

CRYSTAL STRUCTURE OF A MOLECULAR COMPLEX COMPOUND OF ANTIMONY(III) FLUORIDE WITH *L*-LEUCINE

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Single crystal X-ray diffraction analysis is used to determine the crystal structure of a newly synthesized molecular complex compound of antimony(III) fluoride with *L*-leucine of the composition $\text{SbF}_3(\text{C}_6\text{H}_{13}\text{NO}_2)$ (orthorhombic crystal system: $a = 5.7948(8)$ Å, $b = 6.2433(9)$ Å, $c = 28.594(4)$ Å, $Z = 4$, $P2_12_12_1$ space group). The structure consists of SbF_3 molecules and *L*-leucine bound into polymer chains by bidentate bridging carboxyl groups of amino acid molecules. Weak $\text{Sb}\dots\text{F}(1)^b$ bonds combine the adjacent chains into polymer ribbons organized by $\text{N-H}\dots\text{F}$ and $\text{N-H}\dots\text{O}$ hydrogen bonds into a framework.

Keywords: single crystal X-ray diffraction analysis, crystal structure, antimony(III) fluoride, *L*-leucine, molecular complex compound.

Antimony(III) fluoride, which is a Lewis acid, exhibits acceptor properties to both charged and molecular organic ligands containing active donor centers. The acceptor property of SbF_3 to fluoride ions and other acid anions has been thoroughly studied [1, 2]. However, the data on SbF_3 complex compounds with molecular ligands are scarce [3]. We have previously obtained and studied an antimony(III) fluoride molecular complex compound with glycine [4] and *D,L*-valine [5]. The aim of the present work is to perform single crystal X-ray diffraction analysis of a newly synthesized SbF_3 molecular complex compound with *L*-leucine of the composition $\text{SbF}_3(\text{C}_6\text{H}_{13}\text{NO}_2)$.

Experimental. The $\text{SbF}_3(\text{C}_6\text{H}_{13}\text{NO}_2)$ compound was obtained by the interaction of SbF_3 and *L*-leucine in HF aqueous solution. Single crystals of the compound suitable for X-ray diffraction were grown by slow crystallization of aqueous solution at room temperature. Colorless transparent crystals of $\text{SbF}_3(\text{C}_6\text{H}_{13}\text{NO}_2)$ have a plate form and belong to the orthorhombic crystal system. These crystals are readily soluble in water and unstable: under the slightest mechanical action the plates bend and microplates shift along the *ab* plane. The crystal plate selected for the X-ray diffraction study was glued with epoxy to a glass thread, while its deformed edges were dissolved with a wet filter paper under a microscope. Hence, for the measurements we obtained a 0.20 mm thick round plate with a radius of 0.18 mm. The X-ray experiment was performed at 203 K using a Bruker SMART-1000 CCD diffractometer. The main crystallographic data and structure refinement results are listed in Table 1. The data were collected by ω -scanning with a 0.2° step and 20 s exposure time for each frame in three groups of 906 frames with the angle values $\varphi = 0^\circ$, 90° , and 180° and a crystal–detector distance of 45 mm. Absorption was taken into account by equivalent reflections.

The structure was solved by the direct method and refined by the least-squares method in the anisotropic approximation of non-hydrogen atoms. Hydrogen atoms of an *L*-leucine molecule were located geometrically and refined using the riding model.

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TABLE 1. Crystallographic Data, Parameters of the Experiment and SbF₃(C₆H₁₃NO₂) Structural Refinement

Formula	C ₆ H ₁₃ NO ₂ SbF ₃
Molecular weight	309,92
Temperature, K	203(2)
Wavelength, Å	MoK _α (0.71073)
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> , <i>b</i> , <i>c</i> , Å	5.7948(8), 6.2433(9), 28.594(4)
<i>V</i> , Å ³	1034.5(3)
<i>Z</i>	4
<i>d_x</i> , g/cm ³	1.990
<i>μ</i> , mm ⁻¹	2.682
<i>F</i> (000)	600
Crystal size, mm	0.36×0.36×0.20
θ data collection range, deg	4.33–28.54
Ranges of reflection indices	−6 ≤ <i>h</i> ≤ 7, −8 ≤ <i>k</i> ≤ 8, −38 ≤ <i>l</i> ≤ 38
Measured/ independent reflections	8925/2629 (<i>R</i> _{int} = 0.0367)
Reflections with <i>I</i> > 2σ(<i>I</i>)	2551
Refinement variables	122
<i>S</i>	1.262
<i>R</i> factor over <i>I</i> > 2σ(<i>I</i>)	<i>R</i> 1 = 0.0311, <i>wR</i> 2 = 0.0704
<i>R</i> factor over all reflections	<i>R</i> 1 = 0.0323, <i>wR</i> 2 = 0.0707
Res. el. density (max / min), e/Å ³	1.294/−1.563

TABLE 2. Some Bond Lengths (*d*, Å) and Bond Angles (ω, deg) in the SbF₃(C₆H₁₃NO₂) Structure

Bond	<i>d</i>	Bond	<i>d</i>	Angle	ω	Angle	ω
Sb–F(3)	1.9251(6)	Sb–O(1)	2.4745(7)	F(3)SbF(1)	86.38(2)	F(1)SbO(2) ^a	83.02(3)
Sb–F(2)	1.9498(6)	Sb–O(2) ^a	2.5618(7)	F(3)SbF(2)	86.77(3)	F(2)SbO(1)	75.65(3)
Sb–F(1)	1.9736(6)	Sb...F(1) ^b	2.8616(6)	F(3)SbO(1)	79.28(2)	O(1)SbO(2) ^a	115.00(2)
				F(3)SbO(2) ^a	80.73(2)	F(1)SbO(1)	154.37(2)
				F(1)SbF(2)	82.49(3)	F(2)SbO(2) ^a	161.40(2)

Symmetry codes: ^a*x*, *y*−1, *z*; ^b−*x*+1, *y*+1/2, −*z*+3/2.

The data were collected and edited, and the unit cell parameters were refined using the SMART and SAINT Plus programs [6]. All calculations for the structure determination and refinement were performed using the SHELXTL/PC program [7]. The CIF file with full information on the studied structure was deposited to CCDC under No. 745254, and now it is available on request at www.ccdc.cam.ac.uk/data_request/cif. The main bond lengths and bond angles of the studied complex compound are listed in Table 2.

Results and Discussion. In order to gain some preliminary information on the structure of the synthesized SbF₃(C₆H₁₃NO₂) complex compound (**I**) we studied the IR absorption spectrum that was compared to the IR spectrum of the *L*-leucine molecule (the IR absorption spectra of the samples were measured in the range of 400 cm⁻¹ to 4000 cm⁻¹ using the standard method in vaseline oil). In the IR spectrum of *L*-leucine (Fig. 1*a*), the region of stretching vibrational frequencies of the COO group contains an intense absorption band at 1582 cm⁻¹ that corresponds to the deprotonated carboxyl group of amino acid. In the 2600–3100 cm⁻¹ range a broad intense band with several maxima is observed, which belongs to the

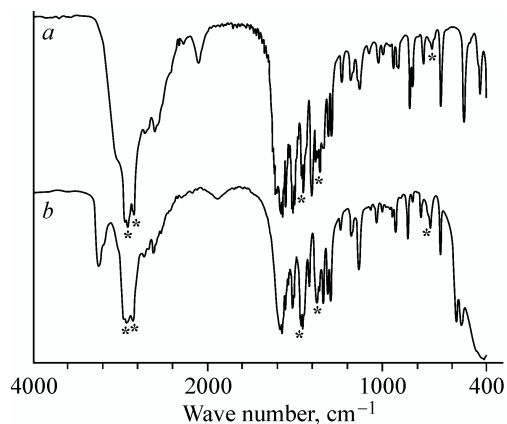


Fig. 1. IR absorption spectra of *L*-leucine (a) and $\text{SbF}_3(\text{C}_6\text{H}_{13}\text{NO}_2)$ (b).

positively charged NH_3^+ group. The presence of the deprotonated COO group and positively charged NH_3^+ group in the *L*-leucine compound indicates the zwitterionic structure of amino acid.

The IR spectrum of complex **I** (Fig. 1b) is almost identical to that of original *L*-leucine in the 600-2000 cm^{-1} frequency range (below 600 cm^{-1} the IR spectrum of complex **I** contains the absorption bands of Sb-F bonds of a SbF_3 molecule). They are slightly different only in the region of stretching vibrational frequencies of NH_3^+ . Along with a broad band at 2600-3110 cm^{-1} the IR spectrum of **I** also contains a moderately intense absorption band with the maximum at 3250 cm^{-1} and a bend at 3190 cm^{-1} . The observed shift of NH_3^+ group absorption bands to the high-frequency range in the IR spectrum of complex compound **I** is likely to be caused by weakening of hydrogen bonding in the complex compound comparing to hydrogen bonding in *L*-leucine.

The presence of the COO^- deprotonated carboxyl group and the positively charged NH_3^+ group in the *L*-leucine molecule entering into complex compound **I** indicates that the zwitterionic structure of the molecule is preserved when the complex compound with SbF_3 forms. Thus, the conclusions made based on the IR spectroscopic analysis of the structure of synthesized compound **I** are confirmed by the crystal structure determination.

The crystal structure of complex compound **I** consists of SbF_3 groups and *L*-leucine molecules bound via oxygen atoms of bidentate bridging carboxyl groups of amino acid molecules into polymer chains along the *b* axis of the crystal.

The antimony atom of complex compound **I** (Fig. 2) is surrounded by three fluorine atoms of a SbF_3 molecule with Sb-F distances of 1.9251(6) Å, 1.9498(6) Å, and 1.9736(6) Å (Table 2) that are slightly different from the Sb-F bond lengths in the SbF_3 crystal structure (Sb-F 1.90(2) Å, 1.90(2) Å, and 1.94(2) Å) [8]. The F-Sb-F bond angles have similar values in the crystal structure of **I** (Table 2) and SbF_3 [8]. These data give evidence of a small distortion of the SbF_3 group in the formation of the complex compound with *L*-leucine.

Along with three F atoms the Sb atom is also surrounded by two carboxyl bridging O atoms of two neighboring *L*-leucine molecules (Sb-O 2.4745(7) Å and 2.5618(7) Å) (Fig. 2). The Sb-O bonds are weak in the structure of **I** in comparison to the Sb-F bonds (mainly ionic) and are typical of bridging Sb-O bonds. The bridging Sb-O bonds of similar lengths (Sb-O 2.524(2) Å and 2.552(2) Å) are observed in the crystal structure of the antimony(III) fluoride complex compound with *D,L*-valine [5], which also has a chain structure.

The crystal structure of compound **I** is significantly different from the structure of the antimony(III) fluoride molecular complex compound with glycine with a similar composition $\text{SbF}_3(^+\text{NH}_3\text{CH}_2\text{COO}^-)$ (**II**) [4]. In the structure of **II**, the SbF_3 group forms a strong bond with one oxygen atom of the deprotonated carboxyl group of a glycine molecule (Sb-O(2) 2.240 Å). The resulted coordination polyhedron of the antimony atom has a form of a SbF_3OE trigonal bipyramid with an unoccupied vertex in the equatorial plane occupied by a lone electron pair (*E*) of the Sb^{3+} ion.

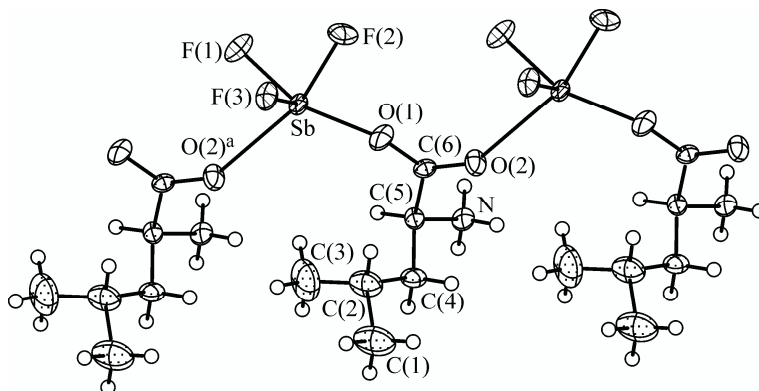


Fig. 2. Fragment of a polymer chain in the structure of **I**.

Geometrical characteristics of the *L*-leucine molecule in the structure of complex compound **I** are similar to those in the *L*-leucine crystal structure [9]. The C–O bond lengths in the carboxyl group of the *L*-leucine molecule entering into complex compound **I** are 1.2448(11) Å and 1.2658(10) Å, which is typical of one-and-a-half C–O bond lengths of the deprotonated COO group in metal carboxylates. Negative charge distribution over both C–O bonds in the carboxyl group of the *L*-leucine molecule provides weak Sb–O bonds in the complex compound. The other bond lengths in the *L*-leucine molecule, i.e. C–C (1.517(2)–1.541(1) Å) and C–N 1.485(1) Å have the values characteristic of amino acid molecules.

The Sb atom has yet another weaker Sb...F(1)^b bond within the second coordination sphere (Table 2), which is used to pairwise organize pairs of polymer chains into ribbons. The latter are combined into a three-dimensional framework by N–H...F and N–H...O hydrogen bonds.

The single crystal X-ray diffraction analysis of SbF₃(C₆H₁₃NO₂) showed that the geometrical characteristics of the SbF₃ group and *L*-leucine entering into the compound composition did not undergo significant changes as compared to those in SbF₃ and *L*-leucine crystals. Therefore, the newly synthesized molecular complex compound of SbF₃(C₆H₁₃NO₂) can be considered as an adduct of SbF₃ and *L*-leucine.

REFERENCES

1. R. L. Davidovich and L. A. Zemnukhova, *Koordinats. Khim.*, **1**, No. 4, 477-481 (1975).
2. A. A. Udovenko and L. M. Volkova, *ibid.*, **7**, No. 12, 1763-1813 (1981).
3. Ya. A. Buslaev and R. L. Davidovich, *ibid.*, **15**, No. 11, 1444-1465 (1989).
4. R. L. Davidovich, V. B. Logvinova, L. A. Zemnukhova, et al., *ibid.*, **17**, No. 10, 1342-1348 (1991).
5. L. A. Zemnukhova, R. L. Davidovich, A. A. Udovenko, and E. V. Kovaleva, *ibid.*, **31**, No. 2, 125-131 (2005).
6. SMART and SAINT-Plus, Versions 5.0, *Data Collection and Processing Software for the Smart System*, Bruker AXS Inc., Madison, Wisconsin, USA (1998).
7. G. M. Sheldrick, *SHELXTL/PC, Versions 5.0, An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*, Bruker AXS Inc., Madison, Wisconsin, USA (1998).
8. A. J. Edwards, *J. Chem. Soc. (A)*, No. 17, 2751-2753 (1970).
9. K. Anitha, S. Athimoolam, and R. K. Rajaram, *Acta Crystallogr.*, **E61**, No. 6, o1604-o1606 (2005).