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Mono- and Binuclear Chloride and Bromide Complexes of Bi(III) with Double-Charged Cations Based on Pyridine: Syntheses and Crystal Structures

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Abstract—The reactions of solutions obtained by the reactions of Bi_2O_3 with 2 M HCl and HBr with the salts containing bis(pyridyl)alkane cations afford mono- and binuclear halide complexes (Py-$(CH_2)_3$-Py)$_3[Bi_2Br_9]_2$ (**I**), (H_3O)(Py-$(CH_2)_4$-Py)$[BiCl_6] \cdot 3H_2O$ (**II**), and $(H_2Bpp)_2[Bi_2Br_{10}] \cdot 2H_2O$ (Bpp is 1,3-bis(4-pyridyl)propane) (**III**). The structures of the synthesized compounds are determined by X-ray diffraction analysis (CIF files CCDC no. 1583338–1583340, respectively).

Keywords: bismuth, chloride complexes, bromide complexes, crystal structure

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INTRODUCTION

In spite of the fact that halide complexes are among the "classical" objects of investigation by coordination chemistry, this area continues attracting attention of researchers. For the compounds of post- and late-transition metals, this is caused, to a significant extent, by the physical properties interesting from the viewpoint of materials science, such as photocatalysis [1–4], ferroelectric properties [5–7], applicability in photovoltaic devices [8–10], and others. From the preparative point of view, these complexes are simple objects: as a rule, they are synthesized by the addition of halide salts of various metals to solutions containing anionic species $[MX_n]^{a-}$ (X = Cl, Br, I). This results in the formation of crystals, whose quality is sufficient for X-ray diffraction analysis. The main problem remaining unsolved is the search for a relationship between the synthesis conditions and the composition and structure of the anionic moiety of these compounds. This is due to the fact that some metals (especially post-transition metals, in particular, Bi(III)) are characterized by a relatively low energy of the M–X bond and the fast kinetics of ligand substitution. Owing to this, solutions containing halometallate anions can be considered as "virtual dynamic libraries" capable of forming polynuclear anions of diverse structures and compositions upon the addition of a large organic cation to the system and solid phase precipitation. It is noted that the most important factors determining the structures of the products are the properties of the solvent used and, to a higher extent, the nature of the cation [11, 12]. At the same time, although the significant body of experimental data on the structures of such compounds has been obtained within the recent years [13–18] and the overall number of deposited crystal structures exceeds 200 (for Bi(III)), it remains to be a perspective task to find correlations in this information array. Evidently, to solve this problem, one has to extend the number of described crystal structures and also to specify boundary parameters, which, in particular, can be synthesis conditions. One of the popular variants is the synthesis of halometalates in aqueous solutions of HX (X = Cl, Br, I), i.e., in an acidic medium in presence of a considerable excess of halide anions.

In this work, we synthesized and structurally characterized three new halide complexes of Bi(III): (Py-$(CH_2)_3$-Py)$_3[Bi_2Br_9]_2$ (**I**), (H_3O)(Py-$(CH_2)_4$-Py)$[BiCl_6] \cdot 3H_2O$ (**II**), and $(H_2Bpp)_2[Bi_2Br_{10}] \cdot 2H_2O$ (Bpp is 1,3-bis(4-pyridyl)propane) (**III**).

EXPERIMENTAL

Compounds **I–III** were synthesized in air. Reagents (reagent grade) were purchased from commercial sources and used as received. Bromides of bis(pyridyl)alkane cations were synthesized by the reaction of pyridine (2 equiv) and 1,3-dibromopro-

pane (1 equiv) or 1,4-dibromobutane in acetonitrile (reflux, 18 h, yield >92%). The purity of the products was monitored by ^{1}H NMR spectroscopy and elemental analysis.

Synthesis of compound I. BiOBr (50 mg, 0.16 mmol) was dissolved in 2 M HBr (8 mL), and a solution of (Py-$(CH_2)_3$-Py)Br_2 (89 mg, 0.27 mmol) in 2 M HBr (7 mL) was added. A pale yellow crystalline precipitate of compound **I** began to form within several minutes. In 2 h, the product was separated by filtration. The yield was 88%.

For $C_{39}H_{48}N_6Br_{18}Bi_4$			
Found, %	C, 16.3	H, 1.8	N, 3.1
Anal. calcd., %	C, 16.3	H, 1.7	N, 2.9

Synthesis of compound II. (Py-$(CH_2)_4$-Py)Br_2 (50 mg, 0.13 mmol) was dissolved in water (4 mL), and $AgNO_3$ (45 mg, 0.27 mmol) was added with vigorous stirring. In 15 min, the formed precipitate of AgBr was filtered off, and concentrated HCl was added to the mother liquor to achieve a concentration of 2 mol/L. Then a solution of Bi_2O_3 (31 mg, 0.067 mmol) in 2 M HCl (1 mL) was added. A gradual formation of colorless crystals of compound **II** was observed for several hours. The yield was 72%.

For $C_{14}H_{27}N_2O_4Cl_6Bi$			
Found, %	C, 23.9	H, 3.7	N, 4.1
Anal. calcd., %	C, 23.7	H, 3.8	N, 4.0

Synthesis of compound III. BiOBr (115 mg, 0.38 mmol) was dissolved in 2 M HBr (8 mL), and a solution of Bpp (150 mg, 0.78 mmol) in 2 M HBr (8 mL) was added. A yellow crystalline precipitate of compound **III** began to form within several seconds. In 2 h, the product was separated by filtration. The yield was 90%.

For $C_{26}H_{36}N_4O_2Br_{10}Bi_2$			
Found, %	C, 19.0	H, 2.1	N, 3.5
Anal. calcd., %	C, 18.9	H, 2.2	N, 3.4

X-ray diffraction analysis. Diffraction data for single crystals of compounds **I–III** were obtained at 130 K on an Agilent Xcalibur diffractometer equipped with an Atlas S2 two-coordinate detector (graphite monochromator, $\lambda(MoK_\alpha)$ = 0.71073 Å, ω scan mode). Integration was performed, an absorption correction was applied, and unit cell parameters were determined using the CrysAlisPro program package [19]. The structures were solved using the SHELXT program [20] and refined by full-matrix least squares in the anisotropic approximation except for hydrogen atoms (SHELXL) [21]. The positions of the hydrogen atoms of the organic cations were calculated geometrically and refined by the riding model. The details of X-ray diffraction analyses and the main crystallographic structural data are presented in Table 1.

The full tables of interatomic distances and bond angles and the coordinates of atoms and parameters of atomic displacements for compounds **I–III** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC 1583338–1583340, respectively; http://www.ccdc.cam.ac.uk/structures) and also are available from the authors.

RESULTS AND DISCUSSION

A specific feature of the Bi(III) halide complexes is a variety of structural types: discrete anions with the nuclearity from 1 to 8 [22–28] and coordination polymers of various topology (predominantly 1D) are known. The formation of the mono- and binuclear anions and chain polymers of the $\{[BiX_5]_n\}^{2n-}$ and $\{[BiX_4]_n\}^{n-}$ types [29] is observed most frequently. Thus, from the structural viewpoint, compounds **I–III** are fairly typical representatives of their class.

The anionic moiety of complex **I** is presented by the binuclear anions $[Bi_2Br_9]^{3-}$ consisting of two octahedral fragments $\{BiBr_6\}$ with the common face. This type is fairly abundant, although the number of bromobismuthates $[Bi_2Br_9]^{3-}$ [30–32] is much lower than that of similar chloride and especially iodide complexes [29]. The $Bi–Br_{term}$ distances (2.6955(8)–2.7670(9) Å) are typical. At the same time, one of the Bi–(μ_2-Br) bonds (2.9626(9) Å) in compound **I** is somewhat shorter than that in the complexes described earlier (cf. 2.98 Å [31]). The crystal packing in the structure of complex **I** is shown in Fig. 1. Interestingly, the crystals in compound **I** are not isostructural to the crystals of the chlorobismuthate complex (Py-$(CH_2)_3$-Py)$_3[Bi_2Cl_9]_2$ described by us previously [33], despite the fact that both empirical composition and structure of anionic moiety are the same.

The reaction with the salt of the pyridine derivative bearing the long $-(CH_2)_4-$ fragment (one additional methylene group) affords mononuclear complex **II** (the crystal packing is shown in Fig. 2). Unlike a similar bromobismuthate [33], this compound is isolated as a solvate (contains three crystallization molecules of H_2O) fairly stable at ambient temperature (according to the elemental analysis data, the composition only insignificantly changes within several days). In addition, the structure contains H_3O^+ cations, whose positions are difficult to determine because of disordering. The Bi–Cl distances in the mononuclear $[BiCl_6]^{3-}$ anion vary in the range 2.726(1)–2.749(1) Å. Thus, the coordination polyhedron (octahedron) of the Bi atoms undergoes in compound **II** only insignificant distortions.

The structure of complex **III** (Fig. 3) contains the binuclear anions $[Bi_2Br_{10}]^{4-}$. As in the case of complex **I**, this structural type is very abundant (at least 45 compounds for X = Cl, Br, and I and at least five compounds for bromobismuthates [29]). The $Bi–Br_{term}$ and Bi–(μ_2-Br) distances (2.7331(8)–2.8563(7) and 2.9664(7)–3.0466(7) Å) are characteristic of this

Table 1. Crystallographic parameters and diffraction experimental details for compounds **I–III**

Parameter	Value		
	I	**II**	**III**
FW	2875.13	709.05	1653.65
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$I2/a$	$P\bar{1}$
a, Å	10.5254(2)	10.6425(3)	11.7125(3)
b, Å	17.9486(4)	14.2898(4)	13.0169(3)
c, Å	18.6680(4)	17.4784(6)	13.7206(4)
α, deg	100.881(2)	90	89.131(2)
β, deg	100.408(2)	95.011(3)	88.059(2)
γ, deg	93.585(2)	90	83.279(2)
V, Å^3	3389.21(13)	2647.94(14)	2076.16(9)
Z	2	4	2
ρ_{calc}, g/cm^3	2.817	1.779	2.645
μ, mm^{-1}	20.996	7.283	18.117
F(000)	2572	1368	1504
Crystal size, mm	0.27 × 0.19 × 0.06	0.44 × 0.36 × 0.20	0.18 × 0.16 × 0.09
Scan range over θ, deg	3.28–25.35	3.46–29.56	3.35–29.10
Range of indices hkl	$-13 < h < 13$, $-21 < k < 22$, $-23 < l < 23$	$-11 < h < 15$, $-15 < k < 20$, $-23 < l < 22$	$-15 < h < 12$, $-13 < k < 17$, $-13 < l < 17$
N_{hkl} measured/independent	25242/12 380	6593/3120	16823/9103
R_{int}	0.0358	0.0153	0.0490
N_{hkl} with $I > 2\sigma(I)$	9854	2713	7378
GOOF for F^2	1.000	1.064	1.014
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0384$, $wR_2 = 0.0713$	$R_1 = 0.0365$, $wR_2 = 0.1076$	$R_1 = 0.0393$, $wR_2 = 0.0684$
R factors (for all reflections)	$R_1 = 0.0568$, $wR_2 = 0.0771$	$R_1 = 0.0426$, $wR_2 = 0.1123$	$R_1 = 0.0545$, $wR_2 = 0.0754$
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	2.477/−2.429	1.658/−1.720	1.983/−1.740

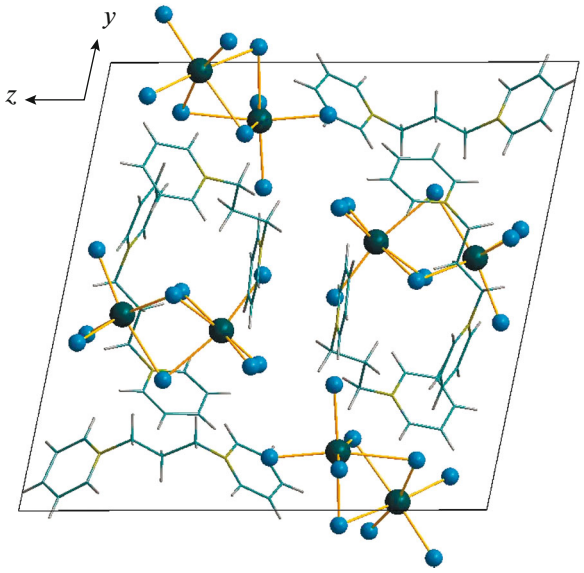

Fig. 1. Molecular packing in the crystal of compound **I**.

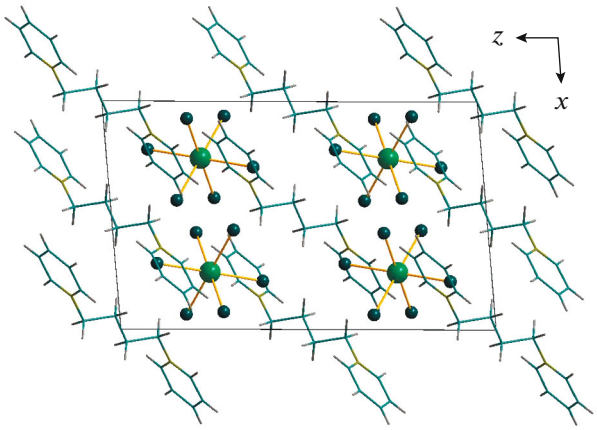

Fig. 2. Packing of the complexes in the crystal of compound **II**. Solvate H_2O molecules and H_3O^+ cations are omitted.

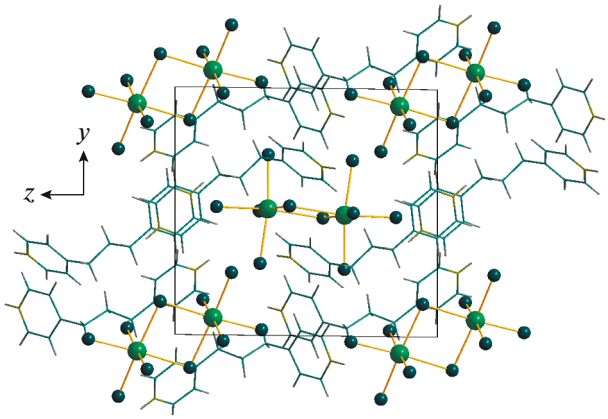

Fig. 3. Packing of the complexes in the crystal of compound **III**. Solvate H_2O molecules are omitted.

type [29]. The structure of complex **III** contains solvate molecules of H_2O, as in the case of complex **II**. The compound is stable on storage for several days.

We have previously [33] mentioned that the structural type $[Bi_2X_{10}]^{4-}$ is most often met in structures of the compounds bearing cations being N-protonated nitrogenous bases. According to the results of analysis of the data presented in the CCDC [33], this structural type is characterized by solvate formation to a higher extent than the $[Bi_2X_9]^{3-}$ complexes. The results obtained in the present work are consistent with these observations.

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