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BIS-OXALATOBISFLUORO-ALUMINATES AND -GALLATES

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SUMMARY

The preparations of some bisoxalatobisfluoroaluminates having the general formula $M_3[Al(C_2O_4)_2F_2].3H_2O$, where $M=K^+$, Na^+ and $[Co(NH_3)_6]^{3+}$, and a bisoxalatobisfluorogallate, $[Co(NH_3)_6][Ga(C_2O_4)_2F_2].3H_2O$, are described. The compounds are characterised by chemical analyses, TGA, IR spectroscopy and X-ray powder photography. IR spectra support the presence of chelating oxalate ligands in these compounds. On isothermal heating at 100-130°C the compounds yield their respective anhydrous products.

INTRODUCTION

Oxalato- and fluoro-aluminates and -gallates are well known [1-4], but no oxalatofluoro-aluminates and -gallates have been reported. In the present paper the isolation and study of several oxalatofluoro-aluminates and an oxalatofluorogallate are described.

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EXPERIMENTAL

Standard silver fluoride solution was prepared by dissolving hydrated silver oxide in the minimum volume of HF and determining the contents of silver and fluorine. $K_3[Al(C_2O_4)_3]\cdot 3H_2O$, $Na_3[Al(C_2O_4)_3]\cdot 3H_2O$ and hexamminecobalt(III) nitrate were prepared by standard methods [1,5]. The fluoride content of the compounds was determined argentometrically after precipitation as PbClF [6]. Aluminium and gallium were estimated gravimetrically as their oxides and K, Na and Co as their sulphates. Oxalate was determined with potassium permanganate adding 1-2 gm boric acid before titration. Nitrogen was determined by Dumas' semi-micro method. The analytical results are reported in Table 1.

TGA data were recorded using a manually operated thermobalance by heating the compounds at a rate of $4^{o}C/min$. IR spectra were recorded in KBr on a Perkin-Elmer spectrophotometer over the range 4000-400 cm^{-1}. Powder X-ray diffraction photographs of $K_3[Al(C_2O_4)_2F_2]\cdot 3H_2O$ and $K_3[Al(C_2O_4)_3]\cdot 3H_2O$ were taken in a Guinier camera using CuK_α radiation and the data are presented in Table 2.

Bisoxalatobisfluoroaluminates

Potassium bisoxalatobisfluoroaluminate, $K_3[Al(C_2O_4)_2F_2]\cdot 3H_2O$: Potassium trisoxalato-aluminate, $K_3[Al(C_2O_4)_3]\cdot 3H_2O$ was dissolved in the minimum amount of water and the calculated amount of silver fluoride solution was added to it. The

TABLE 1

Analytical and IR data of Oxalatofluoro-aluminates and -gallates (*M* = Na, K *or* Co)

	Found (Calcd.) (%)					ν Al/Ga-F	ν C-C
	N	M	Al/Ga	Ox	F	(cm^{-1})	(cm^{-1})
$Na_3[Al(C_2O_4)_2F_2]\cdot3H_2O$	-	19.04 (18.96)	7.50 (7.42)	48.20 (48.35)	10.32 (10.44)	610	560
$Na_3[Al(C_2O_4)_2F_2]$	-	22.11 (22.26)	8.75 (8.71)	56.84 (56.77)	12.36 (12.26)	-	-
$K_3[Al(C_2O_4)_2F_2]\cdot3H_2O$	-	28.37 (28.45)	6.58 (6.56)	42.56 (42.69)	9.31 (9.22)	615	560
$K_3[Al(C_2O_4)_2F_2]$	-	32.50 (32.74)	7.41 (7.54)	49.02 (49.12)	10.55 (10.60)	-	-
$[Co(NH_3)_6][Al(C_2O_4)_2F_2]\cdot3H_2O$	18.54 (18.43)	13.02 (12.92)	5.84 (5.92)	38.32 (38.60)	8.26 (8.34)	610	560
$[Co(NH_3)_6][Al(C_2O_4)_2F_2]$	20.78 (20.90)	14.50 (14.65)	6.81 (6.72)	43.93 (43.79)	9.55 (9.45)	-	-
$[Co(NH_3)_6][Ga(C_2O_4)_2F_2]\cdot3H_2O$	16.65 (16.85)	11.96 (11.81)	13.82 (13.98)	35.39 (35.30)	7.54 (7.62)	480	515
$[Co(NH_3)_6][Ga(C_2O_4)_2F_2]$	19.01 (18.89)	13.35 (13.24)	15.60 (15.68)	39.71 (39.59)	8.60 (8.55)	-	-

TABLE 2

X-ray powder diffraction data of $K_3[Al(C_2O_4)_2F_2].3H_2O$

dA	Relative intensity	dA	Relative intensity	dA	Relative intensity
9.6	w	3.60	s	3.17	m
7.2	ms	3.48	ms	3.06	m
6.3	ms	3.38	m	2.93	w
5.15	ms	3.32	m	2.62	m
4.75	m	3.20	s	2.11	w
3.95	m				

s = strong, ms = medium strong, m = medium and w = weak silver oxalate thus precipitated was filtered off. Alcohol was then added to the filtrate when crystals were obtained. These were filtered, washed with alcohol and dried in air.

Sodium bisoxalatobisfluoroaluminate, $Na_3[Al(C_2O_4)_2F_2]\cdot 3H_2O$, was obtained similarly starting from $Na_3[Al(C_2O_4)_3]\cdot 3H_2O$ and AgF.

Hexamminecobalt(III) bisoxalatobisfluoroaluminate, $[Co(NH_3)_6][Al(C_2O_4)_2F_2]\cdot 3H_2O$ was obtained as orange-yellow crystals on adding a concentrated solution of hexamminecobalt (III) nitrate to the clear solution obtained as above from $K_3[Al(C_2O_4)_3]\cdot 3H_2O$ and AgF. The crystals were filtered, washed with water and dried in air.

Bisoxalatobisfluorogallate

Hexamminecobalt(III) bisoxalatobisfluorogallate, $[Co(NH_3)_6][Ga(C_2O_4)_2F_2]\cdot 3H_2O$ was obtained as orange-yellow crystals on adding a mixture of hexamminecobalt(III) nitrate (1.3 gm) and oxalic acid (0.5 gm) to a saturated solution of $PyHGaF_4\cdot 2.5H_2O$ (Py=pyridine) (1 gm) [7]. The crystals were filtered, washed with water and dried in air.

RESULTS AND DISCUSSION

The potassium and sodium bisoxalatobisfluoroaluminates are readily soluble in water, whereas the hexamminecobalt(III) bisoxalatobisfluoro-aluminate and -gallate are insoluble in water. The isolation of $[Co(NH_3)_6][Al(C_2O_4)_2F_2]\cdot 3H_2O$ shows that the oxalatofluoroaluminate anion is relatively stable in aqueous solution. Although the oxalate can be replaced by two fluorides from the oxalatoaluminate ion, the reverse reaction could not be carried out using a fluoroaluminate and oxalic acid or potassium oxalate. Hence it can be concluded that the Al-F bond strength is greater than that between Al^{3+} and oxalate. On the other hand oxalate displaces fluoride from a fluorogallate, suggesting the opposite order of bond strength for gallium.

The compounds start decomposing around 100°C and show horizontals between 100-200°C which are due to the formation of stable anhydrous intermediates. On the basis of the TGA results, isothermal heating of the compounds was carried out and anhydrous products were obtained. The rate of decomposition of the complexes is maximum between 200-340°C and complete decomposition occurs at ca. 400°C leading apparently to the formation of mixtures of oxides and fluorides.

$$K_3[Al(C_2O_4)_2F_2]\cdot 3H_2O \xrightarrow[-3H_2O]{120^\circ C} K_3[Al(C_2O_4)_2F_2]$$

$$Na_3[Al(C_2O_4)_2F_2]\cdot 3H_2O \xrightarrow[-3H_2O]{90^\circ C} Na_3[Al(C_2O_4)_2F_2]$$

$$[Co(NH_3)_6][Al(C_2O_4)_2F_2]\cdot 3H_2O \xrightarrow[-3H_2O]{120^\circ C} [Co(NH_3)_6]\text{-}[Al(C_2O_4)_2F_2]$$

$$[Co(NH_3)_6][Ga(C_2O_4)_2F_2]\cdot 3H_2O \xrightarrow[-3H_2O]{130^\circ C} [Co(NH_3)_6][Ga(C_2O_4)_2F_2]$$

IR spectra of $K_3[Al(C_2O_4)_2F_2]\cdot 3H_2O$, $Na_3[Al(C_2O_4)_2F_2]\cdot 3H_2O$, $[Co(NH_3)_6][Al(C_2O_4)_2F_2]\cdot 3H_2O$ and $[Co(NH_3)_6][Ga(C_2O_4)_2F_2]\cdot 3H_2O$ show strong bands in the region 520-570 cm^{-1}, 785-825 cm^{-1}, 1980-1430 cm^{-1} and 1700-1725 cm^{-1}, consistent with chelating oxalate groups [8-10]. M-F vibrations generally occur between 400-700 cm^{-1} [11-14]. $K_3[Al(C_2O_4)_3]\cdot 3H_2O$ shows only one band at 585 cm^{-1}, whereas the oxalatofluoroaluminates show bands at 560 cm^{-1} and 615 cm^{-1}. Hence the band at 615 cm^{-1} (Table 1) is assigned to ν Al-F and the other one to oxalate (ν C-C).

All of the hydrated compounds show a strong band at 3400 cm^{-1} from the water of crystallisation [15].

Comparison of the X-ray diffraction data of $K_3[Al(C_2O_4)_2F_2]\cdot 3H_2O$ with those of $K_3[Al(C_2O_4)_3]\cdot 3H_2O$ and KHC_2O_4 confirms that our product is substantially free from these probable contaminants.

Since the above aluminium compounds have been obtained through the replacement of oxalate, occupying cis-positions, the two fluoride ions in the oxalatofluoroaluminate ion probably also occupy cis-positions in it. The similarity of the IR data of hexamminecobalt(III) bisoxalatobisfluorogallate and the corresponding aluminium compound suggest similar structures for both the compounds.

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