# The Visible and Near Infrared Spectrum of

Manganese (III) Complexes

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Spectra of the manganese(III) ion in a variety of molecular environments are reported. In all cases these spectra have two regions of discrete absorption, one about 20 000 cm^{-1} and the other in the range 5 000—15 000 cm^{-1}. The higher energy system is accounted for by the expected spin-allowed d-d transition (O_h)

$${}^5E_g \rightarrow {}^5T_{2g}$$
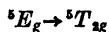
The low energy absorption is considered to be due to a ligand to metal charge transfer process. Such a model is capable of explaining most of the empirically available data.

The spectra of high-spin complexes of trivalent manganese are not well characterized.[1,2] This paucity of experimental data is presumably due to the fact that the $3d^4$ high-spin configuration is thought to be susceptible to oxidation-reduction reactions.[3] There exist, however, numerous references [4-18] in the literature concerning the preparation of Mn(III) compounds and, under specified conditions, many of these complexes are stable, the properties of the free ion having been modified by the ligand environment.

There are several reports [19-27] concerning the spectra of six-coordinated, high-spin Mn(III) complexes and some tentative assignments have been proposed. Jørgensen,[19] Piper and Carlin,[20,21] and Barnum [22] have interpreted their results in terms of an octahedral model and assign the ~20 000 cm^{-1} absorption (ε ~50—300 litres $mole^{-1}$ cm^{-1}) as the spin-allowed, crystal field transition

$${}^5E_g \rightarrow {}^5T_{2g}$$
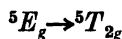
These authors consider a spin-forbidden transition to be responsible for the relatively intense absorption, (ε~50—150) that appears in the vicinity of 10 000 cm^{-1} in the tris bidentate complexes.

McClure [24] did not observe this near infra-red band in the spectrum of $Mn(III)/Al_2O_3$, Hartmann and Schläfer [25] did not report it in the crystal

spectrum of $CsMn(SO_4)_2 \cdot 12H_2O$ and Hatfield *et al.*[26] do not report it in the spectrum of a CsCl disc containing $[Rh(C_3H_{10}N_2)_3]$ $[MnCl_6]$. All three investigations report the quintet-quintet absorption at $\sim 20\ 000$ cm^{-1}.

In a preliminary report [27] we have suggested that the near infra-red band may arise from a spin-allowed transition between components of the ^5E_g ground state which had been split by Jahn-Teller forces in the tris bidentate complexes. In the light of the present, more complete work and other relevant investigations [28-30] it seems more reasonable to consider this lowlying, near infra-red absorption as a ligand to metal charge transfer process.

EXPERIMENTAL

All compounds were prepared by existing methods.[4-18] Solvents were analytical grade and were usually subjected to further drying and purifying processes. Solution spectra, recorded at $23 \pm 1°C$ excepting those of the tris oxalato and bis oxalato diaquo complexes which were obtained at 2—4°C, were measured with a UNICAM SP700 spectrophotometer. On standing most of the solutions show a colour change, the reds and browns fading to yellow or colorless solutions and in a few instances a pale yellow solid is precipitated. In all cases the solutions were stable enough to allow reliable spectra to be obtained. Intensities are reported as molar extinction coefficients ε and they are thought to be accurate to 5 %. If the above mentioned decomposition is a reduction of manganic to manganous then the reported ε values are likely to be low although the qualitative shape of the visible spectrum should not be affected.

Single crystal spectra have been obtained at room temperature and at 77°K using a Beck reflecting microscope and the UNICAM SP 700 monochromator. For the low temperature spectra a stage, similar to that described by Ferguson and Wignall,[31] has been used.

RESULTS

The spectra fall into groups that are essentially characteristic of the molecular arrangement about the central metal ion.

(i) *Tris bidentate complexes.* In these complexes the molecular geometry should be D_3. All spectra show a reasonably intense absorption band in the near infra-red region (in the range $5\ 500—10\ 000$ cm^{-1}; $\varepsilon \sim 50—150$ litres mole^{-1} cm^{-1}) as well as a strong ($\varepsilon \sim 300$), usually multiple absorption at about $20\ 000$ cm^{-1} (in some cases these latter absorptions exist only as shoulders on a much more intense ultraviolet system). Figs. 1, 2, and 3 show representative spectra and the results are summarized in Table 1.

(ii) *Bis bidentate diaquo complexes.* These complexes, generally derived from a parent in (i) by replacing one bidentate ligand with two water molecules, are considered to be *trans* and thus to have an approximate D_{4h} symmetry. The spectra no longer show the near infra-red band found in (i) although it has been replaced by a much less intense absorption at $10\ 000—15\ 000$ cm^{-1}. The $\sim 20\ 000$ cm^{-1} system of (i) persists but it shifted to slightly higher frequencies than found in the parent compound. Fig. 2b shows a typical spectrum and Table 1 summarizes the results.

(iii) *Acid solutions containing Mn(III).* These spectra are similar to those found in (ii) excepting that the shape and the intensity is strongly dependent upon the acid concentration (Fig. 4 and Table 1). An important feature of the spectra is that although the $\sim 20\ 000$ cm^{-1} absorption is strongly dependent

Table 1. Spectral data for some complexes of manganese(III).

Mn(III) Complex Type (i)	ν cm⁻¹	ε l/mole cm	Probable excited state (O_h)	$\varDelta$	$\varDelta'$ [a]	B	β [b]
tris-diethyldithio-carbamato (in carbon tetrachloride)	5 500	103	C.T.	—	13 250	740	0.82
	(16 000) 19 700	{ 250 1250	$^5T_{2g}$ charge transfer or $^5T_{2g}$	16 000 19 700	17 000	—	—
tris-N-piperidyl dithiocarbamato (carbon tetrachloride)	5 600	132	C.T.	—	13 300	740	0.82
	(16 100) 19 600	{ 250 1400	$^5T_{2g}$ charge transfer or $^5T_{2g}$	16 100 19 600	16 800		
tris 2,2-bipyridyl-1,1-dioxide persulphate (dimethylsulphoxide)	6 500 (16 700) (19 000)	112 { 200 400	C.T. / $^5T_{2g}$ or charge transfer	16 700	13 450 15 750	775	0.86
tris-acetylacetonato (carbon tetrachloride)	8 500 17 600 (22 000)	87.6 { 160 300	C.T. $^5T_{2g}$	— 17 600 22 000	13 350 17 750	900	1.0
tris-benzoylacetonato (carbon tetrachloride)	8 600 17 900 (22 500)	93.7 195 ~1250	C.T. $^5T_{2g}$	— 17 900 22 500	13 500 18 200	900	1.0
tris-oxalato ion in oxalate buffer at 2—3°C	9 500 { 19 400 20 500	50 230	C.T. $^5T_{2g}$	— 20 000 (ave)	— 15 250 (ave)	1040	1.16
tris-malonato ion in malonate buffer at 2—3°C	9 600 { 19 600 20 400	70 250	C.T. $^5T_{2g}$	20 000 (ave)	15 250 (ave)	1040	1.16

[a] $\varDelta'$ is calculated by assuming $\varDelta$ for a distorted complex is given by $\varDelta' = \nu_{5T_{2g}} - \tfrac{1}{2}\nu$ near infrared absorption

[b] β is calculated by using $B_{\text{Free ion}} = 900$ cm⁻¹

Type (ii)	ν	ε	Probably exicited state (O_h)	Δ	Δ'	B	β^*
bis-oxaloto diaquo in oxalate buffer	13 500 21 700 22 400	20 130	C.T. $^5T_{2g}$	22 000 (ave)	15 300 (ave)	—	—
bis-malonato diaquo in malonate buffer	14 200 21 600 22 500	20 125	C.T. $^5T_{2g}$	22 000 (ave)	14 000 (ave)	—	—
bis-acetylacetonato diaquo in acac/H_2SO_4, pH = 2	17 600 25 100	28 370	C.T.? $^5T_{2g}$	17 600 25 100	— —	—	—
Type (iii) Mn(III) in dilute H_2SO_4 Mn(III)(H_2O)$_6^{3+}$?	12 000 21 000	— —	C.T. $^5T_{2g}$	21 000	15 000	1140	1.27
Mn(III) in conc. H_2SO_4	11 700 19 400	— —	C.T. $^5T_{2g}$	19 400	13 500	—	—
Mn(III) in dil. HCl	11 800 21 000	18 ~60	C.T. $^5T_{2g}$	21 000	15 000	1130	1.25
Mn(III) in conc. HCl	12 800 17 700 25 600	40 330 1700	C.T. $^5T_{2g}$ charge transfer	17 700	11 300	1050	1.17
Mn(III) in conc H_3PO_4	12 500 (17 800) 18 500 (19 600)	— — —	C.T. $^5T_{2g}$	18 500	12 200	1065	1.18
Mn(III) in 40 % HF	14 000 (18 500) 21 600	5 — 15	C.T. $^5T_{2g}$	20 000 (ave)	13 000	1120	1.25

Type (iv) Mn(III)triethanolamine in 1 % aq. NaOH	13 600	172	C.T.?	—	15 600	1240	1.38
	22 400	116	$^5T_{2g}$	22 400			
Salicylaldehyde ethylenediimine acetate (alcoholic solution)	~17 000	250		20 800?			
	20 800	1 000					
	25 000	5 000					
	(27 800)	~8 000					
	32 000	~9 500					
	35 300	15 000					
tris-picolinato hydrate (aqueous solution)	15 600	200	?				
	18 570	250					
	(25 500)	800					
	(36 900)	~	ligand absorptions				
	37 700						
	38 500	5 000					
	47 000						
ammonium bis-salicylato diaquo dihydrate (alcoholic solution)	18 000	~100	$^5T_{2g}$?				
	(~26 000)						
	33 500	10 000					

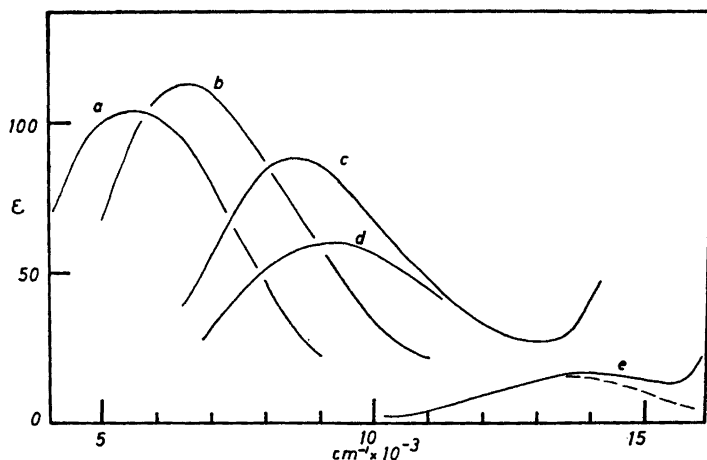*Fig. 1.* The near infrared absorption in manganese(III) complexes.

  a) tris-N, N-diethyldithiocarbamato-Mn(III)
  b) tris-2,2-bipyridyl-1,1-dioxide-Mn(III) ion
  c) tris-acetylacetonato-Mn(III)
  d) tris-oxalato-Mn(III) ion
  e) bismalonato-diaquo-Mn(III) ion.

on the acid strength, the frequency of the $11\,000-13\,000$ cm^{-1} absorption shows very little dependence on the solvent.

(iv) Table 1 also includes results for a number of complexes that, for stereochemical reasons, are difficult to classify in any of the above groups.
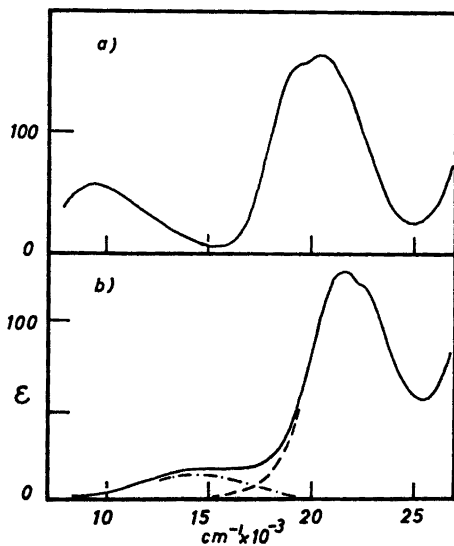
Fig. 2. a) The near infrared/visible spectrum of potassium tris-malonato-Mn(III) trihydrate in a malonic acid/potassium malonate buffer.

b) The potassium bis-malonato-diaquo-Mn(III) dihydrate complex in a malonic acid/potassium malonate buffer solution.
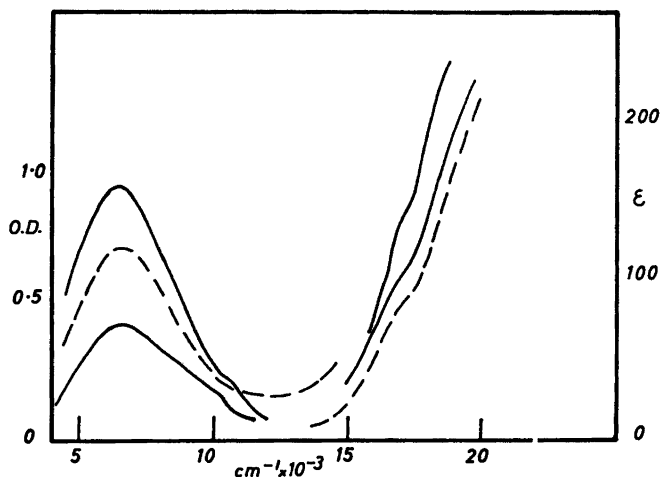
Fig. 3. The near infrared/visible spectrum of tris-2,2-bipyridyl-1,1-dioxide-Mn(III) perchlorate tetrahydrate in dimethylsulphoxide ----; in a pure single crystal polarized in two unknown molecular orientations ————.

If it is assumed that only one absorbing species is present then it is evident from most of the spectra that the effective potential field at the central metal ion is considerably lower than octahedral since the absorption bands at $\sim$20 000 cm^{-1} are either asymmetric or show distinct multiple maxima (Fig. 2). Some of the crystal spectra show further small splittings that are indicative of low field components in the crystals. For both solutions and crystals it is unlikely that assignments in O_h will be capable of explaining the finer features of the spectra although, for estimates of Dq, B, C and β such assignments are probably adequate.
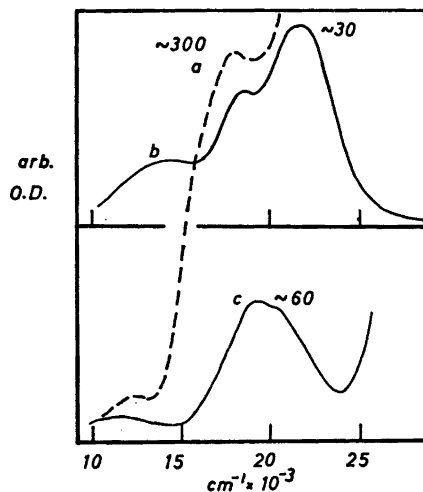

Fig. 4. The visible spectrum of manganese (III) in
a) 10 M hydrochloric acid b) in 40 % hydrofluoric acid c) in 6 M sulphuric acid.

The close agreement between the crystal and the solution spectra (Fig. 3 gives an example) shows that the spectra arise from an intramolecular origin and that they are not unduly affected by solvent or crystal environment.

ASSIGNMENTS

(i) *The 20 000 cm^{-1} absorption.* In all cases it is plausible to propose that the absorptions in the region 17 500—23 000 cm^{-1} are associated with the transition (octahedral notation),

$$^5E_g \rightarrow \, ^5T_{2g} \tag{1}$$

or its components in one or another lower symmetry group. The lower than O_h symmetry, ((i), (ii), and (iii) of the last section) accounts for the appearance of the multiple absorption maxima in the spectra. The movement of the absorption to higher energies in the diaquo bis bidentate complexes follows as a consequence of the tetragonal perturbation if the water molecules are *trans*. This point, plus the fact that there is a $\sim$50 % reduction in intensity on going from (i) to (ii) is good support for the proposed *trans* model.

In the acid solutions it is difficult to be sure of the nature of the absorbing species. Sidgwick [3] proposes *trans* diaquo models in phosphoric and sulphuric acids whereas in hydrochloric and hydrofluoric acids it has been suggested [32] that MnX$_6^{3-}$ complexes exist. More recently, good evidence has been provided [29] for the existence of Mn(H$_2$O)$_5$OH^{2+} in moderately concentrated perchloric acid solutions and it has been suggested [33] that when fluoride ion is added to such solutions a complex Mn(H$_2$O)$_5$F^{2+} is formed.

In the present case it does not matter too much what the exact nature of the absorbing complex in the solution is so long as at least one ligand binds through an atom (oxygen in these cases) that contains non-bonding or weakly π bonding orbitals at about the same energy as the 3d metal orbitals. The correspondence between the spectra in (ii) and (iii) supports this hypothesis.

The absorption bands at 21 000 cm^{-1} in 2 M hydrochloric acid, at 17 500 cm^{-1} in 10 M hydrochloric acid, at 18 200 cm^{-1} in hydrofluoric acid and at $\sim$19 000 cm^{-1} in sulphuric and phosphoric acids provide the relationship

$$Dq_{Cl^-} < Dq_{F^-} < Dq_{SO_4^{2-}} < Dq_{PO_4^{3-}} < Dq_{H_2O}$$

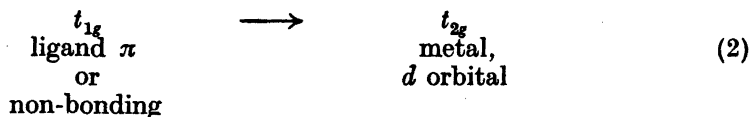which is in good accord with the accepted spectrochemical order for these ligands.

(ii) *The 5 000—15 000 cm^{-1} absorption.* In a near octahedral environment this absorption cannot correspond to any spin-allowed crystal field transition. The radical rearrangement of nuclei required [27] to assign this transition as *d-d* and spin-allowed no longer seems reasonable,[28] at least in the case of the tris bidentate complexes.

On the basis of intensity and frequency values,[27] the earlier assignment of this absorption to a spin-forbidden transition [19—22] no longer appears valid.

The final alternative, that the absorption corresponds to a lowlying, presumably forbidden, charge transfer transition, can be fitted to most of the available data although in one particular case, that of the ammonium penta-

fluoromanganate crystal,[34] a rather drastic assumption is necessary in order to unify the treatment.

If the discussion is restricted to near octahedral complexes involving ligands that have weakly π or non bonding filled orbitals, then there is ample facility for the donation of an electron from such an orbital into the partially filled, essentially d-like t_{2g} orbitals of the metal. It is suggested here that the transition most likely corresponds to the one electron excitation [35]

$$
\begin{array}{ccc}
t_{1g} & \longrightarrow & t_{2g} \\
\text{ligand } \pi & & \text{metal,} \\
\text{or} & & d \text{ orbital} \\
\text{non-bonding} & &
\end{array}
\qquad (2)
$$

DISCUSSION OF ASSIGNMENTS

It is clear that the simple crystal field theory [36] cannot explain these spectra, although it is equally clear that the spectra are intramolecular and in general of a forbidden nature.

The $\sim$20 000 cm^{-1} absorption can be confidently assigned as the only quintet-quintet crystal field transition (however, see Jørgensen [37] for an alternative treatment). We have not provided a general proof of this assignment although the crystal results [34] on ammonium pentafluoromanganate(III) provide a good basis for this proposal.

More interest is attached to the clarification of the situation concerning the near infra-red absorption band.

Our earlier inclination [27] towards a strongly Jahn-Teller distorted ground state has to be replaced by a near octahedral model [28] even though the spectrum is that expected [38] for a strongly distorted Mn(III) complex. The small distortion of the D_3, Mn acac$_3$ complex, found by X-ray means,[28] could be considered the result of a Jahn-Teller effect in the ground state.

Griffith [39] has shown the coupling between $^3T_{1g}(H)$ and $^5T_{2g}$ to be zero in O_h and so it should be zero or very small in these near O_h complexes. If the quintet-triplet assignment is to be retained very large mixing coefficients must therefore be introduced, especially, for instance, in the fluoro complex.

In the series of complexes examined (Table 1) the frequency of this absorption band when considered as $^5E_g - ^3T_{1g}(H)$ does not follow the relationship expected from the simple theory.[36]

The theory predicts that as $\nu_{5T_{2g}}$ increases, $\nu_{3T_{1g}(H)}$ should decrease, however, a better description is given by the correlation

$$\nu_{5T_{2g}} \text{ increases } \nu_{3T_{1g}(H)} \text{ increases.}$$

These relationships depend on the Racah parameter B and we have no independent measure of this quantity but it seems that reasonable values of B do not give agreement with the theory. The values of B, and hence $\beta = B_{complex}/B_{free\ iron}$. ($B_{free\ iron} = 900$ cm^{-1}), derived using the diagonal elements for $^5T_{2g}$ and $^3T_{1g}(H)$ are all rather large. In fact, the β values are mostly greater than unity even though as a result of the Jahn-Teller distortion in the ground state, the $10\ Dq$ values are usually considered to be greater than those

of a "normal" Mn(III) complex (this last effect should decrease B and β values calculated from $^3T_{1g}(H)$).

Finally the appearance of a weak band at $\sim$10 500 cm^{-1} in the 2,2-bipyridyl-1,1-dioxide complex in the solid as well as the stronger band at 6 500 cm^{-1} (Fig. 3) is reasonable evidence that $^3T_{1g}(H)$ is not responsible for the more intense near infra-red band. On these grounds we believe that the quintet-triplet assignment may be safely discarded.

The charge transfer transition that is responsible for the near infra-red band must be rather strongly forbidden ($\varepsilon \sim$5—100). For this reason and because the intensity is greatly decreased in complexes that have a centre of symmetry the transition is considered parity forbidden and transition (2) is preferred.

The first thing the model must be able to do is to explain the appearance or absence of the near infra-red band in the various spectra reported. Of these perhaps the Mn(III)/Al$_2$O$_3$ system [23] is the most important. The crystal structure [40] of Al$_2$O$_3$ shows that each aluminium ion, and hence each Mn(III) ion, is surrounded by a distorted octahedron of oxygen ions whereas each oxygen is surrounded in an approximately tetrahedral manner by four metal ions. Thus, if sp^3 hybridization is assumed, all the oxygen orbitals are involved in σ bond formation; hence there are no filled non-bonding ligand orbitals in the region of the metal t_{2g} orbitals and no lowlying charge transfer can be expected. Alternatively, in an ionic model, crystal field forces would destabilize the oxygen orbitals in such a way that they will fall far out of the "normal", non-bonding oxygen orbital region.

Again the model must be able to explain why the MnCl$_6^{3-}$ disc spectrum shows no absorption [26] at $\sim$ 13 000 cm^{-1} whilst the solution spectrum of the chloro complex in hydrochloric acid shows such an absorption band.[18] To do this, we propose, in line with some earlier work,[29,33] that in the solution OH$^-$ or H$_2$O ligands are coordinated to the metal, that the electron is transferred from a non-bonding or slightly π bonding orbital on these ligands and further that the Cl$^-$ ligands are not greatly involved in any molecular orbital formulation involving this oxygen orbital. In this way the first chlorine to metal charge transfer may be associated with the relatively intense absorption at $\sim$25 000 cm^{-1} (in the fluoro complex this band falls at $>$ 35 000 cm^{-1}).

This explanation resolves another point, namely, that in solution both the fluoro and the chloro complexes have an absorption at $\sim$13 000 cm^{-1}, a result not compatible with the $L{\rightarrow}M$ hypothesis if the chloro and the fluoro ligand were the donating ligand in each case. From this point of view it is encouraging to note that the Mn(H$_2$O)$_5$OH^{2+} spectrum, reported by Diebler and Sutin,[29] has a weak absorption in the region of 13 000 cm^{-1} although as far as we know no such absorption has been seen in the Mn(H$_2$O)$_6^{3+}$ case.

The general question of the frequency variation of this transition can be dealt with in the following way. In the tris bidentate complexes the variation of frequency is in the sense predicted by Jørgensen's optical electronegatively concept.[41] When one bidentate ligand is replaced by two water molecules the absorption invariably moves to higher energy. According to the optical electronegativity scale, if the water molecules participate in the non-bonding ligand molecular orbital from which the electron is excited, then such a blue

shift is to be expected. Furthermore the similarity of the spectra in (ii) and (iii) in this region is now easily explained.

The appearance [34] of an absorption in the region of 13 000 cm^{-1} in the crystal of $(NH_4)_2MnF_5$ cannot be explained by the charge transfer model since, according to Sears,[42] the metal ion is surrounded by six fluoride ions in a distorted octahedron. The crystals used in our optical study [34] have the same X-ray determined characteristics as those reported by Sears although both his and our preparation showed some evidence for the presence of O—H bonds in the infrared spectrum. One possible solution to this dilemma is to propose that in the crystal each Mn ion is surrounded by four fluoride ions and two shared hydroxide ions instead of six fluoride ions and that the formula should be $(NH_4)_2MnF_4OH$. We have mentioned in an earlier report [34] the difficulty of distinguishing between OH^- and F^- in a two dimensional X-ray determination such as that made by Sears.

If the above proposal is correct then the hydroxides can be thought of as forming an sp^2 hydrid to take care of the σ bonding and leaving a filled non-bonding or π bonding p_z orbital to take part in the charge transfer process. This arrangement also provides an explanation of the $\pm 21°$ kinking [42] of the Mn—F—Mn chain since a pure sp^2 hydrid, without strain, only requires a kinking of $\pm 30°$. We are at present carrying out experiments aimed at testing this very tentative hypothesis.

Finally, the instability towards oxidation/reduction reactions may be considered. The decolorization of solutions and the deposition of pale yellow solids is consistent with a decomposition reaction that occurs through a ligand to metal charge transfer process, ultimately described by the equation

$$Mn(III) + e^- \rightarrow Mn(II)$$
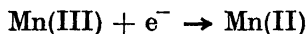
In the solid state several complexes have been found to be sensitive to light. The most striking example is that of potassium tris oxalato manganese (III) trihydrate. This crystal is deep purple; however, after one or two seconds at the focus of the Beck microscope it is bleached colorless and in a few more seconds the crystal explodes. The process is described by the following equation.

$$2Mn(III) + C_2O_4^{2-} \xrightarrow{h\nu} 2Mn(II) + 2CO_2$$
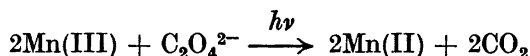
By using various filters the 10 000 cm^{-1} and the 20 000 cm^{-1} regions have been isolated and, although the rate is considerably reduced the decomposition still proceeds when light is absorbed in the 10 000 cm^{-1} region. This is much more likely if the absorption is due to a charge transfer process ($L \rightarrow M$ according to the above arguments) than if the process is d-d when, in the absence of extensive molecular orbital formation, the excitation is essentially localized on the metal ion.

CONCLUSIONS

A consistent description of the visible and near infra-red spectrum of manganese(III) complexes cannot be had from the simple crystal field theory. Inclusion of Jahn-Teller distortions in the ^5E_g ground state do not resolve the problem and the final solution appears to be found in the more general

ligand field theory when the possibility of low energy charge transfer is admitted.

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