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Syntheses, Crystal Structures, and Properties of Heterometallic Iodoplumbates: Bicubane, Ribbon, and Chain Configurations

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Successful introduction of Cu/Ag cations into the Pb/I system has led to the formation of four unprecedented heterometallic iodoplumbates in which the common connection of PbI_6 units has been remarkably altered. Also, interesting long-lived fluorescence properties have been found.

Considerable current interests focus on fundamental as well as more applied studies of iodoplumbates related to their significant excitonic, nonlinear optical, structural, and other physical properties.[1] Lead(II) iodide and its low-dimensional derivatives represent a potential class of functional materials and ideal systems for investigation of the structure−property relationships. Their structural diversity is provided by the flexibility of the Pb^{2+} coordination polyhedron and the nature of iodide anions, which can be modulated by the size and H-bonding properties of the cations. Their anion structures range from isolated anions[2] to infinite chains,[3,4] layered perovskites,[5] and three-dimensional polymeric networks.[1c] Most structures are characterized by PbI_6 octahedra with common faces, edges, or vertexes.

Coordination polymers are attractive targets for crystal design inasmuch as three aspects are controllable: the identity of the metal ion, the linking ligand units, and the counterions.[6] The first two components can have a direct impact on the structure and functionality of a polymer, whereas the physical and structural properties of iodoplumbates can be fine-tuned by organic countercations, especially for the layered perovskite family.[1] The aim of this work is to provide a deeper knowledge of the directly controlling factors regarding the heterometallic bonding nature of iodoplumbate and to explore the formation of new compounds with unusual structural motifs and properties. We here describe the syntheses and crystal structures of four novel heterometallic iodoplumbates: $[PbCu_6I_8](PPh_3)_6]$ (**1**) (PPh_3 = triphenylphosphine), $[PbAg_2(PPh_3)_2I_4]_n{\cdot}[PbI_2(DMF)_2]_n$ (**2**), $[(Bu_4N)(PbCuI_4)]_n$ (**3**), and $[(Bu_4N)(PbAgI_4)]_n$ (**4**), wherein the bond interactions of the transition-metal ions significantly alter the normal combinations of Pb^{2+} octahedra into unexpected structure types, iodoplumbate bicubane, cubane one-dimensional (1D) chain, rigid chain, and ribbon. The optical-gap analyses show that they are all semiconductors; furthermore, **1** exhibits an interesting fluorescence property in the yellow to near-IR range, and **2** shows a yellow emission.

The structure of **1** has been characterized[7] (Figure 1) as the first vertex-sharing bicubane heterometallic iodoplumbate structure type. The structural details of **1** indicate that the large radius difference between Pb^{2+} and Cu^+ ions leads to the distortion of $[PbCu_3I_4]^+$ cubane. Therefore, the larger Ag^+ ion was utilized instead, and the somewhat expected

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(7) Diffraction data collection and refinement details for **1**−**4** are listed in the SI. For **1**, space group $P\bar{1}$, a = 13.3978(14) Å, b = 13.4764(14) Å, and c = 17.5502(18) Å with α = 70.072(4)°, β = 68.740(4)°, and γ = 66.061(3)°. R1 = 0.0293; wR2 = 0.0795 (CCDC 273798). For **2**, $P2_1/c$, a = 8.9561(5) Å, b = 24.4637(18) Å, and c = 25.428(2) Å with β = 99.424(3)°. R1 = 0.0402; wR2 = 0.0885 (CCDC 273799). For **3**, $P2_1/c$, a = 9.690(3) Å, b = 16.869(5) Å, and c = 17.060(5) Å with β = 102.974(4)°. R1 = 0.0260; wR2 = 0.0645 (CCDC 273800). For **4**, $P2_1$, a = 13.5310(11) Å, b = 15.2811(14) Å, and c = 13.5539(11) Å with β = 93.7270(10)°. R1 = 0.0363; wR2 = 0.0828 (CCDC 273801).

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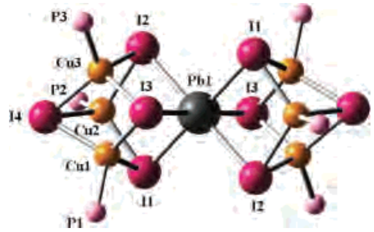

Figure 1. Structural unit in **1**. The C and H atoms of the triphenylphosphorus ligands are omitted for clarity.

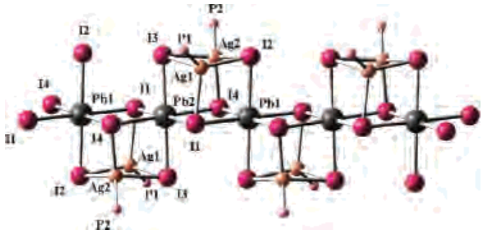

Figure 2. Diagram of the cubic chain $[PbAg_2(PPh_3)_2I_4]_n$ in **2** along the *a* axis. The C and H atoms of the triphenylphosphorus ligands are omitted for clarity.

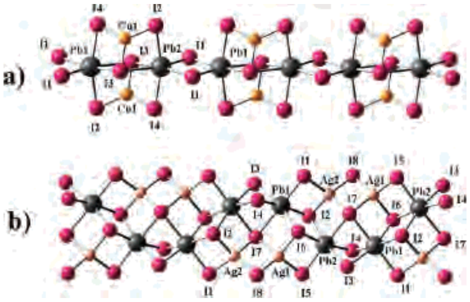

Figure 3. (a) Schematic representation of the rigid anion polymeric chain in **3** along the *a* axis. (b) Section of 1D ribbon in **4** along the *b* axis.

cubane unit with less distortion in a 1D chain, **2**, was found (Figure 2). Considering that the PPh_3 ligand serves as a blocking agent, two more reactions were carried out, purposely omitting any coordinating ligand other than I^-, and these gave the novel heterometallic 1D polymeric $[(PbCuI_4)^-]_n$ chain **3** (Figure 3a) and 1D $[(PbAgI_4)^-]_n$ ribbon **4** (Figure 3b) with $[Bu_4N]^+$ cations. Details about all of these syntheses are listed in the Supporting Information (SI).

The molecular structure of **1** can be described as two $[PbCu_3I_4^+]$ units sharing a vertex to form a bicubane-like cluster, which is unique for an iodoplumbate. This bicube is structurally similar to the neutral Ca_7 subunit in the alkaline-earth metal compound $Li[\{Ca_7(OH)_8I_6(THF)_{12}\}_2(\mu\text{-}I)]\cdot 3THF$.[8] The central Pb1 atom in **1** lies on an inversion center and features an octahedral coordination sphere of six I^- ions. The I_i-Pb-I_i ($i = 1-3$) angles are essentially 180°, and other angular deviations from ideal octahedral symmetry are less than 4.2°. The Pb−I distances are in the range of 3.16−3.22 Å, similar to those found in other iodoplumbates[2,5b] and that in bulk PbI_2 (3.23 Å). Each Cu atom has tetrahedral coordination to one P and three μ_3-I. The $Cu-P_{ave}$ distance is 2.26 Å, as expected. The mean bond length of $Cu-I_{ave}$ is 2.69 Å, which is close to that found in bulk CuI, 2.63 Å. The distortion of the $[PbCu_3I_4]^+$ subunit comes mainly from the large difference between $Pb-I_{ave}$ and $Cu-I_{ave}$ distances (3.20 vs 2.69 Å). The significance of **1** is that it provides a good example of the direct effect of transition-metal ions on the skeletal structure. Therefore, introducing heterometal ions into Pb/I systems opens up more possibilities for new compounds and structures.

Compound **2** has a similar cubane-like subunit $[Pb_2Ag_2I_4]^{2+}$ (Figure 2). The cubic units are vertex-fused into a 1D chain that runs parallel to the *a* axis. The mean $Pb-I_{ave}$ distance is 3.22 Å, similar to that of **1**. The $Ag-P_{ave}$ distance is 2.45 Å, similar to that in the $Ag(PPh_3)NO_3$ salt and naturally longer than the $Cu-P_{ave}$ bond in **1**. The $Ag-I_{ave}$ distance is 2.88 Å. The distortion of the cubane-like subunit is less than that in **1**, as expected, and the angular deviations from the ideal octahedron around Pb1 and Pb2 are less than 2.5°. **2** also has a second linear chain of edge-sharing octahedra about Pb3 (see Figure S2 in the SI).

The anion structure of **3** is shown in Figure 3a. The PbI_6 octahedra are quite distorted. Two neighboring octahedra are joined by two trigonally coordinated Cu^+ ions to form a dimer; the adjacent dimers are connected by a common edge (I1−I1) and extended along the *a* axis as a 1D polymeric chain. Such a motif has a close relationship with $[(PbCu_2I_4)(CH_3CN)_2]$,[9] with the main structural differences coming from different repeat unit $[PbCuI_4^-]$ in **3** vs $[PbCu_2I_4^0]$ and the Cu coordination environment, planar trigonal vs distorted tetrahedral.[9] Because of the Cu−I bonding interaction, Pb1−I4 and Pb1−I2 are bent toward the Cu^+ ions, with the angle being 19° from linear. Cu1 is almost trigonal-planar, deviating from planarity by $\Delta\phi = 0.62°$.[10] The $Cu-I_{ave}$ bond is 2.54 Å, shorter than 2.69 Å in **1** and 2.66 Å in ref 9 and comparable to that in the trigonal-coplanar (CuI_3^{2-}) anion, 2.55 Å.[11]

The anionic motif of **4** is shown in Figure 3b. The Pb−I distances are in the usual range (3.08−3.44 Å). The $Ag-I_{ave}$ length is 2.87 Å, similar to that in **2**. Two octahedra, $Pb(1)\,I_6$ and $Pb(2)I_6$, form an edge-sharing (I2−I6) octahedral dimer that is further joined at a common face (I3−I4−I7) to give a tetramer. These are fused by a tetrahedral AgI_4 dimer via shared edges (I1−I2, I2−I7, I7−I6, and I5−I6) and are further condensed into a heterometallic 1D ribbon running down the *b* axis with a width of 0.8 nm. Such a heterometallic anionic structure is reminiscent of the $[(Pb_2I_6)^{2-}]_n$ chains in $[C_6H_{10}N_2]Pb_2I_6$[12] but differs in that the double chain in **4** is now a heterometallic polymer from replacement of PbI_6 octahedral dimers by AgI_4 tetrahedral dimers. Also, **4** contains face-sharing PbI_6 octahedra in a long−short-stepped Pb1−Pb2 wavey chain motif (Pb1−Pb2 = 4.75 and 4.06 Å alternately). Such a motif has not been previously observed.

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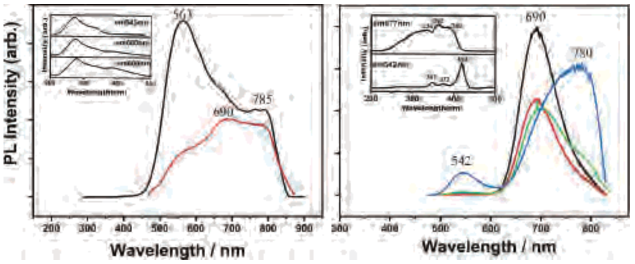

Figure 4. Solid-state emission spectra of **1**. (left) The room-temperature emission spectra are black ($\lambda^{ex} = 275$ nm) and red ($\lambda^{ex} = 397$ nm). The inset shows the excitation spectra of different emission energies. (right) Emission spectra (black and red) at 10 K have $\lambda_{max} = 690$ nm with $\lambda^{ex} = 363$ and 380 nm, respectively; emission (green), $\lambda^{ex} = 408$ nm; blue emission, $\lambda^{ex} = 419$ nm. The inset shows related excitation spectra for emissions at 677 and 542 nm, respectively.

The diffuse-reflectance UV−visible spectral analyses[13] indicate that **1**−**4** have optical band gaps of 2.67, 2.82, 2.54, and 2.77 eV, respectively (see Figure S6 in the SI).

The luminescence properties of all compounds were examined. **3** and **4** are nonemissive at room temperature when excited in the range of 200−1000 nm, whereas both **1** and **2** exhibit long-lived, intense fluorescence. The room-temperature photoluminescence (PL) spectra of **1** show a complicated broad emission band from the yellow to near-IR range with three maxima at 563, 690, and 785 nm (Figure 4, left). Such a broad emission band may indicate a strong electron-vibrational coupling in **1**. To reduce the vibrational influences, the PL spectra at 10 K were also measured (Figure 4, right). The results indicate that the emission band consists of two sets of narrower peaks, depending on the excitation energy, namely, emission centered at 690 nm with excitation wavelength (λ^{ex}) < 380 nm and a pair of peaks at 542 and 780 nm for λ^{ex} > 400 nm. The PL peak at 690 nm has the lifetime $\tau = 25$ μs with $\lambda^{ex} = 363$ nm. When the excitation energy is decreased from 380 to 419 nm, such an emission is weakened, and a 780-nm emission appears first as a shoulder (green line in Figure 4, right) and then as a strong peak, whereas for $\lambda^{ex} = 419$ nm, a luminescence peak at 542 nm and $\tau = 10$ μs is simultaneously exhibited (blue line in Figure 4, right).

The interesting near-IR luminescence emission of **1** ($\lambda_{max} = 780$ nm; $\tau = 17$ μs) has never been observed in any tetranuclear cubic $Cu_4X_4L_4$ complex.[14] The major structural difference is that the Pb heteroatom in **1** is also involved in the construction of the cubic skeleton. With such a consideration, an assignment of the near-IR emission to originate from Pb^{II}-related orbitals is likely. According to a new Pb−Cu heterometallic cluster $PbI_4Cu_2(PPh_3)_4$,[15] wherein the near-IR emission at 732 nm and $\tau = 25$ μs has been assigned to an I(5p)−Pb(6s) to PPh_3−Pb(6p) charge transfer, it is therefore possible to assign the near-IR emission of **1** to that derived from a similar Pb−halide ligand transition.

The higher emission energies of **1** (690 and 542 nm) are very similar to those of $Cu_4X_4L_4$ (L = pyridine, X = I;[14a] L = PPh_3, X = diynyl[14c]). The small dependence of the 690-nm emission energy on the nature of the ligands and bridging X atoms may be suggestive of an emission origin bearing a high percentage of metal-centered character modified by metal−metal interactions over the cubic cluster core. In our case, the Pb heteroatom and the relatively higher delocalized Pb−Cu and Cu−Cu interactions over the bicubic cluster should have significant influences.

The 542-nm emission depends on the excitation energy, and such an emission is not found in the $PbI_4Cu_2(PPh_3)_4$[15] cluster, where the Pb ion has a different C_{2v} four-coordinate sphere. Considering these two facts, we favor the assignment of this 542-nm emission to an exciton emission originating from an octahedrally coordinated Pb^{2+} ion. A similar assignment was suggested for PbI_2[16] and layered PbI_2-based perovskite compounds.[1c,17]

Compound **2** has a yellow emission at 566 nm with $\tau = 12$ μs, as shown in Figure S7 in the SI, which is around 100 nm red-shifted compared to that of cubic $Ag_4I_4(PPh_3)_4$.[18] This emission might be assigned to a transition in the cubic moiety $[Ag_2Pb_2I_4^{2+}]$ at lower energy than that in the Ag_4I_4 cube.[18] This simple correlation may suggest that the delocalization over the Ag and Pb atoms is larger, which is proven by their structural characteristics (1D cubic chain vs discrete cubic cluster). How the heterometallic interactions between Ag and Pb alter the ground and excited electronic states is now under investigation.

In conclusion, we have reported here four unprecedented iodoplumbates that bring heterometallic bonding interactions into the common PbI_6 octahedral unit. This is important in that the bicubane **1**, cubic chain **2**, and ribbon **4** motifs have never been seen before. **1**−**4** are semiconductors, and **1** and **2** exhibit interesting fluorescence properties. We are currently investigating their special optical properties in more detail as well as the possibility of synthesizing layered heterometallic iodoplumbates via other various metal linkers.

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

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