研究简报

一种新颖有机-无机杂化配位聚合物 $[(C_{10}H_{16}N)_2(Pb_2I_6)\cdot 2DMF\cdot H_2O]_n$ 的自组装合成和晶体结构

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Self-Assembly and Crystal Structure of a Novel Inorganic-Organic Hybrid Coordination Polymer: $[(C_{10}H_{16}N)_2(Pb_2I_6)\cdot 2DMF\cdot H_2O]_n$

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A novel coordination polymer $[(C_{10}H_{16}N)_2(Pb_2I_6)\cdot 2DMF\cdot H_2O]_n$ ($C_{10}H_{16}N$=N-butyl-2-Methy-Pyridinium) was synthesized by the reaction of $Pb(NO_3)_2$ with $C_6H_{10}NI$ at room temperature in DMF solvent and structurally characterized by means of X-ray single diffraction. The title compound crystallizes in triclinic system, space group $P\bar{1}$ with a=1.123 7(2) nm, b=1.253 30(16) nm, c=0.808 00(12) nm, α=102.523(4)°, β=92.475(5)°, γ=95.712(10)°, V=1.102 9(3) nm^3, Z=1, D_c=2.470 Mg·m^{-3}, F(000)=738, chemical formula $C_{26}H_{48}N_4O_3Pb_2I_6$ and M_r=1 640.46, μ(Mo$K\alpha$)= 11.849 mm^{-1}, the final R=0.057 8 and wR=0.166 5 for 3 716 observed reflections with $I > 2\sigma(I)$. The title compound consists of cations ($[(C_{10}H_{16}N)^+]$) and anion chain(PbI_3^-),they are combined by static attracting forces in the crystal. DMF and H_2O locate between the organic and inorganic moiety. CCDC: 210812.

Keywords: **coordination polymers** **template synthesis** **lead iodide** **quaternary ammonium**

0 Introduction

Construction of low-dimensional organic-inorganic supramolecular arrays with novel properties represents new directions in solid-state chemistry[1,2]. Generally the physical properties of such low dimensional compounds differ from those of the parent compound. Our current research is focused on the synthesis of low-dimensional crystalline organic-inorganic mental iodides with the possibility of incorpo- ration unique properties associated with functional inorganic and organic moieties. Lead iodide and its low-dimensional compounds are of particular interests due to their significant excitonic, third-order nonlinear optical, ferroelectric and ferroelastic properties[3]. In these compounds, the organic moiety usually contain positively charged groups such as quaternary amonium, which serves to counterbalance the charge of the inorganic

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part and template the inorganic chain or layer. We aim at probing into the impact of organic quaternary ammonium cations on the structure of inorganic chain. Here we report the structure of a novel coordination polymer $[(C_{10}H_{16}N)_2[Pb_2I_6]\cdot 2DMF\cdot H_2O]_n$.

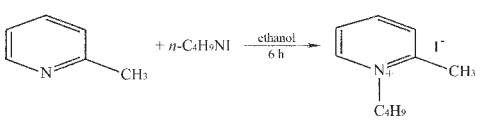
1 Experimental Section

1.1 Reagent and Physical Measurements

All chemicals were of regent grade quality obtained from commercial sources and used without further purification except for N-butyl-2-Methy-Pyridinium iodide, which was synthesized by following literature procedures[4]. IR spectra were carried out on a Nicolet Co. Magna-IR 750 spectrometer with KBr pellets in the 4 000~400 cm^{-1} regions. Fluorescence analysis was carried on a RF-540 instruments. TG-DTA analysis was carried out on Univer V2.4F TA Instruments.

1.2 Synthesis of $C_{10}H_{16}NI$ and $\{(C_{10}H_{16}N)_2[Pb_2I_6]\cdot(DMF\cdot H_2O)\}_n$

$C_{10}H_{16}NI$ (N-butyl-2-Methy-Pyridinium iodide) was prepared as following:



The title compound $[(C_{10}H_{16}N)_2(Pb_2I_6)\cdot 2DMF\cdot H_2O]_n$ was prepared by self-assembling reaction of $Pb(NO_3)_2$ and $C_{10}H_{16}NI$ (N-butyl-2-Methy-Pyridine iodide). $Pb(NO_3)_2$ (0.166 g, 0.5 mmol) was dissolved in 7 mL DMF solvent and then $C_{10}H_{16}NI$ (0.276 g, 0.8 mmol) was dissolved in the above solution. Stirred till it became clear, adjusted pH with 10% NaOH/DMF solution till pH=6.0 and then filtered. The colorless needle-like crystal (0.076 g, yield 45%) was obtained after putting the result solution at room temperature for three days. $C_{10}H_{16}NI(cm^{-1})$: ν(Ar-H)=3 049(s), δ_{as}(-CH_2-)=1 483(s), ν(C-N)=1 173(m). Fluorescence analysis: $\lambda^{(EX)}$=350 nm, $\lambda^{(EM)}$=690 nm. Heat weight analysis shows that the title compound is stable till 250 ℃.

1.3 Crystallographic Studies

A colorless needle single crystal with dimensions of 0.30 mm × 0.20 mm × 0.20 mm was selected and the data collection of the crystal was carried out on Rigaku Weissenbery IP diffractometer with Mo$K\alpha$ (λ= 0.071 069 nm). A total of 8 871 reflections were collected, of which 4 782 are independent in the range of $1.67° < \theta < 27.48°$ at 298 K and 3 716 are observed reflections with $I > 2\sigma(I)$. The corrections for Lp factor were applied. The structure was solved by direct method. All the non-hydrogen atoms were determined with successive difference Fourier syntheses. The structure was refined with anisotropic thermal parameters for non-hydrogen atoms by full-matrix least-squares on F^2 for 167 parameters. All calculations were performed on a computer with SHELX 97 program package[4,5]. The final R=0.057 8 and wR=0.166 5, $w=1/[\sigma^2(F_o^2)+(0.103\,6P)^2+0.000\,0P]$, where $P=(F_o^2+2F_c^2)/3$. $(\Delta/\sigma)_{max}$=0.000, S=1.029, $(\Delta\rho)_{max}$=2 680 e·nm^{-3}, $(\Delta\rho)_{min}$=−2 803 e·nm^{-3}.

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2 Results and Discussion

The selected bond lengths and bond angles are given in Table 1. Hydrogen bonds are listed in Table 2. The structure of $[PbI_3^-]_n$ chain is shown in Fig.1,the crystal packing diagram of title compound is revealed in Fig.2.

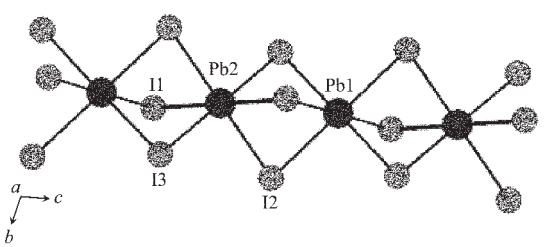

Fig.1 Structure of $[PbI_3^-]_n$ chain (along c-axis)

The whole crystal structure of polymer $[(C_{10}H_{16}N)_2(Pb_2I_6)\cdot 2DMF\cdot H_2O]_n$ consists of organic moiety and inorganic moiety. The inorganic moiety is a infinite chain of PbI_3^-. As shown in Fig.1 the coordination geometry of each Pb(Ⅱ) ion is a slightly distorted octahedral, adjacent units share the same face to form infinite chain. All the Pb atoms have the same coordination environment, in which Pb is six coordination, and I is μ-2. The octahedral is distorted because of the

Table 1　Selected Bond Lengths (nm) and Bond Angles (°)

bond	dist.	bond	dist.	bond	dist.
I(1)-Pb(1)	0.322 52(8)	I(1)-Pb(2)	0.324 34(9)	I(2)-Pb(2)	0.322 56(8)
I(2)-Pb(1)	0.323 73(9)	I(3)-Pb(2)	0.320 67(8)	I(3)-Pb(1)#1	0.323 11(9)
Pb(1)-I(1)#2	0.322 52(8)	Pb(1)-I(3)#3	0.323 11(9)	Pb(1)-I(3)#4	0.323 11(9)
Pb(1)-I(2)#2	0.323 74(9)	Pb(2)-I(3)#4	0.320 67(8)	Pb(2)-I(2)#4	0.322 56(8)
Pb(2)-I(1)#4	0.324 34(9)	N(1)-C(1)	0.135 9(15)	N(1)-C(5)	0.136 5(18)
N(1)-C(7)	0.149 0(16)	C(1)-C(2)	0.136 8(17)	C(1)-C(6)	0.145 3(19)
C(2)-C(3)	0.141(2)	C(3)-C(4)	0.143(3)	C(4)-C(5)	0.140(2)
C(7)-C(8)	0.150 2(17)	C(8)-C(9)	0.151(2)	C(9)-C(10)	0.149(3)
N(2)-C(11)	0.132(2)	N(2)-C(12)	0.147(3)	N(2)-C(13)	0.149(4)
O(1)-C(11)	0.126(3)	O(1)-OW	0.276(4)	O(1)-OW#5	0.277(5)
OW-OW#5	0.275(7)	OW-O(1)#5	0.277(5)	OW-H(101)	0.095(4)
OW-H(102)	0.088(4)				
bond	angle	bond	angle	bond	angle
Pb(1)-I(1)-Pb(2)	77.30(2)	Pb(2)-I(2)-Pb(1)	77.379(19)	Pb(2)-I(3)-Pb(1)#1	77.74(2)
I(1)#2-Pb(1)-I(1)	180.0	I(1)#2-Pb(1)-I(3)#3	86.00(2)	I(1)-Pb(1)-I(3)#3	94.00(2)
I(1)#2-Pb(1)-I(3)#4	94.00(2)	I(1)-Pb(1)-I(3)#4	86.00(2)	I(3)#3-Pb(1)-I(3)#4	180.00(3)
I(1)#2-Pb(1)-I(2)	96.36(2)	I(1)-Pb(1)-I(2)	83.64(2)	I(3)#3-Pb(1)-I(2)	95.01(2)
I(3)#4-Pb(1)-I(2)	84.99(2)	I(1)#2-Pb(1)-I(2)#2	83.64(2)	I(1)-Pb(1)-I(2)#2	96.36(2)
I(3)#3-Pb(1)-I(2)#2	84.99(2)	I(3)#4-Pb(1)-I(2)#2	95.01(2)	I(2)-Pb(1)-I(2)#2	180.0
I(3)-Pb(2)-I(3)#4	180.00(2)	I(3)-Pb(2)-I(2)	94.41(2)	I(3)#4-Pb(2)-I(2)	85.59(2)
I(3)-Pb(2)-I(2)#4	85.59(2)	I(3)#4-Pb(2)-I(2)#4	94.41(2)	I(2)-Pb(2)-I(2)#4	180.00(2)
I(3)-Pb(2)-I(1)#4	86.11(2)	I(3)#4-Pb(2)-I(1)#4	93.89(2)	I(2)-Pb(2)-I(1)#4	96.46(2)
I(2)#4-Pb(2)-I(1)#4	83.54(2)	I(3)-Pb(2)-I(1)	93.89(2)	I(3)#4-Pb(2)-I(1)	86.11(2)
I(2)-Pb(2)-I(1)	83.54(2)	I(2)#4-Pb(2)-I(1)	96.46(2)	I(1)#4-Pb(2)-I(1)	180.00(2)
C(1)-N(1)-C(5)	121.4(11)	C(1)-N(1)-C(7)	120.5(11)	C(5)-N(1)-C(7)	118.1(11)
N(1)-C(1)-C(2)	118.5(12)	N(1)-C(1)-C(6)	120.3(12)	C(2)-C(1)-C(6)	121.2(12)
C(1)-C(2)-C(3)	122.5(13)	C(2)-C(3)-C(4)	118.6(15)	C(5)-C(4)-C(3)	116.1(16)
N(1)-C(5)-C(4)	122.7(15)	N(1)-C(5)-H(5)	118.6	N(1)-C(7)-C(8)	111.5(10)
C(7)-C(8)-C(9)	112.2(13)	C(10)-C(9)-C(8)	115.9(16)	C(11)-N(2)-C(12)	116.7(17)
C(11)-N(2)-C(13)	121(2)	C(12)-N(2)-C(13)	122(2)	C(11)-O(1)-OW	156(2)
C(11)-O(1)-OW#5	144(2)	OW-O(1)-OW#5	59.8(14)	O(1)-C(11)-N(2)	118(2)
OW#5-OW-O(1)	60.3(15)	OW#5-OW-O(1)#5	60.0(16)	O(1)-OW-O(1)#5	120.2(14)
OW#5-OW-H(101)	43.0(15)	O(1)-OW-H(101)	18.0(18)	O(1)#5-OW-H(101)	103(3)
OW#5-OW-H(102)	51.7(18)	O(1)-OW-H(102)	112(3)	O(1)#5-OW-H(102)	8.3(17)
H(101)-OW-H(102)	94(3)				

Symmetry transformations used to generate equivalent atoms: #1: $x, y, z-1$; #2: $-x, -y, -z+1$; #3: $x, y, z+1$; #4: $-x, -y, -z$; #5: $-x+1, -y+1, -z$.

templating of the organic quaternary ammonium cation. But in the structure of $(C_{12}H_{14}N_2)Pb_2I_6$[6], which also has PbI_3^- chain, six PbI_3^- units have different coordination type, including ideal octahedral symmetry, distorted octahedral and trigonal prismatic coordination. Three different coordination types are alternative to from infinite chain. And in the structure of $[Bu_3N(CH_2)_4NBu_3]_2$ $[Pb_3I_{10}]$[7], Pb has two coordination types, which are distorted octahedral and square pyramidal. So our compound is different from other similar compounds.

There are two independent Pb in each unit. The

Table 2 Hydrogen Bonds in the Title Compound (distances in nm, angles in °)

D-H	*d*(D-H)	*d*(H···A)	∠DHA	*d*(D···A)
OW–H10···O1	0.094 9	1.879	153.06	2.759
OW–H10···O1[a]	0.087 9	1.901	167.87	2.767

a: $-x+1, -y+1, -z$.

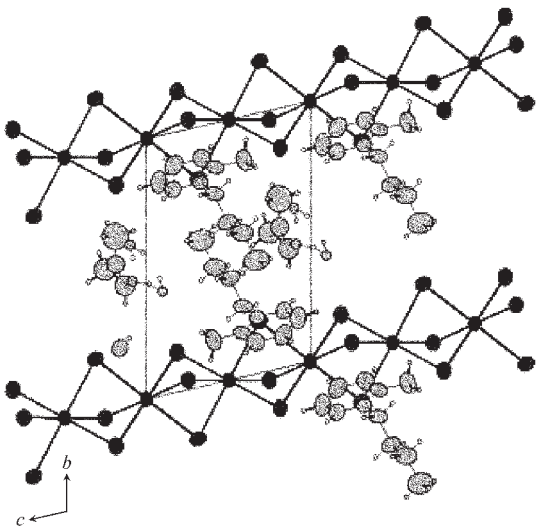

Fig.2 Packing diagram of title compound (along *a*-axis)

bond distances around Pb(1) is from 0.322 52(8) nm to 0.323 74(9) nm, with an average value of 0.323 12 nm. The bond distances around Pb(2) is from 0.320 67(8) nm to 0.324 34 (9) nm, with an average of 0.322 94 nm. These values are slightly longer than the Pb-I distance (0.304 2~0.313 4 nm) of $[Bu_3N(CH_2)_4NBu_3]_2[Pb_3I_{10}]$[7] and generally equal to that in $(C_{12}H_{14}N_2)Pb_2I_6$[6] (0.321 4(1) to 0.324 9(1) nm). The longer bond distance might attribute to the smaller space volume of $C_{10}H_{16}N^+$, which lead to more relax packing of inorganic moiety.

The bond angles around Pb(1) range from 86.00(2)° to 96.36(2)°, and I(1)-Pb(1)-I(1)#2 is 180.00(3)°, I(3)#3-Pb(1)-I(3)#4 is 180.0(3)°. The bond angle around Pb(2) range from 83.59(2)° to 96.46(2)°, and I(2)#4-Pb(2)-I(2) is 180.00(2)°, I(1)-Pb(2)-I(1)#4 is 180.00(2)°. The above angles deviate from ideal octahedral values (90° and 180°).

Neutral molecule DMF and H_2O also stack in the crystal. They are surrounded by the organic quaternary ammonium and attract with each other by H-bond. H-bonds are listed in Table 2.

From Fig.2 we can see that the neighboring PbI_3^- chains act as "cavities" wherein organic cations and neutral molecules lie sandwiched between two adjacent chains. They are combined by non-covalent interaction-static attracting forces to form so-called organic-inorganic hybrid structure.

References

[1] Ouahab L. *Chem. Mater.*, **1997**,**9**,1909.

[2] Mitzi D. B., Wang S., Field C. A., Chess C. A., Guloy A. M. *Science*, **1985**,**267**,1473.

[3] Calabrese J., Jones N. L., Harlow R. L., Herron N., Thorn D. L., Wang Y. J. *J. Am. Chem. Soc.*, **1991**,**113**,2328.

[4] HUANG Shu(黄 枢), XIE Ru-Gang(谢如刚) *Manual for Organic Synthesis Reagent Preparation*(有机合成试剂制备手册), Chengdu: Sichuan University Press, **1988**.

[5] Sheldrick G. M. *SHEKX*97, *Program for Crystal Structure Solution*, University of Gottingen, Germany, **1997**.

[6] Sheldrick G. M. *SHEKX*97, *Program for Crystal Structure Refinement*, University of Gottingen, Germany, **1997**.

[7] Tang Z., Culoy A. M. *J. Am. Chem. Soc.*, **1999**,**121**,452.

[8] Krautscheid H., Vielsack F. *J. Chem. Soc., Dalton Trans.*, **1999**,2731.