

Hydrothermal Synthesis and Crystal Structure of a Novel Pb(II) Coordination Polymer

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The novel coordination polymer, [Pb(1,4-chdc)(L)], **1**, (1,4-H₂chdc = cyclohexane-1,4-dicarboxylic acid and L = 11-fluoro-dipyrido[3,2-a:2',3'-c]phenazine), has been synthesized using a hydrothermal method and characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. Crystal data: C₂₆H₁₉FN₄O₄Pb, triclinic, space group *P*1̄, *a* = 9.074(5), *b* = 9.499(5), *c* = 13.853(5) Å, α = 85.640(5), β = 76.127(5), γ = 74.730(5)°, *V* = 1118.2(9) Å³, *Z* = 2. The 1,4-chdc ligands link the Pb(II) atoms to form a 1D chain structure. The L ligands are attached on both sides of the chains. Further, π - π interactions among neighboring chains lead to a two-dimensional supramolecular layer.

Key words: Coordination Polymer, Crystal Structure,
Cyclohexane-1,4-dicarboxylic Acid,
11-Fluoro-dipyrido[3,2-a:2',3'-c]phenazine

Introduction

The design and synthesis of coordination polymers with infinite two- and three-dimensional networks have been an area of rapid growth in recent years because of the potential of these polymers in various applications, such as catalysis, electrical conductivity, host-guest chemistry, and magnetism [1–4]. So far, studies on coordination polymers have focused mainly on the incorporation of *s*, *d* and even *f* block metal ions as the coordination centers, while less consideration has been given to metals of the *p* block [5]. Lead(II), as a toxic heavy metal of the *p* block, is commonly found in critical life cycles due to its widespread use in numerous industrial applications [6]. The possible molecular mechanisms of the toxicity of Pb(II) may affect several

different types of proteins [7]. Therefore, good knowledge of the coordination properties of Pb(II), including aspects such as the lone pair of electrons, the coordination number and the coordination geometry, is crucial for understanding the toxicity of lead(II) [8].

On the other hand, the selection of the ligand is an important factor that may be utilized in determining framework structures. In this regard, 1,10-phenanthroline (phen) has been widely used to build up supramolecular architectures because of its excellent coordinating ability and its large conjugated system that can easily form π - π interactions [9]. However, far less attention has been given to its derivatives. 11-Fluoro-dipyrido[3,2-a:2',3'-c]phenazine (L) is an important phen derivative. It possesses an aromatic system and is a good candidate for the construction of metal-organic supramolecular architectures. To the best of our knowledge, coordination polymers based on the dicarboxylate ligand and L have not been documented so far [1]. Here, we selected the cyclohexane-1,4-dicarboxylate ligand (1,4-chdc) as an organic linker and L as an N-donor chelating ligand to generate a new coordination polymer, [Pb(1,4-chdc)(L)].

Results and Discussion

Selected bond lengths and angles for **1** are given in Table 1. The single-crystal structure determination has revealed that the compound has a two-dimensional supramolecular structure. As shown in Fig. 1, each Pb(II) atom is seven-coordinated by two nitrogen atoms from one L ligand, and five carboxylate oxygen atoms from three different 1,4-chdc ligands. The Pb–O distances range from 2.378(5) to 2.969(5) Å, and the Pb–N distances vary from 2.737(5) to 2.867(5) Å (Table 1), which are near to the data reported for [Pb(fum)(dpdp)]·H₂O (fum = fumarate and dpdp = dipyrido[3,2-a:2',3'-c]-phenazine) [11]. As depicted in Fig. 2, the 1,4-chdc ligands in *cis*-conformations bridge two neighboring Pb(II) centers to form a one-dimensional chain structure. Notably, the L ligands are attached on both sides of the chains. It is clear that the N-donor chelating ligand L plays an important role in the formation of the chain structure. Two N atoms from the L ligand occupy two coordination positions of the Pb(II) atom, while the remaining coordination positions are

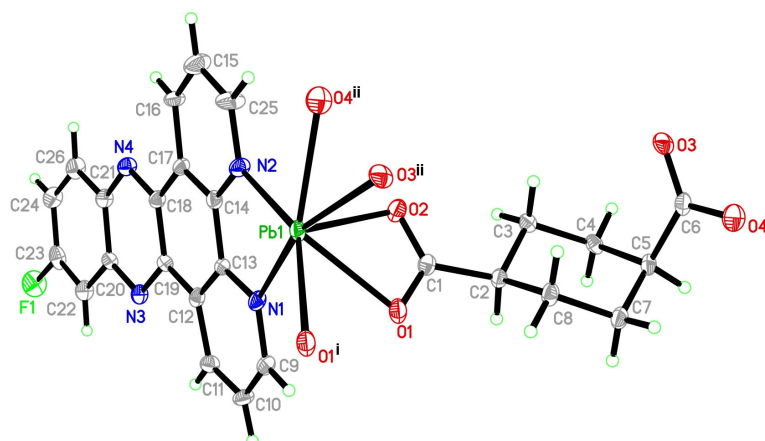


Fig. 1 (color online). The coordination environment of the Pb(II) atom in the molecular structure of [Pb(1,4-chdc)(L)] (1) in the crystal.

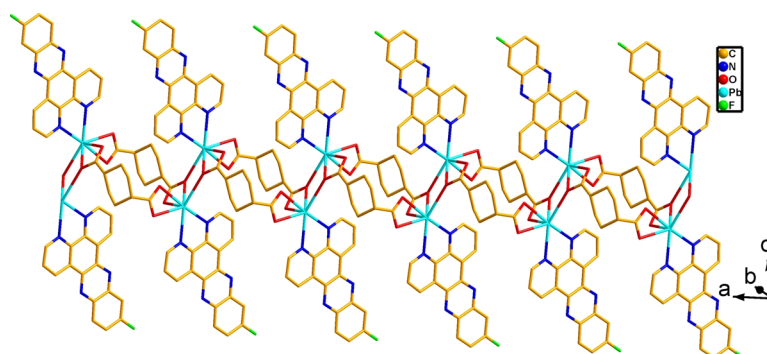


Fig. 2 (color online). View of the one-dimensional chain structure of crystalline [Pb(1,4-chdc)(L)] (1).

available for the 1,4-chdc ligands, allowing the formation of the chain structure. The L ligands are arranged in a parallel fashion at both sides of the chains (Fig. 3), leading to a structure suitable to form π - π interactions. Indeed, the lateral L ligands of adjacent chains are paired to furnish strong π - π interactions (centroid-to-centroid distance 3.42 Å, face-to-face distance 3.35 Å) resulting in an interesting 2-D supramolecular layer (Fig. 3). In fact, the π - π stacking interactions play an important role in the formation and stabilization of the supramolecular structure.

Up to now, several Pb(II) complexes with phen-like chelating ligands have been reported, however, no other Pb(II) coordination polymer containing the chelating ligand L has been observed [11]. It is noteworthy that the structure of **1** is entirely different from that of [Pb(fum)(dpdp)]·H₂O [11], where each fum ligand bridges four Pb(II) centers in a tetradentate mode, generating a novel layer structure. These layers are decorated with dpdp ligands alternating at two sides of each layer. Further, the π - π interactions between

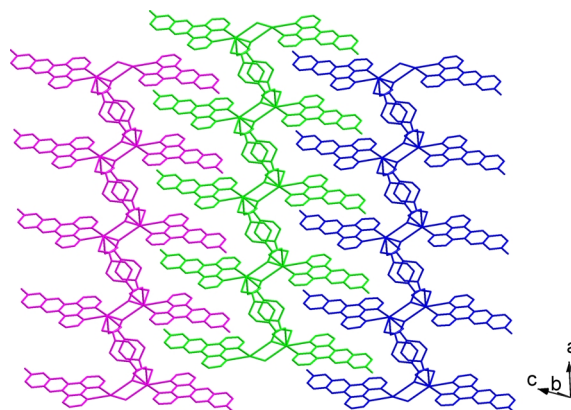


Fig. 3 (color online). Supramolecular layer structure of [Pb(1,4-chdc)(L)] (1) constructed by π - π interactions.

the dpdp ligands lead to a unique three-dimensional supramolecular structure.

The stereochemical activity of the Pb(II) lone pair of electrons is an interesting topic and is often discussed. The geometries of Pb(II) complexes can be classified as holo- and hemidirected [8]. Holodirected

Table 1. Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **1** with estimated standard deviations in parentheses^a.

Pb(1)–O(1)	2.459(5)	Pb(1)–O(2)	2.378(5)
Pb(1)–O(3) ⁱ	2.512(5)	Pb(1)–O(4) ⁱ	2.523(6)
Pb(1)–O(1) ⁱⁱ	2.969(5)	Pb(1)–N(1)	2.867(5)
Pb(1)–N(2)	2.737(5)		
O(2)–Pb(1)–O(1)	53.72(16)	O(2)–Pb(1)–O(3) ⁱ	80.63(19)
O(1)–Pb(1)–O(3) ⁱ	82.11(18)	O(2)–Pb(1)–O(4) ⁱ	80.0(2)
O(1)–Pb(1)–O(4) ⁱ	120.09(19)	O(3) ⁱ –Pb(1)–O(4) ⁱ	51.65(16)
O(2)–Pb(1)–N(2)	80.47(18)	O(1)–Pb(1)–N(2)	121.71(17)
O(3) ⁱ –Pb(1)–N(2)	127.97(17)	O(4) ⁱ –Pb(1)–N(2)	77.50(16)
O(2)–Pb(1)–N(1)	81.66(17)	O(1)–Pb(1)–N(1)	79.65(17)
O(3) ⁱ –Pb(1)–N(1)	159.83(18)	O(4) ⁱ –Pb(1)–N(1)	133.68(16)
N(2)–Pb(1)–N(1)	57.64(15)	O(1)–Pb(1)–O(1) ⁱⁱ	68.31(17)
O(2)–Pb(1)–O(1) ⁱⁱ	118.90(15)	O(3) ⁱ –Pb(1)–O(1) ⁱⁱ	73.60(16)
N(1)–Pb(1)–O(1) ⁱⁱ	107.11(16)	O(4) ⁱ –Pb(1)–O(1) ⁱⁱ	119.01(16)
N(2)–Pb(1)–O(1) ⁱⁱ	155.15(17)		

^a Symmetry transformations used to generate equivalent atoms: (i) $-x+2, -y+1, -z+2$; (ii) $-x+1, -y+1, -z+2$.

refers to Pb(II) complexes in which the bonds to the ligand atoms are located throughout the surface of an encompassing sphere, while hemidirected refers to those cases in which the bonds to the ligand atoms are directed through only part of an encompassing sphere [8]. In compound **1**, the coordination of the ligands at Pb(II) leaves room for a lone pair of electrons. Therefore, this coordination environment can be considered to be somewhat hemidirected.

Experimental Section

Generals

All the materials were of analytical reagent grade and used as received without further purification. The IR spectrum was obtained on a Perkin-Elmer 2400LSII spectrometer. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer.

Synthesis of **1**

Pb(NO₃)₂ (0.5 mmol), 1,4-H₂chdc (0.5 mmol) and L (0.5 mmol) were dissolved in 12 mL distilled water, followed by addition of triethylamine until the pH value of the system was adjusted to about 5–6. The resulting solution was stirred for about 1 h at r. t., sealed in a 23-mL Teflon-lined stainless-steel autoclave and heated at 468 K for 5 d under autogeneous pressure. Afterwards, the reaction system was slowly cooled to r. t. Pale-yellow block-shaped crystals of **1** suitable for single-crystal X-ray diffraction analysis were collected by filtration, washed several times with distilled water and dried in air at ambient temperature. Yield:

Table 2. Crystal structure data for **1**.

Formula	C ₂₆ H ₁₉ FN ₄ O ₄ Pb
<i>M_r</i>	677.64
Crystal size, mm ³	0.19 × 0.15 × 0.14
Crystal system	triclinic
Space group	<i>P</i> $\bar{1}$
<i>a</i> , Å	9.074 (5)
<i>b</i> , Å	9.499 (5)
<i>c</i> , Å	13.853 (5)
α , deg	85.640 (5)
β , deg	76.127 (5)
γ , deg	74.730 (5)
<i>V</i> , Å ³	1118.2 (9)
<i>Z</i>	2
<i>D</i> _{calcd} , g cm ^{−3}	2.01
μ (MoK α), cm ^{−1}	7.6
<i>F</i> (000), e	652
<i>hkl</i> range	−11 ≤ <i>h</i> ≤ 11; −12 ≤ <i>k</i> ≤ 10; −17 ≤ <i>l</i> ≤ 17
θ range, deg	3.0–27.5
Refl. collect. / unique / <i>R</i> _{int}	11090 / 5086 / 0.032
Ref. parameters	319
<i>R</i> 1/ <i>wR</i> 2 [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0318 / 0.0880
<i>R</i> 1/ <i>wR</i> 2 (all data)	0.0372 / 0.1054
GoF (<i>F</i> ²)	1.204
$\Delta\rho_{\max}$ / $\Delta\rho_{\min}$, e Å ^{−3}	1.29 / −1.07

39% based on Pb(II). – Anal. for C₂₆H₁₉FN₄O₄Pb (%): calcd. C 46.04, H 2.80, N 8.26; found C 46.33, H 2.59, N 8.41. – IR (KBr, cm^{−1}): ν = 3043w, 1712w, 1612m, 1581s, 1459s, 1422w, 1359w, 1342s, 840w, 721w, 654w.

X-Ray structure determination

Single-crystal X-ray diffraction data for complex **1** (Table 2) were recorded at 273(2) K on a Rigaku RAXIS-RAPID diffractometer, using the ω scan technique with graphite-monochromatized MoK α radiation (λ = 0.71073 Å). The structure was solved by Direct Methods with SHELXS-97 [12] and refined by full-matrix least-squares techniques using SHELXL-97 [13]. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms of the ligands were refined as rigid groups.

CCDC 790211 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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- [1] N. W. Ockwig, O. Delgado-Friedrichs, M. O’Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176–182.
- [2] M. O’Keeffe, M. A. Peskov, S. J. Ramsden, O. M. Yaghi, *Acc. Chem. Res.* **2008**, *41*, 1782–1789.
- [3] S. R. Batten, *Cryst. Eng. Commun.* **2001**, *3*, 67–73.
- [4] S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558–1595; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460–1494.
- [5] J. Yang, G. D. Li, J. J. Cao, Q. Yue, G. H. Li, J. S. Chen, *Chem. Eur. J.* **2007**, *13*, 3248–3261.
- [6] J. Yang, J. F. Ma, Y. Y. Liu, J. C. Ma, S. R. Batten, *Cryst. Growth Des.* **2009**, *9*, 1894–1911.
- [7] X. L. Wang, Y. Q. Chen, Q. Gao, H. Y. Lin, G. C. Liu, J. X. Zhang, A. X. Tian, *Cryst. Growth Des.* **2010**, *10*, 2174–2184.
- [8] Q. Qiao, G. Q. Wu, T. D. Tang, S. W. Ng, *Acta Crystallogr.* **2009**, *C65*, m146–m148.
- [9] X. M. Chen, G. F. Liu, *Chem. Eur. J.* **2002**, *18*, 4811–4817.
- [10] Z.-G. Kong, X.-Y. Wang, L. Carlucci, *Inorg. Chem. Commun.* **2009**, *12*, 691–694.
- [11] J. Yang, J. F. Ma, Y. Y. Liu, J. C. Ma, S. R. Batten, *Inorg. Chem.* **2007**, *46*, 6542–6555.
- [12] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473.
- [13] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.