ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 1, pp. 109–113. © Pleiades Publishing, Ltd., 2013.

Synthesis and Study of a New Kind of Lead Complex with Variable Coordination Numbers[1]

E. J. Gao*, L. Yang, B. Wang, M. L. Wang, L. Dai, M. C. Zhu, Y. Zhang, and L. Lin

Department of Coordination Chemistry, Shenyang University of Chemical Technology, International Key Laboratory of Shenyang Inorganic Molecule-Based Chemical, Shenyang, 110142 P.R. China

**e-mail: ejgao@yahoo.com.cn*

Received July 7, 2011

Abstract—The crystal $C_{18}H_{12}O_{10}Pb_3$ is synthesized by Pb and phenyl propylene acid. The crystal is characterized by IR and single-crystal X-ray diffraction. The crystal belongs to monoclinic system, space group $P2_1/c$ with the crystal cell parameters of $a = 15.3263(14)$ Å, $b = 16.3479(14)$ Å, $c = 8.1006(7)$ Å, $\beta = 92.3060(10)°$, $V = 2028.0(3)$ Å^3, and $Z = 4$. Through the molecular structure of complex, we can see that Pb has three kinds of coordination modes (5, 6, 7). The compound has formed a 1D surface shape structure through these coordinate modes with the ligand, and this 2D layer piles through C–H···π forms the 3D compound.

DOI: 10.1134/S1070328412110024

INTRODUCTION

During the past decades, coordination polymers with a fascinating and unusual topological structure have drawn researchers' attention due to their physical and chemical properties, host–guest chemistry, magnetic materials, super conducting materials, nonlinear optical materials, catalysis, and biological activity and have already shown excellent potentials in many aspects [1–3]. In the study of biological activity, Pb as a heavy toxic metal have been attracted much attention in recent years. The molecular mechanisms of lead toxicity are probably associated with several different types of proteins [4]. Therefore, it has extensively been studied by using various techniques. As a heavy *p*-lock metal ion, lead may provide potential opportunity to construct novel extended inorganic hybrids with fascinating topologies and interesting properties thanks to its large radius, variable sereochemical activity, and flexible coordination environment [5]. We all know that lead can provide variable coordination numbers, careful selection of suitable polyfunctional organic ligands is helpful for constructing novel coordination polymers [6–8]. Recent reports have focused on the malonate ligand (anion of the malonic acid, hereafter noted Mal) as a flexible and fruitful tool for the design of magnetic systems with different dimensionalities when an appropriate coligand is used [9–11]. In this work, we synthesize the 3D complex $C_{18}H_{12}O_{10}Pb_3$ (**I**).

EXPERIMENTAL

Materials. All chemicals were reagent-grade commercial samples and were used without further purification. Elemental analyses (C, H, and N) were performed on a model Finnigan EA 1112 instrument. The IR spectrum in the range of 400–4.000 cm^{-1} was recorded on a Nicolet IR-470 spectrophotometer using KBr pellets.

Synthesis of complex I. Experiments were all reagent concentration 10 mmol/L phenylmalonic acid (0.1 mmol, 0.019 g), dissolved in the deionize water (10 mL), the resulting solution was then slowly added to $Pb(NO_3)_2$ acid (0.1 mmol, 0.033 g) in demonize water (10 mL). Stirred in air, the mixture turned to lacte turbid, continuing stirring for 2 h. The clear solution was obtained after removing turbines by filtration under atmospheric pressure. Two weeks later, the colorless transparent crystals formed by evaporating the solution at room temperature, which could be collected and suitable for X-ray diffraction.

For $C_{18}H_{12}O_{10}Pb_3$		
anal. calcd, %:	C, 21.41;	H, 1.20.
Found, %:	C, 21.40;	H, 1.21.

IR (KBr; ν, cm^{-1}): ν(=C–H) 3065; ν(–C=O) 1767; ν(COO–) 1610; ν(C=C) 1568, 1520; δ(–C–H) 726.

X-ray crystallography analysis. Single-crystal X-ray data of the complex were collected on a BRUKER SMART 1000 CCD diffractometer with MoK_α radiation ($\lambda = 0.71073$ Å) at 293(2) K, and the intensity data were obtained in the range of $1.82° < \theta < 26.07°$ at 273 K by using an ω scan technique. The structure was resolved by a direct method using SHELXS-97 [12–14]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps. Crystal data and

---

[1] The article is published in the original.

Table 1. Crystallographic data and details of the experiment and refinement of complex **I**

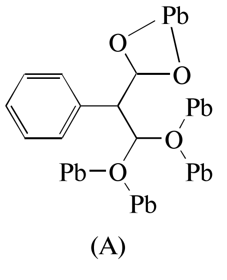
Parameter	Value
Formula weight	1009.05
Crystal system, space group	Monoclinic, $P2_1/c$
a, Å	15.3263(14)
b, Å	16.3479(14)
c, Å	8.1006(7)
β, deg	92.3060(10)
V, Å^3	2028.0(3)
Z	4
ρ_{calcd}, g/cm^{-3}	3.30731
μ, mm^{-1}	None
F(000)	1784
θ Range for data collection, deg	1.02–26.07
Limiting indices	$-16 \le h \le 18$, $-20 \le k \le 19$, $-8 \le l \le 10$
Reflections collected/unique (R_{int})	11868/3996 (0.0452)
Reflections with $I > 2\sigma(I)$	3583
Parameter refinemened	280
Completeness, %	99.7
Goodness-of-fit on F^2	1.045
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0377$, $wR_2 = 0.0942$
R indices (all data)	$R_1 = 0.0422$, $wR_2 = 0.0968$
Largest diffraction peak and hole, e Å^{-3}	4.006 and −1.788

structure refinement details were summarized in Table 1 and selected bond lengths and angles were given in Table 2.

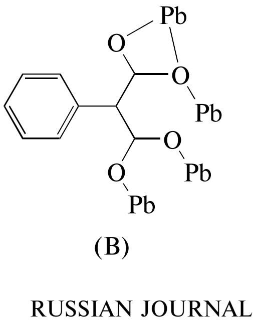
Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 815304; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Carboxylate groups present two different kinds of coordination modes are given bellow:



(A)



(B)

Table 2. Selected bond lengths and bond angles in complex **I**

Bond	d, Å	Bond	d, Å
Pb(1)–O(10)	2.395(5)	Pb(2)–O(10)$^{\#4}$	2.509(5)
Pb(1)–O(9)	2.480(5)	Pb(2)–O(4)	2.856(6)
Pb(1)–O(8)$^{\#1}$	2.544(6)	Pb(2)–O(5)	2.587(6)
Pb(1)–O(4)$^{\#2}$	2.588(6)	Pb(3)–O(3)$^{\#5}$	2.634(6)
Pb(1)–O(7)$^{\#3}$	2.705(7)	Pb(3)–O(6)$^{\#4}$	2.476(6)
Pb(1)–O(8)$^{\#3}$	2.734(7)	Pb(3)–O(9)	2.356(6)
Pb(1)–O(3)	2.923(6)	Pb(3)–O(4)	2.905(5)
Pb(2)–O(9)$^{\#4}$	2.369(6)	Pb(3)–O(1)	2.431(6)
Pb(2)–O(10)	2.347(6)	Pb(3)–O(2)	2.713(7)
Angle	**ω, deg**	**Angle**	**ω, deg**
O(10)Pb(1)O(9)	74.27(17)	O(9)Pb(1)O(4)$^{\#2}$	73.6(2)
O(10)Pb(1)O(8)$^{\#1}$	76.93(19)	O(8)$^{\#1}$Pb(1)O(4)	105.8(2)
O(9)Pb(1)O(8)$^{\#1}$	150.0(2)	O(9)Pb(1)O(8)$^{\#3}$	85.28(19)
O(10)Pb(1)O(4)$^{\#2}$	73.1(2)	O(9)Pb(3)O(1)	81.9(2)
O(9)Pb(3)O(6)$^{\#4}$	79.9(2)	C(6)C(1)C(2)	120.7(10)
O(1)Pb(3)O(6)$^{\#4}$	89.7(2)	C(1)C(2)C(3)	120.7(11)
O(9)Pb(3)O(3)$^{\#5}$	68.38(19)	C(6)C(7)C(8)	113.4(7)
O(1)Pb(3)O(3)$^{\#5}$	78.4(2)	O(3)C(8)O(4)	122.6(9)
O(9)Pb(3)O(2)	127.3(2)	O(2)C(9)O(1)	122.5(8)

As we all know that the lead can exhibit a variable coordination number. In this compound, the Pb–O(COO) bond distances 2.347–2.734 Å are limited in the typical Pb–O bond in range of 2.255–2.734 Å [15]. If the weak Pb–O interactions in a range of 2.78–3.05 Å are considered [16], the Pb groups present three different kinds of coordination modes are given bellow (Fig. 1): Pb(1) can be described as seven-coordinated, Pb(2) – as five-coordinated, and Pb(3) can be described as six-coordinated. Every Pb atom is linked by O atom. As we can see in Fig. 2, the coordination numbers of Pb get a cycling which is variable.

The Pb(1) atom is coordinated to seven carboxylate oxygen atoms, among them, two carboxylate oxygen atoms from two L ligands in mode A, three carboxylate oxygen atoms from two L ligands in mode B, and two oxygen atoms O from the water molecule occupies the remaining coordination sites. Among the two oxygen atoms, O(9) atom links the three lead atoms of the structure unit. O(10) atom links two lead atoms of one structure unit with an lead atom from another structure unit. The Pb(2) atom is coordinated to three oxygen atoms from water and two carboxylate oxygen atoms from two L ligands: a carboxylate oxygen atom from one L ligands in mode A, another carboxylate oxygen atom from one L ligands in mode B. The Pb(3) atom is coordinated to an oxygen atom from water and five carboxylate oxygen atoms from four L ligands: four carboxylate oxygen atoms from three L ligands in

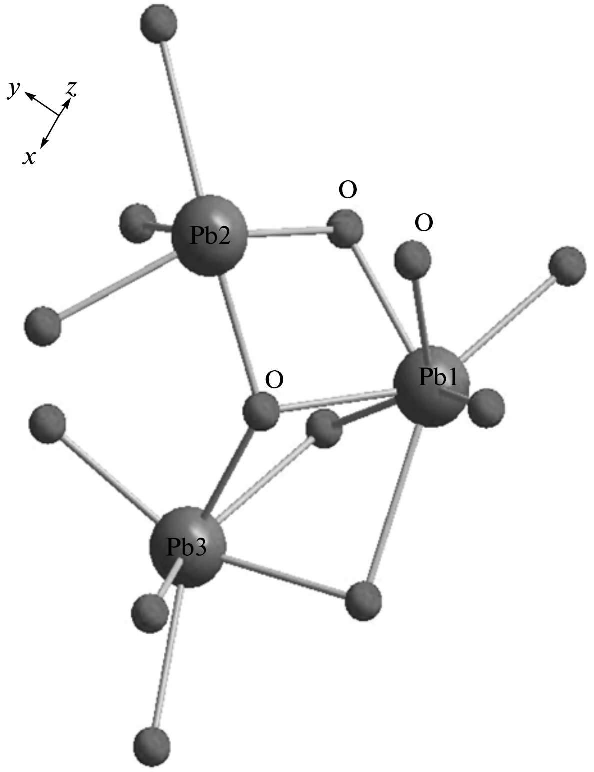


Fig. 1. The structural unit (C and H atoms are omitted for clarity).

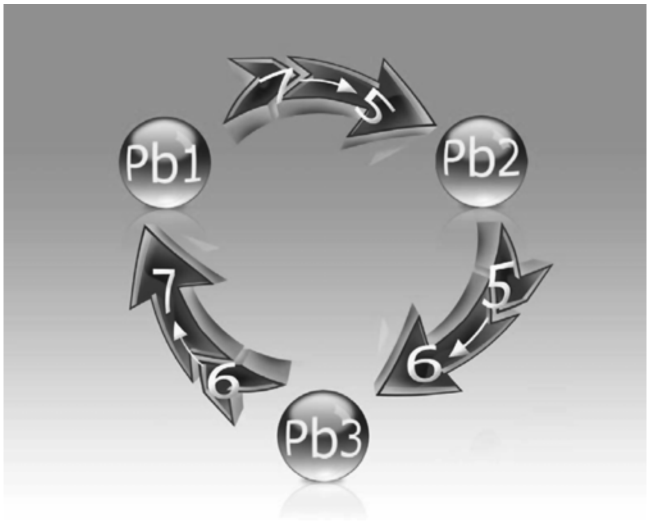


Fig. 2. Cycling of the Pb coordination number.

mode A, one carboxylate oxygen atom from one L ligands in mode B (Fig. 3).

In Fig. 4, every 6 Pb atoms get a group. Groups are joined into a 2D layer structure via bridging carboxylate groups of the L ligand.

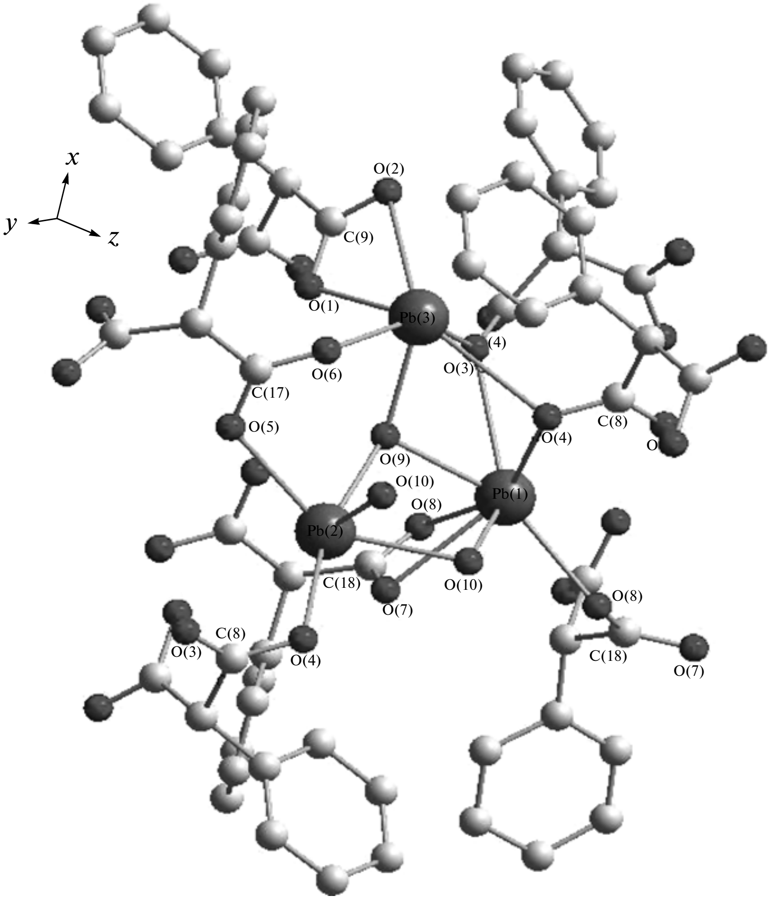


Fig. 3. Molecular structure of the crystal.

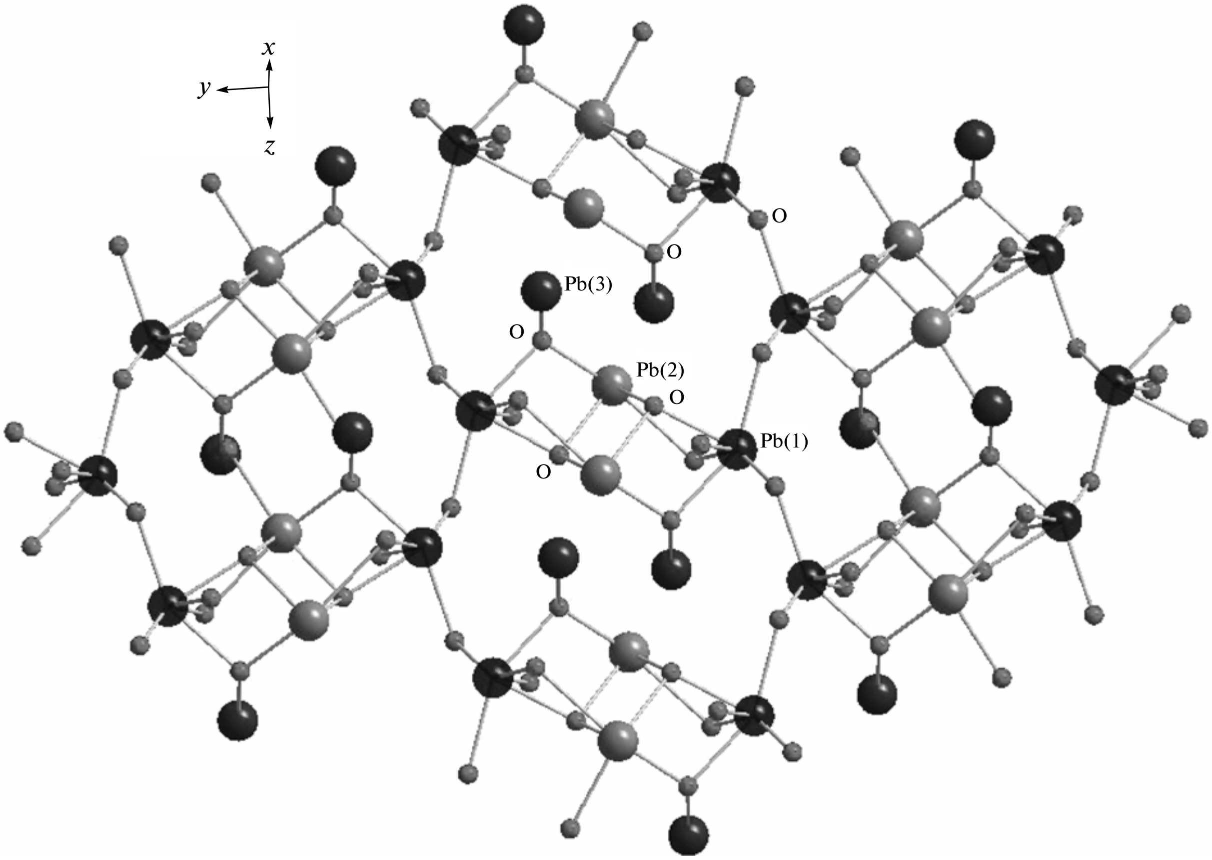


Fig. 4. Molecular structure of the 2D framework (H and C atoms were omitted for clarity).

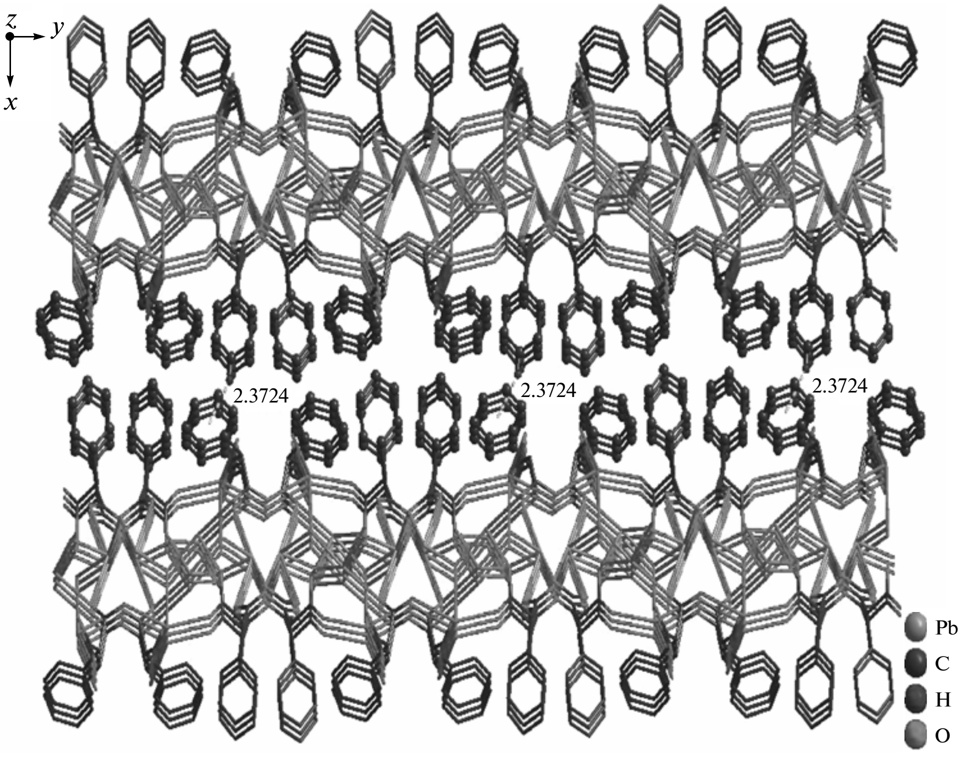


Fig. 5. Stacking interactions between the layer with the C–H···π interactions.

C–H···π interactions of the adduct are with the distances from the closest hydrogen to the plane of the phenyl propylene acid ring being 2.3724 Å [17–19], and the stacking framework of the complex is shown in Fig. 5. The 2D layers are further connected through C–H···π interactions, forming a 3D framework.

ACKNOWLEDGMENTS

We gratefully acknowledge the Natural Science Foundation of China (nos. 20971090, 21171118), the Distinguished Professor Project of Liaoning province, and the Science and Technology Projects fund of Shenyang City (no. F10-215-1-00).

REFERENCES

1. Li, F., Wang, Y.L., Li, G.S., et al., *Inorg. Chem. Commun.*, 2007, no. 10, p. 767.
2. Zhu, H.F., Li, L., and Fan, J., *Chin. J. Inorg. Chem.*, 2003, vol. 19, no. 1, p. 25.
3. Gao, S., Liu, J.W., and Huo, L.H., *Chin. J. Inorg. Chem.*, 2005, vol. 21, no. 9, p. 1349.
4. Gao, E.J., Liu, H.Y., Zhu, M.C., et al., *Russ. J. Coord. Chem.*, 2009, vol. 35, no. 12, p. 903.
5. Lin, J.D., Wu, S.T., Li, Z.H., and Du, S.W., *CrystEngComm.*, 2010, vol. 12, p. 4252.
6. Bu, X.H., Tong, M.L., Chang, H.C., et al., *Angew. Chem. Int. Ed.*, 2004, vol. 43, p. 192.
7. Ghosh, A.K., Ghoshal, D., Zangrando, E., et al., *Dalton Trans.*, 2006, p. 1554.
8. Holmes, K.E., Kelly, P.F., and Elsegood, M.R.J., *Dalton Trans.*, 2004, p. 3488.
9. Rodriguez-Martin, Y., Hernandez-Molina, M., Delgado, F.S., et al., *CrystEngComm.*, 2002, vol. 4, p. 522.
10. Ruiz-Perez, C., Rodriguez-Martin, Y., Hernandez-Molina, M., et al., *Polyhedron*, 2003, vol. 22, p. 2111.
11. Pasan, J., Delgado, F.S., Rodriguez-Martin, Y.M., et al., *Polyhedron*, 2003, vol. 22, p. 2143.
12. Gao, E.J., Wang, L., Zhu, M.C., et al., *Eur. J. Med. Chem.*, 2010, vol. 45, p. 311.
13. Uma, V., Kanthimathi, M., and Weyhermuller, T., *J. Inorg. Biochem.*, 2005, vol. 99, p. 2299.
14. Wang, Y.L., Liu, Y.C., Yang, Z.S., and Zhao, G.C., *Bioelectrochem.*, 2004, vol. 65, p. 81.
15. Song, J.L., Mao, J.G., Sun, Y.Q., and Cleareld, A., *Eur. J. Inorg. Chem.*, 2003, vol. 23, p. 4218.
16. Marandi, F., Mirtamizdoust, B., Soudi, A.A., and Fun, H.K., *Inorg. Chem. Commun.*, 2007, vol. 10, p. 174.
17. Vivek, S.G., Gupta, K., Raina, S., and Gupta, B.D., *J. Chem. Crystallogr.*, 2006, vol. 36, no. 2, p. 121.
18. Ali, B.F., Al-Sou'od, K.A., Al-Far, R., et al., *Struct. Chem.*, 2006, vol. 17, p. 425.
19. Huang, R.B., Zheng, N.F., Xie, S.Y., et al., *J. Incl. Phenom. Macrocycl. Chem.*, 2001, vol. 40, p. 123.