HALIDE COMPLEXES OF MANGANESE

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Except where otherwise specified, the work described in this thesis is the candidate's own.

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SUMMARY

A series of anionic halide complexes of manganese (II) containing alkyl-substituted ammonium cations was prepared from solution. The complexes could be classified in two main groups, those containing the tetrahedral anion $MnX_4^=$ (where X is Cl, Br or I) and those containing the octahedral anion MnX_3^- (where X is Cl or Br). The exception to this general scheme was the complex $(CH_3NH_3)_2MnCl_4$ which was shown by spectroscopic and X-ray powder data to contain octahedrally coordinated manganese (II). A few chloro complexes with potassium and caesium cations were prepared from melts.

Using the strong field scheme of Tanabe and Sugano with a least squares refinement, energy levels were calculated for the spectra of fourteen manganese (II) complexes and were found to agree with the experimentally determined energy levels to within 2%. The dependence of the ligand field parameter Δ on the ligand was found to be in accordance with the spectrochemical series, and the Racah parameter B was found to decrease with the increasing covalent nature of the metal-ligand bond as predicted from the nephelauxetic series.

It was shown from X-ray powder data that the structure of the compound $(CH_3NH_3)_2MnCl_4$ is related to the K_2NiF_4 structure and that the compounds $(CH_3)_4NMnCl_3$ and $(CH_3)_4NMnBr_3$ have the $CsNiCl_3$ type structure.

A series of anionic manganese (III) chloro complexes with alkyl- substituted ammonium cation was isolated from solution and found to conform to two general formula types. The methylammonium and dimethylammonium compounds were shown to have the formula $(R_4N)_4MnCl_7H_2O$ and the remaining complexes the formula $(R_4N)_2MnCl_5$.

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Preface

The introduction of Crystal field theory by Bethe, van Vleck and others aroused new interest in the spectra and magnetic properties of transition metal complexes. The most successful application of the theory has been in the assignment and interpretation of the weaker absorption bands in the visible and ultraviolet regions of the spectrum.

The visible and ultraviolet absorption spectra of both octahedral and tetrahedral complexes of high-spin manganese (II) are due to weak, spin-forbidden transitions and have been successfully interpreted by several workers using crystal field calculations. The colour of manganese (II) complexes has been shown to be characteristic of the stereochemistry of the complex ion; thus green compounds contain tetrahedrally coordinated manganese (II) and pink compounds octahedrally coordinated manganese (II).

An examination of the work of previous authors reveals that inconsistencies in the values of the crystal field parameters, for the same spectrum, are due to different methods of calculation. In the present work an attempt has been made to verify the method of calculation and also to remove some of the difficulties encountered by previous authors. A series of octahedral and tetrahedral halide complexes of manganese (II) was prepared as described in part 1 of this thesis, and the reflectance spectra of these complexes interpreted as described in part 2. The crystal field parameters obtained by previous authors have been calculated in order to provide a self-consistent set of parameters. In part 3 structures of two new octahedral complexes of manganese (II) are described.

Although a great deal of experimental work on the preparation of chloro complexes of manganese (III) has been described in the literature, only in a few cases have these complexes been satisfactorily characterized. Section B of this thesis deals with the preparation, properties and spectra of several chloro complexes of manganese (III).

A. Halide Complexes of Manganese (II)

1. Experimental Methods

(i) Starting Materials

Analytical grade hydrated manganese chloride and bromide were used in the preparations although laboratory grade reagents were found to be satisfactory. Commercially available, hydrated manganese iodide was always badly contaminated with iodine and could not be used in the preparation of iodide complexes. Iodine free manganese iodide was prepared by reacting iodine free hydriodic acid with clean electrolytic manganese metal. The resultant pale pink solution was evaporated down on a rotary evaporator and finally dried for several hours under vacuo. This removes all the free hydriodic acid and thus prevents rapid formation of free iodine on exposure to air. The solution must be filtered and evaporated while still acidic, otherwise a pale pink flocculent precipitate will form. This precipitate, which turns brown on exposure to air and can be removed by addition of more hydriodic acid, is probably manganese (II) hydroxide.

The presence of slight traces of cobalt in the A.R. manganese halides was discovered in the appearance of three unidentifiable bands between 600 and 700 mμ in the absorption spectra of the green tetrahalo-complexes. Precipitation of the cobalt with α-nitroso-β-naphthol[1] was carried out and the group of bands disappeared from the spectra. The spectra of the pink octahedral complexes were found to be unaltered by the presence of cobalt in the hydrated manganese (II) halides.

The alkylammonium halides used were of laboratory grade. Where not available, the compounds were simply prepared by neutralizing an aqueous solution of the required alkyl-amine with a halogen acid and evaporating the resultant solution to dryness on a rotary evaporator. In some cases where purification was necessary to remove water or other contaminants such as the ether soluble tribromides or triiodides, the salts were precipitated from alcoholic solution with peroxide free ether. The resulting precipitate was then filtered and washed with ether to remove any colouration present.

The solvents used in the reaction were commercially available; absolute alcohol, methanol, A.R. glacial acetic acid and A.R. 55% w/w hydriodic acid. With the exception of the hydriodic acid no further purification of the solvents was necessary. The hydriodic acid was freed from iodine by distillation with a small amount of hypophosphorus acid[2]. As iodine is formed on contact of the acid with air it must be used as soon as possible after distillation. To overcome this the acid was usually distilled directly into a reaction vessel and thus used immediately.

(ii) Analyses

All compounds prepared in this work, other than compounds from melts, were analysed for halide and for manganese. The most satisfactory method for determining manganese was by direct titration of an aqueous solution of the complex with standard sodium EDTA at pH = 10 with Eriochrome black T as indicator[3]. Initially halide analyses (only chloride determinations) were carried out gravimetrically. A much more rapid potentiometric titration method was used for all subsequent halide analyses and also to check the previous gravimetric determinations. A Radiometer automatic titrator type SBR2C fitted with a 5 ml syringe burette was used for the potentiometric titrations. Standard silver nitrate solution was delivered by the syringe into an aqueous solution of the halide which had to be stirred at the maximum speed to give reproducible results. The reference electrode used was a standard glass electrode and the indicator electrode a silver/silver chloride electrode.

Compounds prepared in melts were not analysed as pure samples of the compounds could not be obtained. The melts were analysed qualitatively using X-ray powder diffractometry. All analyses are listed in Table (2) at the end of this chapter.

(iii) Preparation of alkylammonium compounds

In general most of the alkylammonium compounds could be prepared by a method analogous to that used by Taylor[4] to prepare pyridinium compounds. In this method hot ethanolic solutions of a hydrated manganese halide and of an alkylammonium halide in stoichiometric proportions are mixed and left to crystallise. Mixed halide complexes were not prepared but their existence has been reported[5]. The use of glacial acetic acid as a solvent as described by Naldini and Sacco[5] proved to be very useful in the isolation of pure bromo complexes and in the preparation of most of the iodo complexes. Due to the very hygroscopic nature of many of the bromo complexes the final stages of the preparations (filtering, washing and drying) were carried out in a dry-box and samples for analysis were weighed out on a Cahn Electrobalance in the dry-box. After filtration all complexes were dried under vacuo over potassium hydroxide pellets. Recrystallisation was not necessary as the complexes were, in most cases, much less soluble than either of the two starting materials.

All compounds of the type R_2MnX_4 with the exception of $(CH_3NH_3)_2MnCl_4$ are pale-yellowish green and have been shown to contain tetrahedrally coordinated manganese(4-9). The compound $(CH_3NH_3)_2MnCl_4$ is pale pink and as this colour indicates octahedrally coordinated manganese the compound must have a polymeric anion. The other compounds obtained in this series of preparations conform to the general formula $RMnX_3$ and are all pink. These compounds must also contain a polymeric anion.

As there are many slight variations to the general method of preparation those which either do not conform exactly to this method or may be prepared in a different way are listed below. A list of all the complexes obtained in this work with alkylammonium cations is listed in Table (1).

It can be seen from the table that, with the exception of the methylammonium compounds, the bromo complexes correspond to the series of chloro complexes for all alkylammonium cations. In the case of the methylammonium compounds only one chloro complex, $(CH_3NH_3)MnCl_4$, was obtained which has been shown to be octahedral by both spectroscopic and X-ray diffraction studies. With the bromide two complexes were formed, one containing the tetrahedral anion $MnBr_4^=$ and the other the octahedral anion $MnBr_3^-$. The trimethylammonium halide in both cases yields only complexes containing the octahedral MnX_3^- anion and the tetraethylammonium halide only yields tetrahedral $MnX_4^=$ anions. The two remaining alkylammonium halides give complexes which contain tetrahedral $MnX_4^=$ anions and also compounds with octahedral MnX_3^- anions. The only iodide complexes formed contained the $MnI_4^=$ anion. Thus the change in size of both cation and anion appears to effect the coordination of the central metal ion.

(a) Methylammonium tetrachloromanganate (II) $(CH_3NH_3)_2MnCl_4$

This compound may be prepared from methanol or ethanol using a wide range of mole proportions of the starting materials. The compound has also been prepared by evaporation of an aqueous solution of the two reactants on a rotary evaporator. Polycrystalline and twinned crystals were obtained from alcoholic solutions of the reactants whereas aqueous solutions yielded single crystals.

(b) Dimethylammonium tetrachloromanganate (II) $((CH_3)_2NH_2)_2MnCl_4$

As this compound is very soluble in ethanol it was usually found necessary to evaporate the solution to effect crystallisation. The compound was also prepared by evaporation of an aqueous solution of the reactants. The compound crystallises as pale yellow-green prisms and is very hygroscopic.

(c) Dimethylammonium trichloromanganate (II) $(CH_3)_2NH_2MnCl_3$

A large excess of hydrated manganese chloride is needed to prevent formation of the yellow-green tetrachloride in this preparation. The compound is prepared from ethanol, but crystallization must not be hastened by scratching or cooling, otherwise immediate precipitation of the tetrachloro compound may occur. A solution of dimethylammonium chloride in thionyl chloride[10] containing solid hydrated manganese chloride was refluxed for two hours to give a pale pink crystalline mass which was shown by analysis to be the trichloromanganate.

(d) Trimethylammonium trichloromanganate (II) $(CH_3)_3NH\ MnCl_3$

This compound is best prepared from hot ethanolic solutions using 100% excess of hydrated manganese chloride. If stoichiometric proportions of the reactants are used the first crop of crystals is grey-green. The pink trichloro compound is then obtained by evaporation of the filtrate. The colourless to grey-green crop of crystals seems to indicate possible formation of a tetrachloro complex. No tetrachloro complex has been isolated from alcohol, although a green deliquescent compound with a variable analysis was obtained from nitromethane. The compound probably contains nitromethane and varying amounts of trimethylammonium chloride as the analysis indicated a manganese to chlorine ratio of nearly 1:7.

(e) Tetramethylammonium trichloromanganate (II) $(CH_3)_4NMnCl_3$

This compound is readily convertible into tetramethylammonium tetrachloromanganate (II) and may be obtained by adding an excess of hydrated manganese chloride to a suspension of the tetrachloride in ethanol and boiling the solution for several minutes. The tetrachloride is obtained in a similar manner from a suspension of the trichloride in an alcoholic solution of tetramethylammonium chloride. The trichloromanganate is an extremely fine pink powder. Large crystals suitable for single crystal work may be prepared by recrystallizing the compound from a solution of hydrated manganese chloride in methanol.

(f) Methylammonium tetrabromomanganate (II) $(CH_3NH_3)_2MnBr_4$

This compound unlike the chloro homologue is yellowish-green and thus 'tetrahedral'. As is the case with most of the bromide preparations, glacial acetic acid is the best solvent. To prevent formation of the tribromomanganate an excess of methylammonium bromide is necessary. Methylammonium bromide is the main product when ethanol and methanol are used as solvents, but iso-propanol and n-butanol give the tetrabromomanganate.

(g) Methylammonium tribromomanganate (II) $CH_3NH_3MnBr_3$

Glacial acetic acid or iso-propanol may be used as solvent in the preparation of this compound which is formed very readily from stoichiometric proportions of the reactants.

(h) Dimethylammonium tribromomanganate (II) $(CH_3)_2NH_2MnBr_3$

This compound is obtained from glacial acetic acid if 100% excess of hydrated manganese bromide is used to suppress formation of the green tetrabromomanganate.

(i) Tetramethylammonium tetrabromomanganate (II) $((CH_3)_4N)_2MnBr_4$

Unlike the majority of the bromide complexes this compound can be readily obtained from ethanol (but not from methanol) using a wide range of proportions of starting materials. The use of glacial acetic acid with stoichiometric proportions of starting materials gives a much better yield of the complex.

(j) Tetraethylammonium tetrabromomanganate (II) $((C_2H_5)_4N)_2MnBr_4$

As with (i) above, this compound may be obtained from both ethanol and glacial acetic acid. A wide range of proportions of starting materials will yield this compound as no tribromomanganate appears to be formed. The original preparation of this compound by Jorgensen[6], using aqueous hydrobromic acid as a solvent, was employed to obtain large crystals for single crystal spectral work.

(k) Tetramethylammonium tetraiodomanganate (II) $((CH_3)_4N)_2MnI_4$

All the iodide complexes with the exception of the tetramethylammonium compound could be obtained from glacial acetic acid. This compound had to be prepared using iodine free aqueous hydriodic acid from which it crystallised out as large rectangular plates. Large crystals of the tetraethylammonium tetraiodomanganate were prepared by this method for single crystal work. Due to rapid decomposition of the iodides together with the difficulty of preparing pure compounds, analyses are not listed for all the compounds. The tetraethylammonium tetraiodomanganate appears to be the most stable compound and has the only satisfactory analysis.

Table 1

Complex Halides of Manganese (II)

Alkylammonium Cation	Complexes Obtained Chloride	Bromide	Iodide
$CH_3NH_3{}^+$	$(CH_3NH_3)_2MnCl_4$ [a]	$(CH_3NH_3)_2MnBr_4$ $CH_3NH_3.MnBr_3$	No complex formed
$(CH_3)_2NH_2{}^+$	$((CH_3)_2NH_2)_2MnCl_4$ $(CH_3)_2NH_2.MnCl_3$	$((CH_3)_2NH_2)_2MnBr_4$ $(CH_3)_2NH_2.MnBr_3$	$((CH_3)_2NH_2)_2MnI_4$
$(CH_3)_3NH^+$	$(CH_3)_3NH.MnCl_3$ [b]	$(CH_3)_3NH.MnBr_3$ [b]	$((CH_3)_3NH)_2MnI_4$
$(CH_3)_4N^+$	$((CH_3)_4N)_2MnCl_4$ $(CH_3)_4N.MnCl_3$	$((CH_3)_4N)_2MnBr_4$ $(CH_3)_4N.MnBr_3$	$((CH_3)_4N)_2MnI_4$
$(C_2H_5)_4N^+$	$((C_2H_5)_4N)_2MnCl_4$	$((C_2H_5)_4N)_2MnBr_4$	$((C_2H_5)_4N)_2MnI_4$

a. This complex has been shown to contain octahedrally coordinated manganese (II).

b. There is some evidence that a tetrahedral complex may exist.

(iv) Preparation of compounds from melts

(a) System $KCl/MnCl_2$

This system was first examined as a means of preparing K_4MnCl_6 which could not be obtained by the methods of Suss[11] or Belanca[12]. Both of these methods do not give full details of the preparation which is carried out by slow evaporation of an aqueous solution of potassium chloride and hydrated manganese chloride. Several attempts to prepare K_4MnCl_6 by either method invariably gave large crystals of potassium chloride.

As the complete crystal structure of K_4MnCl_6 is known (Bellanca)[12] and as its X-ray powder diffraction pattern is listed in the A.S.T.M. index there is no difficulty in identifying the compound.

A series of melts were prepared in a silica tube under anhydrous hydrogen chloride and oxygen free nitrogen. X-ray powder-diffraction patterns were taken to determine the melt compositions. With mole ratios 1/2 : 1, $KCl : MnCl_2$ through to 4 : 1, $KCl : MnCl_2$ two definite X-ray powder patterns emerged. The pattern of $KMnCl_3$ was identified in melts with 1/2 : 1, 1 : 1 and 1 : 2 mole ratios of $KCl : MnCl_2$ using X-ray diffraction data which appeared in the literature (Croft <u>et al</u>[13]) while this work was in progress. The melts with 1 : 3, 1 : 4 and 1 : 5 mole ratios $KCl : MnCl_2$ showed the presence of K_4MnCl_6 with increasing amounts of potassium chloride as the mole ratio increases.

A more recent paper (Seifert and Koknat[14]) which appeared after this work had been completed, included a phase analysis of the system $KCl/MnCl_2$. The phase diagram shows that K_4MnCl_6 has an incongruent melting point at 448°C with 30.5 mole% $MnCl_2$.

(b) System $KBr/MnBr_2$

The system $KBr/MnBr_2$ was investigated in the same manner as the preceding system and showed that a 1 : 1 compound, $KMnBr_3$, may exist. A definite X-ray diffraction pattern could be obtained for the 1 : 1 mole ratio of KBr : $MnBr_2$, but as this pattern did not resemble that for $KMnCl_3$ the compound could not be positively identified.

(c) The system $CsCl/MnCl_2$

This system has been studied by both P. Andersen[15], and Markov and Chernov[16], and the compounds $CsMnCl_3$, Cs_3MnCl_5 and Cs_2MnCl_4 shown to have congruent melting points. Ijdo[17] has managed to prepare α-Cs_2MnCl_4 by fusion, and shows that this pink compound has the K_2NiF_4 structure. Attempts to prepare this compound by fusion always yielded the green compound β-Cs_2MnCl_4 which has been reported by Andersen to have the Cs_2CoCl_4 structure and is therefore tetrahedral. The β-modification could be converted to α-Cs_2MnCl_4 by heating it at 200°C for several days when its colour was observed to change gradually from green to an orange-pink. The α-compound was identified using the X-ray diffraction data of Ijdo[17]. Ijdo could not prepare $CsMnCl_3$ by fusion.

(v) <u>Preparation of caesium complexes from solution</u>

A relatively simple method of preparing both α-Cs_2MnCl_4 and $CsMnCl_3$ is to dehydrate the dihydrates of these compounds at 105°C. The preparation of the dihydrates and their subsequent dehydration at 105°C is described by Saunders[18].

Another method of preparing $CsMnCl_3$ is to mix hot methanolic solutions, one containing caesium chloride and the other hydrated manganese chloride. Immediate precipitation takes place and a very finely divided pink compound results. This compound was shown to be $CsMnCl_3$ by analysis. No definite proportions of the reactants are necessary as the compound $CsMnCl_3$ appears to be the only one formed by this reaction.

(vi) Miscellaneous preparations

The nickel chloro complexes $CsNiCl_3$ and $(CH_3)_4N.NiCl_3$ were prepared by simply mixing ethanolic solutions using stoichiometric proportions of the reactants. The compounds were identified by analysis. The anhydrous manganese halides were all prepared from tetrahydrates and purified by vacuum sublimation.

(vii) Spectra

(a) Reflectance spectra.

Reflectance spectra for all compounds were taken over the range 3200 to 6500 Å using a Unicam S.P.500 U.V.-visible spectrophotometer with a diffuse reflectance attachment. For very hygroscopic or deliquescent samples the sample holder was slightly modified so that a protective stream of dry nitrogen could be passed around the sample whilst the spectrum was being taken. Finely ground samples of each compound were sandwiched between a 1 mm thick silica disc and a microscope cover slide. Even though the glass diffusing screen in the reflectance attachment was replaced with a silica diffusing screen, spectra could not be obtained below 3200 Å.

(b) Single crystal spectra.

Single crystal spectra were obtained photographically for $(CH_3NH_3)_2MnCl_4$, $(CH_3)_4NMnCl_3$, $((C_2H_5)_4N)_2MnBr_4$ and $((C_2H_5)_4N)_2MnI_4$ in an attempt to observe the ^4F transitions which could not be obtained by reflectance methods.

The crystals were mounted over a pin hole in a brass plate and silica lenses used to focus light from a Zenon lamp onto the crystal and then onto the slit of a Hilger quartz spectrometer. The spectra were recorded over the region 2500 to 5000 Å using Kodak B4 plates and calibrated with an iron arc. A microphotometer was used to scan the plates in such a way that the calibration curve could be superimposed on the crystal spectrum. The observed band positions were found to correspond with those obtained from reflectance spectra and no bands due to 4F transitions in the region 2500 to 3200 Å were detected. As the observed band positions were found to agree very well with those obtained by reflectance (differing only by 50 to 100 cm^{-1} at the maximum), they are not listed as errors of this magnitude are well within the limits of the calculated band positions.

(c) Fluorescence spectra.

As all the alkylammonium complexes exhibited a very intense fluorescence under ultraviolet light, fluorescence spectra were obtained for the different anionic complexes, by mounting KCl discs containing the compound in a Beckman DK2 Fluorescence attachment.

(viii) X-ray Diffraction patterns

Powder diffraction patterns were obtained using CuK_{α} radiation. The finely ground sample in petroleum jelly or a nujol mull was spread onto a glass plate and mounted in a Philips PW 1051 Diffractometer. With very hygroscopic compounds, sample preparation was carried out in a dry box using nujol mulls or samples in an aluminium sample holder covered with Mylar film. A few diffraction patterns were obtained photographically using a Philips 57.3 mm Debye-Scherrer camera. Due to fluorescence of the manganese an aluminium foil filter had to be placed on the film to enable the diffraction pattern to be seen above the background. The high background (up to 30% depending on sample preparation) could be reduced considerably with the Diffractometer by switching in the pulse height analyser and employing a nickel exit filter.

Table 2

Metal and Halide Analyses of Complexes

Complex	% Manganese		% Halide	
	Obtained	Calculated	Obtained	Calculated
$(CH_3NH_3)_2MnCl_4$	20.9	21.00	54.3	54.40
$((CH_3)_2NH_2)_2MnCl_4$	18.8	19.01	49.0	49.10
$(CH_3)_2NH_2MnCl_3$	26.4	26.49	51.0	51.29
$(CH_3)_3NHMnCl_3$	24.6	24.80	48.2	48.10
$((CH_3)_4N)_2MnCl_4$	23.0	23.30	45.0	45.10
$(CH_3)_4NMnCl_3$	15.8	15.90	41.1	41.10
$((C_2H_5)_4N)_2MnCl_4$	12.0	12.00	30.9	31.00
$CsMnCl_3$	18.5	18.67	36.4	36.26
Cs_2MnCl_4	11.8	11.88	30.5	30.66
$(CH_3)_4NNiCl_3$	24.4	24.53	44.3	44.47
$(CH_3NH_3)_2MnBr_4$	12.7	12.58	72.4	72.86
$CH_3NH_3MnBr_3$	16.8	16.87	73.6	73.60
$((CH_3)_2NH_2)_2MnBr_4$	11.8	11.82	68.3	68.48
$(CH_3)_2NH_2MnBr_3$	16.5	16.76	70.0	70.35
$(CH_3)_3NH\ MnBr_3$	15.5	15.49	67.7	67.76
$((CH_3)_4N)_2MnBr_4$	10.5	10.51	61.1	61.14
$(CH_3)_4N\ MnBr_3$	15.0	14.92	65.1	65.01
$((C_2H_5)_4N)_2MnBr_4$	8.6	8.66	50.2	50.37
$((C_2H_5)_4N)_2MnI_4$	6.5	6.67	61.6	61.73

2. Spectra of Manganese (II) Complexes.

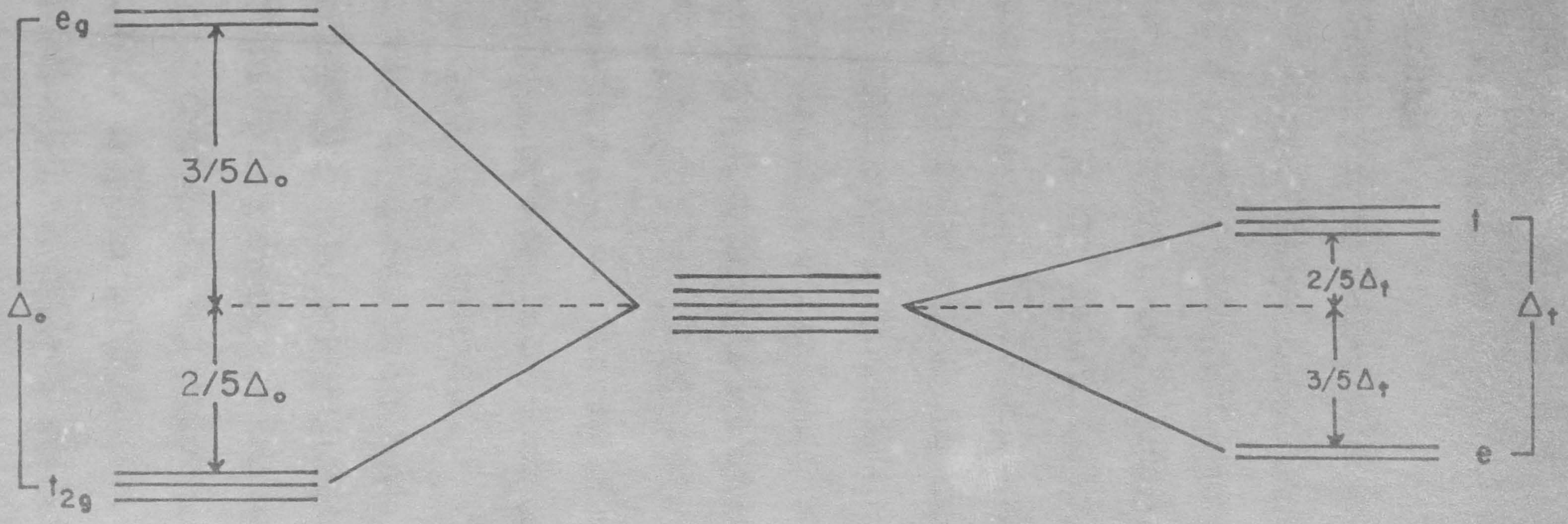
(i) Crystal Field Theory.

The basic idea of crystal field theory, as developed by Bethe[19], van Vleck[20] and others[21-23], is a purely electrostatic concept and does not allow for ionic interaction or partial covalent character in the metal-ligand bond. The central, positively charged, metal ion is considered to be surrounded by negative ions or dipoles oriented with the negative end towards the metal. These groups are termed ligands and those adjacent to the metal ion give rise to the ligand field. The negative field due to these ligands removes the degeneracy of the five d-orbitals of the metal ion. When six ligands are placed at the corners of a regular octahedron any electrons in the d_{z^2} and $d_{x^2-y^2}$ orbitals are closer to the ligands than those in the remaining d_{xy}, d_{xz} and d_{yz} orbitals and thus are increased in energy relative to these latter levels. The higher doubly degenerate e_g set and the lower triply degenerate t_{2g} set are separated by an energy difference Δ, termed the ligand field parameter.

By a similar line of reasoning it can be shown that a tetrahedral distribution of ligands will invert the energies of the e_g and t_{2g} sets giving t_2 and e sets respectively. This splitting of the d-orbitals is represented schematically in Fig. (1). The tetrahedral field has been shown to be $4/9\ \Delta$ if the metal-ligand distance is the same and if the metal and ligand are identical for an octahedral and a tetrahedral distribution of the ligands.

For a particular metal the ligands may be arranged in order of increasing Δ to give the spectrochemical series. The series for the common ligands[24] is:

Schematic diagram showing how degenerate d orbitals are split in octahedral and tetrahedral crystal fields.



Octahedral field

Tetrahedral field

Fig. 1.

$$I^- < Br^- < Cl^- < F^- < OH^- < (C_2O_4)^{2-} < H_2O < NCS^- < py \sim NH_3 < en < NO_2^- \ll CN^-.$$

Until the advent of crystal field theory very little work had been carried out on the absorption spectra of transition metal compounds. The crystal field theory as originated by Bethe and van Vleck was used initially to explain the magnetochemistry of the first row transition elements. Following this work several authors (Abragham and Pryce[25], Ilse and Hartman[26], Schlafer[27], Jorgensen[6,78], and others) started the theoretical investigation of absorption, but not until the work of Tanabe and Sugano[29], and Orgel[30-33] could any quantitative predictions be made. These authors produced two different schemes to describe the effect of crystal fields on d^n systems. These may be conveniently classified as the strong-field scheme due to Tanabe and Sugano and the weak-field scheme of Orgel.

(a) Strong Field.

In the scheme of Tanabe and Sugano the electrons are placed in the e_g and t_{2g} orbitals and their interaction determined. The crystal field is considered to be stronger than the electron-electron repulsions and no information is obtained from the free ion term values. Instead the Racah parameters B and C, parameters of electrostatic interaction, are evaluated independently. In the intermediate field limit this scheme corresponds to that of Orgel.

(b) Weak Field.

In this scheme the free ion terms arising from the ground state are subjected to a crystal field which removes the degeneracy of each term, and gives rise to several excited levels. These levels are not considered to interact in the crystal field which is small compared with the separation of the levels. The crystal field may be considered as a small perturbation which does not alter the original electronic state of the free metal ion. The energies of the excited levels are calculated using first order perturbation theory to describe the effect of the crystal field on each of the atomic terms.

(ii) The Effect of Crystal Field Splitting on Manganese (II)

The manganese (II) ion has five 3d electrons in its outer shell and if the crystal field is weak the electrons obey Hund's rule of maximum multiplicity. The electrons each occupy one orbital and all spins are parallel. This electron configuration is termed the high-spin state of manganese (II). The low-spin state where maximum spin pairing takes place occurs only for the strongest ligands and compounds with this electron configuration have not been considered in this work.

The ground state of manganese (II) with maximum spin multiplicity is denoted by ^6S or to use the symmetry designation $^6A_1(^6S)$. On absorption of energy this ground state gives rise to the quartet states ^4G, ^4D, ^4P, ^4F together with many doublet states. The only possible alteration of the ground state electron distribution $t_{2g}^3e_g^2$ with all spins parallel results in the pairing of two or four spins (but not pairing of electrons as in low spin complexes) thus giving rise to quartet or doublet states respectively. As the doublet states in this case are doubly spin-forbidden it is not expected that transitions to these states will be observed because the quartet transitions have been found to be extremely weak ($e_{max} \sim 0.02$)[27,28].

The quartet terms for the free ion together with the experimental values for these terms are given as combinations of the Racah parameters[34] B and C in Fig.(2). Further splitting of the quartet states by the crystal field removes the degeneracy in these states to give energy levels which

Figure 2

Quartet levels of the free gaseous Mn^{2+} ion

State	Energy in terms of Racah Parameters	Emission[a] Spectrum(cm^{-1})	Calculated[b] energy levels	Least Squares[c] fit of Energy levels
^6S	0	0.0	0.0	0.0
^4G	10B + 5C	26,800	26,800	25,880
^4P	7B + 7C	29,200	32,000	29,590
^4D	17B + 5C	32,300	32,300	32,520
^4F	22B + 7C	43,600	43,800	43,810

a Moore, Ref.49.

b Heidt et al. Ref.36.

c Stout, Ref.37.

are no more than three-fold spacially degenerate. Octahedral and tetrahedral crystal fields give identical energy level diagrams for d^5 systems. The positions of these energy levels are depicted by the energy level diagram (or Orgel diagram) in Fig. (3). This diagram obtained by Orgel has all energy levels referred to a ground state of zero energy.

From the energy matrices of Tanabe and Sugano, Fig. (4), it can be seen that the two ^4E levels are independent of the ligand field parameter Δ and, by solution of the matrix equations for these levels, that the $^4E_g(^4G)$ and $^4A_{1g}(^4G)$ levels are accidentally degenerate. These factors are used in the identification of the observed transitions in manganese (II) spectra[33].

(iii) Identification of observed transitions in Mn(II) spectra

The observed spectrum of the aquated manganous ion[28] Fig. (5) shows the presence of six absorption bands below 30,000 cm^{-1}. The calculated energy level diagram Fig. (3) enables these bands to be readily identified although the Δ independent levels are found to be lower than the corresponding states in the free ion. Orgel[33] assigned the spectrum of the aquated manganous ion by identifying the doublet at 25,000 cm^{-1} as the transitions $^6A_1(^6S) \longrightarrow {}^4E(^4G)$ and $^6A_1(^6S) \longrightarrow {}^4A(^4G)$ since the energies of these transitions are calculated to be degenerate and the ^4G state for the free ion occurs at 26,800 cm^{-1}. Similarly the other sharp band at 29,700 cm^{-1} was identified as the $^6S \longrightarrow {}^4E_g(^4D)$ transition. These two ^4E_g levels appear as relatively sharp bands in the spectrum whereas the remaining levels are much broader. If the energy level diagram is examined it can be seen that the slopes of the energy levels are related to the band widths in the observed spectrum of the aquated manganous ion. Orgel[33] explains this in

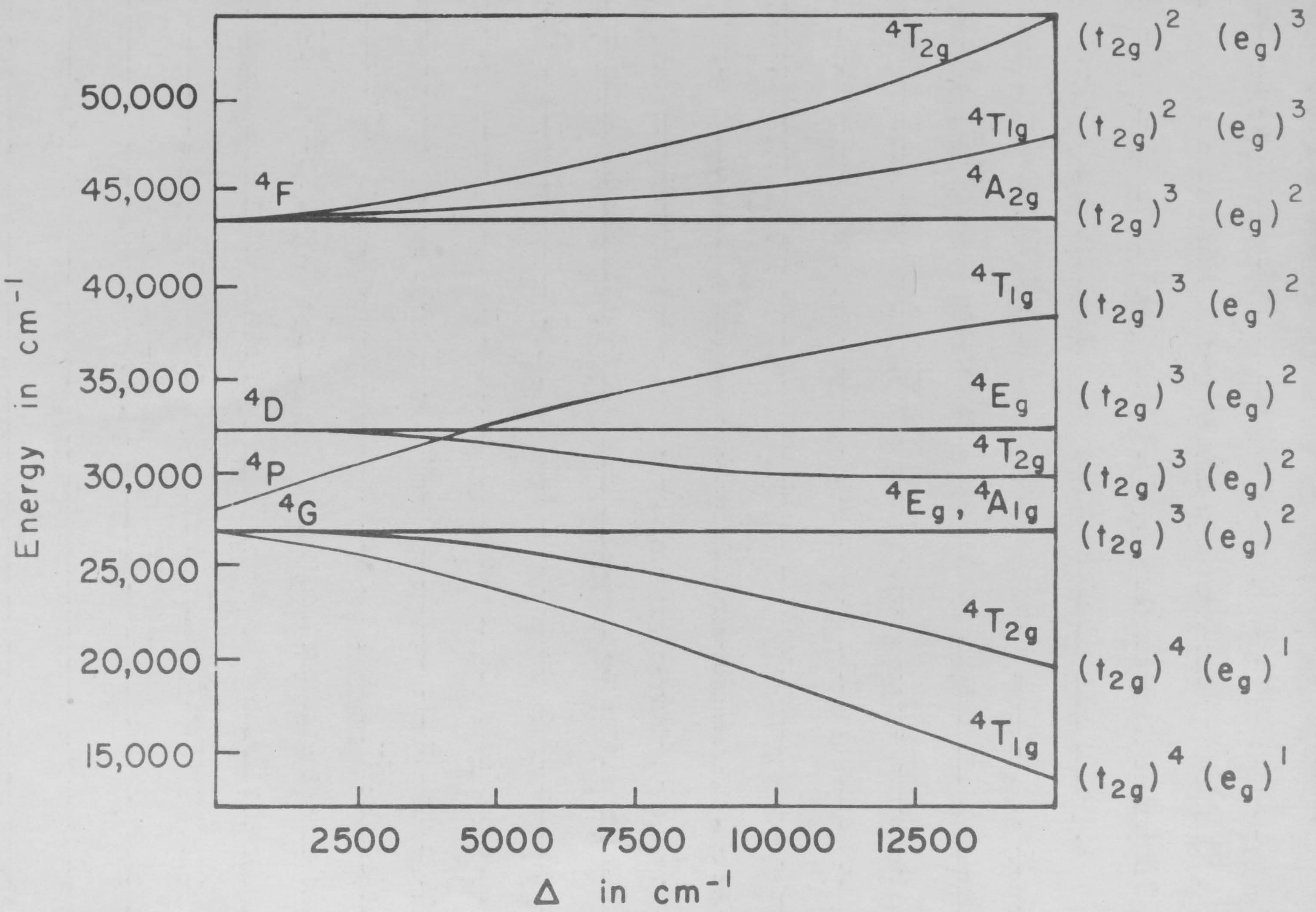


Fig. 3 Energy level diagram for a d^5 ion (Mn^{2+}). The ground state ^6S is taken to have zero energy (After Orgel[60]).

Energy matrices for quartet terms arising from d^5

$$^4E(^4D,\,^4G)\quad \begin{vmatrix} 13B+5C & -2\sqrt{3}B \\ -2\sqrt{3}B & 14B+5C \end{vmatrix}$$

$$^4T_1(^4F,\,^4P,\,^4G)\begin{pmatrix} 10B+6C-\Delta & -3\sqrt{2}B & C \\ -3\sqrt{2}B & 19B+7C & -3\sqrt{2}B \\ C & -3\sqrt{2}B & 10B+6C+\Delta \end{pmatrix}$$

$$^4T_2(^4F,\,^4D,\,^4G)\begin{pmatrix} 18B+6C-\Delta & \sqrt{6}B & 4B+C \\ \sqrt{6}B & 13B+5C & -\sqrt{6}B \\ 4B+C & -\sqrt{6}B & 18B+6C-\Delta \end{pmatrix}$$

$$^4A_1(^4G) = 10B+5C$$

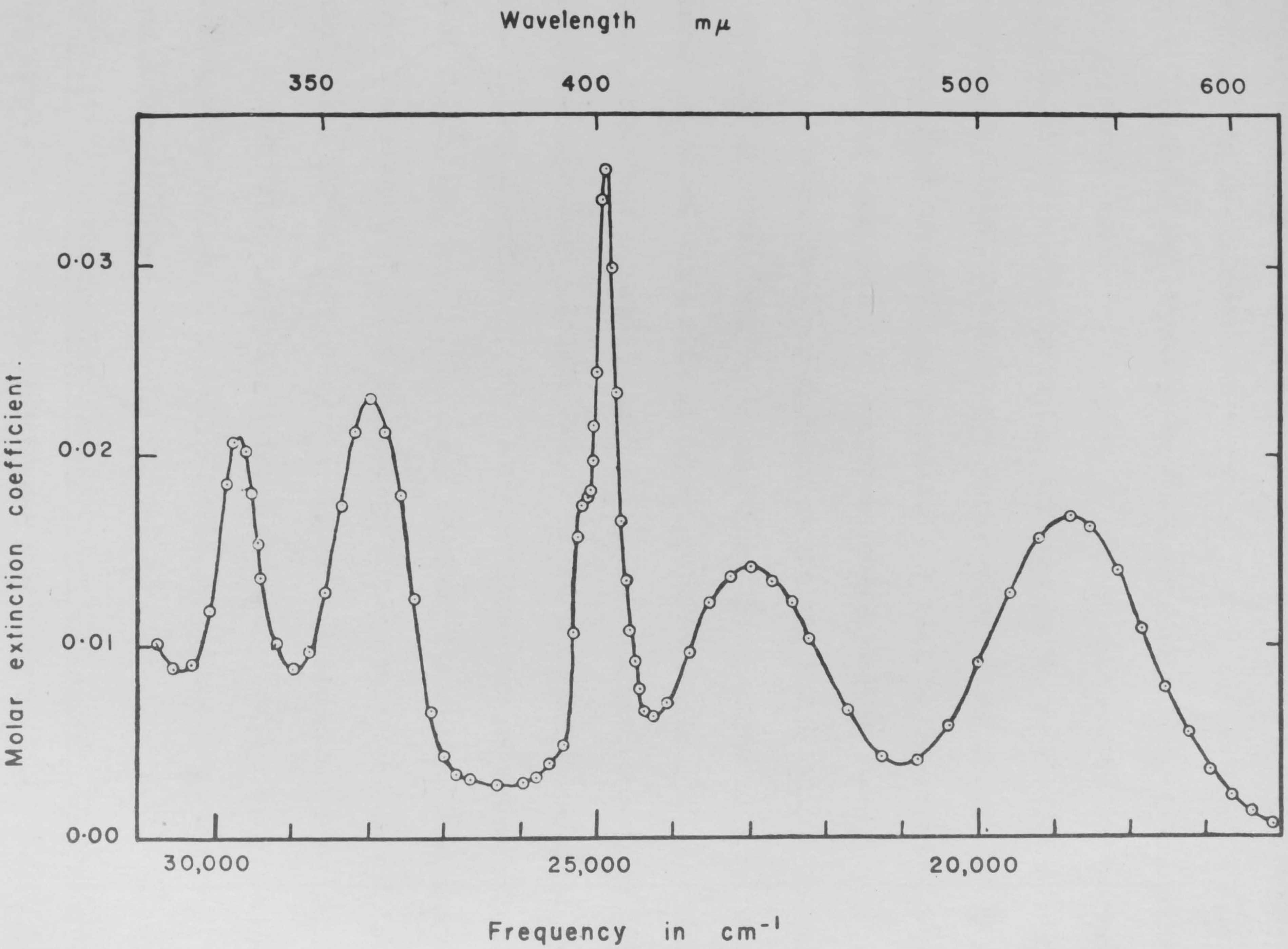
$$^4A_2(^4F) = 22B+7C$$

$$^6A_1(^6S) = 0$$

Fig. 4.

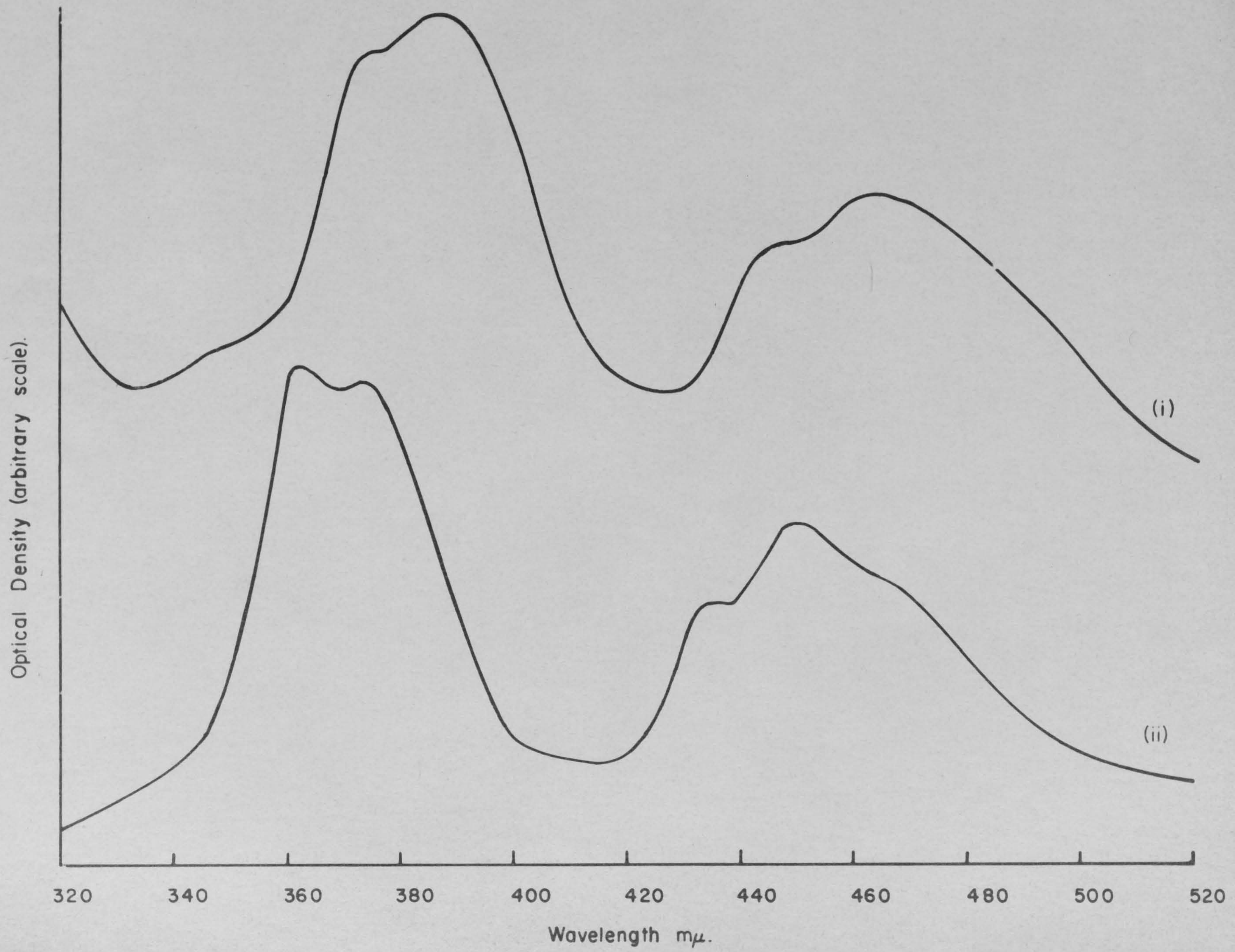
the following way. The transitions which appear as broad bands involve a change in the electron distribution and hence the metal ligand equilibrium distances are altered. By the Frank-Condon principle, equilibrium is not regained during the very rapid optical excitation and the excited states will be vibrationally excited. A change in the metal-ligand bond will affect the ligand field to give an averaged value of the ligand field parameter. Thus transitions dependent on Δ will be temperature broadened and transitions independent of Δ will appear as narrow bands.

With a tetrahedral arrangement of ligands the splitting is much less than with an octahedral arrangement and the spectrum appears as two broad groups of three bands with similar band widths (Fig.6). The assignment of these bands can be made by comparison with the spectrum of an octahedral complex. The only possible change in the observed tetrahedral band positions is the inversion of the order predicted for an octahedral spectrum of the $^4T_1(^4P)$ and the $^4E(^4D)$ energy levels. The energy level diagram for the free ion shows that these two energy levels cross over when Δ is approximately 4000 cm^{-1}. This gives two alternate choices for the position of the $^4E(^4D)$ level when assigning a tetrahedral spectrum. Using the strong field scheme which relies on the calculation of the Racah parameters B and C from two observed ^4E transitions, the correct assignment can be readily checked by solution of the secular equations for the $^4T_1$ and $^4T_2$ levels for the two sets of B and C. The calculated positions of these levels are then compared with the observed positions.



Absorption spectrum of the aquated manganous ion. (After Jorgensen[28])

Fig. 5.



Reflectance spectra of (i) $((C_2H_5)_4N)_2MnI_4$, (ii) $((C_2H_5)_4N)_2MnBr_4$.

Fig. 6.

(iv) Calculations of band positions using crystal field theory

The most commonly used model in crystal field theory considers the effect of an electric field due to the ligands (as point charges) on the electrons of the central metal ion in an isolated octahedral or tetrahedral complex ion. The complex ion is taken to be regular and the other ions and molecules in the crystal (other than the ligands) are assumed to have very little effect on the crystalline field. In reality the true physical picture is far removed from this simple concept. Very few complexes contain perfectly octahedral or tetrahedral units, but in most cases departure from symmetry is difficult to detect. Many factors such as non-equivalence of ligands and physical distortion lead to deviations from regular symmetry even when the ligands are all the same. The influence of the long range forces from other ions in the lattice is also important and the true symmetry is that of the lattice site and not of the ideal complex ion. As the symmetry of the complex is decreased more parameters are required to enable the electronic states of the complex ion to be fully specified but there are usually too few data to determine these parameters. The use of solution spectra overcomes the problem of determining the site symmetry of the complex ion, but in the present work dissociation of the complexes in solution necessitated the use of reflectance or single crystal spectra to obtain the required data. No allowances for solid state effects have been applied to these spectra which have been treated as solution spectra.

The calculations of ligand field parameters for high-spin manganese (II) complexes by methods used in the literature and in the present work using the common assumption of a symmetrical complex are described in the following sections.

The ligand field parameter Δ and the parameters B and C have been calculated by several different methods for the spectra of tetrahedral and octahedral manganese (II) complexes. These methods are based in either the weak-field treatment of Orgel or the strong-field treatment of Tanabe and Sugano but there are numerous variations in detail. On examination of the available values of the crystal field parameters (Table 3), it can be seen that these vary from author to author for the same spectrum. This is because different methods of calculation have been used by the various authors. Thus comparison of the crystal field parameters obtained from different spectra is not reliable unless the same method of calculation is employed for each spectrum.

Table 3

Literature Values for B, C and Δ

	B	C	Δ	Reference
Mn^{2+} (gaseous)	786	3790	0	Heidt et al[36]
	950	3280	0	Stout[37]
Mn^{2+} (aqueous)	-	-	7900	Orgel[33]
	-	-	7800	Jorgensen[34]
	860	3850	12300	Tanabe and Sugano[29]
	671	3710	8480	Heidt et al[36]
$MnCl_2$	758	3082	7630	Low and Rosengarten[41]
	-	-	8300	Stout[39]
MnF_2	801	3158	7520	Low and Rosengarten[41]
	-	-	7800	Stout[37]
$MnBr_2$	-	-	9400	Stout[39]
$(MnCl_4)^{2-}$	558	3524	3600	Cotton et al[35]
	-	-	2650	Buffagni and Dunn[9]
	-	-	3300	Furlani and Furlani[7]
$(MnBr_4)^{2-}$	536	3530	3100	Cotton et al[35]

(a) Weak-field method.

When Orgel assigned the spectrum of the aquated manganous ion he noticed that the Δ independent levels, which correspond to the free ion states with zero ligand field, were considerably lower than the experimental values for the free ion. This lowering in energy was considered to be transmitted to all other excited levels which were then lowered by the same amount as the corresponding ^4E_g levels. An energy level diagram was then constructed for the aquated ion from the energy level diagram for the free ion in the above manner. The ligand field parameter Δ was obtained by fitting a vertical line through the energy level diagram so that its points of intersection with the energy levels agree as closely as possible with the energies of the observed transitions. Using this method no estimate of B and C could be made.

The main problem with this method is that it is an empirical treatment and the positions of the energy levels are no longer described by the energy matrices. This method has been applied to tetrahedral complexes by Furlani and Furlani[7], and by Dunn[9]. However the values of Δ were found to be 3300 cm^{-1} and 2600 cm^{-1} respectively. This discrepancy arises from two reasons; firstly, the method of calculation is very approximate and secondly, there are small differences in the experimental band positions obtained by the two authors. The band assignments, in both cases, list the $^4T_1(^4P)$ level below the $^4E(^4D)$ level as the corresponding free ion terms are in this order. Later work shows these levels to be inverted[35].

(b) Strong-field methods.

This method of calculation originated by Tanabe and Sugano[29] was used by these authors to obtain a value of 12,300 cm^{-1} of Δ from the aquated manganous spectrum. This value has been shown to be anomalous by later workers who found Δ to be between 7000 and 8000 cm^{-1}. A high value was obtained because the energy level diagram was constructed using the Racah parameters for the free ion and only two transitions in the spectrum of the aquated manganous ion were observed. The first successful application of the strong-field scheme was carried out by Heidt, Koster and Johnson[36] for the aquated manganous spectrum. The spectrum was assigned by identification of the ^4E_g transitions followed by taking the predicted order of transitions from an energy level diagram. Racah parameters were obtained for the complexed ion by solving simultaneously the two equations for the ^4E_g energy levels:

$$^4Eg(^4G) = 10B + 5C$$

$$^4E_g(^4D) = 17B + 5C$$

To obtain the values of the $^4T_{1g}$ and $^4T_{2g}$ levels these Racah parameters were substituted in the appropriate energy matrices (Fig. 4) which were solved for a wide range of Δ values. The energy levels obtained in this way agreed very well with the energies of the observed transitions except for the $^4T_{1g}(^4P)$ level which was about 10% higher than the experimental value. In the spectrum of the free ion the calculated position of the ^4P transition was also about 10% high and by allowing this discrepancy to be carried into the crystal field treatment the position of the $^4T_{1g}(^4P)$ level may be accounted for.

Lawson[40] using the same method of calculation as described above, accounted for all of the observed quartet transitions in the spectrum of $MnCl_22H_2O$

below 45,000 cm^{-1}, to within 2%, with the exception of the $^6S \longrightarrow {}^4T_{1g}(^4P)$ transition. This transition was calculated about 10% higher than the experimental value as was found for the same transition by Heidt et al for the spectrum of the aquated manganous ion.

Cotton et al[35] used this same method to calculate band positions in the spectra of the tetrahedral anions $MnBr_4^=$ and $MnCl_4^=$ but, due to insufficient data, could not make any predictions about the spectrum of the $MnI_4^=$ anion. Partial Gaussian analysis of the spectrum of the tetrabromomanganate ion showed that the bands due to the two ^4E levels were narrower than the other observed bands in agreement with the aquated manganous spectrum. To account for the position of the $^4T_1(^4P)$ level the Racah parameters obtained from the two ^4E levels were used to calculate the position of the $^4T_1(^4P)$ level for zero ligand field. This value was then lowered arbitrarily by 7.5% and a value of C chosen to fit the relative positions of the ^4G, ^4P and ^4F terms using the original value for B. These Racah parameters were then used to calculate the relative positions of the $^4T_1$ and $^4T_2$ levels over a range of Δ values. The absolute placement of all the levels was then obtained using the original value for C together with B in the secular equations.

To account for the observed change in term values in going from the spectrum of the free manganous ion to the spectrum of a complexed ion, Stout[37] used the covalency parameter ϵ (ϵ was originally introduced by Koide and Pryce[38]) to reduce the amplitude of the e_g orbitals by $(1-\epsilon)^{1/2}$. The Tanabe and Sugano energy matrices were modified to incorporate this parameter thus giving a new set of energy matrices. These matrices were further altered so that the Racah parameters from the spectrum of the free ion could be used in their evaluation. Stout used the set of Racah parameters which were found to give a statistical best fit between calculated and experimental energy levels in the spectrum of the free ion. It was found that this statistical prodedure removed the discrepancy between the calculated and the experimental ^4P energy levels. For small values of the parameter ϵ as is the case with MnF_2, the calculated positions of all energy levels, including the $^4T_{1g}(^4P)$ level, were shown to be in very good agreement with the experimental values. In this method of calculation second order terms in ϵ have been completely neglected by Stout on the ground that there is no "theoretical justification" for regarding ϵ as more than a first order correction. However this assumption has been shown not to hold for all values of ϵ since the contribution of ϵ^2 to the calculated energies of the E_g levels increases noticeably as ϵ increases. To take an extreme case, the spectra of tetrahedral compounds show discrepancies in the order of 8% between calculated and observed values of the ^4E levels if second order terms are included in the energy equations.

Stout uses this method of calculation to fit the observed spectra of $MnCl_2$ and $MnBr_2$[39]. The covalency parameter behaves as expected and increases from MnF_2 to $MnBr_2$, but the ligand field parameter changes contrary to the predictions of the spectrochemical series.

A more complicated method of calculation including spin-orbit coupling has been described by Low and Rosengarten[41]. The energy matrices used by these authors contain five variable parameters, B, C and Δ the crystal field parameters, the spin-orbit coupling parameter ζ and α the Trees' correction.

This method is purely a mathematical treatment and will not be considered further as it has been found that it is possible to account for all the observed transitions in the spectra of manganese (II) complexes within the simple framework of the Tanabe-Sugano theory.

(v) Least squares method of calculation

Owing to the many approximations involved in crystal field theory it is understandable that some of the predicted energy levels do not agree with the experimentally obtained levels. The 10% discrepancy in the calculated $^4T_{1g}(^4P)$ level has been a noticeable feature of all the calculations previously described which are based on the strong field scheme and methods of calculation have been arbitrarily modified to account for this discrepancy. All the methods of calculation depend upon the experimental values of the two Δ independent ^4E_g levels. These two levels are treated as exact quantities and used to obtain approximate values for all other energy levels.

Stout[37] has shown that the value of the ^4P state in the spectrum of the free manganous ion can be accounted for if the Racah parameters B and C are adjusted to give a best fit of the whole spectrum. As the crystal field theory only gives an approximate description of d^n systems, exact agreement between the calculated and observed spectral band positions in these systems should not be expected. The ^4E_g levels in the spectrum of a complexed manganese (II) ion, even though they appear in the spectrum as narrow absorption bands which are independent of the ligand field parameter, need not necessarily be predicted exactly by the theory. If instead the values of these energy levels are allowed to differ from the experimentally observed values, a best fit of all energy levels can be obtained by varying the parameters B, C and Δ.

This means that the energy matrices do not have to be modified and the energy levels are specified by these parameters which form a unique set for each complex ion. In the least squares method of calculation the Racah parameters B and C for the spectrum of the complex ion were first obtained (as in the method of Heidt et al[36]) by using the values of the ^4E energy levels deduced from the spectrum. A mathematical relationship between the two ^4E levels and the ^4P level for zero ligand field was obtained by combining the energy equations for these three levels, to give the following identity:

$$^4E(^4G) + {}^4E(^4D) = 17B + 10/7(^4P) \quad \ldots\ldots\ldots \qquad \text{(i)}$$

This identity was obtained by assuming the energy levels have a fixed relationship to one another given by two Racah parameters B and C. If now the ^4P level is allowed to vary while the two ^4E levels remain constant, the Racah parameter B in this equation must depend on the value selected for the ^4P level. For most of the methods of calculation based on the strong field scheme which have been previously described, the calculated value of the ^4P level was found to be higher by about 10% than the experimental value derived from the spectrum. Therefore, the value of the ^4P level for $\Delta = 0$, obtained by solution of the following equation,

$$7B + 7C = {}^4P \quad \ldots\ldots\ldots \qquad \text{(ii)}$$

where B and C are evaluated from the experimental ^4E levels, was lowered arbitrarily by 5%. This new value of the ^4P level, together with the experimental values for the two ^4E levels, was substituted into equation (i) which was then solved for B. A corresponding value of the parameter C could be obtained, using this new value of B together with the lowered value of the ^4P level, by solution of equation (ii).

Substitution of this new set of Racah parameters into the equations for the ^4E levels :

$$\left.\begin{array}{l} 10B + 5C = {}^4G = {}^4E(^4G) \\ 17B + 5C = {}^4D = {}^4E(^4D) \end{array}\right\} \ldots\ldots\ldots\ldots \qquad \text{(iii)}$$

gave values for these levels which both differed by about 2% from the values obtained experimentally.

The ^4P level was lowered arbitrarily over a range of 4% to 6%, at 0.5% intervals, as this range was found to enable a reasonable estimate of the ^4E levels to be made. Sets of Racah parameters were obtained for each value of the ^4P level. The energy equations for the $^4T_1$ and $^4T_2$ levels were solved as simple cubic equations for all sets of Racah parameters for a wide range of values of the ligand field parameter Δ. When a value of the ligand field parameter had been estimated, to within 100 cm^{-1}, for the spectrum, the corresponding value of the ^4P level for zero ligand field was varied over a range of ± 0.5% at 0.1% intervals and further sets of Racah parameters were calculated. The energy equations for the $^4T_1$ and $^4T_2$ levels were then solved using these Racah parameters for a small range of Δ values about the first estimate of $\Delta \pm 100$ cm^{-1} at intervals of 50 cm^{-1}.

These calculations were carried out using the I.B.M. 1620 computer at the Australian National University. The sets of calculated band positions were then fitted to the observed band positions by a least squares procedure to obtain the best set of B, C and Δ. Using this method the positions of the spectral bands for several manganese (II) complexes were successfully predicted to within 2% of the observed frequencies.

(vi) Absorption spectra used in crystal field calculations

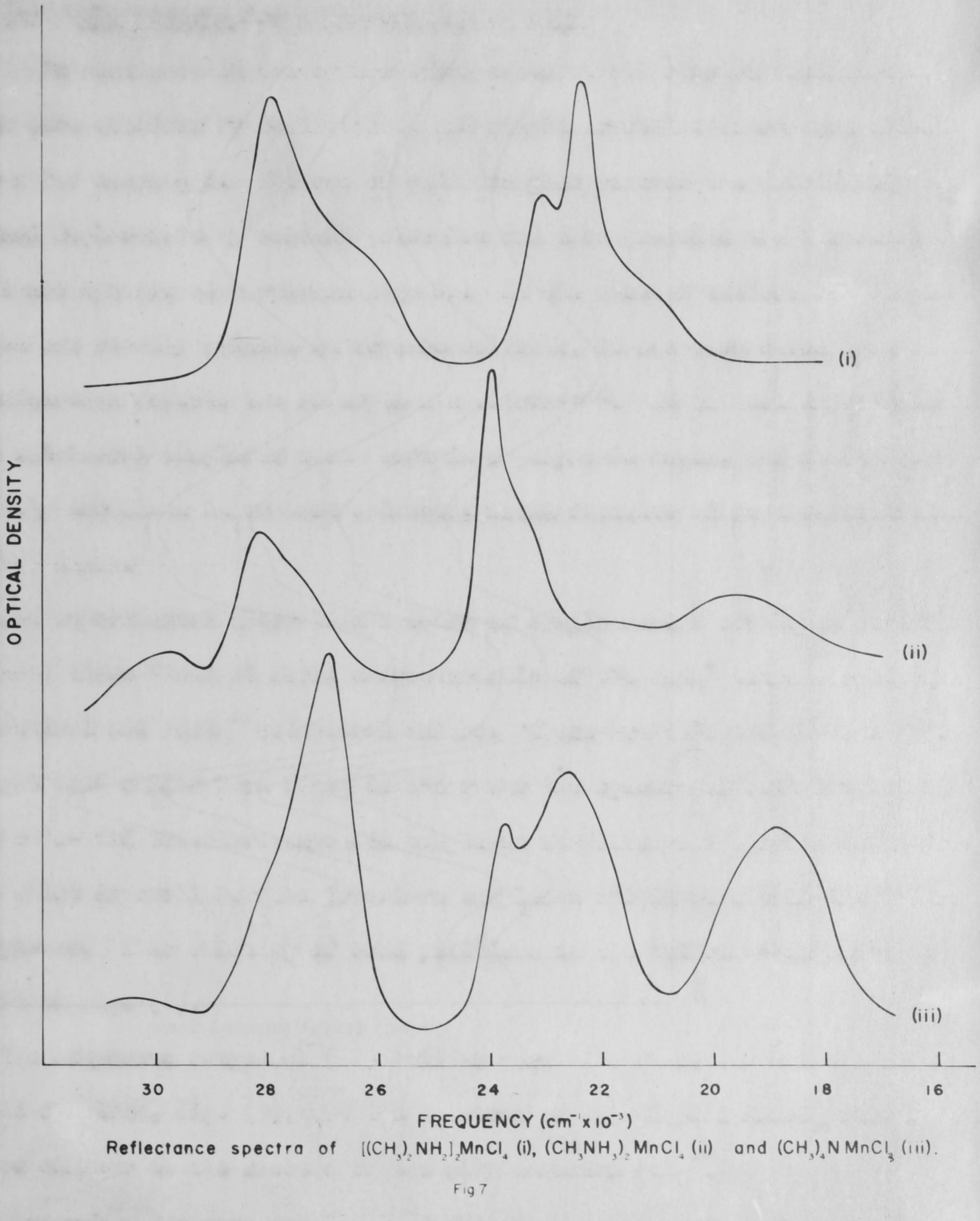
(a) Characteristics of absorption spectra

As mentioned in the experimental section, all spectra used in this work were obtained by reflectance, and single crystal spectra were obtained for a few compounds. The use of solid samples removes the possibility of ligand replacement by solvent molecules and thus prevents the formation of an ionic species with unknown ligands. In the case of tetrahedral complexes which are readily soluble in organic solvents, it has been shown that solvent coordination affects the absorption spectrum[7,42]. It is most improbable that the octahedral complexes which contain a polymeric anion, and which are relatively insoluble in organic solvents, would dissolve without dissociation of the anion.

The experimental absorption spectra of alkylammonium complexes were found to have three distinct forms characteristic of the $MnX_4^=$ tetrahedral, MnX_3^- octahedral and $MnCl_4^=$ octahedral anions. These are depicted in Fig. (7). Slight band shifts were found to occur for the spectra of both octahedral tribromo- and trichloromanganate complexes for different alkylammonium groups. The shift is small for the trichloro complexes and increases in the tribromo complexes. This shifting of band positions in the tribromo-manganate is shown in Fig. (8).

The anhydrous manganese (II) halides were also found to have a characteristic spectrum, Fig. (9), but the spectrum of K_4MnCl_6 and $KMnCl_3$ were found to be similar to the spectra of the alkylammonium MnX_3^-.

Although a few observed $^6S \longrightarrow {}^4F$ transitions have been reported[35,36,37,40],



Reflectance spectra of $[(CH_3)_2NH_2]_2MnCl_4$ (i), $(CH_3NH_3)_2MnCl_4$ (ii) and $(CH_3)_4NMnCl_3$ (iii).

Fig 7

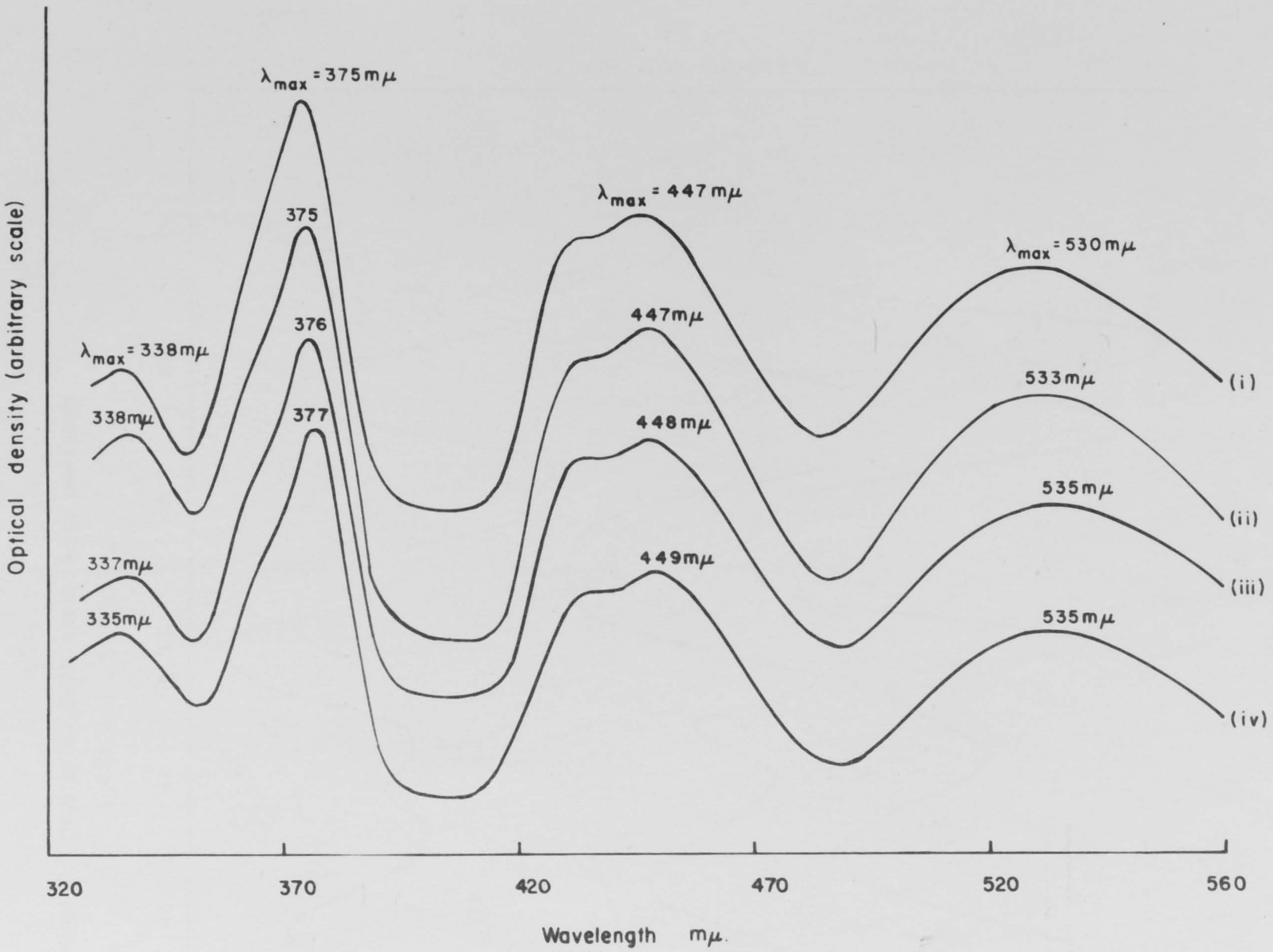


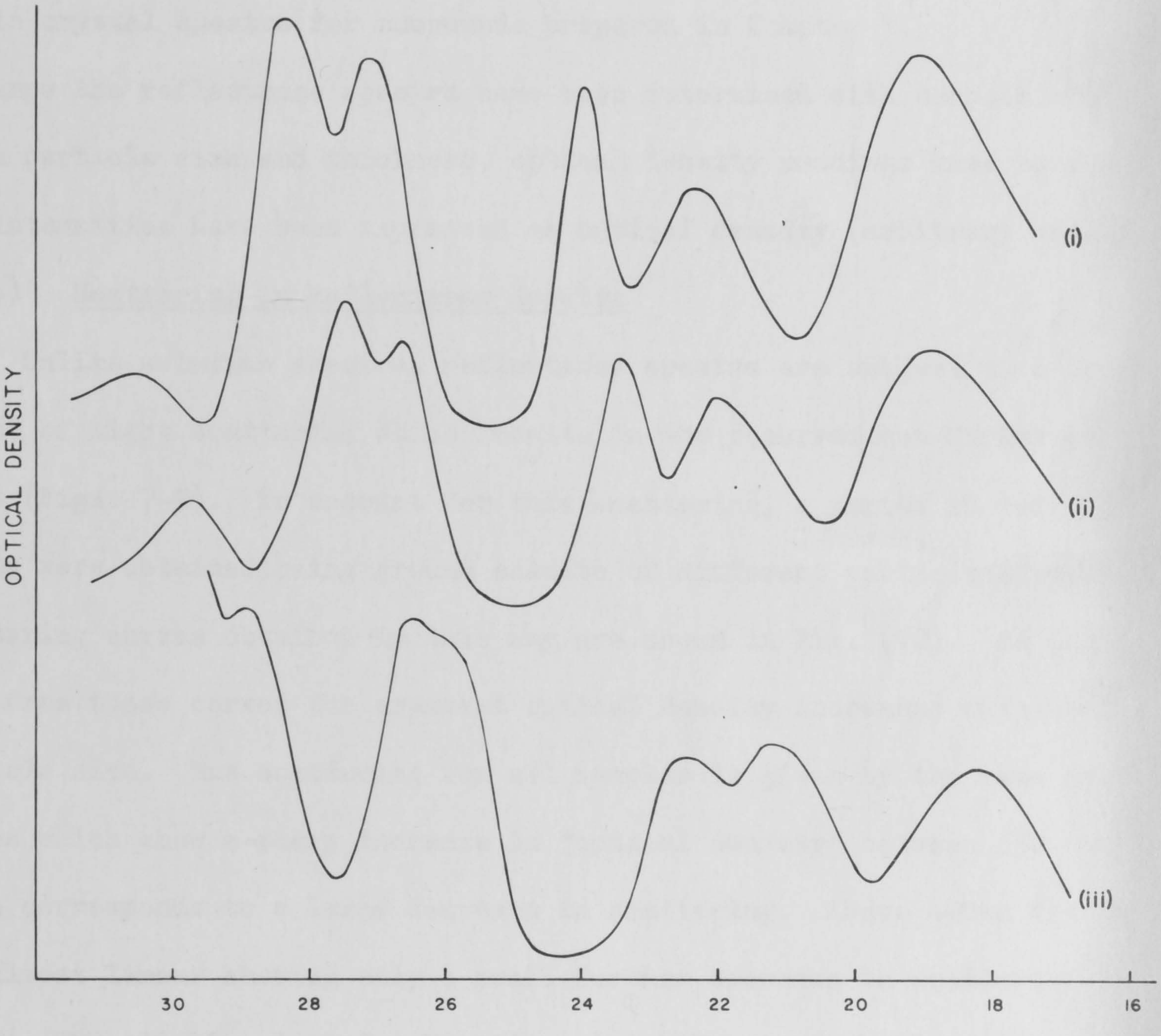
Fig. 8. Observed reflectance spectra of the alkylammonium tribromomanganates showing small band displacements.

(i) $(CH_3)_4NMnBr_3$

(ii) $(CH_3)_3NHMnBr_3$

(iii) $(CH_3)_2NH_2MnBr_3$

(iv) $(CH_3NH_3MnBr_3$



Observed reflectance spectra of $MnCl_2$ (i), $MnBr_2$ (ii), and MnI_2 (iii).

Fig. 9.

the energies of these transitions have not been included in the least squares method of calculation used in this work. Energy values for these transitions could not be obtained either from reflectance spectra or from single crystal spectra for compounds prepared in Chapter 1.

Since the reflectance spectra have been determined with samples of unknown particle size and thickness, optical density readings have no meaning and intensities have been expressed as optical density (arbitrary scale).

(b) Scattering in Reflectance Spectra

Unlike solution spectra, reflectance spectra are subject to a large amount of light scattering which results in the observed non-horizontal base lines (Figs. 7-9). To account for this scattering, a series of reflectance curves were obtained using ground calcite of different particle sizes. The scattering curves obtained in this way are shown in Fig. (10). As can be seen from these curves the apparent optical density increases with increasing particle size. The scattering for all samples is given by the same shaped curves which show a sharp increase in "optical density" between 330 and 400mμ which corresponds to a large decrease in scattering. Above 400mμ the curves are almost linear showing only a small further decrease in scattering to 520mμ. The slight point of inflection at ~410mμ is probably instrumental as a U.V. filter is removed during the recording of the spectrum at 400mμ.

A background correction of the shape shown by these scattering curves was subtracted from the observed reflectance spectrum. This correction resulted in slight changes in the original band positions for all spectra, but the most noticeable change was in the resolution of the band arising from the ^6S to $^4T_{1g}(^4P)$ transition in the spectra of the octahedral complexes. In

Scattering Curves for Calcite.

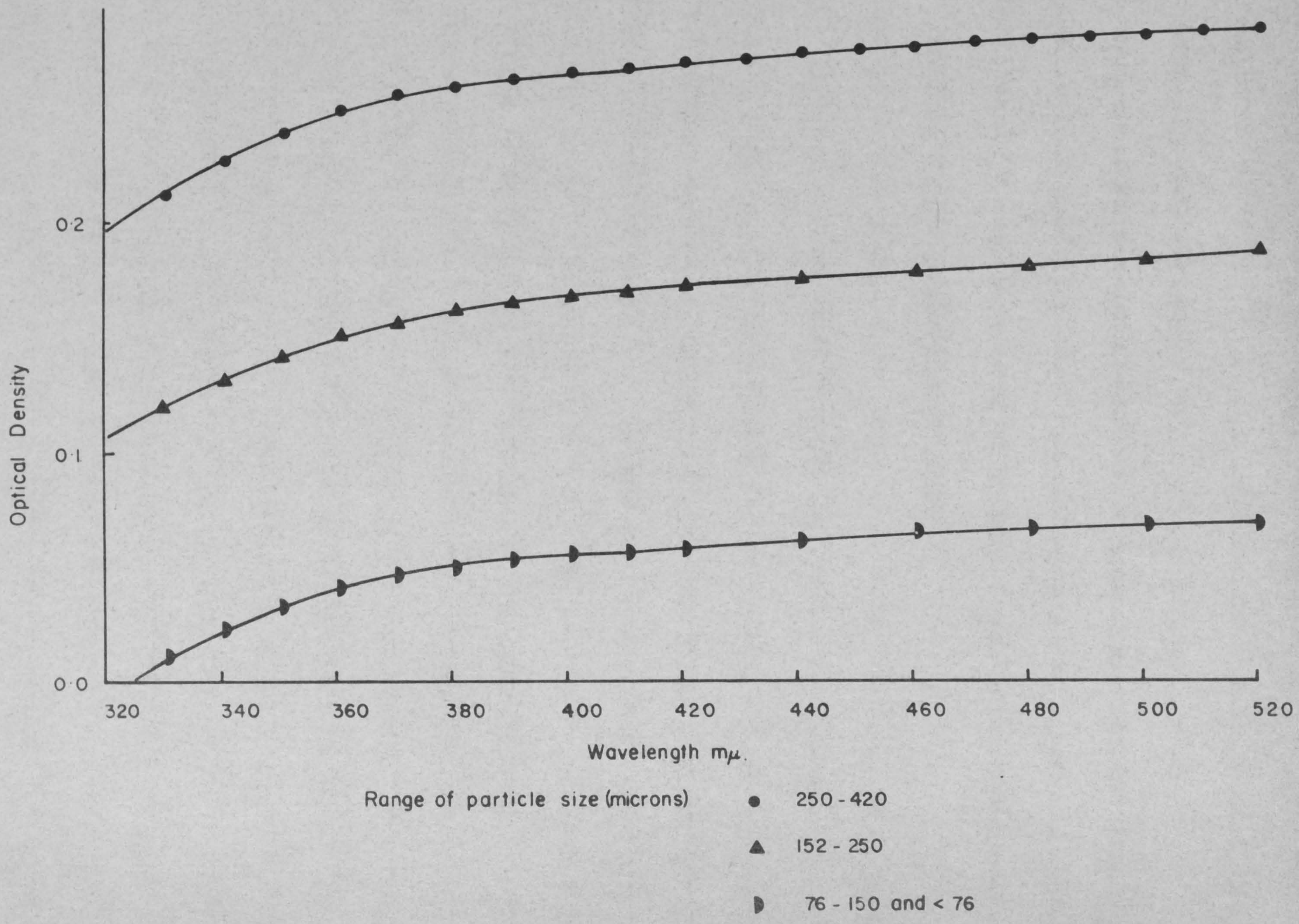


Fig.10.

the spectra of most of the octahedral complexes this transition appeared as a very flat band in the region 330 to 350mμ. Correction of these spectra for scattering resolved the flat bands into definite maxima.

(c) Gaussian error curves

Partial Gaussian analysis was used to obtain band centres for bands which appeared as shoulders on an otherwise symmetrical band. Jorgensen[43] showed that bands in simple spectra of metals of the first transition series could be approximated by Gaussian error curves of the form:

$$\varepsilon = \varepsilon_0 2^{-\left(\frac{\nu-\nu_0}{\delta}\right)^2}$$

where ε_0 is the extinction coefficient in the maximum, and δ is the half-width. To use Gaussian error curves the observed reflectance spectra have to be first corrected for scattering. The isolated bands in the spectra of the octahedral complexes were readily fitted by Gaussian curves as no trouble was encountered in determining half-widths or maximum extinction coefficients. However where two bands overlapped so that one band appeared as a shoulder, some difficulty was experienced in choosing both halfwidths and maximum extinction coefficients. It was found that an indefinite number of combinations of two different bands of varying halfwidths, maximum extinction coefficients and positions could be used to fit the observed band. To prevent this situation from occurring the centre of one of the Gaussian error curves must be kept near to the centre of the most definite observed band. It can be seen that this procedure is only an approximate one and too much reliance must not be placed on the results.

(d) Assignment of the spectrum of the tetraiodomanganate ion

As the spectral data obtained in this work for the tetrahedral chloro- and bromomanganates were essentially the same as those obtained by Cotton et al[35], the band positions quoted by these authors were used in the least squares method of calculation. Contrary to their findings the spectrum of the tetraiodomanganate ion could be used to obtain a value for the ligand field parameter. The assignment of this spectrum differed from that reported by Cotton et al as the presence of a third band in the region of strong absorption at about 26,000 cm^{-1} was indicated by both reflectance and single crystal spectra. The very weak band at about 28,000 cm^{-1} assigned by them to the ${}^6A_1 \longrightarrow {}^4T_1({}^4P)$ transition is possibly due to a transition to a doublet excited state or to a decomposition product of the very unstable tetraiodomanganate ion.

(vii) Fluorescence spectra.

The presence of divalent manganese as an impurity in phosphors and glasses is known to activate fluorescence emission in the green and red regions of the visible spectrum[44-46]. Linwood and Weyl[45] proposed that green fluorescence was due to tetrahedrally coordinated manganese (II) and red fluorescence to octahedrally coordinated manganese (II). Jorgensen[6] was the first person to observe the fluorescence of bis-tetraethylammonium tetrabromomanganate (II), and noticed that the intensity of fluorescence emission with 366mμ excitation was greater than that of uranyl salts. He did not discuss the energy levels responsible for the fluorescence. The fluorescence was attributed to the transition ${}^4T_{1g}({}^4G) \longrightarrow {}^6S$ by Orgel[47] who discussed the position of the fluorescence band in terms of ligand field theory. Orgel's theoretical discussion supports the conclusion reached by Linwood and Weyl that green fluorescence is associated with tetrahedrally coordinated manganese (II).

The following argument may be applied to the fluorescence of both octahedrally and tetrahedrally coordinated manganese (II) complexes. During the period between absorption of the exciting quantum and the emission of fluorescent radiation the metal-ligand bond length has time to adjust to the change in electron configuration from $t_{2g}^3e_g^2$ of the ground state to $t_{2g}^4e_g^1$ of the excited state. It has been shown that the metal-ligand bond length increases with the number of e_g electrons[48], and thus the metal-ligand bond in the excited state must be shortened. However, in the case of optical absorption, the metal-ligand bond has insufficient time to adjust during the very rapid optical excitation and retains the ground state equilibrium distance. The ligand field Δ depends on the length of the metal-ligand bond, increasing as the bond length decreases. Thus in the emission of fluorescence the ligand field of the excited molecule is greater than that concerned with the excited state responsible for the absorption band. From an energy level diagram (Fig.3) it can be seen that the emission should therefore occur at a longer wavelength than the corresponding absorption band. Similarly from an energy level diagram it can be seen that the energy of the $^4T_{1g}(^4G)$ level starts to decrease rapidly as Δ increases above 5000 cm^{-1}. An increase of 1000 cm^{-1} in Δ in this region would give a corresponding decrease of about 1500 cm^{-1} in the $^4T_{1g}(^4G)$ level. This applies to octahedral coordination of the central manganese (II) ion where Δ has been found to vary between 5200 to 7600 cm^{-1}. However a similar argument may be used for the case of tetrahedral manganese (II) compounds. For a change of 1000 cm^{-1} in Δ from

2000 to 3000 cm^{-1} on the energy level diagram the $^4T_{1g}(^4G)$ level decreases by only 800 cm^{-1}. Hence the separation between the fluorescence band and the nearest absorption band should be less for tetrahedral than for octahedral complexes. Van Vleck[50] has shown that in electrostatic theory, Δ is proportional to r^5 where r is the internuclear distance between metal and ligand. Hence a small decrease in r will give a correspondingly large change in Δ.

In the present work the separation between the fluorescence band and the nearest absorption band (the Stokes displacement) was less for tetrahedral than for octahedral complexes as predicted, but the Stokes displacement was not found to change in a predictable manner either with a change in Δ or with a change in halide. These findings are contrary to the results obtained by Furlani _et al_[51] as these authors found the Stokes displacement to decrease as Δ decreased. The differences between the two sets of results, for the spectra of tetrahedral halide complexes, are attributed to differences in experimental band positions obtained by the two authors for both absorption spectra and fluorescence spectra. The most noticeable difference is in the position of the fluorescence band obtained for the $MnCl_4^=$ anion. The large difference of 880 cm^{-1} is probably due to the different tertiary ammonium cations used by the two authors. In the present work only alkylammonium cations were used whereas the tetrahedral chloride complex prepared by Furlani _et al_ contained trimethylbenzylammonium as the cation. In the present work it was found that the experimental errors in determining the positions of both absorption and fluorescence bands for the spectra of tetrahedral halide complexes were in the order of ± 200 cm^{-1}. The variation of values for the band positions in the absorption spectra of tetrahedral complexes in the literature[7,9,35] was found to be in the same order of magnitude as the above errors.

As the Stokes displacement is the difference (in cm^{-1}) between the fluorescence band and the lowest absorption band, the maximum error in the value of this displacement should be approximately 400 cm^{-1}. Thus the differences between the values of the Stokes displacements (of 200 cm^{-1}) obtained by Furlani _et al_ for spectra of the tetrahedral halide anions, are meaningless.

The Stokes displacements, obtained in the present work for the spectra of octahedral complexes, could not be compared with the corresponding Stokes displacements obtained by Furlani _et al_ as the spectral data used by the latter authors were obtained for types of octahedral complexes different from those described in this thesis. The fluorescence spectra together with the Stokes displacements and ligand field parameters obtained in the present work are listed in table 4.

Only the alkylammonium salts of the manganese halide complexes were found to fluoresce at room temperature and then only in the solid state. For the solid samples excitation with the same frequency light as the lowest absorption level gave fluorescence indicating that the ${}^4T_{1g}({}^4G)$ level is responsible for the fluorescence emission. Solutions of the tetrahedral alkylammonium salts of the manganese halide complexes in nitromethane, dimethylformamide or alcohol did not fluoresce.

Table 4

Fluorescence Spectra of Manganese (II) Complexes

Complex Anion	Fluorescence Emission(cm^{-1})	^6S $^4T_{1g}(^4G)$ Absorption(cm^{-1})	Stokes Displacement Φ(cm^{-1})	Ligand Field Parameter Δ (cm^{-1})
$MnCl_4^=$	19,280	21,200[a]	1920	3100
$MnBr_4^=$	19,360	21,350[a]	1990	2700
$MnI_4^=$	18,960	20,480	1520	2700
$MnCl_4^=$ (oct.)	17,100	19,560	2460	5500
$MnCl_3^-$	16,760	18,840	2080	5900
$MnBr_3^-$	16,950	18,760	1810	5600

[a] Data from Ref. 35.

(viii) Discussion of Results obtained using the least squares method of calculation

Using the least squares method of calculation, ligand field parameters and Racah parameters were obtained, not only for the spectra of complexes containing octahedral anionic species $MnCl_6^{4-}$, $MnCl_4^{=}$, $MnCl_3^{-}$, $MnBr_3^{-}$ and the tetrahedral species $MnX_4^{=}$ (where X is the Cl, Br or I), but also for spectra of the anhydrous halides MnX_2 (where X is F, Cl, Br or I) and the aquated manganous ion. The frequency values of the calculated energy levels together with the experimental frequency values for the spectra of these complex species are listed in Table 5. All the spectral data, except where otherwise specified, were obtained in the present work. It can be seen from this table that, with few exceptions, the calculated values of all the listed energy levels deviate by no more than 2% from the values obtained from the spectra. The root mean square error, which is the averaged error between calculated and experimental energy levels for the six lowest transitions, is listed for each complex together with the Racah parameters B and C and the ligand field parameter Δ in Table 6.

The values of the ligand field parameters shown in Table 6 are generally lower than those in the literature (Table 3). The values of the ligand field parameters, described in the literature, depend on the method of calculation, thus exact numerical values of these parameters have no real sifnificance. For a particular metal, as the ligands are changed or as the stereochemistry of the complex is altered, the value of the ligand field parameter changes. To enable a valid comparison of the resulting values for this parameter to be made, the same method of calculation must be used to evaluate all the parameters. Relative values of the ligand field para-

Table 5

Experimental and Calculated band positions (cm^{-1}) for spectra of high spin Mn(II) complexes

Transitions	$(MnCl_4)^=$		$(MnBr_4)^=$		$(MnI_4)^=$	
$^6A_1(^6S)$	(a) Expt.	Calcd.	(a) Expt.	Calcd.	Expt.	Calcd.
$^4T_1(^4G)$	21,200	21,360	21,350	21,480	20,480	20,820
$^4T_2(^4G)$	22,400	22,490	22,180	22,410	21,560	21,750
$^4E, ^4A_1(^4G)$	23,200	22,785	23,000	22,635	22,400	21,995
$^4T_2(^4D)$	26,300	27,000	25,900	26,780	25,800	26,070
$^4E(^4D)$	27,100	27,503	26,700	27,178	25,900	26,468
$^4T_1(^4P)$	27,900	28,480	27,700	28,160	26,800	27,380

Transitions	$(CH_3NH_3)_2MnCl_4$		$MnCl_3^-$		$MnBr_3^-$	
$^6A_1(^6S)$	Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.
$^4T_{1g}(^4G)$	19,560	19,460	18,840	19,410	18,760	18,940
$^4T_{2g}(^4G)$	22,100	22,130	22,560	22,070	22,240	21,640
$^4E_g,A_{1g}(^4G)$	23,980 23,440	23,075	23,660	23,220	23,000	22,650
$^4T_{2g}(^4D)$	27,600	27,360	26,900	26,930	26,480	26,720
$^4E_g(^4D)$	28,120	28,570	27,790	28,230	27,550	27,970
$^4T_{1g}(^4P)$	29,980	29,990	30,400	30,780	29,640	29,630

	K_4MnCl_6		$KMnCl_3$		(b) MnI_2	
$^4T_{1g}(^4G)$	19,460	20,050	19,700	20,220	19,440	19,720
$^4T_{2g}(^4G)$	22,900	22,550	22,960	22,700	23,500	23,260
$^4E_g,A_{1g}(^4G)$	23,980	23,520	24,100	23,612	25,200 25,500	24,980
$^4T_{1g}(^4P)$	27,040	27,470	27,240	27,710	28,120 28,370	29,020
$^4E_g(^4P)$	28,200	28,658	28,380	28,869	30,230	30,750
$^4T_{1g}(^4P)$	30,060	30,810	30,100	30,770	33,060	33,650

Table 5 (cont.)

Transitions	$MnCl_2$		$MnBr_2$		MnI_2	
$^6A_1$ (^6S)	Expt.	Calcd.	Expt.	Calcd.	Expt.	Calcd.
$^4T_{1g}$(^4G)	18,904	19,180	18,797	19,240	18,180	18,447
$^4T_{2g}$(^4G)	22,222	22,130	21,930	21,887	21,100	20,955
^4E_g, $^4A_{1g}$(^4G)	23,866	23,370	23,419	23,000	22,420	22,000
$^4T_{2g}$(^4D)	27,027	27,340	26,738	26,768	25,900	25,613
^4E_g(^4D)	28,249	28,750	27,627	28,047	26,450	26,823
$^4T_{1g}$(^4P)	30,485	30,920	29,762	30,400	28,900	29,048

Transitions	Cs_2MnCl_4		$Mn(H_2O)_6^{2+}$	
$^6A_1$ (^6S)	Expt.	Calcd.	(c)Expt.	Calcd.
$^4T_{1g}$(^4G)	19,920	19,911	18,870	19,066
$^4T_{2g}$(^4G)	22,640	22,412	23,120	22,708
^4E_g, $^4A_{1g}$(^4G)	23,660 24,180	23,240	24,960	24,495
$^4T_{2g}$(^4D)	27,380	27,639	27,980	28,513
^4E_g(^4D)	28,340	28,756	29,750	30,291
$^4T_{1g}$(^4P)	29,900	29,968	32,960	33,087

(a) Data from Cotton *et al*[35].

(b) Data from Stout *et al*[37].

(c) Data from Heidt *et al*[36].

Table 6

Ligand Field Parameters

(cm^{-1})

Compound	B	C	Δ	RMS error cm^{-1}
$Mn(H_2O)_6^{2+}$	828	3243	7600	410
MnF_2	825	3346	7500	471
$MnCl_2$	770	3132	6200	380
$MnBr_2$	721	3158	5800	390
MnI_2	689	3022	5500	294
$(CH_3NH_3)_2MnCl_4$	785	3045	5500	390
Cs_2MnCl_4	788	3072	5200	280
$KMnCl_3$	751	3220	5400	498
K_4MnCl_6	734	3237	5500	525
$(CH_3)_4NMnCl_3$	716	3213	5900	428
$(CH_3)_4NMnBr_3$	700	3260	5600	355
$((CH_3)_4N)_2MnCl_4$	674	3209	3100	445
$((CH_3)_4N)_2MnBr_4$	649	3229	2700	478
$((CH_3)_4N)_2MnI_4$	639	3121	2700	408

meters are important however, as these values give some insight into the nature of the metal-ligand bonding and the metal-ligand stereochemistry.

It can be seen, from the values of the ligand field parameters obtained by the least squares method of calculation in Table 6, that the expected behaviour of Δ in terms of the spectrochemical series is observed for both octahedral and tetrahedral arrangements of ligands about the central manganese ion. Thus Δ increases in the order:

$$I^- \leqslant Br^- < Cl^- < F^- \leqslant H_2O$$

As predicted from crystal field theory, the ligand field parameter is greater for an octahedral arrangement of ligands than for a tetrahedral arrangement of the same ligands. The ratio of the tetrahedral ligand field parameter Δ_t to the octahedral parameter Δ_o (0.56) is greater than the theoretical ratio of 4/9 (0.44) if the values of the ligand field parameters used are 3100 cm^{-1} for the spectrum of tetrahedral $MnCl_4^=$ and 5500 cm^{-1} for the spectrum of K_4MnCl_6. This choice of Δ values was made since K_4MnCl_6[12] is the only octahedral halide complex containing discrete octahedral $MnCl_6^{4-}$ units in the crystal lattice. All the tetrahedral halide complexes contain discrete tetrahedral $MnX_4^=$ units in the crystal structure. The high value of the ratio can be explained from bond length considerations. In K_4MnCl_6 the manganese-chlorine bond length was found to be 2.51 Å.[12] Although no data are available on manganese-chlorine bond lengths in tetrahedral chloro complexes, an estimate of the bond lengths can be made by reference to known bond lengths in tetrahedral chloro complexes of other first row transition metals. For the tetrahedral complex anions $NiCl_4^=$ and $ZnCl_4^=$ in the compounds $(Ph_3MeAs)_2NiCl_4$[61] and $((CH_3)_4N)_2ZnCl_4$,[62] the metal-chlorine bond lengths are

2.27Å and 2.245Å respectively. The ionic radius of divalent manganese (0.80Å)[63] is greater than either that of zinc (0.74Å)[63] or nickel (0.69Å)[63] and thus the manganese-chloride bond length should be approximately 2.30Å. As mentioned previously Δ is inversely proportional to r^5 where r is the internuclear separation. If, for purposes of calculation, the tetrahedral bond length is increased from 2.3Å to 2.51Å using the preceding proportionality, the effective value of Δ_t is decreased and thus the ratio Δ_t/Δ_o is decreased to 0.48 which is to be compared with the theoretical value of 0.44.

From the range of values for Δ obtained for octahedral chloride complexes, Δ must depend on the cation or on the structural arrangement of the $MnCl_6$ octahedra. For the series of $MnBr_3^-$ complexes with alkylammonium cations, the positions of the spectral bands were changed by only a few hundred cm^{-1} as the cation was changed from methylammonium to tetramethylammonium (Fig.8). The error in the calculated band positions, for a value of Δ giving a least squares fit of the observed band positions, lies between 200 to 400 cm^{-1} (Fig.5). Thus a change, of this order of magnitude, in the band positions will not effect the value of Δ very greatly.

From preliminary X-ray work and from known structural data, several different arrangements of $MnCl_6$ octahedra are known to occur in chloride complexes of manganese. The change in arrangement of $MnCl_6$ octahedra appears to be largely responsible for the wide range of Δ values obtained for the corresponding chloride complexes (Table 6).

The values of ligand field parameters obtained for anhydrous manganese chloride and anhydrous manganese bromide are higher than those obtained for complex anions containing the corresponding halides. The anhydrous fluoride and iodide also seem to have relatively high values for the ligand field parameter (Δ for MnI_2 is the same as that obtained for K_4MnCl_6). The high values of the ligand field parameters may be explained in the following way. All the anhydrous manganese halides have structures which contain distorted MnX_6 octahedra. Thus manganese fluoride has the rutile structure[52] in which two chains of octahedra formed by sharing opposite edges of the octahedra are linked to form bands which lie along the crystallographic c-axis of the structure. The structures of the three remaining anhydrous halides[53,54,55] have the same network of octahedra as found in the CdI_2 and $CdCl_2$ structures. In the latter structures the octahedral CdX_6 coordination groups are linked by sharing edges to form infinite layers. Similarly the MnX_6 octahedra share edges to form an infinite two dimensional array of octahedra. Manganese bromide and manganese iodide have the cadmium iodide structure whereas manganese chloride has the cadmium chloride structure. The cadmium chloride structure only differs from the cadmium iodide structure in the geometrical disposition of successive layers of octahedra. In all four anhydrous halide structures the MnX_6 octahedra are distorted and the octahedra are closely packed. Both of these two factors probably contribute to the somewhat higher values of the ligand field parameters obtained for these compounds compared to the values for the anionic complexes. Another factor which may also be considered is that the anhydrous halides contain electrically neutral networks of MnX_6 octahedra whereas in the manganese halide complexes the networks of MnX_6 octahedra have an overall negative charge. This change from a system containing neutral MnX_6 octahedra to one containing MnX_6 octahedra as anions will certainly affect the ligand field around the central metal ion and hence alter the value of the ligand field parameter.

Of the ligand field parameters obtained for octahedral chloro complexes the value of 5900 cm^{-1} for $(CH_3)_4NMnCl_3$ is high compared with the other values of 5500, 5400 and 5200 cm^{-1} obtained for the remaining complexes. From preliminary X-ray analysis it is possible that this compound has the $CsNiCl_3$ structure[56]. In this structure the $NiCl_6$ octahedra share opposite faces to form chains. Although no bond length data are available for compounds containing discrete $NiCl_6$ octahedra it is possible that changes in the Mn-Cl bond lengths may occur when MnX_6 octahedra are linked in the same way. The known Mn-Cl bond lengths for an octahedral arrangement of chloride ions about the central manganese ion have been obtained for complexes containing discrete octahedra (K_4MnCl_6[12] has an Mn-Cl bond length of 2.51Å) or for complexes in which the octahedra are linked by the corners ($KMnCl_3$[13] has an Mn-Cl bond length of 2.50Å). There are no reported bond length data for manganese chloro complexes in which the octahedra are linked by sharing opposite faces. From Van Vleck's relationship between Δ and the internuclear separation, a change in bond length of less than 2% will produce a change in Δ of approximately 400 cm^{-1}. A complete structure analysis would be required to show whether there are any changes in bond length of this magnitude when $MnCl_6$ octahedra share opposite faces.

One other ligand field parameter worthy of comment is that obtained for Cs_2MnCl_4 with the value of 5200 cm^{-1}. This value is 300 cm^{-1} lower than that obtained for $(CH_3NH_3)_2MnCl_4$ (5500 cm^{-1}). The two complexes have basically the same structures in which the arranegment of $MnCl_6$ octahedra for both complexes is the same as the arrangement of NiF_6 octahedra in K_2NiF_4[57]

and thus the change in the ligand field parameter must be caused by the different cations.

The ligand field parameters for the spectra of tetrahedral bromide and iodide complexes were found to have identical values of 2700 cm^{-1}. The corresponding tetrahedral halogeno complexes of nickel (II) were found by Goodgame et al[58] to have identical ligand field parameters and this is in agreement with the ligand field parameters obtained for the tetrahedral iodo- and bromomanganates in the present work. However, the actual values of these ligand field parameters obtained in this work could be separated by as much as 200 cm^{-1}, because a least squares fit of either spectrum could not be obtained for intervals of Δ less than 100 cm^{-1}.

The parameter B depends not only on the coordinated ligand, but also on the stereochemistry of the complex ion and values of this parameter shown in table 6 vary accordingly. The values obtained for the parameter C show no definite trend with changes in the ligand or with changes in the parameters Δ and B. From table 6 it can also be seen that the parameter B decreases through the series of ligands $H_2O \gg F^- > Cl^- > Br^- > I^-$ and also that B is smaller for tetrahedral complexes than for octahedral complexes with the same ligand. This change in B is parallel to an increase in the covalent nature of the metal-ligand bond. It is well known that in metal-fluoride compounds the metal-fluoride bonding is mainly ionic and this ionic character is gradually decreased and the covalent character of the bonding increased as the fluoride ions are successively replaced by chloride, bromide or iodide ions. The proportion of ionic character to covalent character in a metal-ligand bond can be correlated with the metal-ligand bond length. Thus where the interionic separation is decreased by a change from octahedral to tetrahedral coordination of the ligand there is more mixing of the metal and ligand orbitals and the covalent character of the metal-ligand bond is increased.

The interelectronic repulsion forces between the _d_ electrons are decreased by complex ion formation and this decrease is accompanied by an increasing covalent character of the metal-ligand bond. As the Racah parameter B is a parameter of interelectronic repulsion, some correlation between the value of this parameter and the extent to which covalent bonding takes place, should be possible. In the crystal field theory which considers the metal and ligands to be ionic, no allowance is made for interaction between metal and ligand electrons. However there is a decrease of the Racah parameter B from the free ion value to that obtained by crystal field calculations for a complex ion. This shows that complexing the free metal ion alters the electrostatic repulsion forces between _d_ electrons in the ion. The behaviour of the parameter B with respect to the value of this parameter for the free ion which is considered to be purely ionic, gives some measure of the decrease of ionic character of the metal-ligand bond.

Schaffer and Jorgensen[59] have arranged the common ligands in order of increasing $(1-\beta)$ to give the nephelauxetic (cloud expanding) series. For the common ligands this series is:

$F^- < H_2O < \text{urea} < NH_3 < (C_2O_4)^= < \text{en} < \underline{N}CS^- < Cl^- \sim CN^- < Br^- < I^-$

The parameter β is termed the nephelauxetic ratio and is defined by

$\beta = \frac{B_{\text{complex ion}}}{B_{\text{free ion}}}$. It can be seen from this equation that β decreases as $B_{\text{complex ion}}$ decreases and hence (1-β) increases as $B_{\text{complex ion}}$ increases since $B_{\text{free ion}}$ is constant. When the ligands studied in the present work are arranged in order of decreasing B values they correspond to the order of ligands obtained by Schaffer and Jorgensen for the nephelauxetic series.

The following conclusions may be made from the results of crystal field calculations applied to the spectra of 'high spin' manganese (II) complexes in the present work.

(1) To enable a valid comparison of values for ligand field parameters to be made, all values must be obtained by the same method of calculation. The predicted ratios of Δ values for $(MCl_4)^{2-}$ and $(M(H_2O)_6)^{2+}$ complex ions obtained by Cotton et al[35] using Δ values given in the literature, are meaningless.

(2) The value of the ligand field parameter was found to vary with the ligand as predicted from the spectrochemical series.

(3) For the same ligand the value of the ligand field parameter for a tetrahedral complex ion is less than that for an octahedral complex ion as predicted from crystal field theory. The ratio $\frac{\Delta_t}{\Delta_o}$ is greater than the theoretically predicted ratio of 4/9, but the increase may be accounted for if bond lengths are considered.

(4) The variation of Δ values for a particular ligand with the same metal-ligand coordination is due to differing structural arrangements of the metal-ligand coordination groups.

(5) The values obtained for the Racah parameter B are in agreement with expected values of B predicted from the nephelauxetic series of ligands

obtained by Schaffer and Jorgensen[59].

(6) Exact numerical values of the parameters B, C and Δ have no real significance in terms of crystal field theory as it is impossible, due to the approximate nature of the theory, to obtain absolute values for these parameters. Only relative values of these parameters have any real meaning.

(7) The band positions in the observed absorption spectra of "high spin" manganese (II) complexes can be readily accounted for in terms of crystal field theory. Using the strong-field approximation of Tanabe and Sugano[29] it is possible to calculate the positions of the six lowest quartet transitions (assuming the $^4E(^4G)$ and $^4A_1(^4G)$ levels are degenerate) to within 2% for all the experimental band positions. Each spectrum can be characterized by an unique set of the three ligand field parameters B, C and Δ.

(8) Within the simple framework of the Tanabe-Sugano theory in which the energy equations are calculated for a cubic crystalline field due to the octahedrally coordinated ligands, the observed splitting of the $^4E(^4G)$ and $^4A_1(^4G)$ levels for several of the spectra of octahedral complexes cannot be explained, except by assuming distortion of the octahedra.

3. X-Ray Powder Data

(i) The structure of methylammonium tetrachloromanganate (II)

All compounds of the type $(R_4N)_2MnX_4$ with the exception of $(CH_3NH_3)_2MnCl_4$ are greenish yellow and contain tetrahedral $MnX_4^{=}$ anions. The latter compound is pale pink and from spectroscopic evidence has been shown to contain octahedrally coordinated manganese (II).

In a study of the chloride complexes formed by fusing anhydrous transition metal chlorides with caesium chloride, Ijdo[17] prepared a pale pink compound α-Cs_2MnCl_4 which had the K_2NiF_4[65] structure. The parameters of the tetragonal unit cell of α-Cs_2MnCl_4 were found by him to be $\underline{a} = 5.14$, $\underline{c} = 19.63$, (space group D_{4h}^{17} - 14/mmm).

All strong reflections in the powder diffraction pattern of $(CH_3NH_3)_2$-$MnCl_4$ could be indexed on the basis of a tetragonal unit cell (table 7) with dimensions $\underline{a} = 5.09$ Å, $\underline{c} = 19.37$ Å and all reflections were found to conform to the same group as K_2NiF_4.

The cell parameters together with the axial ratios c/a are given for K_2NiF_4, α-Cs_2MnCl_4 and $(CH_3NH_3)_2MnCl_4$ in the table below.

	$\underline{a}$ (Å)	$\underline{c}$ (Å)	c/a
K_2NiF_4[65]	4.00	13.06	3.26
α-Cs_2MnCl_4[17]	5.14	16.93	3.29
$(CH_3NH_3)_2MnCl_4$	5.09	19.37	3.80

It can be seen from this table that there is a definite relationship between the cell parameters for α-Cs_2MnCl_4 and $(CH_3NH_3)_2MnCl_4$. The $\underline{a}$ axis in both cases is almost the same, as would be expected if the two structures have the same arrangement of $MnCl_6$ octahedra. The cell edge a is the distance between the centres of two $MnCl_6$ octahedra linked by sharing a corner. The value of c in $(CH_3NH_3)_2MnCl_4$ is greater by about 2 Å than that in α-Cs_2MnCl_4[17]. This can be explained if the methylammonium cations lie along the crystallographic c-axis of the structure. There are a few weak lines in the powder pattern of $(CH_3NH_3)_2MnCl_4$ which could only be accounted for on the basis of a larger tetragonal unit cell with a' = 2a = 7.20 Å. The cell edge c remains the same at 19.37 Å.

The departure from the K_2NiF_4 type structure is probably due to an unsymmetrical disposition of the methylammonium groups along the c-axis, thus lowering the overall symmetry of the structure.

Table 7

X-Ray Powder diffraction data for $(CH_3NH_3)_2MnCl_4$ obtained using CuK_α radiation

$\sin^2\theta$ (Obs)	$\sin^2\theta$ (Calc)	I	hkl
0.0065	0.0064	S^+	002
0.0245	0.0244	S	111
0.0374	0.0372	M	113
0.0461	0.0456	M	200
0.0525	0.0520	W	202
0.0573	0.0570	M	210
0.0714	0.0714	M	213
0.0914	0.0912	S^-	220
0.0976	0.0976	M	222
0.1012	0.1026	M^+	300
0.1159	0.1156	W	311
0.1284	0.1284	VW	313
0.1483	0.1482	W	320
0.1929	0.1938	W	410

Cell parameters.

a = 7.20 Å, c.= 19.27 Å.

(ii) The structures of $(CH_3)_4MnCl_3$ and $(CH_3)_4N\ MnBr_3$

As mentioned in the previous chapter complexes of the general formula $RMnCl_3$ are known from X-ray crystallographic work to have several different structures. The compound $KMnCl_3$ has a slightly distorted cubic perowskite structure[13], $RbMnCl_3$ has the $BaTiO_3$ structure[14] and $CsMnCl_3$[14,15] is reported to have a unique structure. Ijdo[17] showed that nearly all the first row transition metal complexes with the general formula $CsMCl_3$ had the $CsNiCl_3$ structure. Ijdo could not prepare $CsMnCl_3$, but Siefert and Koknat[14] reported that a crystallographic study of this compound has been carried out by Andersen[15] who showed it to have a unique structure. In this structure the smallest repeat unit consists of three $MnCl_6$ octahedra sharing opposite faces. These repeat units are linked together to form staggered chains which lie along the crystallographic c-axis of the structure. It has not been possible to obtain the original report on the structure determination by Andersen[15] as it has only been published in a conference report, (Andersen, P., Nordiske Kemikermode, 1956, 9 , Åhrus.).

In the present work $CsMnCl_3$ was prepared as described in chapter 1 (page 12). The complex was found to be very hygroscopic and on exposure to air rapidly formed the dihydrate. A sample of the dihydrate was placed in a sample holder which could be heated electrically to 150°C. Temperature control was provided by a rheostat and the temperature could be measured using a chromel/alumel thermocouple. The powder pattern of the sample was first recorded at room temperature. Since the dihydrate dehydrates completely, without decomposition, at 105°C[18], the sample was kept at 110°C for a period of three hours. The diffraction pattern changed during this period and when two successive patterns were found to be identical, dehydration of the sample was assumed to be completed. The resultant pattern showed no resemblence to the powder diffraction pattern of $CsNiCl_3$, indicating that the two compounds are probably not isostructural. (It has not been possible to index the powder pattern of $CsMnCl_3$).

The X-ray powder diffraction patterns obtained for $(CH_3)_4NMnCl_3$ and $(CH_3)_4NMnBr_3$ could be indexed on the basis of a hexagonal unit cell, (tables 8 and 9) which immediately excludes the cubic perowskite structure. The remaining three probable structure types, $BaTiO_3$, $CsNiCl_3$ and $CsMnCl_3$, all belong to the hexagonal system and thus any one of these is possible.

The unit cell parameters obtained for the two tetramethylammonium compounds were a = 9.13 Å, c = 6.49 Å for $(CH_3)_4NMnCl_3$ and a = 9.44 Å, c = 6.76Å for $(CH_3)_4NMnBr_3$. The unit cell parameters of $BaTiO_3$[66], a = 5.735 Å, c = 14.05 Å, do not show any relationship to the corresponding cell parameters for the tetramethylammonium compounds. It is therefore unlikely that these compounds have the $BaTiO_3$ type structure.

The cell parameters for $CsNiCl_3$[56] are a = 7.18 Å and c = 5.93 Å (space group D^6_{4n}-$P6_3mmc$), the ratio c/a being 0.82. The corresponding axial ratios are 0.72 for both alkylammonium compounds. This value is lower than that obtained for $CsNiCl_3$, but this is to be expected as the a axis will be expanded by replacement of the Cs^+ ions with tetramethylammonium ions. The c axis is also longer, which may be due to the larger size of the $MnCl_6$ octahedra relative to the $NiCl_6$ octahedra. The Miller indices of the reflections observed for the two tetramethylammonium compounds also conform to the space group $P6_3mmc$.

No cell parameters have been reported for $CsMnCl_3$[14], but as the smallest repeat unit for this structure consists of three $MnCl_6$ octahedra sharing opposite faces to form staggered chains along the c axis, the dimension of the unit cell along this axis must be at least three times the distance between opposite faces in an $MnCl_6$ octahedron. In the $CsNiCl_3$ structure, however, the unit cell dimension along the c axis is given by twice the width of an $NiCl_6$ octahedron. Three times the width of an $NiCl_6$ octahedron would be 8.89 Å and thus a structure containing units of three $MnCl_6$ octahedra sharing faces in the z-direction would require the c axis of the unit cell to be greater than this value. The large value of the c parameter required for the $CsMnCl_3$ structure thus excludes this structure from consideration. It therefore appears probable that both the tetramethylammonium compounds have the $CsNiCl_3$ type structure. More detailed crystallographic studies using single crystal data would be required to show whether this choice of structure is correct.

Table 8

X-Ray Powder diffraction data for $(CH_3)_4NMnCl_3$ obtained using CuK_α radiation

$\sin^2\theta$ (Obs)	$\sin^2\theta$ (Calc)	I	h k l
0.0097	0.0095	VS	1 0 0
0.0236	0.0236	W	1 0 1
0.0286	0.0285	S	1 1 0
0.0380	0.0380	W	2 0 0
0.0521	0.0521	M	2 0 1
0.0565	0.0564	W	0 0 2
0.0665	0.0665	W	2 1 0
0.0807	0.0806	M^-	2 1 1
0.0850	0.0849	W	1 1 2
0.0939	0.0944	W	2 0 2
0.0991	0.0996	W	3 0 1
0.1142	0.1140	M^-	2 2 0
0.1232	0.1235	M	3 1 0
0.1421	0.1419	W	3 0 2
0.1799	0.1799	M^-	3 1 2
0.1991	0.1995	W^+	4 1 0
0.2132	0.2136	W	4 1 1
0.2515	0.2516	W	5 0 1
0.2553	0.2559	W	4 1 2
0.2653	0.2660	W	4 2 0

Cell parameters.

<u>a</u> = 9.13 Å, <u>c</u> = 6.49 Å.

Table 9

X-Ray Powder diffraction data for $(CH_3)_4NMnBr_3$ obtained using CuK_α radiation

$\sin^2\theta$ (Obs)	$\sin^2\theta$ (Calc)	I	h k l
0.0087	0.0089	S^+	1 0 0
0.0267	0.0267	M	1 1 0
0.0354	0.0356	M^-	2 0 0
0.0397	0.0397	W	1 1 1
0.0487	0.0486	S	2 0 1
0.0514	0.0520	W	0 0 2
0.0622	0.0623	M^-	2 1 0
0.0751	0.0753	S^-	2 1 1
0.0802	0.0801	W	3 0 0
0.0870	0.0876	W	2 0 2
0.0929	0.0931	M	3 0 1
0.1066	0.1068	M	2 2 0
0.1142	0.1143	W	2 1 2
0.1159	0.1159	M	3 1 0
0.1284	0.1287	W	3 1 1
0.1320	0.1321	W	3 0 2
0.1520	0.1526	W	2 0 3
0.1687	0.1691	S	3 2 0
0.1786	0.1793	W	2 1 3
0.1867	0.1869	W	4 1 0
0.1956	0.1944	W	4 0 2
0.1991	0.1999	W	4 1 1
0.2211	0.2211	W	3 2 2
0.2350	0.2355	W	5 0 1
0.2403	0.2403	W	3 3 0
0.2485	0.2492	W	4 2 0

Cell parameters

$\underline{a} = 9.44$ Å, $\underline{c} = 6.76$ Å.

B. Chloro Complexes of Manganese (III)

4. Experimental methods

(i) Introduction

In comparison with the wide variety of manganese (II) compounds, not many manganese (III) compounds are known. This is because the manganese (III) ion is readily reduced and in aqueous solution this ion disproportionates to give manganese (II) and manganese dioxide. The most stable manganese (III) salt of a common anion is the acetate $Mn(C_2H_3O)_3 2H_2O$. An acid sulphate and several phosphates of manganese (III) are also known.

No simple halides, other than MnF_3, are known. However chloro complexes with the general formulae R_2MnCl_5 and $R_2MnCl_5.H_2O$, where R is an alkali metal or univalent organic base, have been isolated from both aqueous and non-aqueous solutions. The "manganese (III) chloride" is soluble in ether, unlike manganese (II) chloride, and dissolves to give a deep violet coloured solution. The Mn (III) ion is also soluble in ethanol, glacial acetic acid and hydrochloric acid. No iodide or bromide complexes of manganese (III) are known and this is probably due to the ability of the iodide and bromide ions to reduce manganese (III).

The starting point in the isolation of manganese (III) chloro complexes is the preparation of either an aqueous or a non-aqueous chloride solution containing manganese (III). Many methods of preparing "manganese (III) chloride" solutions have been described in the literature and these are briefly reviewed below.

A great deal of experimental work has been carried out on the reaction between HCl and the various manganese oxides in aqueous or non-aqueous media.

The bulk of experimental evidence points to the formation of trivalent manganese when manganese dioxide is reduced in a non-aqueous medium and the formation of both trivalent and tetravalent manganese if manganese dioxide is reduced in an aqueous medium.

(a) Reaction between HCl and manganese oxides in non-aqueous media.

One of the earliest reported studies of the hydrogen chloride-manganese oxide system was carried out by Nickles[67] in 1865. Diethyl ether saturated with hydrogen chloride was reacted with manganese dioxide at 0°C and this gave a deep green solution. When this solution was diluted with ether the colour changed from green to a deep violet. A deep green colouration was again produced when the violet ether solution was saturated with hydrogen chloride. Nickles attributed this green colouration to the presence of $MnCl_4$.

Christensen[68] repeated the work of Nickles and showed by analysis that the resulting green solution contained not $MnCl_4$ but $MnCl_3$. By suspending manganese dioxide in anhydrous ether and saturating the ether with chlorine, Christensen obtained a violet solution which he considered to contain the same dissolved substance as the green ether solution.

Christensen's work was later repeated by Franke[69], who obtained the same ratio of manganese to chloride of approximately 1:1, but by a different interpretation of the results showed that not $MnCl_3$ but $MnCl_4.MnCl_2$ or $MnCl_6$ were responsible for the colour of the ether solutions.

During this early stage of investigation no compounds had been isolated from solution and it is not surprising that several different conclusions were reached by the analysis of solutions which probably contained varying amounts of hydrogen chloride and chlorine. It was not until much later that definite compounds were isolated from non-aqueous solutions. Olsen[70] obtained a deep green alcoholic solution by reacting potassium permanganate with hydrogen chloride saturated ethanol on an ice salt bath. To the resulting solution he added solutions of organic bases which were saturated with hydrogen chloride. Dark green salts of the type R_2MnCl_5 were obtained (including $((CH_3)_4N)_2MnCl_5$ and $((C_2H_5)_4N)_2MnCl_5$ which have been prepared in the present work).

Mellor[71] describes a method of preparing an alcoholic "$MnCl_3$ solution" by reacting potassium permanganate with ethanol saturated with hydrogen chloride. (This method is referred to Christensen, but a thorough search of Christensen's published works failed to show his connection with this method of preparation).

Meyer and Best[72] isolated pyridine and quinoline compounds,with the general formula R_2MnCl_5, from a solution of Mn_2O_3 in hydrogen chloride saturated ether. The solutions of pyridine or quinoline in ethanol were saturated with hydrogen chloride and these solutions were then added to the cold ethereal solution. Immediate crystallization of dark green complexes occurred with both of these organic bases. These authors also reported the preparation of K_2MnCl_6, the first authenticated manganese (IV) chloride complex. This complex was prepared by passing hydrogen chloride into a solution of $KMnO_4$ in glacial acetic acid. The complex was obtained as fine black needles and these transmitted red light, showing that the true colour of the compound was red.

Holmes[73] found that analysis of the violet solution, resulting from the reaction of ethereal hydrogen chloride with manganese dioxide, was not possible as this solution always contained an excess of hydrogen chloride which could not be removed. He found that the manganese compounds formed in this reaction did not dissolve in carbon tetrachloride and therefore used this solvent as a reaction medium. Hydrogen chloride was passed through a suspension of manganese dioxide in carbon tetrachloride which was kept cold by means of an ice salt bath. The carbon tetrachloride turned yellow during the reaction but no manganese was found to be present in solution and the yellow colouration was attributed to the presence of dissolved chlorine. A black-green solid, which slowly evolved chlorine at room temperature, was obtained in this reaction. This compound partially dissolved in ether and gave a violet solution. The ether insoluble residue, a red-brown substance, dissolved in ethanol to give a deep wine red coloured solution. By analysis of the ethereal and alcoholic solutions, Holmes identified the black-green compound as $MnCl_3$ and the reddish brown compound as $MnCl_4$ respectively. Thus Holmes showed that both manganese (III) and manganese (IV) were formed in the reaction between manganese dioxide and hydrogen chloride.

As part of a study of the halide complexes of transition metals, Gill[74] reported the preparation of a series of alkylammonium manganese (III) chloride complexes. These complexes were obtained by adding ethanolic solutions of the required alkylammonium chloride to a violet ethereal solution prepared by using Holmes' method. This comfirmed Holmes' claim that the violet ethereal solution contained manganese (III).

(b) Reaction between manganese dioxide and hydrogen chloride in aqueous solution.

Fisher[75] repeated Nickles' experiment but could not analyse the resulting ethereal solutions. To overcome this problem he dissolved manganese dioxide in cold concentrated hydrochloric acid. The resultant brown solution when poured into water gave a brown precipitate which was filtered, dried, ignited and weighed as Mn_3O_4. By chlorine and manganese analysis Fisher showed that $MnCl_4$ was responsible for the brown colour of the solution. Fisher also reduced Mn_2O_3 and Mn_3O_4 with hydrochloric acid and obtained the same result as for MnO_2. Fishers' deductions regarding the formation of $MnCl_4$ were based on the fact that only one substance, manganese dioxide, was formed when the brown hydrochloric acid solutions were diluted with water. Pickering[76] repeated Fishers' work and showed by detailed analyses that the oxide precipitated was not MnO_2 but a variable mixture of MnO_2 and Mn_2O_3, when the brown hydrochloric acid solutions were diluted. Pickering concluded that $MnCl_3$ was formed in the reduction of the three manganese oxides and not $MnCl_4$ as determined by Fisher.

Weinland and Dinkelacker[77], following on the work of Meyer and Best reacted aqueous hydrogen chloride with potassium permanganate or with calcium permanganate to obtain compounds of the type R_2MnCl_6 where R is K^+, Rb^+ or NH_4^+. These authors also reported occasional separation of compounds of the type R_2MnCl_5 or $R_2MnCl_5.H_2O$.

More recently a spectrophotometric study of the solution of manganese dioxide and potassium permanganate in concentrated hydrochloric acid was carried out by Ibers and Davidson[78] and showed that tripositive manganese (III) was definitely present in the solution.

Summarizing the above, rather confused data, it appears that:

(1) The reduction of manganese dioxide (or potassium permanganate) with a saturated solution of hydrogen chloride in ether produces trivalent manganese. This may be inferred as the only complexes isolated from these solutions contain trivalent manganese.

(2) The reaction of hydrogen chloride on potassium permanganate in glacial acetic acid or of concentrated hydrochloric acid on potassium permanganate gives a solution containing both Mn (III) and Mn (IV).

(3) The manganese species responsible for the violet and green ether solutions and the wine red ethanol solutions have not been definitely characterized.

(ii) Starting materials

For the preparation of solutions containing manganese (III) chloride, A.R. potassium permanganate or L.R. manganese dioxide were used as sources of manganese. B.D.H. precipitated manganese dioxide was found to react much more readily than any of the other available samples of manganese dioxide. Hydrogen chloride and hydrogen bromide were obtained from Matheson lecture bottles. Where cylinders of hydrogen chloride were not available, the gas was prepared by reacting concentrated hydrochloric acid with concentrated sulphuric acid in a gas generator. Dry solvents were used when available to minimize the amount of water in the reaction mixture, even though water is a product of the reaction between hydrogen chloride and manganese dioxide (or potassium permanganate). Manganese (II) is formed by disproportionation of manganese (III) in water and the use of dry solvents helps to prevent unnecessary formation of divalent manganese. Peroxides were removed from A.R. anhydrous ether by standing the ether over freshly ground ferrous sulphate crystals for several hours prior to use.

(iii) Analyses

Chloride analyses were carried out using a Radiometer automatic titrator as described in chapter 1, section (ii). The oxidizing power of complexes or solutions containing manganese (III) was determined using standard iodometric techniques. The substance containing manganese (III) was added to a solution of potassium iodide and the liberated iodine titrated with standard 0.01M sodium thiosulphate solution using a starch indicator. Solutions containing ether could not be titrated directly since ether interferes with the starch indicator. The ether was removed by standing the iodine solution on a warm water bath for several minutes. The total manganese analysis could be carried out using the EDTA titration described in chapter 1, section (ii) providing that all the manganese was reduced to manganese (II). Hydroxylamine hydrochloride was used in the reduction of manganese in higher valence states to manganese (II) since this reagent was found not to affect the manganese analysis providing that the solution was neutralized with dilute sodium hydroxide solution before titration with standard EDTA. The determination of the total manganese with standard EDTA solution could be carried out directly on the solution remaining from the iodometric titration, if a "copper-PAR" indicator system was used. The method of analysis used was identical with that described by Flaschka and Abdine[79] in which PAN was used as the indicator. However, as the indicator PAN-(1-(2-pyridylazo)2-napthol) could not be obtained it was successfully replaced by the resorcinol derivative PAR. A 1% solution of PAR in methanol was found to decompose after a few days as indicated by the absence of a sharp end point in the EDTA titration. It was found more convenient to add a few milligrams of the solid indicator to each sample immediately before titration with standard EDTA solution.

(iv) Reduction of manganese dioxide with hydrogen chloride in a non-aqueous medium

One common feature of the early experimental reports[67-70] on reactions between hydrogen chloride and manganese dioxide (or potassium permanganate) is that exact experimental conditions were rarely specified. From preliminary investigations in the present work it was found impossible to give exact data regarding proportions of reagents necessary for complete reduction of manganese in higher valence states to manganese (III). Where the manganese (III) formed in the reaction went into solution the volume of solution was found to be important. Too large a volume of solution was found to give a high proportion of manganese (II) by disproportionation of manganese (III). The following general procedure was found to be quite satisfactory. Manganese dioxide (5 to 10 grams) under ether or ethanol ($\sim$100 mls) at -10°C was reduced by passing anhydrous hydrogen chloride through the solvent for one to two hours. Complete reduction did not take place under these conditions, but a sufficiently high concentration of manganese (III) to enable separation of alkylammonium complexes, was obtained. One important feature of these reduction reactions is that some degree of temperature control is necessary to prevent decomposition of the thermally unstable "manganese (III) chloride" during the exothermic reduction. To prevent rapid disproportionation of the chloride to yield large quantities of unwanted manganese (II) the reaction vessel must be cooled and the temperature of the reaction mixture not allowed to rise over 15°C. In the present work an ice-salt bath at -10°C was used for all reduction reactions except where otherwise specified. The temperature could also be controlled by regulating the flow of hydrogen chloride or the rate of addition of manganese dioxide to the reaction mixture, which must be constantly stirred during the reaction. Using these techniques the temperature of the reaction mixture was generally kept between -10 and +5°C.

Following the work described by Gill[74] on the preparation of alkylammonium compounds, the reduction of manganese dioxide under carbon tetrachloride at 0°C to yield a black-green solid (Holmes, Ref. 73) was carried out. The black-green solid (thought by Holmes to be a mixture of $MnCl_3$ and $MnCl_4$) was separated from the reaction mixture by filtration and then dissolved in various organic solvents. Solutions of alkylammonium chlorides in ethanol were added to the resulting solutions and any compounds formed were separated by filtration. The following results were obtained:

(a) Solution in ether gave the expected deep violet colouration. This solution reacted with methylammonium chloride and tetraethylammonium chloride solutions to yield brown and dark green complexes respectively as reported by Gill[74].

(b) Ethanol gave a deep wine-red solution (described by Holmes[73]) which reacted with methylammonium chloride and tetraethylammonium chloride to yield the same products as in (a).

(c) A 1:1 mixture of glacial acetic acid and acetic anhydride gave a deep red solution. This solution yielded the same brown complex as in (a) and (b) on addition of methylammonium chloride solution, but no complex was formed on the addition of tetraethylammonium chloride solution.

Hydrogen chloride was passed through a suspension of manganese dioxide in ethanol to yield a dark green solution. This solution reacted with tetraethylammonium chloride in ethanol to yield a paler green compound than obtained in (a), (b) and (c) above, indicating that the compound probably contained the yellow-green tetrachloro manganese (II) complex together with the manganese (III) complex. This assumption was confirmed by the separation of only the manganese (II) complex, $(CH_3NH_3)_2MnCl_4$, on addition of methylammonium chloride in ethanol to the dark green solution.

It was not possible to obtain satisfactory analyses for solutions of the black-green solid in methanol or glacial acetic acid. However it was possible to analyse the violet ether solution. The analysis was carried out in a cold room at -10°C to keep the volumetric apparatus and all other containers cold during the analysis, since at room temperature the solution is decolourized in less than an hour. Also the solution could not be pipetted at room temperature as manganese (II) chloride was deposited in the pipette. The best analysis obtained for the violet ether solution gave results which correspond to a manganese (III) content of 90% with 10% manganese (II).

(v) Preparation of alkylammonium chloride compounds

Although the violet ether solution was used successfully by Gill[74] to isolate a pure sample of the complex $(Et_4N)_2MnCl_5$, this solution was found to give methylammonium chloride and methylammonium tetrachloromanganate (II) as well as the brown manganese (III) compound on addition of an alcoholic solution of methylammonium chloride. The presence of these compounds was indicated by X-ray powder diffraction patterns of the brown complex. The precipitation of methylammonium chloride was found to be due to two factors.

Firstly the compound is insoluble in ether and can be precipitated from an alcoholic solution by the addition of ether. Secondly the common ion effect due to the high concentration of chloride ions in the ether extract causes precipitation of methylammonium chloride. To eliminate methylammonium chloride as an impurity, the volume of saturated methylammonium chloride solution in alcohol (at -10°C) which could be added to hydrogen chloride saturated with ether (at -10°C) without causing precipitation, was determined prior to each preparation. However, the decomposition of the Mn (III) chloride to give free chlorine and Mn (II), could not be prevented. It is possible that manganese (II) may be formed in the initial reaction although it was not possible to show this. Methylammonium tetrachloromanganate (II) is less soluble than the manganese (III) complex and if any manganese (II) is present the former complex will also be formed.

The preparation of a manganese (III) chloride solution described by Mellor[71] was carried out. In this method of preparation absolute alcohol (50cc) saturated with HCl at 0°C is diluted with absolute alcohol (50cc) and finely powdered potassium permanganate (5g.) slowly added to the solution. Chlorine is evolved and a deep green solution is formed, which may be kept at -10°C for several days before decolourization is complete. A black residue formed in the reaction was shown, from its X-ray powder pattern, to consist mainly of potassium chloride with a small amount of unreacted potassium permanganate. After separation of the solid material the dark green solution was added to ether, resulting in a violet solution. On dilution of the dark green solution with ethanol a brown solution resulted, but if the ethanol was saturated with hydrogen chloride the green colour remained.

Saturated solutions of alkylammonium chlorides in ethanol were prepared at -10°C and added to the dark green solution described above, yielding the complexes previously obtained by Gill[74]. (This series of preparations was carried out in a cold room at -10°C to prevent undue decomposition of the resulting complexes). The brown methylammonium and dimethylammonium complexes were obtained as coarsely crystalline needles and all the green compounds, with the exception of the crystalline trimethylammonium compound, as fine powders. The complexes were analysed immediately for Mn(III), total manganese and chloride. The green complexes were all found to have a manganese to chlorine ratio of 1:5. Iodometric determination of the manganese showed a 1:1 correspondence with the total manganese analysis for all the alkylammonium compounds indicating that the manganese is present as manganese (III). The most stable complex, the tetraethylammonium compound, was found to have the best analysis and almost exact agreement was obtained between experimental and calculated percentages of chlorine and manganese for the formula $(C_2H_5)_4N)_2$-$MnCl_5$. The analyses are listed in table 10.

It was reported by Gill[74] that the brown compounds probably contained the ionic species $(MnCl_5H_2O)^{2-}$, by analogy with the known brown compounds of the general formula $R_2MnCl_5H_2O$[77,80] where R is NH_4^+ or K^+ or Rb^+. Manganese and chlorine analyses for the brown methylammonium and dimethylammonium compounds however, did not agree with the theoretical percentages based on the formula $(CH_3NH_3)_2MnCl_5H_2O$ and $((CH_3)_2NH_2)_2MnCl_5H_2O$ respectively. Instead, the ratio of manganese to chlorine was found to be approximately equal to 1:7 for several samples of both compounds.

Carbon, hydrogen and nitrogen analyses (table 10) showed these two compounds to have the general formula $(R_4N)_4MnCl_7H_2O$. The presence of water in both complexes was shown by infrared absorption bands at 1600 cm^{-1} and 3000 cm^{-1} for nujol mulls of the complexes. The magnetic moment for the methylammonium compound, determined at room temperature (22°C), was found to be 4.80 Bohr Magneton. This showed that the manganese had four unpaired electrons as the theoretical magnetic moment for a spin free d^4 electron configuration is 4.90 B.M.

X-ray crystallographic studies will have to be carried out to determine the coordination number of the manganese in both of the $(R_4N)_4MnCl_7H_2O$ type structures. The compounds may contain seven or eight coordinate manganese (III), but it is more probable that the two compounds will contain octahedral $(MnCl_5H_2O)^{2-}$ anions in a lattice of methyl- or dimethylammonium ions and chloride ions.

Table 10

Analyses of Manganese (III) complexes

Compound	% C		% H		% N		% Mn		% Cl	
	Calc.	Obtd.	Calc.	Obtd.	Calc.	Obtd.	Calc.	Obtd.	Calc.	Obtd.
$(CH_3NH_3)_4MnCl_7H_2O$	10.6	10.3	5.8	5.2	12.4	11.4	12.2	11.9	55.2	54.9
$((CH_3)_2NH_2)_4MnCl_7H_2O$	19.9	18.5	7.5	6.9	11.6	10.6	11.4	11.2	51.5	50.9
$((CH_3)_3NH)_2MnCl_5$	20.4	21.5	5.7	6.2	8.0	8.6	15.6	15.4	50.3	49.9
$((C_2H_5)_4N)_2MnCl_5$	39.0	38.4	8.2	7.9	5.7	5.5	11.1	11.1	36.0	36.3

Carbon, Hydrogen and Nitrogen analyses were carried out by the Australian Microanalytical Service (C.S.I.R.O. Melbourne) four days after preparation of compounds.

Manganese and Chlorine analyses were carried out immediately after isolation of the complexes from solution.

(vi) Reaction of hydrogen bromide with manganese dioxide (or potassium permanganate)

Attempts to prepare manganese (III) bromide complexes by the reduction of manganese dioxide (or potassium permanganate) with hydrogen bromide in a non-aqueous solvent at-10°C were unsuccessful. In all cases bromine was slowly liberated from the reaction mixture.

Askitopoulos and Galinos[81] have reported the preparation of the complex halogen acid $H(MnBr_4)\ 5Et_2O$ by reacting a solution of hydrogen bromide in ether with finely divided manganese metal. The acid is described as a "light red-brown" oil which fumes strongly in air and reacts with manganese metal to form a solid identified by analysis as $MnBr_3$. No oxidation-reduction titrations were carried out to show the presence of manganese (III) in these compounds.

These "compounds" were prepared several times in the present work, but were shown not to contain manganese (III). Both compounds could be dissolved in water without precipitation of a manganese oxide or without liberation of bromine as would be expected from a manganese (III) bromide. Analysis of the compound "$MnBr_3$" showed this compound to be manganese (II) bromide contaminated with hydrogen bromide.

(vii) Preparation of ammonium pentafluoromanganate(III)

The compound $(NH_4)_2MnF_5$ was prepared using the method described by Cox and Sharpe[82]. Firstly manganese (II) fluoride was prepared as a fine suspension by adding manganese (II) carbonate to 40% aqueous hydrofluoric acid. This suspension was then electrolysed using platinum electrodes (0.75 amps, 2-3 volts) until the colour of the solution turned a deep red-brown (~2 hours). Unreacted MnF_2 was removed by filtration and addition of a saturated aqueous solution of ammonium fluoride to the filtrate yielded deep red needles of the complex $(NH_4)_2MnF_5$. This complex was found to be particularly stable in air and could be kept for several months without appreciable decomposition. (Mn analysis obtained 29.5%, % calculated from formula $(NH_4)_2MnF_5$ is 29.53).

5. Spectra of manganese (III) complexes

From the energy level diagram for a high-spin d^4 system (Fig. 11) it can be seen that there is only one spin allowed transition from the ^5E_g ground state and this is $^5E_g \longrightarrow {}^5T_{2g}$. This transition involves the configurational change from $t_{2g}^3 e_g^1$ to $t_{2g}^2 e_g^2$.

The value of the ligand field parameter Δ is given simply by the energy value of this transition. One of the first reported ligand field parameters for a manganese (III) complex, was that of 21,000 cm^{-1} for the aquated ion $Mn(H_2O)_6^{3+}$ in $CsMn(SO_4)_2 12H_2O$[83].

Dingle[84] carried out a study of the visible and near infra-red spectra of manganese (III) complexes, most of which contained multi dentate ligands. He also obtained spectra from acid solutions of some of the complexes and showed that the values of the ligand field parameter deduced from the observed spin allowed transition $^5E_g \longrightarrow {}^5T_{2g}$ were in the order of increasing Δ as predicted from the spectrochemical series. The ligand field parameter was found to increase in the order $Cl^- < F^- < SO_4^{2-} < PO^{3-} < H_2O$.
As mentioned in the first part of section B of the present work, several differently coloured solutions containing manganese (III) have been obtained during the investigation of the reduction of manganese dioxide (or potassium permanganate) with hydrogen chloride in aqueous or non-aqueous solutions. In aqueous solutions the reduction always gives a red brown solution. In ether the reduction yields either green or violet solutions, depending on the concentration of chloride ions, but in alcohol and glacial acetic acid red-brown solutions are obtained.

Spectra obtained for the brown alcoholic or glacial acetic acid solutions

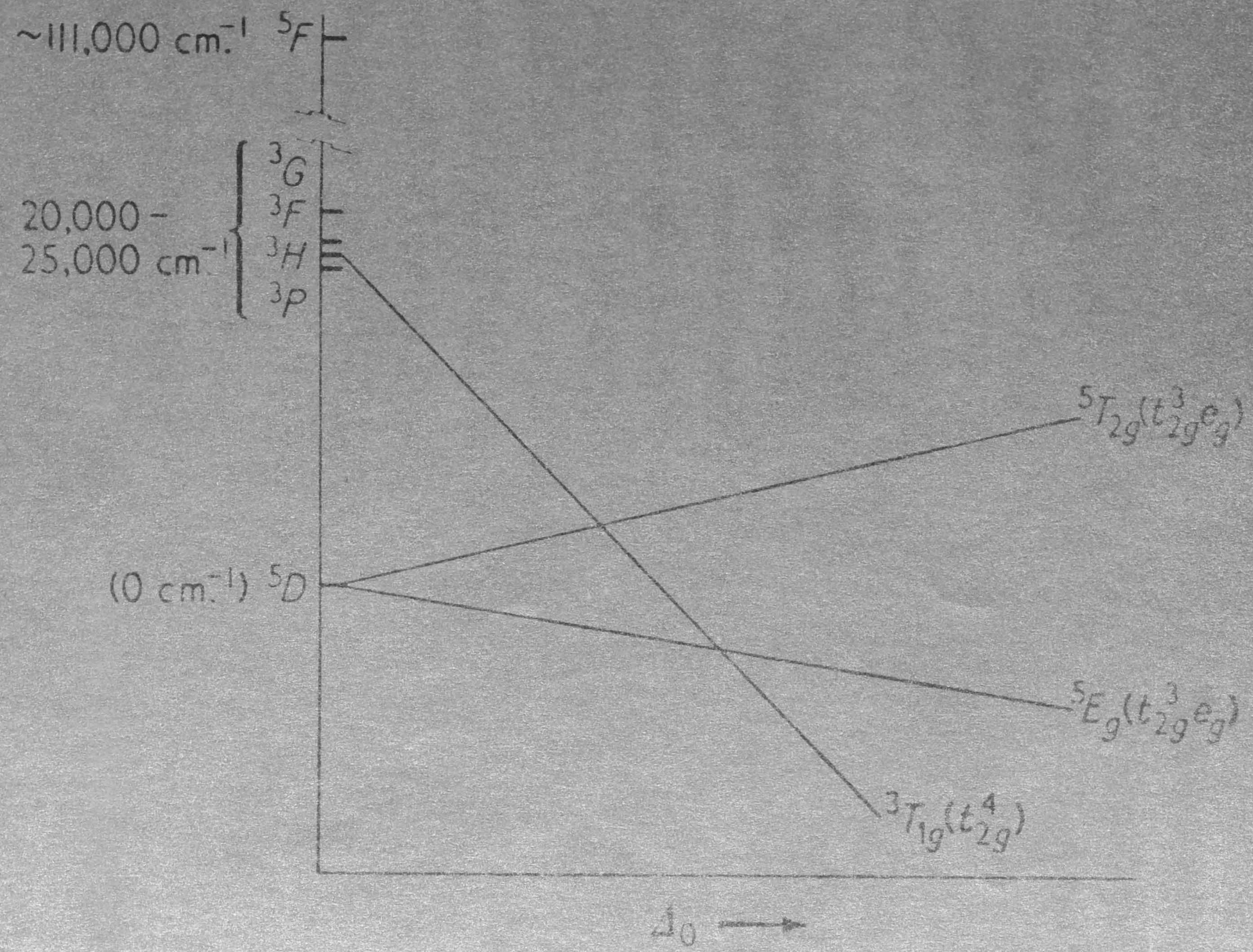


Fig. 11. Simplified energy level diagram for the d^4 system Mn^{III} in octahedral surroundings. (After Cotton and Wilkinson[64])

showed intense absorption over the whole visible range of the spectrum with no definite absorption maxima. The same phenomenon was observed in the reflectance and single crystal spectra of the brown methylammonium and dimethylammonium complexes. Spectra were also obtained for the violet and green solutions in ether and ethanol respectively. The spectrum of the violet ether solution showed a broad absorption band extending from 450 to 650 mμ with a maximum at 580 mμ. The solution showed complete absorption below 420 mμ. The violet colour of the solution is accounted for by the narrow region of transmission between 420 and 450 mμ. The green solution gave a similar absorption spectrum which showed a broad band extending from 510 to 700 mμ with a maximum at 570 mμ. The solution absorbed completely below 480 mμ, thus accounting for its green colour. A nujol mull of the deep red fluoride complex $(NH_4)_2MnF_5$ gave intense absorption from 420 to 600 mμ with an absorption maximum at 485 mμ.

The values of the ligand field parameters obtained from the above absorption maxima together with the value for the aquated Mn (III) ion are listed in table 11 below. These values vary as predicted from the spectrochemical series. The ligand field parameter increases $Cl < H_2O < F$.

Table 11

Compound or ion	Ligand field parameter Δ (cm^{-1})
[a]$Mn(H_2O)_6^{3+}$	20,000
$(NH_4)_2MnF_5$	20,619
Green EtOH solution. Probably containing $MnCl_6^{3-}$	17,540
Violet ether solution of $MnCl_3$	17,240

[a] Value from Hartman and Schläfer, Ref. 83.

The appearance of a single intense absorption band in the visible region of the spectrum shows that the manganese is present as manganese (III), since the spectra are consistent with the crystal field splitting predicted for a d^4 system. The very intense absorption below 420 and 480 mμ in the spectra of the violet and green solutions respectively are probably due to charge transfer bands.

The visible and U.V. spectra of K_2MnCl_6 have been reported[85]. From X-ray structure analysis and magnetic susceptibility measurements, this Mn(IV) compound was shown to be an octahedrally coordinated high spin d^3 complex. Crystal field splitting of the high spin d^3 configuration predicts three spin allowed transitions from the quartet ground state to quartet excited levels. The observed spectrum of K_2MnCl_6 gave intense absorption maxima at 15,000 cm^{-1} (650 mμ) 27,400 cm^{-1} (365 mμ) and 33,300 (300 mμ). This spectrum does not resemble the spectra obtained in the present work for the manganese (III) complexes and furnishes additional proof that manganese (IV) is not present in non aqueous solutions.

From spectroscopic data it has been shown that:

(a) Manganese (III) is formed in the reduction of both manganese dioxide and potassium permanganate by hydrogen chloride in ether or in ethanol.

(b) The ligand field parameter Δ is much greater for manganese (III) complexes than for manganese (II) complexes. This is to be expected as the smaller ionic radius of the Mn^{3+} ion (0.62 Å [63] compared with 0.80 Å for Mn^{2+}) means that the metal ligand bond in a manganese (III) complex will be shorter than that in the corresponding manganese (II) complex.

(c) The dependence of the value of the ligand field parameter Δ on the ligand can be predicted from the spectrochemical series as it can for manganese (II) complexes.

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