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1D-Bromobismuthates of Dipyridinoalkane Derivatives

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Abstract—The following bromobismuthates of organic cations (dipyridinoalkane derivatives) are synthesized and characterized: (4-NH_2PyC_5)$BiBr_5$ (**I**), (2-$MePyC_2$)$BiBr_5$ (**II**), (2-NH_2PyC_{10})$BiBr_5 \cdot 0.65H_2O$ (**III**), (2-NH_2PyC_{10})$_4H_5O_2(BiBr_6)_3$ (**IV**), (2-NH_2PyC_6)$_2KBi_2Br_{11}$ (**V**), (2-NH_2PyC_6)$H_3OBiBr_6 \cdot 2.33H_2O$ (**VI**), and (2-NH_2PyC_6)$_3(BiBr_6)_2 \cdot CH_3CN$ (**VII**). Three compounds obtained (**I–III**) contain the zigzag 1D chain $(BiBr_5)_n$. A new type of 1D chains, $(KBi_2Br_{11})_n$, is found in the structure of compound **V**. Pseudo-1D chains of $BiBr_6^{3-}$ anions can be observed in the 3D structures of compounds **IV**, **VI**, and **VII**. The crystallographic data were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC 1569478 (**I**)–1569484 (**VII**), respectively).

Keywords: hybrid bromobismuthates, crystal structure, optical properties, polynuclear chains

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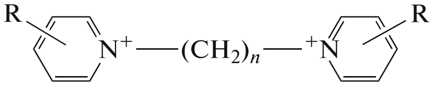
INTRODUCTION

In the recent time, hybrid halobismuthates attract attention of researchers due to their unusual physical properties. In particular, low optical band gaps of the synthesized compounds make them possible candidates for use as light-harvesting materials for solid-state solar cells [1, 2].

We have recently studied the properties of halobismuthates of bis(4-cyanopyridino)-1,1'-alkanes $(4\text{-CNPyC}_n)^{2+}$ and have found [3] that 4-$CNPyC_3BiBr_5 \cdot H_2O$ obtained from aqueous solutions has the $BiBr_5$ anion in the 1D structure. For this semiconductor, the optical band gap is $E_g = 2.24$ eV. The replacement of bromine by iodine in this compound results in the formation of a product with $E_g = 1.70$ eV. Bis(4-cyanopyridino)pentane iodobismuthate has a lower optical band gap ($E_g = 1.59$ eV) [4]. However, attempts to obtain crystals of iodobismuthates of $(4\text{-CNPyC}_n)^{2+}$ and to characterize their structures failed: the recrystallization of these compounds from acidic or hot solutions led to the hydrolysis of the cation. Therefore, we decided to study hybrid halobismuthates of the following organic cations: the dipyridinoalkane derivatives bearing amino and methyl groups as substituents at the aromatic ring. No evident reasons preventing the crystallization of the reaction products from acidic solutions were observed for these compounds. First, we were interested in a relation between the structures of the obtained hybrid halobismuthates and their spectral characteristics.

EXPERIMENTAL

The structure of the bis(*m*-R-1-pyridino)-1,1'-alkane dications (*m* is the substituent position) used in the work is presented in Scheme 1.



I: R = NH_2, *m* = 4, *n* = 5
II: R = CH_3, *m* = 2, *n* = 2
II, IV: R = NH_2, *m* = 2, *n* = 10
V–VII: R = NH_2, *m* = 2, *n* = 6

Scheme 1.

Bromides of organic cations synthesized in air from the corresponding derivatives of pyridine and α,ω-dibromoalkanes in acetonitrile were used. The purity of the products was monitored by the ^1H NMR method.

Synthesis of bis(4-amino-1-pyridino)pentane bromobismuthate (I). A weighed sample of bis(4-amino-1-pyridino)pentane bromide (0.394 g) was dissolved in concentrated HBr (17 mL). A 0.1 M solution of $BiBr_3$ (Lanchit ultra dry 99.998%) (10 mL) in concentrated HBr (Fluka purum ≥ 48%) was added to the reaction mixture. Yellow crystals of (4-NH_2PyC_5)$BiBr_5$ (**I**) precipitated in several days at room temperature were decanted from the mother liquor and washed with anhydrous acetonitrile (Komponent-Reactiv, dry). The yield was 0.82 g (67%).

Synthesis of bis(2-methyl-1-pyridino)ethane bromobismuthate (II). A weighed sample of bis(2-methyl-1-pyridino)ethane (0.50 g) was dissolved in a 4 M aqueous solution of KBr (Reakhim, analytical grade) (6.25 mL). A solution (18.75 mL) containing KBr (23.80 g) and $Bi(NO_3)_3 \cdot 5H_2O$ (Reakhim, special purity grade) (4.750 g) in H_2O (75 mL) was added to the resulting solution. A yellow precipitate formed was filtered off from the solution in vacuum, thoroughly washed with water and ethanol, and dried in air. The yield was 0.73 g (66%) based on the formation of $(2\text{-MePyC}_2)BiBr_5$. The isolated precipitate (0.5 g) was dissolved in a minimum amount of concentrated HBr. Yellow crystals of $(2\text{-MePyC}_2)BiBr_5$ **(II)** precipitated in several days at room temperature were decanted from the mother liquor and washed with anhydrous acetonitrile.

Synthesis of bis(2-amino-1-pyridino)decane bromobismuthates (III) and (IV). Weighed samples of bis(2-amino-1-pyridino)decane bromide (0.43 g) and KBr (2.90 g) were dissolved in H_2O (40 mL). A solution containing KBr (5.80 g), $Bi(NO_3)_3 \cdot 5H_2O$ (1.20 g), and H_2O (10 mL) was added to the reaction mixture. A yellow precipitate formed was filtered off from the solution in vacuum, washed with water and ethanol, and dried in air at room temperature. The yield was 0.65 g (78%) based on the formation of $(2\text{-NH}_2\text{PyC}_{10})BiBr_5 \cdot 0.65H_2O)$. The isolated precipitate (0.5 g) was dissolved in a minimum amount of concentrated HBr. The crystalline mixture precipitated in several days at room temperature was decanted from the mother liquor and washed with anhydrous acetonitrile. The crystalline precipitate contained crystals of two types: $(2\text{-NH}_2\text{PyC}_{10})BiBr_5 \cdot 0.65H_2O$ **(III)** and $(2\text{-NH}_2\text{PyC}_{10})_4H_5O_2(BiBr_6)_3$ **(IV)**.

Synthesis of bis(2-amino-1-pyridino)hexane bromobismuthates (V–VII). Weighed samples of bis(2-amino-1-pyridino)hexane bromide (0.890 g) and KBr (5.046 g) were dissolved in H_2O (10 mL). A solution containing KBr (10.09 g), $Bi(NO_3)_3 \cdot 5H_2O$ (2.07 g), and H_2O (15 mL) was added to the reaction mixture. A yellow precipitate formed was filtered off from the solution in vacuum, washed with water and ethanol, and dried in air. The yield was 1.645 g (94%) based on the formation of $(2\text{-NH}_2\text{PyC}_6)_2KBi_2Br_{11}$. The obtained precipitate (0.5 g) was dissolved in a minimum amount of concentrated HBr. Yellow crystals of $(2\text{-NH}_2\text{PyC}_6)_2KBi_2Br_{11}$ **(V)** precipitated in several days at room temperature were decanted from the mother liquor and dried on the filter.

In order to isolate the product containing no potassium ions, bis(2-amino-1-pyridino)hexane bromide (0.204 g) was dissolved in a minimum amount of HBr. A 0.1 M solution (5 mL) of $BiBr_3$ in concentrated HBr was added to the reaction mixture. Yellow crystals of $(2\text{-NH}_2\text{PyC}_6)H_3OBiBr_6 \cdot 2.33H_2O$ **(VI)** precipitated in several days were decanted from the mother liquor and dried on the filter. An attempt to wash off the crystals from the mother liquor resulted in their dissolution, after which unstable in air crystals of $(2\text{-NH}_2\text{PyC}_6)_3(BiBr_6)_2 \cdot CH_3CN$ **(VII)** were formed within several minutes on the bottom of the beaker.

X-ray structure analysis. Experimental data for compounds **I–VII** were collected on a Bruker SMART APEX2 diffractometer ($\lambda(\text{Mo}K_\alpha)$ radiation, graphite monochromator) [5] (Table 1). Absorption corrections for compounds **I–IV**, **VI**, and **VII** were applied semiempirically by equivalents using the SADABS program [6]. The X-ray structure analysis of compound **V** was carried out on an accretion, and an absorption correction was applied using the TWINABS program [7]. The structures of compounds **I–VII** were determined by a combination of a direct method and Fourier syntheses. The site occupancies of the disordered fragments obtained by the isotropic refinement of the structures with fixed thermal parameters of disordered atoms were not refined in subsequent calculations. The structures were refined by the full-matrix anisotropic–isotropic (some disordered atoms) least-squares method. Hydrogen atoms were partially localized from the difference Fourier syntheses and were calculated in part from geometric concepts. All calculations were performed using the SHELXS-2016 and SHELXL-2016 programs [8]. The single-phase character of compounds **I**, **II**, and **V** was confirmed by X-ray diffraction analysis using the TOPAS program [9]. Refinement parameters: space group *Pbca*, a = 8.9046(2), b = 20.6148(2), c = 25.0894(3) Å, R_{exp} = 2.93%, R_{wp} = 6.76%, R_p = 4.80%, GOOF = 2.31 (**I**); space group $P2_1/c$, a = 9.6577(4), b = 19.7734(3), c = 11.6179(4) Å, β = 113.552(3)°, R_{exp} = 3.54%, R_{wp} = 7.26%, R_p = 5.20%, GOOF = 2.05 (**II**); space group $P\bar{1}$, a = 11.1401(5), b = 11.1567(5), c = 13.1222(4) Å, α = 77.823(3)°, β = 66.613(3)°, γ = 60.675(3)°, R_{exp} = 3.24%, R_{wp} = 5.73%, R_p = 4.24%, GOOF = 1.77 (**V**).

The coordinates of atoms and other parameters for the structures of compounds **I–VII** were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC 1569478–1569484; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

X-ray diffraction analysis was carried out on a Bruker D8 Advance diffractometer with the horizontal axis of the goniometer ($\text{Cu}K_\alpha$) in a 2θ range of 3°–120° at the 2θ increment 0.01°–0.02° and time 0.3–0.5 s per increment. The full-profile analysis of the X-ray diffraction patterns of the crystalline substances was conducted using the TOPAS program [9]. The Chebyshev polynomials of the fourth kind were used to determine the surface area.

Diffuse reflectance spectra were recorded on an Ocean Optics (model QE65000) spectrophotometer in a frequency range of 11000–50000 cm^{-1} at room

Table 1. Selected structural data and refinement results for compounds **I**–**VII**

Parameter	Value						
	I	**II**	**III**	**IV**	**V**	**VI**	**VII**
T, K	120(2)	150(2)	150(2)	150(2)	150(2)	120(2)	150(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$Pbca$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
a, Å	8.7959(4)	9.624(3)	18.641(2)	12.7167(4)	10.9936(11)	11.7922(6)	12.4840(6)
b, Å	20.5377(10)	19.609(6)	16.0199(18)	12.9660(4)	11.0944(11)	13.3966(7)	21.8199(12)
c, Å	24.9416(12)	11.606(4)	9.6422(12)	17.7614(5)	13.0953(12)	15.3074(7)	12.9009(7)
α, deg	90	90	90	104.6030(10)	77.5688(16)	82.819(2)	90
β, deg	90	114.006(4)	105.008(3)	94.5060(10)	66.9079(14)	83.482(2)	91.866(2)
γ, deg	90	90	90	102.7500(10)	60.4064(14)	66.824(2)	90
V, Å^3	4505.6(4)	2000.8(11)	2781.2(6)	2736.01(14)	1277.1(2)	2200.12(19)	3512.3(3)
Z	8	2	4	1	1	3	2
ρ_{calc}, g/cm^3	2.556	2.732	2.266	2.073	2.446	2.315	2.113
μ, mm^{-1}	16.702	18.795	13.541	11.432	15.598	14.207	11.871
$F(000)$	3184	1496	1778	1620	866	1427	2104
Crystal size, mm	0.5 × 0.04 × 0.02	0.14 × 0.12 × 0.02	0.30 × 0.04 × 0.04	0.26 × 0.16 × 0.12	0.22 × 0.2 × 0.1	0.36 × 0.2 × 0.16	0.24 × 0.12 × 0.06
Range of θ, deg	2.145–30.530	2.077–27.873	2.186–25.411	2.179–26.405	2.112–30.032	2.042–27.931	2.234–28.319
Range of indices	$-12 \le h \le 12$, $-29 \le k \le 29$, $-35 \le l \le 35$	$-12 \le h \le 12$, $-25 \le k \le 25$, $-15 \le l \le 15$	$-22 \le h \le 22$, $-18 \le k \le 19$, $-11 \le l \le 11$	$-15 \le h \le 15$, $-16 \le k \le 16$, $-22 \le l \le 22$	$-15 \le h \le 15$, $-15 \le k \le 15$, $-18 \le l \le 18$	$-15 \le h \le 15$, $-17 \le k \le 17$, $-20 \le l \le 20$	$-16 \le h \le 16$, $-29 \le k \le 29$, $-17 \le l \le 17$
Collected reflections	68960	33916	18957	43176	66578	34598	60288
Independent reflections (R_{int})	6888 (0.0649)	4815 (0.0823)	5127 (0.1576)	11167 (0.0529)	7434 (0.0845)	10527 (0.0561)	8735 (0.0842)
Completeness to $\theta = 25.242°$, %	100	100	100	99.9	100	99.9	100
Max, min transmission	0.0998, 0.0412	0.1015, 0.0242	0.0921, 0.0489	0.0932, 0.026	0.05112, 0.00797	0.0955, 0.0284	0.0479, 0.0153
Restraints/parameters	0/226	0/205	165/279	182/624	0/150	60/466	0/347
GOOF	0.990	1.493	0.891	0.994	1.430	0.993	0.992
R_1, wR_2 ($I > 2\sigma(I)$)	0.0265, 0.0483	0.0813, 0.2271	0.0571, 0.1245	0.0412, 0.0949	0.0782, 0.2002	0.0368, 0.0912	0.0340, 0.0683
R_1, wR_2 (all data)	0.0444, 0.0527	0.0906, 0.2434	0.1930, 0.1819	0.0739, 0.1102	0.0987, 0.2218	0.0594, 0.1000	0.0576, 0.0757
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	0.793, –0.927	5.371, –7.617	1.636, –2.061	1.720, –1.239	8.335, –5.308	1.603, –0.991	0.961, –0.851

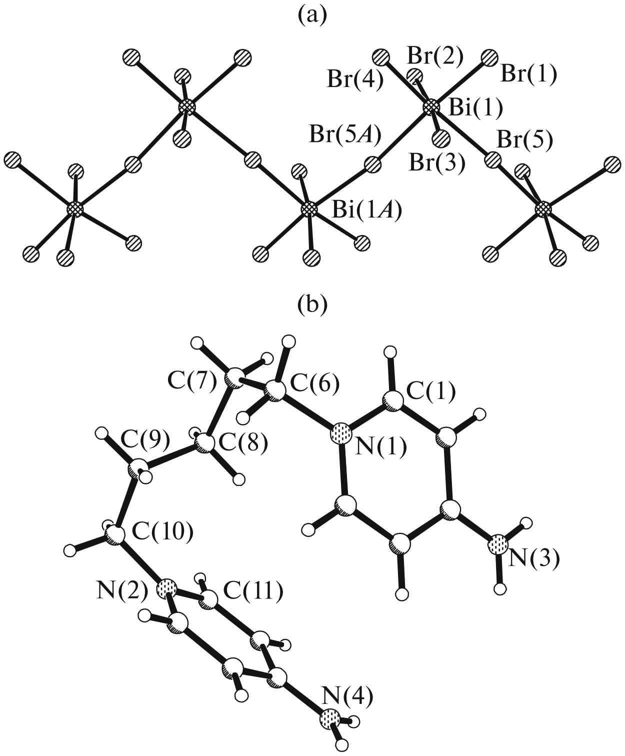


Fig. 1. Structures of the (a) polymeric 1D chain $\{BiBr_5\}_n$ and (b) 4-NH_2PyC_5 cation in compound **I**.

temperature. The spectra were reconstructed in the coordinates of the dependence of the Kubelka–Munk function [10] on the light energy. The following equation was used to obtain the Kubelka–Munk function:

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

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

RESULTS AND DISCUSSION

Compound **I** is formed by 1D chains $\{BiBr_5\}_n$ and $(4\text{-}NH_2PyC_5)^{2+}$ cations (Fig. 1). The octahedral environment of the Bi atom is distorted because of the partial stereochemical activity of the lone electron pair: the Bi(1)–Br(1,2,4) bonds (2.72–2.79 Å) are significantly shorter than Bi(1)–Br(3,5,5*A*) (2.94–3.10 Å) (Table 2). The aliphatic bond of the cation has the (*g*-*g*-*t*-*g*) conformation (*g* is *gauche*, *t* is *trans*). Three of four hydrogen bonds N–H···Br join the cation with one $\{BiBr_5\}_n$ chain, and the fourth bond joins the cation with the adjacent chain. The combined action of the hydrogen bonds results in the formation of layers perpendicular to the *b* axis. The shortest Br···Br contact of the adjacent chains exceeds 4 Å.

Compound **II** is formed by 1D chains $\{BiBr_5\}_n$ and $(2\text{-}MePyC_2)^{2+}$ cations (Fig. 2). In the structure of compound **II**, two Br(2,5) atoms are localized at the inversion centers (Fig. 2a). As usual, the shortest Bi–Br distances are formed by the Br atoms in the *trans* positions to the bridging atoms. The ethylenediimine chain has the *gauche* conformation (Fig. 2b). The shortest Br(3)···Br(3') contact is 3.70 Å.

In the structure of compound **III**, the bridging Br(1) atom is disordered over two positions in a ratio

Table 2. Lengths of Bi–Br bonds (Å) in the structures of compounds **I**–**VII***

Compound	**I**	**II**	**III****	**IV**	**V**	**VI**	**VII**
Bi(1)–Br(1)	2.7193(4)	2.869(2)	3.028(17)[a]	2.8334(9)	2.9906(16)	2.7621(7)	2.8194(5)
Bi(1)–Br(1)[#1]			3.149(17)[a]				
Bi(1)–Br(1*B*)			3.37(3)[b]				
Bi(1)–Br(1*B*)[#1]			2.87(3)[b]				
Bi(1)–Br(2)	2.7938(4)	3.1313(9)	2.830(2)	2.8352(8)	2.7669(17)	2.9723(7)	2.8986(5)
Bi(1)–Br(3)	2.9412(4)	2.820(2)	2.817(2)	2.7695(10)	2.7973(15)	2.8351(7)	2.8030(5)
Bi(1)–Br(4)	2.7210(4)	2.735(2)	2.742(8)	3.0297(10)	2.7858(17)	2.9130(6)	2.8746(5)
Bi(1)–Br(5)	3.1055(4)	3.0497(10)	2.741(8)	2.7594(8)	2.8964(15)	2.8047(7)	2.9950(6)
Bi(1)–Br(5)[#2]	3.0573(4)						
Bi(1)–Br(6)		2.730(2)		3.0134(8)	3.0214(6)	2.8862(7)	2.7900(6)
Bi(2)–Br(7) × 2				2.8432(8)		2.8436(7)	
Bi(2)–Br(8) × 2				2.8671(8)		2.8469(7)	
Bi(2)–Br(9) × 2				2.8498(9)		2.8770(8)	

* Symmetry codes: [#1] $x, -y + 1/2, z - 1/2$; [#2] $x - 1/2, y, -z + 1/2$.
** Site occupancy: 0.65[a], 0.35[b].

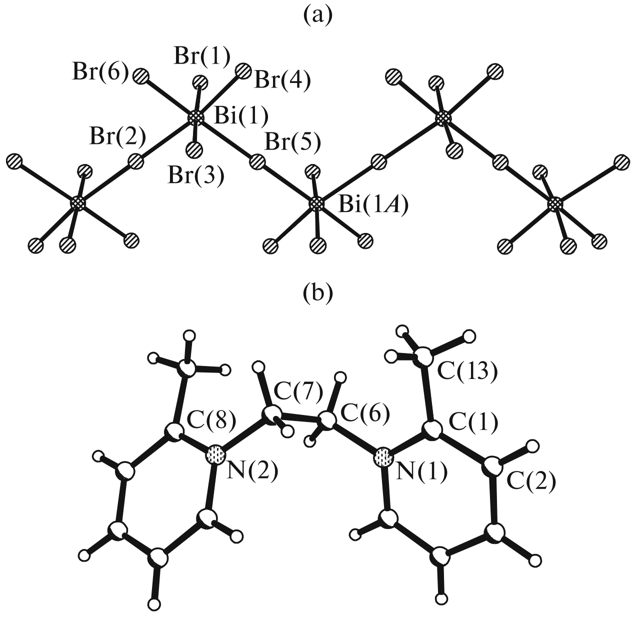


Fig. 2. Structures of the (a) polymeric 1D chain $\{BiBr_5\}_n$ and (b) 2-$MePyC_2$ cation in compound **II**.

of 0.65 : 0.35. The molecule of water of crystallization O(1) (site occupancy 0.65) enters the chain with the high occupancy by two hydrogen bonds (Fig. 3a). The lengths of the bridging Bi–Br(1,1*A*) bonds (3.03, 3.15 Å) in this chain are closer to each other than those in the chain with the lower occupancy (2.87, 3.37 Å). The ratio of the semi-axes of the thermal vibration ellipsoid of the Br(1*B*) atom (0.024 × 0.057 × 0.177) indicates that the bridging Br atom is disordered over more than two positions. The quality of all the four tested single crystals is low and, therefore, we can only state that the Bi atoms with different stereochemically active lone electron pairs coexist in one crystallographic position in a crystal of compound **III** (Figs. 3a, 3b). The aliphatic chain of the cation has the (*t-t-g-t-t-t-g-t-t*) conformation (Fig. 3c). Both amino groups participate in two hydrogen bonds to form $R_2^2(6)$ cycles with two 1D chains $\{BiBr_5\}_n$ resulting, as in the case of compound **I**, in the polymeric structure of compound **III**. The shortest Br···Br contact of the adjacent chains exceeds 4 Å.

The structure of compound **IV** is formed by the $BiBr_6^{3-}$ anions, $(2\text{-}NH_2PyC_{10})^{2+}$ cations, and dioxonium ions $H_5O_2^+$. One of three crystallographically independent cations is localized in the general position (conformation of the aliphatic chain *t-t-t-t-t-t-t-g-t*), the second cation has the crystallographic symmetry –1 (*t-t-t-g-t-g-t-t-t*), and the third cation is disordered around the inversion center (*t-t-g-t-g-t-g-t-g*). The combined action of N–H···Br and O–H···Br hydrogen bonds joins the structural units into a 3D framework. The shortest Br···Br contact is 3.48 Å.

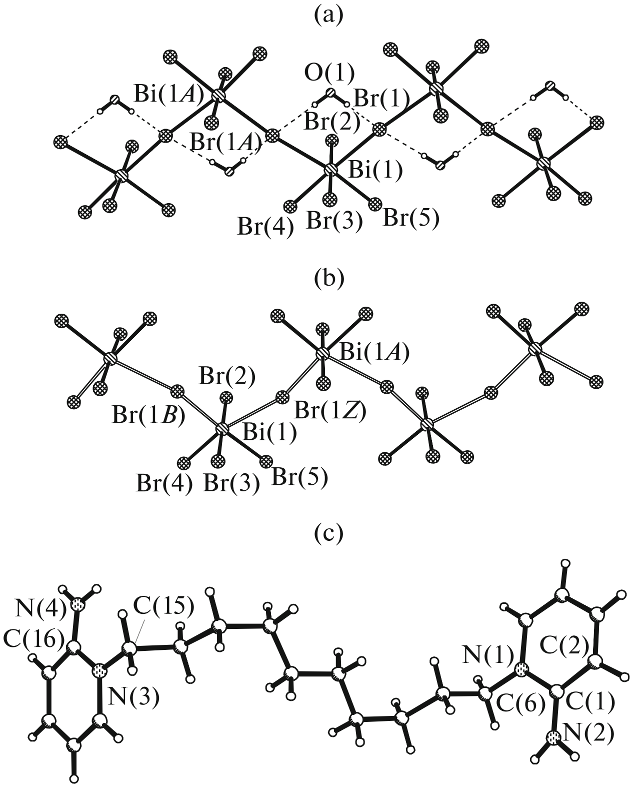


Fig. 3. Structures of the (a, b) polymeric 1D chain $\{BiBr_5\}_n$ of two types and (c) 2-NH_2PyC_{10} cation in compound **III**.

The structure of compound **V** contains K^+ and $(2\text{-}NH_2PyC_6)^{2+}$ cations and $Bi_2Br_{11}^{5-}$ anions. The K atoms join the anions into 1D chains $\{KBi_2Br_{11}\}_n$ (Figs. 4a, 4b). The bridging Br(6) atom (joining the $BiBr_6$ octahedra at the vertex), as the K atom (joining the $BiBr_6$ octahedra at the face), is arranged in the inversion centers. The aliphatic chain of two independent cations (the crystallographic symmetry of one of them is –1, and the second cation is disordered around the inversion center) has the same (*g-t-t-t-g*) conformation. The N–H···Br hydrogen bonds join the cations and anions into a framework. The shortest Br(4)···Br(4') contact is 3.88 Å.

The structure of compound **VI** is formed by two crystallographically independent $BiBr_6^{3-}$ anions (symmetry 1 and –1), two independent $(2\text{-}NH_2PyC_6)^{2+}$ cations (symmetry 1 and –1), oxonium ions, and molecules of water of crystallization. Eleven positions of the O atoms with site occupancies of 0.26–0.68 are localized. The $BiBr_6^{3-}$ anions, oxonium ions, and H_2O molecules form a 3D framework, the cavities of which contain organic cations. The latter enter the framework by the N–H···Br hydrogen bonds. The aliphatic chain of the cation (symmetry 1) has the (*g-t-g-t-t*) conformation, and the chain of symmetry –1 has the

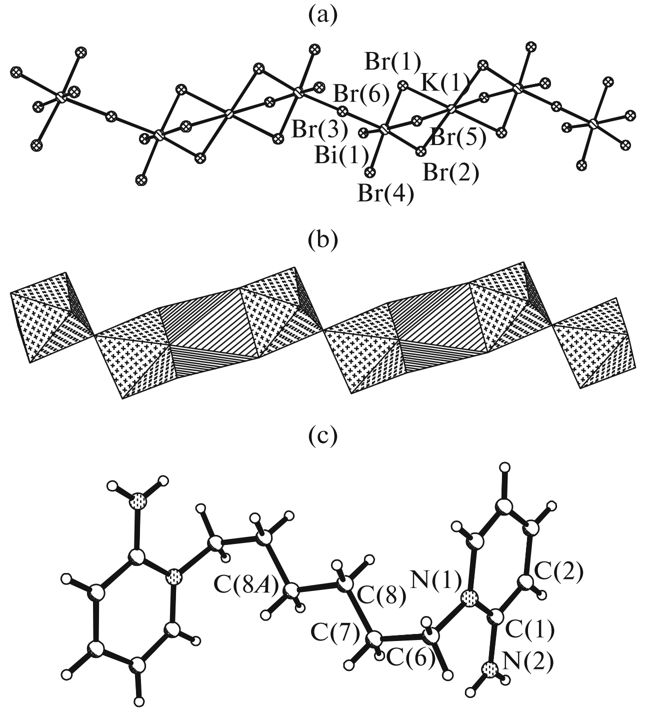


Fig. 4. Structures of the (a, b) polymeric 1D chain $\{\mathrm{KBi_2Br_{11}}\}_n$ and (c) 2-$\mathrm{NH_2PyC_6}$ cation in compound **V**.

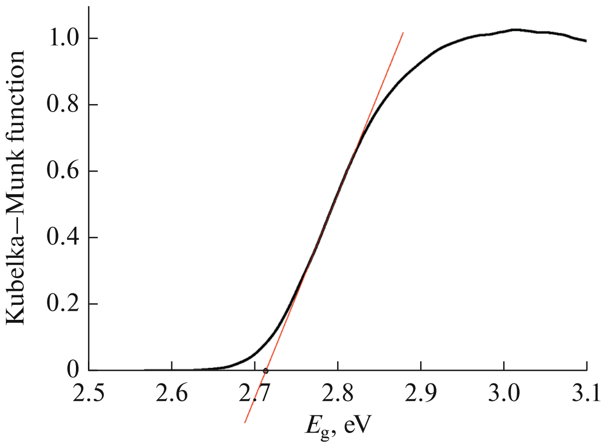


Fig. 5. Diffuse reflectance spectrum of compound **I**.

(*t-t-t-t-t*) conformation. The shortest contacts are Br(1)···Br(7) (3.78 Å) and Br(3)···Br(3') (3.69 Å).

The $\mathrm{BiBr_6^{3-}}$ anion in the structure of compound **VII** exists in the general position, and two crystallographically independent cations have the symmetry 1 and –1. The solvate MeCN molecule is disordered about the inversion center. The aliphatic chain of two independent cations has the same (*g-t-t-t-g*) conformation. The N–H···Br hydrogen bonds join the cations and anions into a 3D framework. The shortest contacts are Br(1)···Br(4) (3.63 Å) and Br(2)···Br(3) (3.74 Å).

Three of seven synthesized compounds (Figs. 1–3) contain polynuclear zigzag 1D chains $(\mathrm{BiBr_5})_n$. According to the proposed [11] classification, these chains are of type A. The Bi(1)–Bi(*1A*)–Bi(*1B*)–Bi(1*C*) torsion angle for this type of compounds is the same and equal to 180°. The characteristics of the chains (distances between two adjacent bismuth atoms in the Bi(1)–Bi(1*A*) chain, increment of the Bi(1)–Bi(1*B*) chain, angles Bi(1)Bi(1*A*)Bi(1*B*) and Bi(1)BrBi(1*A*)) are presented in Table 3. Some more compounds in which the chains are attributed to the same type were described in the literature. The parameters of these compounds are also given in Table 3 and show that all zigzag chains $(\mathrm{BiBr_5})_n$ are of different geometry. The Bi(1)Bi(1*A*)Bi(1*B*) angle in the zigzag chain varies from 80.46° to 102.80°. The deviation from the right angle is due, most likely, to steric factors and stereochemical activity of the lone electron pair of bismuth. The distance between the adjacent bismuth atoms ranges from 5.615 to 6.279 Å. The bridging bromine atom is usually localized at different distances from the bismuth atoms. The chain increment *r*(Bi(1)–Bi(1*B*)) in the bromobismuthates discussed is 7.699–9.642 Å. The fractal dimensionality of the chain log(*r*(Bi(1)–Bi(1*A*)) + *r*(Bi(1*A*)–Bi(1*B*))/log(*r*(Bi(1)–Bi(1*B*)) ranges from 1.109 to 1.214.

All compounds with the zigzag $(\mathrm{BiBr_5})_n$ chains are colored. The optical band gap in these semiconductors obtained from the diffuse reflectance spectra (Fig. 5) is 2.72 eV and lower (Table 3). This is substantially lower than the optical band gap in the compounds with isolated bromobismuthate anions (these compounds are nearly colorless, $E_g \geq 2.79$ eV).

A chain of the new type was found in the structure of compound **V**. In this compound, the 1D chain is formed due to the potassium cations linking the $\mathrm{Bi_2Br_{11}^{5-}}$ anions (Fig. 4). The Bi(1)–Bi(1*A*)–Bi(1*B*)–Bi(1*C*) torsion angle for compound **V**, as for the chains of type A, is 180°. The Bi(1)–Bi(1*A*)–Bi(1*B*) angle is 133.43°. The *r*(Bi(1)–Bi(1*A*)) distance in the $\mathrm{Bi_2Br_{11}^{5-}}$ anion is 6.043 Å. The *r*(Bi(1*A*)–Bi(1*B*)) distance through the potassium cation is 8.184 Å. The value of E_g for compound **V** (2.71 eV) is close to the values for bromobismuthates with the zigzag chains $(\mathrm{BiBr_5})_n$.

No formation of true chains was observed in the structures of compounds **IV**, **VI**, and **VII**. However, pseudo-1D chains of $\mathrm{BiBr_6^{3-}}$ anions can be observed in their 3D frameworks. Two crystallographically independent types of anions were detected in compounds **IV** and **VI**: one type is isolated and another type participates in the formation of the pseudo-1D chain. In compound **IV**, the structure of the anion of the first type is close to the octahedral one ($(\mathrm{Bi{-}Br})_{\max} - (\mathrm{Bi{-}Br})_{\min} = 0.024$ Å), and the structure of the

Table 3. Selected geometric characteristics of the $(BiBr_5)_n$ chains of type A and the spectral characteristics of the compounds containing these chains

Refcode	Bi(1)Bi(1*A*)Bi(1*B*), deg	*r*(Bi(1)–Bi(1*A*)), Å	*r*(Bi(1*A*)–Bi(1*B*)), Å	Bi(1)BrBi(1*A*), deg	E_g, eV
III	102.80	6.169	9.642	161.55, 174.11	Yellow
II	102.24	6.263, 6.099*	9.624	180**	2.70
FEBLOP [12]	94.82	6.279	9.246	171.51	Yellow
PIPRBI [13]	91.87	6.144	8.830	177.59	
I	91.52	6.139	8.796	162.82	2.72
KERGAR [14]	89.98	6.025	8.519	180**	Yellow
ALITAS [15]	87.05	5.898	8.123	159.48**	Brown
OZEMAJ [16]	86.57	5.615	7.699	145.33	2.59
WUJPAU [17]	86.43	5.811	7.958	153.99	2.71
NANNIB [18]	83.53	5.974	7.958	162.00	Yellow
QALVAD [19]	80.46	5.995	7.744	169.15	Red-orange***

* *r*(Bi(1*A*)–Bi(1*B*)).

** The bromine atom is localized at equal distances from the bismuth atoms.

*** The color of the compound is caused by the presence of bromine in the oxidized state.

second type anion is strongly deformed ($(Bi–Br)_{max}$ – $(Bi–Br)_{min}$ = 0.271 Å). For compound **VI**, these values are similarly 0.033 and 0.210 Å, respectively. Only one type of $BiBr_6^{3-}$ anions was observed in compound **VII**. The pseudochain $(BiBr_6)_n$ of the deformed anions ($(Bi–Br)_{max}$ – $(Bi–Br)_{min}$ = 0.205 Å) is formed involving short contacts Br···Br. The value of E_g for compound **VI** (2.90 eV) allows one to assert that the formation of 3D frameworks and pseudochains, unlike true chains, exerts almost no effect on the electronic structures of the compounds.

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