

Short Communication

Electronic spectrum of potassium pentafluoromanganate(IV)

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Few compounds of type AMF_5 are known and only the manganese salts have been investigated in any detail. Unlike the isoelectronic hexafluoro complex, $KMnF_5$ is rather unstable in aqueous HF and a dry technique must be used for its preparation. Peacock and Sharp¹ observed infrared peaks for $KMnF_5$ at 614 and 641 cm^{-1} as compared with 622 cm^{-1} for K_2MnF_6 , and since a discrete MnF_5^- ion would be expected to absorb at a much higher frequency than the MnF_6^{2-} ion, the results suggest that $[MnF_6]$ octahedra are present in the crystal structure.

Clark and Sadana² suggested that $KMnF_5$ has a hexagonal-type lattice, but the precise structure is not known and to our knowledge the electronic spectrum has not hitherto been reported. The diffuse reflectance spectrum of this salt measured at room temperature is shown in Figure 1 and the results are summarised in Table 1. The spectrum was also measured at 77°K but no significant difference was observed. An interesting feature of the spectrum is the rather high intensity of the spin-allowed d-d transitions with respect to those observed for the MnF_6^{2-} and the other 4-valent metal-fluorine complexes³. This, combined with the considerable splitting of the bands, suggests that the octahedrally-coordinated Mn^{IV} ion in $KMnF_5$ undergoes a substantial distortion which results in the disappearance of the centre of inversion. Clearly, a number of possible distortions exist the most probable of which include C_{3v} (D_{3d}), C_{4v} (D_{4h}) or C_{2v} and lower symmetries. The symmetries C_{4v} and C_{3v} are discussed below. C_{2v} symmetry is thought unlikely since the first absorption is observed as a symmetrical and relatively sharp absorption indicating that the first level is not split appreciably. Perumareddi⁴ studied the electronic configurations d^3 and d^7 in non-cubic fields and reported a comparative correlation between the spectra of the octahedrally-coordinated complexes $[Cr(NH_3)_6]X_3$ (quadrately distorted). The spectrum of $KMnF_5$ can be interpreted on a similar basis. In a quadrately-distorted octahedral field, C_{4v} , the cubic field levels split as shown in Figure 2.

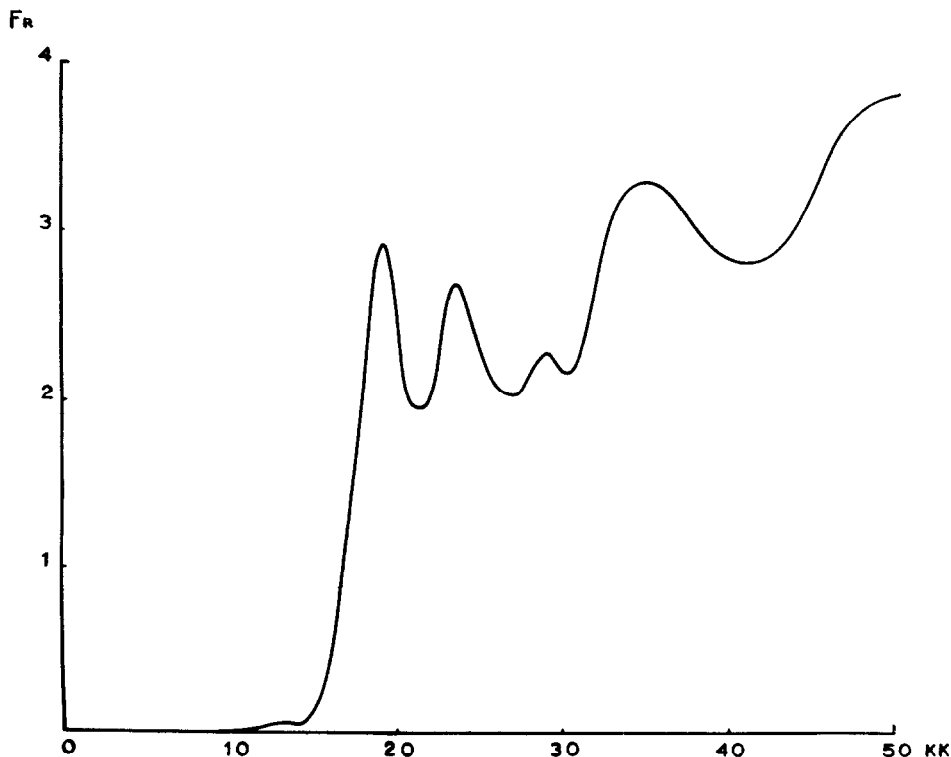


Fig. 1. Diffuse reflectance spectrum of potassium pentafluoromanganate(IV).

Thus, instead of the two bands of the ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4A_{1g}$ transitions observed for MnF_6^{2-} , four bands are expected for the quadrately-distorted $[MnF_6]$ entity in $KMnF_5$ due to the splitting of the triply-degenerate states each into two components. However, as Perumareddi has already shown, it is possible that the 4B_2 component of ${}^4T_{2g}$ and the 4A_2 component of ${}^4T_{1g}(F)$ can come so close to each other that they become nearly degenerate with unresolvable separation, so that only three spin-allowed transitions may be observed. The spectrum shows three spin-allowed d-d bands at 19.38, 23.64 and 28.57 kK which can be assigned as ${}^4B_1 \rightarrow {}^4E$, ${}^4B_1 \rightarrow {}^4B_2$, 4A_2 and ${}^4B_1 \rightarrow {}^4E$ transitions, respectively. Transitions to the two components of the ${}^4T_{1g}(P)$ appear to be obscured by the Laporte-allowed charge-transfer transition at 35.46 kK, and the low-energy position of the charge-transfer band with respect to that observed for MnF_6^{2-} is an indication of the highly oxidising nature of the metal ion. The spectrum also shows a very weak and rather broad absorption at 13.0 kK which can be assigned as a spin-forbidden excitation to the four components 2A_1 , 2B_1 (of 2E_g) and 2E , 2A_2 (of ${}^2T_{1g}$), though the bands are not resolved and only their envelope could be observed, even at 77°K.

TABLE 1
DIFFUSE REFLECTANCE SPECTRUM OF POTASSIUM PENTAFLUOROMANGANATE(IV)

Absorption maxima observed (kK)	C _{4v} Symmetry		C _{3v} Symmetry		Absorption maxima calculated (kK)	Assignment (1)	Assignment (2)
	Absorption maxima calculated (kK)	Assignment	Absorption maxima calculated (kK)	Assignment (1)			
13.0		${}^4B_1 \rightarrow {}^2A_1, {}^2B_1,$ ${}^2E, {}^2A_2$		${}^4A_2 \rightarrow {}^2A_1, {}^2A_2,$ ${}^2E, {}^2A_2$		${}^4A_2 \rightarrow {}^2A_1, {}^2A_2,$ ${}^2E, {}^2A_2$	
19.38	19.36	${}^4B_1 \rightarrow {}^4E$	19.77	${}^4A_2 \rightarrow {}^4E$	20.98	${}^4A_2 \rightarrow {}^4A_1$	${}^4A_2 \rightarrow {}^4A_1$
23.64	23.64	$\left\{ \begin{array}{l} {}^4B_1 \rightarrow {}^4B_2 \\ {}^4B_1 \rightarrow {}^4A_2 \end{array} \right.$	22.36 24.71	${}^4A_2 \rightarrow {}^4A_1$ ${}^4A_2 \rightarrow {}^4E$	22.69 26.08	${}^4A_2 \rightarrow {}^4E$ ${}^4A_2 \rightarrow {}^4A_2$	${}^4A_2 \rightarrow {}^4E$ ${}^4A_2 \rightarrow {}^4A_2$
28.59	28.59	${}^4B_1 \rightarrow {}^4E$	27.55	${}^4A_2 \rightarrow {}^4A_2$	28.78	${}^4A_2 \rightarrow {}^4E$	${}^4A_2 \rightarrow {}^4E$
35.46		Charge transfer		Charge transfer			Charge transfer
		Fitting parameters (cm ⁻¹) $Dq = 2364; Ds = -830;$ $Dt = -417; B = 485.$		Fitting parameters (cm ⁻¹) $Dq = 2309; Ds = 189;$ $Dt = 614; B = 427.$		Fitting parameters (cm ⁻¹) $Dq = 2032; Ds = -189;$ $Dt = -477; B = 507.$	

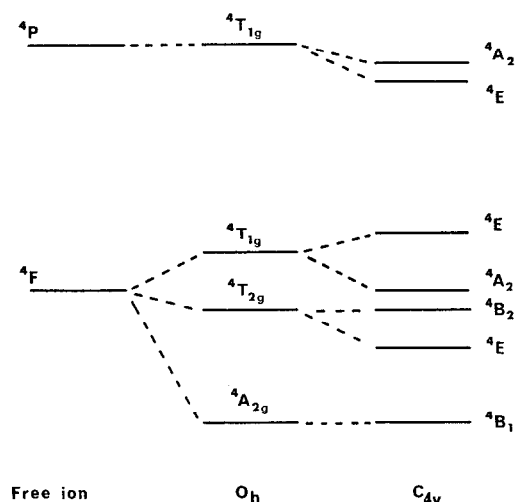


Fig. 2. Energy levels of type d^3 in octahedral (O_h) and quadrate, C_{4v} , environments.

The spectra were fitted using the secular energy matrices for a d^3 configuration derived by Perumareddi⁴. The parameters so obtained are dependent on the exact peak positions but a good fitting was given by the parameters $Dq = 2364 \text{ cm}^{-1}$, $Ds = -830 \text{ cm}^{-1}$, $Dt = -417 \text{ cm}^{-1}$, $B = 485 \text{ cm}^{-1}$. (For K_2MnF_6 , the corresponding values are $Dq = 2200 \text{ cm}^{-1}$ and $B = 587 \text{ cm}^{-1}$.)

Possible alternative assignments for the spin-allowed transitions include (a) ${}^4B_1 \rightarrow {}^4E$, ${}^4B_1 \rightarrow {}^4B_2$, 4E , ${}^4B_1 \rightarrow {}^4A_2$ and (b) ${}^4B_1 \rightarrow {}^4B_2$, ${}^4B_1 \rightarrow {}^4E$, 4A_2 , ${}^4B_1 \rightarrow {}^4E$. These, however, can be eliminated since a negative value for the ratio Ds/Dt is required in both cases.

Calculations were also carried out for trigonal distortion using the appropriate matrices given by Perumareddi⁴. Two possible assignments requiring positive values for the ratio D_σ/D_τ exist, *i.e.* (i) ${}^4A_2 \rightarrow {}^4E$, ${}^4A_2 \rightarrow {}^4A_1$, 4E , ${}^4A_2 \rightarrow {}^4A_2$ and (ii) ${}^4A_2 \rightarrow {}^4A_1$, ${}^4A_2 \rightarrow {}^4E$, 4A_2 , ${}^4A_2 \rightarrow {}^4E$. As Table 1 shows, the fittings are not as good as those obtained for the C_{4v} group, but in the absence of detailed structural information this does not rule out the existence of C_{3v} symmetry in this system.

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