

Solvothermal Synthesis, Crystal Structure, and Characterization of a Heterometallic Iodoplumbate

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Abstract: The design and synthesis of heterometallic iodoplumbates have attracted much interest due to the diverse structures and significant physical properties. A Pb/Cu^I/I heterometallic iodoplumbate, [PbCu₂I₄(bipy)]_n (**1**) (bipy = 2,2'-bipyridine), has been synthesized by solvothermal reaction of PbI₂, Cu(NO₃)₂, bipy, and HI, and characterized by single-crystal X-ray diffraction, powder X-ray diffraction, and thermogravimetric analysis. This compound exhibits one-dimensional neutral structure, which is built upon the linkages of Pb/I chains, Cu/I chains, and Cu(bipy) units. The yellow compound has an optical bandgap of 2.32 eV and shows fluorescent emission at 610 nm which is assigned to iodide-to-copper charge transfer.

Keywords: Heterometallic iodoplumbate; solvothermal synthesis; luminescence property; crystal structure

1. Introduction

Inorganic-organic hybrid iodoplumbates have greatly attracted scientists' attention in recent years due to their diverse structures and significant excitonic, nonlinear optical and other physical properties [1–7]. Their abundant structural diversity, including zero-dimensional clusters, infinite chains, layered perovskites, and three-dimensional polymeric networks, results from the flexibility of the Pb²⁺ coordination geometry and the characteristics of iodide anions [2,7–16]. The structures of iodoplumbates are usually made up of [PbI₆] octahedra by sharing vertexes, edges, or faces.

The introduction of heterometal (HM) ions into the structures of iodoplumbates is likely to produce novel structures as well as new physical properties, such as luminescence and magnetism. The general approach to synthesize heterometallic iodoplumbates is the employment of metal complex cations as templates, for example, [M(en)₃]²⁺ (en = ethylenediamine, M = Cu, Mn, Fe, Ni), [17,18] [Ln(DMSO)₈]³⁺ (Ln = La, Pr, Nd; DMSO = dimethyl sulfoxide) [19] and [Cu(deta)I]⁺ (deta = diethylene triamine) [20]. The results show that bivalent or trivalent metal ions can form such complex cations as templates. On the other hand, it is well known that d¹⁰ Cu⁺ ions can exhibit outstanding luminescence properties [21]. However, its coordination fashion ([CuI₄] tetrahedron) is evidently different from Pb²⁺. Therefore, it is meaningful to prepare Pb/Cu^I/I heterometallic iodoplumbates for the possible formation of novel structures and physical properties. The approach mentioned above cannot be adopted to synthesize the goal compound because it is difficult for monovalent Cu⁺ ions to form such complex cations. Therefore, our strategy is the fabrication of an inorganic-organic hybrid heterometallic iodoplumbate based on coordination compounds through the selection of a proper organic ligand which can join the Pb/I backbone and HM ions or make the Pb/I/HM framework stable.

In this work, we report the synthesis, crystal structure, and characterization of a Pb/Cu^I/I heterometallic iodoplumbate [PbCu₂I₄(bipy)]_n (**1**), which was prepared under solvothermal conditions

in the presence of the organic ligand bipy. This compound is one-dimensional neutral structure and has potential use as a semiconductor with good photoluminescence.

2. Materials and Methods

2.1. Materials and Measurements

All chemicals were obtained from Shanghai Aladdin Reagent (Shanghai, China) and were used without further purification. Powder X-ray diffraction (PXRD) data was tested on a DMAX2500 diffractometer (Rigaku, Tokyo, Japan). Thermogravimetric analysis (TGA) was performed on a Netzsch Sta449C thermoanalyzer (Netzsch, Saierbu, Germany) under N₂ atmosphere in the temperature range of 30–800 °C at a heating rate of 10 °C min^{−1}. Elemental analyses of carbon, hydrogen, and nitrogen were conducted using a Vario EL III (Elementar, Berlin, Germany) element analyzer. Diffuse reflectance spectra were measured at room temperature with a Perkin-Elmer Lambda35 UV-vis spectrometer (Perkin-Elmer, Waltham, MA, USA) equipped with an integrating sphere, and the BaSO₄ plate was used as the reference. Fluorescence spectra were obtained at room temperature with the aid of an Edinburgh FLS920 fluorescence spectrophotometer (Edinburgh Instruments, Livingston, England) with the polycrystalline sample held between two pieces of fused silica slices. The crystal structure was determined by a Rigaku Mercury CCD area-detector diffractometer (Rigaku, Tokyo, Japan) and SHELXL-97 crystallographic software of molecular structure.

2.2. Preparation of [PbCu₂I₄(bipy)]_n (1)

A mixture of PbI₂ (23 mg, 0.5 mmol), 2,2'-bipyridine (156 mg, 1 mmol), Cu(NO₃)₂·3H₂O (482 mg, 2 mmol), HI acid (1 mL), EtOH (5 mL), and H₂O (5 mL) was transferred into a Teflon-lined autoclave (23 mL), heated at 443 K for 4 d and then cooled at a rate of 2 K h^{−1} to room temperature. Yellow crystals suitable for X-ray diffraction analysis were obtained by filtration, washed with distilled water, and dried in air (42% yield based on Pb). Anal. Calcd for **1** (dried) (%): C, 12.03; H, 0.81; N, 2.81. Found: C, 12.31; H, 0.99; N, 2.63. To evaluate the phase purity of the as-synthesized sample, the collected sample was characterized by PXRD at room temperature. The PXRD pattern for the product is consistent with the pattern derived from the single-crystal X-ray solution in position (Figure S1), indicating that our collected sample is pure and can be used in other tests.

2.3. X-ray Crystallography

The crystallographic data for **1** were collected on a Rigaku Mercury CCD area-detector equipped with a graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 293(2) K using an ω -2 θ scan mode. Multi-scan absorption correction was conducted by the CrystalClear program [22]. The structure was solved by direct methods using the SHELXS-97 program and refined by full-matrix least-squares refinement on F^2 with the aid of the SHELXL-97 program [23,24]. All H atoms were positioned geometrically and refined as riding atoms. Data collection and refinements of this compound are listed in Table 1. Selected bond lengths and bond angles of **1** are gathered in Table 2.

Table 1. Crystallographic data and structure refinement parameters for **1**.

Molecular Formula	C ₁₀ H ₈ Cu ₂ I ₄ N ₂ Pb
Formula weight	998.05
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	4.2520(4)
<i>b</i> (Å)	13.1554(8)
<i>c</i> (Å)	16.4353(15)

Table 1. Cont.

Molecular Formula	C ₁₀ H ₈ Cu ₂ I ₄ N ₂ Pb
α (°)	98.231(6)
β (°)	94.171(8)
γ (°)	96.090(7)
V (Å ³)	901.11(13)
Z	2
D _{calc} (g·cm ^{−3})	3.678
μ (mm ^{−1})	18.497
F (000)	868
Crystal size (mm)	0.3 × 0.15 × 0.15
Index range	−5 ≤ h ≤ 5, −16 ≤ k ≤ 17, −19 ≤ l ≤ 22
Reflections collected	7013
Independent reflections	4124
R _{int}	0.0388
θ range (°)	2.76 to 29.31
Data/restraints/parameters	172/0/3056
Goodness-of-fit on F ²	1.028
Final R ₁ , wR ₂ indices	R ₁ = 0.0444, wR ₂ = 0.0855
R ₁ ^a , wR ₂ ^b indices (all data)	R ₁ = 0.0674, wR ₂ = 0.0999
Largest differences peak and hole (e Å ^{−3})	1.038 and −1.780

a. $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, *b.* $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and bond angles (°) for 1.

Bond	Lengths	Bond	Lengths	Bond	Lengths
Pb1–I2	3.0679(8)	Pb1–I1	3.1217(9)	Pb1–I2A	3.1679(9)
Pb1–I4	3.2279(9)	Pb1–I4A	3.3514(9)	Pb1–I3	3.3515(9)
Cu1–N1	2.026(9)	Cu1–N2	2.076(11)	Cu1–I1B	2.5635(17)
Cu1–I1	2.6713(19)	Cu2–I4	2.6012(17)	Cu2–I3C	2.6557(19)
Cu2–I3	2.6603(18)	Cu2–I3B	2.6807(16)		
Bond	Angles	Bond	Angles	Bond	Angles
I2–Pb1–I1	87.33(2)	I4–Pb1–I4A	80.50(2)	N1–Cu1–I1	98.7(3)
I2–Pb1–I2A	85.96(2)	I2–Pb1–I3	84.58(2)	N2–Cu1–I1	128.4(3)
I1–Pb1–I2A	104.78(3)	I1–Pb1–I3	167.95(2)	I1B–Cu1–I1	108.62(6)
I2–Pb1–I4	97.23(2)	I2A–Pb1–I3	83.59(2)	I4–Cu2–I3B	108.63(6)
I1–Pb1–I4	89.98(2)	I4–Pb1–I3	82.20(2)	I4–Cu2–I3	110.62(6)
I2A–Pb1–I4	165.06(3)	I4A–Pb1–I3	81.38(2)	I3C–Cu2–I3	114.96(6)
I2–Pb1–I4A	165.96(3)	N1–Cu1–N2	81.1(4)	I4–Cu2–I3B	111.65(6)
I1–Pb1–I4A	106.46(2)	N1–Cu1–I1B	130.6(3)	I3C–Cu2–I3B	105.35(6)
I2A–Pb1–I4A	92.85(2)	N2–Cu1–I1B	109.8(3)	I3–Cu2–I3B	105.52(6)

Symmetry transformation used to generate equivalent atoms: A: 1 + x, y, z; B: −1 + x, y, z; C: 1 − x, −y, −z.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication, with CCDC-1846939 for 1. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Telephone: +(44)-0123-7629120; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk). These data can be also obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

3. Results and Discussion

3.1. Synthesis

Compound **1** was prepared from the reaction mixture of PbI_2 , $\text{Cu}(\text{NO}_3)_2$, bipy, and HI in the mixed solvents of water and ethanol at 170°C through the solvothermal method. The results indicate that the Cu atoms in this compound are monovalent. However, a reactant containing monovalent Cu was not used; therefore, the production of Cu^{I} could be attributed to the reduction of bivalent Cu^{2+} by I^- under this solvothermal conditions. When CuI taking place of $\text{Cu}(\text{NO}_3)_2$ was directly used as reactant, crystal suitable for X-ray single-crystal analysis was not obtained. Lots of experiments using Cl^- or Br^- ions as halide sources in place of I^- , and other organic ligand such as 1,10-phenanthroline instead of bipy under the same condition have also been done to synthesize compounds similar structurally to **1**, but unfortunately, we did not succeed.

3.2. Structure Description

This compound was synthesized under solvothermal conditions and crystallized in the space group $P\bar{1}$. The asymmetric unit of **1** consists of one Pb atom, two Cu atoms, four I atoms, and one bipy ligand. As shown in Figure 1, the Pb1 atom is surrounded by six I atoms in a familiar $[\text{PbI}_6]$ octahedral environment. The Pb–I distances vary from 3.0679(8) to 3.3515(9) Å (Table 2) and are in accordance with those in many reported iodoplumbates [25,26]. The *cis* I–Pb–I angles are between $80.50(2)$ and $106.46(2)^\circ$, which deviate from the ideal 90° . Based on the charge balance of this structure, Cu1 and Cu2 are assigned as monovalent, which is also supported by the bond-valence sum (BVS) calculations, the valences of atoms Cu1 and Cu2 are 1.03 and 0.98, respectively. Bipy acts as a chelating ligand which bonds to the Cu1 atom by its two N atoms. At the same time, the Cu1 atom is bonded to two I atoms. As a consequence, the Cu1 atom exhibits $[\text{CuI}_2\text{N}_2]$ tetrahedral coordination. Different from the Cu1 atom, the Cu2 atom is coordinated by four I atoms in a $[\text{Cu}_2\text{I}_4]$ tetrahedral geometry. The Cu–N distances are 2.026(9) Å and 2.076(11) Å, and the Cu–I distances are from 2.5635(17) Å to 2.6807(16) Å. $[\text{PbI}_6]$ octahedra are joined by common edges (I2–I4) to form PbI_6 chain. $[\text{Cu}_2\text{I}_4]$ tetrahedra link each other by sharing edges (I3–I3) to engender CuI_4 chain. The $\text{Cu}_2\cdots\text{Cu}_2$ distance of 2.858(3) Å, which is longer than the double van der Waals radius of the Cu^+ ion (1.4 Å), implies a weak $\text{Cu}\cdots\text{Cu}$ interaction. The CuI_4 chain connects two adjacent PbI_6 chains through common edges (I3–I4) to produce Pb/Cu/I chain, which is further linked to $[\text{CuI}_2\text{N}_2]$ tetrahedra by vertex sharing (I1) to give rise to one-dimensional ribbon-like neutral structure $[\text{PbCu}_2\text{I}_4(\text{bipy})]_n$ along the *a* axis (Figures 2 and 3). No distinct interaction is found between neighboring ribbons. As a result of the connectivity of the $[\text{PbI}_6]$ octahedra and $[\text{CuI}_2\text{N}_2]$ and $[\text{Cu}_2\text{I}_4]$ tetrahedra, the iodide ligands act as μ_2 - (I2), μ_3 - (I1 and I4), and μ_4 -bridging (I3) ligands.

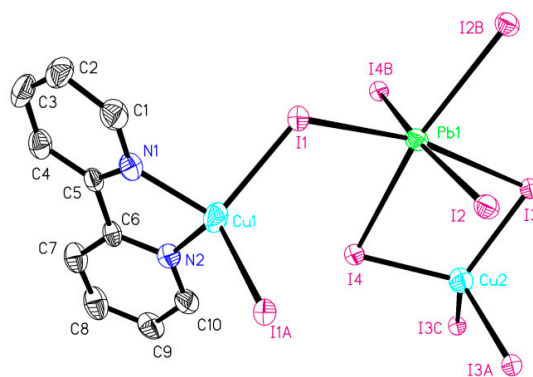


Figure 1. The coordination environment of the Pb and Cu atoms in **1**. All H atoms have been omitted for clarity. Displacement ellipsoids are depicted at the 30% probability level. Symmetry codes: A: $-1 + x, y, z$; B: $1 + x, y, z$; C: $1 - x, -y, -z$.

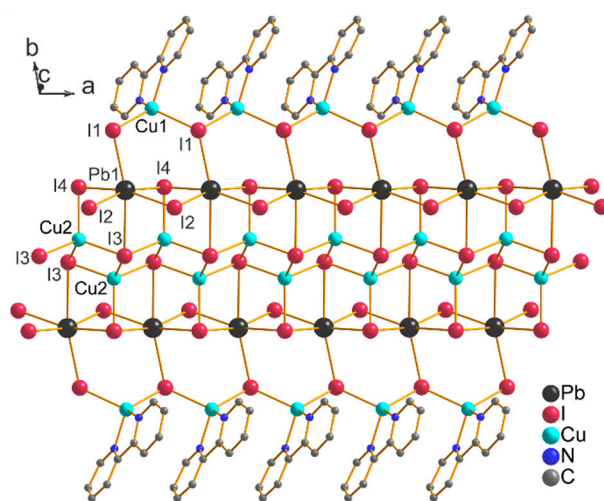


Figure 2. The fragment of the structure of **1** extending along the *a* axis. All H atoms have been omitted for clarity.

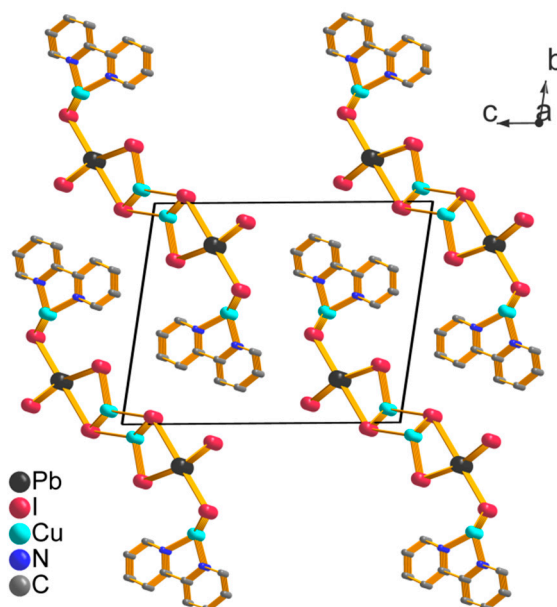


Figure 3. Packing diagram of **1**. All H atoms have been omitted for clarity.

3.3. Thermal Stability

To evaluate the thermal stability of this material, TGA was conducted on the collected powder sample in N_2 atmosphere from 30 °C to 800 °C. TGA reveals that the weight loss in **1** begins at ca. 200 °C up to ca. 395 °C to give a weight loss of 15.3%, corresponding to the loss of one bipy molecule per formula unit (15.6% calculated). In the subsequent weight loss, this compound continues to gradually decompose (Figure S2).

3.4. Diffuse Reflectance Spectroscopy

In order to obtain the optical band gap of **1**, its diffuse reflectance spectroscopy was measured. With the help of the Kubelka-Munk function: $F(R) = (1 - R)^2 / 2R$, in which R is the experimentally observed reflectance [27,28], the plot of $F(R)^2$ vs. photon energy was obtained and is presented in Figure 4. In this plot, the optical band gap is determined by extending the linear portion of the absorption edge to intersect the energy axis. The produced intersection demonstrates that the

optical band gap of **1** is 2.32 eV, which is consistent with its yellow color, showing the potential use as semiconductor.

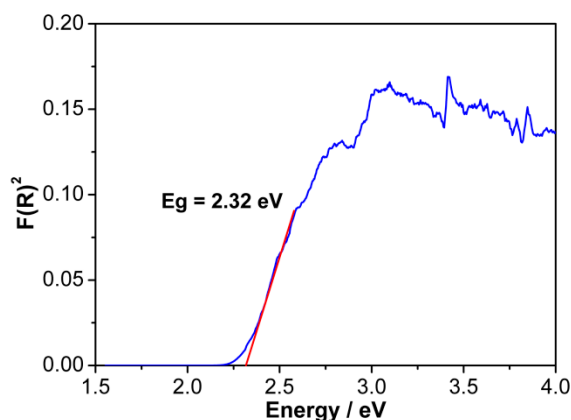


Figure 4. Plot of $F(R)^2$ vs. photon energy for **1**.

3.5. Luminescence Property

As reported in many studies, d^{10} Cu^+ ions present outstanding luminescence properties. To investigate the luminescence property of **1**, its fluorescence spectrum was measured in the solid state at room temperature (Figure 5). Under excitation at 316 nm, a fluorescent emission peak with an intense emission center at 610 nm appeared. According to the reported results of the similar copper(I) halide compounds, the emission band might be assigned to iodide-to-copper charge transfer [29,30]. This result indicates that this compound has potential as a luminescence material.

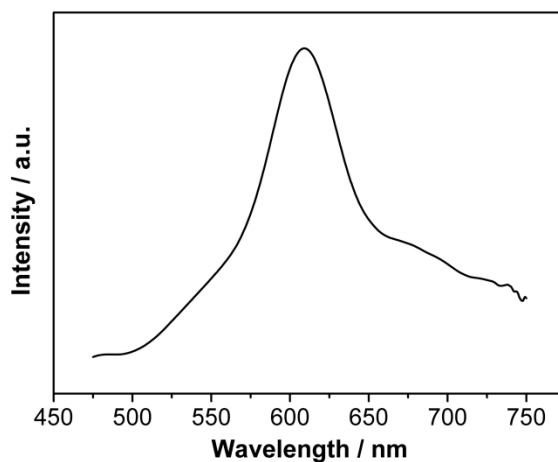


Figure 5. Solid-state emission spectrum for **1** at room temperature (excited at 316 nm).

4. Conclusions

In conclusion, a $\text{Pb}/\text{Cu}^{\text{I}}/\text{I}$ heterometallic iodoplumbate has been prepared by a solvothermal method in presence of the organic ligand bipy. The semiconducting and luminescence properties of **1** are reported. The successful synthesis of **1** shows that the construction of an inorganic-organic heterometallic iodoplumbate based on coordination compounds can be achieved by choosing a proper organic ligand and controlling the synthesis conditions.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4352/8/8/305/s1>, Figure S1: Experimental and simulated powder X-ray diffraction patterns of **1**, Figure S2: TGA curve of **1**.

Author Contributions: Le-Qing Fan designed the experiments and wrote the paper; Xiao-Tong Zhu performed the experiments and analyzed the data.

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Conflicts of Interest: The authors declare no conflict of interest.

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