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Fluorodithiostannates

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Abstract

Fluorodithiostannates, i.e. $(BH)[SnFS_2]\cdot xH_2O$, where B = quinoline, guanidine and 1,10-phenanthroline, are described. These have been characterized by analytical methods, TG and IR data.

Introduction

Tin(IV) is known to form thiostannates and fluorostannates. In the present communication, hitherto unknown fluorodithiostannates of some organic base cations are reported. Analogous germanium compounds are not known.

Experimental

Tin in the fluorothiostannates was determined gravimetrically as SnO_2 after precipitating as its sulphide [1]. For the determination of fluorine, the compounds were fused with sodium carbonate, extracted with water, neutralised with nitric acid and filtered. From the filtrate, lead chlorofluoride was precipitated and then titrated following Volhard's method [2]. Nitrogen was determined by a semi-micro Dumas method. Sulphur was determined gravimetrically as $BaSO_4$ after oxidising sulphide into sulphate with bromine water. The analytical results are reported in Table 1. TG and IR data were recorded as reported previously [3].

Quinolinium fluorodithiostannate hydrate, $(quH)[SnFS_2]\cdot 4H_2O$ was prepared as follows. A solution (10 ml) containing tin(IV) chloride pentahydrate (5 g) and hydrofluoric acid (3 ml, 48%) was saturated by passing H_2S into it. The solution was then added to mechanically stirred quinoline (22 ml) also saturated with H_2S when a yellowish brown precipitate appeared in the mixture (pH ~ 6). This was filtered, washed twice with alcohol, pressed between folds of filter paper and dried over fused calcium chloride. Yield, 0.7 g.

Guanidinium fluorodithiostannate hydrate, $(guH)[SnFS_2]\cdot 10H_2O$ and 1,10-phenanthrolinium fluorodithiostannate hydrate, $(1,10\text{-phenH})[SnFS_2]$-

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TABLE 1

Analytical data for fluorodithiostannates[a]

	Found (Calc.) (%)			
	N	Sn	S	F
(quH)[$SnFS_2$]·$4H_2O$	3.34 (3.46)	29.78 (29.39)	16.01 (15.84)	4.81 (4.70)
(guH)[$SnFS_2$]·$10H_2O$	9.57 (9.51)	27.01 (26.87)	14.66 (14.49)	4.39 (4.30)
(1,10-phenH)[$SnFS_2$]·H_2O	7.04 (6.98)	29.44 (29.6)	15.84 (15.96)	4.83 (4.74)

[a] qu = quinoline; gu = guanidine; 1,10-phen = 1,10-phenanthroline.

·H_2O were prepared as above using the same amounts of tin(IV) chloride and hydrofluoric acid. Guanidinium carbonate (9 g) dissolved in water and 1,10-phenanthroline hydrate (33 g) dissolved in a minimum amount of very dilute hydrofluoric acid were used. The yields of the two compounds, which were dirty white solids, were 0.8 g and 0.6 g, respectively.

Results and discussion

The compounds appeared homogeneous when viewed under a microscope and were sparingly soluble in water and alcohol, but highly soluble in acid. Hence, during their preparation it was essential to maintain the pH of the mother liquor above a value of 6. Attempts to increase the yields of the compounds by varying the quantity of reactants were not successful. The compounds were non-hygroscopic and were, therefore, apparently free from the corresponding hygroscopic amine fluorides which could have been probable contaminants.

The compounds exhibited no X-ray diffraction pattern with CuKα radiation showing them to be amorphous. They were, therefore, substantially free from SnS_2, which is another possible impurity but which is crystalline. The amorphous nature of the compounds suggest them to be polymers probably containing S-bridges or F-bridges or both, so that Sn^{IV} present in the compounds may be hexa-coordinate.

Thermogravimetry of the compounds showed that they decomposed continuously above 40 °C but that decomposition was not complete even at 420 °C. No stable region was noted in the TG curves. It was thus not possible to remove the water to obtain anhydrous compounds.

The IR spectra of the fluorodithiostannates exhibit bands at 350–380 cm^{-1} and 480 cm^{-1}, which are probably due to Sn–S frequencies [4]. The bands observed at 550–670 cm^{-1} may be due to both Sn–F and the organic base [5–7]. The compounds exhibit typical N–H frequencies [8] at 1400–1470

cm^{-1}, 1550–1650 cm^{-1} and 3000–3500 cm^{-1}, but since these ranges include the regions for symmetric and antisymmetric OH stretchings and the H–O–H bending mode due to lattice water [4], superimposition of the bands are likely.

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