



# Synthesis, crystal structure and optical properties of 1,1'-(1,n-alkanediyl)bis(3-methylimidazolium) halobismuthates

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## ABSTRACT

Four hybrid 3,3'-(alkane-1,n-di-yl)-bis(1-methyl-1*H*-imidazole-3-ium) halobismuthates were prepared by a facile solution route and characterized by diffuse reflectance spectra and photoluminescence measurements. Crystal structure of 3,3'-(buthane-1,4-di-yl)-bis(1-methyl-1*H*-imidazole-3-ium) bromobismuthate (**1**) contains zero-dimensional Bi<sub>2</sub>Br<sub>10</sub> anions. Crystal structure of 3,3'-(pentane-1,5-di-yl)-bis(1-methyl-1*H*-imidazole-3-ium) iodobismuthate (**4**) contains zero-dimensional Bi<sub>2</sub>I<sub>9</sub> anions.

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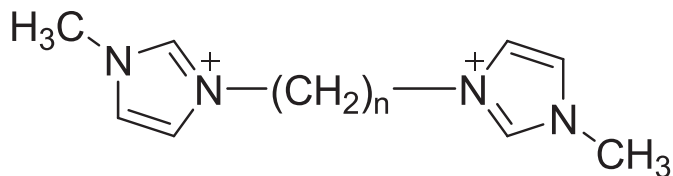
## 1. Introduction

In recent years, the chemistry of organic–inorganic hybrid halobismuthates has attracted growing attention in the advanced materials studies. This interest is inspired by numerous promising physical (and especially optical) properties, specific to the members of this class of compounds, for example, semiconductivity, photochromism, luminescence, etc. Hybrid haloplumbates with perovskite structure [1,2] stand among the most promising photoactive materials. Solar cells based on these materials demonstrate high efficiency conversion of solar energy (up to 20%). In these latter days, hybrid iodobismuthates [3–8] are considered as a possible replacement of hybrid iodoplumbates as a light-harvesting material for solid state solar cells. The efficiency of bismuth-containing elements does not exceed 1–1.5%. However, they have several advantages. Bismuth-containing hybrid compounds are less toxic than lead-containing compounds, besides, they are more stable against moisture and can be obtained from aqueous solutions.

Recently, we have turned to the study of the properties of 1,1'-(1,n-alkanediyl)bis(4-cyanopyridinium) halobismuthates. We have found [9] that PyC<sub>3</sub>BiBr<sub>5</sub>H<sub>2</sub>O (PyC<sub>3</sub><sup>2+</sup> – 1,1'-(1,n-alkanediyl)bis(4-cyanopyridinium cation) obtained from an aqueous solution has 1-D BiBr<sub>5</sub> anion in its structure and the value of optical band gap of E<sub>g</sub> = 2.24 eV. Replacement of bromine by iodine in this compound leads to a product with E<sub>g</sub> = 1.70 eV. An even lower value of E<sub>g</sub> = 1.59 eV had been reported for 1,1'-(1,5-pentanediy)bis(4-cyanopyridinium) iodobismuthate [10]. However, we have not succeeded in crystallizing the obtained 1,1'-(1,n-alkanediyl)bis(4-cyanopyridinium) iodobismuthates. The main reason for this seems to be the hydrolysis of nitrile groups of the cation, which prevents recrystallization of these compounds from acidic or hot aqueous solutions. Therefore, we have turned to study of 3,3'-(alkane-1,n-di-yl)-bis(1-methyl-1*H*-imidazole-3-ium), for which apparently no obstacles for the crystallization of the reaction products from acidic solutions can be expected. The molecular structure of the title dications is presented in Scheme 1. The aim of our study is the obtaining and characterization of crystal structure and optical properties of 3,3'-(alkane-1,n-di-yl) bis(1-methyl-1*H*-imidazole-3-ium) halobismuthates.

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**Scheme 1.** The molecular structure of 3,3'-(alkane-1,n-di-yl)-bis(1-methyl-1H-imidazole-3-ium) dications ( $\text{CH}_3\text{ImC}_n^{2+}$ ).

## 2. Experimental

### 2.1. Materials

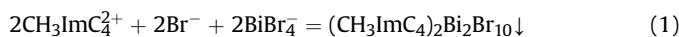
**Synthesis of 3,3'-(alkane-1,n-di-yl)-bis(1-methyl-1H-imidazole-3-ium) bromides.** The starting 1-methylimidazole was prepared according to the procedure described in Ref. [11]. To 1.62 g (0.02 mol) of 1-methyl-1H-imidazole in 25 ml of freshly distilled acetonitrile with vigorous stirring 2.15 g (0.01 mol) of 1,4-dibromobutane or 2.29 g (0.01 mol) of 1,5-dibromopentane were added. The reaction mixture was maintained at the boiling point of the reaction medium for 12 h. The solvent was distilled off on a rotary evaporator, and the residue was taken up in ethyl acetate. The crystallized precipitate was filtered off and dried in air. Purification was carried out by reprecipitation from solutions of dry acetonitrile or methanol with ethyl acetate.

**3,3'-(butane-1,4-di-yl)-bis(1-methyl-1H-imidazole-3-ium) dibromide monohydrate ( $\text{CH}_3\text{ImC}_4\text{Br}_2 \cdot \text{H}_2\text{O}$ ).** Yield 3.5 g (87.9%). M.p. 134 °C (from acetonitrile). Found: C, 36.6; H, 5.84; N, 14.1.  $\text{C}_{12}\text{H}_{20}\text{N}_4\text{Br}_2 \cdot \text{H}_2\text{O}$ . Calculated, %: C 36.2, H 5.6, N 14.1.  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm, J/Hz, Fig. S9 in ESI): 9.57 (s, 2H, by 1H at C (2) in imidazoliums); 7.91 (t, 2H, by 1H at C (4) in imidazoliums,  $J = 1.74$ ); 7.75 (t, 2H, by 1H at C (5) in imidazoliums,  $J = 1.72$ ); 4.36 (t, 4H,  $\text{N}-\text{CH}_2(\text{CH}_2)_2\text{CH}_2-\text{N}$ ,  $J = 6.28$ ); 3.94 (s, 6H, 2  $\text{CH}_3$ ); 1.89 (m, 4H,  $\text{N}-\text{CH}_2(\text{CH}_2)_2\text{CH}_2-\text{N}$ ).

**3,3'-(pentane-1,5-di-yl)-bis(1-methyl-1H-imidazole-3-ium) dibromide ( $\text{CH}_3\text{ImC}_5\text{Br}_2$ ).** Yield 3.5 g (87.9%). M.p. 136–137 °C (from methanol). Found: C, 39.6; H, 5.5; N, 14.2.  $\text{C}_{13}\text{H}_{22}\text{N}_4\text{Br}_2$ . Calculated: C, 39.6; H, 5.6; N, 14.2.  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm, J/Hz, Fig. S10 in ESI): 9.21 (s, 2H, by 1H at C (2) in imidazoliums); 7.81 (t, 2H, by 1H at C (4) in imidazoliums,  $J = 1.73$ ); 7.73 (t, 2H, by 1H at C (5) in imidazoliums,  $J = 1.72$ ); 4.18 (t, 4H,  $\text{N}-\text{CH}_2(\text{CH}_2)_3\text{CH}_2-\text{N}$ ,  $J = 7.19$ ); 3.86 (s, 6H, 2  $\text{CH}_3$ ); 1.85–1.79 (m, 4H,  $\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{N}$ ); 1.25–1.19 (m, 2H,  $\text{N}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{N}$ ).

**Synthesis of 3,3'-(butane-1,4-di-yl)-bis(1-methyl-1H-imidazole-3-ium) halobismuthates.**

The solution of 0.50 g  $\text{CH}_3\text{ImC}_4\text{Br}_2 \cdot \text{H}_2\text{O}$  in concentrated HBr was added to 15 ml of 0.1 M  $\text{BiBr}_3$  (Lanhit ultra dry 99.999%) solution in concentrated HBr. The crystalline substances were being precipitated from light yellow solutions for 1–2 days. The solid ( $\text{CH}_3\text{ImC}_4$ ) $_2\text{Bi}_2\text{Br}_{10}$  (**1**) (0.656 g, 55.1%) was separated from the solution by decantation, washed three times with dry acetonitrile and ethanol, and then dried in air:



The refinements were carried out using TOPAS program [12]. Details of the refinement for **1**, crystalline powder isolated from acid solution (Fig. S4 in ESI), are as follows:  $P2_1/c$ ,  $a = 11.8360$  (2),  $b = 18.8527$  (5),  $c = 10.4385$  (2),  $\beta = 110.036$  (2);  $R_{\text{exp}} = 3.97\%$ ,  $R_{\text{wp}} = 6.51\%$ ,  $R_p = 4.71\%$ ,  $\text{GOF} = 1.64$ . Thus, the structure of single crystals isolated from acid solutions of **1** and crystalline powder **1**

isolated from acid solution is the same. The difference in the parameters can be caused by different temperatures of experiments.

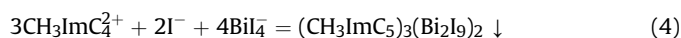
The solution of 0.50 g  $\text{CH}_3\text{ImC}_4\text{Br}_2 \cdot \text{H}_2\text{O}$  and 2.98 g KBr in 6.3 ml of water was added to reaction mixture of 5.95 g KBr, 1.19 g  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and 18.8 ml of water. The solution was filtered under vacuum immediately after crystallization of product. The filtered milky-white precipitate **1a** was washed with water and ethanol, and then dried at room temperature (1.07 g, 89.9%). The refinements were carried out using TOPAS program [12]. Details of the refinement for **1a**, crystalline powder isolated from aqueous solution (Fig. S5 in ESI), are as follows:  $P2_1/c$ ,  $a = 11.8371$  (9),  $b = 18.860$  (2),  $c = 10.4148$  (7),  $\beta = 109.894$  (5);  $R_{\text{exp}} = 3.46\%$ ,  $R_{\text{wp}} = 10.03\%$ ,  $R_p = 6.40\%$ ,  $\text{GOF} = 2.89$ . We found 3 addition reflex in diffractogram ( $d = 2.332$ , 3.216 and 3.808). Thus, the structure of single crystals, isolated from acid solutions of **1** and crystalline powder **1a** isolated from aqueous reaction mixture is the same, but **1a** contains some impurities.

The solution of 0.50 g  $\text{CH}_3\text{ImC}_4\text{Br}_2 \cdot \text{H}_2\text{O}$  and 4.15 g KI in 6.3 ml of water was added to reaction mixture of 8.3 g KI, 1.19 g  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in 18.8 ml of water. Formed orange-red non-crystalline precipitate **2** was filtered, washed with water and ethanol, and then dried at room temperature. (1.05 g).

**Synthesis of 3,3'-(pentane-1,5-di-yl)-bis(1-methyl-1H-imidazole-3-ium) halobismuthates.**

The solution of 0.50 g  $\text{CH}_3\text{ImC}_5\text{Br}_2$  and 2.98 g KBr in 6.3 ml of water was added to reaction mixture of 5.95 g KBr, 1.19 g  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and 18.8 ml of water. The solution was filtered under vacuum immediately after precipitation. The filtered milky-white noncrystalline precipitate **3** was washed with water and ethanol, and then dried at room temperature (0.834 g).

The solution of 0.50 g  $\text{CH}_3\text{ImC}_5\text{Br}_2$  in concentrated HI was added to 15 ml of 0.1 M  $\text{BiI}_3$  (Lanhit, ultra dry 99.998%) solution in 15 ml of concentrated HI. The crystalline substance was being precipitated from red solutions for 1 h. The red solid ( $\text{CH}_3\text{ImC}_5$ ) $_3(\text{Bi}_2\text{I}_9)_2$  (**4**) (0.892 g, 93.2%) was separated from the solution by decantation, washed three times with dry acetonitrile and ethanol, and then dried in air:



The refinements were carried out using TOPAS program [12]. Details of the refinement for **4**, crystalline powder isolated from acid solution (Fig. S6 in ESI), are as follows:  $P2_1/c$ ,  $a = 18.5659$  (7),  $b = 13.3449$  (7),  $c = 17.7328$  (8)  $\beta = 99.953$  (3);  $R_{\text{exp}} = 5.78\%$ ,  $R_{\text{wp}} = 7.74\%$ ,  $R_p = 6.03\%$ ,  $\text{GOF} = 1.34$ . Thus, the structure of single crystals of **4**, isolated from acid solution and crystalline powder of **4** isolated from acid solution is the same. The difference in the parameters can be caused by different temperatures of experiments.

The solution of 0.50 g  $\text{CH}_3\text{ImC}_5\text{Br}_2$  and 4.15 g KI in 6.3 ml of water was added to reaction mixture of 8.3 g KI, 1.19 g  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  in 18.8 ml of water. Formed red noncrystalline precipitate **4a** was filtered, washed with water and ethanol, and then dried at room temperature (0.919 g, 96.0%). The refinements were carried out using TOPAS program [12]. Details of the refinement for **4a**, crystalline powder isolated from aqueous solution (Fig. S7 in ESI), are as follows:  $P2_1/c$ ,  $a = 18.5619$  (6),  $b = 13.3318$  (5),  $c = 17.7188$  (6)  $\beta = 99.948$  (2);  $R_{\text{exp}} = 5.08\%$ ,  $R_{\text{wp}} = 5.95\%$ ,  $R_p = 4.65\%$ ,  $\text{GOF} = 1.17$ . Thus, the structure of single crystals of **4** isolated from acid solution and powder of **4a** isolated from aqueous solution is the same. The difference in the parameters can be caused by different temperatures of experiments.

### 2.2. Analytical methods

The  $^1\text{H}$  NMR spectra were recorded using a Bruker DRX-400

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