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OXALATOFLUORO-INDIUM COMPOUNDS

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SUMMARY

The preparations of indium oxalatofluoride, $In(C_2O_4)F.3H_2O$, and oxalatodifluoro-indates of two types, viz. $M[In(C_2O_4)F_2].xH_2O$, where M = NH_4, Na, K and x = 2,2,3, and $[Co(NH_3)_6][In(C_2O_4)_2F_2].2H_2O$, are described. TGA studies and isothermal heating of these compounds show the formation of stable intermediate mono-hydrates except in the case of ammonium and hexaminecobalt(III) compounds. The IR spectra of these compounds reveal the presence of chelated oxalate groups.

INTRODUCTION

In a previous communication [1] oxalatofluoroaluminates and oxalatofluorogallates were described. The hitherto unknown oxalatofluoro-indium compounds are reported in the present paper.

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EXPERIMENTAL

Hexaminecobalt(III) nitrate was prepared by a standard method [2]. $InF_3.3H_2O$ was prepared as reported earlier [3]. The methods for analysing the constituents were those used before [1,3]. The analytical results are reported in Table 1. TGA and IR data were recorded as before [1].

1. Indium oxalatofluoride, $In(C_2O_4)F.3H_2O$: Indium fluoride, $InF_3.3H_2O$ (1.0 g) was dissolved in water faintly acidified with HF. A solution of oxalic acid (0.6 g) was added and the mixture was evaporated on a steam bath to crystallisation. The crystals were filtered, washed with water and dried in air.

2. Potassium oxalatodifluoroindate, $K[\ In(C_2O_4)F_2\ ].3H_2O$: To a warm solution of indium fluoride (1.0 g) acidified with HF was added a concentrated solution of potassium oxalate (0.8 g) with stirring. After a while crystals were obtained, filtered and dried as above.

3. Ammonium oxalatodifluoroindate, $NH_4[\ In(C_2O_4)F_2\ ].2H_2O$ was obtained as above using ammonium oxalate.

4. Sodium oxalatodifluoroindate, $Na[\ In(C_2O_4)F_2\ ].2H_2O$, was obtained as above using sodium oxalate but evaporation on a water bath was necessary to obtain the crystals of the compound.

5. Hexaminecobalt(III)bisoxalatodifluoroindate, $[Co(NH_3)_6][In(C_2O_4)_2F_2].2H_2O$: A solution containing hexaminecobalt(III) nitrate(1.6 g) and oxalic acid (0.6 g) was

TABLE 1

Analytical data for the fluoroindium compounds

Compound	Found (Calcd.) %				
	N	M	In	Ox	F
In $(C_2O_4)F.3H_2O$	-	-	41.57 (41.62)	31.94 (31.91)	6.95 (6.89)
In $(C_2O_4)F.H_2O$	-	-	47.73 (47.87)	36.94 (36.70)	7.85 (7.92)
K [In $(C_2O_4)F_2$]$.3H_2O$	-	11.78 (11.71)	34.41 (34.38)	26.56 (26.36)	11.28 (11.38)
K [In (C_2O_4) F_2]$.H_2O$	-	13.22 (13.13)	38.54 (38.41)	29.60 (29.54)	12.80 (12.78)
Na [In $(C_2O_4)F_2$]$.2H_2O$	-	7.78 (7.67)	38.15 (38.29)	29.18 (29.35)	12.55 (12.68)
Na [In $(C_2O_4)F_2$]$.H_2O$	-	8.07 (8.16)	40.80 (40.74)	31.19 (31.23)	13.40 (13.48)
NH_4 [In $(C_2O_4)F_2$]$.2H_2O$	4.85 (4.92)	-	40.52 (40.31)	30.94 (30.90)	13.35 (13.34)
[Co $(NH_3)_6$][In $(C_2O_4)_2F_2$]$.2H_2O$	16.10 (15.98)	11.27 (11.20)	21.99 (21.84)	33.63 (33.48)	7.20 (7.23)

M = K, Na or Co; Ox = oxalate

added to a warm solution of indium fluoride (1.0 g) with constant mechanical stirring. Light-yellow crystals appeared immediately, which were filtered, washed with warm water and dried.

Attempts for the isolation of oxalatofluoroindates through the replacement of oxalate group by addition of silver fluoride from the corresponding oxalatoindates were not successful.

RESULTS AND DISCUSSION

The oxalato-fluoroindates are moderately soluble in water except the sparingly soluble corresponding hexamine-cobalt(III) compound, and all are insoluble in common organic solvents.

TGA data for the oxalato-fluoroindates are summarised in Table 2. The results of TGA are further corroborated by isothermal heating of the compounds and analysing the products. Thus monohydrates of indium oxalatofluoroindates were obtained at 180°C, 100°C and 180°C respectively. The stepwise dehydration of the compounds show that the water molecules present in the compounds are differently bonded. Ammonium and hexamminecobalt(III) compounds do not yield any intermediates stable enough for isolation.

The study of the infrared spectra of the oxalatofluoroindates show bands in the region 530-580 cm^{-1}, 790-820 cm^{-1}, 1380-1430 cm^{-1} and 1650-1690 cm^{-1} indicating the presence of

TABLE 2

Summary of TGA data for stable regions along with the decomposition temperatures for the fluoroindium compounds

Compound	Decomposition temp., °C	Stable region found at, °C	% Weight-loss		For the formation of
			Found	Calcd.	
$In\ (C_2O_4)F.3H_2O$	150	200-230	13.25	13.05	$In\ (C_2O_4)F.H_2O$
		350	47.71	49.67	In_2O_3
$Na\ [In\ (C_2O_4)F_2\ ].2H_2O$	40	110-140	6.09	6.00	$Na[In(C_2O_4)F_2\ ].H_2O$
$K\ [\ In\ (C_2O_4)F_2\ ].3H_2O$	50	180-210	11.00	10.78	$K[\ In(C_2O_4)F_2\ ].H_2O$
		400	44.88	44.32	$K\ InO_2$
$NH_4\ [\ In\ (C_2O_4)F_2\ ].2H_2O$	80	300	52.48	51.26	In_2O_3

oxalate groups as chelating ligands [4]. The compounds show a sharp band at around 480 cm^{-1} due to In–F stretching vibrations[5]. The ammonium and hexamminecobalt(III) compounds show typical frequencies for N–H at 3200 and 1400 cm^{-1} [6]. Since chelate oxalato compounds also show bands around 1400 cm^{-1} due to (C–C) and (C–O) stretching frequencies superposition of this band with N–H is very likely in the spectra of the compounds described.

All these oxalatofluoroindium compounds show strong bands in the region 3400-3500 cm^{-1} due to water of crystallisation [7]. Except the hexamminecobalt(III) compound the other oxalatofluoroindates show a strong band around 3580 cm^{-1} confirming the presence of coordinated water [8] as indicated by TGA data.

It may be mentioned that oxalatofluoroaluminates could not be prepared starting from a soluble variety of aluminium fluoride, whilst it was quite easy to prepare oxalatofluoroindium compounds starting from indium fluoride through partial replacement of its fluoride. This observation suggests that Al–F bond is much stronger than In–F bond with the bond strength of Ga–F in between.

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