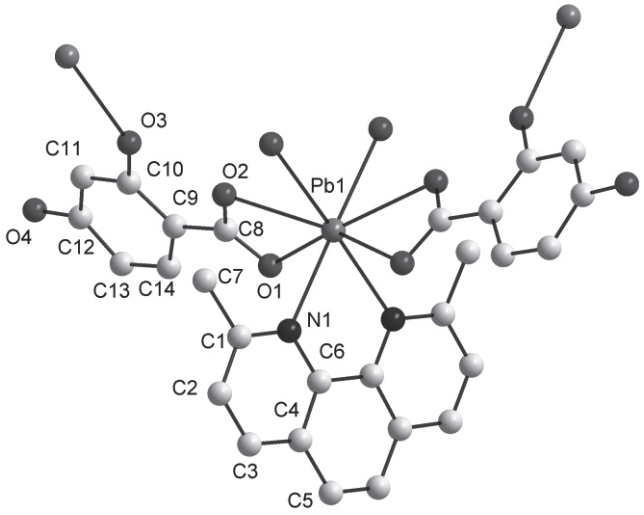
Crystal structure of catena-Poly[bis(μ_2-2,4-dihydroxybenzoato-$\kappa^3O^1,O^{1'}:O^2$)-(2,9-dimethyl-1,10-phenanthroline-κ^2N,N')lead(II)], $C_{28}H_{22}N_2O_8Pb$

Li-Bing Guo[I, II], Dong Xian[*, I] and Jun-Ming Tang[I]

[I] Department of Chemistry, Henan Normal University, Xinxiang 453007, Henan Province, P. R.China
[II] Institute of Chemistry, Henan Academy of Sciences, Zhengzhou 450002, Henan Province, P. R. China

Received February 20, 2015, accepted July 13, 2015, available online July 22, 2015, CCDC no. 1267/4359



Abstract

$C_{28}H_{22}N_2O_8Pb$, orthorhombic, *Pbcn* (no. 60), a = 18.691(2) Å, b = 12.611(1) Å, c = 11.092(1) Å, V = 2614.7 Å^3, Z = 4, $R_{gt}(F)$ = 0.0220, $wR_{ref}(F^2)$ = 0.0671, T = 296 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.35×0.43×0.49 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	65.07 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	18569, 2440
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1844
$N(param)_{refined}$:	180
Programs:	SHELX [15]

Source of material

All reagents and solvents obtained from commercial sources were used without further purification. To a solution of 2,9-dimethyl-1,10-phenanthroline (0.5 mmol), 2,4-dihydroxybenzoate (0.5 mmol) and sodium hydroxide (0.5 mmol) in ethanol/water (v:v = 1:10, 10 ml) was added a solution of $Pb(CH_3COO)_2$ (0.5 mmol) in distilled water (5 ml). The resulting solution was stirred for 10 h at 323 K. After filtration, the clear solution was left to slowly evaporate in air at room temperature to give colourless block-shaped crystals of the title compound suitable for X-ray diffraction over 4 days.

Discussion

The investigation of the coordination chemistry of lead(II) has been carried out in the past decade [1–3] since lead poisoning is a type of metal poisoning caused by the increased levels of the heavy metal in the humans body [4–6]. During the treatment of lead poisoning, the chelating agents with N and O donors such as $CaNa_2$*edta* (*edta* = ethylendiaminetetraacetate) were often used [7]. The high coordinated ability of chelating agent can allow it to form nontoxic complexes with lead, thus this can effectively decrease the content of lead ions [8]. Additionally, new and previously reported lead(II) complexes are unusually diverse due to its antibonding character [9–14]. Therefore, the structural information, obtained from crystallographic data, can help to understand the complicate interacting systems, and has important role in study on the toxicity of lead. Recently, we obtained the title lead(II) complex, by reaction of lead acetate, sodium salicylate and 2,9-dimethyl-1,10-phenanthroline (*DMPHEN*) in ethanol/water mixtures, and herein we report its crystal structure. Closely related Pb(II) complexes can be found in the literature [12–13]. A segment of the polymeric structure of the title compound is given in the figure, and the experimental crystal parameters are summarized in Table1. Each Pb^{II}, located on a two-fold axis, is eight-coordinated by two nitrogen atoms from one *dmphen* ligand (Pb–N= 2.516(3) Å) and six oxygen atoms from three 2,4-dihydroxybenzoate ligands. Amongst them, four oxygen atoms of carboxylate groups from two benzoate ligands behave as bidentate ligands to one Pb ion with Pb–O distances of 2.683 and 2.705 Å, respectively. Two oxygen atoms of hydroxo groups from another two benzoate ligands directly interact with Pb. The molecular structure forms a one-dimensional polymer chain running along the *c* axis linked through two bridging 2,4-hydroxybenzoate groups with a Pb–O distances of 2.901 Å. The distance between adjacent Pb ions is about 6.999 Å. In this crystal, all of the hydroxy groups participate in the formation of the intermolecular and intramolecular O–H···O hydroxy bonds. The intramolecular hydrogen bonds between the hydrogen group on the 4 site and carboxyl O atom stabilizes the conformation of the hydroxybenzoate ligands. Summing up all interactions a three-dimensional framework structure is present. Due to the presence of hydroxy group on 4 site, this compound is largely different to the compound formed by the 2-hydroxybenzoate, which is stabilized by π-π interaction between *DMPHEN* ring to form a simple binuclear structure as reported by Xuan [10]. As for the simple combination of the 4-hydroxybenzoate with *DMPHEN*, only a centrosymmetric binuclear compound was obtained [11].

* Correspondence author (e-mail: xxxiandong@sina.com)

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(4)	8*d*	0.9341	0.0078	0.4133	0.093
H(3)	8*d*	0.6792	0.1625	0.1382	0.075
H(5)	8*d*	0.8111	–0.0039	0.1979	0.049
H(4A)	8*d*	0.7136	0.2654	0.2971	0.047
H(3A)	8*d*	0.7897	0.2804	0.4572	0.049
H(11)	8*d*	1.1121	0.5879	0.5234	0.067
H(10)	8*d*	1.1461	0.4310	0.4409	0.065
H(14A)	8*d*	1.1258	0.1856	0.5519	0.077
H(14B)	8*d*	1.1406	0.2457	0.4307	0.077
H(14C)	8*d*	1.0637	0.2025	0.4588	0.077
H(17)	8*d*	1.0394	0.6887	0.6720	0.069

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(4)	8*d*	0.9096(2)	–0.0062(2)	0.3541(3)	0.067(2)	0.060(2)	0.059(2)	0.043(2)	–0.033(2)	–0.028(2)
O(3)	8*d*	0.7058(2)	0.1110(2)	0.1437(3)	0.052(2)	0.051(2)	0.047(2)	0.015(2)	–0.027(2)	–0.010(1)
O(1)	8*d*	0.8889(1)	0.2285(2)	0.6124(2)	0.032(2)	0.046(2)	0.035(2)	0.009(1)	–0.008(1)	–0.015(1)
O(2)	8*d*	0.9510(2)	0.0958(2)	0.5363(2)	0.042(2)	0.059(2)	0.046(2)	0.026(2)	–0.020(1)	–0.019(1)
C(6)	8*d*	0.7533(2)	0.1271(4)	0.2346(3)	0.031(2)	0.040(2)	0.034(2)	–0.000(2)	–0.011(2)	0.001(2)
C(5)	8*d*	0.8073(3)	0.0537(4)	0.2499(3)	0.051(3)	0.036(2)	0.037(2)	0.012(2)	–0.014(2)	–0.011(2)
C(4)	8*d*	0.7483(2)	0.2138(3)	0.3104(4)	0.033(2)	0.040(2)	0.044(2)	0.014(2)	–0.009(2)	–0.007(2)
C(3)	8*d*	0.7948(2)	0.2232(3)	0.4051(4)	0.036(2)	0.042(2)	0.044(2)	0.013(2)	–0.013(2)	–0.019(2)
C(2)	8*d*	0.8559(2)	0.0664(3)	0.3438(3)	0.035(2)	0.031(2)	0.034(2)	0.013(2)	–0.010(2)	–0.003(2)
C(1)	8*d*	0.8493(2)	0.1502(3)	0.4264(3)	0.025(2)	0.033(2)	0.027(2)	0.003(2)	–0.003(2)	–0.002(2)
C(7)	8*d*	0.8985(2)	0.1593(3)	0.5310(4)	0.028(2)	0.039(2)	0.034(2)	0.001(2)	–0.004(2)	0.001(2)
Pb(1)	4*c*	1	0.16928(1)	¾	0.0246(1)	0.0257(1)	0.0266(1)	0	–0.00497(7)	0
N(1)	8*d*	1.0445(2)	0.3350(2)	0.6485(3)	0.028(2)	0.032(2)	0.031(2)	0.001(1)	0.002(1)	0.001(1)
C(13)	8*d*	1.0241(2)	0.4295(3)	0.6986(4)	0.034(2)	0.033(2)	0.031(2)	–0.002(2)	–0.002(2)	–0.000(2)
C(9)	8*d*	1.0875(2)	0.3354(3)	0.5522(4)	0.034(2)	0.045(3)	0.037(2)	0.000(2)	0.007(2)	0.003(2)
C(11)	8*d*	1.0946(3)	0.5248(4)	0.5551(5)	0.069(3)	0.039(3)	0.060(3)	–0.014(2)	0.016(3)	0.013(2)
C(10)	8*d*	1.1145(3)	0.4318(4)	0.5057(4)	0.055(3)	0.056(3)	0.051(3)	–0.008(2)	0.023(2)	0.009(2)
C(12)	8*d*	1.0482(2)	0.5275(3)	0.6529(4)	0.051(3)	0.032(2)	0.048(3)	–0.005(2)	0.006(2)	0.007(2)
C(14)	8*d*	1.1060(3)	0.2333(4)	0.4932(4)	0.054(3)	0.054(3)	0.047(3)	0.001(2)	0.021(2)	–0.004(2)
C(17)	8*d*	1.0234(3)	0.6246(4)	0.7034(5)	0.076(3)	0.027(2)	0.069(3)	–0.006(2)	0.005(3)	0.007(2)

Acknowledgments. Financial support from the National Natural Science Foundation of Henan Educational Committee (2011 A150018) is gratefully acknowledged.

References

1. Shimoni-Livny, L.; Glusker, J. P.; Bock, C. W.: Lone pair functionality in divalent lead compounds. Inorg. Chem. **37** (1998) 1853–1867.
2. Davidovich, R. L.; Stavila, V.; Marinin, D. V.; Voit, E. I.; Whitmire, K. H.: Stereochemistry of lead(II) complexes with oxygen donor ligands. Coord. Chem. Rev. **253** (2009) 1316–1352.
3. Hu, M. L.; Morsali, A.; Aboutorabi, L.: Lead (II) carboxylate supramolecular compounds: coordination modes, structures and nano-structures aspects. Coord. Chem. Rev. **255** (2011) 2821–2859.
4. Staudinger, K. C.; Roth, V. S.: Occupational lead poisoning. Am. Fam. Physician **57** (1998) 719–726, 731–712.
5. Klein, M.; Kaminsky, P.; Duc, M. L.; Duc, M.: Current diagnosis and treatment of lead poisoning. Rev. Med. Interne. **15** (1994) 101–109.
6. Laraque, D.; Trasande, L.: Lead poisoning: successes and 21st century challenges. Pediatr. Rev. **26** (2005) 435–443.
7. Porru, S.; Alessio, L.: The use of chelating agents in occupational lead poisoning. Occup. Med. (Lond). **46** (1996) 41–48.
8. Gracia, R. C.; Snodgrass, W. R.: Lead toxicity and chelation therapy. Am. J. Health. Syst. Pharm. **64** (2007) 45–53.
9. Gao, J.; Xuan, X. P.: Di-μ-benzoato-κ^3*O,O′:O*;κ^3*O:O,O′*-bis[(acetato-κ*O*)(1,10-phenanthroline-κ^2*N,N′*) lead(II)] dihydrate. Acta Crystallogr. **E65** (2009) m900.
10. Xuan, X. P; Zhao, P. Z.: catena-Poly[[(2,9-dimethyl-1,10-phenanthroline-κ^2*N,N′*)lead(II)]-di-μ-2-hydroxybenzoato-κ^3*O*^{1},*O*$^{1'}$:*O*^{2}; κ^3*O*^{2}:*O*^{1},*O*$^{1'}$]. Acta Crystallogr. **E63** (2007) m2678.
11. Zhao, P. Z.; Xuan, X. P.; Tang, Q. H.: Bis(μ-4-hydroxybenzoato-κ^2*O:O′*)bis[(2,9-dimethyl-1,10-phenanthroline-κ^2*N,N′*)(4-hydroxybenzoato-κ^2*O,O′*) lead(II)]. Acta Crystallogr. **E63** (2007) m3042–m3043.
12. Persson, I.; Lyczko, K.; Lundberg, D.; Eriksson, L.; Placzek, A.: Coordination chemistry study of hydrated and solvated lead (II) ions in solution and solid state. Inorg. Chem. **50** (2001) 1058–1072.
13. Xuan, X. P.; Zhao, P. Z.; Zhang, S. X.: Bis(μ-3-hydroxybenzoato-κ^3*O,O′:O*)bis[aqua(3-hydroxybenzoato-κ^2*O,O′*)(1,10-phenanthroline-κ^2*N,N′*) lead(II)] monohydrate. Acta Crystallogr. **E64** (2008) m152–m153.
14. Zhao, P. Z; Xuan, X. P.: (2,9-Dimethyl-1,10-phenanthroline-κ^2*N,N′*)bis(3-hydroxybenzoato-κ^2*O,O′*)lead(II)-2,9-dimethyl-1,10-phenanthroline-water (1/1/3). Acta Crystallogr. **E63** (2007) m3179.
15. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.