

## A rare 'mesh of trees' (mot) net: poly[aquahemi[ $\mu_4$ -1,6-bis(1,2,4- triazol-1-yl)hexane]( $\mu_2$ -5-nitro- isophthalato)cadmium(II)]

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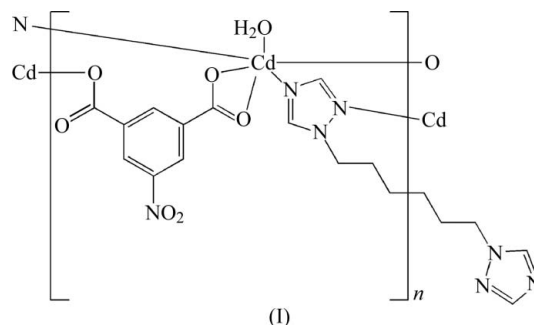
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In the title coordination compound,  $[\text{Cd}(\text{C}_8\text{H}_3\text{NO}_6)(\text{C}_5\text{H}_8\text{N}_3)_2 \cdot 0.5(\text{H}_2\text{O})]_n$ , each  $\text{Cd}^{\text{II}}$  atom is six-coordinated in a distorted octahedral environment surrounded by three carboxylate O atoms from two different 5-nitroisophthalate ( $5\text{-NIP}^{2-}$ ) ligands, two N atoms from two distinct 1,6-bis(1,2,4-triazol-1-yl)hexane (bth) ligands and one water molecule. The  $\text{Cd}^{\text{II}}$  centres are bridged by the bth ligands, which lie across centres of inversion, to give a honeycomb-like two-dimensional layer structure; the layers are further connected by the bridging  $5\text{-NIP}^{2-}$  ligands with a  $\kappa^2;\kappa^1-\mu_2$  coordination mode to generate the final three-dimensional structure. Topologically, taking the  $\text{Cd}^{\text{II}}$  atoms and the bth ligands as different four-connected nodes and the  $5\text{-NIP}^{2-}$  ligands as linkers, the three-dimensional structure can be simplified to a rare 'mesh of trees' (mot) net with the Schäfli symbol  $(6^6)(6^4.8^2)_2$ .

### Comment

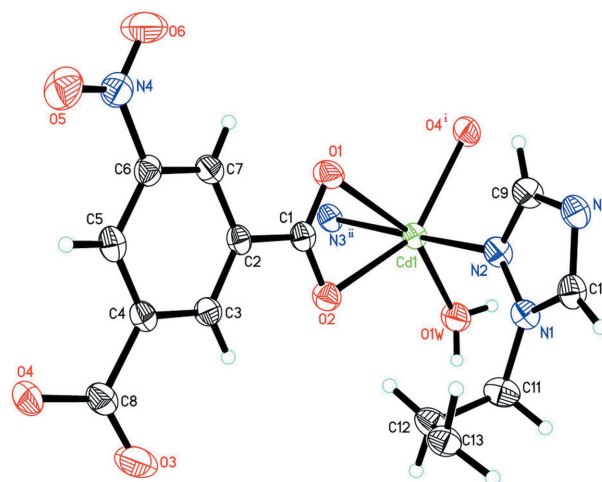
The rational design and synthesis of metal-organic frameworks (MOFs) constructed from organic ligands and metal ions through a self-assembly route has undergone rapid development in recent years owing to their fascinating structural topologies and potential applications as functional materials (Abrahams *et al.*, 1999; Eddaoudi *et al.*, 2001; Farha *et al.*, 2010). The topologies of MOFs can often be controlled and modified by properly selecting the coordination geometry preferred by the metal ion and the chemical structure of the organic ligand chosen. Organic carboxylate ligands have been extensively used to construct MOFs with various properties and topologies (Li *et al.*, 2005; Eddaoudi, Kim, Rosi *et al.*, 2002). 5-Nitroisophthalate ( $5\text{-NIP}^{2-}$ ), as one type of bridging aromatic dicarboxylate ligand, has been widely studied (Liu *et al.*, 2010; Huang *et al.*, 2011; Sarma *et al.*, 2011). The nitro group, which can act as a hydrogen-bond acceptor or coordi-

nate to the metal centres, influences the final coordination structure (Du *et al.*, 2008; Ye *et al.*, 2008).

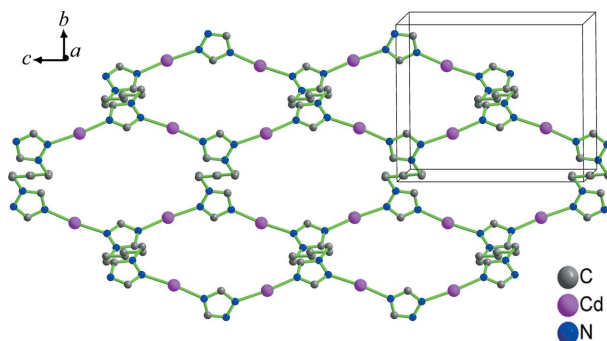


The selection of the second ligand is also significant. In comparison with pyridine-containing ligands, imidazole- or triazole-containing ligands have seldom been used (Ma *et al.*, 2003; Tian *et al.*, 2008). Structures with 1,6-bis(1,2,4-triazol-1-yl)hexane (bth) and  $\text{Cd}^{\text{II}}$  are rare with only a few reported (Liu *et al.*, 2007; Liang *et al.*, 2009). The mot net (mot is 'mesh of trees') is a well known topology, first introduced to crystal design by Batten *et al.* (2009). Reported crystal structures with a mot net are rare (Wen *et al.*, 2009). Here we report the synthesis and structure of poly[aquahemi[ $\mu_4$ -1,6-bis(1,2,4-triazol-1-yl)hexane]( $\mu_2$ -5-nitroisophthalato)cadmium(II)], (I), which crystallizes in this topology.

Selected bond lengths and angles for (I) are given in Table 1. As shown in Fig. 1, the asymmetric unit of (I) contains one  $\text{Cd}^{\text{II}}$  atom, one  $5\text{-NIP}^{2-}$  ligand, one half of a bth ligand and one coordinated water molecule. A centre of inversion falls at the mid-point of the  $\text{C}13-\text{C}13^{\text{iii}}$  bond of the bth ligand [symmetry code: (iii)  $-x + 1, -y, -z + 2$ ]. Each  $\text{Cd}^{\text{II}}$  atom is six-coordinated in a distorted octahedral environment surrounded by three carboxylate O atoms from two different  $5\text{-NIP}^{2-}$  ligands, two N atoms from two distinct bth ligands and one water molecule, with average  $\text{Cd}-\text{O}_{\text{carboxylate}}$  and



**Figure 1**  
The atom numbering and the local coordination of the  $\text{Cd}^{\text{II}}$  cation in the title compound, (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. Only the symmetry-unique half of the bth ligand is shown. [Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ .]

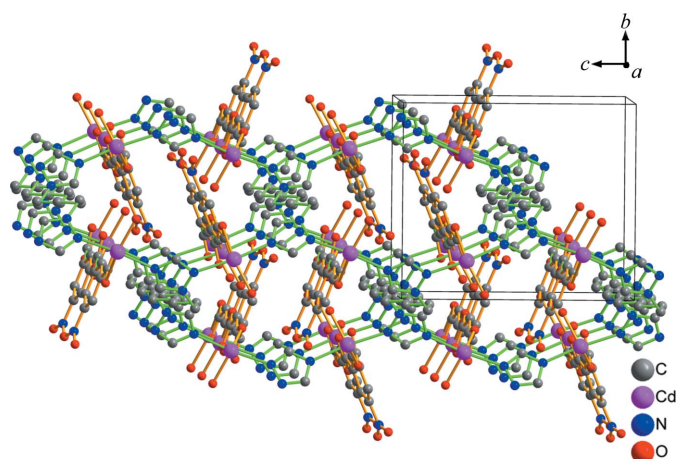
**Figure 2**

The honeycomb-like two-dimensional layer structure of (I) in the  $bc$  plane, constructed from  $\text{Cd}^{\text{II}}$  atoms and bth ligands. H atoms have been omitted for clarity.

$\text{Cd}-\text{N}$  distances of 2.330 (9) and 2.387 (7) Å, respectively. The  $\text{N}2-\text{Cd}1-\text{N}3(x, -y + \frac{1}{2}, z - \frac{1}{2})$  angle, which is close to  $180^\circ$  (Table 1), and the  $\text{N}-\text{Cd}-\text{O}$  angle range of  $84.31(7)-100.12(8)^\circ$  are consistent with a distorted octahedral coordination environment about the  $\text{Cd}$  centre. The  $\text{Cd}^{\text{II}}$  atoms are bridged by the bth ligands to form a honeycomb-like two-dimensional layer structure (Fig. 2) in which the bth ligands act as  $\mu_4$ -bridging ligands with two N atoms in each triazole ring coordinated to different  $\text{Cd}^{\text{II}}$  atoms. This  $\mu_4$ -bridging mode has not been reported before and may be rationalized through the weaker coordination ability of the 2-position N atom because of the steric hindrance from the adjacent hexane carbon chain. The two-dimensional layers are further connected by the bridging 5-NIP $^{2-}$  ligands with the  $\kappa^2;\kappa^1-\mu_2$  coordination mode to generate the final three-dimensional structure (Fig. 3).

It is noteworthy that (I) possesses a three-dimensional net while the  $\text{Cd}^{\text{II}}$  structure  $\{[\text{Cd}_4(\text{D-ca})_4(\text{bth})_4]_3 \cdot 2\text{H}_2\text{O}\}_n$  (D-H $_2$ ca is D-camphoric acid) reported by Liang *et al.* (2009) exists only as a two-dimensional sheet although there are no significant differences between the bond lengths and angles of the coordination bonds in the two structures. This indicates that the 5-NIP $^{2-}$  ligand, which is spatially different from the D-ca $^{2-}$  ligand, influences the final structure of (I).

Using the simplification principle (Natarajan *et al.*, 2009; Tranchemontagne *et al.*, 2009), the  $\text{Cd}^{\text{II}}$  centre and the bth ligands are defined as different four-connected nodes, while the 5-NIP $^{2-}$  ligands serve as linkers. On the basis of this

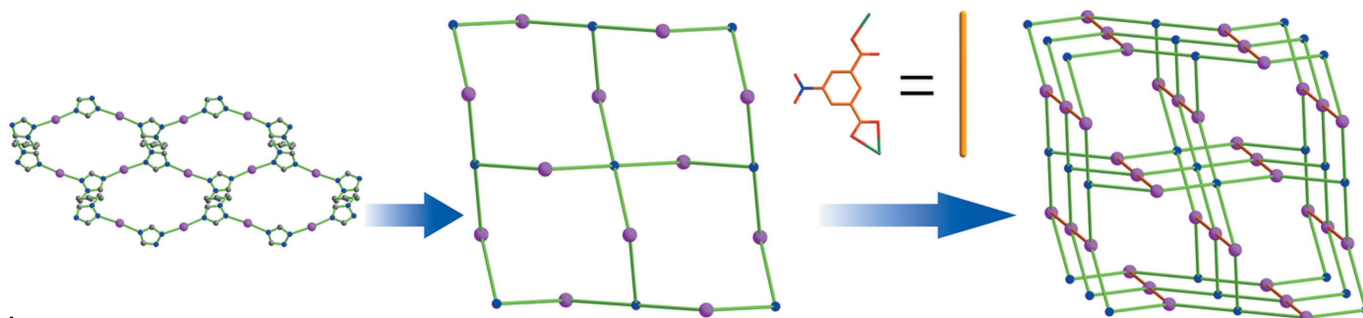
**Figure 3**

A view of the three-dimensional structure of (I). The two-dimensional layers based on  $\text{Cd}^{\text{II}}$  atoms and bth ligands are connected by bridging 5-NIP $^{2-}$  ligands to generate the three-dimensional structure. H atoms have been omitted for clarity.

concept of chemical topology, the overall structure is a three-dimensional mot net with the Schläfli symbol  $(6^6)(6^4.8^2)_2$  (Fig. 4) (Wen *et al.*, 2009). However, as a four-connected net, this mot net, which is named after MOF-112 (Batten *et al.*, 2009; Eddaoudi, Kim, Vodak *et al.*, 2002), is related to the NbO and  $\text{CdSO}_4$  nets (Bai *et al.*, 2010; Friedrichs *et al.*, 2003) although it contains two different square-planar nodes. For one node all its connected neighbours are mutually perpendicular, whereas for the other node half are perpendicular and half are coplanar. Thus, we have constructed an unusual mot net based on 5-NIP $^{2-}$  and bth ligands.

## Experimental

A mixture of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  (0.1 mmol), 5-nitroisophthalic acid (0.1 mmol), 1,6-bis(1,2,4-triazol-1-yl)hexane (0.1 mmol) and NaOH (0.2 mmol) was dissolved in distilled water (12 ml). The resulting solution was stirred for about 30 mins at room temperature, sealed in a 25 ml Teflon-lined stainless steel autoclave and heated at 443 K for 3 d under autogenous pressure. Afterwards, the reaction system was cooled slowly to room temperature. Colourless block-shaped crystals of (I) suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several

**Figure 4**

A schematic representation of the formation of the final three-dimensional mot net. The  $\text{Cd}^{\text{II}}$  centre and the bth ligands act as nodes, while bridging 5-NIP $^{2-}$  ligands act as linkers.

**Table 1**

Selected geometric parameters (Å, °).

Cd1—O4 <sup>i</sup>	2.238 (2)	Cd1—N3 <sup>ii</sup>	2.353 (2)
Cd1—O1W	2.258 (2)	Cd1—O1	2.412 (2)
Cd1—O2	2.342 (2)	Cd1—N2	2.422 (2)
O4 <sup>i</sup> —Cd1—O1W	112.51 (8)	O2—Cd1—O1	55.35 (6)
O4 <sup>i</sup> —Cd1—O2	142.34 (7)	N3 <sup>ii</sup> —Cd1—O1	84.31 (7)
O1W—Cd1—O2	105.10 (7)	O4 <sup>i</sup> —Cd1—N2	86.75 (8)
O4 <sup>i</sup> —Cd1—N3 <sup>ii</sup>	94.87 (8)	O1W—Cd1—N2	100.12 (8)
O1W—Cd1—N3 <sup>ii</sup>	86.89 (8)	O2—Cd1—N2	84.78 (7)
O2—Cd1—N3 <sup>ii</sup>	88.96 (7)	N3 <sup>ii</sup> —Cd1—N2	171.61 (8)
O4 <sup>i</sup> —Cd1—O1	87.71 (7)	O1—Cd1—N2	87.53 (7)
O1W—Cd1—O1	158.59 (7)		

 Symmetry codes: (i)  $x + 1, y, z$ ; (ii)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ .

times with distilled water and dried in air at ambient temperature (yield 72%, based on Cd<sup>II</sup>).

### Crystal data

[Cd(C<sub>8</sub>H<sub>3</sub>NO<sub>6</sub>)(C<sub>5</sub>H<sub>8</sub>N<sub>3</sub>)<sub>0.5</sub>(H<sub>2</sub>O)]  
 $M_r = 449.67$   
 Monoclinic,  $P2_1/c$   
 $a = 10.292 (2) \text{ \AA}$   
 $b = 11.250 (3) \text{ \AA}$   
 $c = 13.339 (3) \text{ \AA}$   
 $\beta = 90.644 (3)^\circ$   
 $V = 1544.4 (6) \text{ \AA}^3$   
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.46 \text{ mm}^{-1}$   
 $T = 296 \text{ K}$   
 $0.26 \times 0.21 \times 0.19 \text{ mm}$

### Data collection

Bruker–Nonius KappaCCD diffractometer  
 Absorption correction: empirical (using intensity measurements) (*SADABS*; Bruker, 1997)  
 $T_{\min} = 0.699, T_{\max} = 0.757$   
 13260 measured reflections  
 3547 independent reflections  
 2898 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.082$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$   
 $wR(F^2) = 0.069$   
 $S = 0.99$   
 3547 reflections  
 226 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.96 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.94 \text{ e \AA}^{-3}$

All C-bound H atoms were placed geometrically and treated as riding on their parent atoms, with C—H = 0.93 (triazole and arene) or 0.97 Å (methylene) and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The water H atoms were located in a difference Fourier map and initially included in the refinement using bond-length restraints of O—H = 0.85 (1) Å and H···H = 1.39 (1) Å. In the final refinement, these H atoms were restrained to ride on their parent O atom, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve

structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL-Plus* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GA3165). Services for accessing these data are described at the back of the journal.

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