

基于 PbBr_2 的有机-无机杂化化合物的合成和晶体结构

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摘要: 合成得到了 2 个新的有机-无机杂化化合物 $\{(4\text{-CH}_3\text{-Bz-4-Ph-Py})[\text{PbBr}_3]\}_n$ (**1**) (4- $\text{CH}_3\text{-Bz-4-Ph-Py}^+=4$ -甲基苄基-4-苯基吡啶离子) 和 $\{(4\text{-F-Bz-4-Ph-Py})[\text{PbBr}_3]\}_n$ (**2**) (4- $\text{F-Bz-4-Ph-Py}^+=4$ -氟苄基-4-苯基吡啶离子)。对化合物 **1** 和 **2** 进行了元素分析、粉末 X 射线衍射等表征, 并利用 X 射线单晶衍射测定了它们的单晶结构, 配合物 **1** 与 **2** 同构, 均属于正交晶系, $P2_12_12_1$ 空间群。结构研究表明, 配合物 **1** 和 **2** 中, 铅溴八面体通过共边连接方式, 形成 $[\text{Pb}_3\text{Br}_9]_n$ 三链, 有机阳离子填充在无机溴化铅链空隙中。配合物 **1** 和 **2** 均未作手性分离。

关键词: 溴化铅; 有机-无机杂化化合物; 晶体结构

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Syntheses and Crystal Structures of Two Homogeneous Organic-Inorganic Compounds Based on PbBr_2

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Abstract: Two homogeneous compounds, $\{(4\text{-CH}_3\text{-Bz-4-Ph-Py})[\text{PbBr}_3]\}_n$ (**1**) (4- $\text{CH}_3\text{-Bz-4-Ph-Py}^+=4$ -methylbenzyl-4-phenylpyridinium) and $\{(4\text{-F-Bz-4-Ph-Py})[\text{PbBr}_3]\}_n$ (**2**) (4- $\text{F-Bz-4-Ph-Py}^+=4$ -fluorobenzyl-4-phenylpyridinium), have been synthesized and characterized by elemental analysis and single-crystal X-ray diffraction. Compounds **1** and **2** are isostructural, and crystallize in orthorhombic, space group $P2_12_12_1$. Structure analyses reveals that haloplumbate ion exhibits octahedron topology in compounds **1** and **2**, and all these octahedron topologies formed 1D polymeric chain through edge-sharing connecting modes. The flack values of **1** and **2** are 0.340(13) and 0.453(10), respectively. No chiral separation was done for both compounds. CCDC: 1572941, **1**; 1572942, **2**.

Keywords: lead bromide; organic-inorganic hybrid compounds; crystal structure

0 Introduction

Haloplumbate-based hybrids have been received considerable research interests due to their tunable structures from the discrete mononuclear or polynuclear species (zero-dimensional; abbr. 0D) to the infinite variety with higher dimensionality^[1-13] (one-

dimensional^[1,3-9], two-dimensional^[10-11] or three-dimensional^[2]; hereafter abbr. as 1D, 2D and 3D, respectively) and the wide range of novel physical properties, beneficial in optics^[14-20] and electronics^[21-22].

In the context of haloplumbate-based hybrids, the perovskite-type ones have attracted tremendous research interest. The 3D haloplumbate-based

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perovskites, $(\text{CH}_3\text{NH}_3)\text{PbI}_{3-x}\text{Cl}_x$, with much lower exciton binding energies and intense light absorption over the whole visible light region have been employed as absorbers in solar cells. It is remarkable that the records of certified power conversion efficiencies have been constantly updated and over merely a few years, the power conversion efficiency has been enhanced to 22.1%^[20]. Most recently, the $(\text{CH}_3\text{NH}_3)\text{PbI}_{3-x}\text{Cl}_x$ perovskites have been found to show amazing bipolar and bistable resistive switching behavior with small on-off voltage (<1.0 V) in a simple metal-dielectric-metal capacitor configuration device memory field^[23]. The 2D haloplumbate-based hybrids, $(N\text{-MEDA})[\text{PbBr}_{4-x}\text{Cl}_x]$ ($N\text{-MEDA}=N\text{-1-methylethane-1,2-diammonium}$, $x=0\sim 1.2$), are single-phase white-light emitters, and their broadband emission across the entire visible spectrum arises from corrugated lead halide sheets. Interestingly, the emission is tunable through halide substitution to afford both “warm” and “cold” white light in such haloplumbate-based wide-band gap semiconductors^[14]. The 1D iodoplumbate-based hybrids were reported to display ferroelectricity, wherein the polarization is switchable under an alternating current electrical field^[24].

In addition, a 3D open-framework hybrid, $\{(\text{EDAMP})_2[\text{Pb}_7\text{I}_{18}] \cdot 4\text{H}_2\text{O}\}_n$ ($\text{EDAMP}^{2+}=\text{Et}_2\text{NHC}_6\text{H}_4\text{-CH}_2\text{C}_6\text{H}_4\text{NHEt}_2$), in which the inorganic framework is built from purely octahedral PbI_6 units and behaves as a quantum-wire array, shows a fascinating wavelength-dependent photochromic behavior^[25]. Its color changes from yellow to olive green under illumination by light with $\lambda=500$ nm and further to dark green by light with $\lambda<500$ nm. Most interestingly, the reversion of the color for the hybrid can be accomplished by heating, indicating that this hybrid possesses switchable photochromic nature. It is well known that a material with switchable functionality through external stimuli, such as thermally-triggered, irradiation-induced and applied pressure, is very useful for application in the fields of sensors, memory and data storage^[26-29].

In this study, we report the syntheses and crystal structures of two haloplumbate-based hybrids, $\{(4\text{-CH}_3\text{-Bz-4-Ph-Py})[\text{PbBr}_3]\}_n$ (**1**) and $\{(4\text{-F-Bz-4-Ph-Py})[\text{PbBr}_3]\}_n$ (**2**).

$\text{CH}_3\text{-Bz-4-Ph-Py})[\text{PbBr}_3]\}_n$ (**1**) and $\{(4\text{-F-Bz-4-Ph-Py})[\text{PbBr}_3]\}_n$ (**2**).

1 Experimental

1.1 Materials and general methods

All chemicals and solvents were reagent grade and used without further purification. $(4\text{-CH}_3\text{-Bz-4-Ph-Py})\text{Br}$ and $(4\text{-F-Bz-4-Ph-Py})\text{Br}$ were synthesized according to a similar procedure described in the literature^[30]. Elemental analyses for C, H and N were performed with an Elementar Vario EL III analytic instrument. Powder X-ray diffraction (PXRD) data for **1** and **2** were collected on a Rigaku/max-2550 diffractometer with $\text{Cu } K\alpha$ radiation ($\lambda=0.154$ 18 nm) at room temperature. The acceleration voltage was 40 kV with a 40 mA current flux. The data were collected in the 2θ range from 5° to 50° .

1.2 Synthesis of $\{(4\text{-CH}_3\text{-Bz-4-Ph-Py})[\text{PbBr}_3]\}_n$ (**1**)

A mixture of $(4\text{-CH}_3\text{-Bz-4-Ph-Py})\text{Br}$, KBr and PbBr_2 with a molar ratio of 1:1:1 in DMF (25 mL) was placed in an oven and slowly evaporated at 55°C for 10~14 days to produce light yellow needle-shaped crystals in *ca.* 95% yield. Elemental analysis calculated for $\text{C}_{38}\text{H}_{36}\text{N}_2\text{Pb}_3\text{Br}_8$ (%): C 25.62, H 2.04, N 1.57; Found (%): C 25.60, H 2.03, N 1.55.

1.3 Synthesis of $\{(4\text{-F-Bz-4-Ph-Py})[\text{PbBr}_3]\}_n$ (**2**)

The synthesis of **2** was the same as that of **1** except that $(4\text{-F-Bz-4-Ph-Py})\text{Br}$ was used instead of $(4\text{-CH}_3\text{-Bz-4-Ph-Py})\text{Br}$. Yellow needle-shaped crystals were gained in *ca.* 95% yield. Elemental analysis calculated for $\text{C}_{36}\text{H}_{30}\text{N}_2\text{Pb}_3\text{Br}_8\text{F}_2$ (%): C 24.16, H 1.69, N 1.57; Found(%): C 24.11, H 1.65, N 1.54.

1.4 X-ray crystallography

Two block single crystals of **1** and **2** with dimensions of both 0.19 mm $\times$ 0.18 mm $\times$ 0.17 mm were selected under an optical microscope and glued to thin glass fibers, respectively. X-ray diffraction intensity data were collected on a Bruker APEX II CCD diffractometer equipped with a graphite monochromated $\text{Mo } K\alpha$ ($\lambda=0.071$ 073 nm) using the φ - ω scan mode at 296(2) K. Data reductions and absorption corrections were performed with the SAINT and SADABS software packages^[31], respectively. Structures were solved by

direct methods and refined by full matrix least-squares with SHELXL-2014/7 software package^[32]. The non-hydrogen atoms were anisotropically refined using the full-matrix least-squares method on F^2 . All hydrogen atoms were placed at the calculated positions and

refined riding on the parent atoms. The details about data collection, structure refinement and crystallography are summarized in Table 1.

CCDC: 1572941, **1**; 1572942, **2**.

Table 1 Crystallographic and structure refinement data for **1** and **2**

Compound	1	2
Formula	$C_{38}H_{36}N_2Pb_3Br_8$	$C_{36}H_{30}N_2Pb_3Br_8F_2$
Formula weight	1 781.54	1 911.29
Space group	$P2_12_12$	$P2_12_12$
Crystal system	Orthorhombic	Orthorhombic
a / nm	2.101 3(2)	2.137 9(2)
b / nm	2.349 6(3)	2.286 2(2)
c / nm	0.442 11(5)	0.435 81(4)
V / nm ³	2.182 8(4)	2.130 1(3)
Z	2	2
D_c / (g·cm ⁻³)	2.711	2.980
$F(000)$	1 608	1 712
μ / mm ⁻¹	18.893	19.368
θ range for data collection / (°)	1.73~27.66	1.30~27.44
Index ranges	$-23 \leq h \leq 27, -30 \leq k \leq 30, -5 \leq l \leq 5$	$-27 \leq h \leq 27, -28 \leq k \leq 29, -5 \leq l \leq 5$
R_{int}	0.086 7	0.036 3
Flack	0.340(13)	0.453(10)
Independent reflection, restraint, parameter	5 045, 0, 105	4 848, 0, 103
Goodness of fit on F^2	1.059	1.061
R_1, wR_2^a [$I > 2\sigma(I)$]	$R_1=0.062$ 7, $wR_2=0.163$ 7	$R_1=0.054$ 8, $wR_2=0.147$ 3
R_1, wR_2^a [all data]	$R_1=0.084$ 7, $wR_2=0.178$ 7	$R_1=0.064$ 8, $wR_2=0.159$ 2
$(\Delta\rho)_{max} (\Delta\rho)_{min}$ / (e·nm ⁻³)	4 402, -4 931	4 416, -3 827

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

2 Results and discussion

2.1 Description of crystal structure

Compound **1** crystallizes in the $P2_12_12$ space group at room temperature and no chiral separation was done. The asymmetric unit, as shown in Fig.1, consists of one Pb^{2+} ion and three different Br^- anions together with one 4-CH₃-Bz-4-Ph-Py⁺ cation. The Pb^{2+} ion is located at an inversion center and coordinated with six Br^- to form the slightly distorted PbI_6 octahedron. The Pb-Br lengths range from 0.271 38(23) to 0.349 15(20) nm and the Br-Pb-Br angles fall within the range of 83.754(46)°~172.861(50)° at 296 K, these geometry parameters within the coordination octahedron are comparable to other haloplumbates. Three

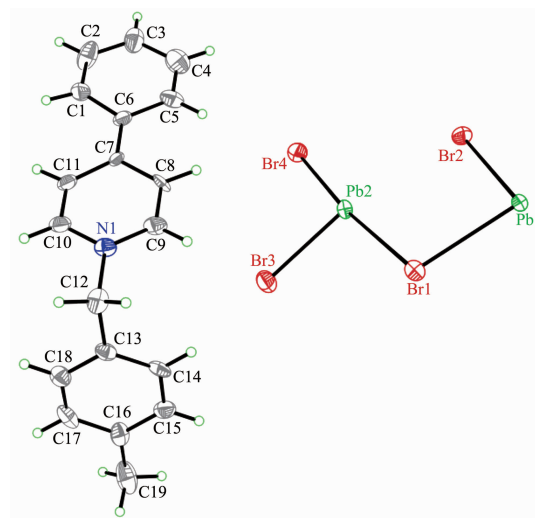
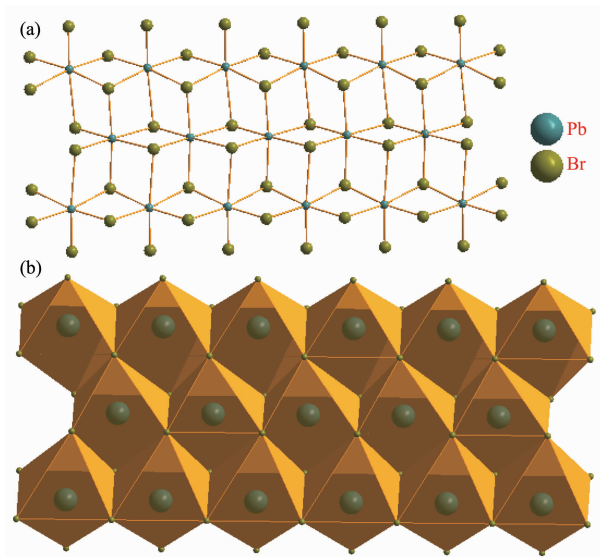


Fig.1 ORTEP view of **1** with thermal ellipsoids at 30% probability level

different Br^- ions are adopted in the μ_3 -bridged model to connect three neighboring Pb^{2+} ions. The adjacent PbBr_6 coordination octahedral are connected together via the edge-sharing mode to form a uniform $[\text{Pb}_3\text{Br}_9]_n$ chain along the a -axis direction (Fig.2).



(a) Stick and ball model; (b) Polyhedron model

Fig.2 Edge-sharing octahedral chain of $[\text{Pb}_3\text{Br}_9]_n$ in compounds **1** and **2**

The cation is composed of a 4-phenylpyridine and a 4-methylbenzyl, and the neighboring cations are aligned into quadrilateral-shaped 1D channels, and the inorganic $[\text{Pb}_3\text{Br}_9]_n$ chains reside in the channels (Fig.3). Charged-assisted H-bonding interactions

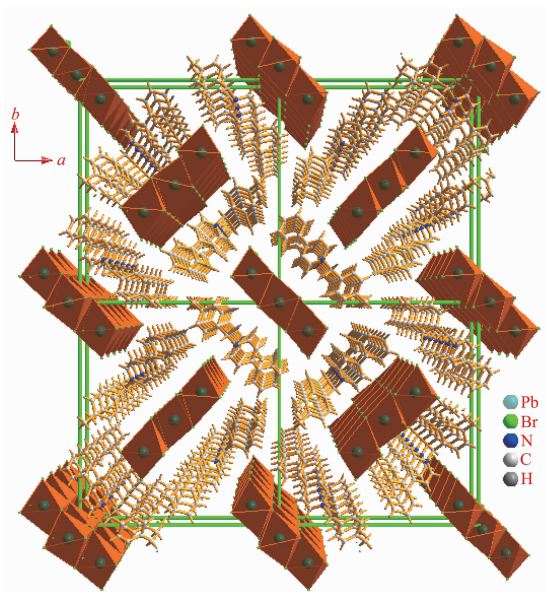


Fig.3 Molecular packing diagram for compound **1**

appear between the CH_2 groups in the cations and the Br^- ions in the inorganic chains. Compound **2** (Fig.4~5) is isostructural with compound **1**.

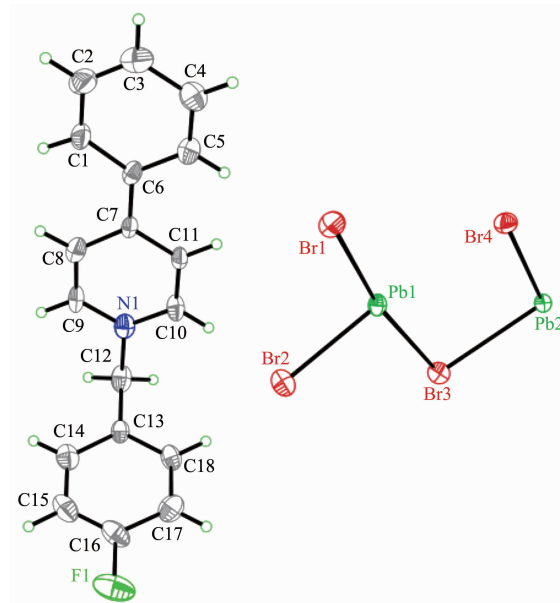


Fig.4 ORTEP view of **2** with thermal ellipsoids at 30% probability level

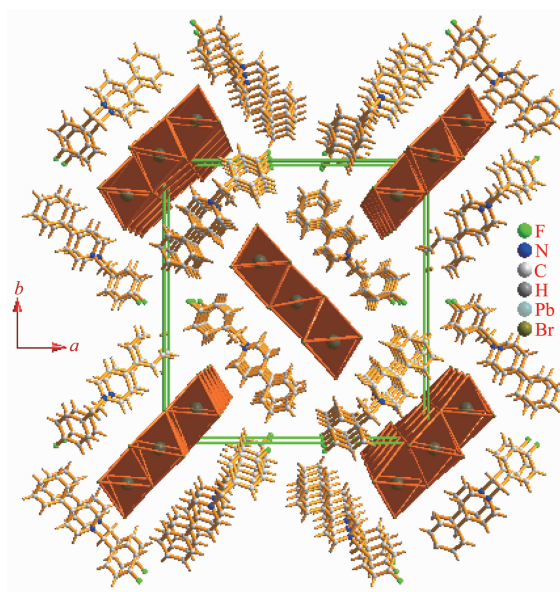


Fig.5 Molecular packing diagram for compound **2**

2.2 Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) analyses were carried out for **1** and **2** at room temperature to characterize their purity. As shown in Fig.6, the measured peak positions closely match the simulated peak positions, indicative of pure products.

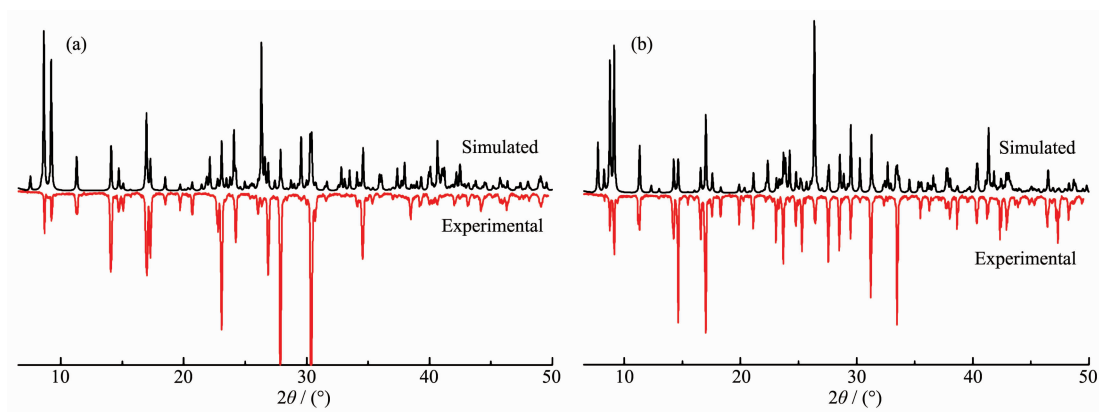


Fig.6 PXRD patterns of compounds **1** (a) and **2** (b)

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