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Tetra- and Pentanuclear Iodobismuthates with the Cation Based on 2,3,5,6-Tetramethylpyrazine: Syntheses and Crystal Structures

A. N. Usoltsev[a], **S. A. Adonin**[a, b, *], **P. A. Abramov**[a, b], **M. N. Sokolov**[a, c], **and V. P. Fedin**[a, b]

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

[b] *Novosibirsk State University, Novosibirsk, 630090 Russia*

[c] *Kazan (Volga region) Federal University, Kazan, Tatarstan, 420008 Russia*

**e-mail: adonin@niic.nsc.ru*

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Abstract—Complexes $(HTMP)_4[Bi_4I_{16}] \cdot 2H_2O \cdot 2(CH_3)_2CO$ (**I**) and $(HTMP)_3[Bi_5I_{18}] \cdot 5THF$ (**II**) have been synthesized by the reactions of BiI_3 and 2,3,5,6-tetramethylpyrazine (TMP) in acetone and tetrahydrofuran (THF), respectively. The crystal structures of both compounds were determined by X-ray diffraction analysis (CIF files CCDC nos. 1817306 (**I**) and 1817307 (**II**)). In both cases, the complexes in the solid state feature supramolecular contacts between the π systems of the cations and iodide ligands of the anions.

Keywords: bismuth, halide complexes, tetramethylpyrazine, X-ray diffraction analysis, supramolecular contacts

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INTRODUCTION

Halide, in particular, iodide, Bi(III) complexes form a large class of coordination compounds [1, 2] differed in diversity of structural types. Discrete anionic iodobismuthate complexes of various compositions and structures, particularly, bi- [3–8], tri- [9–11], tetra- [12–15], penta- [16, 17], hexa- [18, 19], hepta- [20, 21], and octanuclear [14, 22] complexes, as well as various coordination polymers [23–26] are known nowadays. The production of materials for solar cells is among the most interesting areas of application of these substances [27]: the possibility of using iodobismuthates as light-absorbing layers was demonstrated during the recent years [28–30].

In the majority of cases, the procedures for the preparation of iodobismuthates (and in general, halobismuthates) are fairly simple: halide salts of various cations are added to a solution containing anionic forms $[MX_n]^{a-}$ (X = Cl, Br, I). The synthesis leading in aqueous solutions of HX typically results in the formation of a crystalline precipitate. Other approaches (evaporation, slow diffusion of a different solvent, etc.) are used to obtain single crystals in organic solvents. The composition and structure of the anionic moiety of the products are primarily determined by the nature of the cations used [31]. The influence of the reaction medium is studied to a lower extent. However, the effect of the medium also can serve as a significant factor: several examples are described where the reactions between BiX_3 and X_n (X = Cl, I) taken in resembling ratios afford complexes of different types depending on the solvent used [22, 32, 33].

When attempting to synthesize coordination polymers from 2,3,5,6-tetramethylpyrazine (TMP) and BiI_3, we found that the reactions taking place in acetone or tetrahydrofuran (THF) did not give desirable products. In both cases, TMP are protonated and tetra- or pentanuclear iodobismuthates $(HTMP)_4[Bi_4I_{16}] \cdot 2H_2O \cdot 2(CH_3)_2CO$ (**I**) and $(HTMP)_3[Bi_5I_{18}] \cdot 5THF$ (**II**), respectively, are formed. Their structures were determined by X-ray diffraction analysis.

EXPERIMENTAL

The syntheses of compounds **I** and **II** were carried in air. The reagents (reagent grade), including solvents, were obtained from commercial sources and used as received.

Synthesis of compound I. Bismuth triiodide BiI_3 (100 mg, 0.17 mmol) and TMP (46 mg, 0.34 mmol) were dissolved in acetone (10 mL) on heating (50°C) for 1 h. The resulting solution was cooled to room temperature. Dark orange crystals of compound **I** were formed during of the gradual evaporation of the solvent to 1/5 of the initial volume.

Synthesis of compound II was similar to that of compound **I** but THF was used (50°C, 1 h). Dark orange crystals of compound **II** were formed upon the gradual evaporation of the solvent to 1/5 of the initial volume.

Table 1. Crystallographic characteristics and diffraction experimental details for the structures of compounds **I** and **II**

Parameter	Value	
	I	**II**
Empirical formula	$C_{38}H_{68}N_8O_4I_{16}Bi_4$	$C_{52}H_{92}N_8O_5I_{19}Bi_5$
FW	3567.32	4365.33
Crystal system	Triclinic	Triclinic
Space group	*P*1	*P*1
a, Å	10.6498(2)	10.7248(2)
b, Å	13.9029(3)	14.7601(3)
c, Å	14.6123(3)	17.2712(4)
α, deg	81.709(2)	69.104(2)
β, deg	77.986(2)	81.276(2)
γ, deg	72.313(2)	79.243(2)
V, $Å^3$	2008.50(8)	2498.50(10)
Z	1	1
μ, mm^{-1}	14.92	14.68
Crystal sizes, mm	0.20 × 0.06 × 0.06	0.26 × 0.15 × 0.15
Range of data collection over θ, deg	3.3–29.1	3.3–29.0
Ranges of reflection indices	$-14 \le h \le 13$, $-18 \le k \le 16$, $-19 \le l \le 15$	$-14 \le h \le 14$, $-19 \le k \le 17$, $-21 \le l \le 18$
Measured reflections	15267	18723
Independent reflections	11917	14676
Reflections with $I \ge 2\sigma(I)$	11027	13835
Number of refined parameters	632	803
GOOF	1.01	1.02
R_1 (for $\|F\|^2$ (for reflections with $I > 2\sigma(I)$))	0.031	0.037
wR_2 (for $\|F\|^2$ (for all reflections))	0.067	0.080
Residual electron density (max/min), $e/Å^3$	1.34/–1.59	1.54/–1.95

X-ray diffraction analysis. The structures of compounds **I** and **II** were determined using a standard procedure on an Xcalibur diffractometer (Agilent Technologies) at 130 K (MoK_α, $\lambda = 0.71073$ Å, graphite monochromator). The reflection intensities were measured by narrow (0.5°) frame scanning (φ scan mode). An absorption correction was applied empirically using the SCALE3 ABSPACK algorithm (CrysAlisPro, Agilent Technologies, Version 1.171.37.35 (release 13-08-2014 CrysAlis171.NET). The structures were solved by a direct method and refined by full-matrix least squares in the anisotropic (for non-hydrogen atoms) approximation using the SHELX 2014/7 algorithm [34] in the ShelXle program [35]. The crystallographic data and refinement results for the structures of compounds **I** and **II** are presented in Table 1. Selected geometric parameters are given in Table 2.

Complexes **I** and **II** crystallize in the triclinic crystal system, and their crystal structures were solved in the noncentrosymmetric space group *P*1 using the racemic twin approximation with the contribution of

Table 2. Geometric parameters (Å) for complexes **I** and **II**

Bond	*d*, Å	Bond	*d*, Å
I			
I(1)–Bi(1)	2.9116(17)	I(11)–Bi(4)	2.9385(17)
I(2)–Bi(1)	2.9155(14)	I(12)–Bi(1)	3.2705(16)
I(3)–Bi(2)	2.9053(15)	I(12)–Bi(2)	3.0910(13)
I(4)–Bi(1)	2.9447(12)	I(13)–Bi(2)	2.8872(14)
I(5)–Bi(1)	3.3197(13)	I(14)–Bi(2)	3.0641(12)
I(5)–Bi(3)	3.0421(12)	I(14)–Bi(4)	3.3487(14)
I(6)–Bi(3)	2.9305(15)	I(15)–Bi(1)	3.2290(13)
I(7)–Bi(4)	2.9581(12)	I(15)–Bi(2)	3.2864(15)
I(8)–Bi(4)	2.8979(14)	I(15)–Bi(3)	3.3101(13)
I(9)–Bi(3)	3.1280(12)	I(16)–Bi(2)	3.3305(13)
I(9)–Bi(4)	3.2958(16)	I(16)–Bi(3)	3.2610(15)
I(10)–Bi(3)	2.9175(13)	I(16)–Bi(4)	3.2506(13)
II			
I(8)–Bi(1)	3.1774(13)	Bi(3)–I(8)	3.1706(13)
I(10)–Bi(1)	3.3420(13)	Bi(3)–I(9)	3.3257(12)
I(11)–Bi(1)	2.8790(13)	Bi(3)–I(10)	3.2424(13)
I(12)–Bi(1)	2.8888(14)	Bi(4)–I(1)	2.9073(13)
I(13)–Bi(1)	3.0109(14)	Bi(4)–I(2)	2.8997(15)
I(14)–Bi(1)	3.3618(11)	Bi(4)–I(3)	2.8946(14)
Bi(2)–I(4)	3.0208(14)	Bi(4)–I(4)	3.3155(14)
Bi(2)–I(9)	3.1694(13)	Bi(4)–I(5)	3.3127(12)
Bi(2)–I(10)	3.3074(12)	Bi(4)–I(9)	3.3388(13)
Bi(2)–I(14)	3.1537(13)	Bi(5)–I(13)	3.3677(12)
Bi(2)–I(15)	3.0052(13)	Bi(5)–I(14)	3.3599(13)
Bi(2)–I(19)	2.8819(12)	Bi(5)–I(15)	3.3495(13)
Bi(3)–I(5)	3.0230(13)	Bi(5)–I(16)	2.9023(12)
Bi(3)–I(6)	2.9309(13)	Bi(5)–I(17)	2.8877(14)
Bi(3)–I(7)	2.9105(12)	Bi(5)–I(18)	2.8664(13)

the lower component of 0.45 and 0.47, respectively. The hydrogen atoms of water of crystallization in the structure of complex **I** were not localized. The hydrogen atoms of the cations and solvate molecules were refined in the geometrically calculated positions.

The atomic coordinates and other parameters for the structures of compounds **I** and **II** were deposited to the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1817306 and 1817307, respectively; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

In spite of the fact that the solvent effect on the compositions and structures of the halide complexes of post-transition metals was reliably shown earlier

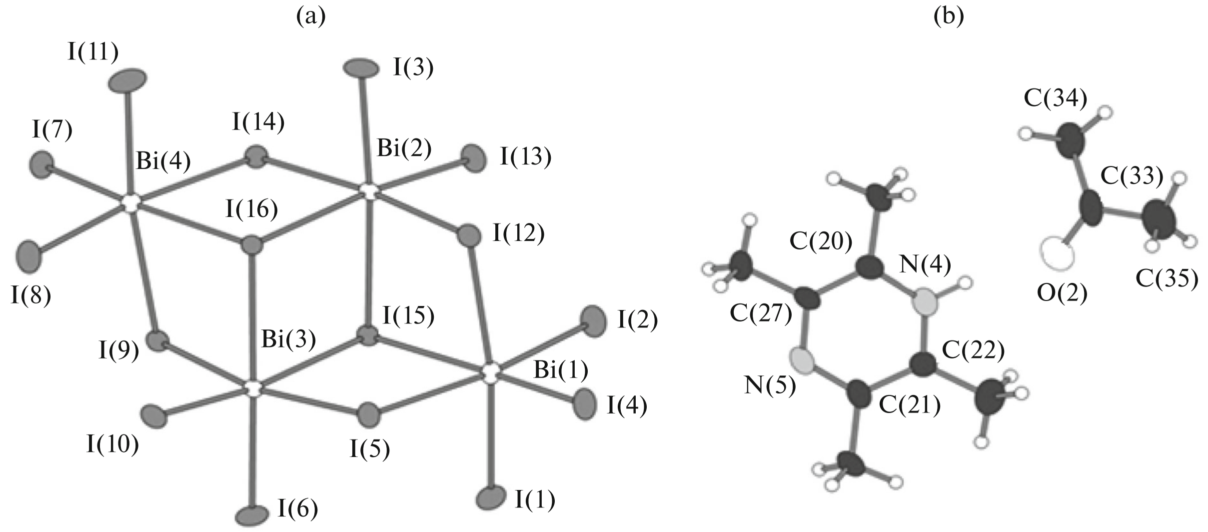

Fig. 1. (a) Structure of $[Bi_4I_{16}]^{4-}$ and (b) an example of the associate between the 2,3,5,6-tetramethylpyrazinium cation and acetone molecule in the crystal structure of complex **I**.

[22, 32, 33], this phenomenon was not almost studied systematically. Available contradictory data do not allow one to judge about the existence of correlations between the characteristics of the solvent (polarity, donor number) and nuclearity of the formed anions.

Compounds **I** and **II** are unstable in the absence of the mother liquor (the crystals are smeared within several seconds), which is explained by the existence of numerous solvate molecules. This impedes their adequate characterization using other physicochemical methods and elemental analysis. At the same time, both syntheses are reproducible when using undried solvents (for the repeated syntheses, the nature of the products was confirmed by the determination of the cell parameters of the isolated crystals). Evidently, in both cases, an impurity of H_2O in the starting solvents is a source of H^+ (and also a source of some solvate molecules for **I**). Attempts of the syntheses in dried acetone and THF did not give compounds **I** and **II**.

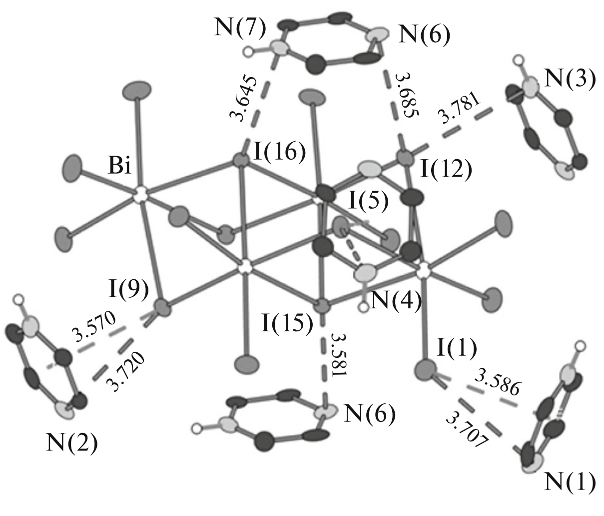

Fig. 2. Cation-anionic interactions in the crystal structure of complex **I**.

The main building block of the crystal structure of complex **I** is the tetranuclear anion $[Bi_4I_{16}]^{4-}$ (Fig. 1a) formed of four $\{BiI_6\}$ octahedra joined by common edges. In the crystal structure, the 2,3,5,6-tetramethylpyrazonium cations form two types of associates built of hydrogen bonds with water and acetone molecules (Fig. 1b), and no extended structures are formed. Other types of interactions also occur in the structure: weak contacts between the I atoms and π systems of the cations. Each anion in the structure is surrounded by a unique spherical shell of the cations arranged in such a way that two types of specific cation-anionic interactions are observed (Fig. 2). In the first case, this is the contact between the whole aromatic π system and iodine atom at the distance about 3.5 Å, which is in the range of the known interactions of the CH···π or π–π type [36–38]. In the second case, the selective interaction between the nitrogen atoms of the cations and iodine atoms at distances of ~3.6–3.8 Å is observed. Similar contacts are met in a series of the homo- and heteroligand halide complexes [39–42].

The crystal structure of compound **II** contains the pentanuclear anions $[Bi_5I_{19}]^{4-}$ (Fig. 3) built by joining

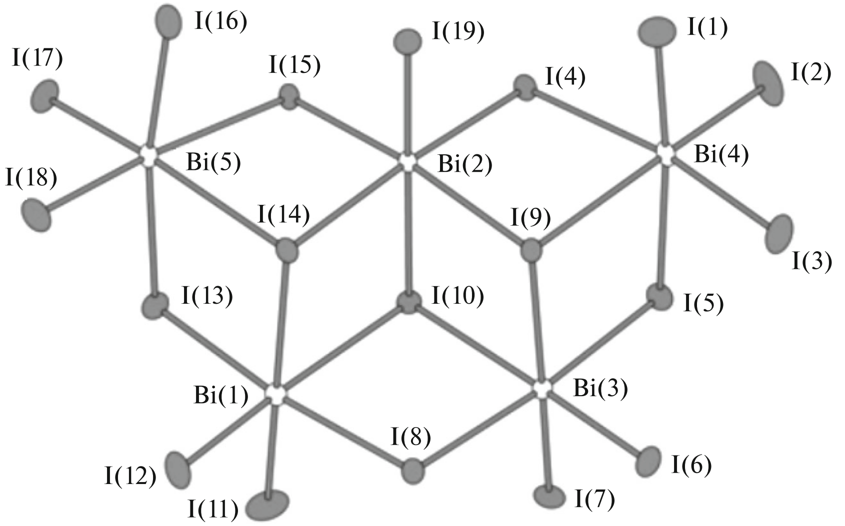

Fig. 3. Structure of anion $[Bi_5I_{19}]^{4-}$.

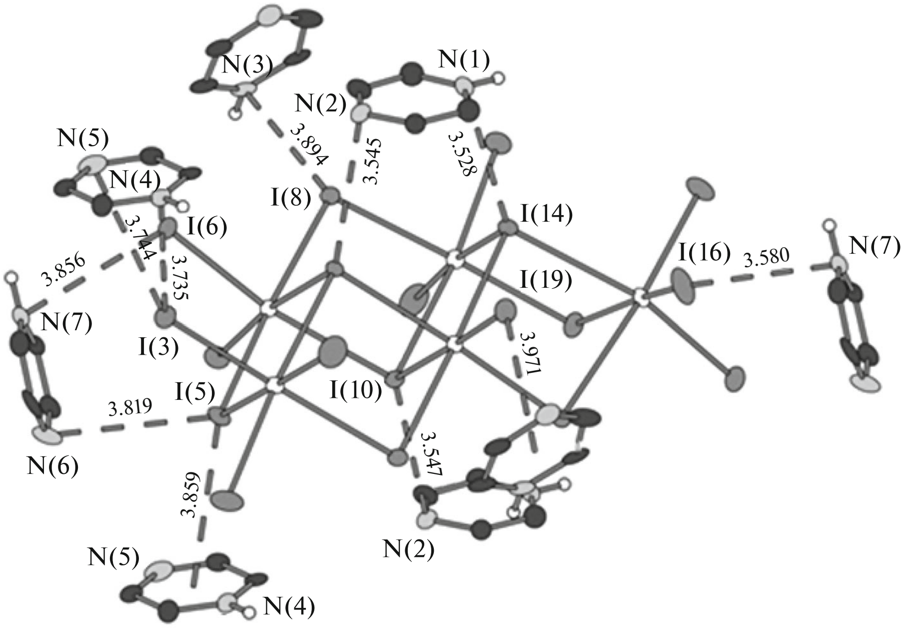

Fig. 4. Cation-anionic interactions in the crystal structure of complex **II**.

$\{BiI_6\}$ octahedra via the common edges. A specific feature of the structure of compound **II** (as well as of **I**) is presented by cation-cationic interactions between the iodine atoms and π systems of the cations.

The structure of compound **II** also contains two types of nonvalent contacts between the iodine atoms and 2,3,5,6-tetramethylpyrazinium cation (Fig. 4). The first type is related to the interaction of the π system of the cation and the iodine atom, and the second type is associated with the interaction of the N atoms of the cation with the I^- anion. In this case, both the variant of the single N···I contact and the variant of two N···I contacts for one cation are observed. The general feature of these interactions in the structures of compounds **I** and **II** is the formation of stable cyclic associates (Fig. 5a) with the shortest N···I distances (3.5 Å in both cases). Interestingly, the $[Bi_5I_{19}]^{4-}$ anion can be considered as a fragment of the layered structure of the CdI_2 type (but not BiI_3!) evidently stabilized by numerous cation-anionic contacts. In turn, each cation forms an associate

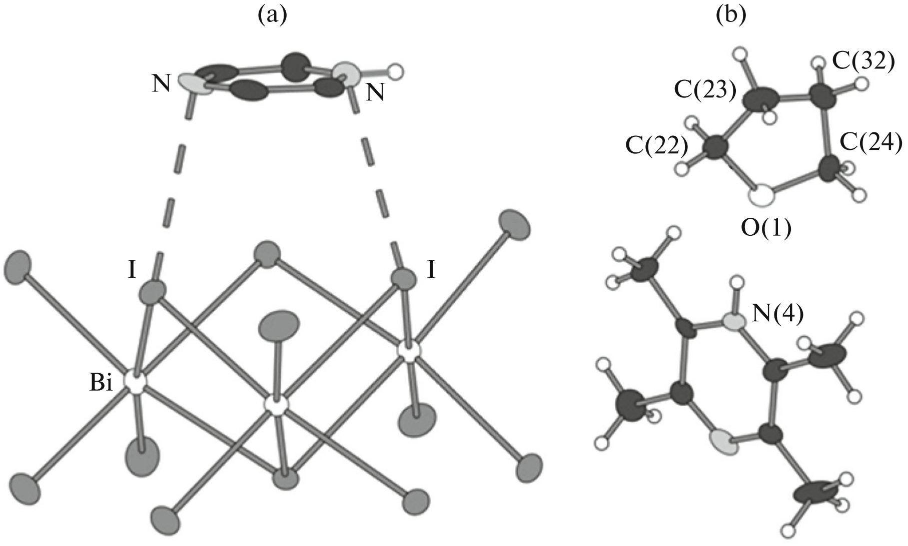

Fig. 5. Structure of the cyclic associate between the cation and anion.

with the THF molecule (Fig. 5b) via the formation of a hydrogen bond. As in the case of compound **I**, no extended structures based on hydrogen bonds are observed in compound **II**.

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