

Haloplumbate hybrids with organically coordinated halometal complexes as templates and mixed halo atoms: Solvothermal syntheses, crystal structures, and optical properties

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ABSTRACT

Inorganic–organic hybrids with mixed halo atoms or organically coordinated halometal-complex cations are rare. A series of haloplumbate hybrids with these structural features, $[\text{Cu}(\text{phen})_2\text{Cl}]_n(\text{PbCl}_3)_n$ (phen = 1,10-phenanthroline) (**1**), $[\text{Cu}(\text{phen})_2\text{Cl}]_n[\text{PbCl}(\text{Cl}_{0.5}\text{I}_{0.5})]_n$ (**2**), and $[\text{Cu}(\text{phen})_2\text{I}]_n(\text{PbI}_3)_n$ (**3**), have been solvothermally synthesized using phen coordinated halocopper(II) complexes as templates and balance cations. Their haloplumbate ions all show 1-D chain structures. Compounds **1–3** feature the hybridization of inorganic–organic hybrids: 1) their absorption edges fall in the range of those of semiconductors, which is typical for bulk lead(II) halides, but show a red shift compared with those of the latter; 2) bulk lead(II) halides are nonluminescent upon UV irradiation, but introduction of the phen coordinated halocopper(II) complexes as templates enable the hybrids to emit blue light. Their luminescent intensities gradually decrease with the increase of I content, which indicates the potential to design and syntheses of new luminescent halide materials by means of variation of halo atoms and that iodoplumbates are not good candidates for luminescent materials.

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Inorganic–organic hybrids have attracted considerable interest during the past decade, not only for their intriguing structural chemistry, but also for many potential applications as electronic, optical, magnetic and storage materials [1–6]. Previous studies have shown that haloplumbate hybrids, with a wide range of interesting optical, semi-conducting, and other physical properties, are technically important [7–9], and their haloplumbate anions exhibit a wide variety of coordination numbers and stereochemistries due to the flexibility of the Pb(II) coordination polyhedron and the templating effect of the cations [10]. Recent development has revealed that introduction of transition metal (TM) complex cations into inorganic systems can produce inorganic–organic hybrids with unique topological structures and interesting physical properties [11,12]. For example, Mercier and co-workers have synthesized an organic–inorganic hybrid $[\text{Cu}(\text{O}_2\text{C}(\text{CH}_2)_3\text{NH}_3)_2]_n\text{PbBr}_4$ with copper paddle-wheel clusters linking perovskite layers [13]. Chen and co-workers have obtained a new stepwise layered iodoplumbate structure templated by $[\text{Ni}(\text{opd})_2(\text{acn})_2]^{2+}$ cations [14]. Our group obtained a new type of hybrid magnetic semiconductor based upon a polymeric iodoplumbate with $[\text{M}(\text{en})_3]^{2+}$ complexes as templates [11].

To the best of our knowledge, inorganic–organic hybrids with mixed halo atoms or organically coordinated halometal complexes cations are rare [15–17]. During our further studies on haloplumbate hybrids with TM complexes as templates, we obtained a series of haloplumbate hybrids, $[\text{Cu}(\text{phen})_2\text{Cl}]_n(\text{PbCl}_3)_n$ (phen = 1,10-phenanthroline) (**1**), $[\text{Cu}(\text{phen})_2\text{Cl}]_n[\text{PbCl}(\text{Cl}_{0.5}\text{I}_{0.5})]_n$ (**2**), and $[\text{Cu}(\text{phen})_2\text{I}]_n(\text{PbI}_3)_n$ (**3**), with mixed halo atoms and phen coordinated halocopper(II)-complex cations. Photoluminescence (PL) analyses illuminated that the presence of different halo atoms in the phen coordinated halocopper(II)-complex cations or haloplumbate anions influence significantly the PL intensities of haloplumbate hybrids. Herein, we report the solvothermal syntheses [18], crystal structures, and optical (UV–vis and PL) properties of **1–3**.

The FT-IR spectra were obtained on a PerkinElmer Spectrum One FT-IR spectrometer using KBr disks in the range of 4000–400 cm^{-1} . The elemental analyses of C, H, and N were measured on an Elementar Vario EL III microanalyzer. Optical diffuse reflectance spectra were measured on a PerkinElmer Lambda-900 UV/Vis/NIR spectrophotometer equipped with an integrating sphere at 293 K, and a BaSO₄ plate was used as the reference. The absorption edges were calculated by the Kubelka–Munk function: $\alpha/S = (1 - R)^2/2R$, where α is the absorption coefficient, S is the scattering coefficient, and R is the reflectance. Solid-state PL excitation and emission spectra were recorded on a HORIBA Jobin Yvon Fluorolog-3 spectrofluorometer equipped with a 450-W Xe lamp. The test condition is the same, including excitation slit and emission slit width, dwell time,

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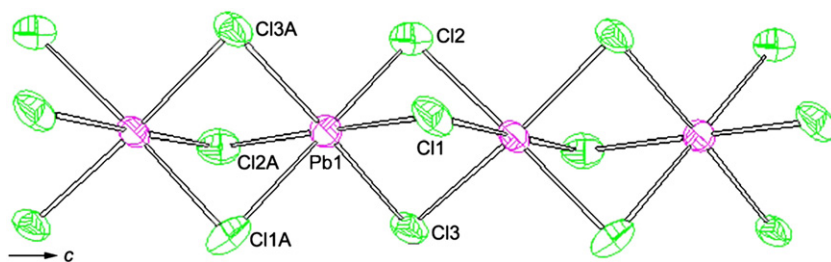


Fig. 1. 1-D chain structure of the chloroplumbate ion in **1** extending along the *c* axis. Symmetry codes: A = $x, 3/2 - y, 1/2 + z$.

repeats number, filter, excitation wavelength, and the same sample holder with a $0.3 \times 1.0 \text{ cm}^2$ at room temperature. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku MiniFlexII diffractometer using $\text{Cu } K_{\alpha}$ radiation ($\lambda = 1.54056 \text{ \AA}$).

The crystallographic data of **3** determined by single-crystal X-ray diffraction analysis was used to calculate its electronic band structure. The calculation of electronic band structure along with density of states (DOS) was performed with the CASTEP code [19,20] based on the density functional theory using a plane-wave expansion of the wave functions. The interactions between the ionic cores and the electrons were described by the norm-conserving pseudopotential, in which the orbital electrons of $1-5s^25p^5$, $\text{Pb}-5d^{10}6s^26p^2$, $\text{Cu}-3d^{10}4s^1$, $\text{H}-1s^1$, $\text{N}-2s^22p^3$, and $\text{C}-2s^22p^2$ were treated as valence electrons. The number of plane waves included in the basis was determined by a cutoff energy E_c of 290.0 eV, and the numerical integration of the Brillouin zone was performed using a $1 \times 1 \times 2$ Monkhorst Pack *k*-point sampling. The convergent criterion of total energy was set by the default value of the CASTEP code [19].

The solvothermal method has been widely used in the syntheses of inorganic–organic hybrids to obtain new compounds with novel structures and properties [21], because the difficulties of differential solubility for organic and inorganic precursors can be overcome under solvothermal condition, but it has scarcely been used in the haloplumbate-based hybrid system [11]. As we know, in a special solvothermal process, many factors can affect the formation and crystal growth of the product phases, such as reactant stoichiometry, initial reactants, pressure, pH value, temperature, reaction time, and so forth.

We had studied the influence of several synthetic parameters on **1–3**: (1) Other solvents such as ethanol cannot gain the same high yield as DMF. (2) The temperature plays a decisive role in the formation of these compounds and directly relates to the yields of the products. Lower temperature, such as $120 \text{ }^\circ\text{C}$, helps the crystals to grow, while the crystals of **1–3** cannot be obtained or their yields are very low under higher temperature, like $180 \text{ }^\circ\text{C}$. (3) The initial reactants of lead nitrate instead of lead chloride can help to raise the yield of compound **1**, but has no help for the yields of **2** and **3**.

Single-crystal X-ray diffraction analysis [22] reveals that compound **1** crystallizes in monoclinic space group $P2_1/c$ and consists of $[\text{Cu}(\text{phen})_2\text{Cl}]^+$ cations and 1-D infinite $(\text{PbCl}_3)_n^-$ chains. As shown in Fig. 1, the $(\text{PbCl}_3)_n^-$ chain extending along the *c* direction is consisted of face-sharing (PbCl_6) octahedra. The average Pb–Cl bond distance is $2.944(2) \text{ \AA}$ and the Cl–Pb–Cl bond angles fall in the range of $81.70(5) - 100.01(6)^\circ$, which agrees well with those reported in the literature [23,24]. In the crystal structure of **1** (Fig. 2), each 1-D chloroplumbate chain is encapsulated in a cricoid channel, which is formed by six $[\text{Cu}(\text{phen})_2\text{Cl}]^+$ cations extending along the *c* axis direction. There are two types of face-to-face $\pi \cdots \pi$ stacking interactions between two neighboring phen molecules in **1** (Fig. S1) with centroid–centroid (the centroids are defined as the geometrical centers of phenyl or pyridyl rings of the phen molecules) distances of $3.462(1)$ and $3.744(1) \text{ \AA}$, respectively, which locate in the ranges of those reported in the literature [25,26]. The $[\text{Cu}(\text{phen})_2\text{Cl}]^+$ cations form a supramolecular chain along the *c* direction through $\pi \cdots \pi$ interactions, which is parallel to the inorganic chains.

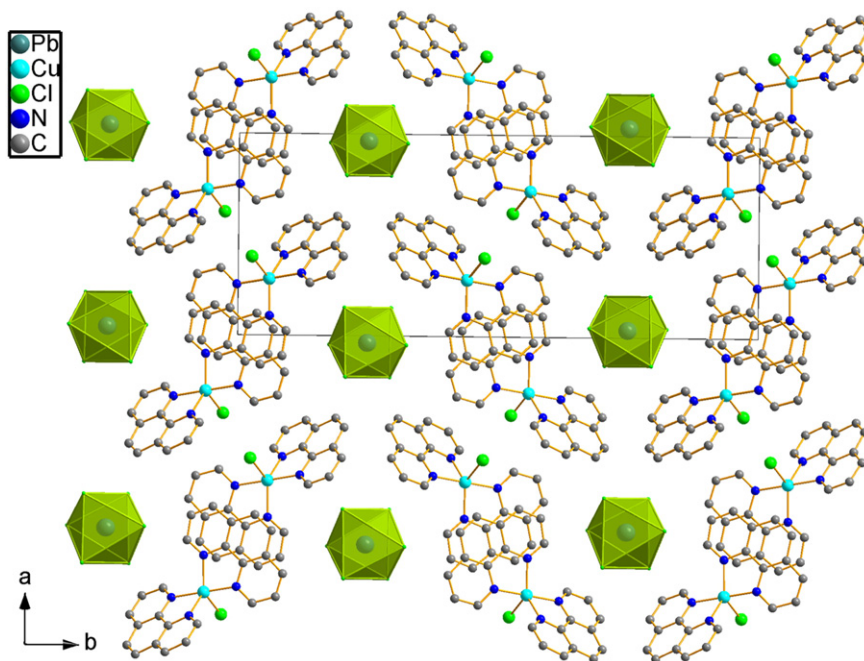


Fig. 2. Crystal structure of **1** viewed along the *c* direction. Hydrogen atoms are omitted for clarity.

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