

The Electronic Structure of Trigonally Distorted Iron(III) Complexes

S. HOLT* and R. DINGLE**

Chemical Laboratory IV, Department of Physical Chemistry, The University of Copenhagen, Copenhagen, Denmark

The 20°K spectra of two trigonally distorted iron(III) complexes are reported. It is shown that while the absorption spectra of high spin iron(III) complexes may be assigned on energy grounds no detailed information as to the nature of the $d-d$ transitions may be obtained from polarization data.

While the optical spectra of Mn^{2+} (d^5) ion in an octahedral field are well characterized, the spectra of the isoelectronic Fe^{3+} species are not well known. The first detailed work on Fe^{3+} was that of Piper and Carlin who reported the polarized spectra of the trigonally distorted species $NaMgFe(Ox)_3$ and $(Fe,Al)(acac)_3$ at 77°C.¹ More recently Hatfield has reported the spectrum of $[Fe(mal)_3]^{3-}$.² As part of an investigation of Fe^{3+} in various environments we wish to report a more detailed assignment of the spectrum of $NaMgFe(Ox)_3$ and to point out some differences which exist between it and the spectrum of similarly trigonally distorted $Fe(urea)_6(ClO_4)_3$.

EXPERIMENTAL

Large single crystals of $NaMgFe(C_2O_4)_3 \cdot 9H_2O$ were grown in a manner analogous to that reported by Piper and Carlin.¹

$Fe(urea)_6(ClO_4)_3$ was prepared by mixing stoichiometric amounts of $Fe(ClO_4)_3 \cdot 6H_2O$ and urea in a weak perchloric acid solution. On standing pale green hexagonal plates appeared.

Spectra have been recorded using the Cary Model 14 spectrophotometer. Low temperature spectra have been obtained using a Cryo-Tip liquid hydrogen cryostat. Polarized spectra were obtained in a manner analogous to that described in previous publications from this laboratory.³

$NaMgFe(Ox)_3 \cdot 9H_2O$ is isomorphous with $NaMgCr(Ox)_3 \cdot 9H_2O$. The space group of $NaMgCr(Ox)_3 \cdot 9H_2O$ was determined by Frossard to be $P\bar{3}c1$ with 2 molecules per

* Present address: Polytechnic Institute of Brooklyn, 333 Jay Street, Brooklyn, New York 11201, USA.

** Present address: Bell Telephone Laboratories, Inc., Murray Hill, New Jersey, USA.

unit cell.⁴ The $[\text{Cr}(\text{Ox})_3]^{3-}$ site symmetry would thus be D_3 . Frossard's data have been shown to be in error however.⁵ The correct data yield 6 molecules per unit cell and space group $P\bar{3}c1$ or $P3c1$. This provides the choice of C_2 or C_3 and D_3 site symmetries for space group $P\bar{3}c1$. For space group $P3c1$ the choice is C_1 or C_3 . As a complete structure analysis was not attempted no choice between the possibilities can be made. Recent spectroscopic work,⁶ however, indicates that optical data for the chromium system can be accounted for by assuming that the effective symmetry of the $[\text{Cr}(\text{Ox})_3]^{3-}$ ion is D_3 .

$\text{Fe}(\text{urea})_6(\text{ClO}_4)_3$ is isomorphous with $\text{Cr}(\text{urea})_6(\text{ClO}_4)_3$. In $\text{Cr}(\text{urea})_6(\text{ClO}_4)_3$ the metal ion is reported to be on a site of D_3 symmetry.⁷

RESULTS

$\text{Fe}(\text{urea})_6(\text{ClO}_4)_3$. The room temperature spectrum of $\text{Fe}(\text{urea})_6(\text{ClO}_4)_3$ exhibits two broad bands at low energy. The first band occurs at 12 800 cm^{-1} in the σ polarization and 12 700 cm^{-1} in the π polarization. The second band exhibits a σ component at 17 000 cm^{-1} and a π component at 16 500 cm^{-1} . On cooling to 20°K the absorption maxima are shifted to lower energy. There is also a slight increase in ϵ and a splitting appears in the lowest σ component.

Table 1. Band maxima and extinction coefficients.

$\text{Fe}(\text{urea})_6(\text{ClO}_4)_3$			$\text{NaMgFe}(\text{Ox})_3$		
	Band max. cm^{-1}	ϵ		Band max. cm^{-1}	ϵ
σ	11 750	0.17	σ	10 500	0.95
σ	12 600 (sh)	—	σ	15 000	1.13
π	12 000	0.13	π	10 750	0.05
σ	16 700	0.38	π	15 000	0.09
π	15 900	0.27			
σ	22 990	0.70	σ	22 130	2.00
σ	23 320	0.60	σ	22 350 (sh)	—
σ	23 530 (sh)	—	π	22 130	4.40
π	22 990	3.15	π	22 380	3.02
π	23 250 (sh)	—			
π	23 320	3.90			
π	23 600 (sh)	—			
π	23 950 (sh)	—			
σ	~25 500 (sh)	—			
σ	~25 700 (sh)	—			
σ	~26 000 (sh)	—			

A band system in the visible is also observed at room temperature. This system consists of two maxima, one at 23 030 cm^{-1} and another at 23 320 cm^{-1} and exhibits strong polarization behavior. Higher energy transitions are masked by the onset of an allowed transition. On cooling to 20°K, in contrast with the near IR system, no shift in maxima occur and fine structure appears.

Of further interest is the appearance at liquid H_2 of a band system in the near ultra-violet. As may be seen in Fig. 1, two maxima are present in the σ polarization, $\nu_1 = 25 500 \text{ cm}^{-1}$ and $\nu_2 = 25 700 \text{ cm}^{-1}$ but only a broad absorp-

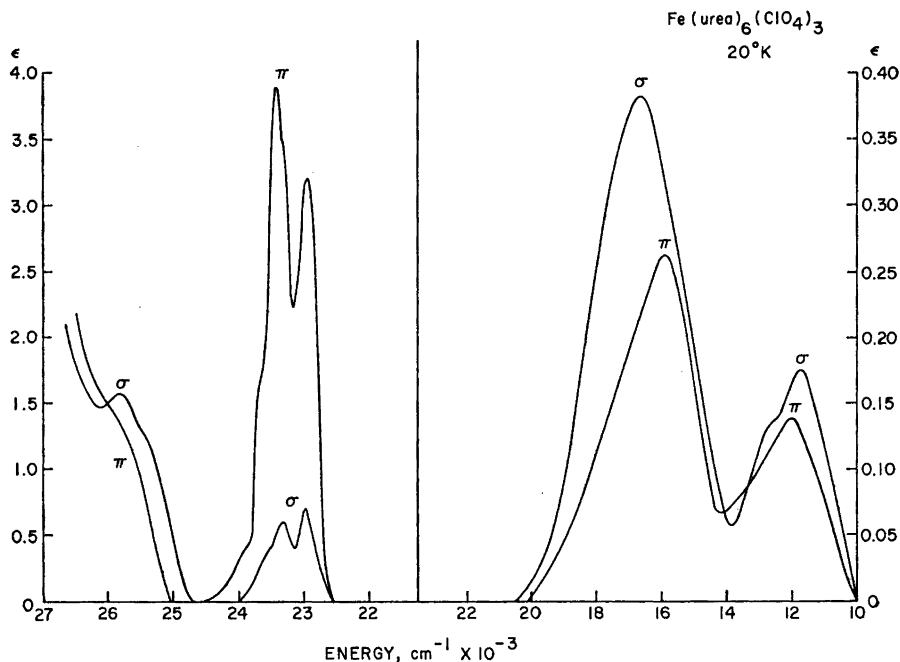


Fig. 1. The 20°K spectrum of $\text{Fe}(\text{urea})_6(\text{ClO}_4)_3$.

tion at $\approx 26\,000$ is present in the π direction. The axial and σ spectra are coincident indicating that the observed transitions are electric dipole in nature.

$\text{NaMgFe}(\text{Ox})_3$. Our spectra of $\text{NaMgFe}(\text{Ox})_3$ agree in overall character with those reported by Piper and Carlin¹ with the exception that there appears to be a 300–500 cm^{-1} difference in the respective reported band maxima. We also find that the bands exhibit little temperature dependence.

The spectrum of $\text{NaMgFe}(\text{Ox})_3$, recorded at 20°K, is exhibited in Fig. 2. As can be seen, the near IR bands are allowed in the σ polarization and almost completely forbidden in the π polarization. The visible system, in contrast is strongly allowed in the π direction and only moderately reduced in intensity in the σ direction.

DISCUSSION

In spin free d^5 systems there exists an orbital configuration $t_{2g}^3 e_g^2$ leading to a 6A_1 ground electronic state. As all electronic excitations lead to a spin change, there are only doublet and quartet excited states. All transitions must therefore be spin forbidden. Spectra are observed, however, for both Mn^{2+} and Fe^{3+} ions. There are two mechanisms by which these transitions may become weakly allowed; through spin-orbit mixing with spin allowed

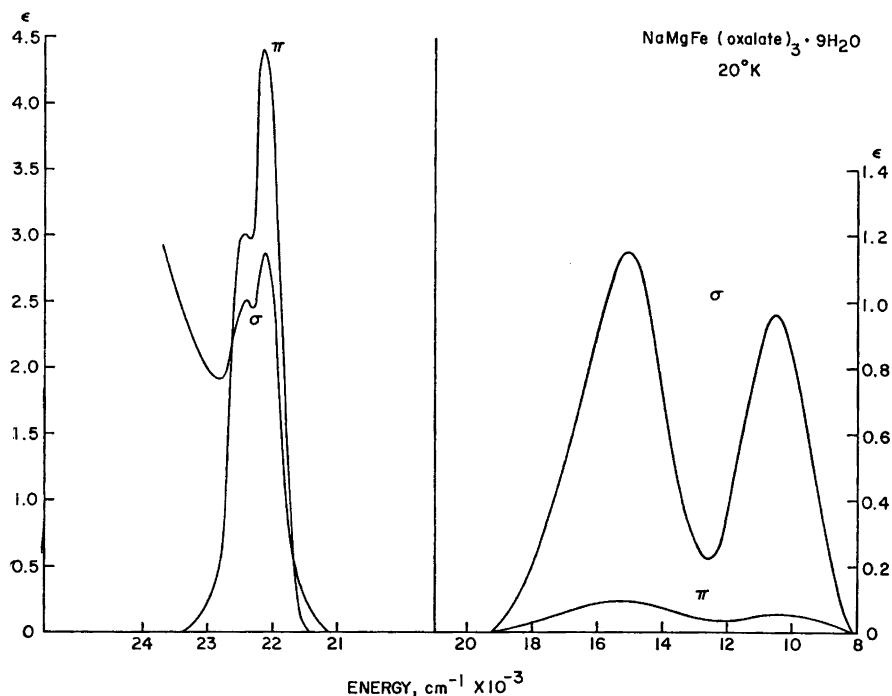


Fig. 2. The 20°K spectrum of $\text{NaMgFe}(\text{Ox})_3 \cdot 9\text{H}_2\text{O}$.

transitions or by magnetic exchange interaction. Ignoring the latter mechanism (the materials under discussion are reasonably magnetically dilute)⁶ and concentrating on the spin-orbit process we note that intensity transfer may occur through coupling with either intraligand or charge transfer transitions. This coupling will occur *via* matrix elements of the type $\langle {}^4X|l \cdot s|{}^6Y \rangle$ where 6Y is some excited state localized on the ligand to which transitions from the 6A_1 ground state is allowed. Thus, in order to explain the polarization behavior

Table 2. Selection rules for D_3 and D_3' .

	Transition	Allowed
D_3	$A_1 \rightarrow E$	σ
	$A_1 \rightarrow A_2$	π
	$A_1 \rightarrow A_1$	forbidden
D_3'	$\Gamma_4^4 \rightarrow \Gamma_4^4$	σ and π
	$\Gamma_4^4 \rightarrow \Gamma_5^4$	σ
	$\Gamma_4^4 \rightarrow \Gamma_6^4$	σ
	$\Gamma_5^4 \rightarrow \Gamma_5^4$	π
	$\Gamma_5^4 \rightarrow \Gamma_6^4$	forbidden
	$\Gamma_6^4 \rightarrow \Gamma_6^4$	π

of any d^5 system we must concern ourselves with the selection rules governing the electronically allowed transitions and the relative magnitude of the appropriate matrix elements.

$NaMgFe(Ox)_3$. As we may see from Table 2, in D_3 symmetry the ${}^6A_1 \rightarrow {}^6E$ transition is xy allowed, the ${}^6A_1 \rightarrow {}^6A_2$ transition is z allowed while the ${}^6A_1 \rightarrow {}^6A_1$ transition is symmetry forbidden. Comparing double group representations which are held in common between 6A_1 , 6A_2 , 6E , 4A_2 , 4A_1 , and 4E states, we may predict the polarizations which can occur. From Table 3 we see that in the D_3' double group all quartet and all sextet states under consideration contain representations of Γ_4 and $\Gamma_{5,6}$ symmetry. We could therefore reasonably expect absorption bands for all ${}^6A_1 \rightarrow {}^4X$ transitions in both σ and π polarizations. This symmetry treatment while predicting the possible polarizations cannot tell us what the intensities of a transition will be in a given polarization, however. This is determined by the mixing of states having different multiplicity, *i.e.*:

$$\psi' = \psi({}^4X) + \sum_j \frac{\int \psi({}^4X) \left[\sum_i \zeta_{ni} l_i s_i \right] \psi_j({}^6Y) d\tau}{E_a - E_j} \cdot \psi_j({}^6Y) \quad (1)$$

where the square of mixing coefficient, \sum_j , determines the transition probability. Abbreviating the expression \sum_j , we have, in terms of oscillator strength $f_{4,6} = f^\circ (a\zeta_{ni}/\Delta E)^2$ or that the oscillator strength of the spin forbidden transition is dependent on the product of the oscillator strength of the spin allowed transition times the square of the mixing coefficient. Therefore, intensities of

Table 3. Correlation table $O_h \rightarrow D_3'$.

O_h	D_3	D_3'
6A_1	6A_1	$2\Gamma_4 + (\Gamma_5, \Gamma_6)$
6A_2	6A_2	$2\Gamma_4 + (\Gamma_5, \Gamma_6)$
6E	6E	$3\Gamma_4 + 2(\Gamma_5, \Gamma_6)$
4A_1	4A_1	$\Gamma_4 + (\Gamma_5, \Gamma_6)$
4E	4E	$3\Gamma_4 + (\Gamma_5, \Gamma_6)$
4T_1	4A_2	$\Gamma_4 + (\Gamma_5, \Gamma_6)$
	4E	
4T_2	4A_1	
	4E	

spin forbidden bands are really a function of three separable quantities: the square of the numerator, which includes the spin-orbit coupling constant, the square of the separation between 4X and 6Y states and the oscillator strength of the ${}^6A_1 \rightarrow {}^6Y$ transition. The contribution from the ζ_{ni}^2 term poses a problem in evaluation so will be ignored for now. Needless to say, however, this numerator is very dependent on the wave function for various 4X and 6Y and will therefore have very different values for the various transitions involved.

Looking at the denominator one would expect that the smaller the value of $(\Delta E)^2$ the greater would be the intensity of the transition in question and

if 6Y is much lower in wavelength than any other 6Y the more pronounced would be the polarization behavior of the ${}^6A_1 \rightarrow {}^4X$ excitation. Comparing the two lowest energy bands for both $\text{Fe(urea)}_6(\text{ClO}_4)_3$ and NaMgFe(Ox)_3 we see that this expectation is borne out as the complex with the lowest C-T onset, NaMgFe(Ox)_3 , shows an intensity in its ${}^6A_1 \rightarrow {}^4T_1$ and ${}^6A_1 \rightarrow {}^4T_2$ transitions \sim three times that of the corresponding transitions in $\text{Fe(urea)}_6(\text{ClO}_4)_3$. Although the effect is not quite so dramatic in the third, ${}^6A_1 \rightarrow {}^4E$, transition it is there none-the-less.

It can be seen for NaMgFe(Ox)_3 that the lower two bands are strongly polarized in the σ direction. This occurs because $\Delta E({}^6A_1 \rightarrow {}^6E) < \Delta E({}^6A_1 \rightarrow {}^6A_2)$. In the case of $\text{Fe(urea)}_6(\text{ClO}_4)_3$ polarization is weak because there are both σ and π allowed bands at $\sim 25\,000\text{ cm}^{-1}$.

The visible bands in both the oxalate and hexaurea compounds display some interesting characteristics. First, there appears to be a vibrational mode of $\sim 300\text{ cm}^{-1}$ associated with the $\text{Fe(urea)}_6(\text{ClO}_4)_3$ spectrum. This is in agreement with the infrared active frequency of 330 cm^{-1} reported for $\text{Fe(urea)}_6\text{Cl}_2$.⁹ Secondly, the ${}^6A_1 \rightarrow {}^4A_1$ and ${}^6A_1 \rightarrow {}^4E$ are non degenerate, and thirdly, it is clearly pointed out that assignments of quartet states, in these systems, based on polarization data alone are not very meaningful. The following example serves as an illustration of this point. From our spectra it can be seen that the E state is more strongly coupled with π allowed components for both the urea and oxalate compounds. Even when, as in the case of the oxalate, a σ allowed ${}^6A_1 \rightarrow {}^6E$ transition overlaps with the spin-forbidden band, thereby making $(\Delta E)^2$ small indeed, we still have more intensity in the π component.

Our conclusion then is that, although the observed absorptions in the near infrared and visible regions of the spectrum in these pseudo octahedral iron(III) complexes can be associated with certain spin forbidden $d-d$ transitions on the basis of frequency alone, no assignments can be made of these transitions because the more detailed information made available, *via* the crystal spectra, is still ambiguous.

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