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The Polarized Single Crystal Spectrum of Ammonium Pentafluoromanganate(III)

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The tetragonally elongated molecular unit MnF_6^{2-} has been used to assign the symmetry properties of the three more intense visible absorption bands in the crystal spectrum. The ground state may not be deduced from the spectral properties although the crystallographic evidence is consistent with axial stabilization and a $^5B_{1g}$ ground state in a D_{4h} symmetry. The two higher energy transitions are associated with $^5T_{2g}$ of O_h, whereas the absorption that appears at 12,750 cm.$^{-1}$ is not easily assigned to any particular crystal field transition. The origin of this absorption is discussed. The solution spectrum in hydrofluoric acid and the diffuse reflectance spectrum of potassium pentafluoromanganate(III) hydrate are considered and it is concluded that the Mn(III) environment in these latter instances is tetragonally distorted.

Introduction

The spectral properties of trivalent manganese complexes are not well characterized. A number of reports concerning solution spectra[2,3] and more recently crystal spectra[4-7] have appeared, but none of these investigations has been able to provide rigorous assignments of the spectral transitions observed.

Sears[8] has determined the crystal structure of the ammonium pentafluoromanganate(III) complex, and it is on this basis that the polarized crystal spectrum of this complex may acquire some significance.

The Jahn–Teller theorem is applicable to the degenerate ground state of manganese(III) complexes in octahedral symmetry and it is of interest to consider the structure and spectrum of this complex from such a viewpoint, especially from the comparison of the crystal spectrum with that observed in solution.

Experimental

The complex was prepared by the method of Christensen.[9] The crystals grow as needles elongated along the b axis and with faces (001) and (100) well developed. Attempts to cut these crystals normal to the needle axis have inevitably led to their destruction.

Spectra have been recorded single beam, using a Beck reflecting microscope as illuminator and a Unicam SP 700 monochromator, and double beam using the microscope and a Cary Model 14 spectrophotometer. Low-temperature spectra have been obtained using a stage similar to that described by Ferguson and Wignall.[10] Solution and diffuse reflectance spectra have been obtained using standard equipment.

Crystal Structure[8]

Ammonium pentafluoromanganate(III) is orthorhombic, space group P_{nma}-D_{2h}^{16}.

a = 6.20 Å.	Mn(III) site symmetry, C_i
b = 7.94 Å.	Factor group symmetry, D_{2h}
c = 10.72 Å.	Molecular symmetry, D_{4h}
z = 4	

The complex is tetragonally distorted; the in-plane Mn–F bond lengths are 1.84 and 1.85 Å. and the axial bond lengths are 2.12 Å. The long bonds link octahedra into infinite, kinked chains, the appropriate fluorines being shared by two octahedra.

The molecular z axis (of the D_{4h} molecular unit) is taken parallel to this 2.12 Å. bond direction and thus makes an angle of ±20.6° with the b crystallographic axis.

Spectra taken on (001) and (100) were recorded perpendicular and parallel to the b axis and hence $\parallel b$ spectra contain 90% of the z polarized transition intensity and $\perp b$ spectra about 90% of the x,y polarized transition intensity.

Results

The spectra taken on (001) and on (100) are very similar. Figure 1 shows spectra taken on (001). Figure 2 compares the unpolarized spectrum taken on (001) with that obtained when this complex (or $K_2Mn^{III}F_5 \cdot H_2O$) is dissolved in 40% hydrofluoric acid in the presence of excess fluoride ion or when the solute is at low concentration (<0.03 M) in 40% hydrofluoric acid.

The diffuse reflectance spectrum of potassium pentafluoromanganate(III) hydrate is not shown, but it is very similar to those of Figure 2 excepting that several, very sharp, weak bands appear in the region 15,000–25,000 cm.$^{-1}$.

All spectra are summarized in Table I.

In all cases there are three broad bands located at ~21,000, ~18,000, and ~13,000 cm.$^{-1}$. The solids show the presence of some weak bands in the 15,000–25,000 cm.$^{-1}$ region and for the ammonium salt a weak, sharp, band at 6400 cm.$^{-1}$ (2 × 3195 cm.$^{-1}$, NH_4^+ absorbs strongly at 3195 cm.$^{-1}$).

Assignments and Discussion

The marked spectral dichroism indicates that the effective symmetry is less than octahedral although probably higher than rhombic. If a vibronic coupling mechanism is assumed it is possible to reach an assignment in D_{4h} symmetry. It is also possible that other, lower symmetries may be able to provide an analysis.

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TABLE I

EXPERIMENTAL DETAILS FOR SOME MANGANESE(III) FLUORO COMPLEXES

Complex		Strong, broad			Weak, sharp			
$(NH_4)_2MnF_5$	ν, cm.$^{-1}$	12,750	18,200	21,000	16,700	18,100	19,800	23,800
	$\epsilon_{\perp}'/\epsilon_{\|\|}$	0.6	$\gg$1.0	2.5–3.0	<1.0?	?	<1.0	
	$\epsilon_{\perp}$ cryst., ±10%	3.5	8.0	15.0				
$K_2MnF_5 \cdot H_2O$ (diffuse reflectance MgO standard)	ν, cm.$^{-1}$	12,000	18,000	21,250	18,000	19,230	19,800?	23,250
MnF_6^{3-} (0.1 *m* in 40% HF, excess NH_4F)	ν, cm.$^{-1}$	14,000	18,500	21,600	...			
	ϵ_{soln}, l. mole^{-1} cm.$^{-1}$	4.7	7.6	12.1				

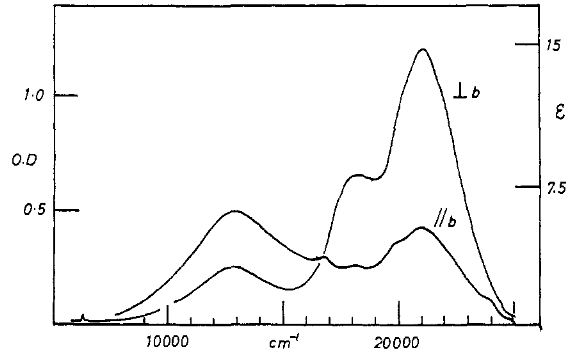

Figure 1.—Polarized crystal spectrum of ammonium pentafluoromanganate(III) taken on (001) with the electric vector || and ⊥ to the *b* crystallographic axis. Low-temperature spectra sharpen the bands somewhat but no gross changes occur.

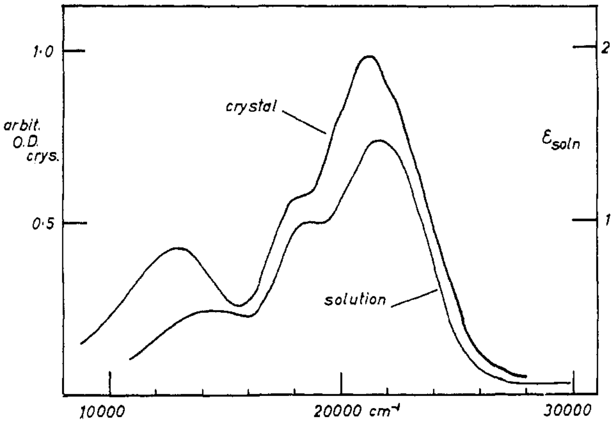

Figure 2.—Unpolarized crystal spectrum of ammonium pentafluoromanganate(III) and the solution spectrum in 40% hydrofluoric acid in the presence of excess fluoride ion.

However, more exacting experimental circumstances, that may reveal small splittings and more subtle intensity effects, are required before this aspect may be checked.

If the x and y axes point at the in-plane fluoride atoms, then assuming an axial stabilization in D_{4h}, the d orbitals will be arranged so that d_{xz}, d_{yz} are degenerate and most stable through d_{xy} and d_{z^2} with $d_{x^2-y^2}$ least stable. In this scheme, the four 3d electrons will generate a $^5B_{1g}$ ground state with $^5A_{1g}$ some distance to higher energies, both levels correlating with ^5E_g ground state of O_h symmetry. The only quintet excited state, $^5T_{2g}$ of O_h, becomes $^5B_{2g} + {}^5E_g$ in this arrangement.

With a $^5B_{1g}$ ground state the possible quintet-quintet transitions and their associated vibronic character are those listed in Table II. From Table I it is seen that if the odd vibrations b_{2u} and/or a_{2u} are more effective at intensity stealing than is e_u then the experimentally observed polarizations are in agreement with the predicted vibronic coupling scheme.

TABLE II

POSSIBLE VIBRONIC SPECTRAL ASSIGNMENTS OF MANGANESE(III) IN A TETRAGONAL ENVIRONMENT

Transition	$2a_{2u}$	b_{2u}	$3e_u$	Polarization ratios $\epsilon_{\perp}/\epsilon_{\|\|}$[a]
$^5B_{1g} \rightarrow {}^5A_{1g}$	...	$A_{2u}(z)$	$E_u(x,y)$	~3
$^5B_{1g} \rightarrow {}^5B_{1g}$	$A_{2u}(z)$	...	$E_u(x,y)$	~$^3/_2$
$\rightarrow {}^5B_{2g}$	...	...	$E_u(x,y)$	$\gg$1
$\rightarrow {}^5E_g$	$E_u(x,y)$	$E_u(x,y)$	$A_{2u}(z)$	~1

[a] All vibrations equally efficient.

On this basis, the symmetry properties of the absorption bands have been assigned as follows.

$^5B_{1g} \longrightarrow {}^5A_{1g}$ or $^5B_{1g}$	12,750 cm.$^{-1}$
$\longrightarrow {}^5B_{2g}$	18,200 cm.$^{-1}$
$\longrightarrow {}^5E_g$	21,000 cm.$^{-1}$

The correlation between the odd vibrations of an octahedron, MX_6, and those generated in a tetragonally distorted D_{4h} model is shown below and the vibrations are pictorially displayed in Figure 3.

O_h	D_{4h}
$2t_{1u}$	$2a_{2u} + 2e_u$
t_{2u}	$b_{2u} + e_u$

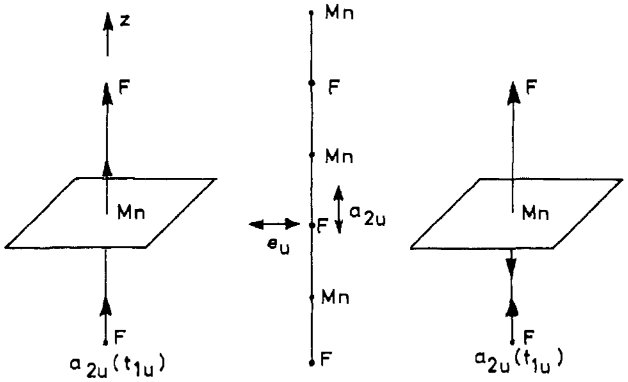

Figure 3.—Metal–ligand vibrations in the $(NH_4)_2MnF_5$ crystal.

As shown in the figure, the a_{2u} modes (which may be mixed) represent essentially symmetrical and antisymmetrical stretching motions along the ···F–Mn–F–Mn··· chain, whereas their associated e_u components are mostly chain bending modes.

The b_{2u} mode also has most motion along the chain, although in this case the motion represents a bending of the F–Mn–F bonds that lie at right angles to the F–Mn–F chain. The associated e_u mode likewise represents a bending of the infinite Mn–F chain.

If it is the a_{2u} modes that are most efficient, then, because the motion along the chain must be strongly inhibited relative to that involving the free fluorine atoms, these particular vibrations can be expected to have considerably lower frequencies than their e_u counterparts. Since the spectra do not display any strong temperature dependence between 300 and 77°K. it can be anticipated that the important, ground-state, odd vibrations are considerably less than 200 cm.$^{-1}$, and these could easily correspond to the a_{2u} modes described above.

The question of the parentage of these vibronic levels in octahedral symmetry is of some importance. This is so because in the D_{4h} model there can be a maximum of three spin-allowed d–d transitions (in addition there are a number of spin-forbidden transitions), but there are arguments against assigning the three more intense transitions to such a set of d–d transitions.

Firstly, there seems little doubt that the levels identified here as $^5B_{2g}$ and ^5E_g arise from $^5T_{2g}$ of O_h.

The ~13,000 cm.$^{-1}$ absorption is not so easily dealt with. If, for instance, the effective symmetry is less than tetragonal it may be the third component of $^5T_{2g}$ of O_h. The splitting of $^5T_{2g}$ would then be very large, and in view of the assignment of the $^5B_{2g}$ and ^5E_g components in D_{4h} this alternative does not seem likely.

The theory[11] predicts a number of spin triplets, arising from the ^3H, ^3P, ^3G, and ^3F atomic terms, to be in the visible–near-infrared region. The weak, sharp lines observed in the range 15,000–25,000 cm.$^{-1}$ must surely represent some of these quintet–triplet transitions but probably not the $^3T_{1g}$ component of the ^3H term. This latter level has been assumed by some authors[2a,3,4–6] to be responsible for the relatively intense near-infrared band in some tris bidentate Mn(III) complexes. The present author[7] has suggested an alternative assignment involving a strongly Jahn-Teller distorted ground state in those complexes although a recent X-ray study[12] on tris(acetylacetonato)-manganese(III) has indicated such an interpretation to be inappropriate, at least in that complex. On the basis of a more extended investigation[13] it seems likely that the near-infrared band, in the complexes where the ligands bind through oxygen or sulfur atoms, can be explained not as a d–d transition but as a charge-transfer excitation involving oxygen or sulfur π orbitals and the metal d orbitals.

In the present case, if the transition is a quintet-triplet and if mixing, *via* spin–orbit coupling, to $^5T_{2g}$ is important, then the absorption appears to have the wrong polarization properties. Furthermore, Griffith[14] has calculated a zero mixing coefficient between $^3T_{1g}$ and $^5T_{2g}$ in octahedral symmetry. In addition, there are other spin-forbidden transitions that have the same symmetry properties and that lie closer to $^5T_{2g}$ that show no enhanced intensity, and it is concluded that the transition is probably not to do with the $^5E_g \rightarrow {}^3T_{1g}(^3H)$ transition of O_h. Mixing of $^3T_{1g}$ with charge-transfer states could give rise to the observed polarizations, but if this is the case very large mixing coefficients must be introduced, especially in the fluoro complex.

The only other d–d transition that can be introduced is that arising from a transition between the two components of the $^5E_g(O_h)$ ground state, split by the tetragonal field in the crystal. Such tetragonal splittings are large; 12,750 cm.$^{-1}$ in the ground state and 2800 cm.$^{-1}$ in the excited state. Values of the axial parameters *Ds* and *Dt*, calculated from such splittings, are very large and of the same order of magnitude as *Dq* and are thus not meaningful.[15] Tetragonal fields of this magnitude have been invoked before, for instance by Holmes and McClure[16] and by Ballhausen and Gray.[17] The latter case is supported by good evidence, although in the former case this does not appear to be the case. The present example seems to fall between these two "extremes," since a bond elongation of 0.27 Å. is not inconsiderable and it might be expected to have a profound influence on the spectrum. Even so the spectrum requires the ground-state distortion to be very large and without further evidence it is dangerous to assign the transition in this manner.

The final alternative is that the absorption band is not d–d in origin but that it represents a ligand-to-metal charge-transfer transition. If this is the case and if the transition is parity forbidden but spin-allowed, then the intensity is reasonable and the excited state may be either $^5A_{1g}$ or $^5B_{1g}$. If the transition is both parity and spin-forbidden then the polarization data do not allow an assignment of the symmetry properties.

A similar band has been observed in Mn(III)–HCl solutions[13,18] but not in a KBr disk containing the $MnCl_6^{3-}$ ion.[19] If the solution result is due to an essentially octahedral or tetragonal complex of the type being discussed here, then the correspondence between the chloro and the fluoro complexes is difficult to explain. Perhaps the solid disk spectrum is the more reliable, although in a variety of oxygen-binding D_{4h} Mn(III) complexes an absorption has been observed[13] at about the same region, both in solution and in crystals.[20]

At the present time we are unable to decide which

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[11] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

[12] B. Morosin and J. R. Brathovde, *Acta Cryst.*, **17**, 705 (1964).

[13] R. Dingle, to be published.

[14] J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, 1961.

[15] In D_{4h}, the transition energy of $^5B_{1g} \rightarrow {}^5B_{2g}$ represents the value of 10*Dq* that would be obtained for a regular octahedral complex of the type MnF_6^{3-}. Hence $\Delta_F = 18{,}500$ cm.$^{-1}$ and in a regular octahedron of fluoride ions the transition $^5Eg \rightarrow {}^5T_{2g}$ should occur at this energy.

[16] O. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).

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[18] J. A. Ibers and N. Davidson, *J. Am. Chem. Soc.*, **72**, 4744 (1950).

[19] W. E. Hatfield, R. C. Fay, C. E. Pluger, and T. S. Piper, *ibid.*, **85**, 265 (1963).

[20] It is difficult to imagine a charge-transfer level in this region in a fluoro complex whereas it is not unreasonable in the case of the oxygen-binding ligands. In solution, the existence of complexes of the type MnF_5OH^{3-}, $MnF_5H_2O^{2-}$, etc., cannot be ruled out, although it is not likely that the crystal contains impurities sufficient to give rise to a band of such intensity. It must be noted, however, that in a two-dimensional X-ray study it would be rather difficult to distinguish F^- and OH^-.

of the above alternatives is the best since, in each case, there seems good reasons for *not* accepting any particular assignment of the 12,750 cm.$^{-1}$ absorption.

On dissolving this complex (or $K_2MnF_5 \cdot H_2O$) in 40% hydrofluoric acid it is thought that a MnF_6^{3-} complex ion is formed.[21] Recently it has been demonstrated[22] that in <6 *M* perchloric acid solutions containing Mn(III) and a large excess of Mn(II) the ion $Mn(H_2O)_5OH^{2+}$ exists. Furthermore, when free fluoride ion is added, it has been suggested[23] that a complex $Mn(H_2O)_5F^{2+}$ is formed.

In the present experiments (in 40% HF with and without excess F^-) the spectrum has been found to be very sensitive to the $Mn(III)/F^-$ ratio in the solutions, thus agreeing with the previous reports.[21,23] The spectrum shown in Figure 2 is that observed when a large excess of fluoride ion is present, and the absorbing species is thought to be anionic,[21] and, from the correspondence between solution and crystal, both in terms of energy and intensity, we consider the absorbing complex to be MnF_6^{3-}. We cannot, however, rule out complexes of the type $MnF_x(H_2O)_y^{3-x}$ where $x \geq 4$ and $y \leq 2$.

Under normal circumstances the MnF_6^{3-} units in solution should have a regular octahedral configuration, but since the ground state is $^5E_g(O_h)$ a large Jahn–Teller distortion may be anticipated. The correspondence between the crystal and the solution spectrum, Figure 2, indicates that if a single absorbing species is present then it exists in a conformation that is as distorted as that seen in the crystal.

Presently we prefer to think that single MnF_6^{3-} units exist in the solution and that the assignments discussed for the crystal may be transferred directly to the solution spectrum. Even if the actual assignments, especially with regard to the 12,750 cm.$^{-1}$ absorption, are in doubt, the correspondence between the spectrum of the tetragonally distorted ammonium pentafluoromanganate and that of the solution must be considered as strong evidence for a distorted ground-state conformation, perhaps of a Jahn–Teller origin for the complex in solution.

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Raman Spectra of Crystalline Chlorothallates

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Raman spectra have been obtained for a series of crystalline compounds containing the complex anions $TlCl_6^{-3}$, $TlCl_5^{-2}$, $Tl_2Cl_9^{-3}$, and $TlCl_4^-$. Comparison with solution spectra leads to the conclusion that addition of chloride to aqueous $TlCl_4^-$ involves a tetrahedral–octahedral transition, although both structures are somewhat distorted by water.

Introduction

Raman spectra of chloride complexes of thallium(III) have recently been determined in aqueous solution.[1] The solution data raise some questions about the structures of the complexes which seemed worth exploring further through investigation of crystalline materials containing these species. A number of chlorothallate salts can be prepared and several crystal structures have been determined. Thus, $K_3TlCl_6 \cdot 2H_2O$ contains $TlCl_6^{-3}$ octahedra,[2] while $Cs_2TlCl_5 \cdot H_2O$ contains square pyramidal $TlCl_5^{-2}$,[3] with a water molecule occupying the sixth octahedral position. In $Cs_3Tl_2Cl_9$, on the other hand, the complex consists of two octahedra fused at a face.[4] The tetrachloro complex in crystalline $(C_6H_5)_4AsTlCl_4$ is tetrahedral.[5] Raman spectra arising from these structural units are presented in this work and their implications for the structures of chlorothallates formed in solution are discussed.

Experimental

The crystalline compounds of known structure were prepared following the methods of the investigators who determined the structure. Thus $K_3TlCl_6 \cdot 2H_2O$[2] and $Cs_3Tl_2Cl_9$[4] were prepared according to Hoard and Goldstein, $Cs_2TlCl_5 \cdot H_2O$ according to Watanabe and Atoji,[3] and $(C_6H_5)_4AsTlCl_4$ according to Cotton, *et al.*[5] In addition, $K_2TlCl_5 \cdot 2H_2O$ and the pyridinium salt of $TlCl_4^-$, $(C_5H_5NH)TlCl_4$, were prepared according to Meyer,[6] and $(CH_3)_4NTlCl_4$ was prepared according to Cotton, *et al.*[5] In all cases the method consisted of adding a proper amount of a solution containing the appropriate chloride salt to a solution of

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