphur-chelate compounds and offers a possible explanation of the non-reversibility observed for several such compounds.

Wave 3 corresponds to the process

\[ \text{CoL}_2^- \leftrightarrow \text{CoL}_2^2 \text{ k'} \text{ Products} \]  

(9-4)

Slow scan cyclic voltammograms establish the non-reversibility of the CoL$_2$ oxidation. However, under very fast scan rate steady state conditions (e.g., 20th scan of cyclic voltammogram), the kinetic complication is no longer of importance, and two reversible couples are evident (Fig. 9-5). The compounds CoL$_2$-, CoL$_2$ and CoL$_2$+ are therefore produced during the redox processes and are lined by the 

\[ \text{CoL}_2^- \leftrightarrow \text{CoL}_2 \leftrightarrow \text{CoL}_2^+ \]  

(9-5)

A polarographic study on the compounds FeL$^+$, FeL$^{+2}$, FeL$_2^+$, FeL$_3^+$, FeL$_3^-$ and FeL$_3$ (where L = acac) has shown these compounds are also linked both by electron transfer and chemical reactions coupled to the heterogeneous electron transfers.

(b) M(SacSac)$_3$ (M = Co, Rh, Ir) REDUCTIONS

The reductions of these complexes have been investigated previously at a dme. It was established that the first Co(SacSac)$_3$ reduction is a two-electron process occurring at the same potential as the first Co(SacSac)$_2$ reduction. In the present study separate single-electron waves corresponding to the processes of equations (9-1) and (9-3) could not be obtained under any conditions. The Co(SacSac)$_3$ electrode processes under all time scales are a non-reversible two-electron reduction

\[ \text{Co(SacSac)}_3 + 2e \rightarrow \text{Co(SacSac)}_2^- + \text{SacSac}^- \]  

(9-6)

and a subsequent reversible one-electron reduction.

\[ \text{Co(SacSac)}_2^- \leftrightarrow \text{Co(SacSac)}_2^-^2 \]  

(9-7)
Figure 9-4. Cyclic voltammogram of Co(Bu'SacBu'ac)_3 at a mercury electrode.
The similarity with the behaviour of Co(Bu^tSacBu^tac)_3 (above) is obvious. In the Co(SacSac)_3 example however, access to both Co(SacSac)_3 and Co(SacSac)_2 provides direct evidence for the mechanism proposed for Co(Bu^tSacBu^tac)_3.

Rh(SacSac)_3 has also been shown to undergo a two-electron reduction to give a product postulated as Rh(SacSac)_{2}^- . The dc polarographic behaviour of Ir(SacSac)_3 is complicated at natural drop times, but rapid polarographic techniques have established the presence of two waves corresponding to consecutive, reversible, one-electron reductions separated by about 100 mV. Bond et al. comment that Ir(SacSac)_3 may undergo

"... a rapid dissociative equilibrium upon reduction. For example, the iridium(II) or iridium(I) species could be degraded to a bis complex. Insertion of electrons in the O-antibonding orbitals should labilize the metal-ligand bonds and increase the possibility of rapid reversible loss of a bidentate ligand. ..."

(c) Co(OEtSacSac)_3

A further example of this mechanism is provided by Co(OEtSacSac)_3. Both Co(OEtSacSac)_3 and Co(OEtSacSac)_2 are known, and reductions of millimolar solutions of Co(OEtSacSac)_3 have been shown to proceed via the mechanism observed for Co(Bu^tSacBu^tac)_3.

(d) Co(DITHIOCARBAMATO)_3 REDUCTIONS

The reduction processes of a series of cobalt(III) tris-dithiocarbamates have been reported previously and their non-reversibility noted. In the present study, the Co(dtc)_3 complexes of the N,N-dibenzyl- and pyrrolidyl-dithiocarbamates were chosen for examination and the ligands N,N-dibenzyl- pyrrolidyl-, and N,N-diisopropyl-dithiocarbamate used in titrametric experiments with cobalt(II) perchlorate. The reduction potentials of the tris-species are presented in Table 9-1.

---

† Dithiocarbamate ligands and complexes used in the present work were supplied by Drs. N.M. Rohde and A.R. Hendrickson.
Figure 9-5. Rapid scan rate cyclic voltammograms of Co(Bu$_3$SacBu$_3$ac)$_3$ at a dme. A and B initial scans, C steady state. Scan rates: A, 1 V sec$^{-1}$; B, 10 V sec$^{-1}$; C, 100 V sec$^{-1}$. Potential ranges: A and B, +0.75 V to -2.25 V; C, -0.3 V to -1.4 V.
(1) Platinum Electrode Studies

One non-reversible reduction wave is observed for the Co(dtc)$_3$ complexes at a platinum electrode. Ligand loss from the reduction product is revealed by the observation of the electrode process

\[ \text{dtc}^- \rightarrow \frac{1}{2} (\text{thiuram disulphide}) + e \]  
(9-8)

on the reverse scan of the cyclic voltammograms. These oxidation waves can be assigned by comparisons with published oxidation potentials, or, more conveniently, by addition of the relevant sodium dithiocarbamate.

The observation of the process (9-8) on the reverse scan of the cyclic voltammograms is consistent with reduction of Co(dtc)$_3$ being followed by ligand loss to give Co(dtc)$_2$. Accordingly, redox processes of the Co(dtc)$_2$ complexes were studied by in situ generation of these species. Similarly to the behaviour of Co(SacSac)$_2$, the first Co(dtc)$_2$ reduction wave occurs at the same potential as that of the first Co(dtc)$_3$ reduction. However, in contrast to Co(SacSac)$_2$, this first Co(dtc)$_2$ reduction is non-reversible. Thus, the Co(dtc)$_2^-$ species appear to be far less stable than the Co(SacSac)$_2^-$ and Co(Bu$^t$SacBu$^t$ac)$_2^-$ species. This trend is reflected in the relative stabilities of the neutral bis-chelates of these ligands. The overall electrode processes of the cobalt(III) dithiocarbamate reductions then seem to be

\[ \text{Co(dtc)}_3 + 2e \rightarrow \text{Co(dtc)}_2^- + \text{dtc}^- \]  
(9-9)

and those of the cobalt(II) dithiocarbamates to be

\[ \text{Co(dtc)}_2 \leftrightarrow \text{Co(dtc)}_2^- \rightarrow \text{Products} \]  
(9-10)

(ii) Mercury Electrode Studies

Under dc polarographic conditions, the reduction waves of the Co(dtc)$_3$ compounds are again very complex. The first region of electroactivity is assigned to the processes of equation (9-9). Partial resolution of this complex reduction into two apparently one-electron
## Table 9-1. Electrochemical data for reductions of Co(dithiocarbamate)$_3$ complexes. Data abstracted from reference 146.

<table>
<thead>
<tr>
<th>Dithiocarbamate</th>
<th>$E_{1/2}$ ($V$)</th>
<th>$E_{3/4} - E_{1/4}$ ($mV$)</th>
<th>$E_P$ ($V$)</th>
<th>$W_{1/2}$ ($mV$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N,N-dibenzylidithiocarbamate</td>
<td>-0.80</td>
<td>58</td>
<td>-0.80</td>
<td>92</td>
</tr>
<tr>
<td>pyrrolidyldithiocarbamate</td>
<td>-0.83</td>
<td>58</td>
<td>-0.82</td>
<td>93</td>
</tr>
<tr>
<td>N,N-diisopropylidithiocarbamate</td>
<td>-1.09</td>
<td>50</td>
<td>-1.12</td>
<td>98</td>
</tr>
</tbody>
</table>

$E_P$ and $W_{1/2}$ refer to potentials in Volt vs. Ag/AgCl in acetonitrile - 0.1 M tetraethylammonium perchlorate.
steps is under ac polarographic conditions. A further poorly defined wave (or waves) is observed at more negative potentials, its possible origin being reduction of residual Co(dtc)$_2^-$ and/or its products. Again, generation of ligand at the electrode can be established by observation of the relevant mercury oxidation waves (established as such by ligand addition experiments) on the reverse cyclic voltammetric scans. The oxidation of Co(dtc)$_2^-$ could be observed at very rapid cyclic voltammetric scans at a dme.

A complex polarographic reduction of Co(dtc)$_2$ was observed at a potential close to that of the Co(dtc)$_3$ reduction. An electron transfer series similar to that of Co($^{t}$SacBu$^{t}$ac)$_2$ (equation 9-5) was also evident in this case under high scan rate cyclic voltammetric conditions at a dme.

Reductions of all of the above tris cobalt(III) compounds are thermodynamically equivalent (i.e., in all cases, the reversible $E_{1/2}^R$ potentials of the CoL$_2$ compounds are more positive than those of the analogous CoL$_3$ compounds). The degree to which the CoL$_3$ reduction is shifted from its $E_{1/2}^R$ potential is determined by the magnitudes of the kinetic terms of the follow-up chemical reactions. Kinetically, the behaviour is governed by the inertness of cobalt(III), the lability of Co(II)L$_3^-$ species, the stability of Co(II)L$_2$ species relative to the Co(II)L$_3^-$ species, and the ready accessibility of a univalent cobalt oxidation state. In view of these factors, non-reversible electrochemical behaviour in cobalt(III) sulphur-chelates is perhaps not unexpected.

The deduction that $E_{1/2}^R$ for the Co(II)L$_2$ reduction is more positive than that for the Co(III)L$_3$ reduction offers a possible explanation of other electrochemical observations.

Non-reversible oxidations of ML$_2$ dithiocarbamates (M=Mn, Fe) have been observed to occur at the same potentials of those of the corresponding ML$_3$ compounds. The ML$_2$ compounds were prepared by titrametric methods, in situ. Should the inverse of the above ordering of $E_{1/2}^R$-values apply to oxidations (that is, that $E_{1/2}^R$ for a M(II)L$_2$ oxidation is more positive than that for the corresponding M(III)L$_3$ oxidation), and the rate of formation of M(III)L$_3$ be sufficiently rapid, then the ML$_2$/ML$_2^+$ oxidation could occur at the ML$_3$/ML$_3^+$ potential.
might be made available for electrochemical oxidation via exchange reactions of the kind

\[ ML_2^+ + ML_2 \rightleftharpoons ML_3 + ML^+ \]

or may co-exist in equilibrium with other \( ML_{n+x}^+ \) species. In the case of \( M = \text{Fe(III)} \), the system is known to be very labile and the rates of formation of the various complexes are very fast. Hendrickson et al.\(^{246}\) and Lachenal\(^{147}\) report that voltammetric oxidation of \( \text{Ni(dtca)}_2 \) compounds yields \( \text{Ni(dtca)}_3^+ \) compounds, and Rohde\(^{146}\) has shown that copper(I) dithiocarbamates undergo complex multi-electron oxidations in the same potential regions as the corresponding \( \text{Cu(dtca)}_2/\text{Cu(dtca)}_2^+ \) couples, with the processes

\[
\begin{align*}
\text{Cu(dtca)}_2^+ + e & \longrightarrow \text{Cu(dtca)}_2 \\
\text{Cu(dtca)}_2 + e & \longrightarrow \text{Cu(dtca)}_2^-
\end{align*}
\]

being evident on the reverse cyclic voltammetric scans (the system is further complicated by the polymeric nature of the copper(I) dithiocarbamates).

The studies outlined in this Chapter have demonstrated that non-reversible behaviour in several sulphur-chelate compounds is a consequence not of slow heterogeneous electron transfer kinetics, but rather is due to the influence of chemical reactions coupled to the electron transfer. These reactions occur when at least one member of the redox pair is labile on the electrochemical time scale. The extent to which these chemical reactions influence the reversibility of the system is dependent upon the magnitude of the associated kinetic parameters.

These observations correlate well with the findings of the previous two Chapters where it was shown that dithio-\( \beta \)-diketonato complexes undergo very rapid heterogeneous electron transfers. Such rapid electron transfers have now been demonstrated for mnt,\(^{218}\) monothio- and dithio-\( \beta \)-diketonato and dithiocarbamato systems which, as evidenced by the work of this Chapter, suggests that coupling of chemical reactions to the electron transfer is a more likely source of non-reversibility in sulphur-chelates than is a slow heterogeneous
electron transfer. This is exemplified in the next Chapter, wherein some new redox processes leading to unusually high or low oxidation states are investigated and in those cases in which non-reversible behaviour is observed and investigated, it is found to arise from factors other than electron transfer kinetics.
CHAPTER 10

NEW ELECTRODE PROCESSES OF SULPHUR-CHELATES
Figure 10-1. Dependence of peak heights of ac polarographic waves for \( \text{Ni(mnt)}_2^{-1/2} \) oxidation and reduction upon ac frequency.
Numerous communications have reported transition-metal chelate compounds in apparently high or low metal oxidation states. In many cases, the redox processes leading to these unusual oxidation state compounds have subsequently been shown to be ligand- rather than metal-based. Thus, when a number of oxidation states is available to both metal and ligand, redox processes can be centred on either or both entities. If however, successive electron transfers "exhaust" the number of such oxidation states of either metal or ligand, and accessible oxidation states are available to the other species, then further electron transfer steps can be expected. In such an example, an extensive electron transfer series would be observed, the nature of the series changing from metal- to ligand-based (or vice versa).

An extensive electron transfer series is known for the 1,2-dithio chelate compounds and comparisons have been drawn between these and the $\text{M(SacSac)}_n$ series. Commenting on such comparisons, Bond et al. remark,

"... Comparisons (of the $\text{M(SacSac)}_n$ complexes) with the electron-transfer properties of the dithiolenes must be drawn carefully. The most reduced (dithiolato) forms of these, $\text{MS}_4^{2-}$ and $\text{MS}_6^{3-}$, formally contain dinegative ligands and place the metals in the ordinary oxidation states, M(II) and M(III), respectively. The dithiolato complexes are susceptible to stepwise oxidations which remove electrons from molecular orbitals of predominantly ligand character. ...

... It is emphasized that $\text{Ni(SacSac)}_2$ is properly compared with the dianionic "dithiolate" rather than the neutral "dithiene". Stepwise oxidations of the dithioacetyl-acetonates are obviously relatively inaccessible, since the present polarographic range extends only to $+0.8 \text{ V}$ with reference to Ag-AgCl, though their possible occurrence could be further investigated. ..."

† Author's comment: platinum or glassy carbon electrodes were not used by Bond et al. in this study.
Table 10-1. Parameters for Ni(mnt)$_2$ reduction.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{1/2}$</td>
<td>-1.529 V</td>
</tr>
<tr>
<td>$D$</td>
<td>$1.60 \times 10^5$ cm$^2$ sec$^{-1}$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>0.45</td>
</tr>
<tr>
<td>$k_S$</td>
<td>$&gt; 0.1$ cm sec$^{-1}$</td>
</tr>
</tbody>
</table>
Two inferences may be drawn from this quotation. Firstly, if the neutral $\text{M(SacSac)}_n$ complexes are to be compared with the anionic $\text{M(III)}(\text{S-S})_3^{-3}$ and $\text{M(II)}(\text{S-S})_2^{-2}$ ($\text{S-S} = 1,2$-dithio chelate) complexes, then reduction processes of the $\text{M(III)}(\text{S-S})_3^{-3}$ and $\text{M(II)}(\text{S-S})_2^{-2}$ compounds may be accessible to voltammetric experiments, since all the $\text{M(SacSac)}_n$ complexes studied undergo at least one reversible (with regard to the rate of heterogeneous electron transfer) reduction. Additionally, if the $\text{M(SacSac)}_n$ reductions are metal-based, then these extra reductions of the 1,2-dithio chelate compounds might be expected to be metal-based, such behaviour thereby realising the expectation of an extensive electron transfer series ranging from ligand- to metal-based redox processes. In this regard, studies on the effects of chelate-ring substituents upon $E_{1/2}$-values have shown that for both metal- and ligand-based processes, the $-\text{CN}$ substituent group facilitates reduction to the greatest degree.\(^2,112,243\) In fact, the reversible

$$\text{Ni(mnt)}_2^{-2} \leftrightarrow \text{Ni(mnt)}_2^{-3}$$

reduction was reported recently\(^2\) and was subsequently shown by esr studies to be metal-based.\(^{271}\)

Conversely, it can also be inferred that voltammetric oxidations of the $\text{M(SacSac)}_2$ complexes may be observed at electrodes such as platinum which has a greater anodic range than does mercury. Such oxidations may be either metal- or ligand-based. However, as indicated elsewhere in this thesis, the most likely product of ligand oxidation is the 3,5-dimethyl-1,2-dithiolium cation (halogen oxidation of $\text{Ni(SacSac)}_2$, for example, is known to afford the tetrahalonickelate salt of this cation\(^82\)). This species is unlikely to remain co-ordinated to the metal-ion, and exhibits well-defined electrochemical behaviour at a platinum electrode,\(^{257}\) and so should be readily detected on reverse cyclic voltammetric scans. Therefore, reversible voltammetric oxidations of $\text{M(SacSac)}_n$ complexes might intuitively be expected to be metal-based.\(^\dagger\) Chelate-ring substituent variation studies have indicated that the ligand most likely to support an oxidation process is

\(^\dagger\) However, the close interligand sulphur ... sulphur interactions observed in $\text{M(SacSac)}_n$ structures, indicate the possibility of alternative forms of the oxidised ligand which may support a ligand-based oxidation.\(^2\)
Figure 10-2. Cyclic voltamogram of Cr(mnt)$_3^{3+}$ oxidations at 100 mV sec$^{-1}$ at 0 °C. Note that current axis is inverted. Inset, scan rate = 2 V sec$^{-1}$. Platinum electrode cleaned between scans.
NH₂SacNH₂Sac⁻ (Chapter 2). However, synthetic problems have so far restricted the range of characterised compounds of this ligand to the divalent nickel, palladium and platinum derivatives of Chapter 2. Oxidation of Ni(NH₂SacNH₂Sac)₂ has been shown to be quite complex, possibly resulting in [Ni(NH₂SacNH₂Sac)₃]⁺ in a manner analogous to oxidation of nickel(II)dithiocarbamate complexes,¹⁴⁶-¹⁴⁸ viz.,

\[ 3\text{NiL}_2 \rightarrow 2[\text{NiL}_3]⁺ + \text{Ni}^{2+} + 4e⁻ \]

and the system is as yet incompletely characterised. Indications of a polarographic oxidation of Os(OEtSacSac)₃ at the anodic limit have been reported,² and Os(OEtSacSac)₃ or Os(SacSac)₃ appear to be the dithio-β-diketonato compounds for which an oxidation wave is most likely to be observed.

Accordingly, the possibilities of an Os(SacSac)₃ oxidation and new M(mnt)⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓—⁻→ νίζ.

Although the reductions of "Co(mnt)₂⁻²⁻" and "Fe(mnt)₂⁻²⁻" are as yet not fully characterised, they are included here as they provide useful introductions to further work in this field.

(a) Ni(mnt)₂⁻²⁻

The reduction process

\[ \text{Ni(mnt)}₂⁻²⁻ \leftrightarrow \text{Ni(mnt)}₂⁻³⁻ \]

has been reported and found to be metal-based.²,²⁷¹ This reduction has been further characterised in the present work to provide a reference for the study of other mnt-compounds. The oxidation of Ni(mnt)₂⁻²⁻ has previously been assigned a \( k_s \) value in excess of 1 cm sec⁻¹ at a platinum electrode in acetonitrile.²¹₈ Ac polarographic studies (Fig. 10-1) establish that both the oxidation and reduction of Ni(mnt)₂⁻²⁻ are characterised by very large \( k_s \) values. Parameters describing the reduction process are collected in Table 10-1. These data were determined via the procedures of Chapter 5. The diffusion coefficient of \( 1.6 \times 10^{-5} \) cm² sec⁻¹ agrees well with the value of \( 1.36 \times 10^{-5} \) cm² sec⁻¹ determined by Lingane.²¹₈
Figure 10-3. Cyclic voltammogram of Cu(mnt)$_2$ reduction at a platinum electrode at room temperature. Potential range 0 V to -1.3 V. Scan rate is 50 mV sec$^{-1}$. Inset is cyclic voltammogram of dotted region (-0.4 V to -0.8 V) at 5 V sec$^{-1}$. 
Dimer/monomer associations are known to complicate the electrochemistry of both of these systems, although both dianions can be generated at the electrode (\((\text{Et}_4\text{N})_2[\text{Fe(mnt)}_2]\) was used as a possible source of \(\text{Fe(mnt)}_2^-\)). Further reduction waves were observed for both of these compounds (Fe: \(E_{1/2} = -1.575\ V\), Co: \(E_{1/2} = -1.497\ V\)) in addition to other processes corresponding to the known electrochemistry of these systems. The gradient of the \(E/\log \left(\frac{i_d}{i_p}\right)\) plot for the dc polarographic \(E_{1/2} = -1.575\ V\) wave of the iron derivative is 61.1 mV, and a linear dependence of the ac polarographic peak height upon the square root of the frequency is evident over the frequency range 80 < \(f< 1100\ Hz\).

Whilst the cyclic voltammogram of the \(\text{Co(mnt)}_2^-\) process appears reversible (\(\Delta E_p = 67\ \text{mV}\) at \(20\ \text{mV sec}^{-1}\)), two ac polarographic waves develop as the ac frequency is increased (at 1000 Hz, \([E_{dc}]\) values are \(-1.450\ V\) and \(-1.495\ V\)). However, a plot of the \(I_p vs. f^{1/2}\) behaviour of the peak at \([E_{dc}] = -1.495\ V\) is linear. At \(-5\ \text{°C}\) a reversible cyclic voltammogram is obtained (at \(200\ \text{mV sec}^{-1}\), \(\Delta E_p = 70\ \text{mV}, \frac{i_f}{i_p} = 1.04\)).

The natures of the species involved in these reductions have not yet been resolved, but it is tempting to include the couples in the possibilities. Further characterisation is necessary, this discussion being included to indicate possible investigations.

\(\text{Fe(mnt)}_2^- \leftrightarrow \text{Fe(mnt)}_2^3^-\)

\(\text{Co(mnt)}_2^- \leftrightarrow \text{Co(mnt)}_2^3^-\)


d) \(\text{Cr(mnt)}_3^-\)

The dc polarogram showed two small oxidation waves and a large reduction wave at \(E_{1/2} \approx -1.43\ V\). This reduction was investigated by cyclic voltammetry at a mercury electrode. No peak was evident on the reverse cyclic voltammetric scan and the forward scan wave was severely distorted. A reversible cyclic voltammogram was not obtained in this potential region under rapid scan rate or low temperature conditions. The oxidation waves correspond to the known single-electron oxidations...
Table 10-2. Characteristics of Cu(mnt)$_2^{-2/-1}$ process.
Cyclic voltammetry at a platinum electrode at 22 °C.

<table>
<thead>
<tr>
<th>Scan Rate (mV sec$^{-1}$)</th>
<th>$E_{1/2}$ (V)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$i_f/i_b$</th>
<th>$i_f$ (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>+0.549</td>
<td>65</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>+0.547</td>
<td>65</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>+0.549</td>
<td>65</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>+0.549</td>
<td>65</td>
<td>0.94</td>
<td></td>
</tr>
</tbody>
</table>

Table 10-3. Comparison of Cu(mnt)$_2^{-2}$ oxidation and reduction waves at -28 °C. Cyclic voltammetry at a platinum electrode.

<table>
<thead>
<tr>
<th>Couple</th>
<th>$E_{1/2}$ (V)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$i_f/i_b$</th>
<th>$i_f$ (μA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(mnt)$_2^{-2/-1}$</td>
<td>+0.495</td>
<td>50</td>
<td>1.09</td>
<td>19.8</td>
</tr>
<tr>
<td>Cu(mnt)$_2^{-2/-3}$</td>
<td>-0.610</td>
<td>50</td>
<td>1.19</td>
<td>18.0</td>
</tr>
</tbody>
</table>
of Cr(mnt)$_3$$^{3^-}$, and comparison of the limiting currents of the oxidation waves and the reduction wave shows the latter to correspond to a complex multi-electron process. Thus, although a new reduction of Cr(mnt)$_3$$^{3^-}$ is observed, the total wave does not correspond only to the simple electron transfer

$$\text{Cr(mnt)}_3^{3^-} \leftrightarrow \text{Cr(mnt)}_3^{4^-}$$

but rather a complex multi-electron process with the products uncharacterised as yet.

The oxidation waves observed polarographically were studied at a platinum electrode. These oxidations occur at $E_{1/2} = +0.05$ V and $E_{1/2} = +0.27$ V and are assigned to the redox steps.

$$\text{Cr} (\text{mnt})_3^{2^-} \leftrightarrow \text{Cr} (\text{mnt})_3^{-1}$$

Cyclic voltammetric scans at the usual scan rates ($20 \text{ mV sec}^{-1}$ - $500 \text{ mV sec}^{-1}$) show the Cr(mnt)$_3$$^{3^-/2^-}$ couple to be reversible and the Cr(mnt)$_3$$^{2^-/1^-}$ couple to be non-reversible (Fig. 10-2). The structures of the Cr(mnt)$_3^x$ compounds are thought to change from a trigonal prismatic to an "octahedral" geometry as $x$ decreases from 0 to $-3$. Accordingly, the non-reversibility of the more positive oxidation may be a consequence of a structural change following oxidation. Under rapid scan rate conditions (Fig. 10-2 inset) the oxidation at $E_{1/2} = +0.27$ V becomes more nearly reversible. It may therefore be possible to isolate Cr(mnt)$_2^-$ in two different geometries, depending upon the temperature at which it is prepared.

(e) Cu(mnt)$_2$$^{2^-}$

Both an oxidation and a reduction of Cu(mnt)$_2$$^{2^-}$ can be detected polarographically. Cyclic voltammetry at a platinum electrode established that the oxidation at $E_{1/2} = +0.549$ V corresponds to a reversible, one-electron oxidation with a rapid heterogeneous electron transfer (Table 10-2). This process is therefore assigned to the

$$\text{Cu} (\text{mnt})_2^{2^-} \leftrightarrow \text{Cu} (\text{mnt})_2^{-1}$$
Figure 10-4. Cyclic voltammograms of oxidation and reduction processes of Cu(mnt)$_2$ at -28 °C. Scan rate is 50 mV sec$^{-1}$. 
couple. Comparison of the polarographic limiting currents established that the reduction process is quite complicated and is a seemingly multi-electron step. Cyclic voltammetry at a platinum electrode showed the reduction to be very non-reversible at normal scan rates (Fig. 10-3). However, rapid scan rate (> 2 V sec\(^{-1}\)) experiments yielded a reversible wave in the region of this reduction (Fig. 10-3 inset). Accordingly, the reduction was investigated at low temperature. At -28°, cyclic voltammetric experiments showed a reversible reduction in this region (~ -0.5 V). The oxidation and reduction waves at this temperature are superimposed in Figure 10-4 (note that the current axis is inverted for the oxidation). It is evident from this Figure that the peak currents of both waves are equal (see also Table 10-3) and so the reduction is assigned to the

\[
\text{Cu(mnt)}_2^{2-} \leftrightarrow \text{Cu(mnt)}_2^{-3}
\]

couple. This process is evidently highly reversible with respect to the kinetics of heterogeneous electron transfer, but at room temperature \(\text{Cu(mnt)}_2^{-3}\) obviously undergoes some form of follow-up chemical reaction. Although the products of this reaction have not been established, the very large peak current for the reduction at room temperature (Fig. 10-3) is consistent with a product or products being electro-active at this potential.

These results indicate that the new complex \(\text{Cu(mnt)}_2^{-3}\) should be synthetically accessible at low temperatures. It is difficult to envisage further reduced forms of the ligand and it is therefore tempting to assign the compound as a copper(I) derivative. However, isolation of \(\text{Cu(mnt)}_2^{-3}\) should enable the metal- or ligand-based character of the \(\text{Cu(mnt)}_2^{-2}\) reduction to be established.

(f) \(\text{Os(SacSac)}_3\)

This complex has been shown to undergo a reversible, one-electron, diffusion controlled reduction at a dme in acetone with \(E_{1/2} = -0.05\) V.\(^{169}\) A reversible reduction is also observed in DMF at \(E_{1/2} = -0.151\) V vs. sce at a rotating platinum electrode.\(^{112}\) The reduction has been assumed to be metal-based, and the ease of reduction correlated with completion of the metal \(t_{2g}\) sub-shell.\(^{169}\)
Figure 10-5. Cyclic voltammogram of Os(SacSac)$_3^{3-1/0/+1}$ system at a platinum electrode. Scan rate is 50 mV sec$^{-1}$. 
The cyclic voltammogram at a platinum electrode of Os(SacSac)$_3$ is illustrated in Figure 10-5. Both oxidation and reduction processes of Os(SacSac)$_3$ are evident and both can be seen to possess a considerable degree of reversibility. As a prelude to the study of the previously unknown Os(SacSac)$_3$ oxidation, the reduction was characterised at a platinum electrode. At room temperature this wave corresponds to a reversible, one-electron reduction (typically, at 100 mV sec$^{-1}$, $\frac{i_r}{i_b} = 0.97$, $\Delta E_p = 65$ mV and $E_{1/2} = -0.050$ V). The system is also reversible at -40 °C ($\Delta E_p = 67$ mV, and $E_{1/2} = -0.026$ V) or at cyclic voltammetric scan rates of 5 V sec$^{-1}$.

Superposition of the reduction and oxidation waves (Fig. 10-6) shows the wave heights to be the same. Os(SacSac)$_3$ is therefore oxidised in a one-electron step at $E_{1/2} = +0.920$ V. Some assymetry of the wave is apparent, the ratio $\frac{i_r}{i_b}$ and the scan rate dependence of this ratio (Table 10-4) indicating complications due to slow chemical reaction of Os(SacSac)$_3$$^+$. This assymetry is not evident at a scan rate of 5 V sec$^{-1}$ nor at -40 °C (Table 10-4) at which temperature $E_{1/2} = +0.885$ V.

Os(SacSac)$_3$, then, undergoes an *electrochemically* reversible, one-electron oxidation at $E_{1/2} = +0.920$ V to which is coupled a relatively slow, follow-up chemical reaction. Thus, the occurrence of a reversible oxidation of a neutral M(SacSac)$_n$ complex has been demonstrated for the first time. Os(SacSac)$_3$ is the central member of the electron transfer series

Os(SacSac)$_3^-$ $\rightleftharpoons$ Os(SacSac)$_3$ $\rightleftharpoons$ Os(SacSac)$_3$$^+$

To what extent this series is metal- or ligand-based has yet to be established, although Bond *et al.*$^{169}$ favour the metal-based description for the Os(SacSac)$_3$$^{-1/6}$ couple. Of particular significance is the lack of evidence for the 3,5-dimethyl-1,2-dithiolium cation in the cyclic voltammogram of Figure 10-5, perhaps suggesting that the Os-S bond is sufficiently strong to prevent S-S bonding.

The ease of reduction and of oxidation of Os(SacSac)$_3$ is consistent with Os(SacSac)$_3^-$ and Os(SacSac)$_3$$^+$ being amenable to synthesis. Both species should be stable in air. On the basis of the above results, it is suggested that the isolation of Os(SacSac)$_3$$^+$ should
Figure 10-6. Cyclic voltammograms of Os(SacSac)$_3$ reduction (dashed/left hand curve, upper potential scale) and oxidation (solid/right hand curve, lower potential scale) processes at a scan rate of 100 mV sec$^{-1}$ at a platinum electrode.
be attempted at low temperatures, but that the cation may be stable as a solid at room temperature. Preparation of these new compounds would enable the degree of metal- or ligand-based character of the redox process to be ascertained and a comparative crystallographic study of the series Os(SacSac)$_3^{-1/0/+1}$ would be of great interest.

The preliminary studies reported in this Chapter have established the presence of several new reduction processes for the M(mnt)$_n^{-n}$ ($n = 2, 3$) species and a new oxidation of Os(SacSac)$_3$. In particular, the Cu(mnt)$_2^{2/-3}$ and Os(SacSac)$_3^{0/+1}$ couples are reversible with respect to the rate of heterogeneous electron transfer, and both the syntheses of Cu(mnt)$_2^{3/-3}$ and Os(SacSac)$_3^+$ should be possible at low temperatures. The possible existence of other highly reduced species has been demonstrated and several of these compounds may be isolable. Characterisation of the Os(SacSac)$_3$ oxidation points to other possible M(SacSac)$_n$ oxidations, and confirms that extended one-electron transfer series are by no means confined to transition metal complexes of the 1,2-dithiolenes.

Table 10-4. Parameters for Os(SacSac)$_3$ oxidation. Cyclic voltammetry at a platinum electrode.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Scan Rate (mV sec$^{-1}$)</th>
<th>$E_{1/2}$ (V)</th>
<th>$\Delta E_p$ (mV)</th>
<th>$i_{E_{1/2}}/i_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>100</td>
<td>+0.920</td>
<td>80</td>
<td>1.26</td>
</tr>
<tr>
<td>22</td>
<td>200</td>
<td>+0.920</td>
<td>70</td>
<td>1.14</td>
</tr>
<tr>
<td>22</td>
<td>500</td>
<td>+0.923</td>
<td>75</td>
<td>1.04</td>
</tr>
<tr>
<td>-40</td>
<td>50</td>
<td>+0.885</td>
<td>58</td>
<td>0.90</td>
</tr>
<tr>
<td>-40</td>
<td>100</td>
<td>+0.885</td>
<td>60</td>
<td>0.85</td>
</tr>
<tr>
<td>-40</td>
<td>200</td>
<td>+0.890</td>
<td>60</td>
<td>0.83</td>
</tr>
</tbody>
</table>
CHAPTER 11

EXPERIMENTAL DETAILS
SYNTHESSES

Compounds prepared by published methods are collected in Table 11-1. Satisfactory elemental analyses were obtained in all cases. Other compounds were prepared as follows (analytical data in Table 11-2). All solutions saturated unless specified.

(i) Bis(malondithioamidato)nickel(II) \([\text{Ni(NH}_2\text{SacNH}_2\text{Sac)}_2]\)

A warmed aqueous solution of nickel acetate tetrahydrate (0.004 mol) was added to a stirred solution of dithiomalonamide (0.008 mol) in hot water. The dark green product separates immediately.

(ii) Bis(malondithioamidato)palladium(II) \([\text{Pd(NH}_2\text{SacNH}_2\text{Sac)}_2]\)

A warmed aqueous solution of disodium tetrachloropalladate(II) (0.005 mol) was added to a stirred solution of dithiomalonamide (0.01 mol) and sodium acetate trihydrate (0.01 mol) in hot water. The orange product separates immediately.

(iii) Bis(malondithioamidato)platinum(II) \([\text{Pt(NH}_2\text{SacNH}_2\text{Sac)}_2]\)

The mustard-coloured product was prepared similarly to the palladium analogue.

All complexes were recrystallised for dimethyl sulphoxide by the slow addition of methanol and dried at 0.05 Torr at 80° (yield 60 - 80%). However, repeated efforts failed to remove completely occluded solvent from \([\text{Pt(NH}_2\text{SacNH}_2\text{Sac)}_2]\).
Table 11-1. Compounds prepared by published methods.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Preparation from Reference Number</th>
<th>Studied in Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_2$SacNH$_2$SacH</td>
<td>14, 311</td>
<td>2</td>
</tr>
<tr>
<td>3,5-Diamino-1,2-dithiolium iodide</td>
<td>110</td>
<td>2</td>
</tr>
<tr>
<td>Ni(NH$_2$SacNH$_2$SacH)$_2$Cl$_2$</td>
<td>104</td>
<td>2</td>
</tr>
<tr>
<td>Ni(dtb)$_2$</td>
<td>312</td>
<td>2</td>
</tr>
<tr>
<td>Zn(SacSac)$_2$</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Bu$_4$SacBu$_4$acH</td>
<td>21</td>
<td>4</td>
</tr>
<tr>
<td>Ni(Bu$_4$acBu$_4$ac)$_2$</td>
<td>130</td>
<td>4, 8</td>
</tr>
<tr>
<td>Ni(Bu$_4$SacBu$_4$ac)$_2$</td>
<td>21</td>
<td>4, 8</td>
</tr>
<tr>
<td>Ni(Bu$_4$'SacBu$_4$'ac)$_2$</td>
<td>45</td>
<td>4, 8</td>
</tr>
<tr>
<td>Ni(CF$_3$SacSac)$_2$</td>
<td>83</td>
<td>4</td>
</tr>
<tr>
<td>Cr(acac)$_3$</td>
<td>313</td>
<td>7</td>
</tr>
<tr>
<td>Mn(acac)$_3$</td>
<td>314</td>
<td>7</td>
</tr>
<tr>
<td>Fe(acac)$_3$</td>
<td>315</td>
<td>7</td>
</tr>
<tr>
<td>Co(acac)$_3$</td>
<td>316</td>
<td>7</td>
</tr>
<tr>
<td>Ni(Sac(NMe)ac)$_2$</td>
<td>$a$</td>
<td>8</td>
</tr>
<tr>
<td>Ni(mnt)$_2$(Et$_4$N)$_2$</td>
<td>317</td>
<td>10</td>
</tr>
<tr>
<td>Cu(mnt)$_2$(Et$_4$N)$_2$</td>
<td>317</td>
<td>10</td>
</tr>
<tr>
<td>Fe(mnt)$_2$(Et$_4$N)</td>
<td>318</td>
<td>10</td>
</tr>
<tr>
<td>Cr(mnt)$_3$(Ph$_3$As)$_3$</td>
<td>319</td>
<td>10</td>
</tr>
<tr>
<td>Co(mnt)$_2$(Et$_4$N)$_2$</td>
<td>320</td>
<td>10</td>
</tr>
</tbody>
</table>

$^a$ after the method of reference 75.

The substituted 1,2-dithiolium iodides, dithiocarbamates of sodium and cobalt(III), and Os(SacSac)$_3$ were presented by Dr. A.R. Hendrickson.
(iv) Tris(4-thiolo-3-ene-2-thione)chromium(III)
[Cr(SacSac)₃]

An acidified aqueous solution of chromous chloride (0.02 mol) was added to finely divided 3,5-dimethyl-1,2-dithiolium iodide (2.55 g, 0.01 mol) under nitrogen. The resulting slurry was stirred for 4 hours, then the dark solid was washed with diethyl ether and recrystallised from chloroform to yield the product [Cr(SacSac)₃] (0.48 g, 36%).

(v) "Sodium Dithioacetylacetonate Solution"

Sodium borohydride (0.34 g) was dissolved in basic methanol, and added slowly with stirring to a solution of 3,5-dimethyl-1,2-dithiolium bromide (1 g) in methanol at 0 °C.

(vi) Bis(π-cyclopentadienyl)(dithioacetylacetonato)-vanadium(IV)tetrafluoroborate [cp₂V(SacSac)][BF₄]

A solution of bis(π-cyclopentadienyl)vanadium dichloride (1.2 g) in acetone-water (50%) was added to the "sodium dithioacetylacetonate solution". The resultant solution was filtered and added to a solution of sodium fluoroborate (0.5 g) in water, the mixture then being cooled to 0 °C for thirty minutes. Dark green crystals of [cp₂V(SacSac)][BF₄] were precipitated. These were collected by filtration, washed with methanol and diethyl ether, and dried at 80 °C.

(vii) Tetraphenylarsonium Dithioacetylacetonate
[Ph₄As]⁺[SacSac]⁻

Tetraphenylarsonium chloride (2 g) in a 50% aqueous methanol solution was added at 0 °C to a solution of sodium dithioacetylacetonate and left to stand at 0 °C. Red crystals separated after approximately thirty minutes and were collected by filtration and washed with diethyl ether.

(viii) C₁₀H₁₄S₄

3,5-Dimethyl-1,2-dithiolium bromide (2 g) in methanol was added at 0 °C to a solution of sodium dithioacetylacetonate (prepared as
Table 11-2. Analytical data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>C (%)</th>
<th>H (%)</th>
<th>S (%)</th>
<th>N (%)</th>
<th>M (%)</th>
<th>Halogen (%)</th>
<th>Mol. Wt. or B (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiC₆H₆N₆S₄</td>
<td>22.16</td>
<td>22.28</td>
<td>3.11</td>
<td>3.46</td>
<td>39.44</td>
<td>38.97</td>
<td>17.23</td>
</tr>
<tr>
<td>PdC₆H₆N₆S₄</td>
<td>19.33</td>
<td>19.52</td>
<td>2.71</td>
<td>2.72</td>
<td>34.40</td>
<td>34.09</td>
<td>15.03</td>
</tr>
<tr>
<td>PtC₆H₆N₆S₄</td>
<td>15.61</td>
<td>16.00</td>
<td>2.18</td>
<td>2.31</td>
<td>27.79</td>
<td>27.45</td>
<td>12.14</td>
</tr>
<tr>
<td>Cr₅H₄S₆</td>
<td>40.4</td>
<td>40.2</td>
<td>4.7</td>
<td>4.7</td>
<td>43.1</td>
<td>43.1</td>
<td>-</td>
</tr>
<tr>
<td>VC₅H₇S₂BF₄</td>
<td>45.00</td>
<td>45.36</td>
<td>4.25</td>
<td>4.35</td>
<td>16.1</td>
<td>16.2</td>
<td>-</td>
</tr>
<tr>
<td>C₆H₄S₄</td>
<td>45.8</td>
<td>45.52</td>
<td>5.35</td>
<td>5.47</td>
<td>48.8</td>
<td>48.8</td>
<td>-</td>
</tr>
<tr>
<td>CoC₃₃H₅₇O₃S₃</td>
<td>60.33</td>
<td>60.51</td>
<td>8.75</td>
<td>8.61</td>
<td>14.64</td>
<td>13.58</td>
<td>-</td>
</tr>
</tbody>
</table>

a  Calculated values for PtC₆H₁₀N₄S₄ +1/8 DMSO (see text): C, 15.92%; H, 2.30%; N, 11.93%; S, 28.04%; Pt, 41.38%.

b Vapour pressure osmometry in pyridine.

c Solubility in pyridine too low to obtain a reasonably accurate figure.

d Vapour pressure osmometry in chloroform.
above, but using 3,5-dimethyl-1,2-dithiolium bromide (1 g). The white crystals separated directly and were filtered and washed several times with diethyl ether.

(ix) 1,2-Dithiolium Iodide

Dry, gaseous hydrogen chloride was bubbled into methanol (150 ml) at 0 °C, until a 33% w/v solution was obtained. Iodine (9 g) was added and hydrogen sulphide bubbled into the solution for two minutes. Malonic dialdehydetetraethylacetal (15 ml) was then added, and the mixture stirred for two hours with hydrogen sulphide bubbling through. The red solution was filtered, and the yellow product precipitated by addition of copious amounts of diethyl ether. The product was filtered, washed with ethanol and diethyl ether, and recrystallised with difficulty from glacial acetic acid.

(x) Bis(1,2-dithiopropanedialato)nickel(II)

Solid 1,2-dithiolium iodide (2 g) and nickel chloride hexahydrate (1 g) were ground together with a mortar and pestle at 0 °C. Solid sodium borohydride (0.7 g) was added, and the mixture ground further with several small pieces of ice. When the solid mixture was completely black, dilute hydrochloric acid (5 ml) was added. After five minutes the black solid was filtered and washed several times with methanol and diethyl ether.

(xi) Tris(monothio-2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt(III) [Co(Bu^tSacBu^tac)_3]

This compound was prepared by the reaction of cobaltous acetate tetrahydrate (0.01 mol) with monothiodipivaloylmethane (0.02 mol) in methanol (50 ml) in the presence of oxygen. The dark green crystals were recrystallised from dichloromethane/methanol (nmr spectrum in CDCl₃ δCOOME₃ 1.12 ppm, δCSCMe₃ 1.32 ppm, δCH 6.64 ppm).
(b) ANALYSES

Elemental analyses and molecular weight determinations were performed by the ANU Microanalytical Service.

(c) INSTRUMENTATION

(i) Infra-red Spectra

Infra-red spectra were obtained with Perkin-Elmer 225 and 457 grating infra-red spectrophotometers. Samples were suspended in potassium bromide or cesium iodide discs.

(ii) Nuclear Magnetic Resonance Spectra

Nuclear Magnetic Resonance spectra were recorded with a Varian Associates HA100, hundred megacycle instrument. Tetramethylsilane was used as internal reference.

(iii) Electronic spectra

Electronic spectra were obtained with a Cary 14 recording spectrophotometer.

(iv) Electron Paramagnetic Resonance Spectra

Electron paramagnetic resonance spectra were recorded with a Varian X-band spectrometer.

(v) Mass Spectra

The mass spectra of Chapter 4 were measured on an AEI MS 902 instrument at 70 eV with ion source temperatures in the range 150 to 215 °C. The metal complexes and dithiolium iodides were introduced on the direct insertion probe, while the ligands were introduced through the all glass heated inlet which was maintained at 190°. Accurate mass measurements were made by means of high resolution scans recorded and processed by an on-line Raytheon 706 computer. Metastable ions
fragmenting in the first field-free region were recorded using the HV scan technique. The compositions of all ions referred to in the text were confirmed by accurate mass measurements, and first or second field-free region metastable ion peaks, or both, were found corresponding to all ion reactions referred to in the text. All peaks are tabulated using $^{58}\text{Ni}$ and $^{32}\text{S}$ isotopes. Other mass spectral measurements were made at low resolution with an AEI MS 902 instrument.

(vi) Electrochemistry

Electrochemical studies utilised a Princeton Applied Research Corporation (PAR) Model 170 Electrochemistry System and a PAR Model 172A Polarographic Stand. All measurements were made in acetone with tetraethylammonium perchlorate (0.1 M) as supporting electrolyte. Argon was bubbled through all solutions prior to, and passed over all solutions during recording. A three-electrode configuration as described in reference 82 was employed with a Metrohm Ag/AgCl EA425 (0.1 M LiCl) reference electrode in a 0.1 M Et$_4$NClO$_4$ salt bridge and a platinum wire auxiliary electrode. Potentials are quoted vs. Ag/AgCl unless otherwise noted. All voltammograms were undamped and measurements made on maximum currents. Total iR compensation was used in all cyclic and ac voltammetric measurements, and phase sensitive detection was utilised in ac voltammetric studies. Coulometric measurements were made at mercury pool and platinum gauze working electrodes with a three-electrode system, and spectrophotometric results were obtained with the Cary 14 spectrophotometer utilising a cell designed by Dr. A.R. Hendrickson and described in reference 146. Working electrodes were glass capillary dropping mercury electrodes, Metrohm E-410 hanging drop mercury electrode, and Beckman platinum disk and hanging drop mercury electrodes. All measurements were made at 22 °C.

May and Baker 'Pronalys' acetone was used as received.\textsuperscript{†} Tetraethylammonium perchlorate was either synthesised by neutralising

\textsuperscript{†} This product was found to be the most suitable for voltammetric measurements, required no further purification and provided the largest potential range.\textsuperscript{2}
BDH 25% tetraethylammonium hydroxide solution with 20% perchloric acid or purchased from Pfaltz and Bauer, Inc. Before use the tetraethylammonium perchlorate was recrystallised twice from 95% ethanol and finally from A.R. methanol, dried and stored under vacuum over silica gel.

Cyclic voltammograms at scan rates greater than 500 mV sec\(^{-1}\) were recorded with Tektronix 5031 and 7613 Oscilloscopes and photographed with a Tektronix C-70 Oscilloscope Camera.

Conductance measurements were obtained with a Phillips Conductivity Measuring Bridge type GM 4144/01.
REFERENCES

REFERENCES


46. R.C. Haddon, personal communication.


148. A.R. Hendrickson, R.L. Martin, and N.M. Rohde, to be submitted for publication.


APPENDIX I

LIGAND ABBREVIATIONS

- acac
- Sacoc
- SacSac
- NH₂SacNH₂Sac
- dtb
- OEtSacSac
- Bu'SacBu'ac
- CF₃SacSac
- (NR)acSacSac
- PMe₂Phos