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Bromobismuthates of 1,1'-(1,*N*-Alkanediyl)bis(picolines): Synthesis, Thermal Stability, Crystal Structures, and Optical Properties

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Abstract—Hybrid bromobismuthates of *N*-alkylated derivatives of 2- and 3-methylpyridine, $(C_{15}H_{20}N_2)_2Bi_2Br_{10}$ (**I**), $(C_{17}H_{24}N_2)_2Bi_2Br_{10}$ (**II**), $(C_{18}H_{26}N_2)_3(Bi_2Br_9)_2$ (**III**), $(C_{14}H_{18}N_2)(H_3O)BiBr_6 \cdot 2H_2O$ (**IV**), $(C_{14}H_{18}N_2)_2BiBr_6IBr_2$ (**V**), $(C_{16}H_{22}N_2)_3(Bi_2Br_9)_2$ (**VI**), and $(C_{18}H_{26}N_2)_3(Bi_2Br_9)_2$ (**VII**), are synthesized in concentrated HBr and characterized by physicochemical methods. The structures of complexes **I–VII** are studied by X-ray structure analysis (CIF files CCDC nos. 1946844–1946850). Complexes **I** and **II** contain anions $[Bi_2Br_{10}]^{4-}$. Anions $[Bi_2Br_9]^{3-}$ are found in the structures of compounds **III**, **VI**, and **VII**. Bis(3-methyl-1-pyridino)ethane bromobismuthate **IV** contains cations H_3O^+ and anions $[BiBr_6]^{3-}$ and, unlike other bromobismuthates, decomposes at low temperatures. In presence of HI vapors, double bromobismuthate **V** containing the $[BiBr_6]^{3-}$ and IBr_2^- anions crystallizes along with compound **IV**.

Keywords: hybrid halobismuthates, semiconductors, crystal structure, bromobismuthate anions
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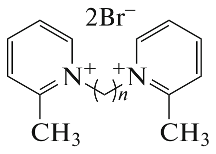
INTRODUCTION

Hybrid halobismuthates are promising materials for solar power engineering [1–4]. They are lowly toxic and highly resistant to external actions, in particular, to high moisture contents. Among the readily formed hybrid halobismuthates, one can find compounds with low values of the optical band gap ($E_g <$ 1.8 eV) [5–9]. Among the latter, mixed methyl viologen chloroiodobismuthate [7] and methyl viologen iodobismuthate [8] contain linear 1D chains $[BiX_5]_n^{2n-}$. When searching for the compounds with linear polymeric anions, we synthesized several bromo- and iodobismuthates of *N*-substituted picolines [9–12]. The linear $[BiI_5]_n^{2n-}$ anion we are interested in was found in the structure of iodobismuthate of the 4-methylpyridine derivative. The optical band gap for this compound was 1.73 eV [9]. Isolated anions $[Bi_2Br_{10}]^{4-}$, $[Bi_2Br_{11}]^{5-}$, and $[BiBr_6]^{3-}$ [10], as well as the zigzag polymeric anion $[BiI_5]_n^{2n-}$ [11], were found in the structures of the obtained bromobismuthates of the picoline derivatives. An unusual linear anionic agglomerate $[(BiBr_6)\cdots(BiBr_5)\cdots(BiBr_6)]^{8-}$ is observed in the structure of 1,1'-(1,4-phenylenebis(methylene))bis(3-methylpyridin-1-ium) bromobismuthate. The high values of E_g for this compound [12] and the compounds with the zigzag polymeric anion $[BiBr_5]_n^{2n-}$ [11] are consistent with the conclusion that only the presence of a linear anionic chain in the compound is the condition for decreasing the optical band gap of the semiconductor. Bromobismuthates, iodobismuthates, and mixed bromoiodobismuthates of the single-charge picoline derivatives are known [13–15]. However, no compounds with low E_g were found among them.

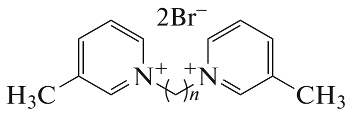
The purpose of this work is to investigate the earlier unstudied hybrid bromobismuthates of *N*-alkylated 2- and 3-picoline dications.

EXPERIMENTAL

Bis(2-methyl-1-pyridino)-1,1'-alkane bromide (a) and bis(3-methyl-1-pyridino)-1,1'-alkane bromide (b) were synthesized in air.



(a)



(b)

A mixture of methylpyridine taken in excess (6 equiv) and dibromoalkane (1 equiv) was dissolved in acetonitrile. The resulting solution was refluxed for 20 h. The formed precipitate was filtered off and washed with acetonitrile. The purity of the formed products was monitored by the ^{1}H NMR method.

Bis(2-methyl-1-pyridino)-1,1'-propane bromide: ^{1}H NMR (300 MHz; DMSO-d^6; δ, ppm): 9.08 (d, J = 6.0 Hz, 2H), 8.46 (t, J = 7.8 Hz, 2H), 8.13 (d, J = 8.1 Hz, 2H), 8.05–7.95 (m, 2H), 4.57 (s, 4H), 2.87 (s, 6H), 1.95 (s, 2H).

Bis(2-methyl-1-pyridino)-1,1'-pentane bromide: ^{1}H NMR (300 MHz; DMSO-d^6; δ, ppm): 9.18 (s, 2H), 8.50 (s, 2H), 8.11 (s, 2H), 7.99 (s, 2H), 4.64 (s, 4H), 2.90 (s, 6H), 1.97 (s, 4H), 1.51 (s, 2H).

Bis(2-methyl-1-pyridino)-1,1'-hexane bromide: ^{1}H NMR (300 MHz; DMSO-d^6; δ, ppm): 9.11 (d, J = 6.1 Hz, 2H), 8.48 (t, J = 7.8 Hz, 2H), 8.14–7.90 (m, 2H), 4.70–4.49 (m, 4H), 2.87 (s, 6H), 1.88 (s, 4H), 1.45 (s, 4H).

Bis(3-methyl-1-pyridino)-1,1'-ethane bromide: ^{1}H NMR (300 MHz; DMSO-d^6; δ, ppm): 9.15 (s, 2H), 8.88 (d, J = 5.9 Hz, 2H), 8.53 (d, J = 7.9 Hz, 2H), 8.06 (t, J = 7.0 Hz, 2H), 5.31 (s, 4H), 2.50 (s, 6H).

Bis(3-methyl-1-pyridino)-1,1'-butane bromide: ^{1}H NMR (300 MHz; DMSO-d^6; δ, ppm): 9.18 (s, 2H), 9.05 (d, J = 5.8 Hz, 2H), 8.48 (d, J = 7.9 Hz, 2H), 8.07 (t, J = 6.9 Hz, 2H), 4.72 (s, 4H), 2.50 (s, 6H), 2.02 (s, 4H).

Bis(3-methyl-1-pyridino)-1,1'-hexane bromide: ^{1}H NMR (300 MHz; DMSO-d^6; δ, ppm): 9.15 (s, 2H), 9.03 (d., J = 6.0 Hz, 2H), 8.46 (d, J = 8.0 Hz, 2H), 8.09–8.02 (m, 2H), 4.62 (t, J = 7.4 Hz), 2.51 (s, 6H), 1.99–1.91 (m, 4H), 1.34 (s, 4H).

Synthesis of $(C_{15}H_{20}N_2)_2Bi_2Br_{10}$ (I). A weighed sample of bis(2-methyl-1-pyridino)propane bromide (0.50 g) was dissolved in a 4 M aqueous solution of KBr (6.25 mL). A solution containing KBr (23.8 g) and $Bi(NO_3)_3 \cdot 5H_2O$ (4.75 g) in H_2O (75 mL) was added to the reaction mixture. A formed greenish precipitate was filtered off in vacuo, washed with water and ethanol, and dried in air. The yield was 0.82 g. The obtained precipitate was dissolved in a minimum amount of concentrated HBr, and the solution was left to evaporate at room temperature. A finely crystalline substance formed in several days was separated from the solution and dried in air. According to the X-ray structure analysis data, the obtained crystals had the composition $(C_{15}H_{20}N_2)_2Bi_2Br_{10}$ (**I**). The X-ray diffraction analysis (XRD) data showed that the substance obtained after recrystallization was single-phase. The details of the Rietveld refinement were the following: $P2_1/n$, a = 11.1050(3), b = 10.0430(4), c = 19.9647(6) Å, β = 101.993(2)°, R_{exp} 3.10, R_{wp} 8.08, R_{p} 5.38%, GOOF 2.61.

Synthesis of $(C_{17}H_{24}N_2)_2Bi_2Br_{10}$ (II). A weighed sample of bis(2-methyl-1-pyridino)pentane bromide (0.50 g) was dissolved in a 4 M aqueous solution of KBr (6.25 mL). A solution containing KBr (23.8 g) and $Bi(NO_3)_3 \cdot 5H_2O$ (4.75 g) in H_2O (75 mL) was added to the reaction mixture. A formed greenish precipitate was filtered off in vacuo, washed with water and ethanol, and dried in air. The yield was 0.635 g. The obtained precipitate was dissolved in a minimum amount of concentrated HBr, and the solution was left to evaporate at room temperature. A finely crystalline substance formed in several days was separated from the solution and dried in air. According to the X-ray structure analysis data, the obtained crystals had the composition $(C_{17}H_{24}N_2)_2Bi_2Br_{10}$ (**II**). The XRD data showed that the substance obtained after recrystallization contained compound **II** as the major phase and an unidentified impurity with the most intense peaks at 2θ = 20.0, 30.1, and 40.3. The details of the Rietveld refinement were the following: $C2/m$, a = 14.4137(6), b = 18.0306(9), c = 9.8775(4) Å, β = 114.822(4)°, R_{exp} = 3.49%, R_{wp} = 14.41%, R_{p} = 9.67%, GOOF 4.13.

Synthesis of crystals of $(C_{18}H_{26}N_2)_3(Bi_2Br_9)_2$ (III). A weighed sample of bis(2-methyl-1-pyridino)hexane bromide (0.50 g) was dissolved in a 4 M aqueous solution of KBr (6.25 mL). A solution containing KBr (23.8 g) and $Bi(NO_3)_3 \cdot 5H_2O$ (4.75 g) in H_2O (75 mL) was added to the reaction mixture. A formed greenish precipitate was filtered off in vacuo, washed with water and ethanol, and dried in air. The yield was 1.02 g. The obtained precipitate was dissolved in a minimum amount of concentrated HBr, and the solution was left to evaporate at room temperature. A powder formed in several days was separated from the solution and dried in air. Several crystals of compound **III** suitable for X-ray structure analysis were isolated from the obtained powder. According to the XRD data, compound **III** was not the major substance of the isolated product.

Synthesis of $(C_{14}H_{18}N_2)(H_3O)BiBr_6 \cdot 2H_2O$ (IV). A weighed sample of bis(3-methyl-1-pyridino)ethane bromide (0.50 g) was dissolved in a 4 M aqueous solution of KBr (6.25 mL). A solution containing KBr (23.8 g) and $Bi(NO_3)_3 \cdot 5H_2O$ (4.75 mL) in H_2O (75 mL) was added to the reaction mixture. A formed colorless precipitate was filtered off in vacuo, washed with water and ethanol, and dried in air. The yield was 1.57 g. The obtained precipitate was dissolved in a minimum amount of concentrated HBr, and the solution was left to evaporate at room temperature. A mixture formed in several days was separated from the solution and dried in air. Crystals of two types suitable for X-ray structure analysis were found in the mixture: compound **IV** and $(C_{14}H_{18}N_2)_2BiBr_6IBr_2$ (**V**). According to the XRD data, the products contained compound **IV** as the major phase and an unidentified impurity different from compound **V** with the most intense peaks at $2\theta = 9.4°$, 10.6°, 11.8°, 12.1°, and 16.8°. The details of the Rietveld refinement were the following: $P2_1/n$, $a = 10.4093(4)$, $b = 18.2135(8)$, $c = 13.8881(6)$ Å, $\beta = 99.444(5)°$, R_{exp} 2.05, R_{wp} 12.72, R_p 8.70%, GOOF 6.21. The formation of the minor phase of compound **V** was related, most likely, to the action of HI vapors on the reaction mixture with the simultaneous storage of a series of solutions containing HBr or HI in a fume hood.

Synthesis of $(C_{16}H_{22}N_2)_3(Bi_2Br_9)_2$ (VI). A weighed sample of bis(3-methyl-1-pyridino)butane (0.50 g) was dissolved in a 4 M aqueous solution of KBr (6.25 mL). A solution containing KBr (23.8 g) and $Bi(NO_3)_3 \cdot 5H_2O$ (4.75 g) in H_2O (75 mL) was added to the reaction mixture. A formed pale green precipitate was filtered off in vacuo, washed with water and ethanol, and dried in air. The yield was 1.168 g. The obtained precipitate was dissolved in a minimum amount of concentrated HBr, and the solution was left to evaporate at room temperature. The crystals formed in several days were separated from the solution and dried in air. The X-ray structure analysis data showed that the obtained crystals had the composition $(C_{16}H_{22}N_2)_3(Bi_2Br_9)_2$ (**VI**). According to the XRD data, the substance obtained after recrystallization was single-phase. The details of the Rietveld refinement were the following: $P2_1/n$, $a = 16.4908(9)$, $b = 11.3762(10)$, $c = 41.7608(26)$ Å, $\beta = 95.189(5)°$, R_{exp} 2.88, R_{wp} 12.56, R_p 8.06%, GOOF 4.37.

Synthesis of crystals of $(C_{18}H_{26}N_2)_3(Bi_2Br_9)_2$ (VII). A weighed sample of bis(3-methyl-1-pyridino)hexane bromide (0.50 g) was dissolved in a 4 M aqueous solution of KBr (6.25 mL). A solution containing KBr (23.8 g) and $Bi(NO_3)_3 \cdot 5H_2O$ (4.75 g) in H_2O (75 mL) was added to the reaction mixture. A formed pale green precipitate was filtered off in vacuo, washed with water and ethanol, and dried in air. The yield was 1.07 g. The obtained precipitate was dissolved in a minimum amount of concentrated HBr, and the solution was left to evaporate at room temperature. A precipitate formed in several days were separated from the solution and dried in air. Several crystals of compound **VII** suitable for X-ray structure analysis were isolated from the precipitate. According to the XRD data, compound **VII** was not the major substance of the isolated product.

X-ray structure analysis. Experimental data for compounds **I–VI** were obtained on a Bruker SMART APEX2 diffractometer (MoK_α radiation, $\lambda = 0.71073$ Å, graphite monochromator) [16]. An absorption correction was applied semiempirically by equivalents (SADABS) [17]. The data for compound **VII** were obtained at the BM01 diffraction station of the European Synchrotron Radiation Facility (PILATUS@SNBL diffractometer, Grenoble, France) [18]. The experimental data were processed using the SNBL ToolBox [18] and CrysAlis software (Rigaku Oxford Diffraction) programs. The structures solved by a combination of a direct method and Fourier syntheses and refined by full-matrix anisotropic–isotropic least squares. The populations of the disordered fragments in the structures of compounds **IV** and **VI** were obtained by the isotropic refinement with fixed thermal parameters of disordered atoms and were fixed in the subsequent refinement. All calculations were performed using the SHELXS and SHELXL programs [19]. Selected crystallographic data are presented in Tables 1 and 2.

The experimental data for the structures of compounds **I–VII** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1946844–1946850); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

XRD analysis was carried out on a Bruker D8 Advance diffractometer (CuK_α, Ni filter, LYNXEYE detector, reflection geometry). The full-profile analysis of the powders was conducted using the TOPAS 4.2 program [20]. The Rietveld refinement was performed using the structural models of compounds **I**, **II**, **IV**, and **VI**.

Diffuse reflectance spectra were recorded on an Ocean Optics spectrophotometer (model QE65000) in a frequency range of 11000–50000 cm^{-1} at room temperature. The spectra were reconstructed in the coordinates of the dependence of the Kubelka–Munk function [21] on the light energy. To obtain the Kubelka–Munk function, the following equation was used:

$$F(R_d) = \frac{(1 - R_d)^2}{2R_d},$$

where $F(R_d)$ is the absolute reflection of the sample layer. The optical band gap was estimated by the extrapolation of the linear section of the corresponding curve to $F(R_d) = 0$.

Thermogravimetric (TG) analysis of the samples was carried out using an SDT Q600 V8.3 Build 101 Module DSC-TGA infrared scanner. The sample was heated with a heating rate of 10°C/min from 25 to 300°C and an air flow rate of 250 mL/min in an open aluminum ware.

^{1}H NMR spectra were recorded on a Bruker AM300 spectrometer (300 MHz) in DMSO-d^6.

RESULTS AND DISCUSSION

The structure of compound **I** is formed by bis(2-methyl-1-pyridino)propane cations and centrosymmetric anions Bi_2Br_{10} (Fig. 1a). The N(2) pyridine

Table 1. Selected crystallographic data and structure refinement results for compounds **I–IV**

Parameter	Value			
	I	**II**	**III**	**IV**
Formula	$C_{30}H_{40}N_4Br_{10}Bi_2$	$C_{34}H_{48}N_4Br_{10}Bi_2$	$C_{54}H_{78}N_6Br_{18}Bi_4$	$C_{14}H_{25}N_2O_3Br_6Bi$
FW	1673.72	1729.82	3085.52	957.80
T, K	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group; *Z*	$P2_1/n$; 2	$C2/m$; 2	$P2_1/n$; 2	$P2_1/n$; 4
a, Å	11.0210(4)	14.2567(5)	9.9964(4)	10.3705(4)
b, Å	10.0180(4)	17.9650(6)	16.4091(7)	18.0471(7)
c, Å	19.8331(7)	9.8582(3)	24.7686(11)	13.8346(5)
β, deg	101.7340(10)	114.6920(10)	95.401(2)	99.5630(10)
V, Å^3	2143.98(14)	2294.04(13)	4044.8(3)	2553.27(17)
ρ_{calc}, g/cm^3	2.593	2.504	2.533	2.492
μ, mm^{-1}	17.542	16.399	17.602	16.311
F(000)	1528	1592	2812	1760
Sample size, mm	0.28 × 0.28 × 0.14	0.24 × 0.24 × 0.12	0.2 × 0.1 × 0.08	0.32 × 0.32 × 0.28
Range of measuring over θ, deg	2.098–31.022	2.267–31.512	2.278–26.058	2.257–30.058
Ranges of reflection indices	$-15 \le h \le 15$, $-14 \le k \le 14$, $-28 \le l \le 28$	$-20 \le h \le 20$, $-26 \le k \le 25$, $-13 \le l \le 14$	$-12 \le h \le 12$, $-20 \le k \le 20$, $-30 \le l \le 30$	$-14 \le h \le 14$, $-25 \le k \le 25$, $-19 \le l \le 19$
Number of measured reflections	54585	16735	43742	47092
Number of independent reflections (R_{int})	6793 (0.0644)	3794 (0.0464)	7987 (0.0870)	7490 (0.0727)
Completeness to θ = 25.242°, %	100.0	100.0	99.9	100.0
Max, min transmission	0.1007, 0.0319	0.1015, 0.0286	0.0926, 0.0322	0.099, 0.0314
Refinement method	Least squares for F^2	Least squares for F^2	Least squares for F^2	Least squares for F^2
Number of restraints/parameters	0/209	0/121	0/373	0/236
S	1.033	1.002	0.974	1.037
R_1, wR_2 ($I > 2\sigma(I)$)	0.0269, 0.0564	0.0270, 0.0610	0.0369, 0.0617	0.0360, 0.0768
R_1, wR_2 (all data)	0.0383, 0.0593	0.0366, 0.0643	0.0719, 0.0716	0.0537, 0.0830
$\Delta\rho_{max}/\Delta\rho_{min}$, e/Å^3	2.253/–0.942	1.703/–0.970	1.214/–1.522	2.532/–1.291

fragment is involved in the stacking interaction to form a centrosymmetric dimer (shortest contacts C...C 3.46, 3.53, 3.54 Å). The shortest Br...Br contacts are 4.15 and 4.16 Å.

In the structure of compound **II**, the bis(2-methyl-1-pyridino)pentane cation lies on the axis 2, and the Bi_2Br_{10} anion has the crystallographic symmetry $2/m$ (Fig. 1b). The pyridine fragment participates in the stacking interaction (shortest contacts C...C 3.25, 3.35, 3.43 Å) with two symmetrically dependent fragments to form 2D layers. The shortest Br...Br contact is 4.20 Å.

The structure of compound **III** contains two crystallographically independent bis(2-methyl-1-pyridino)hexane cations. One of them is localized in the general position, the second cation lies on the inversion center, and the Bi_2Br_9 anion is arranged in the general position (Fig. 1c). The shortest Br...Br contact (3.92 Å) joins the anions into 1D chains.

Table 2. Selected crystallographic data and structure refinement results for compounds **V–VII**

Parameter	Value		
	V	**VI**	**VII**
Formula	$C_{28}H_{36}N_4Br_8IBi$	$C_{48}H_{66}N_6Br_{18}Bi_4$	$C_{54}H_{78}N_6Br_{18}Bi_4$
FW	1403.77	3001.36	3085.52
T, K	150(2)	100(2)	150(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group; *Z*	$P\bar{1}$; 1	$P2_1/n$; 4	$P2_1/n$; 2
a, Å	9.7162(4)	16.4918(7)	10.6567(3)
b, Å	10.1351(5)	11.2389(5)	16.5173(4)
c, Å	11.5665(5)	41.1424(18)	23.2031(5)
α, deg	82.1770(10)	90	90
β, deg	65.5040(10)	94.7070(10)	92.411(3)
γ, deg	68.6170(10)	90	90
V, Å^3	964.99(8)	7600.0(6)	4080.59(18)
ρ_{calc}, g/cm^3	2.416	2.623	2.511
μ, mm^{-1}	13.674	18.732	15.261
F(000)	648	5432	2812
Sample size, mm	0.16 × 0.14 × 0.08	0.24 × 0.16 × 0.12	0.04 × 0.02 × 0.01
Range of measuring over θ, deg	2.158–31.509	2.066–27.118	1.669–26.750
Ranges of reflection indices	$-13 \le h \le 14$, $-14 \le k \le 14$, $-16 \le l \le 16$	$-21 \le h \le 21$, $-14 \le k \le 14$, $-52 \le l \le 51$	$-13 \le h \le 13$, $-22 \le k \le 22$, $-30 \le l \le 30$
Number of measured reflections	18762	63868	25299
Number of independent reflections (R_{int})	6095 (0.0459)	16731 (0.0791)	8782 (0.0421)
Completeness to θ = 25.242°, %	100.0	99.9	92.3
Max, min transmission	0.1015, 0.0342	0.0285, 0.0054	1, 0.39459
Refinement method	Least squares for F^2	Least squares for F^2	Least squares for F^2
Number of restraints/parameters	0/195	9/695	0/370
S	1.019	0.990	1.016
R_1, wR_2 ($I > 2\sigma(I)$)	0.0332, 0.0812	0.0571, 0.1388	0.0658, 0.1590
R_1, wR_2 (all data)	0.0435, 0.0851	0.0881, 0.1546	0.0925, 0.1755
$\Delta\rho_{max}/\Delta\rho_{min}$ e/Å^3	1.749/–2.333	2.028/–2.209	3.229/–3.492

The structure of compound **IV** is formed by the bis(3-methyl-1-pyridino)ethane cations, $BiBr_6$ anions (Fig. 1d), oxonium ions, and molecules of water of crystallization. All positions of the O atoms of the oxonium ions and water molecules are disordered (population 0.24–0.76), which does not allow one to objectively localize the H atoms.

All structural units in the impurity phase **V**, two crystallographically independent bis(3-methyl-1-pyridino)ethane cations and $BiBr_6$ and IBr_2 anions (Fig. 2a), are in the partial positions (inversion centers). One of the cations forms the 1D chain by stacking interactions of the pyridine fragment. The I...Br contact (4.16 Å) links the anions into the 1D chain.

The structure of compound **VI** contains two crystallographically independent Bi_2Br_9 anions and four independent bis(3-methyl-1-pyridino)butane cations (Fig. 2b). One of the anions is disordered over two positions in a ratio of 0.85 : 0.15, two cations are in the general position, the third cation lies on the inversion center, and the fourth cation is disordered about the inversion center. The disordered Br atom with a popu-

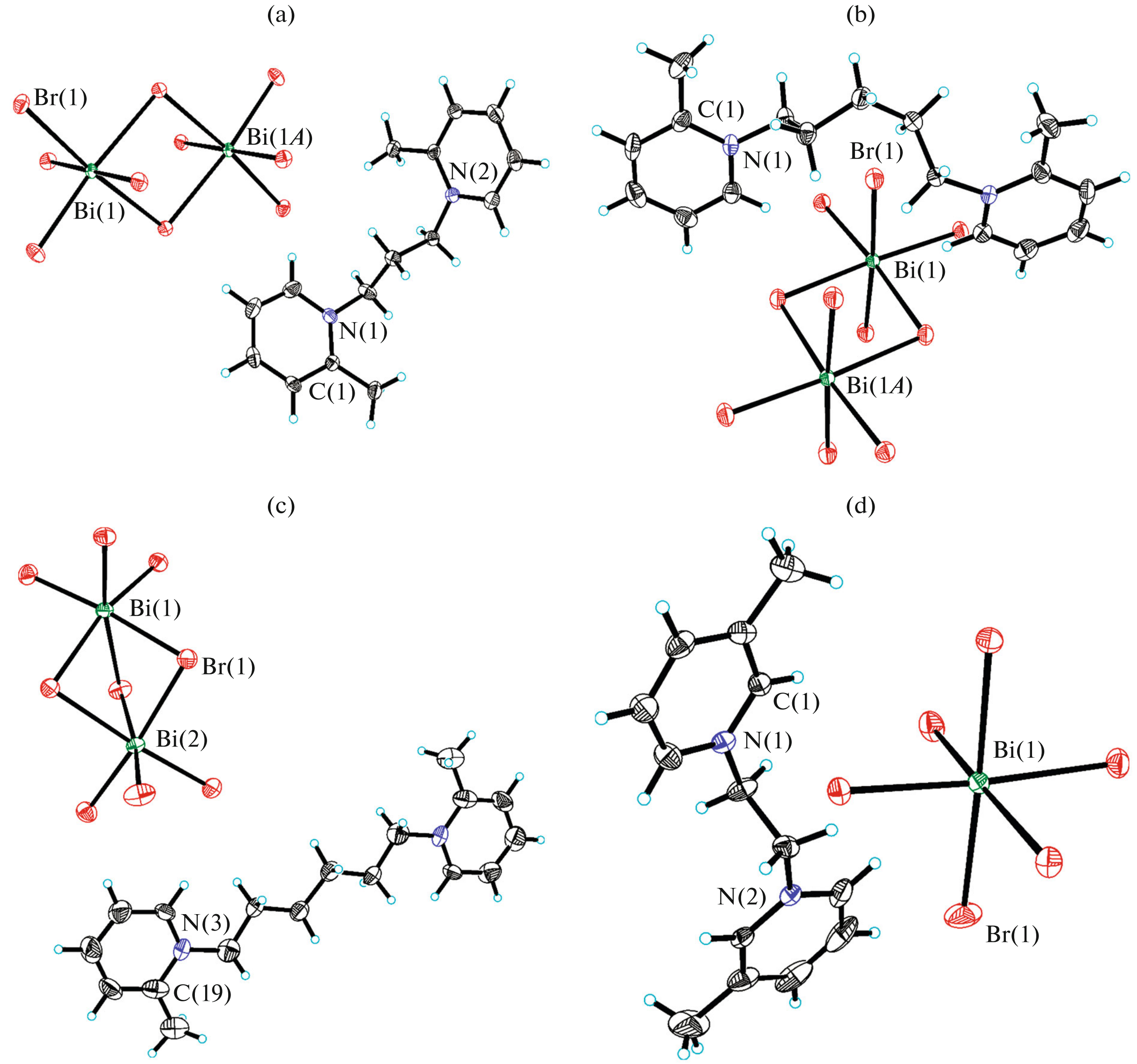


Fig. 1. Fragments of the structures of compounds (a) **I**, (b) **II**, (c) **III**, and (d) **IV**.

lation of 0.15 is involved in the shortest Br...Br contact (3.73 Å).

The structure of compound **VII** is formed by the Bi_2Br_9 anions and two crystallographically independent bis(3-methyl-1-pyridino)hexane cations, one of which is arranged on the inversion center (Fig. 2c). Although the conformation of the aliphatic chains in the cations can be described as ttttt, the range of absolute values of the NCCC and CCCC torsion angles in the centrosymmetric cation (174°–180°) and that arranged in the general position (148°–174°) indicates a less distorted conformation of the first cation. The shortest Br...Br contact is 3.90 Å.

The thermal analysis of the crystalline powder of compound **IV** (Fig. 3) showed that the compound lost one HBr molecule and two H_2O molecules when the temperature reached 140°C. Other compounds are more stable. Compound **I** remains stable to 270°C and then undergoes melting with decomposition at 279°C. The decomposition of compound **II** started already at 250°C. Compound **III** melts at 250°C, compound **VI** melts at 234°C, and compound **VII** melts at 250°C.

According to the data of diffuse reflectance spectroscopy, the optical band gaps for compounds **I**, **II**, **IV**, and **VI** were 2.83, 2.85, 2.88, and 2.85 eV. The formal values for the products containing compounds **III** and **VII** are equal to each other being 2.86 eV. Thus, the spectral characteristics of all isolated compounds are typical of the 0D hybrid bromobismuthates.

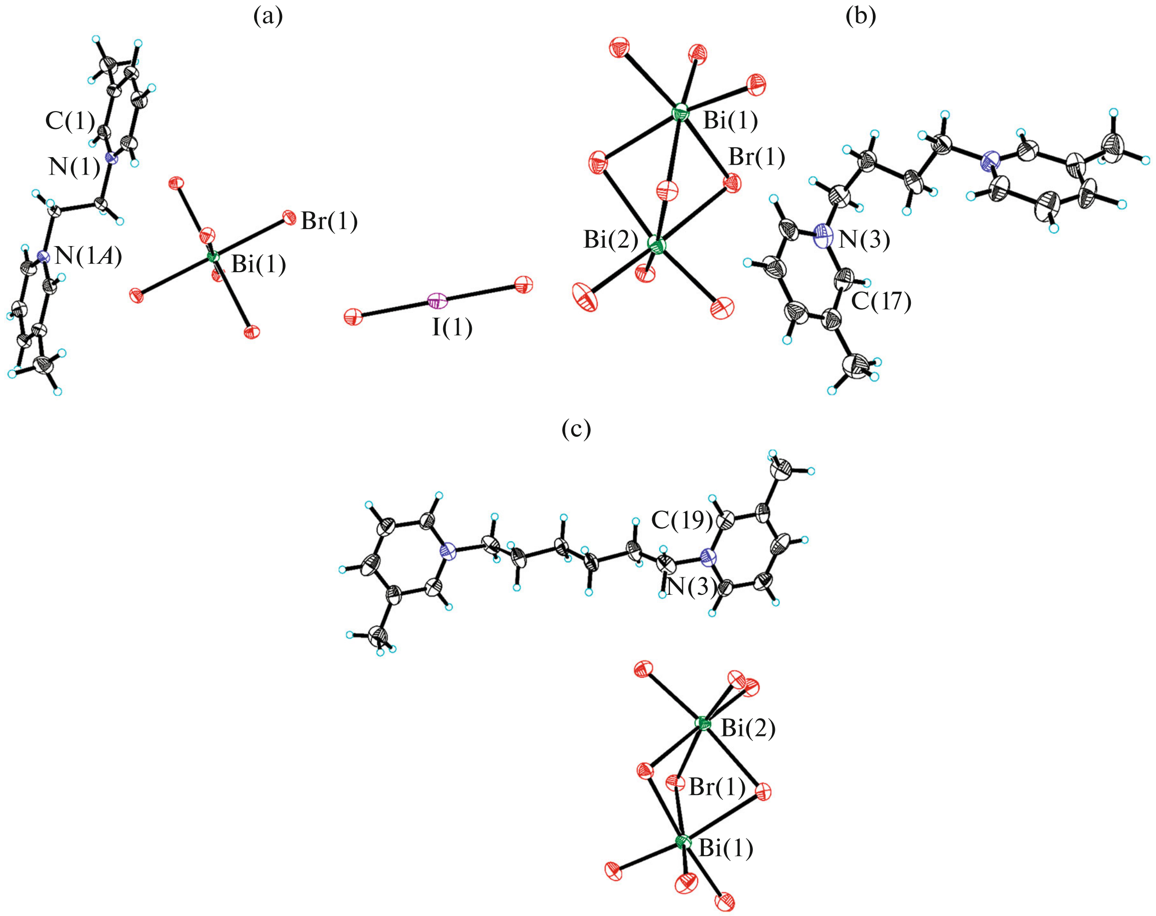


Fig. 2. Fragments of the structures of compounds (a) **V**, (b) **VI**, and (c) **VII**.

Hybrid bromobismuthates of *N*-substituted 2- and 3-picolines contain various anions, namely, $[BiBr_6]^{3-}$, $[Bi_2Br_9]^{3-}$, and $[Bi_2Br_{10}]^{4-}$. We have also found previously the $[BiBr_5]_n^{2n-}$ and $[Bi_2Br_{11}]^{5-}$ anions in the structures of bromobismuthates of *N*-substituted 2- and 4-bromopicolines [10, 11]. Thus, we cannot predict the possible composition and structure of the anionic moiety of bromobismuthates in the series of *N*-substituted picolines even for the same initial stoichiometric ratio of the reagents (doubly charged organic cation : bismuth). We mentioned that the products with the organic cation to bismuth ratio equal to 1 : 1 crystallized for bromobismuthates of *N*-substituted 4-picolines in all cases studied. For bromobismuthates of *N*-substituted 2-picolines, the deviation from this ratio is observed only for the compound in which the cation contains the alkane chain bearing six carbon atoms, while the alkane chain should already contain four and six carbon atoms for bromobismuthates of *N*-substituted 3-picolines. However, since the products of the reactions of bis(*p*-methyl-1-pyridino)hexane cations with bromobismuthate anions are not single-phase, we cannot assert that a tendency for changing the organic cation to bismuth ratio was observed in the series of the isolated compounds.

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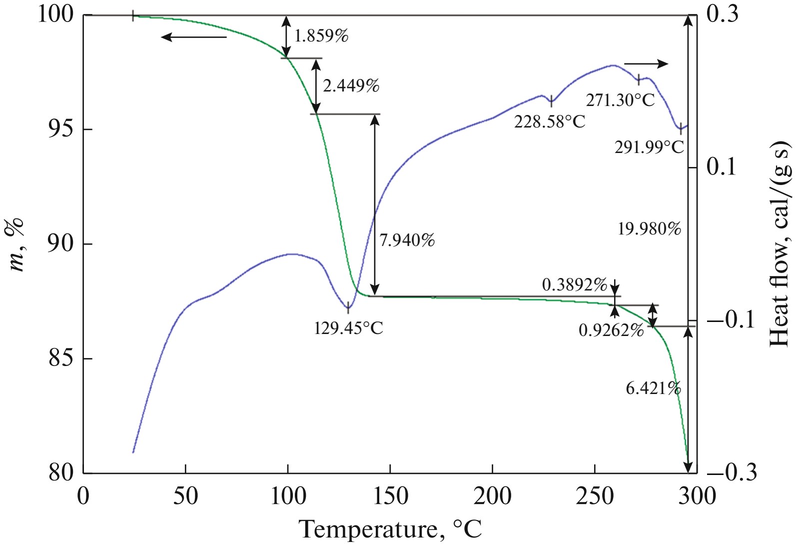

Fig. 3. DSC–TG curves for compound **IV**.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Singh, T., Kulkarni, A., Ikegami, M., and Miyasaka, T., *ACS Appl. Mater. Interfaces*, 2016, vol. 8, p. 14542.
2. Zhang, Z., Li, X.W., Xia, X.H., et al., *J. Phys. Chem. Lett.*, 2017, vol. 8, p. 4300.
3. Sanders, S., Stummler, D., Pfeiffer, P., et al., *MRS Advances*, 2018, vol. 3, p. 3085.
4. Fabian, D.M. and Ardo, S., *J. Mater. Chem. A*, 2016, vol. 4, p. 6837.
5. Kotov, V.Y., Ilyukhin, A.B., Sadovnikov, A.A., et al., *Mendeleev Commun.*, 2017, vol. 27, p. 271.
6. Kotov, V.Y., Ilyukhin, A.B., Birin, K.P., et al., *New J. Chem.*, 2016, vol. 40, p. 10041.
7. Leblanc, N., Mercier, N., Zorina, L., et al., *J. Am. Chem. Soc.*, 2011, vol. 133, p. 14924.
8. Chen, Y., Yang, Z., Guo, C.X., et al., *Eur. J. Inorg. Chem.*, 2010, p. 5326.
9. Kotov, V.Y., Ilyukhin, A.B., Korlyukov, A.A., et al., *New J. Chem.*, 2018, vol. 42, p. 6354.
10. Kotov, V.Y., Ilyukhin, A.B., Simonenko, N.P., and Kozyukhin, S.A., *Polyhedron*, 2017, vol. 37, p. 122.
11. Buikin, P.A., Rudenko, A.Y., Baranchikov, A.E., et al., *Russ. J. Coord. Chem.*, 2018, vol. 44, p. 373. https://doi.org/10.1134/S1070328418060015
12. Kotov, V.Y., Safiullina, E.S., Ilyukhin, A.B., et al., *J. Mol. Struct.*, 2019, vol. 119, p. 944.
13. Li, H.H., Wang, M., Huang, S.W., et al., *Synth. React. Inorg. Met.-Org. Nano-Metal Chem.*, 2011, vol. 41, p. 1351.
14. Adonin, S.A., Gorokh, I.D., Novikov, A.S., et al., *Polyhedron*, 2018, vol. 13, p. 282.
15. Adonin, S.A., Gorokh, I.D., Samsonenko, D.G., et al., *Polyhedron*, 2019, vol. 15, p. 318.
16. *APEX2 and SAINT,* Madison, Bruker AXS Inc., 2007.
17. Sheldrick, G.M., *SADABS*, Göttingen: Univ. of Göttingen, 1997.
18. Dyadkin, V., Pattison, P., Dmitriev, V., and Chernyshov, D., *J. Synchrotron Radiat.*, 2016, vol. 23, p. 825.
19. Sheldrick, G.M., *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, vol. 71, p. 3.
20. Caelho A.A., *TOPAS-Academic. Version 4.2*, Brisbane: Caelho Software, 2009.
21. Kubelka, P. and Munk, F., *Z. Techn. Phys.*, 1931, vol. 12, p. 593.

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