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Synthesis, Thermal Stability, Crystal Structure and Optical Properties of 1,1'-(1,n-Alkanediyl)bis(4-methylpyridinium) Bromobismuthates

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Abstract

Four hybrid 1,1'-(1,n-alkanediyl)bis(4-methylpyridinium) bromobismuthates, namely $(PiC_2)_2Bi_2Br_{10}$ (1), $PiC_4(H_5O_2)BiBr_6\cdot 2H_2O$ (2), $(PiC_5)_2Bi_2Br_{10}$ (3) and $(PiC_6)_2(H_5O_2)Bi_2Br_{11}$ (4), were prepared by a facile solution method. The crystal structures of 1 and 3 contain zero-dimensional Bi_2Br_{10} anion units. A 2-D network structure consisting of $\{H_5O_2\}[BiBr_6]\cdot 2H_2O$ interconnected by hydrogen bonds was found in 2 and a 1-D network structure consisting of $\{H_5O_2\}[Bi_2Br_{11}]$ was observed in 4.

Keywords: Bismuth complexes, optical band gap, crystal structure, thermal stability

Introduction

In recent years, the chemistry of organic-inorganic hybrid halobismuthates has attracted growing attention in advanced materials studies [1]. This interest was inspired by promising physical properties characteristic for this class of compounds, for example, semiconductivity, photochromism, luminescence, etc. Typically, the crystal structures of hybrid halobismuthates are build up by isolated, corner-sharing or edge-sharing BiX_6 octahedra, forming naturally isolated ion units (0-D, eg. $BiBr_6$ [2], Bi_2Br_{11} [3], Bi_2Br_{10} [4,5], Bi_2Br_9 [6,7]), infinite chains (1-D, eg. ($BiBr_5$)_n [8] or ($BiBr_4$)_n [9]) or two dimensional networks (2-D). The inclusion of hydroxonium ions into a structure is more likely to occur when hybrid halobismuthates are isolated from an acid medium [10]. However, not all organic cations are stable in such media. In particular, the recrystallization of 1,1'-(1,n-alkanediyl)bis(4-cyanopyridinium) halobismuthates from acidic solutions can be complicated by the hydrolysis of the cationic nitrile groups [11]. In this study we have focused on 1,1'-(1,n-alkanediyl)bis(4-methylpyridinium) bromobismuthates, for which the cation has a structure close to that of 1,1'-(1,n-alkanediyl)bis(4-cyanopyridinium) and no obstacles for the crystallization from acidic solutions are expected.

Results

The molecular structure of the title dications is presented in Scheme 1. The 1,1'-(1,n-alkanediyl)bis(4-methylpyridinium) bromides (**PiC_nBr**₂), n = 2, 4-6 were synthesized from 4-methylpyridine and α,ω -dibromalkanes in acetonitrile [12,13].



Scheme 1. The molecular structure of the 1,1'-(1,n-alkanediyl)bis(4-methylpyridinium) cations.

Synthesis of the bis(4-cyano-1-pyridino)propane halobismuthates

The interaction of 1,1'-(1,n-alkanediyl)bis(4-methylpyridinium) cations (n = 2, 4-6) with bromobismuthate anions in concentrated HBr resulted in the formation of yellow solutions. Upon standing in air at room temperature, beige or light yellow crystal solids (1-4) were formed in the solutions (n = 2, 4-6):

$$2\text{PiC}_{2}^{2^{+}} + 2\text{Br}^{-} + 2\text{BiBr}_{4}^{-} = (\text{PiC}_{2})_{2}\text{Bi}_{2}\text{Br}_{10}\downarrow \qquad (Compound 1)$$

$$\text{PiC}_{4}^{2^{+}} + 2\text{Br}^{-} + \text{BiBr}_{4}^{-} + \text{H}_{3}\text{O}^{+} + 3\text{H}_{2}\text{O} = \text{PiC}_{4}(\text{H}_{5}\text{O}_{2})\text{BiBr}_{6} \cdot 2\text{H}_{2}\text{O}\downarrow \qquad (Compound 2)$$

$$2\text{PiC}_{5}^{2^{+}} + 2\text{Br}^{-} + 2\text{BiBr}_{4}^{-} = (\text{PiC}_{5})_{2}\text{Bi}_{2}\text{Br}_{10}\downarrow \qquad (Compound 3)$$

$$2\text{PiC}_{6}^{2^{+}} + 3\text{Br}^{-} + 2\text{BiBr}_{4}^{-} + \text{H}_{3}\text{O}^{+} + \text{H}_{2}\text{O} = (\text{PiC}_{6})_{2}(\text{H}_{5}\text{O}_{2})\text{Bi}_{2}\text{Br}_{11}\downarrow \qquad (Compound 4)$$

X-ray diffraction study.

The structure of **1** is formed from 1,1'-ethane-1,2-diylbis(4-methylpyridinium) cations and centrosymmetric Bi_2Br_{10} anions (Fig. 1). The Bi atom is located in an octahedral environment; the Bi-Br bond lengths are different. The longest bonds were found for the bridging Br(3) atoms, the shortest bonds were observed for Br atoms in trans positions to the bridge. The aliphatic fragment has a gosh-conformation with a N(1)C(6)C(7)N(2) torsion angle equal to -57.6°. The cationic and anionic "chains" (Fig. S1 in ESI) are staggered relative to each other. The short contacts in the cationic chain, N(1)...N(1') 3.383, N(1)...C(1') 3.343, C(10)...C(10') 3.364 Å, can be interpreted as stacking interactions.

Fig. 1. The crystal structure of **1**. Atoms are represented at the 50% probability level. Selected bond lengths and angles are given in Table. S1 in the ESI.

The structure of **2** is formed from dioxonium and 1,1'-butane-1,4-diylbis(4-methylpyridinium) cations, BiBr₆ anions and crystal water molecules (Fig. 2a). The H₅O₂ cations and BiBr₆ anions are situated in inversion centers. The C(6)-C(9) aliphatic chain has a gosh-trans-gosh (g-t-g) conformation with torsion angles -62.3, 177.7, and 79.1°. Hydrogen bonds (HB) interconnect the dioxonium cations, BiBr₆ anions and crystal water molecules into layers (Fig. 2b, and Fig. S2 in the ESI). Short C...C contacts between the cations exceed 3.6 Å. Short Bi-Br distances are formed by Br atoms (2,4), which are involved in the HBs with the dioxonium ions.

Fig. 2. The crystal structure of **2** (a). Atoms are represented at the 50% probability level. Selected lengths and angles are given in Table. S1, ESI. The 2D network structure of $\{H_5O_2\}[BiBr_6]$ 2H₂O in **2** stabilized by hydrogen bonds (b).

The structure of **3** is similar to that of **1**. This structure is formed by 1,1'-pentane-1,5-diylbis(4methylpyridinium) cations and centosymmetric Bi_2Br_{10} anions (Fig. 3). The Bi atoms have an octahedral environment. The Bi-Br bond lengths are different for different Br atoms. The longest bonds were found for the bridging Br(2) atoms, the shortest bonds were observed for the Br atoms in the trans-position to the bridge. The aliphatic N(1)...N(2) fragment has a g-t-t-g conformation with torsion angles -52.3, -179.6, -166.6, and -64.1°. The cationic and anionic "chains" (Fig. S3 in the ESI) are staggered relative to each other. The shortest contact in the cationic C(2)...C(2') "chain" is 3.439 Å, The shortest contact distance in the anionic Br(6)...Br(6') "chain" is 7.35 Å.

Fig. 3. The crystal structure of **3**. Atoms are represented at the 50% probability level. Selected bond lengths and angles are given in Table. S1 ESI[‡].

All the structure units in **4**, namely the two crystallographically independent 1,1'-hexane-1,6diylbis(4-methylpyridinium) cations, dioxonium cation and Bi_2Br_{11} anion, are located at inversion centers (Fig. 4a). The difference in the Bi-Br bond lengths in the structure of **4** is caused not only by the dimeric structure of the anion, but also by partial stereochemical activity of the lone electron pairs of Bi atoms. Three Bi-Br bonds with Br atoms of one octahedral face (Br(1), Br(3), Br(5)) are more than 0.2 Å shorter than the same bonds with the Br atoms of the opposite face (Br(2), Br(4), Br(6)).

The conformations of the aliphatic chains of two independent cations are the same, namely g-t-t-t-g (the torsion angles are 65.0, 179.4, 180.0, 179.4, 65.0 and 65.1, -178.2, 180.0, -178.2, 65.0°). The dioxonium cations unite the anions into 1D chains parallel to the c axis (Fig. 4b). In the structure of **4**, one can identify separate layers formed by organic cations and $\{H_5O_2\}[Bi_2Br_{11}]$ (Fig. S4 in the ESI).

Fig.4. The crystal structure of **4**. Atoms are represented at the 50% probability level. Selected bond lengths and angles are given in Table. S1, ESI. 1D network structure of the $\{H_5O_2\}[Bi_2Br_{11}]$ containing chain in **4** (b).

Thermal stability

According to the DSG-TGA results, decahalodibismuthates 1 and 3 are stable up to $230 \,^{\circ}$ C (Fig. S5 and Fig. S7 in the ESI[†]). For compounds 2 and 4 the first stage of mass loss occurs at 70-160 $\,^{\circ}$ C (Fig. 5, Fig. S6 and Fig. S8 in the ESI[†]) and this corresponds to the loss of one HBr molecule and 4 or 2 water molecules per formula unit:

 $2\text{PiC}_{4}(\text{H}_{5}\text{O}_{2})\text{BiBr}_{6} \cdot 2\text{H}_{2}\text{O} = (\text{PiC}_{4})_{2}\text{Bi}_{2}\text{Br}_{10} + 8\text{H}_{2}\text{O} + 2\text{HBr}$ $(\text{PiC}_{6})_{2}\text{H}_{5}\text{O}_{2}\text{Bi}_{2}\text{Br}_{11} = (\text{PiC}_{6})_{2}\text{Bi}_{2}\text{Br}_{10} + 2\text{H}_{2}\text{O} + \text{HBr}$

DSG-TGA: exp. 15.17% for **2** (Fig. S5, ESI), calc. 15.24% for $PiC_4(H_5O_2)BiBr_6 \cdot 2H_2O$, exp. 6.30% for **4** (Fig. S7, ESI), calc. 6.27% for $(PiC_6)_2H_5O_2Bi_2Br_{11}$.

Fig. 5. TGA curve of 2.

After the loss of solvent molecules, the formed 1,1'-(1,n-alkanediyl)bis(4-methylpyridinium) decabromodibismuthates are stable up to 190 °C. Further heating of samples **2-4** results in their melting: $T = 242\pm1$ °C (**2**), 243 ± 1 °C (**3**), 194 ± 1 °C (**4**), $\Delta H= 5.96$ cal/g (**2**), 5.60 cal/g (**4**). The decomposition of the compounds starts at temperatures above 270 ± 5 °C (**1**), 260 ± 5 °C (**2**), 260 ± 5 °C (**3**) and 250 ± 5 °C (**4**) (Fig. S5-S8 in the ESI†).

Optical properties

Corre

The diffuse reflectance spectra (DRS) of **1**, **2** and **4** are shown in Fig. S9 in the ESI[†] as the Kubelka-Munk function vs light energy. The Kubelka-Munk equation is expressed as follows [14]:

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

where R_d is the absolute reflectance of the sample layer. The optical band gap energies (E_g) were estimated from extrapolation of the linear parts of the corresponding curves to $F(R_d) = 0$. The optical band gap values are 2.86 eV (1), 2.92 eV (2), 2.91 eV (3) and 2.77 eV (4). These values are typical for compounds containing bromobismuthate anions with a 0-D structure [2-4,7].

ACCEPTED MANUSCRIPT Table 1. Crystal data and structure refinement for 1-4.

Identification code	1	2	3	4	
Empirical formula	$C_{28}H_{36}Bi_2Br_{10}N_4$	C ₁₆ H ₃₁ BiBr ₆ N ₂ O ₄	$C_{34}H_{48}Bi_2Br_{10}N_4$	$C_{36}H_{57}Bi_{2}Br_{11}N_{4}O_{2}$	
Formula weight	1645.67	1003.87	1729.82	1874.82	
Temperature, K	120(2)	120(2)	150(2)	120(2)	
Wavelength, Å	0.71073	0.71073	0.71073	0.71073	
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic	
Space group	$P2_1/n$	P-1	$P2_{1}/n$	P-1	
a, Å	11.9860(6)	9.8287(7)	12.5224(5)	10.4373(5)	
b, Å	11.5401(6)	10.1037(7)	11.8981(4)	10.6116(5)	
c, Å	14.8312(7)	15.1922(12)	16.3877(6)	14.3397(6)	
α , °	90	85.297(2)	90	107.1050(10)	
β, °	92.117(2)	71.244(2)	90.3920(10)	95.5130(10)	
γ, °	90	81.141(2)	90	114.9560(10)	
Volume, Å ³	2050.05(18)	1410.67(18)	2441.59(16)	1331.07(11)	
Z	2	2	2	1	
D (calc), Mg/m^3	2.666	2.363	2.353	2.339	
μ , mm ⁻¹	18.343	14.769	15.408	14.890	
F(000)	1496	932	1592	868	
Crystal size, mm	0.32 x 0.28 x 0.08	0.1 x 0.08 x 0.04	0.36 x 0.24 x 0.18	0.28 x 0.26 x 0.2	
θ range, °	2.146, 29.130	2.041, 26.732	2.361, 31.572	2.279, 27.483	
Index ranges	-16<=h<=16	-12<=h<=12	-18<=h<=18	-13<=h<=13	
-	-15<=k<=15	-12<=k<=11	-17<=k<=17	-13<=k<=13	
	-20<=l<=20	-19<=l<=19	-23<=l<=23	-18<=l<=18	
Reflections collected	25709	15233	35772	15409	
Independent reflections, Rint	5522, 0.0723	5962, 0.0393	8124, 0.0684	6109, 0.0470	
Completeness to $\theta = 25.242^{\circ}$	100.0 %	99.6 %	99.9 %	99.9 %	
Absorption correction	Semi-empirical	Semi-empirical	Semi-empirical	Semi-empirical	
-	from equivalents	from equivalents	from equivalents	from equivalents	
Max., min. transmission	0.7462, 0.2838	0.0752, 0.0375	0.7462, 0.2558	0.5642, 0.2083	
Refinement method	Full-matrix	Full-matrix	Full-matrix	Full-matrix	
	least-squares on F ²	least-squares on F ²	least-squares on F^2	least-squares on F ²	
Data / restraints / parameters	5522 / 0 / 199	5962 / 0 / 265	8124 / 0 / 226	6109 / 0 / 250	
Goodness-of-fit	1.028	1.169	0.971	0.999	
R1, wR2 [I>2sigma(I)]	0.0347, 0.0896	0.0423, 0.1017	0.0328, 0.0711	0.0300, 0.0740	
R1, wR2 (all data)	0.0458, 0.0949	0.0541, 0.1063	0.0535, 0.0784	0.0378, 0.0769	
Largest diff. peak and hole, e $Å^{-3}$	2.270, -1.860	2.336, -1.746	1.925, -1.667	2.530, -2.087	

Conclusions

Two neutral and two acid hybrid 1,1'-(1,n-alkanediyl)bis(4-methylpyridinium) bromobismuthates were prepared by a facile solution method and characterized by X-ray diffraction, DRS and TGA. The later method demonstrated that for acid compounds 2 and 4 the first stage of mass loss occurs at 70-160 °C and corresponds to the loss of HBr and water molecules with the formation of stable hybrid decabromodibismuthates.

Experimental

Materials

1,1'-(1,n-alkanediyl)bis(4-methylpyridinium) bromides. A mixture containing 5 ml of α , ω -dibromalkane (Aldrich, 97%) and 20 ml of 4-picoline(Aldrich, 98%) was slightly heated with stirring on a magnetic stirrer for one day. The obtained precipitate, PiC_nBr₂, was successively washed with acetonitrile (Komponent-Reactive, dry) and ethanol (Komponent-Reactive, 96%), and then dried in air. In the case of 1,5-dibrompentane, the formed product was hygroscopic. Therefore, after washing with dry acetonitrile, it was immediately dissolved in water or concentrated HBr (Fluka, purum p.a. 48%), with the formation of a 2 M solution.

1,1'-(1,n-alkanediyl)bis(4-methylpyridinium) bromobismuthates. A 3 ml solution of 2 M PiC_nBr_2 in concentrated HBr was added to 15 ml of 0.1 M $BiBr_3$ (Lanhit, ultra dry, 99.999%) solution in 15 ml of concentrated HBr. Crystalline substances precipitated from the light yellow solutions in 1-2 days. The solids of 1-4 were separated from solution by decantation, successively washed three times with dry acetonitrile and ethanol, and then dried in air.

Analytical methods

The reflectance spectra were measured with a Cary 5000 spectrophotometer in the frequency range 10000-50000 cm⁻¹ at room temperature.

The thermal behavior of the samples was studied by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) using an SDT Q600 V8.3 Build 101 Module DSC-TGA thermal analyzer instrument. The samples were heated at 10°/min from 25 to 300 °C in air atmosphere in an alumina open pan.

Single crystal X-ray diffraction data were collected on a Bruker SMART APEX2 instrument [15] (Table 1). Absorptions were taken into account by a semi-empirical method based on equivalents using SADABS [16]. The structures were determined using a combination of the direct method and Fourier syntheses. The positions of hydrogen atoms in the organic cations were calculated from geometrical considerations. The positions of the H atoms of H₂O molecules

and H_5O_2 cations, (2, and 4) were partly localized from the difference Fourier syntheses and partly calculated from geometric considerations. The structures were refined by the full-matrix anisotropic least squares method. All calculations were carried out using SHELXS-2014, SHELXS-2016, SHELXL-2014 and SHELXL-2016 software [17]. X-ray powder diffraction analysis was carried out on a Bruker D8 ADVANCE X-ray diffractometer (CuK α , Ni-filter, LYNXEYE detector, reflection geometry). Further experimental details for reflectance spectroscopy and TGA-DTA can be found in the Electronic Supplementary Information.

Appendix A. Supplementary data

CCDC 1547684-1547687 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

[†]Electronic supplementary information (ESI) available: CIF files of the structural data for compounds **1-4**, CCDC 1547684-1547687, additional figures, DRS and TGA TGA-DTA curves for **1-4**. For ESI and crystallographic data in CIF or other electronic format see DOI:

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