

Notes

Synthesis, Structure and Physical Properties of Cd-Coordination Polymer with (4, 5, 10)-Connected Topology Based on Trinuclear Clusters

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Investigations into coordination polymers remain intensely active because of their intriguing supramolecular compositions and versatile framework topologies as well as their potential applications in many fields, such as ion-exchange, heterogeneous catalysts, optical devices, magnets, electrical conductivity, *etc.*¹⁻³ It is known that the structures of coordination polymers is usually influenced by many factors in the self-assembly process, such as the geometry of the central metal ions, the organic ligands, the counter-ions, the solvents, the temperature and the reaction conditions.⁴ Among these parameters, the nature of the organic ligands is a key factor for constructing coordination polymers with interesting structures. In recent years, multicarboxylate ligands have been widely used in the construction of coordination polymers because of their diversities in coordination modes and conformations.^{5,6} However, 5-*tert*-butyl isophthalic acid (H₂tbip) as a substituted isophthalate ligands at meta-disposed 5-position have received less attention in the construction of coordination polymers.⁷ On the other hand, flexible ligands coordinating to metal centres may bend or rotate to adopt different conformations and often form novel coordination polymers. 1,3-Bis(1,2,4-triazol-1-yl)propane (btp) can adopt different conformations compared with the corresponding 1,2,4-triazole ligand because of the presence of a flexible $-(CH_2)_3-$ group.⁸ The flexibility and conformation freedom of btp can offer the possibility for the construction of an unpredictable and interesting coordination polymers. In this communication, a novel coordination polymer involving the 5-*tert*-butyl isophthalic acid and 1,3-bis(1,2,4-triazol-1-yl)propane mixed ligands [Cd₄(tbip)₄(btp)·H₂O]_n (**1**), has been reported.

Experimental Section

Materials and Physical Measurements. The 1,3-bis(1,2,4-triazol-1-yl)propane (btp) ligand was synthesized according to the literature method.⁸ All other reagents and solvents were commercial available and used without further purification. Infrared spectrum was obtained within the 4000–400

cm⁻¹ as KBr disks on a VECTOR 22 spectrometer. Elemental analysis was performed on a Perkin Elmer 240C elemental analyzer. Fluorescent spectrum was recorded on a Fluoro Max-P spectrophotometer. Thermal gravimetric analysis (TGA) was collected on a Perkin-Elmer Pyris 1 TGA analyzer from room temperature to 650 °C with a heating rate of 20 °C min⁻¹ under nitrogen.

Synthesis of [Cd₄(tbip)₄(btp)·H₂O]_n (1**).** A mixture of Cd(NO₃)₂·6H₂O (34.6 mg, 0.100 mmol), H₂tbip (44.4 mg, 0.200 mmol), btp (17.8 mg, 0.100 mmol), KOH (22.4 mg, 0.400 mmol) in H₂O (10 mL) was sealed in a 16 mL Teflon-lined stainless steel container and heated at 180 °C for 72 h. After cooling to room temperature, colorless block crystals were collected by filtration and washed by water and ethanol several times. (yield 13.6%, based on btp). Elemental analysis for C₅₅H₆₀Cd₄N₆O₁₇ (*M*_r = 1526.73): C 43.27, H 3.96, N 5.50%; found: C 43.38, H 3.97, N 5.52%. Selected IR (KBr) spectra for **1**: m (cm⁻¹) 3612 (w), 3066 (w), 1634 (s), 1570 (s), 1521 (s), 1423 (m), 1442 (w), 1331 (w), 1042 (m), 831 (w), 813 (m), 731 (w), 702 (w).

Structural Determination and Refinement. Structural data for **1** were collected on a Bruker Smart Apex CCD with graphite-monochromated Mo K α radiation (λ = 0.71073 Å) at 291 K. Absorption correction was applied using multi-scan technique. The structure was solved by direct method using the program SHELXL-97 and refined by full-matrix least-squares technique on *F*² with SHELXL-97.⁹ Six C atoms within two *tert*-butyl groups (C10, C11, C12, C22, C23, C24) were modelled as disordered over two sites. In complex **1**, two sets of positions are defined by atoms C10A/C11A/C12A and C10B/C11B/C12B, with refined site occupancies of 0.347 (5) and 0.653 (5), respectively. The C22, C23 and C24 atoms are refined as disordered over two positions, with site occupancies of 0.82 (3) and 0.18 (3). All non-hydrogen atoms were located in difference Fourier maps and refined with anisotropic temperature parameters. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. A summary of the structural determination

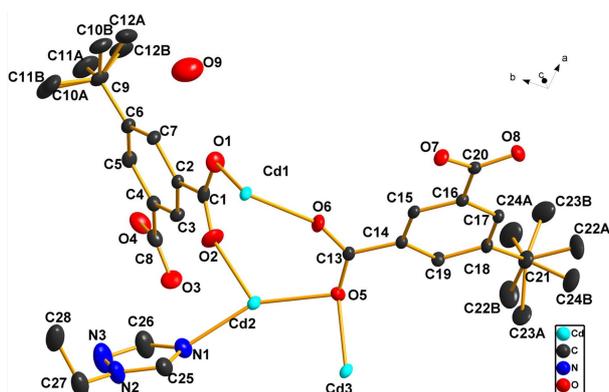
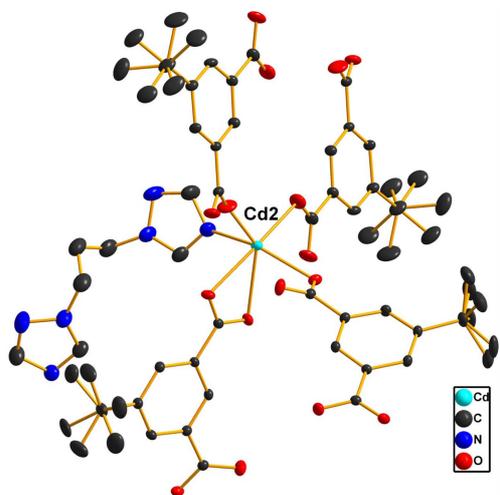


Figure 1. View of the asymmetric unit in complex **1**. Six C atoms within two tert-butyl groups (C10, C11, C12, C22, C23, C24) show orientational disorder. All hydrogen atoms are omitted for clarity.

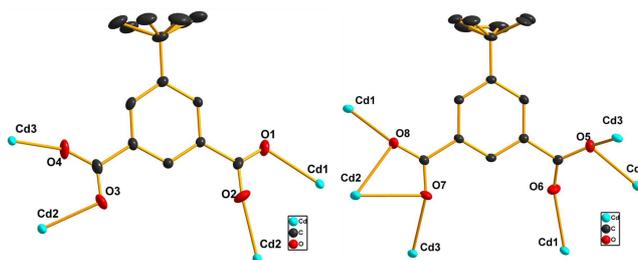
and refinement for the title complex is summarized in Table S1 (Supporting Information) and the selected bond distances and angles are shown in Table S2.

Results and Discussions

The single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the centrosymmetric orthorhombic space group *Fddd* with an asymmetric unit consisting of three crystallographically distinct divalent cadmium atoms (two of which, Cd1 and Cd3, rest on an inversion center), two types of separate fully deprotonated tbip^{2-} (tbip-A , O1–O4; tbip-B , O5–O8) ligands, one half of a btp ligand as well as one-half water molecules of crystallization (Figure 1). The Cd1 and Cd3 centers both are six-coordinated by six oxygen donor atoms from chelating carboxylate groups belonging to six different tbip^{2-} ligands, resulting in an octahedral coordination environment. On the other hand, Cd2 displays a distorted $\{\text{CdO}_5\text{N}\}$ octahedral geometry, with the axial positions taken up by one triazole nitrogen donor atom



Scheme 1. View of the coordination mode of Cd2 metal in complex **1**.



Scheme 2. View of the coordination mode of tbip^{2-} ligands in complex **1**.

from one btp ligand and one oxygen donor atom from chelating carboxylate group belonging to one tbip^{2-} ligand as shown in Scheme 1. The equatorial plane filled by four oxygen atom donors from three chelating carboxylate groups from another three different tbip^{2-} ligands. The Cd–N bond length is 2.306(3) Å and the Cd–O bond lengths are in the range 2.191(2)–2.600(2) Å, which are well comparable to those reported for other cadmium complexes,¹⁰ and the O–Cd–O bond angles fall in the range of 52.42(7)–175.84(9)°.

Notably, two types of tbip^{2-} ligands show different coordination modes in complex **1**. One tbip^{2-} ligand links four Cd(II) cations in $\mu_2\text{-}\eta^1: \eta^1, \mu_2\text{-}\eta^1: \eta^1$ coordination fashions through its two carboxylate groups, whereas the remaining one links six Cd(II) cations in $\mu_3\text{-}\eta^2: \eta^1, \mu_3\text{-}\eta^2: \eta^2$ coordination fashions through its two carboxylate groups as shown in Scheme 2. In these manners, three crystallographically independent Cd(II) centers are linked by tbip^{2-} ligands with these coordination modes into a triangular trinuclear Cd(II)

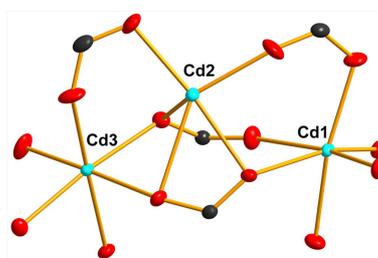


Figure 2. View of triangular trinuclear Cd(II) cluster.

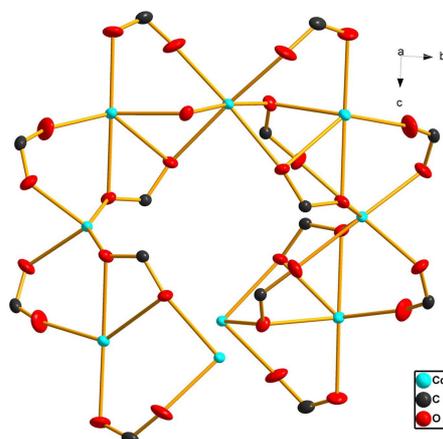
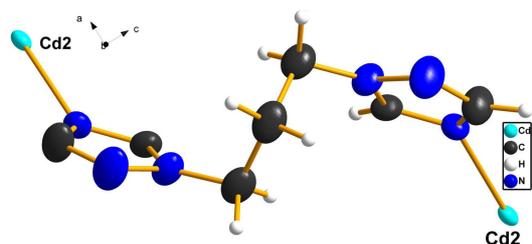


Figure 3. The infinite rod-shaped SBU along *a*-axis.



Scheme 3. View of the coordination mode of btp ligand in complex **1**.

clusters (Figure 2) with Cd...Cd distances in the range of 3.2921(6)–5.6861(7) Å. As shown in Figure 3, these trinuclear Cd(II) clusters are further connected by oxygen atoms of four carboxylate groups from two different tbip^{2-} ligands to form an infinite rod-shaped secondary building units (SBUs) along a -axis. In such SBUs, the trinuclear Cd(II) clusters are arranged in nonlinear fashion with intercluster center distance of 5.224 Å. Moreover, the tbip^{2-} ligands link rod-shaped SBUs to give rise to a complicated three-dimensional framework. On the other hand, the btp exhibits the *gauche-gauche* conformation with the dihedral angle between two triazole planes of $37.8(2)^\circ$, bridging two Cd2 atoms in complex **1** as shown in Scheme 3. The Cd2...Cd2 contact distances through btp ligand is 9.5813(13) Å. The 3D networks only constructed by tbip^{2-} ligands are further connected by btp ligands to result in a new three-dimensional framework of complex **1** (Figure 4). Moreover, the lattice water molecule (O9) participates in two H-bonds [O(9)–H(9A)...O(1) and O(9)–H(9B)...O(2)^{#1}; symmetry codes: #1 5/4- x , y , 1/4- z], which further stabilize the 3D networks architecture.

A further insight into the nature of this intricate framework can be acquired by using topological analysis. A topological analysis of this net was performed with TOPOS software.¹¹ In complex **1**, each tbip-A ligand links four trinuclear Cd(II) clusters and serves as a 4-connected node, and each tbip-B ligand bridges five trinuclear Cd(II) clusters and acts as a 5-

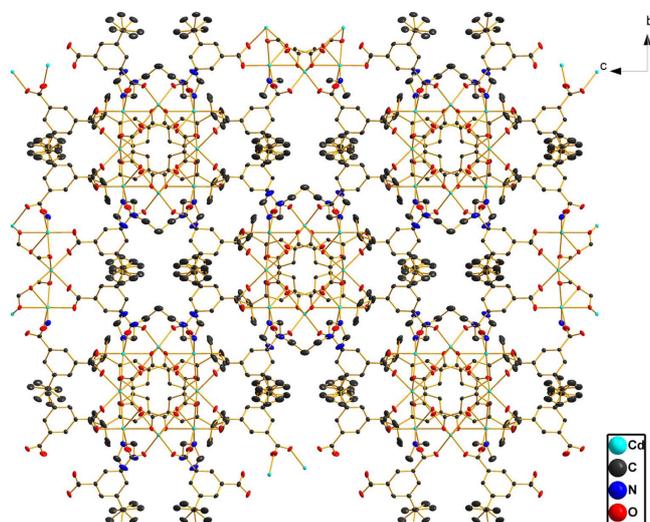


Figure 4. A view of the 3D framework of complex **1**.

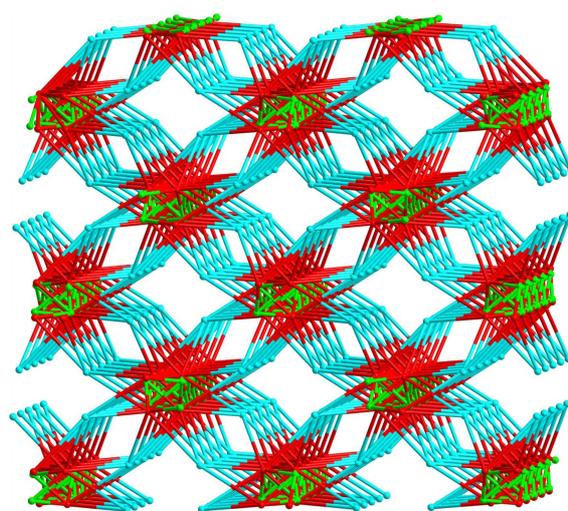


Figure 5. A schematic representation of the (4, 5, 10)-connected topology of complex **1**.

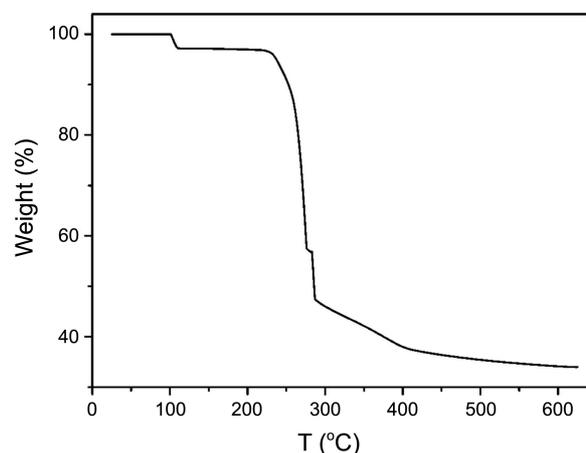


Figure 6. Thermogravimetric curve of complex **1**.

connected node; while each trinuclear Cd(II) cluster separately joins four tbip-A ligands, five tbip-B ligands and another one trinuclear Cd(II) clusters, thus, it can be simplified as a 10-connected node. As a whole, the topology of the resulting

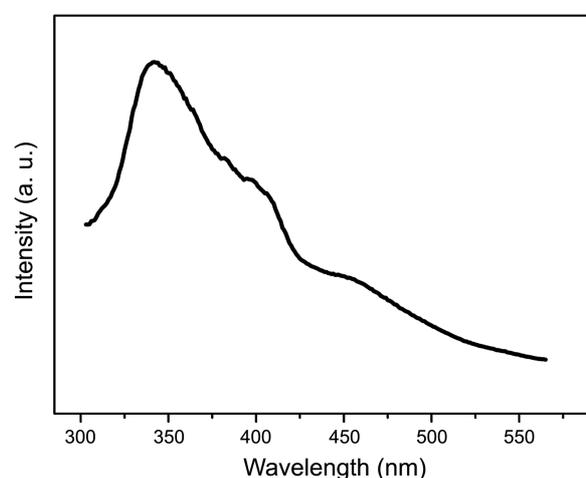


Figure 7. The solid-state emission spectra of complex **1**.

3D framework can be described as a unique trinodal (4, 5, 10)-connected net with the Schläfli symbol of (3.4⁸.5) (3².4²⁸.5¹⁰.6⁵) (4³.6².7) (Figure 5). To the best of our knowledge, this trinodal topology has neither been reported. The unligated water molecules occupy a solvent-accessible incipient space comprising 2.7% of the unit cell volume, according to PLATON.¹²

The thermostability of **1** was studied by thermogravimetric analyses (TGA) (Figure 6). Thermogravimetric analysis of **1** demonstrates that the first weight loss before 108 °C corresponds to the release of the water molecules of crystallization (obsd. 1.98%, calcd. 1.18%). The organic ligands began to decompose at 225 °C, with the 33.99% mass remnant at 620 °C consistent with production of CdO (33.64% calcd).

The fluorescent property of complex **1** was studied in the solid state at room temperature. The free H₂tbip shows emission peaks at 320 nm.¹³ Irradiation of crystalline samples of complex **1** with ultraviolet light ($\lambda_{\text{ex}} = 295$ nm) in the solid state resulted in intense emission violet visible light emission with a λ_{max} of 343 nm (Figure 7). According to a recent review of d¹⁰ metal coordination polymer luminescence, the emissive behavior of **1** can be ascribed to ligand-centered electronic transitions.¹⁴

In summary, a new Cd(II) coordination polymer, [Cd₄(tbip)₄(btp)·H₂O]_n (**1**) was successfully synthesized through a hydrothermal reaction of Cd(II) ions, 5-*tert*-butyl isophthalic acid (H₂tbip) and 1,3-bis(1,2,4-triazol-1-yl)propane (btp). The complex features 3-D framework with (4, 5, 10)-connected (3.4⁸.5) (3².4²⁸.5¹⁰.6⁵) (4³.6².7) topology based on trinuclear Cd(II) cluster motifs. In addition, complex **1** exhibits strong fluorescent emissions in the solid state at room temperature.

Supplementary Material. CCDC-954475 (**1**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via <http://www.ccdc>.

cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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