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Isolation and properties of bis-oxalatodifluorochromates(III) and oxalatotetrafluorochromates(III)

A.K. Sengupta, B.B. Bhaumik *, Partha Sarathi Bose

Department of Chemistry, University of Kalyani, Kalyani, 741235, West Bengali, India

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Abstract

Preparation of bis-oxalatodifluorochromates(III), $M^I_3[Cr(C_2O_4)_2F_2]\cdot nH_2O$, where, $M = Na^+$, K^+, NH_4^+ and $n = 5$; $\frac{1}{3}[Co(NH_3)_6]^{3+}$ ($n = 6$), $\frac{1}{3}[Co(en)_3]^{3+}$ ($n = 7$, en = ethylenediamine) and oxalatotetrafluorochromates(III), $M^I_3[Cr(C_2O_4)F_4]\cdot nH_2O$, where, $M = Na^+$ ($n = 9$), K^+ ($n = 3$), NH_4^+ ($n = 4$), $\frac{1}{3}[Co(NH_3)_6]^{3+}$ ($n = 4$) and $\frac{1}{3}[Co(en)_3]^{3+}$ ($n = 3$) are described. The compounds are characterized by elemental analyses, molar conductance, magnetic susceptibility, thermogravimetry and IR spectral studies. The general properties of the compounds are given.

Keywords: Bis-oxalatodifluorochromate(III); Oxalatotetafluorochromates(III)

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1. Introduction

Mixed ligand oxalatofluorometallates of many transition and non-transition metals are known [1–3]. Chromium(III) forms well known oxalato-, and fluorochromates but compounds containing both oxalate and fluoride as ligands have not been reported. In the present paper the preparation and study of several compounds of two yet unknown oxalatofluorochromate(III) anions viz. $[Cr(C_2O_4)_2F_2]^{3-}$ and $[Cr(C_2O_4)F_4]^{3-}$ have been described.

2. Experimental

$K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ and $M^I[Cr(C_2O_4)_2(H_2O)]\cdot 2H_2O$ where, $M = Na^+$, K^+ and NH_4^+ were prepared by standard procedures [4]. The compounds were analysed by standard procedures [5]. Magnetic susceptibility, IR and thermogravimetric measurements were carried out as reported earlier [6]. Data are given in Table 1.

For the preparation of $K_3[Cr(C_2O_4)_2F_2]\cdot 5H_2O$, 0.024 mol $K[Cr(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$ was dissolved in 40 ml water and to it potassium fluoride solution (0.048 mol, 10 ml) was added and the resulting deep green solution was concentrated on a water bath for about 30 min when a small amount of pale green precipitate separated. The precipitate was filtered off and the filtrate was further concentrated in a vacuum desiccator. After 3–4 days green crystals separated. The crystals were filtered, dried in air and analysed. $M^I_3[Cr(C_2O_4)_2F_2]\cdot 5H_2O$ ($M = Na^+$ and NH_4^+) were obtained as green solids in the same manner by using $M^I[Cr(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$ and the appropriate amounts of sodium or ammonium fluorides in a 1:2 molar ratio of the two reactants. $K_3[Cr(C_2O_4)_2F_2]\cdot 5H_2O$ was also obtained from the reaction between aqueous $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$ and HF in a 1:2 molar ratio. $[Co(NH_3)_6][Cr(C_2O_4)_2F_2]\cdot 6H_2O$ and $[Co(en)_3][Cr(C_2O_4)_2F_2]\cdot 7H_2O$ were obtained as pale green solids on adding 5% aqueous $[Co(NH_3)_6]Cl_3$ and $[Co(en)_3]Cl_3$ solutions respectively to a solution of $K_3[Cr(C_2O_4)_2F_2]\cdot 5H_2O$. The compounds separated immediately from the solution.

For the preparation of $M^I[Cr(C_2O_4)F_4]\cdot nH_2O$ [$M = Na^+$ ($n = 9$), K^+ ($n = 3$) and $NH^+{}_4$ ($n = 4$), 20 ml, M^IHF_2 (0.046 mol) was mixed with $M^I[Cr(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$ (0.023 mol, 40 ml) and fractionally crystallized on a water bath. The desired compounds were obtained in the second crop. These were filtered and dried in air. $[Co(NH_3)_6][Cr(C_2O_4)F_4]\cdot 4H_2O$ and $[Co(en)_3][Cr(C_2O_4)F_4]\cdot 3H_2O$ were obtained by metathesis between $K_3[Cr(C_2O_4)F_4]\cdot 3H_2O$ and 5% aqueous $[Co(NH_3)_6]Cl_3$ or $[Co(en)_3]Cl_3$ solution. Pale green precipitates separated from the solution immediately.

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* Corresponding author.

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Table 1
Analytical, conductance and magnetic moment data for oxalatofluorochromates(III)

Compound	Found (calculated) %					μ_{obs} (B.M.)	Λ_m at 30° (Ohm^{-1})
	Na/K	N	Cr	C_2O_4	F		
$Na_3[Cr(C_2O_4)_2F_2]\cdot 5H_2O$	15.88 (16.23)	-	12.28 (12.23)	41.52 (41.41)	8.84 (8.94)	3.89	460
$K_3[Cr(C_2O_4)_2F_2]\cdot 5H_2O$	24.50 (24.73)	-	10.82 (10.99)	37.18 (37.20)	8.11 (8.03)	3.90	549
$[NH_4]_3[Cr(C_2O_4)_2F_2]\cdot 5H_2O$	-	10.52 (10.24)	12.48 (12.68)	43.15 (42.93)	9.19 (9.27)	3.88	530
$[Co(NH_3)_6][Cr(C_2O_4)_2F_2]\cdot 6H_2O$	-	15.33 (15.70)	9.64 (9.72)	32.60 (32.90)	7.01 (7.10)	-	-
$[Co(en)_3][Cr(C_2O_4)_2F_2]\cdot 7H_2O$	-	12.80 (13.31)	7.78 (8.24)	27.65 (27.89)	5.74 (6.02)	-	-
$Na_3[Cr(C_2O_4)F_4]\cdot 9H_2O$	16.12 (15.43)	-	10.99 (11.63)	18.88 (19.68)	17.01 (17.00)	3.83	449
$K_3[Cr(C_2O_4)F_4]\cdot 3H_2O$	29.77 (30.23)	-	13.26 (13.44)	22.98 (22.74)	19.84 (19.64)	3.88	502
$[NH_4]_3[Cr(C_2O_4)F_4]\cdot 4H_2O$	-	12.31 (12.28)	14.95 (15.20)	26.07 (25.73)	22.25 (22.22)	3.89	464
$[Co(NH_3)_6][Cr(C_2O_4)F_4]\cdot 4H_2O$	-	18.51 (18.71)	11.37 (11.58)	19.30 (19.60)	17.64 (16.93)	-	-
$[Co(en)_3][Cr(C_2O_4)F_4]\cdot 3H_2O$	-	16.86 (16.50)	9.89 (10.22)	17.98 (17.29)	15.03 (14.93)	-	-

Λ_m = Molar conductance [10^{-3} (M)]. μ_{obs} = Observed magnetic moment.

[a] Due to poor yield of compounds containing cobalt complex cations the magnetic susceptibility values could not be measured.

3. Results and discussion

Alkali metal oxalatofluorochromates(III) are needle-shaped, crystalline and non-hygroscopic in nature. They are soluble in water but insoluble in common organic solvents. The observed molar conductivities (Table 1) of their freshly prepared aqueous solutions (10^{-3} M) were higher than that of a 3:1 electrolyte, suggesting partial hydrolysis of the complex anions in solution. The compounds containing cobalt complex cations are sparingly soluble in water. On dehydration over P_2O_5 in vacuum, all alkali metal compounds produced corresponding anhydrous products. The observed magnetic moment values at room temperature for potassium, ammonium and sodium salts of both the anions correspond to the spin only value (Table 1) for the high spin $3d^3$ Cr(III) ion. Thermogravimetric data (in air) indicated low thermal stability of the compounds. From 50 to 400°C the compounds decomposed gradually without showing the formation of any stable intermediate product and at around 400°C they left yellowish green hygroscopic residues. IR data showed several strong bands in the regions 500–550 cm^{-1}, 720–800 cm^{-1}, 1230–1450 cm^{-1} and 1650–1700 cm^{-1} due to the presence of chelated oxalato groups [7–9]. Due to the overlapping of the characteristic νCr–F [10] band with an oxalate band at 500–550 cm^{-1}, the former could not be assigned precisely. Bands at 1400 cm^{-1} and 3100 cm^{-1} for νN–H, 1650 cm^{-1} for δH_2O and 3400 cm^{-1} for νOH [9] were also observed in the IR spectra.

References

[1] A.J. Edwards, D.R. Slim, J. Salapala and J.E. Guerchais, *Bull. Chem. Soc. Fr*, (1975) 2015.

[2] A.K. Sengupta and K. Sinha, *J. Fluorine Chem.*, *24* (1984) 153.

[3] A.K. Sengupta, B.B. Bhaumik and S.K. Nath, *Indian J. Chem.*, *22A* (1983) 535.

[4] W.G. Palmer, Experimental Inorganic Chemistry, Cambridge University Press, 1959, pp. 386, 387.

[5] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, ELBS and Longman, London, 1978, pp. 343, 350, 361.

[6] B.B. Bhaumik and S. Ghosh, *J. Fluorine Chem.*, *56* (1992) 353.

[7] J. Fujita, E. Martell and K. Nakamoto, *J. Chem. Phys.*, *36* (1962) 324; 331.

[8] N.F. Curtis, *J. Chem. Soc.*, (1963) 4109; (1964) 2644; (1968) 1584.

[9] K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley–Interscience, New York, 1970, pp. 151, 155, 166, 245.

[10] R.D. Peacock and D.W.A. Sharp, *J. Chem. Soc.*, (1959) 2762.