The d-d Bands of Hexachloroferrate(III) Ion

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Spectra of finely powdered solid samples of hexacoordinated iron(III) chloride complexes were obtained in the visible and near infrared region with a Carl Zeiss PMQII spectrophotometer equipped with the reflectance attachment RA3.

The spectrum of $(NH_4)_4[FeCl_6][SbCl_6]$, which is representative of hexachloroferrate(III) spectra, is shown in Fig. 1. The bands associated with $[FeCl_6]^{3-}$ can easily be distinguished from those due to NH_4^+ vibrations by comparing the spectrum with that of $(NH_4)_2SnCl_6$, which is essentially isomorphous with $(NH_4)_4[FeCl_6][SbCl_6]$. The band at 12800 cm^{-1} corresponds to the first (lowest in wave number) band so far observed,[1-3] and the band at 8900 cm^{-1} has not been reported.

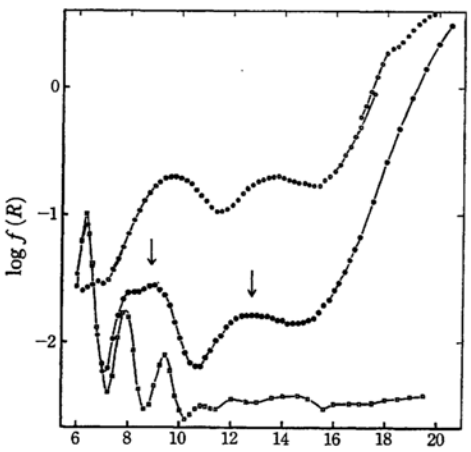

Fig. 1. Spectra* of $(NH_4)_4[FeCl_6][SbCl_6]$ (-●-), $Cs_3Fe_2Cl_9$ (-○-) and $(NH_4)_2[SnCl_6]$ (-□-).

* $f(R)$ [$=(1-R)^2/2R$, where R represents the reflecting power] is nearly proportional to the absorption coefficient for finely powdered weakly absorbing substances. [See, for example, G. Kortüm and H. Schöttler, *Z. Electrochem.*, **57**, 253 (1953).]

The bands at 8900 cm^{-1} and 12800 cm^{-1} are assigned to the $^6A_{1g}\rightarrow{}^4T_{1g}(G)$ and $^6A_{1g}\rightarrow{}^4T_{2g}(G)$ transitions, respectively. With this assignment, a narrow band due to the $^6A_{1g}\rightarrow{}^4A_{1g}$, $^4E_g(G)$ transitions is expected to appear near 18000 cm^{-1}. Closer examination of the spectrum in this region disclosed a slight but discernible rise at about 18000 cm^{-1} on the slope of the intense charge transfer band. Moreover, the spectrum of $Cs_3Fe_2Cl_9$, which also contains $FeCl_6$ chromophores, clearly showed a shoulder at 17900 cm^{-1}, in addition to the two bands at 9800 cm^{-1} and 13600 cm^{-1}.

This assignment unfortunately disagrees with the assignment given by Hatfield *et al.*,[2] but it gives more reasonable values for the ligand field and interelectronic repulsion parameters: $\Delta=$ 11100 cm^{-1} and B=605 cm^{-1} (with the assumption C=4B). Jørgensen's estimation[4] of his spectrochemical and nephelauxetic functions, $f=$ 0.80 and $h=2.0$ for Cl^- and $g=1.4$kK and $k_{35}=$ 0.24 for Fe(III), leads to a prediction of $\Delta=$ 11200 cm^{-1} and B=572 cm^{-1}, if B for the free Fe^{3+} is assumed to be 1100 cm^{-1} by interpolation. Our result compares well with this prediction.

Full results and detailed discussions will be given elsewhere.

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3) A. P. Ginsberg and M. B. Robin, *Inorg. Chem.*, **2**, 817 (1963).
4) C. K. Jørgensen, *Discussions Faraday Soc.*, **26**, 110 (1958); "Structure and Bonding," Vol. 1, ed. by C. K. Jørgensen, J. B. Neilands, R. S. Nyholm, D. Reinen and R. J. P. Williams, Springer-Verlag, Berlin (1966), p. 3.