Short Communication

Preparation and properties of ammonium zinc hexafluoroferrate(III) hexahydrate, $NH_4ZnFeF_6 \cdot 6H_2O$

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In a previous communication[1] the preparation and properties of ammonium zinc hexafluorotitanate(III) hexahydrate, $NH_4ZnTiF_6 \cdot 6H_2O$, were described. A similar investigation has been undertaken on the chemistry of trivalent iron. A new compound, the hexafluoroferrate ion, FeF_6^{3-}, has been prepared in this laboratory and its electronic spectra studied. The observed transitions were different from those reported in the literature for a d^5 ion in a regular or slightly distorted O_h symmetry[2]. The procedure for the preparation of the compound is described below.

A typical preparation of $NH_4ZnFeF_6 \cdot 6H_2O$ may be accomplished by adding 4 g of $Fe(OH)_3$ to *ca.* 50 ml of 20% HF in a platinum crucible and heating to a slow boil until the solution turns white or clear when 5 g of $ZnCO_3$ and 2 g of NH_4F are added. The solution can then be filtered and allowed to evaporate slowly at room temperature until white crystals of the desired product are formed. These crystals are filtered off and washed with cold absolute ethanol. On occasions the compound separates as a fine powder and at other times as well-defined crystals, their white color being characteristic of fluoroferrate compounds. The material is efflorescent, but if stored under kerosene or CCl_4 it may be kept indefinitely. Analysis: Found: Fe, 15.30; NH_3, 4.80; Zn, 17.77; F, 31.60%. Calculated for $NH_4ZnFeF_6 \cdot 6H_2O$: Fe, 15.51; NH_3, 4.71; Zn, 18.00; F, 31.87%.

The electronic absorption spectra of the solid were measured using a Beckman DB-GT instrument with a diffuse reflectance attachment. The bands observed are recorded in Table 1.

In keeping with our previous observation, it is noted that the cationic effect and its concomitant distortion of the O_h symmetry is clearly revealed in the spectral data.

The assignments of the absorption bands have been made assuming the presence of a cubic field. Fluorine, acting as the ligand, creates a medium crystal field and so the left-hand side of the so-called Tanabe–Sugano diagram[3] for a d^5

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system may be used to calculate the 10 Dq value. Utilizing such a diagram for a C/B value of 4.48 it is found that $Dq/B = 1.3$, and on this basis $B = 700$ cm^{-1} and 10 Dq $= 9100$ cm^{-1}.

TABLE 1

Transition	Fe^{3+} (in beryl)[2] (cm^{-1})	FeF$_6^{3-}$ (present communication) (cm^{-1})
$^6A_{1g} \rightarrow {}^4T_{1g}(t_{2g})^4(e_g)$	14 200	15 100
$^6A_{1g} \rightarrow {}^4T_{2g}(t_{2g})^4(e_g)$	17 500 20 000	18 100 20 800
$^6A_{1g} \rightarrow {}^4E_g(t_{2g})^3(e_g)^2$ $^6A_{1g} \rightarrow {}^4A_{1g}(t_{2g})^3(e_g)^2$ }	23 000	25 000
$^6A_{1g} \rightarrow {}^4T_{2g}(t_{2g})^3(e_g)^2$	>26 500	>27 800

The free ion value of B for the Fe^{3+} ion is approximately 1300 cm^{-1}. The magnitude of B is therefore considerably reduced in this complex. The corresponding value in Fe(CN)$_6^{3-}$ is 720 cm^{-1}. Bearing this in mind, the value for 10 Dq of Fe^{3+} will now be discussed. To start with, trivalent Fe^{3+} has a very low 10 Dq value. The values[4] for M(H$_2$O)$_6^{3+}$ when M $=$ Ti, V, Cr, Mn and Co are 20 300, 18 600, 17 000 and 18 200 cm^{-1}, respectively; a complete analysis of the spectrum of Fe(H$_2$O)$_6^{3-}$ has not been undertaken very effectively, but an estimated value of 14 000 cm^{-1} is usually accepted for Fe(H$_2$O)$_6^{3+}$. The values of 10 Dq for FeF$_6^{3-}$ calculated from the spectra of NH$_4$ZnFeF$_6$•6H$_2$O and the calculated value of Dvir and Low are both below 10 000 cm^{-1}. However, the calculations were based on the assumption of a pure cubic field so that some of the assignments may become uncertain on perturbation with (say) a trigonal field.

Oxygen and fluorine are comparable as ligands and the 10 Dq value of FeF$_6^{3-}$ in NH$_4$ZnFeF$_6$•6H$_2$O has been found to be slightly greater than the calculated value for Fe^{3+} in beryl. The frequency shift of the absorption maxima of the present compound as compared to Fe^{3+} in beryl is not constant for each transition, one transition being shifted to a greater extent than the others. This frequency (the fourth from the top in Table 1) is, however, the result of a combination of two different transitions so that this slight deviation is not unexpected. The percentage contribution of the transition $^6A_{1g} \rightarrow {}^4E_g(t_{2g})^3(e_g)^2$ may differ in NH$_4$ZnFeF$_6$•6H$_2$O from Fe^{3+} in beryl, but since this particular transition results from two others this slight deviation is not significant.

REFERENCES

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