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Synthesis and structural characterization of a novel 2D supramolecular lead coordination polymer with phenanthroline derivate and adipic acid

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Abstract: A new metal-organic coordination polymer, $[Pb(L)(adip)_{0.5}]$ (**1**) was synthesized under hydrothermal conditions by using 1-(1*H*-imidazo[4,5-f][1,10]phenanthrolin-2-yl)naphthalen-2-ol (HL) and adipic acid (H_2adip). The complex **1** was characterized by diffraction and elemental analyses. In complex **1**, the binuclear $[Pb_2L_2]$ units were formed by the OH-deprotonation bridging neighboring Pb(II) atoms, and the adipate linked the binuclear $[Pb_2L_2]$ units to form a symmetric one-dimensional chain. The 1D chain was further extended to the 2D supramolecular layer structure through π-π interactions between the L ligands.

Keywords: lead(II) complex, phenanthroline derivate, π-π stacking, crystal structure

Recently, the designing assemblies of polymeric coordination complexes have attracted considerable attention and a variety of remarkable complexes have been prepared so far (Li et al., 2012, 2020; Tang et al., 2006), owing to their fascinating architectures and more to their potential applications in a number of fields, such as magnetism, asymmetric catalysis, gas storage, electric conductivity, and photoluminescence (Cai et al., 2012; Hu et al., 2021; Senthilkumar et al., 2017). The multifunctional organic ligands can be used as linkers to connect the adjacent metal centers for coordination bonding to assemble polymers (Gotthardt et al., 2012; Lan et al., 2019). It is well known that the typical N-donor ligands (such as 1,10-phenanthroline and 2,2-bipyridine) have witnessed an upsurge in interest due to their free conformation and coordination versatility can give rise to diverse structural motifs (Schöne et al., 2018; Takeuchi et al., 2020; Zhang et al., 2020). Especially, 1,10-phenanthroline (phen) as the bidenate chelating reagent can display interesting supramolecular interactions such as aromatic stacking due to the plane conjugation of its multiple large rings. Our group used the heterocyclic nitrogen-derivative ligands, 1-(1*H*-imidazo[4,5-f][1,10]phenanthrolin-2-yl) naphthalen-2-ol (HL), to synthesis the 2D coordination polymer (Kong et al., 2019).

Based on, we report a new 2D supramolecular lead coordination polymer $[Pb(L)(adip)_{0.5}]$ (**1**) with adipic acid (H_2adip) and the derivative 1-(1*H*-imidazo[4,5-f][1,10]phenanthrolin-2-yl)naphthalen-2-ol ligands (see Scheme 1; for the synthesis of the ligand, see: Kong et al., 2015). The complex **1** was characterized by X-diffraction and elemental analyses.

As shown in Figure 1, the asymmetric unit of **1** contains one unique Pb(II) atom, one L ligand and one half unique adipate ligand. Each Pb(II) atom adopts a distorted $[:Pb(L)(adip)_{0.5}]$ octahedral geometry coordinated by two N atoms from one L ligands, one oxygen atom from another deprotonated OH group and two O atoms of the one half adipate ligand (Yang et al., 2007). Two nitrogen atoms (N(1), N(2)) and two O atoms (O(2), $O(3^i)$) make up the basal plane, and axial position

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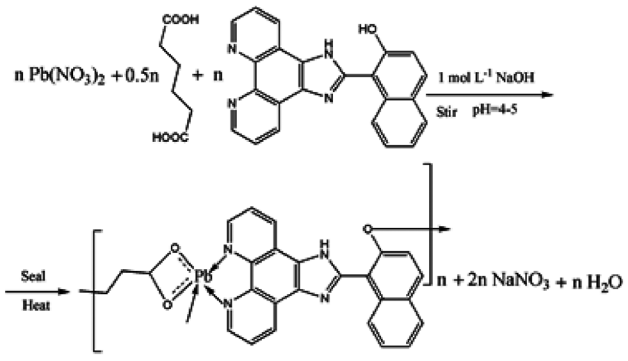
is occupied by the lone pair of electrons and one O atom (O(1)). The Pb–N distances are 2.487(4) and 2.598(4) Å, and the Pb–O varies from 2.313(3) to 2.715(4) Å (Table 1). The Pb-N and Pb-O bond lengths are similar to those found in other crystallographically characterized Pb(II) complex (Wang et al., 2011). As illustrated in Figure 2, the deprotonated OH groups bridge neighboring Pb(II) atoms to form a binuclear $[Pb_2L_2]$ unit with the Pb•••Pb separation of 9.581 Å. Further link of these $[Pb_2L_2]$ units by adipate ligand forms a one-dimensional chain with equatorial plane symmetry along the *a* axis. As seen in Figure 3, the conjugated L ligands from the chains furnish strong π-π stacking interactions between the L ligands of neighboring chains [N(1)/C(1)–C(5), C(18)–C(23) at (x, –y+1/2, z+1/2), centroid-to-centroid distance of 3.746(3) Å and face-to-face distance of 3.5680(19) Å, and dihedral angle of 0.8(3)°], generating a two-dimensional supramolecular layer structure.

In conclusion a novel 2D supramolecular polymer $[Pb(L)(adip)_{0.5}]$ (**1**) has been successfully synthesized and characterized under hydrothermal conditions. The central Pb(II) ion in **1** shows a distorted octahedral coordination environment, in which the lone pair of Pb occupies additional position. And adipate ligands link the binuclear $[Pb_2L_2]$ units forming a symmetric one-dimensional chain. Finally, the π-π stacking interactions among the neighboring chains extend the chains into a 2D supramolecular layer structure.



Scheme 1: Synthesis of complex **1**.

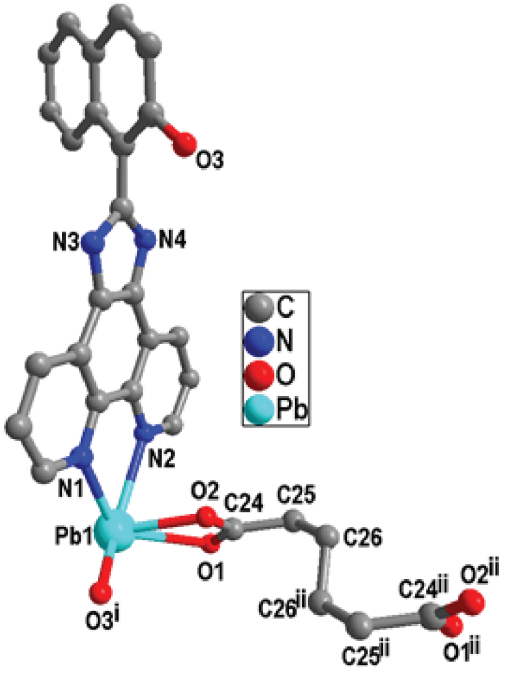


Figure 1: View of the coordination environment of the Pb(II) atom of **1**.

Table 1: Selected bond lengths (Å) and angles (°) for the complex **1**

Pb(1)–N(1)	2.487(4)
Pb(1)–N(2)	2.598(4)
Pb(1)–O(1)	2.374(3)
Pb(1)–O(2)	2.715(4)
Pb(1)–O(3)^{i}	2.313(3)
O(1)–Pb(1)–O(3)^{i}	82.90(11)
N(1)–Pb(1)–O(3)^{i}	79.23(12)
N(1)–Pb(1)–O(1)	85.77(11)
N(2)–Pb(1)–O(3)^{i}	136.60(11)
N(2)–Pb(1)–O(1)	71.93(12)
N(1)–Pb(1)–N(2)	64.49(11)
O(2)–Pb(1)–O(3)^{i}	112.55(12)
O(1)–Pb(1)–O(2)	50.66(11)
N(1)–Pb(1)–O(2)	129.98(12)
N(2)–Pb(1)–O(2)	77.78(13)

Symmetry codes: ^{i} –*x*+2, –*y*, –*z*; ^{ii} –*x*+1, –*y*, –*z*.

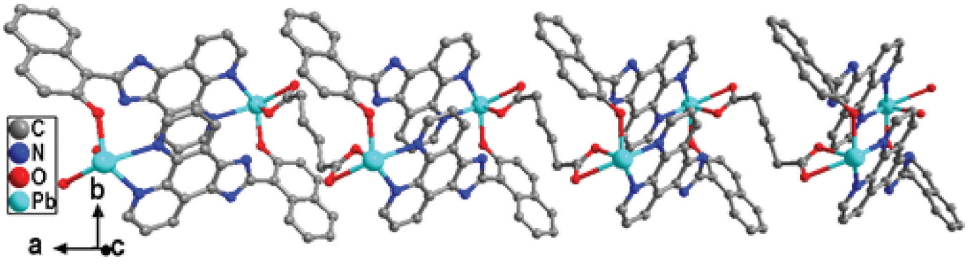


Figure 2: View of the 1D chain structure of **1**.

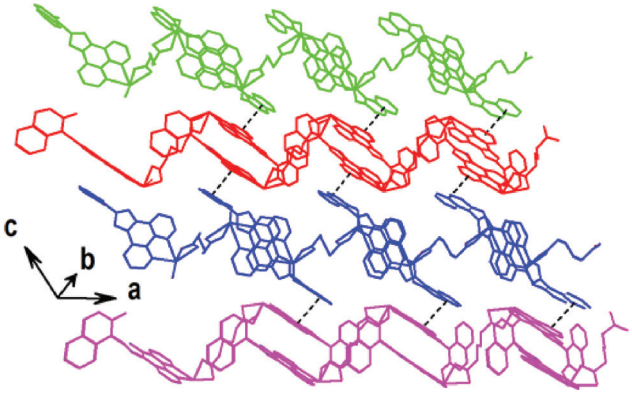


Figure 3: View of the two-dimensional supramolecular layer structure of **1** formed by π-π interactions.

Experimental

All reagents and solvents used in the synthesis procedure were bought from the commercial companies (Shanghai yiyan biological technology Co. Ltd and Tianjin Yuzhou Chemical Sales Co., Ltd, China). Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240 CHN elemental analyzer (Perkin Elmer, North Waltham, USA).

Preparation of $[Pb(L)(adip)_{0.5}]$ (1)

$Pb(NO_3)_2$ (0.066 g, 0.2 mmol), H_2adip (0.029 g, 0.2 mmol), HL (0.036 g, 0.1 mmol), and 9 mL H_2O were added to the 50 mL beaker, while stirring. And the pH value of the solution was adjusted to 4-5 with 1 mol L^{-1} NaOH aqueous solution (about 0.45 mL). The solution is weakly acidic, and the hydroxyl groups on the naphthalene rings of the HL ligands are partially deprotonated. Then the mixture was transferred to the sealed 15 mL Teflon-lined Parr and heated at 195°C for 5 days. After being cooled to room temperature, the light yellow block-shaped crystalline products of **1** were obtained and washed the products repeatedly with water until free from impurities (4 times by 15 mL). The yield was 0.025 g (ca. 39%, based on the L). Analytical calculated for $C_{26}H_{17}N_4O_3Pb$, %: C, 48.75; H, 2.67; N, 8.75; Found %: C, 48.01; H, 2.61; N, 8.59.

X-ray crystallography

The intensity data for the X-ray diffraction analysis of 1 were measured at 298 (2) K on a Bruker-AXS Smart CCD diffractometer with graphite-monochromatized Mo-*K*α radiation (λ = 0.71073 Å) using the ϕ and ω scan technique.

Table 2: Crystalline data and refinement parameters for complex **1**

Empirical formula	$C_{26}H_{17}N_4O_3Pb$
Formula weight	640.62
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	12.342(2)
b (Å)	11.797(2)
c (Å)	16.324(3)
β (°)	111.995(2)
Volume (Å^3)	2203.6(7)
Z	4
D_c (g·cm^{-3})	1.931
μ (mm^{-1})	7.694
F(000)	1228
θ range *(°)*	1.780 to 25.037
Crystal size (mm)	0.208 × 0.185 × 0.171
Tot. reflections	11101
Uniq. reflections, R_{int}	3887, 0.0315
GOF on F^2	0.966
R_1 indices [$I>2\sigma(I)$]	0.0259
wR_2 indices (all data)	0.0578
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e·Å^{-3})	−0.425, 0.982
CCDC No.	2076592

The structure was solved by direct methods using SIR2014 (Burla et al., 2014) and refined by a full-matrix least squares technique on F^2 using SHELXL2018/3 program (Sheldrick, 2015). All H atoms were found by generated calculations with refining as riding, and the non-hydrogen atoms were refined with anisotropic temperature parameters. The crystallographic parameters and refinements are summarized in Table 2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 2076592.

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Conflict of interest: Authors state no conflict of interest.

Data availability statement: All data generated or analysed during this study are included in this published article.

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