Rapid Communication

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# A new cadmium(II) coordination polymer with 1,4-cyclohexanedicarboxylate acid and phenanthroline derivate: Synthesis and crystal structure

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**Abstract:** A new Cd(II) coordination polymers, formulated as $[Cd(1,4\text{-chdc})(L)]_n$ (**1**) (L = 1-(1*H*-imidazo[4,5-*f*][1,10] phenanthrolin-2-yl)naphthalen-2-ol ligands and 1,4-$H_2$chdc = 1,4-cyclohexanedicarboxylate acid), were successfully synthesized by using L ligand and 1,4-$H_2$chdc acid under hydrothermal conditions and characterized by single crystal X-ray elemental analyses, diffraction, and IR spectroscopy. Each Cd(II) atom is a distorted pentagonal bipyramidal geometry connecting the deprotonated 1,4-chdc anion to form a 2D layer, and a 2D layer is formed into a 3D supramolecular structure by the π–π stacking interactions between neighboring layers.

**Keywords:** Cd(II), coordination polymer, phenanthroline derivate, crystal structure

Over the past decades, more and more researchers have focused on the design and synthesis of coordination polymers, because of their unique structures and their potential applications in magnetism, fluorescence, biological, gas storage, and so forth (Guillem et al., 2012; Liu et al., 2021; Song et al., 2021; Wang et al., 2020; Yang et al., 2010). Many different factors such as solvent, organic ligands, temperatures, pH, metal ions, and non-covalent interactions (aromatic stacking interactions) have influence on the final structures and properties of coordination polymers (Li et al. 2021; Martin et al. 2008). So far, most of the coordination polymers have been constructed from carboxylic acid ligands, nitrogen-containing organic ligands, and transition metal ions through intermolecular interactions or coordination bonds (Shimomura et al., 2010; Tiwari et al., 2021; Zhang et al., 2021). Phenanthroline derivative ligands are the typical N-donor ligands, which could adopt diverse conformations in the coordination of the center metal (Ma et al., 2009). Phenanthroline derivatives are rigid structures due to their central ring resulting in the two N-atoms being held in juxtaposition; so they can coordinate with transition metal ions quickly (Hu et al., 2021; Llabrés i Xamena et al., 2008; Song et al., 2021; Wei et al., 2020). In our research, nitrogen-containing organic ligands formed the π–π stacking interactions, and the existences of these π–π stacking interactions contribute considerably to the stability of coordination polymers (Wang et al., 2011).

With the above considerations, Cd(II) coordination polymers with derivative 1-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)naphthalen-2-ol ligands (L) and the 1,4-cyclohexanedicarboxylate acid (1,4-$H_2$chdc), formulated as $[Cd(1,4\text{-chdc})(L)]_n$ (**1**) was constructed under hydrothermal conditions.

X-ray crystallographic analysis reveals that the asymmetric unit of **1** contains one Cd(II) atom, one 1,4-chdc anion and one L ligand. Each Cd(II) atom is coordinated by five carboxylate oxygen atoms from three 1,4-chdc anions (Cd(1)–O(2) = 2.301(2), Cd(1)–O(3) = 2.413(2), Cd(1)–$O(4)^{i}$ = 2.487(2), Cd(1)–$O(5)^{i}$ = 2.362(2), Cd(1)–$O(5)^{ii}$ = 2.400(2) Å) and two

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nitrogen atoms from one chelating L ligand (Cd(1)–N(1) = 2.292(2), Cd(1)–N(2) = 2.405(3) Å) in a distorted [$CdN_2O_5$] pentagonal bipyramidal geometry (Figure 1). The distances of the Cd-O bonds range from 2.301(2) to 2.487(2) Å, which are close to those of $[Cd(L\text{-pheA})(Ac)]_n$ (from 2.248(14) to 2.426(13) Å) (L-pheHA = L-phenylalanine hydroxamic acid) (Chen et al., 2020). The full deprotonated 1,4-chdc anion serves as a $\mu_3$-bridge linking three Cd(II) ions, in which one carboxylic group adopts chelating mode to connect one Cd(II) ions; the other carboxylic group adopts $\mu_2$-$\eta^1$:$\eta^2$-chelating/bridging mode to coordinate with two Cd(II) ions. The 1,4-chdc ligand, linking three Cd(II) ions to form a 2D layer, is shown in Figure 2, and the farthest Cd···Cd distance is 11.277 Å.

Strikingly, the secondary N-donor L ligands are situated on both sides of the 2D layer (Figure 3), which allow the formation of π–π stacking between the pyridine ring and benzene ring of the L ligands with the centroid-to-centroid distance of 3.633(2) Å and face-to-face distance of 3.6158(12) Å, and the dihedral angle between the two planes is ca. 2.78(16)° (the pyridine ring and benzene ring are composed of N(2)/C(6)–C(10) and C(18)$^{viii}$–C(23)$^{viii}$, respectively; symmetry code: $^{viii}$ *–x, –y + 1, –z + 1*) (Figure 4). These π–π stacking interactions connected the neighboring layers into a 3D supramolecular architecture (Figure 5). Additionally, as illustrated in Figure 6, O–H···N hydrogen bond (O(1)–H(1 A)···O(3)$^{vii}$, symmetric code: $^{vii}$ *–x, –y + 2, –z + 1*, as seen in Table 1,) and N–H···O hydrogen bonds (N(4)–H(4)···O(1) and N(4)–H(4)···O(4)$^{vi}$, symmetric code: $^{vi}$ *–x, y–1/2, –z + 1/2*, as illustrated in Table 1) further consolidate the 3D supramolecular structure of **1**.

For the IR spectrum of 1 (Figure 7), one strong and wide peak at 3,421 $cm^{-1}$ was observed, which is characteristic

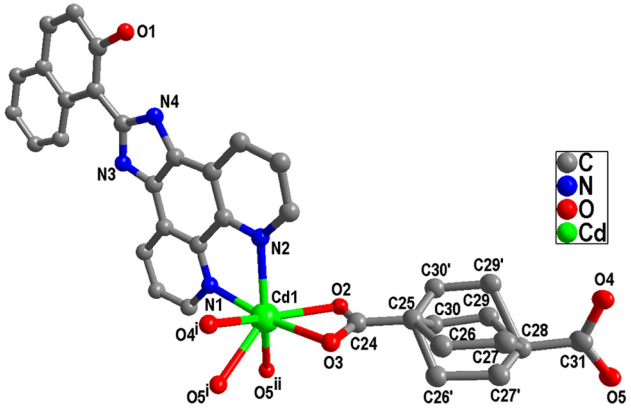


**Figure 1:** View of the coordination environment of the **Cd**(II) atom of **1** (the central ring of the 1,4-chdc is disordered over two positions, symmetric code: $^{(i)}$*x, –y + 5/2, z–1/2*; $^{(ii)}$*–x + 1, y + 1/2, –z + 1/2*).

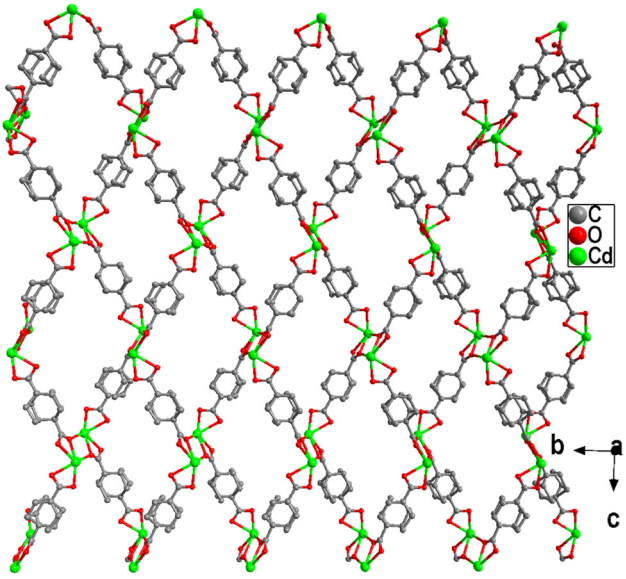


**Figure 2:** View of the 2D layer structure of **1** constructed by the 1,4-chdc.

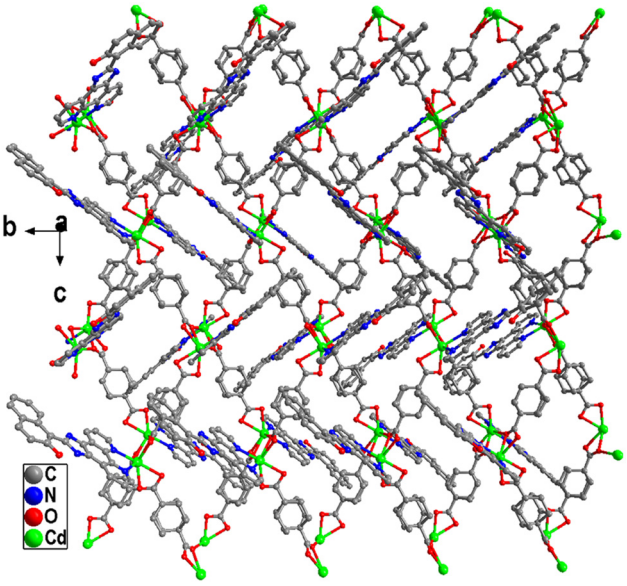


**Figure 3:** View of the 2D layer structure of **1** constructed by the 1,4-chdc and L ligands.

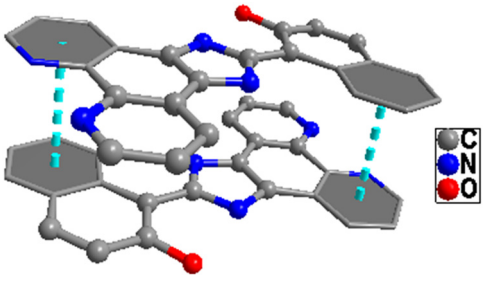


**Figure 4:** View of the π–π interactions between two L ligands of neighboring layers.

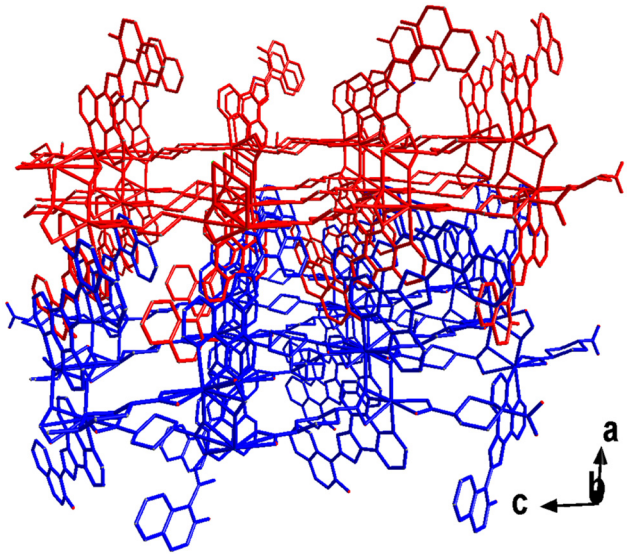


**Figure 5:** View of the 3D supramolecular structure of **1** formed by π–π interactions.

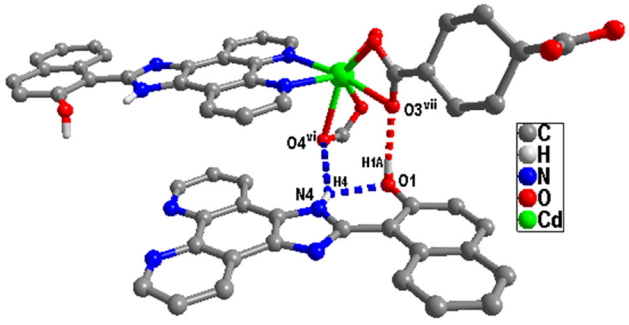


**Figure 6:** View of the O–H···N and N–H···O hydrogen bonds interactions (symmetric code: $^{vi}$–*x*, *y*–1/2, –*z* + 1/2, $^{vii}$–*x*, –*y* + 2, –*z* + 1).

**Table 1:** H-bonding geometry parameters (Å, °) for complex **1**

| D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | D–H···A (°) |
|---|---|---|---|---|
| N(4)–H(4)···O(1) | 0.86 | 2.05 | 2.617(4) | 122.3 |
| N(4)–H(4)···O(4)$^{vi}$ | 0.86 | 2.63 | 3.415(4) | 152.0 |
| O(1)–H(1A)···O(3)$^{vii}$ | 0.82 | 1.86 | 2.671(3) | 172.8 |

Symmetry codes: $^{vi}$–*x*, y–1/2, –*z* + 1/2; $^{vii}$–*x*, –*y* + 2, –*z* + 1.

of the O–H stretching frequency of the L ligand. Two peaks at 1,626 and 1,545 $cm^{-1}$ probably correspond to the *vas*(COO–) and *vs*(COO–) stretching vibration of dicarboxylate in the 1,4-chdc anion. Peaks at 1,413 and 1,072 $cm^{-1}$ could be assigned to *v*(C–N) and *v*(C=N) stretching vibration of the L ligand.

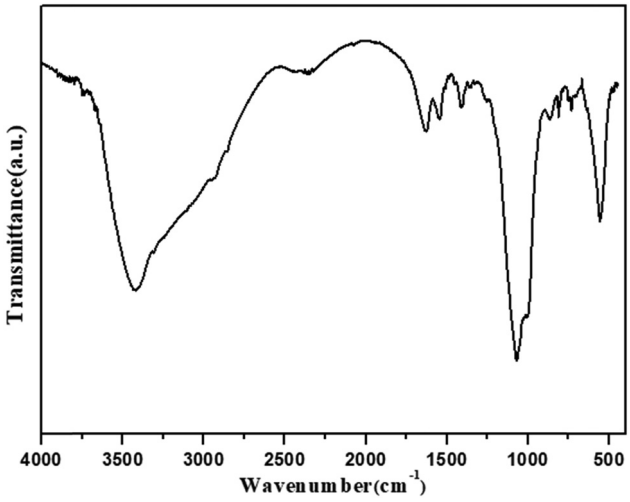


**Figure 7:** IR spectroscopy curve of **1**.

In summary, we report a 2D coordination polymer $[Cd(1,4\text{-chdc})(L)]_n$ (**1**) obtained under hydrothermal conditions with 1-(1*H*-imidazo[4,5-*f*][1,10]phenanthrolin-2-yl)naphthalen-2-ol (L) and 1,4-cyclohexanedicarboxylate acid (1,4-$H_2$chdc). The central Cd(II) atom is coordinated by 1,4-chdc anion and L ligand in a distorted $[CdN_2O_5]$ pentagonal bipyramidal coordination environment to generate a 2D layer. The adjacent 2D layers are further expanded into 3D supramolecular structure via π–π stacking interactions.

## Experimental

All the starting materials 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 PerkinElmer 240 CHN elemental analyzer (PerkinElmer, North Waltham, USA). IR spectrum was recorded on an Alpha Centaurt FT/IR Spectrophotometer (Mattson Technology, USA).

### Preparation of $[Cd(1,4\text{-chdc})(L)]_n$ (1)

A mixture of $CdCl_2{\cdot}2.5H_2O$ (0.2 mmol, 0.046 g), L (0.2 mmol, 0.072 g), 1,4-$H_2$chdc (0.2 mmol, 0.034 g), and 1 mL of anhydrous ethanol was placed in a 50 mL beaker. The mixture was stirred at room temperature. Then, the solution

mixture was sealed in 15 mL Teflon-lined stainless steel vessel which was kept at 195°C for 4 days. After cooling to room temperature, yellow block crystals of **1** were obtained with the yield of 0.067 g (ca. 48%, based on the Cd). Anal. (%) calcd. for $C_{31}H_{22}CdN_4O_5$, %: C, 57.91; H, 3.45; N, 8.71. Found %: C, 57.56; H, 3.40; N, 8.63.

## X-ray crystallography

Crystallographic data for **1** were collected at 298 (2) K on a Bruker-AXS Smart CCD diffractometer, with graphite-monochromatized Mo-Kα radiation ($\lambda$ = 0.71073 Å) using the $\phi$ and $\omega$ scan technique. The crystal structures were resolved by direct methods using SIR2014 (Burla et al., 2015) and refined by full-matrix least-squares methods based on $F^2$ using SHELXL2018/3 program (Sheldrick, 2015). All the non-hydrogen atoms were treated anisotropically. The hydrogen atoms were set in calculated positions and refined as riding atoms. The cyclohexane ring of 1,4-chdc in **1** was disordered over two positions, the occupancies of the two orientations were refined with their sum set to equal 1. Detailed information about the crystallographic parameters are listed in Table 2, with selected bond lengths and bond angles of coordination polymers **1** are summarized in Table 3. Full details of the X-ray structure determination of coordination polymers **1** have been deposited with the Cambridge Crystallographic Data Center, and the CCDC numbers for **1** is 2168486.

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

| | |
|---|---|
| Empirical formula | $C_{31}H_{22}CdN_4O_5$ |
| Formula weight | 642.92 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$ (Å) | 12.6565(9) |
| $b$ (Å) | 10.6227(8) |
| $c$ (Å) | 19.6911(14) |
| $\beta$ (°) | 96.3450(10) |
| Volume (Å$^3$) | 2631.2(3) |
| $Z$ | 4 |
| $D_c$ (g·cm$^{-3}$) | 1.623 |
| $\mu$ (mm$^{-1}$) | 0.880 |
| $F$(000) | 1,296 |
| $\theta$ range (°) | 1.619–25.010 |
| Crystal size (mm) | 0.289 × 0.235 × 0.153 |
| Tot. reflections | 4,647 |
| Uniq. reflections, $R_{int}$ | 13,351, 0.0249 |
| GOF on $F^2$ | 1.017 |
| $R_1$ indices [$I > 2\sigma(I)$] | 0.0321 |
| w$R_2$ indices (all data) | 0.0827 |
| $\Delta\rho_{min}$, $\Delta\rho_{max}$ (e·Å$^{-3}$) | −0.252, 0.609 |
| CCDC No. | 2168486 |

**Table 3:** Selected bond lengths (Å) and angles (°) for the complex **1**

| | |
|---|---|
| Cd(1)–N(1) | 2.292(2) |
| Cd(1)–N(2) | 2.405(3) |
| Cd(1)–O(2) | 2.301(2) |
| Cd(1)–O(3) | 2.413(2) |
| Cd(1)–O(4)$^{i}$ | 2.487(2) |
| Cd(1)–O(5)$^{i}$ | 2.362(2) |
| Cd(1)–O(5)$^{ii}$ | 2.400(2) |
| N(1)–Cd(1)–O(2) | 126.26(9) |
| N(1)–Cd(1)–O(5)$^{iii}$ | 93.40(9) |
| O(2)–Cd(1)–O(5)$^{iii}$ | 134.54(9) |
| N(1)–Cd(1)–O(5)$^{iv}$ | 88.09(8) |
| O(2)–Cd(1)–O(5)$^{iv}$ | 87.97(8) |
| O(5)$^{iii}$–Cd(1)–O(5)$^{iv}$ | 70.30(8) |
| N(1)–Cd(1)–N(2) | 70.95(9) |
| O(2)–Cd(1)–N(2) | 87.32(9) |
| N(2)–Cd(1)–O(5)$^{iii}$ | 130.72(8) |
| N(2)–Cd(1)–O(5)$^{iv}$ | 149.70(9) |
| N(1)–Cd(1)–O(3) | 166.95(9) |
| O(2)–Cd(1)–O(3) | 54.99(8) |
| O(3)–Cd(1)–O(5)$^{iii}$ | 91.74(8) |
| O(3)–Cd(1)–O(5)$^{iv}$ | 104.94(9) |
| N(2)–Cd(1)–O(3) | 96.68(9) |
| N(1)–Cd(1)–O(4)$^{iii}$ | 88.12(8) |
| O(2)–Cd(1)–O(4)$^{iii}$ | 136.12(8) |
| O(5)$^{iii}$–Cd(1)–O(4)$^{iii}$ | 53.53(7) |
| O(5)$^{iv}$–Cd(1)–O(4)$^{iii}$ | 123.31(7) |
| N(2)–Cd(1)–O(4)$^{iii}$ | 78.84(8) |
| O(3)–Cd(1)–O(4)$^{iii}$ | 85.31(8) |

Symmetry codes: $^{i}x, -y + 5/2, z - 1/2$; $^{ii}-x + 1, y + 1/2, -z + 1/2$; $^{iii}x, -y + 5/2, z + 1/2$; $^{iv}-x + 1, y - 1/2, -z + 1/2$.

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**Author contributions:** Beihao Su: writing – original draft and writing – review and editing; Yihan Shi: writing – original draft, conceptualization and methodology; Xuehan Peng: writing – review and editing and software; Zhiguo Kong: writing – review and editing, visualization, and software; Limin Chang: data curation and validation.

**Conflict of interest:** Authors state no conflict of interest.

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

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