

一种新颖一维铅碘聚合物 $[(\text{Pb}_2\text{I}_5)(\text{L}-\text{H}^+)\cdot 2\text{DMF}]_n$ ($\text{L}=\text{Piperazine}$) 的自组装合成和晶体结构

李浩宏 陈之荣* 黄长沧 赵 斌 肖荣平 倪朝霞

(福州大学化学化工学院, 福州 350002)

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The Self-assembly Synthesis and Structure of a Novel 1-D Lead Iodide Adduct: $[(\text{Pb}_2\text{I}_5)(\text{L}-\text{H}^+)\cdot 2\text{DMF}]_n$ ($\text{L}=\text{Piperazine}$)

LI Hao-Hong CHEN Zhi-Rong* HUANG Chang-Cang ZHAO Bin XIAO Rong-Ping NI Zhao-Xia

(Department of Chemistry, Fuzhou University, Fuzhou 350002)

Abstract: The lead iodide adduct $[(\text{Pb}_2\text{I}_5)(\text{L}-\text{H}^+)\cdot 2\text{DMF}]_n$ ($\text{L}=\text{piperazine}$) has been prepared by self-assembly and structurally characterized. It presents one dimensional structure and crystallizes in Triclinic, $P\bar{1}$ space group with the crystal cell parameter: $a=0.922\ 06(18)$ nm, $b=1.237\ 5(3)$ nm, $c=1.297\ 2(3)$ nm, $\alpha=99.05(3)^\circ$, $\beta=102.98(3)^\circ$, $\gamma=105.30(3)^\circ$, and $V=1.353\ 8(6)$ nm³, $Z=2$, $D_c=3.078$ Mg \cdot m⁻³, $\mu(\text{Mo K}\alpha)=18.127$ mm⁻¹, $F(000)=1\ 085$, chemical formula $\text{C}_{16}\text{H}_{43}\text{N}_8\text{O}_4\text{Pb}_4\text{I}_{10}$ and $M_r=2\ 509.39$, the final $R=0.053\ 3$ and $wR=0.146\ 4$ for 3 889 observed reflections with $I>2\sigma(I)$. CCDC: 250760.

Key words: coordination polymers; lead iodide; organic-inorganic hybrid; X-ray single crystal structure

0 Introduction

Increasing interest is focused on the study of magnetic, electronic and optoelectronic properties of low-dimensional organic-inorganic hybrid compounds [1-3]. Studies show that complex consisting of organic and inorganic components have great potential for the creation of functional materials utilizing the wide variety of properties associated with these compounds. For lead(II) the available structure determinations are sporadic and diverse, exhibiting a wide variety of coordination number and stereochemistries with or without the suggestion of a "lone-pair" in the coordination

sphere. On the other hand, lead iodide and its low-dimensional compounds are of particular interests due to their significant excitonic, third-order nonlinear optical, ferroelectric and ferroelastic properties^[4]. In these compounds, the organic moiety usually contains positively charged groups such as quaternary ammonium, which serve to counterbalance the charge on the inorganic part and template the inorganic chain or layer. However, the lead halide adducts $\text{Pb}(\text{L})\text{X}_2$ ($\text{X}=\text{halide}$, $\text{L}=\text{ligand}$) with ligands coordinatively linked to the inorganic framework have attracted little attention, and structure information on these compounds is still rare

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*通讯联系人。E-mail: lihhfzu@tom.com

第一作者: 李浩宏, 男, 26 岁, 博士生; 研究方向: 有机-无机杂化配位聚合物。

scare. Furthermore, the ligand sever two functions: coordinating with inorganic backbone and protonizing to counterbalance the charge of inorganic chain. This kind of compound is more scare. Our current research is focused on such compounds. Herein we report the synthesis of 1-dimensional lead halide-base hybrid polymers, measure its spectrum properties and determine the structure.

1 Experimental

1.1 Preparation of title compound

The title compound $[(\text{Pb}_2\text{I}_5)(\text{L-H}^+)\cdot 2\text{DMF}]_n$ (L= piperazine) was prepared by self-assembly reaction of $\text{Pb}(\text{NO}_3)_2$, NaI and piperazine. All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. Piperazine (0.084 g, 1 mmol) was dissolved in 10 mL DMF, and then $\text{Pb}(\text{NO}_3)_2$ (0.166 g, 0.5 mmol) was added in above solution. Stirred till it became yellow clear, and then NaI (0.187 g, 1.25 mmol) was dissolved, adjusted pH with 10% HI/DMF solution to pH=3.0 and then the mixture solution was filtered. The result solution was kept at room temperature for three days. The colorless needle single crystal was obtained. The IR spectra were recorded in the $4\,000\sim 400\text{ cm}^{-1}$ region using KBr pellets on a Nicolet Co. Magna-IR 750 spectrometer. Piperazine, DMF(cm^{-1}): $\nu_{-\text{CH}_2}^{\text{as}}=1\,455.38$; $\nu_{\text{C-N}}=1\,172.83$; $\nu_{\text{C-C}}=1\,586.21$, $\nu_{-\text{CH}_2}=1\,450.41$, $\nu_{\text{N-H}}=3\,445.32$, $\nu_{\text{C=O}}=1\,665.77$, $\nu_{-\text{CH}_3}=1\,383.94$.

1.2 X-ray Structure Determination

A colorless needle single crystal with dimensions of $0.20\text{ mm} \times 0.12\text{ mm} \times 0.10\text{ mm}$ was selected and the measurement of the crystal was carried out on Rigaku Weissenberg IP diffractometer with Mo $K\alpha$ ($\lambda=0.071\,069\text{ nm}$) for the data collection. A total of 11 458 reflections were collected, of which 5 078 are independent in the range of $1.66^\circ < \theta < 25.99^\circ$ at 298 K and 3 889 are observed reflections with $I > 2\sigma(I)$. All the collected independent reflections were used in the structure analysis. The heavy atoms was solved by Patterson method, other non-hydrogen atoms were solved by successive difference Fourier syntheses. Hydrogen atoms were determined with theoretic calculation. The structure was refined by full-matrix least-

squares using anisotropic thermal parameters for all the non-hydrogen atoms (except C9). All calculations were performed on a computer with SHELX-97 program package^[5,6]. The final $R=0.053\,3$ and $wR=0.146\,4$, $w=1/[\sigma^2(F_o^2)+(0.100\,2P)^2+0.000\,0P]$, where $P=(F_o^2+2F_c^2)/3$. $(\Delta/\sigma)_{\text{max}}=0.000$, $S=1.079$, $(\Delta\rho)_{\text{max}}=2\,250\text{ e}\cdot\text{nm}^{-3}$, $(\Delta\rho)_{\text{min}}=-3\,145\text{ e}\cdot\text{nm}^{-3}$.

CCDC: 250760.

2 Results and discussion

The selected bond lengths and bond angles are given in Table 1. The structure of $[(\text{Pb}_2\text{I}_5^-)(\text{L-H}^+)]_n$ chain is shown in Fig.1. The crystal packing diagram of the title compound is revealed in Fig.2.

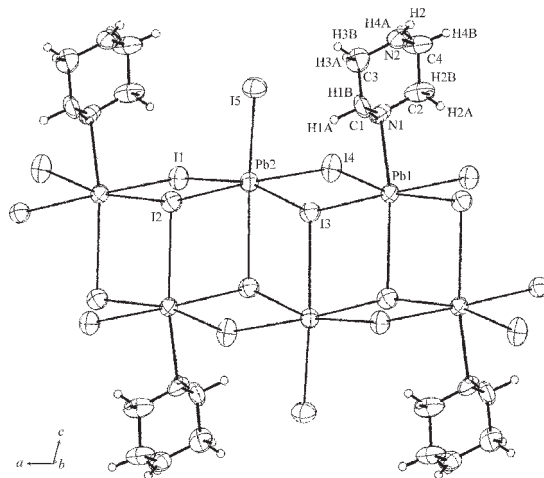


Fig.1 Structure of $(\text{Pb}_2\text{I}_5^-)(\text{L-H}^+)$ chain

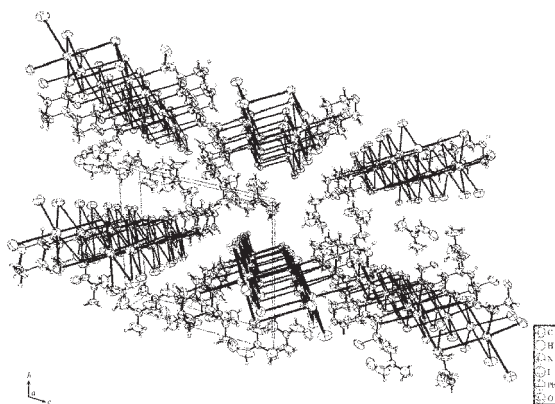


Fig.2 Packing diagram of title compound

There are two kinds of coordination environment of Pb(II) ions in each repeated unit $(\text{Pb}_2\text{I}_5^-)(\text{L-H}^+)$. The coordination number of Pb(2) is six and the $\text{Pb}(2)\text{I}_6$ unit forms a distorted octahedron coordination geometry. Pb(1) ion also has coordination number of six, but

Table 1 Selected bond lengths (nm) and bond angles ($^\circ$)

Bond	Dist.	Bond	Dist.	Bond	Dist.
Pb(1)-N(1)	0.2632(10)	Pb(1)-I(4)	0.310 88(13)	Pb(1)-I(1)	0.321 00(14)
Pb(1)-I(3)	0.324 53(14)	Pb(1)-I(2)a	0.330 85(13)	Pb(1)-I(2)b	0.342 56(16)
Pb(2)-I(5)	0.304 91(15)	Pb(2)-I(1)c	0.321 80(12)	Pb(2)-I(4)	0.323 80(14)
Pb(2)-I(2)	0.325 31(14)	Pb(2)-I(3)	0.328 07(13)	Pb(2)-I(3)b	0.34253(16)
I(1)-Pb(2)a	0.321 80(12)	I(2)-Pb(1)c	0.330 85(13)	I(2)-Pb(1)b	0.342 56(16)
I(3)-Pb(2)b	0.342 53(16)	O(1)-C(8)	0.121(2)	O(2)-C(5)	0.122(3)
N(1)-C(2)	0.141(2)	N(1)-C(1)	0.145 5(17)	N(2)-C(3)	0.145 2(18)
N(2)-C(4)	0.147 6(18)	C(2)-C(4)	0.156 1(19)	N(3)-C(8)	0.137 9(19)
N(3)-C(9)	0.142(3)	N(3)-C(10)	0.144(2)	N(4)-C(5)	0.124(3)
N(4)-C(6)	0.134(2)	N(4)-C(7)	0.136(3)	C(1)-C(3)	0.151 8(19)
Bond	Angle	Bond	Angle	Bond	Angle
N(1)-Pb(1)-I(4)	83.2(2)	N(1)-Pb(1)-I(1)	95.6(3)	I(4)-Pb(1)-I(1)	87.36(3)
N(1)-Pb(1)-I(3)	86.0(3)	I(4)-Pb(1)-I(3)	92.64(3)	I(1)-Pb(1)-I(3)	178.30(3)
N(1)-Pb(1)-I(2)a	88.0(2)	I(4)-Pb(1)-I(2)a	168.15(3)	I(1)-Pb(1)-I(2)a	85.62(3)
I(3)-Pb(1)-I(2)a	94.66(3)	N(1)-Pb(1)-I(2)b	171.5(2)	I(4)-Pb(1)-I(2)b	94.10(4)
I(1)-Pb(1)-I(2)b	92.30(4)	I(3)-Pb(1)-I(2)b	86.01(4)	I(2)a-Pb(1)-I(2)b	95.70(4)
I(5)-Pb(2)-I(1)c	98.06(4)	I(5)-Pb(2)-I(4)	85.87(5)	I(1)c-Pb(2)-I(4)	98.10(3)
I(5)-Pb(2)-I(2)	96.27(4)	I(1)c-Pb(2)-I(2)	86.41(3)	I(4)-Pb(2)-I(2)	174.70(3)
I(5)-Pb(2)-I(3)	95.89(4)	I(1)c-Pb(2)-I(3)	164.46(3)	I(4)-Pb(2)-I(3)	89.67(3)
I(2)-Pb(2)-I(3)	85.30(3)	I(5)-Pb(2)-I(3)b	176.88(3)	I(1)c-Pb(2)-I(3)b	84.29(4)
I(4)-Pb(2)-I(3)b	91.78(4)	I(2)-Pb(2)-I(3)b	85.89(4)	I(3)-Pb(2)-I(3)b	82.03(4)
Pb(1)-I(1)-Pb(2)a	95.22(3)	Pb(2)-I(2)-Pb(1)c	92.69(3)	Pb(2)-I(2)-Pb(1)b	93.95(4)
Pb(1)c-I(2)-Pb(1)b	84.30(4)	Pb(1)-I(3)-Pb(2)	87.26(3)	Pb(1)-I(3)-Pb(2)b	94.09(4)
Pb(2)-I(3)-Pb(2)b	97.97(4)	Pb(1)-I(4)-Pb(2)	90.36(3)	C(2)-N(1)-C(1)	111.0(10)
C(2)-N(1)-Pb(1)	109.0(8)	C(1)-N(1)-Pb(1)	114.9(8)	C(3)-N(2)-C(4)	110.8(11)
C(3)-N(2)-H(2)	124.6	C(4)-N(2)-H(2)	124.6	C(8)-N(3)-C(9)	117.8(16)
C(8)-N(3)-C(10)	119.4(16)	C(9)-N(3)-C(10)	122.8(17)	C(5)-N(4)-C(6)	124.7(19)
C(5)-N(4)-C(7)	115(2)	C(6)-N(4)-C(7)	120(2)	N(1)-C(1)-C(3)	113.2(12)
N(1)-C(2)-C(4)	113.9(13)	N(2)-C(3)-C(1)	111.3(11)	O(1)-C(8)-N(3)	124.6(16)
N(2)-C(4)-C(2)	110.8(11)	O(2)-C(5)-N(4)	122(2)		

Symmetry transformations used to generate equivalent atoms: a: $x+1, y, z$; b: $-x, -y+1, -z+2$; c: $x-1, y, z$.

five of which are linked with I atoms and the rest one is linked with N atom from piperazine. The coordination geometry of $\text{Pb}(1)\text{NI}_5$ is also a distorted octahedron. The $\text{Pb}(2)\text{I}_6$ unit connects with $\text{Pb}(1)\text{NI}_5$ unit by sharing with the same edge to form a structure unit of $\text{Pb}_2\text{I}_9(\text{L}-\text{H}^+)$. Each $\text{Pb}_2\text{I}_9(\text{L}-\text{H}^+)$ unit connect with adjacent unit by sharing two same edges to form a double infinite chain.

The atom distance of Pb (1)-I ranges from 0.310 88(13) nm to 0.342 65(16) nm, with an average value of 0.324 81(14) nm. The distances of Pb(2)-I range from 0.304 91(15) nm to 0.342 53(16) nm, with an average value of 0.319 88(1) nm. These values are

slightly longer than the Pb-I distance (0.304 2~0.313 4 nm) of $[\text{Bu}_3\text{N}(\text{CH}_2)_4\text{NBu}_3]_2[\text{Pb}_3\text{I}_{10}]^{[7]}$ and generally equal to that in $(\text{C}_{12}\text{H}_{14}\text{N}_2)\text{Pb}_2\text{I}_6^{[8]}$ (0.321 4(1) to 0.324 9(1) nm). The longer bond distance might attribute to the smaller space volume of piperazine, which lead to more relax packing of inorganic moiety. The distance of Pb(1)-N(1) is 0.263 3(11) nm, which is slightly longer than the accepted strong Pb-N bonds within 0.024 0~0.026 0 nm^[9]. The angel of N(1)-Pb(1)-I range from 83.2(2) $^\circ$ to 95.6(3) $^\circ$. The angels of I(5)-Pb(2)-I range from 85.30(3) $^\circ$ to 178.30(3) $^\circ$, indicating that tetragonal pyramid is distorted. The position of the H^+ ion can be extracted from the fact that there is one

nitrogen atom in each cation has significantly longer C-N distance than other ones. The nitrogen atoms N(2) clearly has longer C-N distances in this case (Table 1), thus indicating that it is protonated^[10].

Free solvent molecules DMF are also found in the crystal, which fill up the interstice of shell frame to stabilize the structure. From the Fig.1 we also can see that the structure of piperazine is chair configuration.

As the formal oxidation state of lead is +2, the 6s orbital is populated by a pair of non-bonding electrons. The presence of the lone pair generally results in a non-spherical charge distribution around lead cations in solids. And furthermore, to a lowering of the symmetry of the co-ordinate of the negative ions around them. It has previously been suggested that metal-ligand distances are shorter in lead complexes where the lone pair is stereochemically active^[8].

Compared with other reported series compound of $\text{PbX}_2(\text{L})$, such as $\text{PbI}_2(\text{bpy})$ ^[11], $\text{PbI}_2(\text{phen})$ ^[12], $\text{PbI}_2(3\text{-MeC}_5\text{H}_4\text{N})_2$ ^[13], the worth mentioned character of our compound is that ligand(piperazine) not only coordinates with inorganic backbone, but also protonates to counterbalance the charges of inorganic chain.

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