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Properties of Fluoroantimonates(III) Complexes with Amino Acids

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Abstract—Crystalline complex fluoroantimonates(III) with amino acids (glycine, β-alanine, DL-serine, DL-valine, L-leucine, and L-phenylalanine) have been prepared. The complexes stability in aqueous solutions has been studied with the cementation method. ^{1}H NMR studies of aqueous solutions of the amino acids complexes with SbF_3 at pH 1–6 and room temperature are reported. Preparation of polycrystalline metal antimony in aqueous solutions of tetrafluoroantimonates(III) complexes with the protonated amino acids has been demonstrated.

Keywords: antimony(III) fluoride, amino acid, fluoroantimonate(III), ^{1}H NMR

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Antimony trifluoride is known as excellent acceptor of fluoride ions and therefore forms a wide family of complex compounds, their composition, structure, and properties being dependent on the nature of interacting species. Fluoride complexes of antimony(III) with cations of alkali metals and ammonium are the most well studied; among these compounds, substances with important utilitarian properties have been found, for instance, piezoelectrics and ion conductors [1, 2], biologically active compounds inhibiting growth of the tumor (Ehrlich's carcinoma) cells and affecting activity of the marine bacteria [3, 4]. Antimony trifluoride, as a representative of *p*-element compound in the non-complete valence state can form complexes with organic ligands. Such complexes, in particular, those with amino acids, are scarcely studied compared to complexes of amino acids with transition metals [5, 6]. To date, the SbF_3 complexes with glycine (Gly) [7, 8], β-alanine (Ala) [9], DL-serine (Ser) [10], DL-valine (Val) [11], L-leucine (Leu) [12, 13], and L-phenylalanine (Phe) [14] have been described in the literature. Thermal properties of the complexes with Leu and Val as well as their ionic mobility as function of temperature at 150–420 K have been studied [15].

Extending our previous studies of complexes of antimony(III) fluoride with amino acids, herein we report on properties of their aqueous solutions as studied by cementation method and ^{1}H NMR spectroscopy.

Composition of the prepared complex fluoro-antimonates(III) and some of their structural features are collected in Table 1. According to the composition, the compounds could be divided into two groups: molecular adducts $n SbF_3 \cdot X$ (X = Gly, Val, Leu, and Phe; n = 1, 2) and tetrafluoroantimonates(III) of univalent cations of protonated amino acids (Gly, β-Ala, Ser, Val, and Leu). Coordination polyhedrons of antimony(III) were either tetragonal (SbF_4E, SbF_3OE) or octahedral (SbF_5E, SbF_3O_2E) bipyramid with one of the vertexes being occupied with lone pair (E) of Sb^{3+}. Antimony atoms generally occupied the equivalent positions in the crystal unit cell, the $[LeuH]SbF_4$ complex with two different positions of the central atom being an exception. In the molecular adducts and in the complex tetrafluoroantimonates(III), antimony polyhedrons were combined with the amino acid or its protonated cation into three-dimensional scaffold or polymeric chains, the $[GlyH]SbF_4$, complex containing isolated SbF_4E groups being an exception.

Table 1. Complex fluorides of antimony(III) with amino acids and their structural features

Amino acid	Complex composition	Antimony polyhedron	Arrangement type
Glycine	$2SbF_3 \cdot Gly$ [8]		
	$SbF_3 \cdot Gly$ [8]	SbF_4E	Three-dimensional scaffold
	$SbFO \cdot Gly$ [8]		
	$[GlyH]SbF_4$ [8]	SbF_4E	Isolated groups SbF_4
β-Alanine	$[\beta\text{-}AlaH]SbF_4 \cdot H_2O$ [9]	SbF_4E	Polymeric chains $[SbF_4]_n^{n-}$
	$[\beta\text{-}AlaH]SbF_4$ [9]	SbF_4E	Polymeric chains $[SbF_4]_n^{n-}$
DL-Serine	$[SerH]SbF_4$ [10]	SbF_4E	Polymeric chains $[SbF_4]_n^{n-}$
DL-Valine	$SbF_3 \cdot Val$ [11]	SbF_3O_2E	Polymeric chains
	$[ValH]SbF_4 \cdot H_2O$ [11]		
L-Leucine	$SbF_3 \cdot Leu$ [12]	SbF_3OE	Three-dimensional scaffold
	$[LeuH]SbF_4$ [13]	SbF_4E,[a] SbF_5E[b]	Polymeric chains $[Sb_2F_8]_n^{2n-}$
L-Phenylalanine	$SbF_3 \cdot Phe$ [14]	SbF_3O_2E	Polymeric chains of SbF_3 and Phe groups

[a] Fig. 1. [b] Fig. 2.

Stability of antimony(III) fluoride complexes was studied by cementation method; results are summarized in Table 2. Yield of antimony was affected the starting compound composition and ranged in between 47.6% and 96.2%. Recovery of antimony from the solutions containing fluoride complexes of antimony (III) with the F : Sb ratio of 3 was of 50–62.5%. 74.5% of the pure metal could be isolated from the solution of KSb_2F_7 (F : Sb of 3.5), whereas solutions of complex pentafluoroantimonates(III) (F : Sb of 5) yielded 47.6–85.7% of metal antimony. The highest yield of antimony (about 96%) could be obtained from the solutions of tetrafluoroantimonates(III) with protonated amino acids.

Morphology of the metal antimony specimens is shown in Fig. 1. The antimony particles were built of complex needle-shaped crystals (dendrites), 2 to 20 μm long and about 1.2 μm thick. Composition of metal antimony samples isolated from solutions of the complex fluorides was close to that recommended for production of lead antimonate, anti-frictional alloys and alloys for cable shell and universal batteries [16].

In order to find the best source of metal antimony, solution of antimony trichloride in aqueous hydrochloric acid were studied. In that case, cementation yielded the precipitate containing metal antimony (52.8%) and antimony(III) oxochloride crystal hydrate $Sb_8O_{11}Cl_2 \cdot 6H_2O$ (47%). Compound of the latter composition was prepared earlier under different conditions [17]. Hence, in order to obtain the highest yield of antimony, application of aqueous solutions of antimony(III) complex fluorides is advantageous, the best results being achieved in the case of tetrafluoroantimonates(III) with the amino acids cations.

Rate of the metal precipitation depends on its concentration in the solution [18]. Evidently, amount

Table 2. Yield of metal antimony from aqueous solutions of complex fluorides of antimony(III) as function of their composition[a]

Compound	Sb yield, %	Compound	Sb yield, %
SbF_3	62.5	NH_4SbF_4	91.8
SbF_3Leu	51.4	$AlaHSbF_4$	94.6
SbF_3Phe	50.0	$ValHSbF_4H_2O$	96.2
KSb_2F_7	74.5	$LeuHSbF_4$	81.5
$NaSbF_4$	92.8	K_2SbF_5	85.7
$KSbF_4$	73.0	$(NH_4)_2SbF_5$	47.6
$CsSbF_4$	70.5		

[a] Fluoride complexes of antimony(III) were prepared as described elsewhere [1, 3].

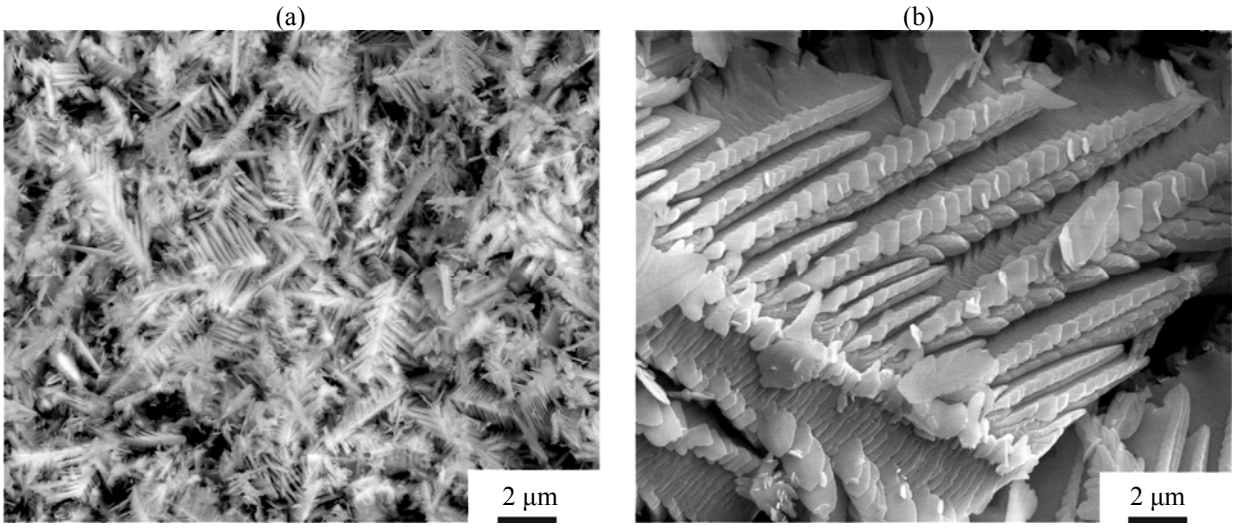

Fig. 1. Microscopy of metal antimony. (a) Magnification ×500; (b) magnification ×1000.

of metal antimony formed in course of cementation depends on the ions concentration [or, in other words, on stability of Sb(III) fluoride complexes in aqueous solutions] as well. Noteworthily, attempts to elucidate the complexes structure in solution have been described [19], but their hydrolysis has not been yet studied in detail.

Stability of fluoroantimonates(III) with amino acids in aqueous solutions has been studied by ^{1}H NMR spectroscopy. The most prominent change of chemical shifts as function of pH was observed in the case of proton of the $NH_2C\underline{H}^{\alpha(\beta)}$ group, the closest to the protonation site; that was in agreement with the published data [20]. Changes of ^{1}H NMR chemical shifts of the amino acids (Glu, β-Ala, Val, Leu, and Phe) and their complexes with antimony(III) fluorides correlated with dissociation constant of the amino aids COOH group (pK_1 2 and 3 [20]) (Fig. 2).

Chemical shifts of the α-protons[1] in the amino acids complexes with SbF_3 were close to those of the corresponding amino acids, pointing at fairly low stability constant in aqueous solutions. In neutral solutions, in the cases of all the studied complexes except for that with leucine, $LeuHSbF_4$, (Fig. 2c), chemical shift of the α-proton equaled that of the pure amino acid.

In the case of complex with glycine SbF_3·Gly, position of the α-proton signal at pH of 2–5 deviated more from that of the pure amino acid than in the case of $2SbF_3$·Gly complex (Fig. 2a). However, at pH > 5 chemical shifts of the 1 : 1 complex signals coincided with those of the pure amino acid.

In the case of complex with valine SbF_3·Val, at pH 1.5–2.5 signal of the α-proton moved downfield as compared to pure valine, pointing at the complex formation. Under such conditions, COOH group of the amino acid dissociated. Cleavage of the O–Sb bonding occurred at higher pH (Fig. 2b).

Chemical shifts of the β-protons in the complex with β-alanine $\beta\text{-}AlaHSbF_4$ were practically the same as those in the case of pure β-alanine (Fig. 2b), pointing at fairly weak bond between Sb atom and the ligand.

Complex with leucine $LeuHSbF_4$ was more stable than the complexes of other amino acids, and existed over wider pH range. Even at pH 7, the α-proton chemical shift deviated from that of the pure amino acid (Fig. 2c).

Complex with phenylalanine SbF_3·Phe revealed upfield shift of the α-proton signal as compared with that of the pure amino acid; the complex was stable at pH ≤ 4 (Fig. 2c).

The low yield (about 50%) of metal antimony upon cementation of the complexes with leucine and phenylalanine (Table 2) coincided with the higher stability of those complexes as compared with complexes of other amino acids, derived from ^{1}H NMR data (Fig. 2).

Structure of SbF_3 complexes with the amino acids in the crystal state was relatively complex (Table 1).

[1] β-Protons in the β-alanine spectrum.

Interaction of the SbF_3 molecules with organic molecules as well as with other antimony(III) fluoride molecules significantly affected the charge transfer upon the complexes formation. Low stability of the complexes in aqueous solutions complicates interpretation of ^1H NMR shifts of the complexes.

EXPERIMENTAL

Morphology of the obtained antimony samples was observed using a EVO-50 XPV scanning electron microscope (LEO, Germany).

^1H NMR spectra of aqueous solutions of the amino acids complexes with SbF_3 (Table 1) were recorded using a Bruker Avance 300 spectrometer (room temperature, pH of 1–6). The chemical shifts δ were determined with accuracy of ±0.01 ppm and referenced to sodium 3-(trimethylsilyl)propanesulfonate. The salt acted as internal reference: 200 mg of the sample was added to the reference salt solution in deuterated water, and the spectrum was registered.

Complex fluorine-containing compounds of antimony(III) were prepared starting from the following substances: antimony(III) fluoride (*pure* grade), glycine, β-alanine, DL-serine, DL-valine, L-leucine, and hydrogen fluoride (all of *chemical pure* grade), and L-phenylalanine (Ajinomoto).

The amino acids complexes with SbF_3 were prepared in the aqueous solution at the reactants molar ratio of 0.5–1 : 1 [8–14]. Purity of the prepared compounds was determined by chemical and X-ray diffraction studies taking advantage of the standard procedures. X-ray diffraction patterns were recorded using a Bruker D8 ADVANCE diffractometer (CuK_α), the compounds were identified using the EVA software and the database of powder diffraction data PDF-2.

Stability of the prepared complexes in aqueous solutions was studied with cementation method, in comparison with antimony trifluoride as well as alkali metals and ammonium complex fluoroantimonates(III).

The cementation method is based on the ability of more electropositive metal ions to be reduced from the solution upon interaction with more electronegative metals [21]. With no external electromotive force, at the electrode made of the more active metal (for example, iron with respect to antimony), the less active metal precipitates from the solution (for the above example, $2Sb^{3+} + 3Fe^0 \rightarrow 2Sb^0 + 3Fe^{2+}$).

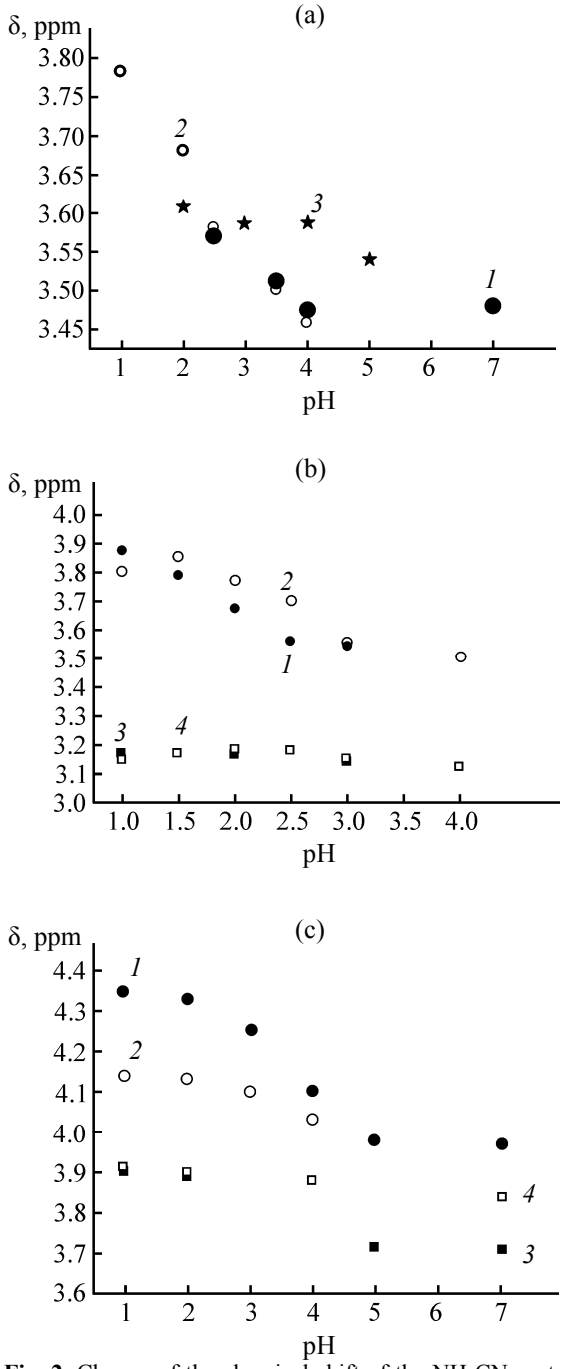

Fig. 2. Change of the chemical shift of the NH_2CN proton in the ^1H NMR spectrum. (a): (*1*) Glycine, Gly; (*2*) complex $2SbF_3$·Gly; (*3*) complex SbF_3·Gly; (b): (*1*) valine, Val; (*2*) complex SbF_3·Val; (*3*) β-alanine, Ala; (*4*) complex $AlaHSbF_4$; (c): (*1*) phenylalanine, Phe; (*2*) complex SbF_3·Phe; (*3*) leucine; (*4*) complex $HLeuSbF_4$.

In the experiment, we used the electrode made of St3 steel (20 × 20 × 3 mm) that was polished, washed with distilled water, and dried in dessicator prior to use. The electrode was then immersed into aqueous

solution (pH 1) of the tested antimony(III) fluorine-containing compound. In particular, 0.7 g/L of the studied compound was dissolved in aqueous HCl (0.1 mol/L) at room temperature. After 20–30 min of incubation, silver-white precipitate with metal luster appeared at the electrode surface; X-ray diffraction study confirmed its identity to metal antimony. The longest incubation time was of 120 h.

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