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Layered Heterometallic Iodoplumbate Containing a Novel $Pb_3Cu_6I_{16}$ Net: Structure and Optical Properties

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A new heterometallic iodoplumbate was synthesized solvothermally. The complex, $[Co(phen)_3]_2[Pb_3Cu_6I_{16}]\cdot C_2H_5OH$, contains a novel $Pb_3Cu_6I_{16}$ net made up of linked Pb_3I_{11} and Cu_6I_{11} clusters. The clusters form a BN-type layer, where the Pb_3I_{11} and Cu_6I_{11} clusters take the place of B and N. The layers, which are separated by $[Co(phen)_3]^{2+}$ cations, contain cavities in which ethanol molecules are located.

Iodoplumbates, including the class of organic/inorganic layered perovskite iodoplumbates, have been investigated for their tunable structural and physical properties, in particular their intriguing optical and transport properties.[1−8] Moreover, because these materials are amenable to solution processing and film casting, there exists great potential and interest in their use in future applications.[9−12] To fine-tune their structures and properties, researchers continue to vary the organic cation layer, which greatly influences the physical properties. Syntheses are typically carried out in concentrated hydroiodic acid solutions, and products are often obtained as single crystals that form during the slow cooling of the solution containing the organic species.[13]

A second class of compounds is based on iodoplumbate anions, an area dominated by the work of Krautscheid and co-workers.[14−16] These anions result from the reaction of PbI_2 in polar organic solvents with organic cations and can form as isolated clusters, infinite chains, two-dimensional sheets, and three-dimensional constructs. A large variety of compositions are known, including $Pb_3I_9^{3-}$, $Pb_3I_{10}^{4-}$, $Pb_3I_{11}^{5-}$, $Pb_5I_{12}^{2-}$, $Pb_7I_{18}^{4-}$, $Pb_{10}I_{28}^{8-}$, $Pb_{15}I_{34}^{4-}$, and $Pb_{18}I_{44}^{8-}$, where different connectivities of the PbI_6 octahedra via corner-, edge-, or face-sharing can lead to different structures for the same overall anion composition. For these materials, the structure and dimensionality of the iodoplumbate is extremely sensitive to the specific reaction conditions and organic counterions used.[4,9,17−19]

Compounds containing metals other than Pb, for example, Sn, Bi, Sb, Ag, and Cu, are known and have been synthesized using a variety of organic counterions, as well as, more recently, transition-metal coordination compounds.[20−26] Among those, the iodocuprates have been extensively investigated, and the work, in particular, of Hartl and co-workers has resulted in the synthesis and characterization of a large number of copper iodide clusters, including $Cu_5I_7^{2-}$, $Cu_6I_{10}^{4-}$,

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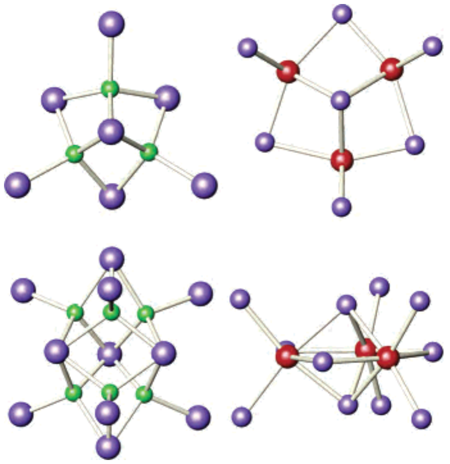

Figure 1. Structures of the Cu_6I_{11} cluster (left, top and bottom) and the Pb_3I_{11} cluster (right, top and bottom) that connect to form the $Pb_3Cu_6I_{16}$ net. Cu is green, Pb is red, and I is purple. The I atoms that link the clusters together are shown facing each other in the lower half of the figure.

$Cu_6I_{11}^{5-}$, $Cu_8I_{13}^{5-}$, and $Cu_{36}I_{56}^{20-}$, while other systems have given rise to extended $Cu_3I_4^-$ and CuI_2^- chains.[27−33]

Because relatively few heterometallic halometallates are known and because of the potential synergistic effect two metals can have on the physical and optical properties of halometallates, we decided to investigate the solvothermal synthesis and characterization of heterometallic Bi−Ag, Bi−Cu, Pb−Ag, and Pb−Cu iodometallates.[26,34−36] Because the cation is known to greatly impact the physical properties, we decided to use d-metal coordination complexes, such as $[Co(phen)_3]^{2+}$, as counterions. This approach has proven to be highly successful, and herein we report on a novel heterometallic iodoplumbate, $[Co(phen)_3]_2[Pb_3Cu_6I_{16}]\cdot C_2H_5OH$ (**1**), containing a complex $Pb_3Cu_6I_{16}$ net made up of linked $[Pb_3I_{11}]^{5-}$ and $[Cu_6I_{11}]^{5-}$ clusters, which is the first example of a two-dimensional Pb−Cu−I iodometallate (Figure 1). Prior to this, the only mixed lead−copper iodides were a $[PbCu_6I_8(PPh_3)_6]$ cluster and $[(Bu_4N)(PbCuI_4)]$ and $PbCu_2I_4\cdot 2MeCN$ chains.[32,36]

The solvothermal reaction of PbI_2, CuI, $Co(NO_3)_2\cdot 6H_2O$, 1,10-phenanthroline, and HI in a 50/50 H_2O/EtOH mixture at 160 °C for 3 days resulted in plentiful crystals. A total of three crystal phases were present: yellow needles (plentiful, $(phenH)(H_2O)[Pb_{3.5}I_8]$), yellow plates (sparse, $[Co(phen)_3][Pb_3I_8](H_2O)$), and red hexagonal block crystals (plentiful, major phase **1**). The structure of **1** was determined by single-crystal X-ray diffraction in space group $P6_3/m$, with $a = 14.7797(3)$ Å and $c = 25.3168(9)$ Å.[37] The structure contains $Pb_3Cu_6I_{16}$ nets, consisting of $[Pb_3I_{11}]^{5-}$ and $[Cu_6I_{11}]^{5-}$ iodometallate clusters that are linked via pairs of bridging iodide ligands into a hexagonal BN-type net. The $[Pb_3I_{11}]^{5-}$ and $[Cu_6I_{11}]^{5-}$ iodometallate clusters are rare in iodometallate chemistry and have never before been found to coexist in the same structure.

The $[Pb_3I_{11}]^{5-}$ cluster,[38] which exhibits the $[Cs_{11}O_3]$ structure,[39] is best described as consisting of three PbI_6 octahedra that share two faces, one with each adjacent octahedra. The two shared faces of each octahedron are cis with respect to one another, leading to the formation of a discrete anionic cluster rather than an extended chain. Three sets of Pb−I bonds are present in the $[Pb_3I_{11}]^{5-}$ anion: six Pb−μ_2-I(3) bonds with an average distance of 3.32 Å, six symmetry-equivalent Pb−μ_3-I(1) bonds of 3.279(1) Å, and six equivalent cluster-bridging Pb−I(2)−Cu bonds of 3.158(1) Å, all of which are comparable in length to bonds of the same type in other iodoplumbate compounds. μ_2-I(3) is disordered over two closely separated positions (see the Supporting Information for details). For comparison, the average Pb−I bond in bulk PbI_2 is 3.23 Å.[36] The PbI_6 octahedra in the $[Pb_3I_{11}]^{5-}$ cluster are distorted, as is typically observed in iodoplumbate clusters, with trans I−Pb−I bond angles ranging from 155 to 168°.

The $[Cu_6I_{11}]^{5-}$ cluster[27] consists of six fairly regular CuI_4 tetrahedra with I−Cu−I bond angles ranging from 107.7 to 113.1°. The six Cu atoms are arranged in a trigonal prism, connected via bridging iodide ligands. The cluster can also be described as consisting of six CuI_4 tetrahedra sharing three edges each, resulting in two apical μ_3-iodides, three equatorial μ_4-iodides, and six terminal iodides (which are shared with a Pb cation in the sheet structure). The six equivalent Cu atoms forming the trigonal prism have Cu−Cu distances of 2.801(1) Å (Cu_3 triangle) and 3.190(1) Å (rectangular face edge). There are three sets of Cu−I bonds present: six equivalent Cu−μ_3-I bonds of 2.674(1) Å, 12 equivalent Cu−μ_4-I bonds of 2.670(1) Å, and six equivalent Cu−I−Pb bonds of 2.591(1) Å. By comparison, the average Cu−I bond in bulk CuI is 2.63 Å.[36]

The $[Pb_3I_{11}]^{5-}$ and $[Cu_6I_{11}]^{5-}$ clusters, which have S_3 site symmetry (idealized symmetry D_{3h}), are connected via pairs of bridging iodides such that each cluster is connected to three clusters of the other type. This generates the anionic $[Pb_3Cu_6I_{16}]^{4-}$ net having the BN-sheet-type structure shown in Figure 2. The six-cluster ring structures are filled with disordered ethanol molecules of solvation.

The $[Co(phen)_3]^{2+}$ cations are situated between the $[Pb_3Cu_6I_{16}]^{4-}$ nets and are located above the apex of the $[Pb_3I_{11}]^{5-}$ clusters and above the three-ethanol-molecule region (Figure S1 in the Supporting Information). No $[Co(phen)_3]^{2+}$ cations are located above the significantly taller $[Cu_6I_{11}]^{5-}$ clusters, which are positioned directly above and

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(37) Diffraction data collection and refinement details for **1** are listed in the Supporting Information. Crystal data for **1**: $C_{74}H_{54}Co_2Cu_6I_{16}N_{12}OPb_3$, fw = 4278.36, hexagonal, $P6_3/m$ (No. 176), $a = 14.7797(3)$ Å, $c = 25.3168(9)$ Å, $V = 4789.3(2)$ Å^3, $T = 150(1)$ K, $Z = 2$, $D_{calc} = 2.967$ g cm^{-3}, μ(Mo Kα) = 12.095 mm^{-1}, R1(F) = 0.0289, wR2(F^2) = 0.0569 for all 4068 data.

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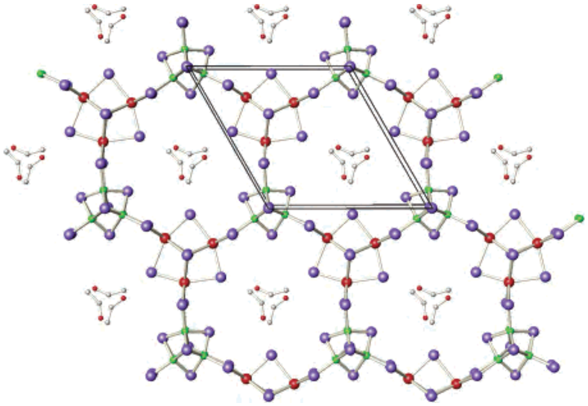

Figure 2. Hexagonal sheet structure of the $Pb_3Cu_6I_{16}$ net made up of linked Pb_3I_{11} and Cu_6I_{11} clusters. Ethanol molecules occupy the spaces between the clusters.

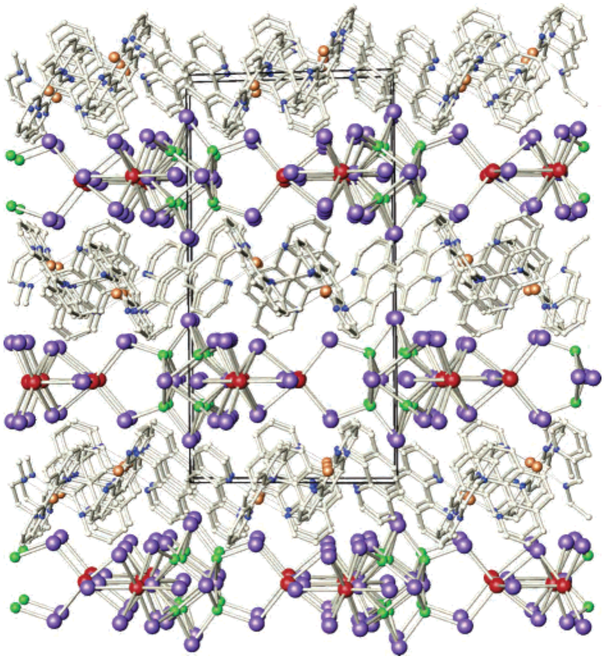

Figure 3. [100] view of the overall structure. The $Pb_3Cu_6I_{16}$ sheets are separated by $[Co(phen)_3]^{2+}$ clusters. Successive sheets are rotated by 60° with respect to each other.

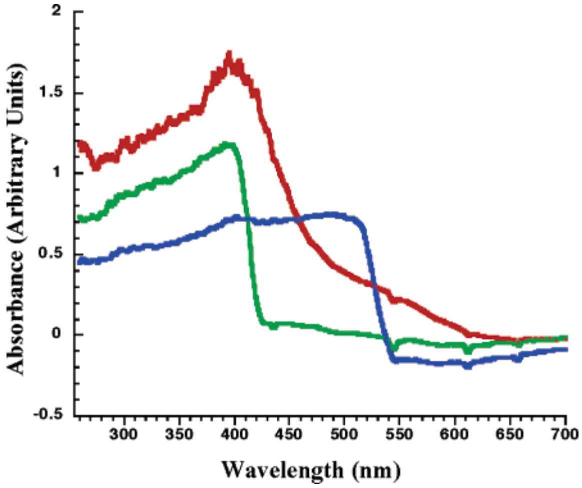

Figure 4. Diffuse-reflectance data for **1** (red), polycrystalline CuI (green), and polycrystalline PbI_2 (blue).

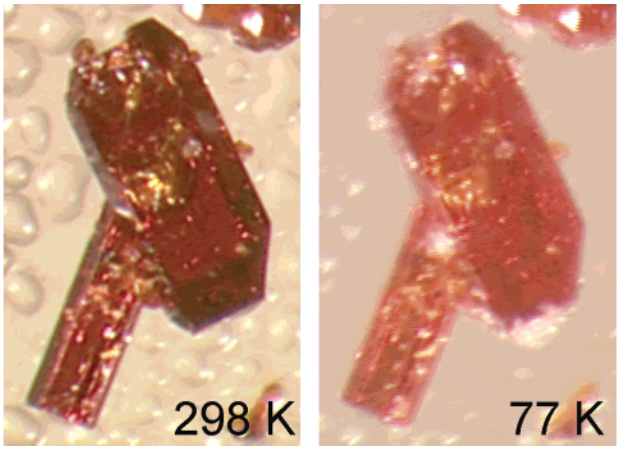

Figure 5. Thermochromism of **1**. The dark-red color changes to bright orange upon cooling to liquid-nitrogen temperature.

below each other in adjacent $[Pb_3Cu_6I_{16}]^{4-}$ layers. Successive $[Pb_3Cu_6I_{16}]^{4-}$ nets are rotated by 60° with respect to each other, forming the extended structure shown in Figure 3.

The diffuse-reflectance data for **1**, shown in Figure 4, indicate that the material is a semiconductor with a poorly defined band edge at 492 nm, corresponding to 2.52 eV. This value is intermediate to that of CuI (2.92 eV) and PbI_2 (2.30 eV).

Interestingly, **1** is a thermochromic material;[40] that is, it changes color as a function of temperature, as can be seen in Figure 5, where images of a crystal at room and liquid-nitrogen temperature are shown. Thermochromic behavior in halometallates is known and thought to be due to shifts in the band edge caused by the lattice contraction during cooling. We have observed similar behavior in iodobismuthates,[41] where, in fact, BiI_3 itself is thermochromic.

In summary, we have synthesized a new heterometallic iodometallate containing Pb and Cu, **1**, that exhibits a novel $Pb_3I_6I_{16}$ net structure.

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Supporting Information Available: Crystallographic data (CIF) and other supporting figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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