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Syntheses and properties of bis-oxalatodifluoroferrates(III), bis-oxalatofluoroferrates(III) and oxalatodifluoroferrates(III)

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Abstract

The preparation and properties of the new oxalatofluoroferrates(III), $M_3^I[Fe(C_2O_4)_2F_2] \cdot xH_2O$ (**I**), where $M = Na^+, K^+$ and NH_4^+, $x = 4$, 2.8 and 1, respectively; $M_2^I[Fe(C_2O_4)_2F] \cdot x_1H_2O$ (**II**), where $M = K^+$, $\frac{1}{3}[Co(NH_3)_6]^{3+}$, $\frac{1}{3}[Coen_3]^{3+}$, $x_1 = 3$, 9 and 4, respectively; and $M^I[Fe(C_2O_4)F_2] \cdot nH_2O$, where $M = Na^+, K^+, NH_4^+$, $\frac{1}{3}[Co(NH_3)_6]^{3+}$, $\frac{1}{3}[Coen_3]^{3+}$, $n = 2$, 2, 3, 6 and 0, respectively, are reported.

Keywords: Syntheses; Bis-oxalatodifluoroferrates(III); Bis-oxalatofluoroferrates(III); Oxalatodifluoroferrates(III)

1. Introduction

Iron(III) forms well-known oxalato, and fluoro complexes [1–3], but with the exception of $(pyH)[Fe(C_2O_4)F_2] \cdot 2H_2O$ (py = pyridine) [4] no other oxalatofluoroferrate is known. In the present communication the preparation and properties of the salts of two new anions, viz. $[Fe(C_2O_4)_2F_2]^{3-}$ and $[Fe(C_2O_4)_2F]^{2-}$, and some salts of the known anion, $[Fe(C_2O_4)F_2]^-$, are reported.

2. Experimental details

$FeC_2O_4 \cdot 2H_2O$, $M_3^I[Fe(C_2O_4)_3] \cdot nH_2O$, $M = Na^+$, K^+ and NH_4^+, were prepared by standard methods [5]. Standard AgF solution was prepared by dissolving hydrated silver oxide in the minimum volume of HF.

2.1. Oxalatodifluoroferrates(III)

For the preparation of $K[Fe(C_2O_4)F_2] \cdot 2H_2O$, H_2O_2 (10 ml, 30%) was added dropwise with stirring to a hot aqueous suspension (20 ml) containing KHF_2 (0.005 mol) and $FeC_2O_4 \cdot 2H_2O$ (0.005 mol). When the vigorous reaction had subsided, the resulting clear yellowish green solution was heated on a water bath for 1 h and then concentrated in a vacuum desiccator over conc. H_2SO_4 for 3–4 d when yellowish green crystals separated. These were filtered and dried over fused $CaCl_2$. The compounds $Na[Fe(C_2O_4)F_2] \cdot 2H_2O$ and $NH_4[Fe(C_2O_4)F_2] \cdot 3H_2O$ were obtained in a similar manner using $NaHF_2$ and $NH_4HF_2$$\cdot$$[Co(NH_3)_6][Fe(C_2O_4)F_2]_3 \cdot 6H_2O$ and $[Coen_3][Fe(C_2O_4)F_2]_3$. They were obtained as orange yellow precipitates on adding the chlorides (5% aqueous solution) of the corresponding cobalt ammine cations to the concentrated aqueous solution of $K[Fe(C_2O_4)F_2] \cdot 2H_2O$. These were filtered, washed with water and dried as before.

2.2. Bis-oxalatodifluoroferrates(III)

For the preparation of $(NH_4)_3[Fe(C_2O_4)_2F_2] \cdot H_2O$, AgF solution (0.008 mol) was added dropwise with stirring to an aqueous solution (10 ml) of $(NH_4)_3[Fe(C_2O_4)_3] \cdot 4H_2O$ (0.004 mol). After filtering off the $Ag_2C_2O_4$ precipitate, the green filtrate (pH ~ 6) was concentrated in a vacuum desiccator over conc. H_2SO_4 for 2–3 d, when green polyhedral crystals separated. These were filtered and dried in air.

For the preparation of $K_3[Fe(C_2O_4)_2F_2] \cdot 2.8H_2O$ and $Na_3[Fe(C_2O_4)_2F_2] \cdot 4H_2O$, $AgNO_3$ solution was added to a solution containing $M_3^I[Fe(C_2O_4)_3] \cdot 3H_2O$ and M^IF in the ratio 2:1:2 ($M = Na^+$ and K^+). The precipitated $Ag_2C_2O_4$ was filtered off and to the green filtrate (pH ~ 6) was added rectified spirit (100 ml) with vigorous stirring when a light green solid separated. The colourless mother liquor was decanted off and the residue dried in air.

2.3. Bisoxalatofluoroferrates(III)

Using $K_3[Fe(C_2O_4)_3] \cdot 3H_2O$ and AgF solution in the ratio 1:2, and following the same preparative method as

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Table 1
Analytical, molar conductance and thermal decomposition data for oxalatofluoroferrates(III) [a]

Compound	Analysis: Found (Calc.) (%)					T_d (°C)	Λ_{1028} (Ω^{-1}), 26 °C
	N	M	Fe	C_2O_4	F		
$K[Fe(C_2O_4)F_2]\cdot 2H_2O$	–	14.93	21.33	33.83	14.49	60	102
		(15.17)	(21.78)	(34.24)	(14.78)		
$Na[Fe(C_2O_4)F_2]\cdot 2H_2O$	–	9.50	23.67	36.96	15.29	50	102
		(9.54)	(23.23)	(36.57)	(15.76)		
$NH_4[Fe(C_2O_4)F_2]\cdot 3H_2O$	5.76	–	22.49	34.86	15.21	50	155
	(5.57)		(22.04)	(34.64)	(14.96)		
$[Co(NH_3)_6][Fe(C_2O_4)F_2]_3\cdot 6H_2O$	9.57	–	19.82	31.88	5.28	–	–
	(10.30)		(20.61)	(32.39)	(4.66)		
$[Co(en)_3][Fe(C_2O_4)F_2]_3$	10.32	–	20.75	33.21	13.87	–	–
	(10.70)		(21.40)	(33.63)	(14.52)		
$(NH_4)_3[Fe(C_2O_4)_2F_2]\cdot H_2O$	11.46	–	16.77	50.68	11.66	60	350
	(12.28)		(16.37)	(51.46)	(11.11)		
$Na_3[Fe(C_2O_4)_2F_2]\cdot 4H_2O$	–	16.92	13.92	42.52	8.82	50	316
		(16.79)	(13.62)	(42.82)	(9.24)		
$K_3[Fe(C_2O_4)_2F_2]\cdot 2.8H_2O$	–	26.92	13.45	40.84	8.78	50	377
		(26.75)	(12.80)	(40.24)	(8.69)		
$K_2[Fe(C_2O_4)_2F]\cdot 3H_2O$	–	19.76	14.75	45.88	5.42	80	180
		(20.36)	(14.92)	(45.95)	(4.96)		
$[Co(NH_3)_6]_2[Fe(C_2O_4)_2F]_3\cdot 9H_2O$	13.85	–	13.37	43.80	4.58	50	–
	(13.58)		(13.58)	(42.68)	(4.67)		
$[Coen_3]_2[Fe(C_2O_4)_2F]_3\cdot 4H_2O$	–	–	12.82	40.53	4.83	–	–
			(12.89)	(40.62)	(4.37)		

[a] T_d = initial decomposition temperature; Λ = molar conductance.

$(NH_4)_3[Fe(C_2O_4)_2F_2]\cdot H_2O$, we obtained $K_2[Fe(C_2O_4)_2F]\cdot 3H_2O$. $[Co(NH_3)_6]_2[Fe(C_2O_4)_2F]_3\cdot 9H_2O$ and $[Coen_3]_2[Fe(C_2O_4)_2F]_3\cdot 4H_2O$ were obtained as orange yellow crystals on adding the chlorides (5% solution) of corresponding cobalt complexes to the concentrated aqueous solution of $K_2[Fe(C_2O_4)_2F]\cdot 3H_2O$. The compounds were filtered and dried in air.

Analyses of the compounds were carried out by standard methods [6] and the results are presented in Table 1.

2.4. General properties

Alkali metal oxalatofluoroferrates(III) are all crystalline and highly soluble in water but insoluble in common organic solvents. Salts of the $[Fe(C_2O_4)F_2]$ anion are slightly hygroscopic. $K[Fe(C_2O_4)F_2]\cdot 2H_2O$ could be recrystallised from its aqueous solution, but solutions of the salts of $[Fe(C_2O_4)_2F]^{2-}$ and $[Fe(C_2O_4)_2F_2]^{3-}$ decompose on standing. The molar conductance values of freshly prepared aqueous solutions (10^{-3} M) and the initial decomposition temperatures are reported in Table 1. The IR spectral data of the alkali metal oxalatofluoroferrates(III) indicated the presence of chelated oxalato groups [7,8]. The '*d*' values found from X-ray powder diffraction spectra of $K[Fe(C_2O_4)F_2]\cdot 2H_2O$, $K_2[Fe(C_2O_4)_2F]\cdot 3H_2O$ and $K_3[Fe(C_2O_4)_2F_2]\cdot 2.8H_2O$ are different from one another and also different from that of $K_2C_2O_4\cdot H_2O$.

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