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CRYSTAL STRUCTURES OF BINUCLEAR Bi(III) CHLORIDE AND BROMIDE COMPLEXES WITH SOME CATIONS – ALKYLATED PYRIDINE DERIVATIVES

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By a reaction of $[BiX_6]^{3-}$ with salts of various N-alkylated pyridine derivatives in 2M HX (X = Cl, Br), $(N\text{-}BzPy)_4[Bi_2X_{10}]$ complexes (X = Cl (**1**), Br (**2**), $(4\text{-}MePyH)_4[Bi_2Cl_{10}]$ (**3**)) are obtained and structurally characterized.

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One of the key problems in the chemistry of polynuclear halide complexes of bismuth(III) (polyhalide bismuthates, PHBs) remains the establishment of the relationship between synthesis conditions, the composition and structure of the anionic part of these compounds [1-3]. This is due to an important feature of PHBs, which consists in their high lability because of a relatively low binding energy of Bi(III)–X (X = Cl, Br, I) and a rapid kinetics of ligand substitution in the Bi(III) coordination sphere. During crystallization, complex $[BiX_6]^{3-}$ anions existing in the solution can transform into PHBs with diverse geometries and nuclearities (from 1 to 8) [4-15]. It has previously been noted [1-3] that the nature of a solvent and a cation used to extract PHB are the most significant factors affecting the product structure. Taking into account that single crystal and powder XRD are the main methods for identifying PHB complexes (the use of other physical methods is very limited because of low information content), it is an essential task to obtain new data on their crystal structure.

In this work, three new complexes are structurally characterized: $(N\text{-}BzPy)_4[Bi_2X_{10}]$ (X = Cl (**1**), Br (**2**), and $(4\text{-}MePyH)_4[Bi_2Cl_{10}]$ (**3**).

EXPERIMENTAL

Synthesis was carried out in the air. Precursors (HBr, HCl, $BiCl_3$, BiOBr, pyridine, 4-methylpyridine (4-picoline), and benzyl bromide) were purchased and used as received. N-benzylpyridinium bromide (N-BzPyBr) was obtained by a reaction of benzyl bromide and pyridine (1.1:1) in a benzene:acetone (1:1) mixture at room temperature [16] and identified by the ^1H NMR spectrum.

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$(N\text{-}BzPy)_4[Bi_2Cl_{10}]$ (1). 47 mg (0.15 mmol) of $BiCl_3$ were dissolved in 4 ml of 2M HCl and added to a solution of 75 mg (0.3 mmol) of N-benzylpyridinium bromide in 2 ml of 2M HCl. In several hours a colorless crystalline precipitate formed, from which crystals of **2** suitable for single crystal XRD were selected.

$(N\text{-}BzPy)_4[Bi_2Br_{10}]$ (2). 61 mg (0.2 mmol) of BiOBr were dissolved in 5 ml of 2M HBr and added to a solution of 100 mg (0.4 mmol) of N-benzylpyridinium bromide in 5 ml of 2M HBr. In several seconds a light yellow fine crystalline precipitate formed, from which crystals of **2** suitable for single crystal XRD were selected.

$(4\text{-}MePyH)_4[Bi_2Cl_{10}]$ (3). 150 mg (0.48 mmol) of $BiCl_3$ were dissolved in 4 ml of 2M HCl and added to a solution of 93 μl (0.96 mmol) of 4-methylpyridinium in 3 ml of 2M HCl. After evaporation for five days large colorless crystals suitable for single crystal XRD formed.

Single crystal XRD. Diffraction data on single crystals **1-3** were measured at 130 K on an automated Agilent Xcalibur diffractometer equipped with a two-dimensional AtlasS2 detector (graphite monochromator, $\lambda(MoK_\alpha) = 0.71073$ Å, ω-scanning). Integration, absorption correction, and determination of unit cell parameters were performed using the CrysAlisPro program package [17]. The structure was solved by direct methods and refined by full-matrix LSM in the anisotropic approximation (except hydrogen atoms) using the SHELX-2013/2014 program package [18]. Positions of hydrogen atoms of the organic cation were calculated geometrically and refined in the riding model. Details of single crystal XRD and the main crystal structural data are summarized in Table 1; the main interatomic distances and bond angles are given in Tables 2-4. Full tables of interatomic distances and bond angles, atomic coordinates, and atom displacement parameters have been deposited with the Cambridge Crystallographic Data Center (CCDC-1511679, 1511680, 1511681); http://www.ccdc.cam.ac.uk/data_request/cif), and also can be received from the authors.

TABLE 1. Crystallographic Parameters and Details of Single Crystal XRD Experiments for **1-3**

Parameter	**1**	**2**	**3**
Chemical formula	$C_{48}H_{48}Bi_2Cl_{10}N_4$	$C_{48}H_{48}Bi_2Br_{10}N_4$	$C_{24}H_{32}Bi_2Cl_{10}N_4$
M, g/mol	1453.36	1897.96	1148.99
Crystal symmetry	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P{-}1$
a, Å	9.85463(9)	9.9742(2)	8.9652(7)
b, Å	23.45377(16)	24.1623(7)	10.2539(8)
c, Å	11.71389(10)	11.7437(3)	10.6852(9)
α, deg			98.858(2)
β, deg	106.5606(9)	105.163(3)	109.666(2)
γ, deg			96.964(2)
V, $Å^3$	2595.10(4)	2731.69(13)	897.99(13)
Z; ρ(calc.), g/cm^3	2; 1.860	2; 2.307	1; 2.125
F(000); μ, mm^{-1}	1400; 7.325	1760; 13.783	540; 10.552
Crystal dimensions, mm	0.26×0.22×0.17	0.64×0.15×0.07	0.21×0.12×0.11
θ scanning range, deg	3.31–32.84	3.30–30.99	2.05–28.06
Range of *hkl* indices	$-15 < h < 15$, $-35 < k < 36$, $-17 < l < 17$	$-13 < h < 7$, $-30 < k < 34$, $-17 < l < 17$	$-12 < h < 12$, $-14 < k < 14$, $-15 < l < 15$
Number of meas. / indep. reflections	57370 / 9041	17567 / 7595	24908 / 4339
R_{int}; number of reflections with $I > 2\sigma(I)$	0.0188; 8526	0.0467; 5991	0.0265; 4236
GOOF on F^2	1.066	1.023	1.179
R-factors $I > 2\sigma(I)$	$R_1 = 0.0237$, $wR_2 = 0.0656$	$R_1 = 0.0469$, $wR_2 = 0.1033$	$R_1 = 0.0117$, $wR_2 = 0.0293$
R-factors (over all reflections)	$R_1 = 0.0260$, $wR_2 = 0.0667$	$R_1 = 0.0660$, $wR_2 = 0.1134$	$R_1 = 0.0123$, $wR_2 = 0.0295$
Res. electron density (max / min), e/$Å^3$	2.178 / –1.075	3.735 / –2.856	0.428 / –0.905

TABLE 2. Main Bond Lengths and Bond Angles in **1**

Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
Bi(1)–Cl(1)	2.6283(6)	Cl(1)–Bi(1)–Cl(2)	91.959(19)	Cl(3)–Bi(1)–Cl(5)	176.01(2)
Bi(1)–Cl(2)	2.9034(6)	Cl(1)–Bi(1)–Cl(2)$^{\mathrm{i}}$	175.373(19)	Cl(4)–Bi(1)–Cl(2)$^{\mathrm{i}}$	89.87(2)
Bi(1)–Cl(2)$^{\mathrm{i}}$	2.9881(6)	Cl(1)–Bi(1)–Cl(3)	90.50(2)	Cl(4)–Bi(1)–Cl(2)	178.08(2)
		Cl(1)–Bi(1)–Cl(4)	89.75(2)	Cl(4)–Bi(1)–Cl(3)	93.02(2)
		Cl(1)–Bi(1)–Cl(5)	89.03(2)	Cl(4)–Bi(1)–Cl(5)	90.94(2)
		Cl(2)–Bi(1)–Cl(2)$^{\mathrm{i}}$	88.359(17)	Cl(5)–Bi(1)–Cl(2)	89.968(19)
		Cl(3)–Bi(1)–Cl(2)$^{\mathrm{i}}$	84.913(19)	Cl(5)–Bi(1)–Cl(2)$^{\mathrm{i}}$	95.588(19)
		Cl(3)–Bi(1)–Cl(2)	86.09(2)	Bi(1)–Cl(2)–Bi(1)$^{\mathrm{i}}$	91.643(16)

Coordinates of dependent atoms are obtained by the following symmetry operations: $^{\mathrm{i}}$ $-x$, $1-y$, $-z$.

TABLE 3. Main Bond Lengths and Bond Angles in **2**

Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
Bi(1)–Br(1)	2.8863(6)	Br(1)–Bi(1)–Br(2)$^{\mathrm{i}}$	88.522(18)	Br(4)–Bi(1)–Br(2)	84.858(18)
Bi(1)–Br(2)	3.0621(6)	Br(1)–Bi(1)–Br(2)	94.514(18)	Br(4)–Bi(1)–Br(2)$^{\mathrm{i}}$	86.065(19)
Bi(1)–Br(2)$^{\mathrm{i}}$	3.0160(7)	Br(2)$^{\mathrm{i}}$–Bi(1)–Br(2)	88.379(17)	Br(5)–Bi(1)–Br(1)	91.53(2)
Bi(1)–Br(3)	2.7533(6)	Br(3)–Bi(1)–Br(1)	89.910(19)	Br(5)–Bi(1)–Br(2)$^{\mathrm{i}}$	177.83(2)
Bi(1)–Br(4)	2.7971(6)	Br(3)–Bi(1)–Br(2)$^{\mathrm{i}}$	91.261(19)	Br(5)–Bi(1)–Br(2)	89.458(19)
Bi(1)–Br(5)	2.7514(7)	Br(3)–Bi(1)–Br(2)	175.550(19)	Br(5)–Bi(1)–Br(3)	90.90(2)
		Br(3)–Bi(1)–Br(4)	90.69(2)	Br(5)–Bi(1)–Br(4)	93.86(2)
		Br(4)–Bi(1)–Br(1)	174.57(2)	Bi(1)$^{\mathrm{i}}$–Br(2)–Bi(1)	91.622(17)

Coordinates of dependent atoms are obtained by the following symmetry operations: $^{\mathrm{i}}$ $1-x$, $1-y$, $1-z$.

TABLE 4. Main Bond Lengths and Bond Angles in **3**

Bond	*d*, Å	Angle	ω, deg	Angle	ω, deg
Bi(1)–Cl(1)	2.5801(5)	Cl(1)–Bi(1)–Cl(2)	89.696(17)	Cl(3)–Bi(1)–Cl(2)	91.886(15)
Bi(1)–Cl(2)	2.6727(5)	Cl(1)–Bi(1)–Cl(3)	93.577(18)	Cl(3)–Bi(1)–Cl(4)	89.266(15)
Bi(1)–Cl(3)	2.5864(5)	Cl(1)–Bi(1)–Cl(4)	90.528(17)	Cl(3)–Bi(1)–Cl(5)$^{\mathrm{i}}$	90.125(15)
Bi(1)–Cl(4)	2.7303(5)	Cl(1)–Bi(1)–Cl(5)	93.797(17)	Cl(3)–Bi(1)–Cl(5)	172.619(16)
Bi(1)–Cl(5)	2.8310(5)	Cl(1)–Bi(1)–Cl(5)$^{\mathrm{i}}$	175.121(14)	Cl(4)–Bi(1)–Cl(5)	90.975(14)
Bi(1)–Cl(5)$^{\mathrm{i}}$	2.9674(5)	Cl(2)–Bi(1)–Cl(4)	178.810(13)	Cl(4)–Bi(1)–Cl(5)$^{\mathrm{i}}$	86.340(15)
		Cl(2)–Bi(1)–Cl(5)	87.845(14)	Cl(5)–Bi(1)–Cl(5)$^{\mathrm{i}}$	82.529(14)
		Cl(2)–Bi(1)–Cl(5)$^{\mathrm{i}}$	93.360(16)	Bi(1)–Cl(5)–Bi(1)$^{\mathrm{i}}$	97.471(14)

Coordinates of dependent atoms are obtained by the following symmetry operations: $^{\mathrm{i}}$ $1-x$, $1-y$, $1-z$.

Powder XRD. The powder XRD analysis of polycrystals was conducted on a Shimadzu XRD-7000 diffractometer (room temperature, CuK_α radiation, Ni filter, 2θ range 5-60°, step 0.03° 2θ, acquisition time 1 s). Samples for the study were prepared as follows: polycrystals were ground in an agate mortar; powder was deposited on the polished side of the standard quartz cuvette covered with a thin layer of vaseline oil. The fact that compounds are single phase was established by a comparison of the indexed powder X-ray diffraction pattern by analogy with a theoretical diffraction pattern of the complex, which was calculated from the structure of a single crystal obtained by single crystal XRD.

RESULTS AND DISCUSSION

Compounds **1** and **2** are isostructural and crystallize in the monoclinic symmetry (space group $P2_1/n$). The asymmetric unit contains one Bi(III) cation. The Bi(III) cation is in the octahedral coordination environment composed of six halide ligands. Two Bi(III) cations are linked with each other by two bridging halide ligands, forming a binuclear $[Bi_2(\mu\text{-}X)_2X_8]^{4-}$ anionic complex (X = Cl and Br for **1** and **2** respectively) (Fig. 1). The Bi–Cl(terminal) distances are in the range 2.6283(6)-2.7567(6) Å. The Bi–Cl(bridging) distances are 2.9034(6) Å and 2.9881(6) Å. In bromide complex **2** the Bi–Br(terminal) distances are in the range 2.7514(7)-2.8863(6) Å, and the Bi–Br(bridging) distances are 3.0160(7) Å and 3.0621(6) Å. The $[Bi_2(\mu\text{-}X)_2X_8]^{4-}$ anions are located in position 2*c* (one of the systems of inversion centers: 0, 1/2, 0; 1/2, 0, 1/2). Organic cations are located in general positions. The cation and anion packing is shown in Fig. 2. Complex anions form layers parallel to the *ac* plane, and between them organic cations are located. Interactions between the components of the structure have an exclusively van der Waals and ionic character. Between the organic cations there are π–

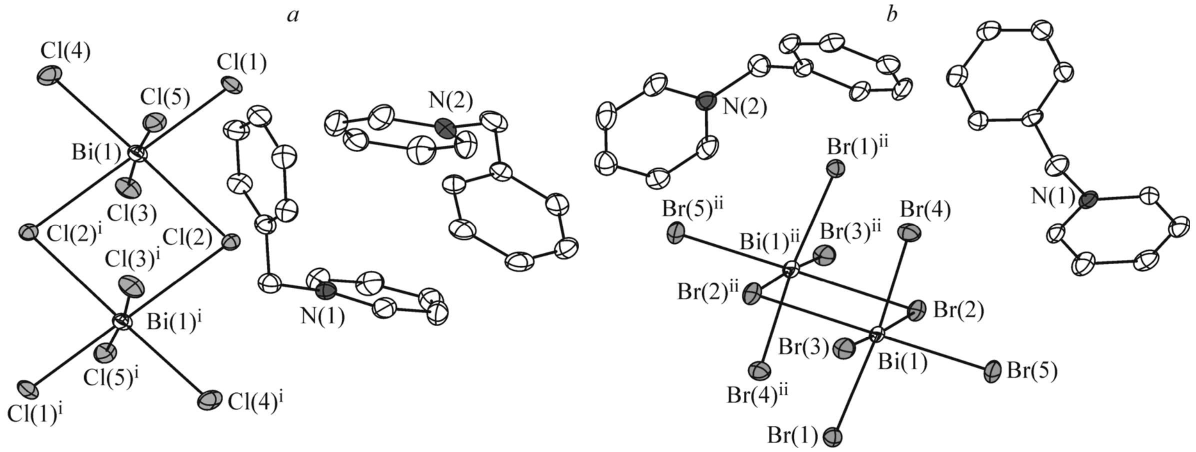

Fig. 1. Structure of the organic cation and the complex anion in **1** (*a*) and **2** (*b*). Hydrogen atoms are omitted. 50% probability ellipsoids. Coordinates of dependent atoms are obtained by the following symmetry operations: ^{i} –*x*, 1–*y*, –*z*; ^{ii} 1–*x*, 1–*y*, 1–*z*.

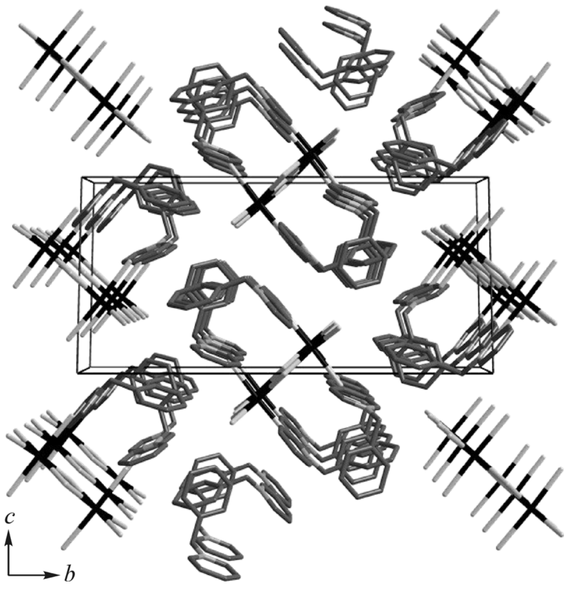

Fig. 2. Cation and anion packing in the structure of **1** (view along the *a* axis). Hydrogen atoms are omitted.

π interactions; the shortest C…C distances are 3.282 Å and 3.335 Å, C…N distances are 3.169 Å and 3.216 Å for **1** and **2** respectively.

Compound **3** crystallizes in the triclinic symmetry (space group *P*–1). The asymmetric unit contains one Bi(III) cation; it is in the octahedral coordination environment of six chloride ligands. Two Bi(III) cations are linked with each other by two bridging chloride ligands (μ-Cl), forming a binuclear $[Bi_2(\mu\text{-}Cl)_2Cl_8]^{4-}$ anionic complex (Fig. 3). The Bi–Cl(terminal) distances are in the range 2.5801(5)-2.7303(5) Å. The Bi–Cl(bridging) distances are 2.8310(5) Å and 2.9674(5) Å. The $[Bi_2(\mu\text{-}X)_2X_8]^{4-}$ anions are located in position 1*h* (one of the systems of inversion centers: 1/2, 1/2, 1/2). Organic cations are located in general positions. The cation and anion packing is shown in Fig. 4. Complex anions form layers (parallel to the *bc* plane) between which the organic cations are located. The organic cations and complex anions form intermolecular

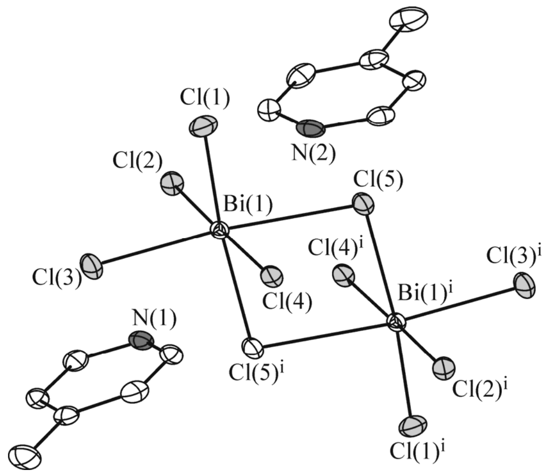

Fig. 3. Structure of the organic cation and the complex anion in **3**. Hydrogen atoms are omitted. 50% probability ellipsoids. Coordinates of dependent atoms are obtained by the following symmetry operations: ^{i} 1–*x*, 1–*y*, 1–*z*.

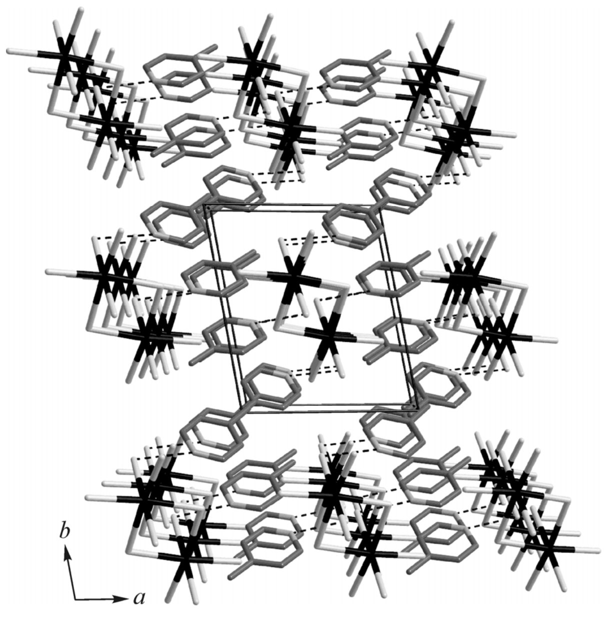

Fig. 4. Cation and anion packing in the structure of **3** (view along the *c* axis). Hydrogen atoms are omitted.

N–H…Cl(terminal) contacts; the N…Cl distances are 3.130 Å and 3.204 Å (Fig. 4, shown by a dashed line). Between the organic cations there are π–π interactions; the shortest C…C and C…N distances are 3.393 Å and 3.309 Å respectively.

According to the powder XRD data, compounds **1** and **3** are isolated in the pure form whereas in the solid phase of **2** an unidentified impurity is present (here **2** is the main component). Attempts to optimize the synthesis by changing the reagent ratio were unsuccessful.

The $[Bi_2X_{10}]^{4-}$ structure type is common for PHBs. In particular, the formation of anions with this structure is most often observed when hydrohalic acid solutions serve simultaneously as a solvent and a source of halide ligands [2]. It should be noted, however, that, unlike chlorobismuthates, for bromide complexes the most often occurring type is $[Bi_2Br_9]^{3-}$ [2]. Not infrequently, the formation of $[Bi_2X_{10}]^{4-}$ occurs during the crystallization with cations that are the protonated forms of N-containing bases. The crystal structure contains characteristic cation-anion contacts of the N–H···X type (compare, e.g., with **3**). In the structures of **1** and **2**, similar interactions are observed between hydrogen atoms belonging to methylene groups of N-BzPy$^+$ and terminal chloride and bromide ligands (average values of 2.63 Å and 2.77 Å respectively).

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