A New Coordination Mode of 5-Aminoisophthalate in Lead Coordination Polymers: Synthesis, Structure, and Photoluminescence Properties

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A new lead coordination polymer $[Pb(aip)]_n$ (H_2aip = 5-aminoisophthalic acid) was synthesized and characterized by IR, elemental and X-ray single-crystal analyses. X-ray crystallographic study of this complex revealed that H_2aip ligand adopts a new coordination mode different from any reported modes in the title complex. The thermogravimetric experiment was carried out to examine the thermal stability, and the photoluminescence property of the title complex was investigated.

INTRODUCTION

In recent years, the chemistry of the crystal engineering of coordination polymeric frameworks stems has been actively investigated [1], due to their potential application as new functional solid materials and their intriguing architectures and topologies [2]. Of the reported complexes, many are based upon polyfunctional organic ligands containing both carboxylate and amino groups, such as 2-aminoterephthalic acid [3], 3-aminobenzoic acid [4] and 5-aminoisophthalic acid [5]. 5-Aminoisophthalic acid (H_2aip) is a rigid triangular ligand similar to 1,3,5-benzenetricarboxylate (H_3BTC). The carboxylate group at the fifth carbon atom of H_3BTC is substituted by one amino group in H_2aip; however, H_2aip keeps the triangle-shape of H_3BTC. Though the amino group shows a single coordination mode, the relatively weaker coordination ability of amino groups make it possible to arbitrarily participate in the coordination to metal cations. This characteristic of the amino group provides more possibility for the coordination of H_2aip, which shows rich coordination

modes [6]. Thus, H_2aip has been widely used as a ligand in the assembly of coordination polymers, in which the following four coordination modes of two carboxylate groups have been observed with the amino group participating coordination: [7] (1) one carboxylate group adopts chelate mode, and the other adopts bisdentate; (2) one carboxylate group shows chelate, and the other shows unidentate; (3) two carboxylate groups both adopt unidentate mode. (4) One carboxylate group exhibits unidentate mode, and the other doesn't coordinate to metal ions (summarized in Scheme 1 (b-h)). According to the combination of the coordination modes of carboxylate groups and amino group, it is possible to obtain more coordination modes of H_2aip.

It has been reported that metal ions and synthesis method are two important factors affecting coordination modes of H_2aip ligand [8]. Compared with the transition and lanthanide metal coordination polymers of H_2aip [9], less effort has been devoted to its main group metal polymers, except $(C_8H_{13}CaNO_8)n(H_2O)1.33n$ [10] and $C_{32}H_{38}N_4Na_2O_{22}$ [11]. To obtain new coordination modes of H_2aip and synthesize interesting compounds, our research has focused on the synthesis of coordination complexes with main group metals.

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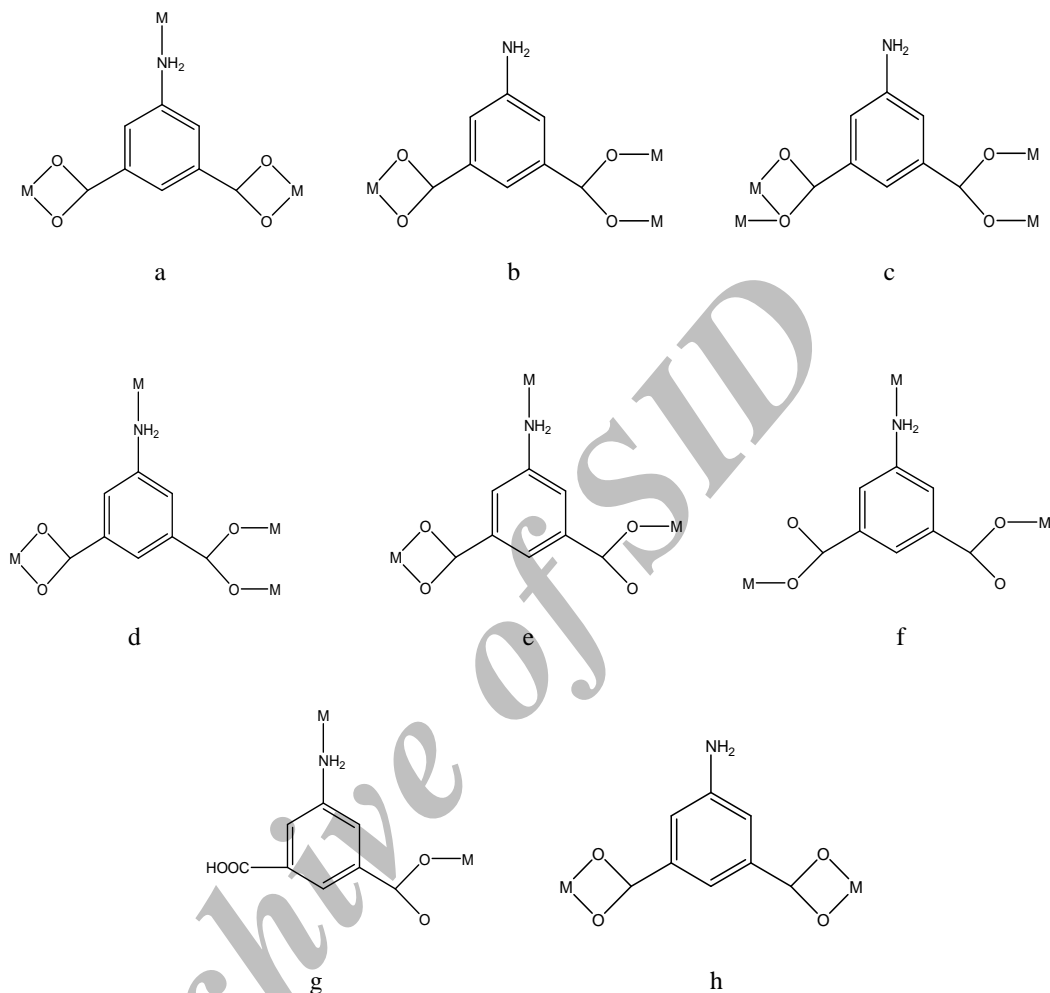
Scheme 1. Coordination modes of 5-aminoisophthalate ligand

Among main group metals, lead has attracted special attention, owing to not only their biological activities [12], but also their large radius, variable stereochemical activity and flexible coordination environment, which provide unique opportunities for obtaining new coordination modes of H_2aip [13]. To the best of our knowledge, no structural data on any lead-aip compounds have been presented though many H_2aip complexes have been reported.

In this study, we adopted the hydrothermal method to synthesize coordination polymers and obtain single-crystals, because it is a well-known technique for the construction of extended structures, such as zolites, organic/inorganic hybrid materials and metastable compounds in crystalline form [14].

For hydrothermal method, reaction temperature is very important. In the synthesis of the title compound, we chose 200 °C as the reaction temperature, because higher temperature may favor the coordination of amino group and richer coordination modes of carboxylate groups [13b]. Herein, we report the hydrothermal synthesis, structure, thermal analysis and luminescent property of compound **1** ([Pb(aip)]$_n$), where H_2aip adopts a new coordination mode.

EXPERIMENTAL

General Methods and Materials

All reagent-grade chemicals were commercially available

and used without further purification. The FT-IR spectra were obtained using a Perkine Elmer Spectrum and one Fourier transform infrared spectrometer (KBr pellet). Elemental analysis for C, H and N was carried out using a PerkineElmer 2400II instrument. The fluorescence spectral analysis was conducted on a PerkineElmer LS55 luminescence spectrometer with a xenon lamp as the light source. Thermogravimetric analysis (TGA) was performed using Shimadzu TGA-7 apparatus from ambient temperature (25 ℃) to 800 ℃, with heating rate of $20°$ min^{-1}, in a nitrogen atmosphere. The single-crystal X-ray data of **1** was collected using a Rigaku Mercury CCD area detector (Mo Kα, λ = 0.71073 Å), at 173 K. The structure was solved by direct methods [15] and refined on F^2 by fullmatrix least-squares using the SHELXTL-97 program package [16]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of C atoms were positioned geometrically and refined using a riding model. The hydrogen atoms bonded to N atoms were located from Fourier difference maps.

Synthesis of [Pb(aip)]ₙ, 1

A mixture of $Pb(CH_3COO)_2.3H_2O$ (0.033 g, 0.14 mmol) and 5-aminoisophthalic acid (0.024 g, 0.13 mmol) in 15 ml distilled water was sealed in a Teflon-lined Stainless autoclave and heated at 200 °C for 15 h under autogenous pressure, and then cooled to room temperature. Colorless block crystals were obtained with a yield of ca. 49%. Anal. Calcd. for $C_8H_5NO_4Pb$ (386.33): C, 24.85; H, 1.29; N, 3.62. Found: C, 25.01; H, 1.17; N, 3.60. IR data (KBr pellet, ν[cm⁻¹]): 3250 m, 1580 s, 1370 vs, 1250 m, 980 m, 750 m, 625 w.

RESULTS AND DISCUSSION

Single-crystal X-ray diffraction study revealed that the compound **1** crystallizes in triclinic system with *P-1 s*pace group. The crystallographic data and experimental details of the structure determination are listed in Table 1. In **1**, the amino group and two carboxylate groups, all participate in coordination to metal centers, where both carboxylate groups adopt chelate coordination modes (Scheme 1a). As far as we know, it is a new coordination mode of H_2aip, and has not been reported before. The coordination ability of amino group is weaker than that of carboxylate group. However, Pb ions

prefer to bind to groups containing nitrogen atoms according to Nierboer and Richardson's classification of metal ions [17]. This characteristic of Pb ions provides more opportunity for the coordination of amino group to metal ions, which is in favor of the simultaneous coordination of amino group and carboxylate group of aip^{2-}. That is why we chose Pb as metal centers to study the reaction with H_2aip. When we adopted higher reaction temperature, both carboxylate groups showed chelate coordination modes with the coordination of amino group, which were different from any reported modes.

As shown in Fig. 1, the Pb(IV) is coordinated by four O atoms from two different aip^{2-} (Pb(1)-O(1A) = 2.449(6), Pb(1)-O(2A) = 2.690(7), Pb(1)-O(3B) = 2.698(6) Pb(1)-O(4B) = 2.399(6) Å), one N atom from the third aip^{2-} (Pb(1)-N(1) = 2.531(7) Å), displaying a distorted square-pyramidal coordination geometry. Thus, each Pb(IV) is coordinated by three aip^{2-}, and each aip^{2-} bridges three metal centers in compound **1**. Through sharing metal centers, three aip^{2-} connect three Pb(IV) to a metal-organic ring. Two of the three aip^{2-} provide one carboxylate group and one amino group to each metal-organic ring, respectively, and the third aip^{2-} offers two carboxylate groups to the ring (Fig. 2). The left carboxylate groups and amino group of these three aip^{2-} are parts of other metal-organic rings, and extend the ring to a 2D network at [011] plane. Interestingly, the 2D networks look like staircases, where Pb-N bonds connect separate levels as supporting structures. This is because each Pb(IV) center shows square-pyramidal coordination geometry, and the N atom occupies the vertex position.

Another interesting feature of compound **1** is that its 2D network is extended to a 3D supramolecular architecture by strong N-H…O hydrogen bonds, π⋯π interactions, and weak Pb…O interactions. As shown in Table 2 and Fig. 3, there are strong N-H…O hydrogen bonds of the amino group and the carboxyl group of aip^{2-} (N…O distance from 2.951-3.060 Å). Aside from the hydrogen bonds, the π…π interaction is another useful organizing force in supramolecular assembly. In **1**, the π…π interactions between the benzene rings of the nearest adjacent layers are 3.525 Å. Furthermore, two 2D layers are connected by weak Pb…O interactions with Pb…O distance 2.825 and 2.929 Å. Undoubtedly, the hydrogen bonds, π…π interactions and weak Pb…O interactions play important roles in the stabilization of the supramolecular architectures [9d].

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Table 1. Crystal Data and Structure Refinement Parameters for **1**

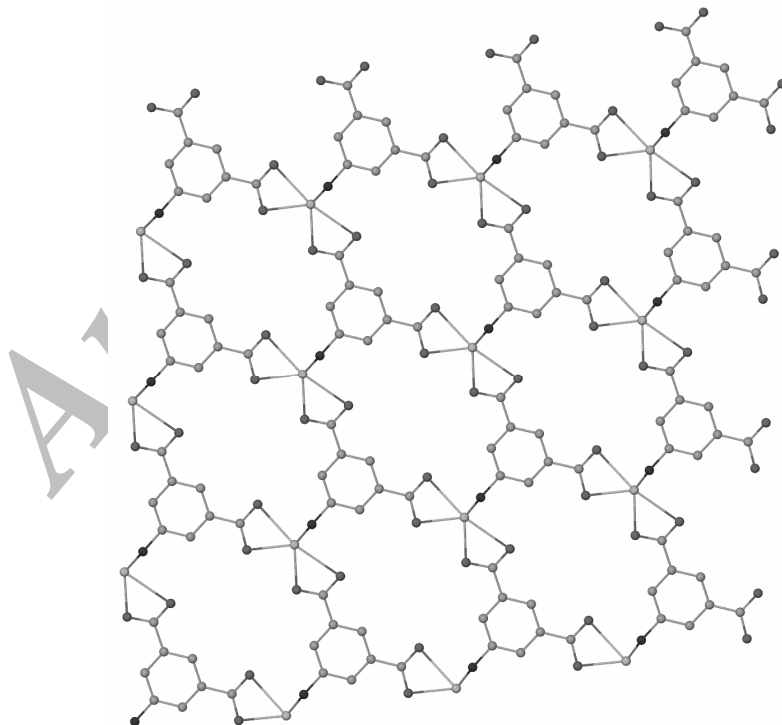| Compound	**1**
Empirical formula	$C_8H_5NO_4Pb$
T (K)	173(2)
λ (Å)	0.71073
Radiation	Molybdenum
Crystal system	Triclinic
F_w	386.33
Color	Colorless
Space group	*P*-1
a (Å)	6.843(3)
b (Å)	8.024(4)
c (Å)	8.086(4)
α (deg)	78.188(19)
β (deg)	69.101(16)
γ (deg)	82.33(2)
$V (Å^3)$	405.2(3)
Z	2
D [g cm^{-3}]	3.167
μ [mm^{-1}]	20.804
F (000)	348
Crystal size (mm)	$0.27 \times 0.18 \times 0.09$
$θ_{min}$, $θ_{max}$ (°)	2.60, 27.79
Reflections collected/unique	3177/1842 [R(int.) = 0.0361]
Completeness to theta = 27.49	98.9%
Data/restraints/parameters	1842/2/135
Goodness-of-fit on *F2*	1.073
final R_1, wR_2 [$I > 2σ(I)$]	0.0433, 0.1068
R1, wR2 (all data)	0.0446, 0.1081

In order to examine the thermal stability of the compound, thermal gravimetric (TG) analyses were carried out. The thermal gravimetric curve (Fig. 4) of compound **1** shows that it can be heated to 420 ℃ without any weight loss, which is consistent with the structure without any guest molecules and/or small coordinated molecules. When the temperature was higher than 420 ℃, it started to lose weight, which corresponds to the decomposition of framework. The weight loss was completed at 690 ℃, and the final residual weight was 61.9% (Calcd. 61.9%) corresponding to PbO_2. But for free H_2aip, it decomposes at 303 ℃ [18]. Upon coordination, the coordinated aip^{2-} is more stable than free H_2aip.

Based on the relevant reports, H_2aip exhibits a broad fluorescent emission centered on 450 nm with an excitation

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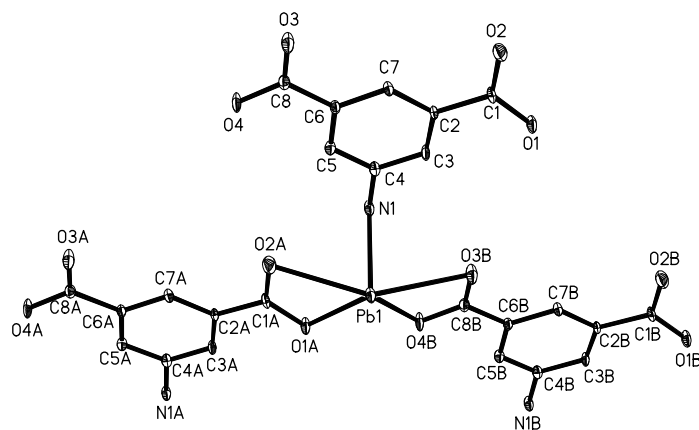
Fig. 1. The coordination environment of lead ions in compound **1** with the thermal ellipsoids at 30% probability level (all H atoms were omitted for clarity). Selected bond distances [Å] and angles [°]: Pb(1)-O(1A) 2.449(6), Pb(1)-O(2A) 2.690(6), Pb(1)-N(1), 2.531(7), Pb(1)-O(3B) 2.698(6), Pb(1)-O(4B) 2.399(6), O(1A)-Pb(1)-N(1) 89.8(2), N(1)-Pb(1)-O(2A) 71.7(2), N(1)-Pb(1)-O(3B) 74.9(2), O(4B)-Pb(1)-N(1) 85.0(2), O(4B)-Pb(1)-O(1A) 76.53(18), O(4B)-Pb(1)–O(2A) 120.7(2), O(1A)-Pb(1)-O(2B) 50.62(19), O(4B)-Pb(1)-O(3B) 51.06(18), O(1A)-Pb(1)-O(3B) 125.89(17), O(2A)-Pb(1)-O(3B) 146.3(2). Symmetry codes: A x,y,z-1; B x,y-1,z.

Fig. 2. The 2D layer structure of the compound **1** showing the linking of Pb(IV) ions through 5-aminoisophtha-late along the a-axis, all the hydrogen atoms are omitted for clarity.

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Table 2. Hydrogen Bonding Geometry (Å and °) for the Compound **1**

D-H	d(D-H)	d(H···A)	<DHA	d(D···A)	A
N1-H1A	0.899	2.227	137.30	2.951	O4 [-x+1, -y+2, -z]
N1-H1A	0.899	2.580	114.17	3.060	O2 [x, y, z-1]
N1-H1B	0.899	2.211	149.84	3.022	O1 [-x+1, -y+1, -z+1]
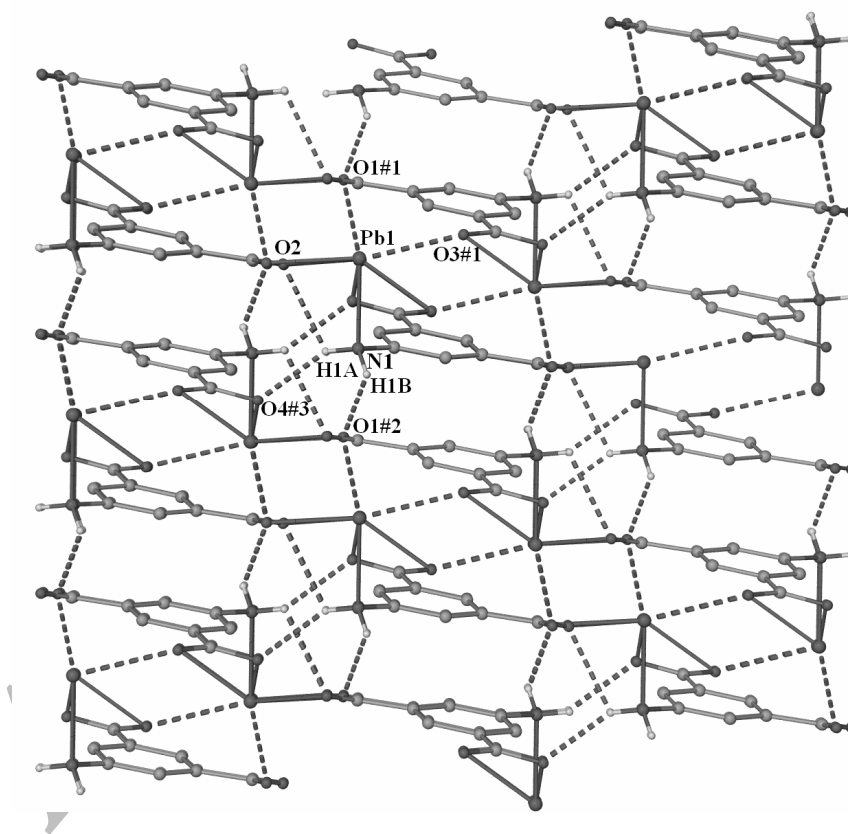
Fig. 3. 3D Supramolecular Network of Compound **1**.

maximum at 300 nm [5]. The solid-state emission spectrum of the complex at room temperature (Fig. 5) shows a red-shifted photoluminescence with emission at 488 nm (excited at 271 nm), which corresponds to the coordination of H_2aip to metal ions. The difference between the free ligand and the complex shows that the emission at 488 nm may have arisen from a ligand-to-metal charge transfer (LMCT).

CONCLUSIONS

Hydrothermal reaction of lead acetate with H_2aip gave rise to a 2D network $[Pb(aip)]_n$, where aip^{2-} adopts a new
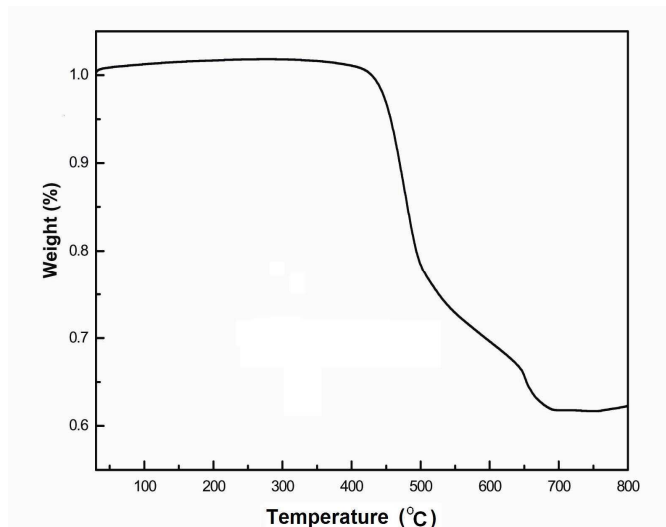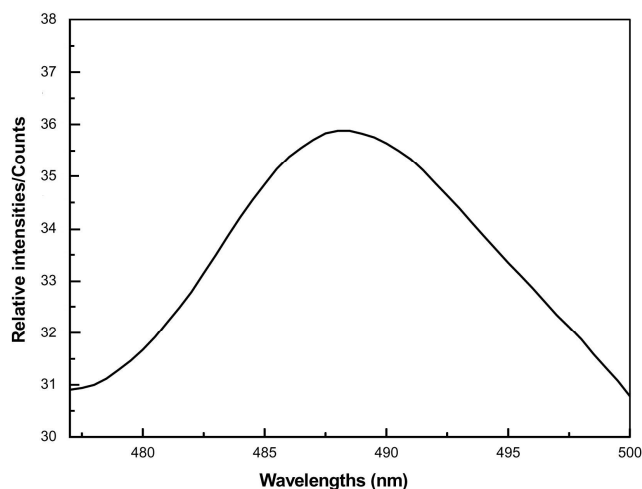
Fig. 4. TGA plots of the compound **1**.

Fig. 5. The emission spectra of compound **1** in the solid state at room temperature.

coordination mode. For obtaining new coordination mode of H_2aip, hydrothermal method with higher temperature and Pb centers with large radius, variable stereochemical activity and flexible coordination environment as well as the preference of binding to nitrogen atoms play important roles. Containing amino group, deprotonated carboxylate groups and benzene

ring, aip^{2-} may donate/accept hydrogen bonding as well as form $\pi \dots \pi$ interactions. All 2D networks in **1** are assembled into a 3-D supramolecular architecture via interlayer $\pi \dots \pi$ interactions, strong N-H…O hydrogen bonds and weak Pb…O interactions.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structure reported in the present paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication no. CCDC 749932. These data can be obtained free of charge upon application to CCDC, 12 UnionRoad, Cambridge CB21EZ, UK[fax (+44) 1223-336-033; email deposit@ccdc.cm.ac.uk.

ACKNOWLEDGMENTS

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