# Synthesis and Crystal Structure of a New Pb(II) Coordination Polymer Constructed by a 1,10-Phenanthroline Derivative and a Flexible Dicarboxylate

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The new coordination polymer, [Pb(L)(*trans*-1,4-chdc)] **1** (L = 1-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)-naphthalen-2-ol and *trans*-1,4-$H_2$chdc = *trans*-1,4-cyclohexanedicarboxylic acid), has been hydrothermally synthesized and characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction. Crystal data: $C_{31}H_{24}N_4O_5Pb$, monoclinic, space group $P2_1/c$, $a$ = 13.579(2), $b$ = 9.7831(15), $c$ = 19.958(3) Å, $\beta$ = 105.058(2)°, $V$ = 2560.3(7) Å$^3$, $Z$ = 4. The Pb(II) atoms are bridged by the flexible *trans*-1,4-chdc ligands to form a zigzag chain. The ligands L are located on both sides of the zigzag chains, where $\pi$-$\pi$ interactions among neighboring zigzag chains give rise to a two-dimensional supramolecular network. In addition, O–H···O and N–H···O hydrogen bonding interactions further stabilize the supramolecular network structure of **1**.

*Key words:* Coordination Polymer, Crystal Structure, *trans*-1,4-Cyclohexanedicarboxylic Acid, 1-(1H-Imidazo[4,5-f][1,10]phenanthrolin-2-yl)naphthalen-2-ol

## Introduction

The design and synthesis of coordination polymers on the basis of metal ions and multifunctional organic ligands have undergone revolutionary growth over the past decades not only because of the potential applications of the products in the fields of ion exchange, gas storage, luminescence, and heterogeneous catalysis, but also due to their undisputed aesthetic network structures [1]. Consequently, a large number of coordination polymers with interesting topological structures have been generated by self-assembly processes [2]. Generally, the molecular architectures greatly depend on the coordination geometry of the central metal and of the organic ligand [3]. In this regard, the design of suitable organic ligands is one of the keys for the construction of coordination architectures [4]. Up to now, typical chelating $N,N'$-based secondary ligands, such as the traditionally employed 1,10-phenanthroline (phen), have been extensively studied to build novel supramolecular architectures due to their excellent coordinating ability [5 – 7]. However, its derivatives such as 1-(1H-imidazo[4,5-f][1,10]phenanthrolin-2-yl)naphthalen-2-ol (L), also a good candidate for the construction of supramolecular architectures, has not been well studied in coordination chemistry [8]. As far as we know, coordination polymers based on L in combination with flexible dicarboxylate ligands have never been investigated [9 – 11]. In this paper, we describe the synthesis of a new Pb(II) coordination polymer [Pb(L)(*trans*-1,4-chdc)] (**1**) (*trans*-1,4-chdc = *trans*-1,4-cyclohexanedicarboxylate).

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

| | | | |
|---|---|---|---|
| Distances | | | |
| Pb(1)–O(1) | 2.731(3) | Pb(1)–O(2) | 2.527(3) |
| Pb(1)–O(4)$^{i}$ | 2.311(3) | Pb(1)–O(3)$^{ii}$ | 2.795(3) |
| Pb(1)–N(1) | 2.560(4) | Pb(1)–N(2) | 2.578(3) |
| Angles | | | |
| O(4)$^{ii}$–Pb(1)–O(2) | 95.27(12) | O(4)$^{ii}$–Pb(1)–N(1) | 79.65(11) |
| O(2)–Pb(1)–N(1) | 142.52(11) | O(4)$^{ii}$–Pb(1)–N(2) | 74.50(10) |
| O(2)–Pb(1)–N(2) | 78.90(10) | N(1)–Pb(1)–N(2) | 63.89(11) |
| O(4)$^{ii}$–Pb(1)–O(1) | 81.30(10) | O(2)–Pb(1)–O(1) | 49.45(9) |
| N(1)–Pb(1)–O(1) | 158.48(10) | N(2)–Pb(1)–O(1) | 119.94(10) |
| O(4)$^{ii}$–Pb(1)–O(3)$^{ii}$ | 50.09(10) | O(2)–Pb(1)–O(3)$^{ii}$ | 122.82(11) |
| N(1)–Pb(1)–O(3)$^{ii}$ | 82.08(11) | N(2)–Pb(1)–O(3)$^{ii}$ | 119.48(10) |
| O(1)–Pb(1)–O(3)$^{ii}$ | 78.04(10) | | |

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

## Results and Discussion

### *Structure description*

Single-crystal X-ray structural analysis has shown that the title compound has a two-dimensional supramolecular network structure. Selected bond lengths and angles for **1** are given in Table 1. As shown in Fig. 1, the asymmetric unit of **1** contains one unique Pb(II) atom, one kind of *trans*-1,4-chdc anion, and one kind of L ligand.

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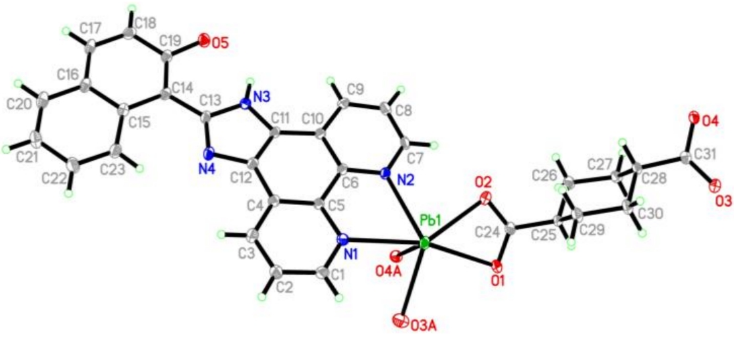

Fig. 1. The coordination environment of the Pb(II) atom in [Pb(L)(*trans*-1,4-chdc)].

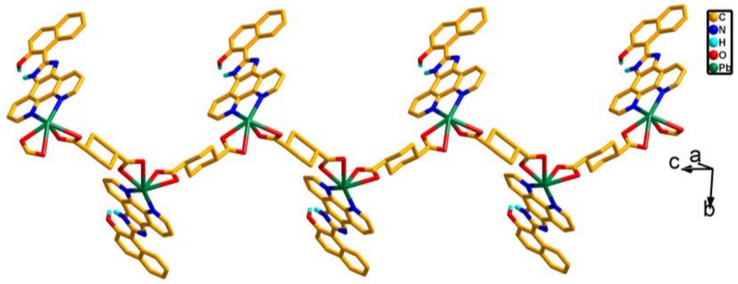

Fig. 2. View of the zigzag chain structure of [Pb(L)(*trans*-1,4-chdc)] in the crystal.

The Pb(II) center is six-coordinated by four carboxylate oxygen atoms from two different *trans*-1,4-chdc anions [Pb(1)–O(1) = 2.731(3), Pb(1)–O(2) = 2.527(3), Pb(1)–O(4)$^{i}$ = 2.311(3) and Pb(1)–O(3)$^{ii}$ = 2.795(3) Å] and two nitrogen atoms from one L ligand [Pb(1)–N(1) = 2.560(4) and Pb(1)–N(2) = 2.578(3) Å]. The Pb–O and Pb–N distances are near to the data reported for [$Pb_2(ndc)_2(tcpp)$] (ndc = 1,4-naphthalenedicarboxylate and tcpp = 4-(1H-1,3,7,8-tetraazacyclopenta[l]phenanthren-2-yl)phenol) [7]. Interestingly, the two carboxylate groups of the *trans*-1,4-chdc are in a bidentate chelating coordination mode. In this mode, each *trans*-1,4-chdc dianion connects two Pb(II) atoms to form a zigzag chain (Fig. 2). In the chain, the Pb···Pb distance bridged by the *trans*-1,4-chdc is about 11.35 Å.

Notably, the L ligands are located on both sides of the zigzag chains. The lateral L ligands from adjacent chains are paired to furnish strong $\pi$-$\pi$ interactions (centroid-to-centroid distance 3.41 Å and face-to-face distance 3.35 Å). Therefore, these chains are extended into two-dimensional supramolecular networks (Fig. 3). It is clear that the $\pi$-$\pi$ stacking interactions play an important role in the formation and stabilization of the supramolecular network structure. In addition, O–H···O and N–H···O hydrogen bonding interactions further stabilize the structure of **1**.

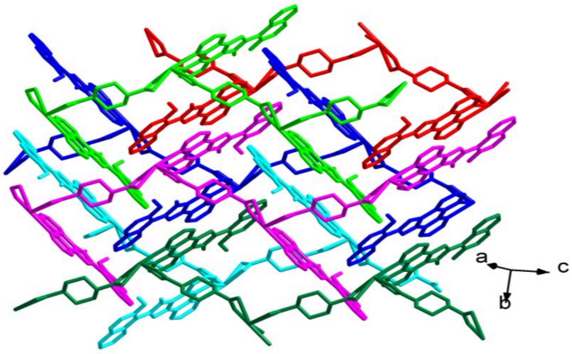

Fig. 3. View of the two-dimensional supramolecular network constructed by $\pi$-$\pi$ interactions in [Pb(L)(*trans*-1,4-chdc)].

The stereochemical activity of the Pb(II) lone pair of electrons is an interesting topic. Pb(II) coordination is classified as holodirected which refers to complexes in which the bonds to ligand atoms are directed throughout the surface of the encompassing sphere, while hemidirected refers to those cases in which the bonds to ligand atoms are directed only to a part of the coordination sphere, leaving a gap in the distribution of the bonds to the ligand [8]. This gap may be due to a stereochemically active lone pair at Pb(II). In compound **1**, the arrangement of O and N atoms for Pb(II) suggests a gap or hole in the coordination geometry around this atom and its coordination sphere is, thus, hemidirected.

It is noteworthy that the structure of **1** is entirely different from that of the related compound [$Pb_2(ndc)_2(tcpp)$] [7]. In that reported compound, the ndc ligands link the Pb(II) atoms to generate a novel two-dimensional layer structure with (4,4) grids. Each corner of a (4,4) grid is occupied by a binuclear Pb(II) subunit. The $\pi$-$\pi$ stacking interactions among neighboring layers extend the layers into a unique double-layer structure.

The carboxylate group of the *trans*-1,4-chdc dianion shows asymmetric and symmetric stretching vibrations at 1613, 1582 $cm^{-1}$ ($\nu(OCO)_{asym}$) and 1360, 1347 $cm^{-1}$ ($\nu(OCO)_{sym}$), respectively [4]. The peak at 1453 $cm^{-1}$ could be assigned to $\nu$(C=N) stretching vibrations of the phen-like ligand L.

## 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 compound **1***

A mixture of $Pb(NO_3)_2$ (1 mmol), *trans*-1,4-$H_2$chdc (1 mmol) and L (1 mmol) was dissolved in 12 mL distilled water. Then, triethylamine was added to the mixture until the pH value of the system was adjusted to about 5.5. 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 462 K for 5 d under autogeneous pressure. Afterwards, the reaction system was slowly cooled to r. t. Pale-yellow 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: 43 % based on Pb(II). – Anal. for $C_{31}H_{24}N_4O_5Pb$ (%): calcd. C 50.33, H 3.27, N 7.57; found C 50.61, H 3.08, N 7.25. – IR (KBr, $cm^{-1}$): $\nu$ = 1712w, 1613m, 1582s, 1459w, 1453s, 1360w, 1347s, 846w, 825w, 721w, 658w.

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

| | |
|---|---|
| Formula | $C_{31}H_{24}N_4O_5Pb$ |
| $M_r$ | 739.73 |
| Crystal size, $mm^3$ | $0.24 \times 0.20 \times 0.17$ |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| $a$, Å | 13.579(2) |
| $b$, Å | 9.7831(15) |
| $c$, Å | 19.958(3) |
| $\beta$, deg | 105.058(2) |
| $V$, $Å^3$ | 2560.3(7) |
| $Z$ | 4 |
| $D_{calcd}$, $g\,cm^{-3}$ | 1.92 |
| $\mu(MoK_\alpha)$, $mm^{-1}$ | 6.6 |
| $F(000)$, e | 1440 |
| $hkl$ range | $-16 \le h \le 15$; $-11 \le k \le 9$;<br>$-22 \le l \le 23$ |
| $\theta$ range, deg | 1.55 – 25.06 |
| Refl. collect. / unique / $R_{int}$ | 12913 / 4526 / 0.0313 |
| Data / ref. parameters | 4526 / 374 |
| $R1$ / $wR2$ [$I \ge 2\sigma(I)$] | 0.0268 / 0.0551 |
| $R1$ / $wR2$ (all data) | 0.0404/ 0.0591 |
| GoF ($F^2$) | 0.999 |
| $\Delta\rho_{max/min}$, e $Å^{-3}$ | 1.29 / −0.44 |

### *X-Ray structure determination*

Single-crystal X-ray diffraction data for complex **1** were recorded at a temperature of 293(2) K on a Bruker Apex CCD diffractometer, using the $\omega$ scan technique with $MoK_\alpha$ radiation ($\lambda$ = 0.71073 Å). The structure was solved by Direct Methods with SHELXS-97 [12] and refined by full-matrix least-squares techniques using the program SHELXL-97 [13]. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms of the ligands were refined as part of rigid groups. Details of the X-ray structure determination are listed in Table 2.

CCDC 815736 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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