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Structural Diversities of a Series of Cd(II) Coordination Complexes Based on a Flexible Tripodal N-donor Ligand

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Abstract: Three Cd(II) coordination complexes with unique structures and topologies, namely, $\{[\text{Cd}(\text{ttmb})(\text{Hbtc})] \cdot 5\text{H}_2\text{O}\}_n$ (1), $\{[\text{Cd}(\text{ttmb})(\text{m-phda})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}\}_n$ (2), and $\{[\text{Cd}(\text{ttmb})(\text{o-cpla})] \cdot (\text{CH}_3\text{CN}) \cdot (\text{H}_2\text{O})_{1.5}\}_n$ (3), have been successfully synthesized under hydro(solvo)thermally condition based on a flexible tripodal N-contained ligand 1,3,5-tris(1,2,4-triazol-1-ylmethyl)-2,4,6-trimethylbenzene (ttmb) and aromatic polycarboxylate acids (H_3btc = 1,2,4-benzenetricarboxylic acid, $\text{m-H}_2\text{phda}$ = 1,3-phenylenediacetic acid and $\text{o-H}_2\text{cpla}$ = Homophthalic acid). Complexes 1–3 were characterized by elemental analysis, IR spectroscopy, X-ray single-crystal diffraction and thermogravimetric analyses. 1 crystallize in the orthorhombic chiral space group $P2_12_12_1$ and feature 3D coordination networks. 2 reveals a 2D ladder-like structure with (4,4) topology containing alternating $\text{Cd}(\text{II})/\text{m-phda}^{2-}$ left- and right-handed helical motifs. 3 exhibits a 3D net with $(6^3)(6^6)(7 \cdot 8^2)$ topology. The structural and dimensional diversity of these complexes not only indicates that the flexible ligand ttmb exhibits strong coordination ability and diverse coordination modes, but also shows that aromatic polycarboxylates play important roles in constructing the frameworks of complexes. Moreover, the different photoluminescence behaviors of 1–3 have been studied in the solid state.

Keywords: coordination polymer; chiral space group; ladder-like structure; luminescence

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1. Introduction

In order to obtain unique MOFs with interesting properties, many flexible ligands have been widely employed as linkers of metal ions, specifically flexible N-donor bridging ligands [1–5]. The introduction of N-rich functional ligands into MOFs is an available strategy to realize the functionalization of materials, as the accessible N sites, such as NH_2 groups, imidazole, and N-rich triazole units, can enhance their catalytic performance and gas adsorption capacity [6–10]. Triazole containing ligands usually have strong coordination ability to transition metal ion centers. For example, as multifunctional organic linkers, 1,2,4-triazole and its derivatives can possess a combination of the advantages of the coordination geometries of both pyrazole and imidazole, and provide more potential coordination sites [11,12]. Compared with the rigid ligands, conformation of the flexible 1,2,4-triazole-containing ligands can often be influenced by exterior factors; thus, specific structures and functions can be used to coordinate different metal ions. At the same time, the flexible ligand itself is easy to rotate and twist in the process of self-assembly.

Meanwhile, polycarboxylate organic ligands, which have good coordination ability and various coordination modes, have proven to be excellent structural contributors [13–15]. The coordination complexes based on the mixed 1,2,4-triazole-containing and polycarboxylate-based ligands were explored with complicated coordination environments. A series of 1,2,4-triazole-containing ligands with distinct orientation and flexibility were reported, as 1,4-bis(1,2,4-triazol-1-ylmethyl)-benzene (bbtz), 4,4'-bis(1,2,4-triazol-1-ylmethyl)biphenyl (btmb), 1,4-bis(1,2,4-triazol-1-yl)butane (btb), 1,3,5-tris(1,2,4-triazol-1-

ylmethyl)-2,4,6-trimethylbenzene (tttmb) [16–26]. For further understanding of the coordination principle, systematic study was carried out for 1,2,4-triazole-containing tripodal ligand Cd(II) coordination complexes, and three Cd(II) coordination complexes, namely, $\{[\text{Cd}(\text{tttmb})(\text{Hbtc})] \cdot 5\text{H}_2\text{O}\}_n$ (**1**, H_3btc = 1,2,4-benzenetricarboxylic acid), $\{[\text{Cd}(\text{tttmb})(m\text{-phda})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}\}_n$ (**2**, $m\text{-H}_2\text{phda}$ = 1,3-phenylenediacetic acid), and $\{[\text{Cd}(\text{tttmb})(o\text{-cpla})] \cdot (\text{CH}_3\text{CN}) \cdot (\text{H}_2\text{O})_{1.5}\}_n$ (**3**, $o\text{-H}_2\text{cpla}$ = homophthalic acid) were successfully synthesized. In addition, the crystal structures and topology of **1–3** were characterized and discussed. Moreover, the thermal stability and photoluminescence properties of **1–3** were also studied.

2. Materials and Methods

2.1. Reagents and Instruments

All reagents and solvents, except for tttmb, were purchased from commercial sources and used directly without further purifications. The ligand tttmb was synthesized according to the literature (see the Supplementary Information for a more detailed description of the synthesis) [21]. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were recorded on a Bruker Tensor 27 spectrometer (Bruker, Bremen, Germany) with KBr pellets. C, H, N elemental analyses were carried out on a Flash EA 1112 elemental analyzer (Nicolet, Ventura, CA, USA). Powder X-ray diffraction data were collected on a PANalytical X'Pert PRO diffractometer (PANalytical, Almelo, The Netherlands) with Cu-K α radiation ($\lambda = 1.5406\text{ \AA}$). Thermal analyses were performed on a Netzsch STA 449C thermal analyzer (Netzsch, Selb, Germany) from room temperature at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ in air. The solid-state luminescent spectra were performed on a Hitachi 850 fluorescent spectrometer (Hitachi, Chiyoda, Japan) using Xe lamp as the light source.

2.2. Single-Crystal X-ray Diffraction

Determination of the crystal structures of **1–3** by X-ray diffractions was carried on a Rigaku Saturn 724 CCD diffractometer with MoK α radiation ($\lambda = 0.71073\text{ \AA}$) at $290 \pm 1\text{ K}$. The structures were solved with the Olex2 program as an interface, together with the SHELXT and SHELXL programs [27,28]. In the refinement, all non-hydrogen atoms were provided with anisotropic displacement parameters and all hydrogen atoms were treated by a riding model. CCDC 1901158, 1901159, and 1901160 contains the supplementary crystallographic data for **1**, **2**, and **3**. Crystallographic crystal data and structure processing parameters for **1–3** are summarized in Table 1. Selected bond lengths and bond angles of **1–3** are listed in Table S1.

Table 1. Crystallographic parameters for compounds **1–3**.

Compound	1	2	3
Formula	$\text{C}_{27}\text{H}_{35}\text{N}_9\text{O}_{11}\text{Cd}$	$\text{C}_{28}\text{H}_{35}\text{N}_9\text{O}_7\text{Cd}$	$\text{C}_{29}\text{H}_{30}\text{N}_{10}\text{O}_5\text{Cd}$
Formula weight	774.0319	722.05	711.03
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$C2/c$	$C2/c$
a (Å)	11.281 (2)	30.639 (6)	19.825 (4)
b (Å)	13.642 (3)	12.889 (3)	13.620 (3)
c (Å)	22.337 (5)	19.841 (4)	23.123 (5)
α (°)	90.00	90.00	90.00
β (°)	90.00	121.18 (3)	95.43 (3)
γ (°)	90.00	90.00	90.00
V (Å ³)	3437.7 (12)	6704 (2)	6216 (2)
Z	4	8	8
D_{calc} (g·cm ^{−3})	1.476	1.431	1.520
μ (mm ^{−1})	0.703	0.707	0.758

Table 1. Cont.

Compound	1	2	3
$F(000)$	1544	2960	2944
R_1^a, wR_2^b ($I > 2\sigma(I)$)	0.0758, 0.1916	0.0747, 0.1686	0.0630, 0.1571
R_1, wR_2 (all data)	0.0864, 0.2002	0.0912, 0.1800	0.0803, 0.1806
GOF	1.061	1.140	1.180

$$^a R = [\sum ||F_o| - |F_c|| / \sum |F_o|], ^b R_W = \sum [|F_o|^2 - |F_c|^2]^2 / \sum (|F_o|^2)^{1/2}.$$

2.3. Preparation of Compounds 1–3

2.3.1. Synthesis of $\{[\text{Cd}(\text{ttmb})(\text{Hbtc})] \cdot 5\text{H}_2\text{O}\}_n$ (1)

$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.023 g, 0.1 mmol), ttmb (0.037 g, 0.1 mmol), H_3btc (0.021 g, 0.1 mmol) were dissolved in H_2O (8 mL). Following this, the mixed solution was kept in a Teflon-lined autoclave at 403 K for 3 days. Then, the reaction mixture was cooled down to room temperature, and the colourless crystals were obtained with a yield of 75% (based on Cd). Anal. Calc. For $\text{C}_{27}\text{H}_{35}\text{N}_9\text{O}_{11}\text{Cd}$ (%): C, 41.9; H, 4.6; N, 16.3. Found: C, 41.9; H, 4.4; N, 16.6. IR (KBr, cm^{-1}): 3440 (w), 3407 (w), 2958 (m), 2924 (s), 2360 (s), 2341 (s), 1748 (s), 1717 (s), 1647 (s), 1559 (s), 1436 (s), 1386 (s), 1134 (s), 669 (s), 515 (m), 449 (m).

2.3.2. Synthesis of $\{[\text{Cd}(\text{ttmb})(\text{m-phda})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}\}_n$ (2)

Compound 2 was obtained using a similar method as 1, except m- H_2phda (0.019 g, 0.1 mmol) was used instead of H_3btc . Colorless crystals were collected with a yield of 60% based on Cd. Anal. Calc. For $\text{C}_{28}\text{H}_{35}\text{N}_9\text{O}_7\text{Cd}$ (%): C, 46.6; H, 4.9; N, 17.5. Found: C, 46.9; H, 4.4; N, 16.9. IR (KBr, cm^{-1}): 3416 (w), 3125 (m), 2925 (m), 1561 (s), 1396 (s), 1261 (s), 1019 (s), 889 (m), 816 (m), 749 (s), 633 (s), 525 (m), 438 (w).

2.3.3. Synthesis of $\{[\text{Cd}(\text{ttmb})(\text{o-cpla})] \cdot (\text{CH}_3\text{CN}) \cdot (\text{H}_2\text{O})\}_n$ (3)

$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.023 g, 0.1 mmol), ttmb (0.037 g, 0.1 mmol), o- H_2cpla (0.018 g, 0.1 mmol) were dissolved in a mixture of H_2O (10 mL) and CH_3CN (1 mL). Following this, the mixed solution was kept in a 25 mL Teflon-lined autoclave and heated at 403 K for 3 days. After the mixture had been cooled to room temperature, colourless crystals were obtained with a yield of 75% based on Cd. Anal. Calc. $\text{C}_{29}\text{H}_{33}\text{N}_{10}\text{O}_{5.5}\text{Cd}$ (%): C, 49.0; H, 4.3; N, 19.7. Found: C, 47.3; H, 4.8; N, 18.5. IR (KBr, cm^{-1}): 3424 (w), 3134 (m), 3092 (m), 2923 (m), 1586 (s), 1519 (s), 1445 (m), 1389 (s), 1277 (s), 1134 (s), 1010 (s), 983 (s), 737 (s), 675 (s).

3. Results and Discussion

3.1. Structural Description

3.1.1. Crystal Structure of 1

1 is a 3D net and also crystallizes in the chiral orthorhombic space group $P2_12_12_1$ with Flack parameter of -0.01 (6) refined from the X-ray data. The asymmetric unit of 1 consists of one Cd(II) ion, one ttmb ligand, one Hbtc^{2-} ligand and five crystallization water molecule. As shown in Figure 1a, the Cd(II) ion is seven-coordinated, adopting a distorted pentagonal bipyramidal geometry via coordinating to four carboxylate oxygen atoms and three nitrogen atoms. The Cd–N distances are in the range of 2.303–2.352 Å and the Cd–O bond lengths vary from 2.410–2.460 Å.

Figure 1. (a) Coordination environment of Cd(II) ion in **1**. (b) The 3D Cd(II)/tttmb architecture extended by alternately left- and right-handed helical chains. (c) Schematic representation of **1** with $(5^3 \cdot 6 \cdot 7^3 \cdot 8^3)(5^2 \cdot 7)$ topology. Yellow node: Cd(II) ion; red stick: tttmb; blue stick: Hbtc²⁻.

The interesting feature of **1** is that the linkages between the Cd(II) ions and tttmb ligands form two kinds of helices. The tttmb ligands choose tridentate chelating coordination mode and bridge the adjacent Cd(II) ions to afford fascinating helical chains with left- and right-handed helical loops (Figure 1b). The pitches of left- and right-handed helix along the *a* axis both are equal to the length of the *a* axis. Each incompletely deprotonated Hbtc²⁻ anions displayed the bidentate coordinated mode coordinates of two Cd(II) centers. If the Cd(II) ion was taken as a 5-connected node, tttmb groups were regarded as 3-connected nodes and Hbtc²⁻ ligands were considered as linkers, **1** can be classified as a 3D structure with a point symbol of $(5^3 \cdot 6 \cdot 7^3 \cdot 8^3)(5^2 \cdot 7)$ (Figure 1c).

Comparing **1** with $[\text{Cd}_2(\text{tttmb})_2(\text{btc})\text{Cl}] \cdot 3\text{H}_2\text{O}$ (**1a**) [21], both of which were prepared from similar starting reactants, some important differences were found as follows: (i) The conformation of tttmb ligand. The tttmb ligand adopts *cis, cis, cis*-conformation in **1**, while *cis, trans, trans*-conformation in **1a**. (ii) The coordination mode of btc³⁻ anions. It is bidentate in **1**, but bidentate (carboxylate group at the 2,4-position) and monodentate (carboxylate group at the 1-position) in **1a**. (iii) The coordination geometry of Cd(II) ions.

It is in pentagonal bipyramid for **1**, while in octahedron for **1a**. (iv) The space group. Compound **1** crystallizes in the chiral orthorhombic space group, while **1a** in the triclinic space group. (v) The synthesis conditions in **1**, $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was used as the metal source, while $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ used in **1a**. Pure H_2O solvent was used for synthesis of **1**, while the use of NaOH in H_2O solvent for that of **1a**. Obviously, the addition of a strong base results in ligand H_3btc becoming completely deprotonated.

3.1.2. Crystal Structure of **2**

Compound **2** crystallizes in the monoclinic space group C2/c and exhibits a two-dimensional ladder-like layer structure. Each asymmetric unit of **2** contains one $\text{Cd}(\text{II})$ ion, one ttmb ligand, one $m\text{-phda}^{2-}$ ligand, one coordinated water molecule, and two lattice water molecules. The $\text{Cd}(\text{II})$ ion exhibits a distorted pentagonal bipyramidal geometry with a CdN_2O_4 coordination sphere, completed by four oxygen atoms from two different $m\text{-phda}^{2-}$ and one oxygen atom from a coordinated water molecule as well as two nitrogen atoms from two ttmb (Figure 2a). The $\text{Cd}-\text{N}$ bonds lengths are 2.288 and 2.318 Å, while $\text{Cd}-\text{O}$ bond lengths are in the range of 2.354–2.569 Å. The completely deprotonated $m\text{-phda}^{2-}$ ligands connect $\text{Cd}(\text{II})$ ions to form a 1D infinite helical chain with the right-handed and left-handed helices arranged alternately along the b axis with the pitch of 12.889(3) Å (Figure 2b), which is further interconnected through the ttmb ligands to generate a 2D wave-like structure with (4,4) sheets (Figure 2c).

Figure 2. (a) Coordination environment of $\text{Cd}(\text{II})$ ions in **2** with hydrogen atoms omitted for clarity. (b) The right- and left-handed helical chains built by $\text{Cd}(\text{II})$ ions and $m\text{-phda}^{2-}$ ligands. (c) View of the 2D ladder-like sheet with 4^4 topology (green ball: Cd^{II} ; Red line: $m\text{-phda}^{2-}$; green line: ttmb).

3.1.3. Crystal Structure of **3**

Complex **3** also crystallizes in the monoclinic space group C2/c . As shown in Figure 3a, the $\text{Cd}(\text{II})$ ion is seven-coordinated, adopting a distorted pentagonal bipyramidal geometry via coordinating to four oxygen atoms from two $o\text{-cpla}^{2-}$ anions and three nitrogen atoms from three ttmb ligands. The $\text{Cd}-\text{O}$ bond distances vary from 2.306 to 2.596 Å, while

the Cd–N bond lengths vary from 2.304 to 2.376 Å. In **3**, ttmb adopts a *cis, trans, trans*-conformation. N1 and N9 atoms of ttmb connect Cd(II) ions to form a 1D wave-like chain. The 1D chain is further linked by N6 atoms of ttmb to expand to a 3D framework (Figure S1). The carboxylic acid groups of *o*-cpla^{2−} anions choose bidentate chelating coordination mode and bridge the adjacent Cd(II) ions to afford fascinating helical chains with left- and right-handed helical loops. (Figure 3b). The pitches of left- and right-handed helix along the *b* axis both are equal to the length of the *b* axis. In addition, the Cd(II)/*o*-cpla^{2−} and Cd(II)-ttmb share Cd(II) ions to form a 3D architecture. Topological methods can provide better insight into such an elegant framework. The Cd(II) ion and ttmb ligand can be considered as five- and three-connected nodes, respectively, thus, the framework of **3** can be described as a rare (2,3,5)-connected net with the Schläfli symbol of (6³)(6⁶·7·8²·10) (Figure 3c).

Figure 3. (a) Coordination environment of Cd(II) ions in **3** with hydrogen atoms omitted for clarity. (b) The Cd(II)/*o*-cpla^{2−} left- and right-handed helical chains along the *b*-axis. (c) Three-dimensional network and schematic representation of **3**. Blue line: ttmb; yellow node: Cd(II) ion; red line: *o*-cpla^{2−} group.

3.1.4. Coordination Modes of ttmb Ligand in 1–3

According to the above structure description, the flexible tripod ligand ttmb has three different coordination modes in complexes **1–3**, as depicted below in Figure 4. In **1**, ttmb ligands adopt the *cis, cis, cis*- μ_3 coordination modes and coordinate with three Cd(II) atoms to form left- and right-handed helices (mode I in Figure 4). In **2**, ttmb ligands show the *cis, trans, trans*- μ_2 coordination modes (mode II in Figure 4) and coordinate with only two Cd(II) atoms to form 1D chains. In **3**, ttmb ligands show similar *cis, trans, trans*-conformations, but act as a μ_3 -bridge linking three Cd(II) atoms to expand to a 3D framework (mode III in

Figure 4). The results show that the coordination modes and the conformations of ttmb ligands obviously influence the structures of the complexes.

Figure 4. The different conformations of ligand ttmb in complexes.

3.2. Powder X-ray Diffraction (PXRD) and Thermal Analyses

The simulated and experimental PXRD patterns of compounds 1–3 (obtained at room temperature) are shown in Figure S2. Their peak positions correspond well with each other, indicating the phase purity of the solids.

The thermal stability of the complexes was investigated, as shown in Figure 5. For 1, there is an initial weight loss at 30.0–302.5 °C, which arises from the loss of five water molecules (observed, 11.7%; calculated, 11.6%). Then the framework begins to decompose. For 2, weight loss of 8.0% occurs from 30.0 to 267.5 °C, which corresponds to the loss of one coordinated water molecule and two guest molecules (calculated, 7.8%). Then the network begins to decompose. For 3, weight loss of 3.1% occurs from 30.0 to 145.0 °C, which corresponds to the loss of solvent water molecules (calculated, 2.5%).

Figure 5. TG plots of complexes 1–3.

3.3. Photoluminescence Properties

The solid state photoluminescent behaviors of Cd(II) complexes 1–3, the free ttmb ligand and aromatic polycarboxylic acids (H_3btc , m - H_2phda and o - H_2cpla) were investigated at ambient temperature under the same experimental conditions. The emission spectra of ttmb, H_3btc , o - H_2cpla and m - H_2phda are shown in Figure 6a. Intense bands were observed at 307 nm (λ_{ex} = 290 nm) for ttmb, 345 nm (λ_{ex} = 306 nm) for H_3btc , 318 nm (λ_{ex} = 274 nm) for o - H_2cpla , and 358 nm (λ_{ex} = 314 nm) for m - H_2phda . The emission spectra of complexes 1–3 are shown in Figure 6b. Intense bands were observed at 454 nm (λ_{ex} = 348 nm) for 1, 441 nm (λ_{ex} = 379 nm) for 2, and 420 nm (λ_{ex} = 306 nm) for 3. All these bands can be assigned to intraligand ($\pi^* \rightarrow \pi$ or $\pi^* \rightarrow n$) emission [29,30]. The emission bands of 3

present red shifts (62 nm) in contrast to those of the free carboxylate ligands (*m*-H₂phda). In view of similar excitation wavelengths for the complex and carboxylate ligands, the coordination of ligands with the Cd(II) ions can improve the conjugation degree of ligands, which may cause the red-shifts [31]. The different photoluminescent behaviors of 1–3 with the same metal center and N-donor ligand may be caused by the coordination environment, auxiliary aromatic polycarboxylate ligand.

Figure 6. Solid-state photoluminescent spectra of (a) free ligands and (b) Complexes 1–3.

4. Conclusions

In summary, we have successfully synthesized three new Cd(II) complexes based on tttmb and different aromatic polycarboxylate ligands under hydro(solvo)thermal conditions. Our research demonstrates that tttmb is a good candidate for the assembling of coordination complexes with charming frameworks and topologies and has the potential to form chiral coordination complexes. Moreover, the structural versatility of 1–3 shows that the coordination modes and the conformations of tttmb ligands can effectively tune the final structural features, as well as the aromatic polycarboxylate coligands. Subsequent studies about this flexible tripodal ligand tttmb are underway.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/cryst12010053/s1>. The description of the synthesis of 1,3,5-tris(1,2,4-triazol-1-ylmethyl)-2,4,6-trimethylbenzene ligand. Table S1: Selected bond lengths (Å) and bond angles (°) for 1–3, Figure S1: The 3D framework of complex 3; Figure S2: Experimental (red) and simulated (black) PXRD patterns of compound 1–3.

Author Contributions: H.W. synthesized the three compounds. J.Q. performed the X-ray structure determination and analyzed the results. H.W. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Crystallographic crystal data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (accessed on 15 November 2021), or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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