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Hybrid halobismuthates: a coordinated $BrIBr^-$ anion

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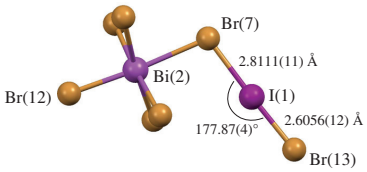
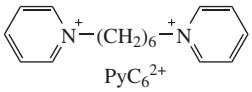
A new organic-inorganic hybrid material containing bromobismuthate anions and bis(1-pyridino)hexane cations was synthesized and characterized. The reaction between $(C_{16}H_{22}N_2)_2Bi_2Br_{10}$ and HBr in the presence of HI vapor afforded $(C_{16}H_{22}N_2)_3(BiBr_6)_2$ as the main product and $(C_{16}H_{22}N_2)_3(BiBr_6)(BiBr_7I)$ as a by-product containing the $BrIBr^-$ anion coordinated by bismuth.



The chemistry of organic-inorganic hybrid halobismuthates is of considerable current interest in advanced materials studies.[1] This interest is inspired by promising physical (especially, optical) properties specific to this class of compounds, for example, semiconductivity, photochromism and luminescence. One of the hallmark features of halobismuthates is a tendency to form polyhalobismuthate complexes in which the halogen-to-bismuth atomic ratio can exceed 6 : 1, *i.e.*, a typical ratio in $[BiX_6]^{3-}$ anions. Recently, it was shown[2] that the reaction between $[BiBr_6]^{3-}$ and Br_2 in the presence of *N*-methylpyridinium cations results in a polymeric structure where $[Bi_2Br_9]^{3-}$ anions are interconnected by Br_2 linkers into a 1-D polymer chain. In general, this feature is typical of bromobismutate complexes: at least four structural types of polybromobismuthates can be obtained by varying the cation. Recently, one of such compounds with the bis(1-pyridino)butane cation was prepared.[2] Here, we studied hybrid halobismuthates with the bis(1-pyridino)hexane cation (PyC_6^{2+}). We increased the size of the cation to stabilize the resulting compound anion in the form of a 1-D polymer chain. This could lead to the formation of products with unusual chemical or optoelectronic properties.



PyC_6^{2+}

Bis(1-pyridino)hexane bromide [1,1′-(1,6-hexanediyl)bispyridinium dibromide], $C_{16}H_{22}N_2Br_2$ (PyC_6Br_2) was synthesized from pyridine and 1,6-dibromohexane in acetonitrile.† The crystals of $(C_{16}H_{22}N_2)_3(BiBr_6)_2$ **1**‡ [Figure 1(*a*)] were isolated in 89% yield from a solution of PyC_6Br_2 and $BiBr_3$ in concentrated HBr.†

$$3\,PyC_6^{2+} + 2\,BiBr_4^- + 4\,Br^- \rightarrow (PyC_6)_3(BiBr_6)_2\downarrow$$

1

The bis(1-pyridino)hexane cations rapidly interact with bromobismuthate anions (as the reaction products of bismuth nitrate with an excess of potassium bromide) in aqueous solution with the formation of lemon-yellow product **2**.

$$2\,PyC_6^{2+} + 2\,Br^- + 2\,BiBr_4^- \rightarrow (PyC_6)_2Bi_2Br_{10}\downarrow$$

2

According to TGA and DTA data (Figure S1, see Online Supplementary Materials), product **2** is anhydrous (it has less

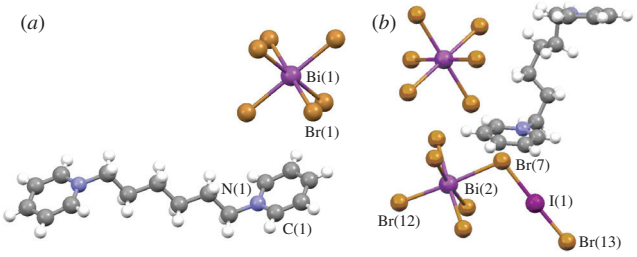


Figure 1 Structure fragment of (*a*) **1** and (*b*) **3**.

† For procedures, see Online Supplementary Materials.

‡ *Crystal data for* **1**. $C_{48}H_{66}Bi_2Br_{12}N_6$, M = 2103.94. Yellow block (0.24×0.22×0.10 mm), monoclinic, space group $P2_1/c$, at 120 K: a = = 12.1975(7), b = 16.4376(9) and c = 15.7622(9) Å, β = 91.116(2)°, V = 3159.7(3) Å^3, Z = 2, d_{calc} = 2.211 g cm^{-3}. Total of 45 185 reflections were collected (2.1° < θ < 31.6°), μ = 13.186 mm^{-1}, 10 136 independent reflections (R_{int} = 0.069) and 6506 with $I > 2\sigma(I)$. Data/restraints/parameters: 10136/108/378. The final refinement parameters were: R_1 = = 0.0360, wR_2 = 0.0666 for reflections with $I > 2\sigma(I)$; R_1 = 0.0819, wR_2 = = 0.0781 for all reflections; largest diff. peak/hole: 2.021/–1.546 eÅ^{-3}. GOF = 0.982.

Crystal data for **3**. $C_{48}H_{66}Bi_2Br_{13}IN_6$, M = 2310.75. Yellow block (0.16×0.08×0.02 mm), monoclinic, space group $P2_1/n$, at 120 K: a = = 17.1056(13), b = 22.0465(16) and c = 17.3915(13) Å, β = 93.587(2)°, V = 6545.8(8) Å^3, Z = 4, d_{calc} = 2.345 g cm^{-3}. Total of 109324 reflections were collected (2.2° < θ < 27.9°), μ = 13.813 mm^{-1}, 15 572 independent reflections (R_{int} = 0.061) and 11 136 with $I > 2\sigma(I)$. Data/restraints/parameters: 15572/0/634. The final refinement parameters were: R_1 = 0.0452, wR_2 = = 0.1235 for reflections with $I > 2\sigma(I)$; R_1 = 0.0749, wR_2 = 0.1385 for all reflections; largest diff. peak/hole: 2.357/–2.452 eÅ^{-3}. GOF = 1.070.

All calculations were fulfilled with the SHELXS and SHELXL programs.[14] Experimental intensities were measured on a Bruker SMART APEX II diffractometer (graphite monochromated MoKα radiation, λ = = 0.71073 Å) using ω-scan mode. The structures were solved by direct methods and refined by full matrix least-squares on F^2 with anisotropic thermal parameters for all non-hydrogen atoms.

CCDC 1530632 and 1530633 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.

than 0.3 absorbed H_2O molecules per formula unit) and stable up to 200 °C. The TGA curve of compound **1** is similar (Figure S2), but unlike **2**, compound **1** melts with decomposition at 249 °C. Our attempts to crystallize **2** from aqueous KBr solutions were unsuccessful. According to EDX microanalysis data (Figure S3), product **2** has the atomic ratio Bi : K : Br = 1 : (1.0±0.1) : (6.1±0.2), and it can be described as the double hexabromobismuthate salt PyC_6KBiBr_6 or a fine mixture of pentabromobismuthate [PyC_6BiBr_5 or $(PyC_6)_2Bi_2Br_{10}$] and KBr. According to XRD data, product **2** contained KBr (Figure S4). Our attempts to wash **2** with water resulted in hydrolysis with the formation of white product. The diffuse reflectance spectra[3] of **1** and **2** are shown in Figure S5. The optical band gap energies (E_g) were estimated from the extrapolation of the linear parts of corresponding curves to $F(R_d) = 0$. The optical band gap of **2** is 2.78 eV. This value is close to E_g = 2.88 eV of bis(4-cyano-1-pyridino)pentane bromobismuthate[4] having the 0-D anion $Bi_2Br_{10}^{4-}$ or to E_g = 2.89 eV of **1** having 0-D anion $BiBr_6^{3-}$ in its structure and substantially higher than E_g of bis(4-cyano-1-pyridino)propane bromobismuthate[5] (2.34 eV) bearing the 1-D polyanion $(BiBr_5)_n^{2n-}$. Therefore, we believe that product **2** is $(PyC_6)_2Bi_2Br_{10}$ contaminated with KBr.

The reaction of **2** with concentrated HBr in the presence of HI vapor and the products of HI oxidation in air produced **1** as the main product and $(C_{16}H_{22}N_2)_3(BiBr_6)(BiBr_7I)$ **3**‡ [Figure 1(*b*)] as a by-product.

$$3\,(PyC_6)_2Bi_2Br_{10} + 4\,Br^- + 2\,I_3^- \rightarrow$$
$$\rightarrow 4\,I^- + 2\,BiBr_4^- + 2\,\underset{\mathbf{3}}{(PyC_6)_3(BiBr_6)(BiBr_7I)}\downarrow$$

The anion $BiBr_7I^{3-}$ in **3** contains the polyhalogen ligand $BrIBr^-$ coordinated to bismuth with a Bi(2)–Br(7)–I(1) angle of 103.15(3)°. The anion $BrIBr^-$ is almost linear. The Br(7)–I(1)–Br(13) angle is 177.87(4)°. In the anion $BrIBr^-$, the iodine atom is shifted to the terminal bromine atom. The Br(7)–I(1) and Br(13)–I(1) distances are 2.8111(11) and 2.6056(12) Å, respectively. Note that the distance Br–I at symmetric non-coordinated $BrIBr^-$ anions varied from 2.679 to 2.928 Å with a median value of 2.707 Å.[6] The Br–I distance between the terminal atoms of the $Br_4I_3^-$ polyhalogen anion reduced to 2.537 Å.[7] Based on the ratio of Bi–Br distances Bi(2)–Br(7) 3.0574(10) Å and Bi(2)–Br(12) 2.7339(10) Å, we can conclude that $BrIBr^-$ is a weak field ligand compared to Br^-. According to the data obtained from the Cambridge Crystallographic Data Centre[8] (CSD version 5.38, November 2016), there are only three compounds incorporating coordinated iodobromo polyhalogen anions: two compounds with the coordinated BrI_2^- anion[9,10] and a host–guest compound with the $Br_{1.16}I_{1.84}^-$ anion.[11]

Thus, bis(1-pyridino)hexane halobismuthate $(C_{16}H_{22}N_2)_3(BiBr_6)(BiBr_7I)$ is a first compound with the coordinated $BrIBr^-$ anion. This and similar compounds can be promising materials for the selective halogenation of organic compounds.[12] Normally, most reported hybrid halobismuthate structures suggest a stabilizing influence of organic ammonium cations through hydrogen bonding.[13] An interesting aspect of the organic cations used in this work is that they do not have hydrogen bonding interactions with the inorganic octahedral units. In this regard, halobismuthate anions in such compounds may be stabilized due to the Bi···X or X···X interactions with the formation of oligomeric (0-D) or polymeric (1-D, 2-D or 3-D) sublattices. A systematic study of hybrid halobismuthates will allow us to determine the regularities of formation of compounds with unusual optoelectronic properties and to receive new light-harvesting materials.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.09.007.

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