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Oxo-nonafluoro diferrates (III)

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Abstract

The isolation and properties of novel oxofluoro-diiron (III) complexes, viz. $K_4HFe_2OF_9$, $Ba_5[Fe_2OF_9]_2 \cdot 2H_2O$, $[Co(NH_3)_6]_4H_3[Fe_2OF_9]_3 \cdot 2H_2O$ and $[Coen_3]_4H_3$ $[Fe_2OF_9]_3 \cdot 8H_2O$ (en = ethylenediamine) are described.

Keywords: Oxo-nonafluoro diferrates preparation; Molar conductance; Magnetic moment; IR spectroscopy

1. Introduction

Some μ-oxochloro complexes containing the $[Fe_2O]^{4+}$ unit have been reported in the literature [1–3] but oxo-iron (III) complexes containing fluoride as ligand are unknown. We report here the preparation and properties of four oxo-diiron (III) fluoro compounds.

2. Experimental details

For the preparation of $K_4HFe_2OF_9$, an aqueous solution (10 ml) of KHF_2 (0.022 mol) was warmed on a water bath and $FeC_2O_4 \cdot 2H_2O$ (0.011 mol) [4] added. To this mixture, H_2O_2 (10 ml) (100 volume) was added dropwise. When the vigorous reaction ceased, a yellowish green solution resulted and within a short time a white solid separated. After half an hour the precipitate was filtered, washed once with water and dried over conc. H_2SO_4. Yield, 0.5 g [Analysis: Found: K, 34.11; Fe, 24.67; F, 37.8%. $K_4HFe_2OF_9$ requires: K, 34.21; Fe, 24.56; F, 37.50%].

$Ba_5[Fe_2OF_9]_2 \cdot 2H_2O$ was obtained as a white gelatinous precipitate on adding barium chloride solution (5%) to a saturated aqueous solution of $K_4HFe_2OF_9$ (1.0 g) (pH ~ 5). The precipitate was centrifuged and the colourless mother liquor (pH ~ 2.8) decanted off. The residue was then washed several times with water and dried over conc. H_2SO_4. Yield, 0.85 g [Analysis: Found: Ba, 52.62; Fe, 16.70; F, 25.70%. $Ba_5[Fe_2OF_9]_2 \cdot 2H_2O$ requires: Ba, 51.94; Fe, 16.96; F, 25.90%].

$[Co(NH_3)_6]_4H_3$ $[Fe_2OF_9]_3 \cdot 2H_2O$ and $[Coen_3]_4H_3$-$[Fe_2OF_9]_3 \cdot 8H_2O$ precipitated immediately as orange needle-shaped crystals on adding 5% aqueous $[Co(NH_3)_6]Cl_3$ and $[Coen_3]_6Cl_3$ solutions, respectively, to a saturated solution of the potassium salt. These were filtered, washed with water and dried in air. [Analysis: Found: N, 21.06; Fe, 21.12; F, 31.80%. $[Co(NH_3)_6]_4H_3[Fe_2OF_9]_3 \cdot 2H_2O$ requires: N, 21.26; Fe, 21.26; F, 32.46%. Found: N, 16.56; Fe, 16.94; F, 25.72%. $[Coen]_4H_3[Fe_2OF_9]_3 \cdot 8H_2O$ requires: N, 16.80; Fe, 16.80; F, 25.65%].

3. Results and discussion

The oxofluoro-diiron compounds are crystalline and non-hygroscopic. They are sparingly soluble in water. At room temperature, the solubility of $K_4HFe_2OF_9$ was found to be 11.8 g l^{-1}. $K_4HFe_2OF_9$ could be recrystallised from water. The molar conductance value of its 10^{-3} molar solution was 545 Ω^{-1} at 26 °C, the value remaining unchanged even after a week. The barium salts and others on dehydration over P_2O_5 yielded the corresponding anhydrous compounds. Thermogravimetry showed that $K_4HFe_2OF_9$ was stable up to 40 °C and then decomposed gradually at higher temperature. The observed magnetic moment value μ_{BM} at 298 K was 9.56 for $K_4HFe_2OF_9$ corresponding to 4.78 BM for each Fe^{III} in the compound. The data indicate the high-spin nature of the complex. The IR data for $K_4HFe_2OF_9$ and $Ba_5[Fe_2OF_9]_2$ showed no band at ca. 1200 cm^{-1} corresponding to ν(Fe–OH) [5,6].

It has been shown [2] that two $FeOCl_3$ tetrahedra are bridged via the oxygen atom in the complex anion $[Fe_2OCl_6]^{2-}$. In $[Fe_2OF_9]^{5-}$ ion each iron atom is probably

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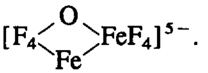
hexacoordinated in the following way,  $[\mathrm{F_4}\langle\overset{\mathrm{O}}{\underset{\mathrm{Fe}}{\quad}}\rangle\mathrm{FeF_4}]^{5-}$. Although evidence for ν(Fe–OH) has not been found in the IR spectra, in the potassium acid salt the H-atom is probably linked to oxygen a fluorine atom rather than to less electronegative oxygen atom.

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