

# THE EFFECT OF TEMPERATURE ON THE ELECTRONIC SPECTRA OF OCTAHEDRAL IRON(II) COMPLEXES

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[Manuscript received August 7, 1968]

## Summary

Spectral changes in iron(II) complexes caused by temperature changes have been examined. When the iron(II) ion is surrounded by six equivalent ligands ( $\text{FeCl}_2$ ,  $\text{FeBr}_2$ ,  $\text{FeI}_2$ ,  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ ) the band separation that arises from the splitting of the  ${}^5E_g$  level decreases on cooling. The variation is proportional to the magnitude of the band separation. In complexes with tetragonal distortion ( $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 2\text{CH}_3\text{OH}$ ,  $\text{FeCl}_2 \cdot 4\text{pyridine}$ ,  $\text{FeCl}_2 \cdot 2\text{pyridine}$ ,  $\text{FeCl}_2 \cdot 4\text{isoquinoline}$ ,  $\text{FeBr}_2 \cdot 4\text{isoquinoline}$ ) the variation in band separation with change in temperature is smaller and is inversely related to the magnitude of the band separation.

The spin-allowed transition  ${}^5T_{2g} \rightarrow {}^5E_g$  in octahedral iron(II) complexes is usually observed in the near-infrared region as an absorption band that is either split into two components or is broad and asymmetric. This may arise from splitting of the  ${}^5E_g$  level as a result of tetragonal distortion of  $O_h$  symmetry when non-equivalent ligands surround the metal atom<sup>1</sup> or may be the result of what is described as a dynamic Jahn–Teller effect by Cotton and Myers.<sup>2</sup> More recently, Hatfield and Piper<sup>3</sup> expressed the view that the distortion in  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  is static rather than dynamic.

Ferrous chloride crystallizes in the rhombohedral system with the space group  $R\bar{3}m$  and with one molecule per rhombohedral cell.<sup>4</sup> The iron atoms occupy positions with symmetry  $\bar{3}m$ . This requires the iron environment to have a threefold symmetry axis, so that any splitting of the  ${}^5T_{2g} \rightarrow {}^5E_g$  transition cannot be the result of a tetragonal distortion. The only permissible distortion is a trigonal one which causes splitting of  ${}^5T_{2g}$ ,<sup>5</sup> but this will be small and is unlikely to be observed. Ferrous bromide and iodide have the hexagonal  $\text{Cd}(\text{OH})_2$  structure, where an analogous situation will also prevail.

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<sup>1</sup> Goodgame, D. M. L., Goodgame, M., Hitchman, M. A., and Weeks, M. J., *Inorg. Chem.*, 1966, **5**, 635.

<sup>2</sup> Cotton, F. A., and Myers, M. D., *J. Am. chem. Soc.*, 1960, **82**, 5023.

<sup>3</sup> Hatfield, W. E., and Piper, T. S., *Inorg. Chem.*, 1964, **3**, 1295.

<sup>4</sup> Pauling, L., and Hoard, J. L., *Z. Kristallogr.*, 1930, **A74**, 546.

<sup>5</sup> Ballhausen, C. J., "Introduction to Ligand Field Theory." (McGraw-Hill: New York 1962.)

In contrast, there is a strong tetragonal distortion of the octahedral metal environment in the dihydrate of  $\text{FeCl}_2$ , whose structure consists of planar chains of metal and chlorine atoms separated by water molecules.<sup>6</sup>

The spectrum of anhydrous  $\text{FeCl}_2$ ,  $\text{FeBr}_2$ , and  $\text{FeI}_2$ , of  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  and the corresponding dimethanolate have been examined in detail, and their variations with temperature are now reported. Included were also  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ , and some heterocyclic amine adducts of  $\text{FeCl}_2$  and  $\text{FeBr}_2$  whose room-temperature spectra were discussed some time ago by Cotton and Myers<sup>2</sup> and Goodgame *et al.*<sup>1</sup>

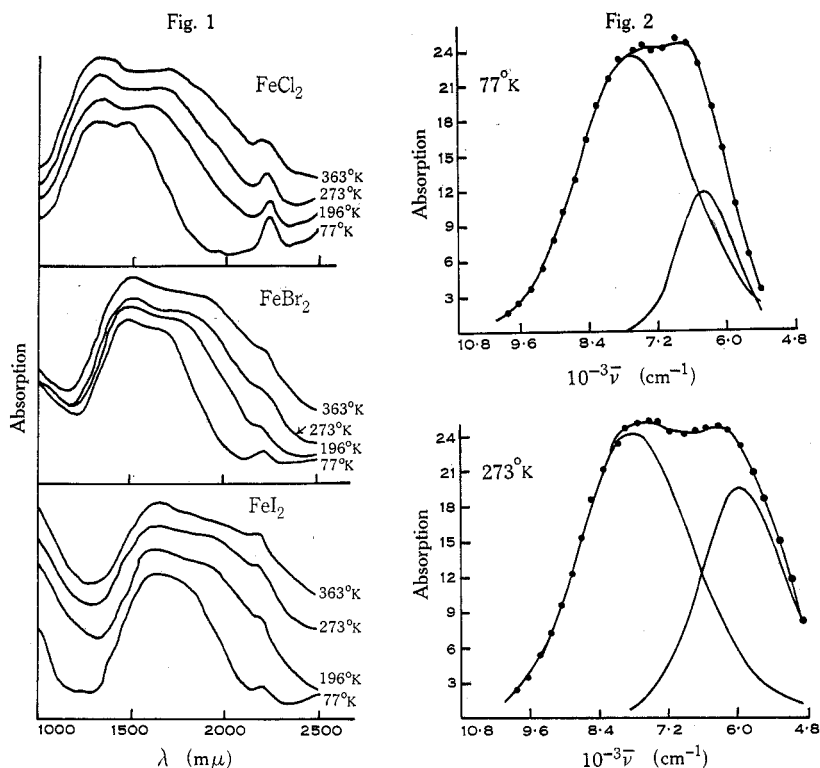


Fig. 1.—Electronic spectra of anhydrous  $\text{FeCl}_2$ ,  $\text{FeBr}_2$ , and  $\text{FeI}_2$ .

Fig. 2.—The two Gaussian components in the spectra of  $\text{FeCl}_2$ . ●, Experimental points; full line, calculated values. (Absorption in arbitrary units.)

## RESULTS

The diffuse reflection of the anhydrous halides in the near-infrared region at temperatures ranging from 77 to 363°K are shown in Figure 1. The broad absorption in the 1200–2000  $\text{m}\mu$  region clearly consists of at least two components whose separation decreases markedly with decrease in temperature. The weak and relatively narrow band at 2200  $\text{m}\mu$  is likely to be vibrational in origin. Using the

<sup>6</sup> Morosin, B., and Graeber, J. E., *J. chem. Phys.*, 1965, **42**, 898.

method of Fraser and Suzuki,<sup>7</sup> and employing their Fortran IV programme for the CDC 3600 computer, the broad electronic bands were resolved into two Gaussian components as shown in Figure 2 for  $\text{FeCl}_2$ . For reflectance spectra such a fitting can only be approximate but is considered satisfactory for this work since relative band positions are being sought. Band positions and half-widths thus obtained for  $\text{FeCl}_2$ ,  $\text{FeBr}_2$ , and  $\text{FeI}_2$  are listed in Table 1. Similarly the spectra of the  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  ions in

TABLE 1  
ELECTRONIC SPECTRA OF  $\text{Fe}^{\text{II}}$  COMPLEXES  
Band positions ( $\bar{\nu}_{\text{max}}$ ), half-widths ( $W_{\frac{1}{2}}$ ), and band separations ( $\delta$ ), in  $\text{cm}^{-1}$

Compound	$T$ ( $^{\circ}\text{K}$ )	1st Band		2nd Band		$10^{-3}\delta$
		$10^{-3}\bar{\nu}_{\text{max}}$	$10^{-3}W_{\frac{1}{2}}$	$10^{-3}\bar{\nu}_{\text{max}}$	$10^{-3}W_{\frac{1}{2}}$	
$\text{FeCl}_2$	363	7.6	2.6	5.6	1.6	2.0
	273	7.6	2.5	5.8	1.4	1.8
	196	7.6	2.5	5.9	1.3	1.7
	77	7.6	2.2	6.4	1.1	1.2
$\text{FeBr}_2$	363	6.8	1.7	5.2	1.5	1.6
	273	6.8	1.6	5.4	1.5	1.4
	196	6.8	1.5	5.5	1.3	1.3
	77	6.8	1.4	5.9	1.0	0.9
$\text{FeI}_2$	363	6.2	1.5	4.9	1.3	1.3
	273	6.1	1.5	4.9	1.1	1.2
	196	6.1	1.4	5.0	1.1	1.1
	77	6.2	1.5	5.4	0.9	0.8
$\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$	290	10.7	3.5	8.3	2.5	2.4
	196	10.8	3.4	8.6	2.4	2.2
	77	10.8	3.2	9.1	2.1	1.7
$\text{FeCl}_2 \cdot 2\text{pyridine}$	290	9.5	3.0	5.3	1.8	4.2
	77	9.9	3.0	5.7	1.4	4.2
$\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$	290	10.0	3.3	6.1	1.9	3.9
	77	10.0	2.5	6.1	1.8	3.9
$\text{FeBr}_2 \cdot 4\text{isoquinoline}$	290	10.9	3.1	7.2	2.0	3.7
	77	11.1	2.8	7.6	1.6	3.5
$\text{FeCl}_2 \cdot 2\text{CH}_3\text{OH}$	290	9.5	2.5	5.8	1.5	3.7
	77	9.7	2.2	6.2	1.5	3.5
$\text{FeCl}_2 \cdot 4\text{isoquinoline}$	290	11.1	4.1	8.7	1.8	2.4
	77	11.2	3.8	9.1	1.7	2.1
$\text{FeCl}_2 \cdot 4\text{pyridine}$	290	10.7	4.2	8.5	2.2	2.2
	77	10.9	3.9	9.1	1.8	1.8
$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	290	10.9	3.3	8.4	1.7	2.5
	77	10.8	3.1	8.8	1.7	2.0

$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and in  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$  were also resolved into two components. For the latter compound the band separation ( $\delta$ ) at room temperature, of  $2400 \text{ cm}^{-1}$  observed in the present study (see Table 1), is somewhat larger than that reported by

<sup>7</sup> Fraser, R. D. B., and Suzuki, E., *Analyt. Chem.*, 1966, **38**, 1770.

Cotton and Myers,<sup>2</sup> but is more in accord with the separation observed for the hexaaquo ion in aqueous ferrous sulphate ( $2100\text{ cm}^{-1}$ ) or in the Tutton salt,  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $2400\text{ cm}^{-1}$ ). The band positions and separations in the spectra at  $290^\circ\text{K}$  of  $\text{FeCl}_2 \cdot 4\text{pyridine}$ ,  $\text{FeCl}_2 \cdot 2\text{pyridine}$ ,  $\text{FeCl}_2 \cdot 4\text{isoquinoline}$ , and  $\text{FeBr}_2 \cdot 4\text{isoquinoline}$  are substantially in agreement with those reported by Goodgame *et al.*<sup>1</sup>

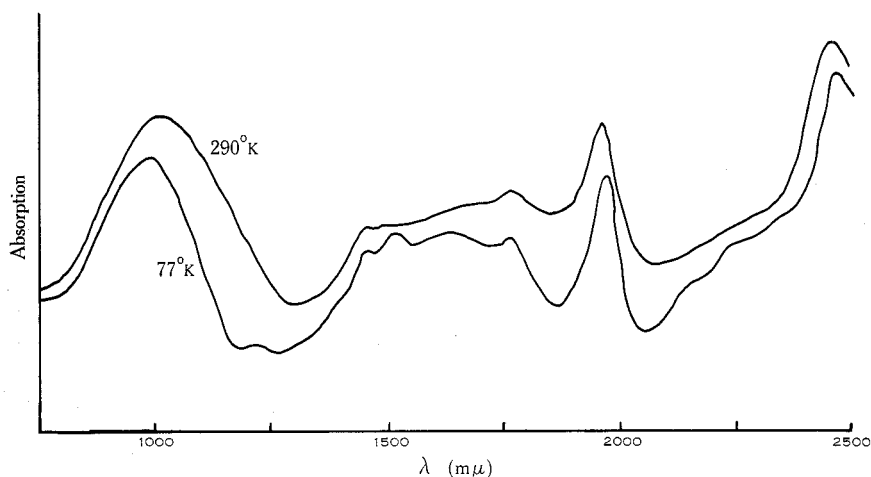


Fig. 3.—Spectra of  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  at  $290^\circ\text{K}$  and  $77^\circ\text{K}$ . (Absorption in arbitrary units.)

The spectra of  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  at  $290^\circ\text{K}$  and  $77^\circ\text{K}$  shown in Figure 3 obviously consist of a number of narrow bands superimposed on two broad bands. Each spectrum may nevertheless be resolved into eight Gaussian components. The widths and intensities of the two major bands leave little doubt that they are electronic transitions, whereas the narrow bands are vibrational. The spectra of the dimethanolate were treated similarly, and the positions and widths of the electronic bands are included in Table I.

#### DISCUSSION

The present series of compounds may be divided into two groups according to the effect of temperature variation on their spectrum. In the first group the broad and asymmetric absorption band in the near-infrared region consists of two overlapping components and there is a gradual decrease in width of both as the temperature is decreased. Although the positions of the high-energy components remain unaltered, the lower-energy components shift towards higher energy on cooling. The variations in separation ( $\delta$ ) with temperature are gradual (see Fig. 4(a)), so that they are unlikely to be the result of a phase change. The variations are proportional to the magnitude of the separations as shown in Figure 4(b), where  $d\delta/dT$  is plotted against  $\delta$  for the values at  $300^\circ\text{K}$ . The compounds exhibiting this behaviour ( $\text{FeCl}_2$ ,  $\text{FeBr}_2$ ,  $\text{FeI}_2$ , and  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ ) have six equivalent ligands surrounding the metal and there is no tetragonal distortion. Cotton and Myers<sup>2</sup> proposed a dynamic Jahn-Teller effect

to explain the splitting in the spectrum of the  $\text{Fe}(\text{H}_2\text{O})_6^{2+}$  ion in  $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ , and it is tempting to extend this explanation to the splitting observed in the spectra of the anhydrous chloride, bromide, and iodide. The general effect of the ligand fields in this series is as expected:  $\text{H}_2\text{O} \gg \text{Cl} > \text{Br} > \text{I}$ . A similar reduction in band separation by cooling  $\text{AgCl}$  and  $\text{AgBr}$ , both doped with  $\text{Fe}^{2+}$ , was reported by Koswig and Kunze<sup>8</sup> who discuss their observation in terms of a dynamic Jahn-Teller effect.\*

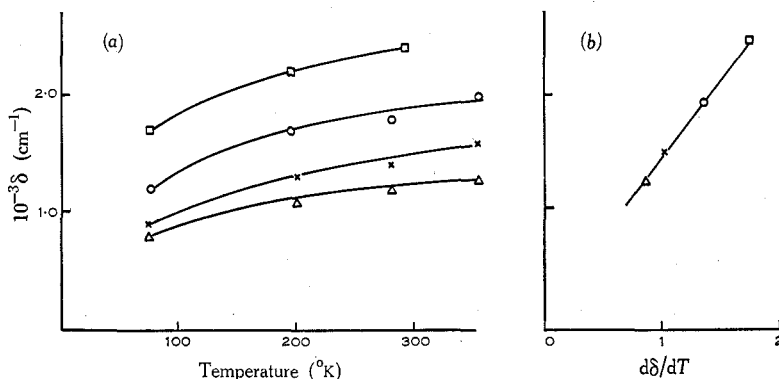


Fig. 4.—(a) Variation of band separation ( $\delta$ ) with change in temperature.  $\square$   $\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ ;  $\circ$   $\text{FeCl}_2$ ;  $\times$   $\text{FeBr}_2$ ;  $\triangle$   $\text{FeI}_2$ . (b) Plot of  $d\delta/dT$  against  $\delta$  for the values at  $300^\circ\text{K}$ .

The absorption observed in the second group is either an asymmetric band that can be resolved into two overlapping components or consists of two well-separated bands. Again, there is a sharpening of the bands at lower temperatures, accompanied sometimes by small shifts towards higher energy. This is probably due to slight increases in ligand field caused by the contraction of the structures on cooling. Contrasting sharply to the behaviour of the compounds in the first group, the variation in the band separation with change in temperature for the second group is much smaller and is inversely related to the magnitude of the separation, becoming unobservable as a band separation of  $4000 \text{ cm}^{-1}$  is approached. The compounds comprising this group are the dihydrate, the dimethanolate, and the heterocyclic amine adducts, where in each case the metal ion is surrounded by non-equivalent ligands and permanent splitting of the  $^5E_g$  level is to be expected. However, a mechanism similar to that observed for the first group appears also to be involved, becoming more pronounced as the effect of permanent distortion decreases.

It is not surprising that the variation in separation for the Tutton salt over a similar temperature range is somewhat greater (see Table 1), where there is a tetragonal distortion of the field, although the  $\text{Fe}^{2+}$  ion is surrounded by identical ( $\text{H}_2\text{O}$ ) ligands.

Thus, there is a clear difference in the behaviour of the two types of compounds; i.e. the ones which do not have a tetragonal distortion show a pronounced temperature-

\* Since this work was completed the results reported by G. D. Jones (*Phys. Rev.*, 1967, **155**, 259) and a discussion on the effect of temperature on the dynamic Jahn-Teller effect by M. D. Sturge (*Solid St. Phys.*, 1967, **20**, 191) have been brought to our notice.

<sup>8</sup> Koswig, H. D., and Kunze, I., *Phys. Status Solidi*, 1965, **8**, 319.

dependent dynamic Jahn-Teller effect, while those with the permanent tetragonal distortion only show this effect when the tetragonal splitting is small.

## EXPERIMENTAL

### Materials

$\text{FeCl}_2$ ,  $\text{FeBr}_2$ , and  $\text{FeI}_2$  were prepared by dissolving high-purity iron wire in the appropriate aqueous mineral acid. The mineral acids were de-aerated, and a blanket of inert gas was maintained over the liquid. After filtration and evaporation the solid was heated to  $200^\circ\text{C}$  for 4 hr under reduced pressure. ( $\text{FeCl}_2$ —Found: Fe, 55.9; Cl, 43.7. Calc.: Fe, 55.9; Cl, 44.1%.  $\text{FeBr}_2$ —Found: Fe, 25.9; Br, 73.8. Calc.: Fe, 25.9; Br, 74.1%.  $\text{FeI}_2$ —Found: Fe, 18.3; I, 80.9. Calc.: Fe, 18.1; I, 81.9%.)

$\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  was prepared as described for  $\text{FeCl}_2$ , but omitting the heating at  $200^\circ\text{C}$ . (White crystals. Found: Fe, 34.5; Cl, 43.0; H, 2.4. Calc.: Fe, 34.3; Cl, 43.6; H, 2.5%.)

$\text{FeCl}_2 \cdot 2\text{CH}_3\text{OH}$  was prepared as described for  $\text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  but substituting methanolic HCl for the aqueous acid. (Pale green crystals. Found: Fe, 19.5; Br, 56.3; C, 8.3; H, 2.9. Calc.: Fe, 20.0; Br, 57.3; C, 8.6; H, 2.8%.)

$\text{FeSiF}_6 \cdot 6\text{H}_2\text{O}$ .—Silicic acid was added to approx. 50% aqueous hydrofluoric acid in a polythene beaker until reaction ceased. Iron powder was then added and the suspension heated under a blanket of inert gas until solution was completed. The pale green needles appearing on cooling were separated by filtration. (Found: Fe, 18.0; F, 37.5; H, 3.8. Calc.: Fe, 18.3; F, 37.3; H, 3.9%.)

$\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ .—Analytical reagent grade, used without further purification.

*Heterocyclic amine adducts* were prepared by the methods described in the literature.<sup>1,9</sup>

### Spectra

The spectra were obtained on a Beckman DK2 spectrophotometer using the sealed cell described by Scaife.<sup>10</sup>

### Analyses

These were performed by the Australian Microanalytical Service, Melbourne.

<sup>9</sup> Gill, N. S., and Nyholm, R. S., *J. inorg. nucl. Chem.*, 1951, **18**, 88.

<sup>10</sup> Scaife, D. E., *J. scient. Instrum.*, 1966, **43**, 484.