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Silver Iodobismuthates: Syntheses, Structures, Properties, and Theoretical Studies of $[Bi_2Ag_2I_{10}{}^{2-}]_n$ and $[Bi_4Ag_2I_{16}{}^{2-}]_n$

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Two novel silver iodobismuthates have been obtained: $(Et_4N)_{2n}$-$[Bi_2Ag_2I_{10}]_n$ (**1**) with one-dimensional infinite chains built from bimetallic tetranuclear units and $(Et_4N)_{2n}[Bi_4Ag_2I_{16}]_n$ (**2**) with a two-dimensional 4^4 grid assembly of the tetranuclear Bi_4I_{16} subunits as nodes and Ag atoms as linkages. Their optical band gaps, 2.05 and 1.93 eV, fit nicely in a size correlation of the Bi/I subunit, which is further supported by the density functional theory studies.

Iodometalates (AM_xI_y, where A = countercation) related to the corresponding metal iodides CuI, AgI, AuI, SnI_2, or PbI_2, etc., have been widely investigated for several decades.[1] Since the first single-crystal characterization of $Cs_3Bi_2I_9$ in 1968,[2] about 60 iodobismuthates have been reported with diverse and unexpected structural and physical features. The majority of these compounds have a general formula $A_n(Bi_xI_y{}^{m-})$ ($m = y - 3x$), in which A covers a large spectrum of cations, inorganic,[2,3] organic,[4] or complex cations.[5] Recently, we found that the introduction of heterometallic bonding into iodoplumbate systems can directly affect the common connection of the PbI_6 units and thus form unusual structural motifs and bring new properties.[1i,j] Although some ternary phases, such as $AgBiI_4$ and Ag_3BiI_6,[3b] have been successfully synthesized and characterized, in iodobismuthates families, the heterometallic anionic analogues are very rare up to now because only one example, $[CuBi_5I_{19}{}^{3-}]_n$, is known.[6] It is therefore a challenge to explore the syntheses of new heterometallic iodobismuthate derivatives and the understanding of their structure–property relationships. Our strategy is to introduce transition-metal (TM) ions into Bi/I systems in consideration of the fact that the incorporation of additional TM–I bonding may modulate the mother Bi/I structure. Such an approach can be expected to provide more flexibility in the self-organization of the building units. Generally, the building blocks of the iodobismuthates consist of BiI_6 octahedra that are either isolated or linked together at vertexes, edges, or faces to form oligomeric clusters or polymeric one-dimensional infinite chains (e.g., $BiI_6{}^{3-}$, $Bi_2I_{10}{}^{4-}$, $Bi_4I_{16}{}^{4-}$, $Bi_6I_{22}{}^{4-}$, $[Bi_4I_{14}{}^{2-}]_n$, etc.).[4,5,7] Among

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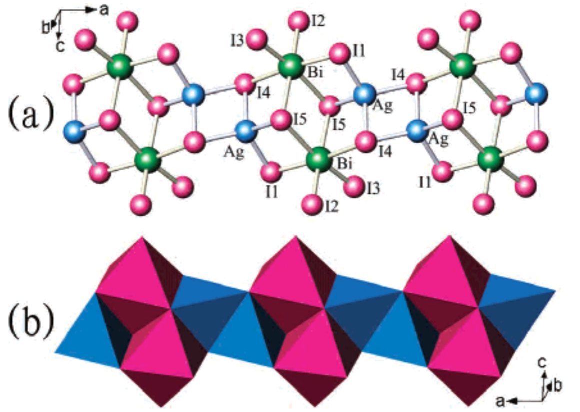

Figure 1. (a) Structure of a chain in **1** along the *a* axis. (b) Polyhedral representation of the chain: BiI_6 octahedra, red; AgI_4 tetrahedra, blue.

discrete clusters such as $Bi_2I_{10}^{4-}$ [4l] and $Bi_4I_{16}^{4-}$,[5d] we consider that their unsaturated terminal μ_t-I and μ_2-I are still coordination-active as far as other Bi atoms or Ag atoms are concerned. Thus, new heterometallic structures are possible via the competition and balance between the two metal−I bonding interactions. Here we report two novel compounds: $(Et_4N)_{2n}[Bi_2Ag_2I_{10}]_n$ (**1**) with a one-dimensional (1D) infinite chain and $(Et_4N)_{2n}[Bi_4Ag_2I_{16}]_n$ (**2**) with a novel two-dimensional (2D) grid array. An interesting optical band gap−size and dimensional relationship of the Bi/I substructures and the corresponding electronic structure studies based on density functional theory (DFT) calculations are also reported.

Both **1** and **2** are air-stable and were synthesized with a mixture of BiI_3, AgI, and Et_4NI (with molar ratios of 1:1:1 and 2:1:1, respectively) by solvothermal reactions (see details in the Supporting Information). A solvothermal condition is the key to obtaining both **1** and **2**. Several other synthetic efforts at room temperature or even under refluxing conditions in various organic solvents (Me_2CO, CH_3CN, *N*,*N*-dimethylformamide, etc.) with different molar ratios only afforded two simple iodides suitable for single-crystal diffraction characterization: $(Et_4N)_3(Bi_2I_9)$[7] and $(Et_4N)_n[AgI_2]_n$.[8]

The structure of **1** (Figure 1), the first anionic silver iodobismuthate (see full crystallographic data in the Supporting Information), features a linear anionic chain constructed from tetranuclear $Bi_2Ag_2I_{10}^{2-}$ units via shared (I4−I4) edges along the *a* axis. The repeat unit can be viewed as a $Bi_2I_{10}^{4-}$ dimer[4l] coordinated by two AgI_4 tetrahedra into a geometry that is similar to the discrete $Bi_4I_{16}^{4-}$ cluster.[5d] Each metal ion in **1** exhibits an ordinary coordination polyhedron, a AgI_4 tetrahedron, and a BiI_6 octahedron, respectively. The former shows angular deviations from the ideal of <6° and Ag−I bonds that are quite uniform, ranging from 2.824(1) to 2.859(2) Å with an average (av) of 2.84 Å. These are comparable to those of other silver iodides, e.g., $Ag_2I_6^{4-}$, in which Ag−I = 2.828(1)−2.918(2) Å and $(Ag-I)_{av}$ = 2.87 Å.[9] While the latter, BiI_6 octahedra, are quite distorted with Bi−I = 2.866(1)−3.420(1) Å and $(Bi-I)_{av}$ = 3.12 Å, these are reasonable and comparable to 2.97−3.22 Å in the $Bi_2I_{10}^{4-}$ dimer[4l] and 2.96−3.36 Å in the $Bi_4I_{16}^{4-}$ tetramer.[5d]

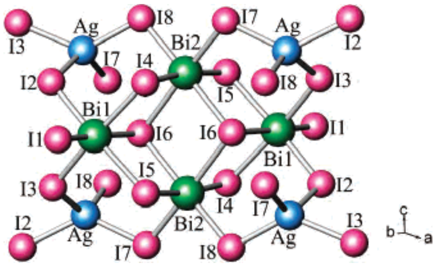

Figure 2. Structure of the anionic repeat unit in **2**.

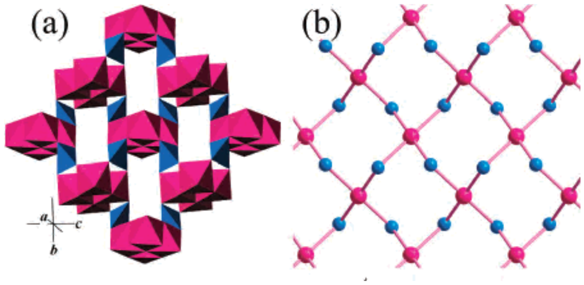

Figure 3. (a) Polyhedral representation of the 4^4 grid of the anion in **2** with BiI_6 octahedra (red) and AgI_4 tetrahedra (blue). (b) Topological scheme of the layer in which the Bi_4I_{16} cluster is treated as a node (red) and the Ag atom as a linkage (blue).

Compound **2** crystallizes in the monoclinic system and exhibits a unique 2D-layered structure motif (Figures 2 and 3). The building unit is the tetranuclear Bi_4I_{16} cluster coordinated by four AgI_4 tetrahedra shown in Figure 2. The AgI_4 tetrahedra are more distorted with a maximum angular deviation of 20° from the ideal, but the average Ag−I bond of 2.85 Å is similar to that in **1**.

Two crystallographically independent Bi atoms are octahedrally coordinated as usual and differ only in that Bi1 has one terminal I with $Bi-I_t$ = 2.903 Å whereas Bi2 does not. Four Bi atoms lie in the *ac* plane with a geometry similar to that in Bi_4I_{16},[5d] and four individual AgI_4 tetrahedra are connected to this center via shared iodides (I2, I8 or I3, I7) with a 2-up and 2-down motif. Remarkably, such a building block $Bi_4Ag_{4/2}I_{16}^{2-}$ further extends in the *bc* plane to form a 4^4 topological network (Figure 3), which features an eight-membered ring (Figure 3b) in which the Bi_4I_{16} cluster and the Ag atom act as a node and a linkage, respectively. Such a novel motif is the first layered heterometallic example in a Bi/I system, and only a few compounds are even remotely related. For example, the hexagonal BiI_3 (ICSD #26083) has six-membered-ring layers in the *ab* plane that are constructed from uniform edge-sharing (BiI_6) octahedra. A ternary distant example, $Rb_3Bi_2I_9$, has corrugated layers formed by (BiI_6) octahedra sharing three corners.[3a] In the hybrid perovskite $(H_2AEQT)Bi_{2/3}I_4$, the anionic layer consists of four corner-sharing (BiI_6) octahedra.[4b]

In summary, both **1** and **2** are packed with Et_4N^+ countercations but with totally different anionic structures.

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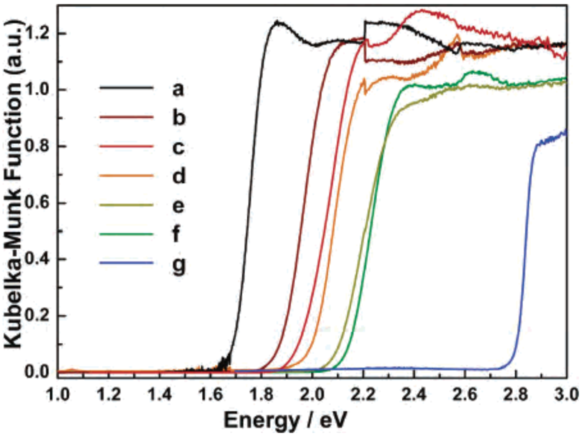

Figure 4. Room-temperature optical absorption spectra for solid samples of (a) BiI_3, (b) **2**, (c) **5**, (d) **1**, (e) **4**, (f) **3**, and (g) β-AgI.

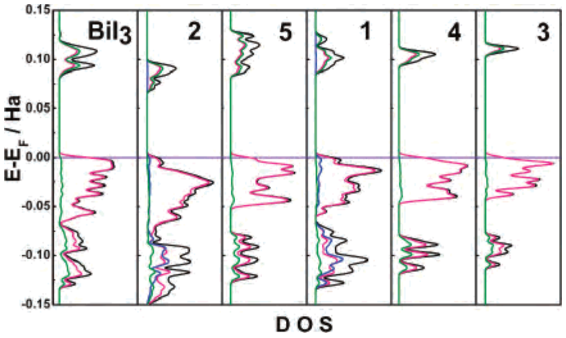

Figure 5. Total and partial densities of states plots of bulk BiI_3 and **1**−**5** with the Fermi level setting as zero. The black line represents the total density of states, while the olivine, pink, and blue lines represent the partial densities of states of Bi, I, and Ag, respectively.

Their distinct anionic constructions might be understood in terms of the geometric limitations. The dimeric $Bi_2I_{10}^{4-}$ block in **1** provides two coordination sites to Ag^+; thus, a two-direction extension is allowed to generate a 1D chain. Dissimilarly, the tetrameric $Bi_4I_{16}^{4-}$ subunit in **2** supplies four sites for Ag^+, which leads to a four-direction growth to form a 2D network.

The optical absorption spectra of **1** and **2** and some related compounds—dimeric $(PhCH_2NEt_3)_3(Bi_2I_9)$ (**3**),[7] tetrameric $(PhCH_2NEt_3)_4(Bi_4I_{16})$ (**4**),[5d] a tetranuclear-unit 1D chain $(n\text{-}Bu_4N)_{2n}[Bi_4I_{14}]_n$ (**5**)[10]—and the binary iodides BiI_3 and β-AgI have been measured for their powdered crystals. All measured spectra are plotted according to the Kubelka−Munk function[11] in Figure 4. The optical band gaps (E_g) for **1**−**5** are found to be located between those of β-AgI (2.81 eV)[12] and of BiI_3 (1.73 eV)[5c] and decrease according to the following trend: **3** (2.19 eV), **4** (2.16 eV), **1** (2.05 eV), **5** (2.02 eV), and **2** (1.93 eV) (SFig. 3 in the Supporting Information). Such a reduction apparently follows an increase in the dimensions of the anion structure.

The ab initio calculations reveal that there are almost no contributions of Ag to the frontier orbitals. The total density of states at the top of the valence band (Figure 5) derives nearly entirely from I in all cases, and the partial densities of states of I and Bi together make up the bottom of the conduction band. On the other hand, the partial density of states of Ag hardly contributes in these regions. Accordingly, the bonding of the Ag does not directly change the electronic structures around the frontier orbitals but rather influences it by modulating the Bi/I substructures. Further partial density of states analyses show that the absorption peaks of all six compounds can be assigned as charge-transfer transitions from occupied I 5p nonbonding states to empty Bi 6p and I 5p antibonding states. Their linear optical property studies indicate that the values of the onset of the transition edges (SFig. 4 in the Supporting Information) are decreasing with an increase of the size and dimension of the Bi/I unit, which is consistent with the experimental trend shown in Figure 4.

Thermogravimetric analyses were also performed on polycrystalline samples of **1** and **2** (SFig. 5 in the Supporting Information). The results show no weight loss or transitions up to ∼200 °C. Decompositions are seen upon further heating.

In conclusion, the successful introduction of Ag^+ into the Bi/I system leads to two novel silver iodobismuthates with 1D $[Bi_2Ag_2I_{10}^{2-}]_n$ infinite chains and 2D $[Bi_4Ag_2I_{16}^{2-}]_n$ 4^4 topological grids, respectively. Their optical band gaps display a size-dependent relationship on the Bi/I subunit. DFT calculations reveal a negligible effect of heterometallic Ag atoms therein, and the simulated optical absorption spectra are in agreement with the experimental results. Explorations of the incorporation of some functional metallic ions into the Bi/I system, such as magnetic Mn^{2+}, Co^{2+}, and Ni^{2+} or luminescent Ln^{3+} (Ln = rare earth metal), are ongoing.

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Supporting Information Available: X-ray data in the form of CIF files for **1** and **2**, refinement details and crystal data, the details of synthesis experiments, experimental measurements of optical properties, theoretical calculation details, and other supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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