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Bromide Complexes of Sb(III) with the 4,4'-Dimethyl-1,1'-butanediylbis(pyridinium) Cation: Unexpected Formation of Polymorphs with Complex Cations of Various Nuclearity

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Abstract—The reaction of solutions of Sb_2O_3 and 4,4'-dimethyl-1,1'-butanediylbis(pyridinium) dibromide ((4-MePyC_4)Br_2) in concentrated HBr affords polymorphs: binuclear (4-MePyC_2)[Sb_2Br_8] (**I**) or tetranuclear (4-MePyC_4)$_2$[Sb_4Br_{16}] (**II**) complexes, depending on the reaction conditions. The structures of the complexes are studied by X-ray structure analysis (CIF files CCDC nos. 2061368 (**I**) and 2061369 (**II**)).

Keywords: antimony, bromide complexes, polynuclear complexes, X-ray structure analysis, polymorphism
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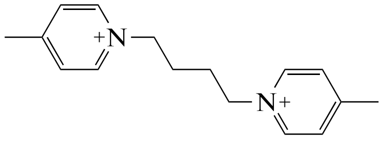
INTRODUCTION

The study of the Sb(III) halide complexes is among a variety of recent trends [1–9] in the coordination chemistry of antimony [10–12]. On the whole, this is due to increasing interest in the chemistry of halometallates of elements of the main groups [13–16]. In turn, this interest is significantly related to the development of the so-called perovskite solar cells [17–20].

As was multiply mentioned earlier [21, 22], halometallates of elements of groups 14 and 15 differ by rich structural types of complex anions (discrete anions of diverse nuclearity; 1D, 2D, and 3D coordination polymers were described) [23]. However, it is impossible to predict even approximately the compositions and structures of halometallate anions depending on the synthesis conditions, which remains so far to be an unsolved problem [22]. Taking into account that no theoretical models that could help in solving this problem were proposed [22], it is most likely that the only reasonable approach is the further accumulation of new experimental (especially X-ray structure analysis (XSA)) data on the structures of halometallates. We hope that in future the amount of these data would provide their quality.

We have recently found [24] that bromoantimonates(III) can be characterized by polymorphism leading to substantial distinctions in optical properties (absorption in the visible range). Further we have found another pair of polymorphs: the reaction of solutions of Sb_2O_3 in HBr with 4,4'-dimethyl-1,1'-butanediylbis(pyridinium) bromide salt ((4-MePyC_4)Br_2) leads to the formation of (4-MePyC_4)[Sb_2Br_8] (**I**) or (4-MePyC_4)$_2$[Sb_4Br_{16}] (**II**) depending on the ratio of the reactants (see below). Their structures are discussed in the present work.

The structure of the (4-MePy)C_4^{2+} cation is shown in Scheme 1.



Scheme 1.

EXPERIMENTAL

The starting reactants used were purchased from commercial sources, and (4-MePyC_4)Br_2 was synthesized by the reaction of 4-methylpyridine and 1,4-dibromobutane (2.05 : 1) in acetonitrile (reflux, 12 h) in the yield close to the quantitative one. In all cases, concentrated HBr was used. The synthesis was carried out in air.

Synthesis of compound I. Antimony oxide Sb_2O_3 (50 mg, 0.17 mmol) was dissolved in HBr (2 mL), and a solution of (4-MePyC_4)Br_2 (68 mg, 0.17 mmol) in HBr (1 mL). Then the solution was kept at 5°C for

Table 1. Crystallographic data and structure refinement parameters for compounds **I** and **II**

Parameter	Value	
	I	**II**
Empirical formula	$C_{16}H_{22}N_2Br_8Sb_2$	$C_{32}H_{44}N_4Br_{16}Sb_4$
FW	1125.13	2250.27
Crystal system, space group	Monoclinic, *P*2/*c*	Monoclinic, $P2_1/n$
a, Å	26.3128(13)	11.4661(3)
b, Å	6.4010(2)	19.7236(4)
c, Å	17.9886(8)	12.5217(3)
β, deg	109.026(5)	92.726(2)
V, $Å^3$	2864.3(2)	2828.61(12)
Z	4	2
ρ_{calc}, g/cm^3	2.609	2.642
μ, mm^{-1}	13.05	13.22
F(000)	2056	2056
Scan range over θ, deg	3.4–28.9	3.3–28.9
Range of indices *hkl*	$-25 \le h \le 35$ $-8 \le k \le 8$ $-22 \le l \le 24$	$-14 \le h \le 15$ $-20 \le k \le 26$ $-12 \le l \le 16$
N_{hkl} measured/independent	15045/6312	14028/6140
R_{int}	0.031	0.027
N_{hkl} with $I > 2\sigma(I)$	5059	5354
R ($F^2 > 2\sigma(F^2)$)	0.033	0.031
$wR(F^2)$, *S*	0.060, 1.03	0.067, 1.05
Residual electron density (min/max), e/Å^3	−1.06/1.06	−1.51/0.87

12 h, and colorless crystals of compound **I** suitable for XSA were formed. The yield was 79%.

For $C_{32}H_{44}N_4Br_{16}Sb_4$

Anal. calcd., %	C, 17.2	H, 2.0	N, 2.5
Found, %	C, 17.4	H, 2.0	N, 2.6

Synthesis of compound II was carried out according to the procedure similar to that for complex **I** using Sb_2O_3 (100 mg, 0.34 mmol) in HBr (3 mL). The yield was 81%.

For $C_{32}H_{44}N_4Br_{16}Sb_4$

Anal. calcd., %	C, 17.2	H, 2.0	N, 2.5
Found, %	C, 17.5	H, 2.1	N, 2.6

XSA of single crystals of compounds **I** and **II** were obtained at 130 K on an Agilent Xcalibur automated diffractometer with an AtlasS2 two-coordinate detector (graphite monochromator, λ(MoK_α) = 0.71073 Å, ω scan mode). Integration was performed, an absorption correction was applied, and the unit cell parameters were determined using the CrysAlisPro program package. The crystal structures were solved using the SHELXT program and refined by full-matrix least squares in the anisotropic (except for hydrogen atoms) approximation using the SHELXL program [25]. The positions of the hydrogen atoms of the organic ligands were calculated geometrically and refined by the riding model. The crystallographic data and details of diffraction experiments are presented in Table 1.

The full tables of interatomic distances and bond angles, coordinates of atoms, and atomic shift parameters were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 2061368 (**I**) and 2061369 (**II**); https://www.ccdc.cam.ac.uk/structures/).

A topological analysis of the molecular packing was performed using the ToposPro program package [26].

RESULTS AND DISCUSSION

The anionic moiety of compound **I** consists of the binuclear anions $[Sb_2Br_8]^{2-}$ that can be presented as the result of condensation of two tetragonal pyramidal fragments $\{SbBr_5\}$ at one of the edges of the base (Fig. 1a). This structural type is rare (only four com-

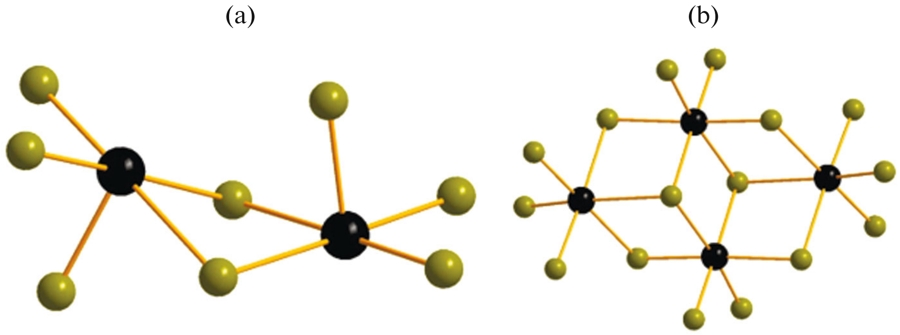


Fig. 1. Structures of the bromoantimonate(III) anions in compounds (a) **I** and (b) **II**.

pounds containing these anions have been described previously [27–30]) and is met more frequently among chloroantimonates(III) [31, 32]. The shortest Sb–Br bond corresponds to the bromide ligands lying at the vertices of the {$SbBr_5$} pyramids (2.524 Å), and other Sb–Br_{term} bonds are somewhat elongated (2.609–2.630 Å). The Sb–μ_2-Br bonds are characterized by the maximum length (2.940–3.044 Å). An analysis of the Sb···Br distances and a comparison of them with the sum of the corresponding van der Waals radii (3.89 Å [33]) do not allow one to suggest any noncovalent interactions of this type. The structure of compound **I** contains the H···Br cation-anionic contacts (the shortest of them are 2.829 Å) typical of the halometallate salts with organic cations.

Compound **II** has an identical empirical composition, but its structure includes the tetranuclear bromoantimonate(III) anions $[Sb_4Br_{16}]^{4-}$. The Sb atoms lie in one plane to form a rhombus (Fig. 1b). The coordination sphere of Sb contains three or two terminal bromide ligands (Sb–Br_{term} 2.568–2.627 and 2.582–2.596 Å, respectively), and the Sb–μ_2-Br (2.693–3.095 Å) and especially Sb–μ_3-Br (3.123–3.241 Å) bonds are longer (this effect is common for the halometallate anions [21]). This structural type is most abundant among discrete tetranuclear halobismuthates(III) [21], and the number of the described corresponding Sb(III) complexes is significantly lower [34–37].

The crystals of compounds **I** and **II** were initially isolated from the identical samples differed in the storage time of the crystals in the mother liquor (10 and 7 days, respectively). We were surprised that the pure phase of compound **I** was formed, according to the X-ray diffraction data, when the synthesis was reproduced with the ratio of the reactants corresponding to the composition of compound **I** or **II** (organic cation salt : Sb_2O_3 = 1 : 1) and the solid phase was isolated within 1 day. No traces of the phase of compound **II** were observed even upon a prolonged (>14 days) storage of the sample in the mother liquor at room temperature. This indicates that the primary results can be considered as an artifact. At the same time, a change in the reactant ratio (twofold increase in the load of Sb_2O_3, i.e., synthesis under the conditions of an organic cation salt deficient) leads to the formation of the pure phase of compound **II** (in both cases, the optimized procedures are presented in Experimental). Reasons for this phenomenon remain unclear.

The packings in the crystals of compounds **I** and **II** are shown in Figs. 2 and 3, respectively. In the structure of compound **I**, the organic cations form a primitive cubic unit (pcu) containing the binuclear anions in the cavities, and the topology of the full packing is body centered cubic (bcc, type CsCl, bcu-x, Fig. 4). In the structure of compound **II**, the bcc motif is strongly distorted, although its elements can be monitored: the tetranuclear anions are linked to each other via the pcu motif, and the cations form an additional short contact; i.e., each molecule has the environment 1 + 6 (the pcu motif is also formed without this contact). The phase transition between compounds **I** and **II** in the solid phase is not theoretically impossible.

The data obtained confirm our previous observations: polymorphism related to distinctions in the structure of the anionic moiety is more typical, most likely, of halide complexes of Sb(III) rather than Bi(III). Although this phenomenon is not very abundant, its manifestation can be expected in other compounds of this class. In addition, it cannot be excluded that similar polymorphism can be related to reversible phase transitions [38] and can substantially affect some physical properties (e.g., piezo- and segnetoelectrical properties), which can be interesting from the viewpoint of materials science.

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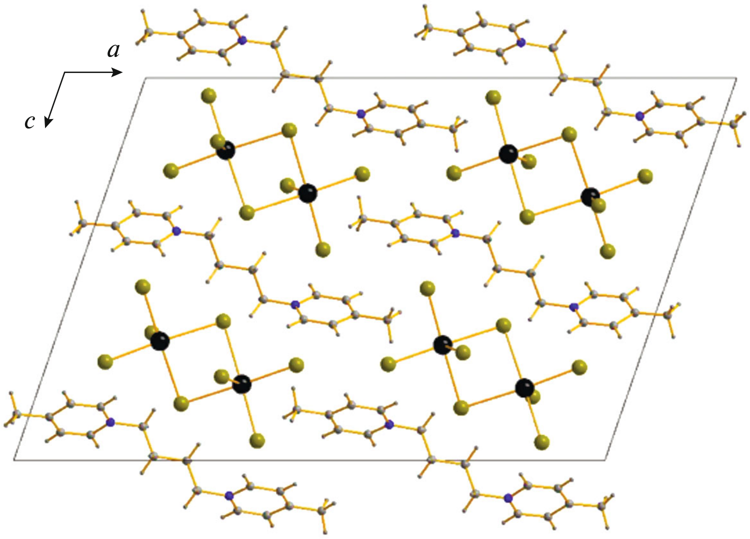

Fig. 2. Packing in the crystal of compound **I**.

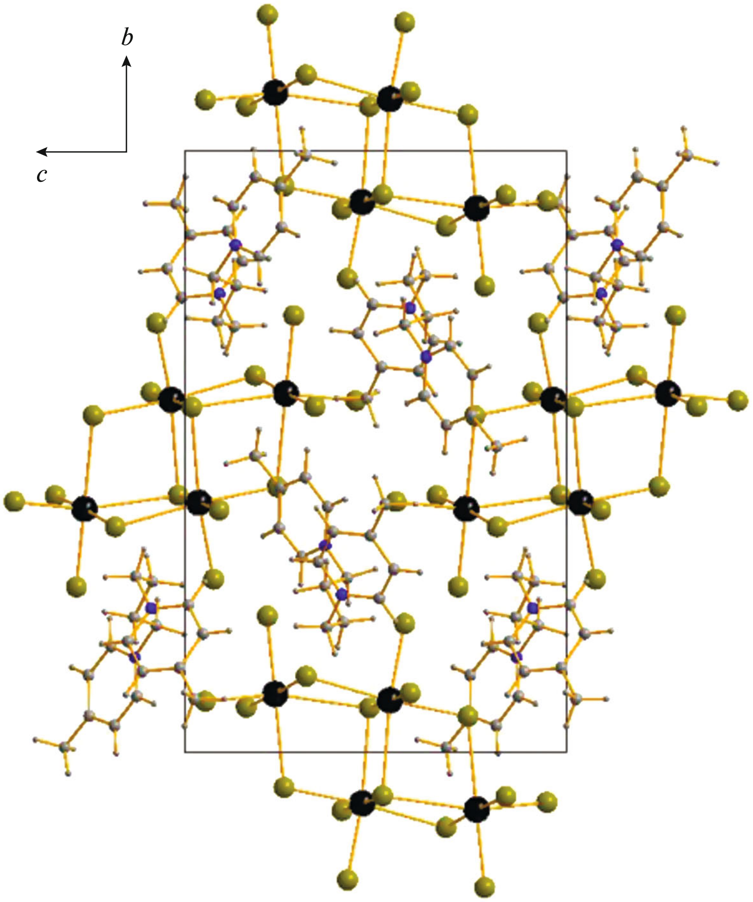

Fig. 3. Packing in the crystal of compound **II**.

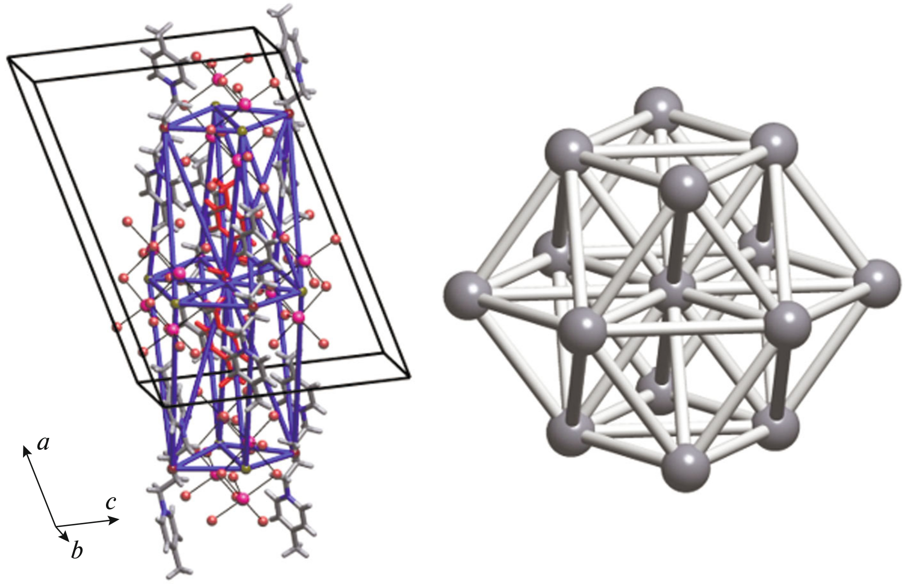

Fig. 4. The bcc packing of molecules in the structure of compound **I**: (a) nearest environment of 4,4'-dimethyl-1,1'-butanediyl-bis(pyridinium) by the cations and anions (centers of gravity are blue-colored) and (b) environment of the atom in the bcc packing.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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