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A Novel 3D Lead(II) Organometallic Framework with Four Lead(II) Nuclei as a Secondary Building Unit: Synthesis and Characterization[1]

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Abstract—A new 3D layered compound, $[Pb_2(L)_2H_2O]_n$ (L is phenylmalonic acid) was hydrothermally synthesized and characterized by single-crystal X-ray diffraction. In the compound, lead has four coordination modes. The compound has formed a 2D surface shape structure through these coordinate modes with the ligand, and this 2D layer piles through C–H···π forms the 3D compound.

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INTRODUCTION

Recently, the design and synthesis of polymeric coordination network are of great interest in supramolecular chemistry owing to the realization of their potential for use as functional materials in catalysis, molecular recognition, separation, and nonlinear optics [1–5]. In this aspect, considerable progress has been made on the theoretical prediction and network-based approaches for controlling the topology and geometries of the networks to produce useful functional materials [6]. However, to predict the exact structures through controlling the factors that affect the framework formation is still a challenge. Therefore, systematic research on this topic is still very necessary for understanding the roles of the factors in the formation of metal coordination frameworks.

On the other hand, lead is a heavy toxic metal found in critical life cycles as a result of its widespread use in industry. The molecular mechanisms of lead toxicity are probably associated with several different types of proteins. Therefore, it has extensively been studied by using various techniques. As is known, the lead can exhibit a variable coordination number, structural diversities in lead complexes will inevitably occur, careful selection of suitable polyfunctional organic ligands is helpful for constructing novel metal coordination polymers [7–9]. In this work, the self-assembly of $Pb(NO_3)_2$, and phenylmalonic acid (**L**) under hydrothermal conditions generates a 3D lead(II) framework, $[Pb_2(L)_2H_2O]_n$ (**I**).

[1] The article is published in the original.

EXPERIMENTAL

Materials and measurements. All reagents were obtained from commercial sources and used without further purification. Elemental analyses (C, H, and N) were performed on a model Finnigan EA 1112 instrument. IR spectra were run as KBr pellets on a Nicolet IR-470.

Synthesis of I. A mixture of $Pb(NO_3)_2$ (0.3 mmol, 0.099 g), phenylmalonic acid (0.3 mmol, 0.056 g), and water (12 ml) was stirred for 30 min in air. The mixture was then transferred to a 23-ml Teflon reactor and kept at 120°C for 3 days under autogenous pressure, and then cooled to room temperature at a rate of 10.5°C/h, Colorless crystals of **I** were obtained, and washed with deionized water and absolute ethanol. The FT-IR main absorption bands are centered at 3449, 3061, 1556, 1517, 1450, 1411, 1385, 1248, 952, 825, 720, 695 cm^{-1}. The absence of IR bands at 1700 cm^{-1} indicates that the acetate groups are fully deprotonated [10]. In addition, the FT-IR spectra show characteristic bands of carboxylate groups at 1556 and 1517 cm^{-1} for the asymmetric stretching and at 1450 and 1411 cm^{-1} for symmetric stretching. The separations between ν_{as}(COO) and ν_s(COO) indicate the presence of bidentate coordination modes of the COO ligand [11].

For $C_{18}H_{14}O_9Pb_2$			
anal. calcd, %:	C, 27.40;	H, 1.78;	O, 18.26.
Found, %:	C, 27.35;	H, 1.80;	O, 18.30.

X-ray diffraction analysis. Data were collected on a Bruker Smart 100 CCD X-ray single-crystal diffractometer with MoK_α radiation (λ = 0.71073 Å) at 293 K. The structures were solved by a direct method using the SHELXL-97 package [12, 13]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms.

Table 1. Crystallographic data and details of the experiment and refinement of $[Pb_2(L)_2H_2O]_n$ complex

Parameter	Value
Formula weight, g/mol	788.67
Space group	$P\,2_1$
Crystal system	Monoclinic
Unit cell dimensions	
a, Å	12.8657(10)
b, Å	10.4443(8)
c, Å	14.6512(11)
β, deg	90.4800(10)
V, Å^3	1968.66(26)
Z	4
ρ_{calcd}, g cm^{-3}	2.661
μ_{Mo}, mm^{-1}	17.130
F(000)	1432
Crystal size, mm	0.43 × 0.31 × 0.23
θ range for data collection, deg	1.39 < θ < 25.34
Limiting indices	$-15 \le h \le 9$, $-12 \le k \le 12$, $-17 \le l \le 17$
Reflections collected/unique	10542/6963 (R_{int} = 0.0227)
Number of reflection with $I > 2\sigma(I)$	6464
Number of refined parameters	523
Completeness, %	99.9
Goodness-of-fit on F^2	0.997
Final R indices ($I > 2\sigma(I)$)	R_1 = 0.0283, wR_2 = 0.0595
R indices (all data)	R_1 = 0.0321, wR_2 = 0.0610
Residual electronic density (max/min), e Å^{-3}	233 and –0.950

Table 2. Selected bond lengths for structure **I***

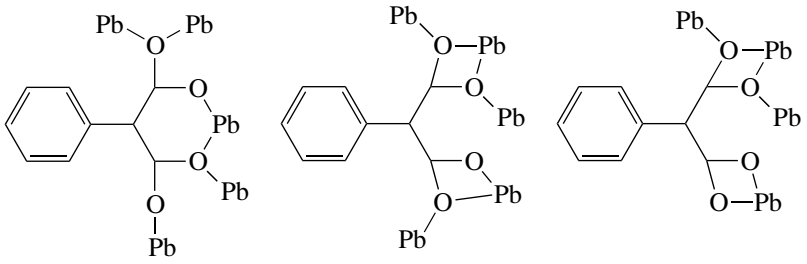
Bond	d, Å	Bond	d, Å
Pb(1)–O(2)$^{\#1}$	2.556(8)	Pb(1)–O(12)	2.568(8)
Pb(1)–O(11)	2.595(8)	Pb(1)–O(1)$^{\#2}$	2.616(8)
Pb(1)–O(8)	2.621(7)	Pb(1)–O(3)$^{\#2}$	2.732(9)
Pb(1)–O(13)	2.796(9)	Pb(1)–O(16)	2.822(10)
Pb(2)–O(4)	2.495(8)	Pb(2)–O(16)$^{\#3}$	2.515(8)
Pb(2)–O(15)$^{\#3}$	2.612(8)	Pb(2)–O(12)$^{\#4}$	2.706(9)
Pb(2)–O(5)	2.708(8)	Pb(2)–O(6)$^{\#4}$	2.725(8)
Pb(2)–O(7)	2.816(7)	Pb(3)–O(6)$^{\#4}$	2.389(7)
Pb(3)–O(7)	2.398(8)	Pb(3)–O(9)$^{\#4}$	2.462(7)
Pb(3)–O(10)$^{\#4}$	2.608(10)	Pb(3)–O(11)	2.800(11)
Pb(4)–O(3)$^{\#4}$	2.380(9)	Pb(4)–O(14)	2.428(8)
Pb(4)–O(2)$^{\#2}$	2.543(7)	Pb(4)–O(1w)	2.583(7)
Pb(4)–O(13)	2.709(9)	Pb(4)–O(13)	2.876(8)

* Symmetric codes: $^{\#1}$ $-x, y - 1/2, -z$; $^{\#2}$ $x - 1, y, z$; $^{\#3}$ $x + 1, y, z$; $^{\#4}$ $-x, y + 1/2, -z$.

Hydrogen atoms were located from difference Fourier maps. The crystal data and structure refinement are given in Table 1. Selected bond lengths (Å) and bond angles (deg.) are listed in Table 2. The coordinates of the atoms and the thermal parameters were deposited with the Cambridge Crystallographic Data Center (no. 716732; deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

In **I** (Fig. 1), the Pb–O(COO) bond distances 2.389(7)–2.732(9) Å are imited in the typical Pb–O bond in range of 2.255–2.734 Å [14], and carboxylate groups present three different kinds of coordination modes (**A**, **B**, and **C**) are given bellow:



(A) (B) (C)

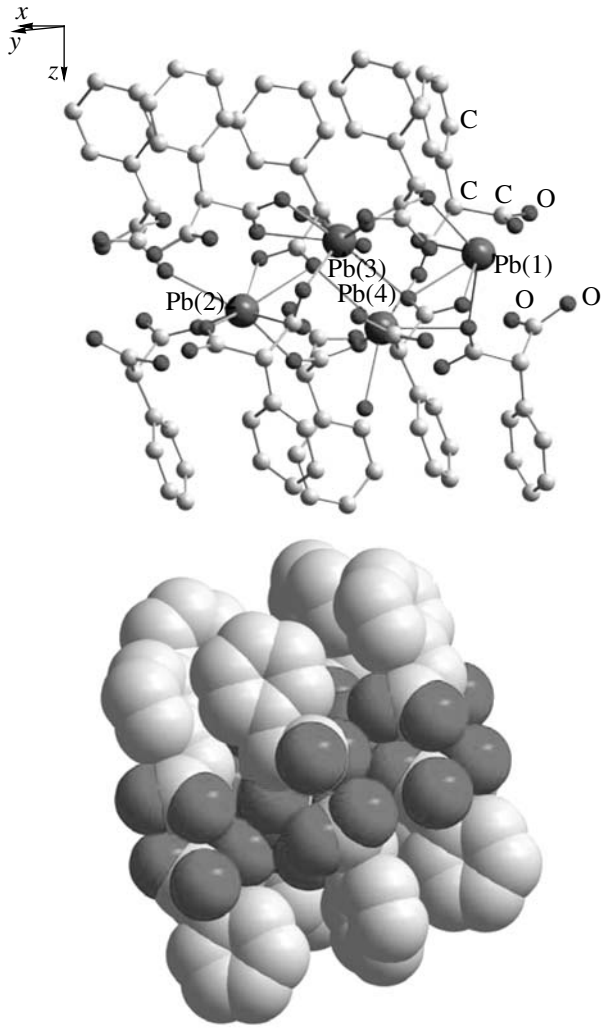


Fig. 1. Molecular structure of showing the local geometry around the metal center and ligand (H atoms were omitted for clarity).

However, if the weak Pb–O interactions in a range of 2.78–3.05 Å are considered [15], Pb(1) can be described as eight-coordinated, Pb(2) can be described as seven-coordinated, Pb(3)—as five-coordinated, and Pb(4)—as six-coordinated. One unit contains 25 Pb–O(COO) bonds and additionally one Pb–O(H_2O) bond (Fig. 2).

The Pb(1) atom is coordinated to eight carboxylate oxygen atoms from six L ligands: four carboxylate oxygen atoms from three L ligands in mode A, two carboxylate oxygen atoms from two L ligands in mode B, two carboxylate oxygen atoms from one L ligand in mode C. The Pb(2) atom is coordinated to seven carboxylate oxygen atoms from five L ligands: among them, four carboxylate oxygen atoms from three L ligands in mode A, two carboxylate oxygen atoms from one L ligands (in mode B), one carboxylate oxygen atoms from one L ligands in mode C. The Pb(3) atom is coordinated to five carboxylate oxygen atoms from four L ligands: among them, three carboxylate oxygen atoms from two L ligands in mode C, and the others are in mode A. The Pb(4) atom is coordinated to an oxygen atom from water and five carboxylate oxygen from four L ligands: among them, two carboxylate oxygen atoms from one L ligand in mode B, two carboxylate oxygen atoms from two L ligands in mode A, one carboxylate oxygen atoms from a L ligand in mode C. All the Pb(II) centers are still in the hemidirected geometry, indicating that the lone electron pairs of the Pb(II) centers are all stereochemically active [16, 17].

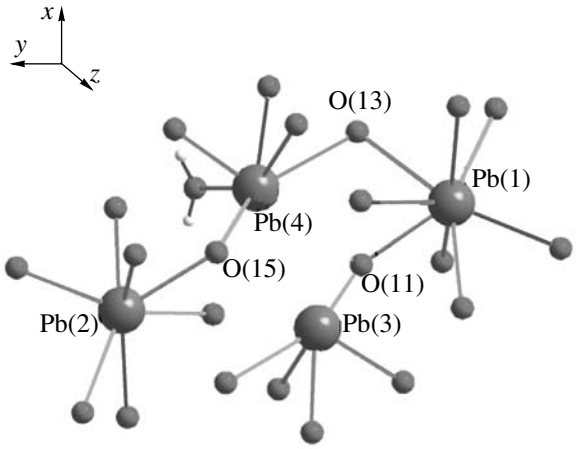


Fig. 2. The structural unit (C and H atoms are omitted for clarity).

As for the 2D framework in Fig. 3, it can be seen that the subunits are extended via ten L dianions (as shown

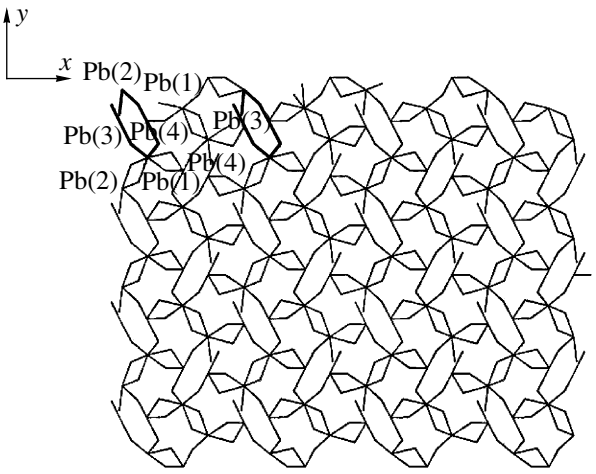


Fig. 3. Molecular structure of the 2D framework (H and C atoms were omitted for clarity, bold is subunit). The geometry being similar to hexagon consisting of four Pb represents the subunit.

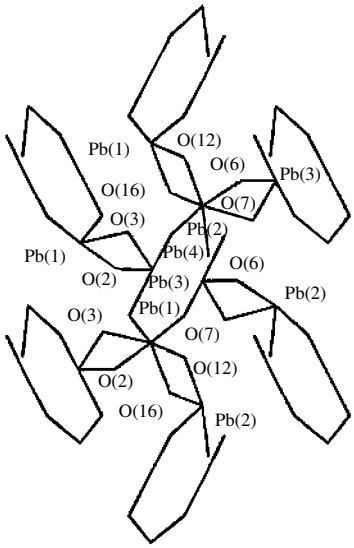


Fig. 4. Subunits joined via three bridging carboxylate groups of the L ligand.

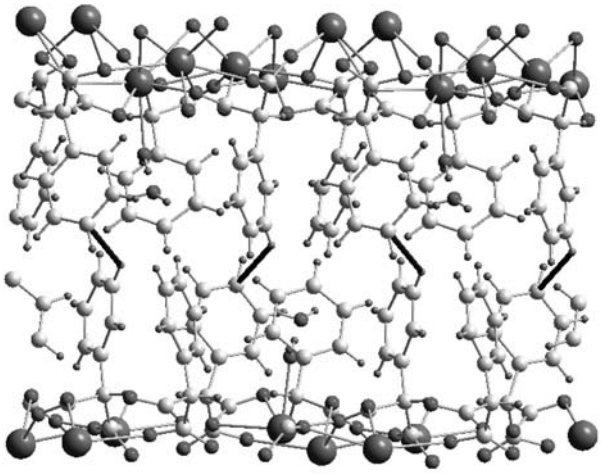


Fig. 5. Stacking interactions between the layer with the CH···π interactions (shown as dark lines).

in Fig. 1) linking neighboring subunits. As a consequence, the formation of strong intramolecular Pb···Pb distances can be observed (Pb(3)···Pb(4) 3.6808(2), Pb(1)···Pb(4) 4.3280(3), Pb(1)···Pb(3) 4.2548(2), Pb(2)···Pb(3) 4.3414(3), Pb(2)···Pb(4) 4.2730(2), Pb(1)···Pb(2) 7.7693(5) Å). These separations are much shorter than the previously reported Pb···Pb values [18, 19]. Four centrosymmetrical Pb cores occur in the same plane, which are joined together via three carboxylate oxygen atoms of the L ligand in mode B and mode C, Pb(2)···Pb(4) and Pb(1)···Pb(4) are joined via carboxylate oxygen atoms in mode B (O(15) and O(16)), and Pb(1)···Pb(3) are joined via carboxylate oxygen O(11) atoms in mode C. Two subunit are linked via three groups of carboxylate oxygen atoms: O(12), O(16), O(6), O(7), O(2), and O(3) (Fig. 4). Subunits are joined into a 2D layer structure via bridging carboxylate groups of the L ligand.

Furthermore, the 2D layers were stacked along by the CH···π interactions, and the CH···π interactions of the compound are with the distances from the closest hydrogen to the plane of the phenyl ring being 2.899 Å (Fig. 5). The layers are connected through CH···π contacts into the 3D framework.

In conclusion, a novel 3D lead(II) MOF with four lead(II) nuclei as a secondary building unit was isolated successfully. We described the unit structure and the

coordination mode of Pb, displaying the 2D structure and 3D framework.

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