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CRYSTAL STRUCTURE OF *DL*-SERINIUM HEPTAFLUORODIANTIMONATE(III)

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The crystal structure of *DL*-serinium heptafluorodiantimonate(III) $(C_3H_8NO_3)Sb_2F_7$ (**I**) synthesized for the first time is determined (monoclinic crystal system: $a = 6.6367(1)$ Å, $b = 5.9521(1)$ Å, $c = 13.5562(3)$ Å, $Z = 2$, space group $P2_1$). The structure of $(C_3H_8NO_3)Sb_2F_7$ represents a new structure type of complex antimony(III) fluoride with a protonated amino acid cation. It is formed of *DL*-serinium $(C_3H_8NO_3)^+$ cations and dimeric $[Sb_2F_7]^-$ anion complexes. The complex $[Sb_2F_7]^-$ anions consist of two trigonal SbF_4E bipyramids sharing a vertex. The structural units are arranged into a three-dimensional framework via N–H···F, O–H···O, and O–H···F hydrogen bonds.

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INTRODUCTION

The study of formation regularities of metal coordination compounds with amino acids (AAs) is of interest for tackling problems such as the mechanisms of element bioaccumulation, design of drugs for directed drug delivery to target organs, chemical modification of proteins by attaching certain groups to AA residues in a protein molecule. Complex compounds of *p* elements with AAs are less studied, as compared to transition metal complexes [1] despite the fact that antimony is still an important part of the modern arsenal of medications [2].

The need to determine the mechanisms of action of antimony(III)-based drugs in a body generates interest in studying the structure of trivalent antimony coordination compounds with various organic ligands. The interaction of antimony(III) halides with nitrogen-containing ligands, especially with AAs, mainly results in the formation of molecular adducts [3, 4]. Antimony trifluoride reacts with neutral organic donor ligands to form molecular complexes and fluoroantimonates(III) with cations of alkali metals, ammonium, thallium, divalent metals and protonated cations of organic bases. Among many and compositionally diverse complex fluoroantimonates(III), which have been structurally investigated, the crystal structures of tetrafluoroantimonates(III) are most fully represented [5]. On studying the interaction of antimony trifluoride with aliphatic AAs (glycine, β-alanine, *DL*-valine, *L*-leucine), hydroxy-AA *DL*-serine, and aromatic *L*-phenylalanine in an aqueous medium a series of compounds were prepared. The synthesis of four SbF_3 complex compounds with simplest AA (glycine) with the composition $2SbF_3(^+NH_3CH_2COO^-)$, $SbF_3(^+NH_3CH_2COO^-)$, $SbFO(^+NH_3CH_2COO^-)$, and $(NH_3CH_2COOH)SbF_4$ was described in [6]. The molecular complexes of antimony trifluoride with *DL*-valine [7], *L*-leucine

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[8], *L*-phenylalanine [9] and tetrafluoroantimonates(III) of protonated AAs β-alanine (monohydrate and anhydrous) [10], *DL*-serine [11], *L*-leucine [12] and *DL*-valine (monohydrate) [13] were synthesized and structurally studied. Within the systematic study of the chemistry and structure of complex compounds of antimony(III) fluoride with AAs, *DL*-serinium heptafluorodiantimonate(III) $(C_3H_8NO_3)Sb_2F_7$ was synthesized for the first time. The structure of the newly synthesized compound was compared with those of previously studied *DL*-serinium tetrafluoroantimonate(III) (**II**) and rubidium and 1,2,4-triazolium heptafluorodiantimonates(III).

EXPERIMENTAL

The complex compound was synthesized preparatively by the interaction chemically pure SbF_3 and reagent grade *DL*-serine (preliminary recrystallized from water) taken in a 1:0.5 molar ratio in an aqueous solution in the presence of hydrofluoric acid. The portions of precursors were dissolved in water; the solutions heated to ~50-60 °C were mixed together. The solution acidity was adjusted to pH 1-2 by adding hydrofluoric acid. The obtained solution was evaporated to 1/3 of the initial volume and left for slow crystallization at room temperature. The crystalline substance formed was vacuum filtered and dried in the air until reaching a constant weight. The individuality of the prepared compound was determined by chemical (found Sb, %: 50.65; for $(C_3H_8NO_3)Sb_2F_7$ calculated Sb, %: 50.46) and IR spectroscopic analyses. The IR absorption spectra of the samples were recorded in a range 400-4000 cm^{-1} using the standard procedure in paraffin oil (IRAffinity-1 Fourier spectrometer, Shimadzu).

Single crystal X-ray diffraction study. Colorless transparent crystals of $(C_3H_8NO_3)Sb_2F_7$ are monoclinic ($M = 482.60$, $a = 6.6367(1)(2)$ Å, $b = 5.9521(1)$ Å, $c = 13.5562(3)$ Å, $\beta = 92.14(1)°$, $V = 535.13(2)$ Å^3, $Z = 2$, $d_{calc} = 2.995$ g/cm^3, $\mu(MoK_\alpha) = 5.142$ mm^{-1}, space group $P2_1$). The X-ray experiment was carried out with a 0.20×0.18×0.05 mm single lamellar crystal at a temperature of 296 K on a Bruker KAPPA APEX II diffractometer (MoK_α radiation, graphite monochromator, ω-scanning with a step of 0.3° covering a hemisphere of reciprocal space and 20 s acquisition per scan; the crystal-to-detector distance was 45 mm). X-ray absorption in the sample was taken into account based on equivalent reflections. The intensities of 16804 reflections, including 6816 [$R(\text{int}) = 0.0193$)] independent, were measured in an angle range $2\theta \leq 90.12°$. The structure of **I** was determined by a direct method and refined by the least squares method in the anisotropic approximation for non-hydrogen atoms to $R_1 = 0.0187$ and $wR_2 = 0.0412$ for 6416 reflections with $F^2 > 2\sigma(F^2)$, $GOOF = 1.011$. The positions of hydrogen atoms in the protonated serine molecule were calculated geometrically and included in the refinement using the riding model.

The data were collected and edited and the unit cell parameters were refined using the Bruker APEX2 software [14]. All calculations related to the structure determination and refinement were performed using the SHELXTL/PC software [15]. The main bond lengths and bond angles are given in Table 1 and the geometric parameters of hydrogen bonds are reported in Table 2.

The CIF file containing full information on the studied structure has been deposited with CCDC under number 1563434 and is available free on request via the following website: www.ccdc.cam.ac.uk/data_request/cif.

RESULTS AND DISCUSSION

Prepared complex compound **I** is stable when stored in the air, very soluble in water. The IR absorption spectra of complexes **I**, **II** and serine are shown in Fig. 1. A protonated COOH group of AA is known to have an intense band in the IR spectrum at 1700 cm^{-1}; and a deprotonated COOH group in the zwitterion form, at ~1600 cm^{-1}. The IR spectrum of the initial *DL*-serine has no absorption bands at 1700 cm^{-1} and 1200 cm^{-1} characteristic of the protonated carboxyl group and an intense absorption band at 1574 cm^{-1} is observed in the stretching frequency range of the COO group, which agrees well with the literature data [16].

TABLE 1. Interatomic Distances and Bond Angles in the Structure of **I**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
Sb(1)–F(1)	1.922(1)	Sb(2)–F(5)	1.944(1)	C(1)–O(1)	1.417(4)
Sb(1)–F(2)	1.939(2)	Sb(2)–F(6)	1.946(2)	C(1)–C(2)	1.515(3)
Sb(1)–F(3)	1.971(1)	Sb(2)–F(7)	1.989(1)	C(2)–N	1.485(3)
Sb(1)–F(4)	2.361(2)	Sb(2)–F(4)	2.314(2)	C(2)–C(3)	1.523(3)
Sb(1)···F(7)[a]	2.698(1)	Sb(2)···F(4)[c]	2.621(2)	C(3)–O(2)	1.200(3)
Sb(1)···F(5)[b]	3.039(2)	Sb(2)···F(2)	3.110(2)	C(3)–O(3)	1.311(3)
		Sb(2)···F(5)[c]	3.140(2)		
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
F(1)Sb(1)F(2)	91.59(7)	F(5)Sb(2)F(6)	86.60(8)	O(1)C(1)C(2)	109.9(2)
F(1)Sb(1)F(3)	86.54(7)	F(5)Sb(2)F(7)	82.35(7)	C(1)C(2)N	110.8(2)
F(1)Sb(1)F(4)	78.99(7)	F(5)Sb(2)F(4)	75.37(6)	C(1)C(2)C(3)	113.8(2)
F(2)Sb(1)F(3)	84.70(8)	F(6)Sb(2)F(7)	84.96(10)	NC(2)C(3)	107.7(2)
F(2)Sb(1)F(4)	74.58(6)	F(6)Sb(2)F(4)	80.75(8)	C(2)C(3)O(2)	122.6(2)
F(3)Sb(1)F(4)	154.22(8)	F(4)Sb(2)F(7)	154.10(9)	C(2)C(3)O(3)	111.2(2)
Sb(1)F(4)Sb(2)	114.91(7)			O(2)C(3)O(3)	126.2(2)

Symmetry codes: [a] *–x*+1, *y*+1/2, *–z*; [b] *–x*, *y*+1/2, *–z*; [c] *–x*, *y*–1/2, *–z*.

TABLE 2. Geometric Parameters of Hydrogen Bonds in the Structure of **I**

D—H···A bond	Distance, Å			DHA angle, deg
	D—H	H···A	D···A	
O(1)–H(1)···F(3)[a]	0.82	1.88	2.683(3)	166
O(3)–H(3)···O(1)[b]	0.82	1.89	2.638(3)	152
N–H(0A)···F(1)[c]	0.89	1.93	2.790(2)	163
N–H(0B)···F(2)[d]	0.89	1.99	2.862(2)	167
N–H(0C)···F(5)[e]	0.89	1.91	2.785(2)	166
C(2)–H(2)···F(3)[f]	0.98	2.39	3.223(3)	143
C(2)–H(2)···F(7)[e]	0.98	2.54	3.372(3)	143
C(1)–H(1A)···O(2)[g]	0.97	2.62	3.510(3)	152

Symmetry codes: [a] *–x*+1, *y*+1/2, *–z*+1; [b] *–x*, *y*–1/2, *–z*+1; [c] *–x*, *y*+1/2, *–z*+1; [d] *–x*+1, *y*+1/2, *–z*+1; [e] *x*, *y*, *z*+1; [f] *–x*+1, *y*–1/2, *–z*+1; [g] *x*+1, *y*, *z*.

In a range 2100-3200 cm^{-1} there is a group of bands corresponding to vibrations of a positively charged NH_3^+ group. In the IR spectrum of **I**, as distinct from the spectrum of serine, there are an intense absorption band at 1732 cm^{-1} and a medium intense band with a maximum at 1256 cm^{-1}. These absorption bands unambiguously indicate that the $(C_3H_8NO_3)^+$ cation in the composition of the fluoride antimony(III) complex contains the protonated COOH group.

The assumptions made from the IR spectroscopic study of compound **I** were confirmed by the determination of its crystal structure.

A unit cell of the crystal structure of $(C_3H_8NO_3)Sb_2F_7$ (Fig. 2) contains two crystallographically independent Sb atoms, seven F atoms, and one $(C_3H_8NO_3)^+$ cation.

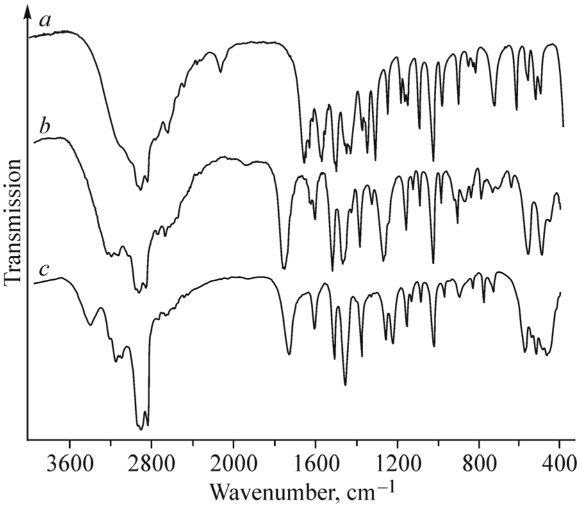

Fig. 1. IR spectra: serine (*a*), complexes **I** (*b*) and **II** (*c*).

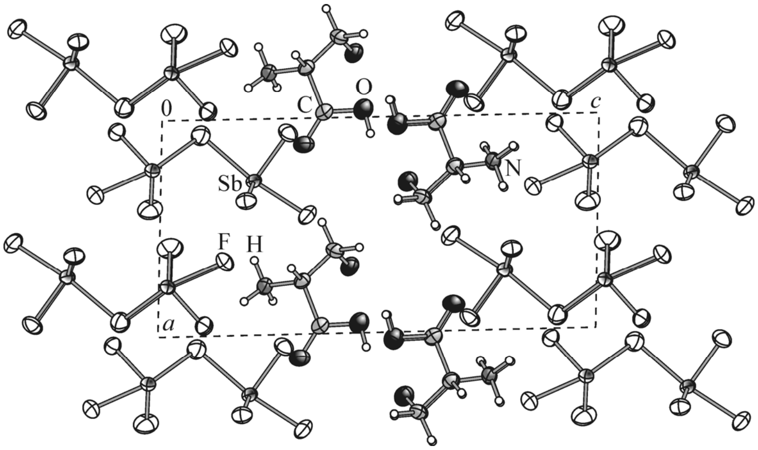

Fig. 2. Structure of the crystal structure of $(C_3H_8NO_3)Sb_2F_7$.

In the structure of $(C_3H_8NO_3)Sb_2F_7$ the coordination polyhedra of the Sb1 and Sb2 atoms within the first coordination sphere [17] are ψ-trigonal SbF_4E bipyramids (Fig. 3), which are joined together by a common vertex with the F4 atom into a dimeric $[Sb_2F_7]^-$ complex anion.

In the polyhedra (Table 1) the Sb-F distances and the F–Sb–F bond angles are 1.922(1)-2.361(2) Å and 74.58(6)-91.59(7)° respectively and are typical of a ψ-trigonal bipyramidal configuration [18].

The Sb(1)–Sb(2) distance in the dimer is 3.940(1) Å. In addition to short Sb–F bonds, the antimony atoms within the second coordination sphere have yet another five weaker Sb···F bonds of 2.621(2)-3.140(2) Å (Table 1), by which the dimeric anion complexes are arranged into $[Sb_2F_7]_n^{n-}$ anion layers parallel to the (001) plane. The minimum Sb···Sb distances in the layers are 4.198 Å, 4.263 Å, and 4.293 Å, which correspond to intermolecular interactions [19].

In the structure of **I** the $(C_3H_8NO_3)^+$ cation has a typical geometry (Fig. 4) analogous to that in the structure of **II** [11]. In both cations the geometric parameters of the bonds are characteristic of protonated AA cations: in the carboxyl groups of the $(C_3H_8NO_3)^+$ cations of complexes **I** and **II** the C–O bond lengths are 1.311(3) Å and 1.313(2) Å and the C=O bond lengths are 1.200(3) Å and 1.202(2) Å respectively. The lengths of the C–N and C–C bonds are also typical of such bonds.

The serinium cations and the $[Sb_2F_7]^-$ complex anions in the structure of **I** are organized into a framework by hydrogen bonds formed with the involvement of all hydrogen atoms of the cation, excluding the H(1B) atom of the (–CH_2–) moiety.

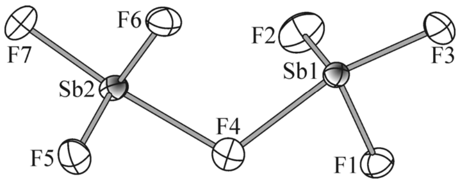

Fig. 3. Structure of the dimeric $[Sb_2F_7]^-$ complex in the structure of **I**.

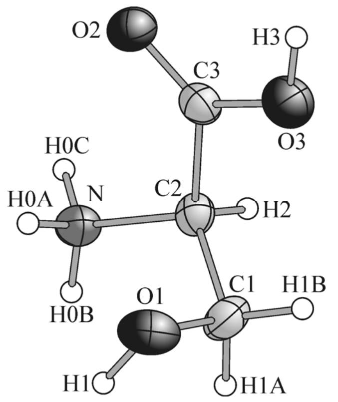

Fig. 4. Structure of the $(C_3H_8NO_3)^+$ cation in the structure of **I**.

The crystal structure of **I** substantially differs from that of previously synthesized compound **II** whose structure is formed of $(C_3H_8NO_3)^+$ cations and $[SbF_4]_n^{n-}$ complex anions having a polymer chain structure. Unlike **I**, in the structure of **II** the coordination polyhedra of the Sb atom, which also have a ψ-trigonal bipyramidal configuration, are linked via the bridging fluorine atoms into bent polymer anion chains extended along the *b* crystal axis (in a polymer chain the Sb···Sb distance is 4.372 Å).

The analysis of structural data shows that in the previously studied complex heptafluorodiantimonates(III) with the composition MSb_2F_7 ($M = K^+$, Rb^+, Cs^+, Tl^+, $C_2N_3H_4^+$) the antimony polyhedra are very diverse [5]. The number of non-equivalent positions of antimony atoms in a unit cell depends on the cation nature and varies from 2 to 6. The structural motifs in antimony(III) complexes with the F:Sb ratio of 3.5 are mostly different. The crystal structure of **I** is much similar to the structures of previously studied heptafluorodiantimonates(III) formed of rubidium cations and 1,2,4-triazolium and dimeric $[Sb_2F_7]^-$ complex anions. The coordination polyhedra of the antimony atoms in $RbSb_2F_7$ [20] are ψ-trigonal $Sb(1)F_4E$ and $Sb(2)F_4E$ bipyramids arranged into layers. 1,2,4-Triazolium heptafluorodiantimonate(III) also has a similar structure [21]; it is found that there are also two non-equivalent positions of antimony atoms $Sb(1)F_4E$ and $Sb(2)F_4E$ in its unit cell. The $C_2N_3H_4^+$ cations in this compound, being located in the cavities between the layers of dimeric $[Sb_2F_7]^-$ anions, link the layers themselves and the dimer complexes in the layers through hydrogen bonds.

Therefore, in the group of coordination compounds of antimony trifluoride with AAs, complex antimony(III) fluoride with the protonated AA cation was synthesized for the first time. Its structure is formed of *DL*-serinium $(C_3H_8NO_3)^+$ cations and dimeric $[Sb_2F_7]^-$ anion complexes.

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