

A novel two-dimensional (4,4) network based on dinuclear cadmium secondary building units: poly[(μ_5 -benzene-1,4-diacetato)[μ_2 -1,4-bis(1,2,4-triazol-1-yl)butane]-cadmium(II)]

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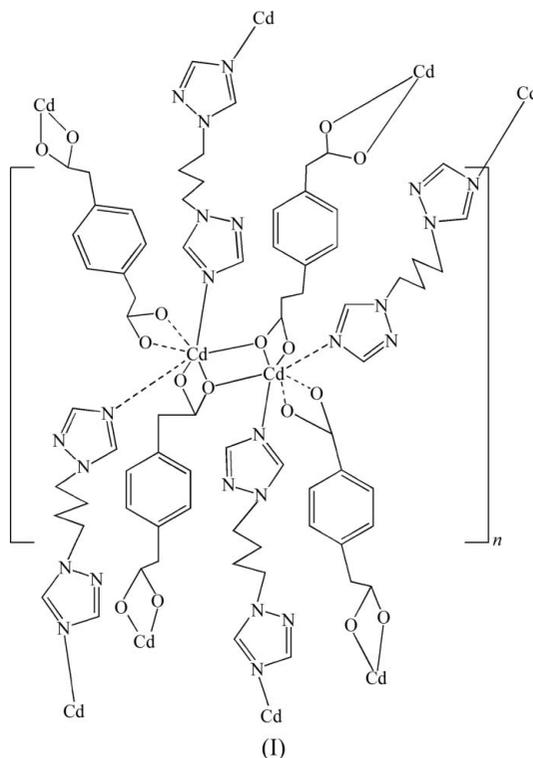
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In the title mixed-ligand metal–organic polymeric compound, $[\text{Cd}(\text{C}_{10}\text{H}_8\text{O}_4)(\text{C}_8\text{H}_{12}\text{N}_6)]_n$ or $[\text{Cd}(\text{PBEA})(\text{BTB})]_n$ [H_2PBEA is benzene-1,4-diacetic acid and BTB is 1,4-bis(1,2,4-triazol-1-yl)butane], the asymmetric unit contains one Cd^{II} ion, one BTB molecule and one PBEA^{2-} anion. The Cd^{II} ion is in a slightly distorted pentagonal–bipyramidal geometry, coordinated by five carboxylate O atoms from three distinct PBEA^{2-} anions and by two BTB N atoms. There are two coordination patterns for the carboxylate groups of the PBEA^{2-} ligand, one being a $\mu_1\text{-}\eta^1\text{:}\eta^1$ chelating mode and the other a $\mu_2\text{-}\eta^2\text{:}\eta^1$ bridging mode, while the BTB molecule shows a *trans–trans–trans* conformation. The crystal structure is constructed from the secondary building unit (SBU) $[\text{Cd}_2(\text{CO}_2)_4\text{N}_2\text{O}_2]_n$, in which the two metal centres are held together by two PBEA^{2-} linkers. The SBU is connected by BTB and PBEA^{2-} bridges to form a two-dimensional grid-like (4,4) layer with meshes of dimensions $14.69 \times 11.28 \text{ \AA}$.

Comment

Considerable attention has been paid to the construction of highly connected metal–organic frameworks (MOFs) with enhanced stability and stable porosity, not only because of their fascinating structures and topologies but also owing to their potential applications in many fields (Kitagawa *et al.*, 2004; Ferey *et al.*, 2005; Roy *et al.*, 2009; Zhang *et al.*, 2009; Jiang *et al.*, 2010). A feasible pathway toward highly connected MOFs is to use a polynuclear metal cluster as a secondary building unit (SBU), because such clusters can effectively reduce steric hindrance between organic ligands. The mainstream method of constructing such clusters is to utilize carboxylate-containing ligands, since carboxylate groups have

excellent coordination capability and flexible coordination patterns. Furthermore, carboxylate groups can prompt core aggregation *via* bridging metal ions (Eddaoudi *et al.*, 2001).



Compared with the corresponding rigid terephthalic acid, benzene-1,4-diacetic acid (H_2PBEA) may show a variety of coordination modes and conformations owing to the increased flexibility of its two carboxylate groups (Pan *et al.*, 2003; Chen *et al.*, 2006; Braverman & LaDuca, 2007; Wang, Yang *et al.*, 2008). Meanwhile, 1,4-bis(1,2,4-triazol-1-yl)butane (BTB) can adopt different conformations on the basis of the relative orientation of its CH_2 groups (Zhou *et al.*, 2006; Gu *et al.*, 2008; Wang, Zhang *et al.*, 2008; Zhu *et al.*, 2009). However, to the best of our knowledge, coordination polymers constructed from H_2PBEA and BTB ligands have not been documented so far. We have selected H_2PBEA and BTB as organic linkers, generating the title new Cd^{II} coordination polymer, $[\text{Cd}(\text{PBEA})(\text{BTB})]_n$, (I), the crystal structure of which we now report.

Compound (I) crystallizes in the monoclinic space group $P2_1/c$, and the asymmetric unit contains one Cd^{II} ion, one PBEA^{2-} ligand and one BTB molecule. Each Cd^{II} centre is seven-coordinated by two triazole N atoms (N1 and N4ⁱⁱⁱ) from two different BTB ligands and five O atoms (O1, O2, O3ⁱ, O4ⁱ and O4ⁱⁱⁱ) from three distinct PBEA^{2-} ligands, resulting in a distorted pentagonal–bipyramidal geometry (Fig. 1) [symmetry codes: (i) $x - 1, y, z - 1$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $x, y, z - 1$]. The equatorial plane is defined by the carboxylate O atoms, while the axial positions are occupied by two BTB N atoms. The Cd–N bond lengths are 2.324 (2) and 2.3243 (19) Å, while the Cd–O bond lengths vary greatly, from 2.3171 (17) to 2.4980 (17) Å. The average Cd–O and

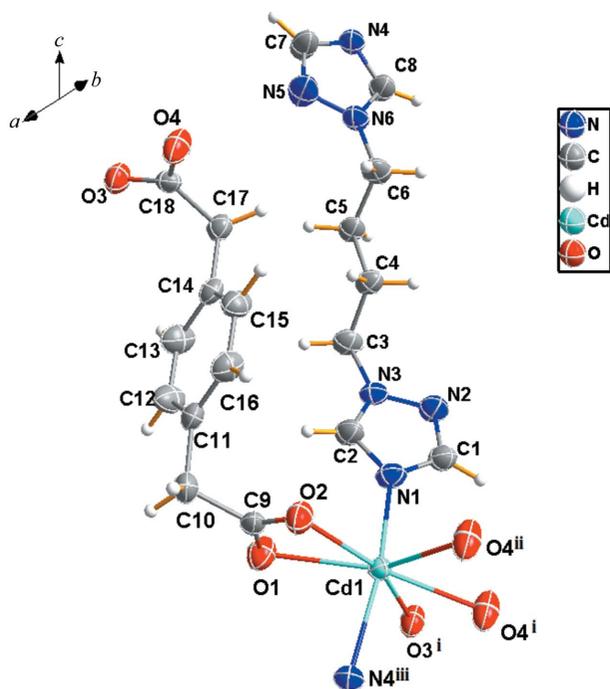


Figure 1
A view of the local coordination of the Cd^{II} cations in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x - 1, y, z - 1$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $x, y, z - 1$.]

Cd–N distances in (I) are comparable with those reported for Cd-based compounds (Liu *et al.*, 2008).

Importantly, each H₂PBEA ligand in (I) is completely deprotonated and links three Cd^{II} atoms, while there are two

coordination patterns for the PBEA²⁻ ligand, one being a $\mu_1\text{-}\eta^1\text{:}\eta^1$ chelating mode and the other a $\mu_2\text{-}\eta^2\text{:}\eta^1$ bridging mode. Two crystallographically equivalent Cd^{II} atoms are bridged by two tridentate bridging carboxylate groups to form a binuclear motif (the SBU), with a Cd···Cd separation of 3.9848 (3) Å, and the SBUs are joined by PBEA²⁻ ligands to form an infinite ladder-like one-dimensional chain along [010]. The separation between the SBUs in the chain is 11.2773 (6) Å. Furthermore, a two-dimensional layer (Fig. 2) perpendicular to the *b* axis is formed by SBUs double-joined by both BTB and PBEA²⁻ units. The Miller indices of this plane are (010), in which the BTB molecule shows a *trans–trans–trans* conformation with a Cd···Cd separation of 14.6837 (8). These sheets are further arranged parallel to the (010) plane and these sheets are connected by weak C–H···O hydrogen bonds between an alkyl C atom and a neighbouring carboxylate O atom (Table 1).

In conclusion, we have synthesized a two-dimensional coordination polymer based on the secondary building unit [Cd₂(CO₂)₄N₂O₂], in which the PBEA²⁻ ligand forms a one-dimensional ladder-like chain based on a dinuclear Cd₂ SBU and the BTB ligand is used to extend the framework.

Experimental

A mixture of Cd(NO₃)₂·6H₂O (34.5 mg, 0.1 mmol), H₂PBEA (19.4 mg, 0.1 mmol), BTB (19.2 mg, 0.1 mmol) and NaOH (8.0 mg, 0.2 mmol) in H₂O (10 ml) was sealed in a 16 ml Teflon-lined stainless steel container and heated at 413 K for 72 h. After cooling to room temperature, white block-shaped crystals of (I) were collected by filtration and washed several times with water and ethanol (yield 32.5%, based on H₂PBEA). Elemental analysis for C₁₈H₂₀CdN₆O₄: C 43.52, H 4.06, N 16.92%; found: 43.61, H 4.08, N 16.94%.

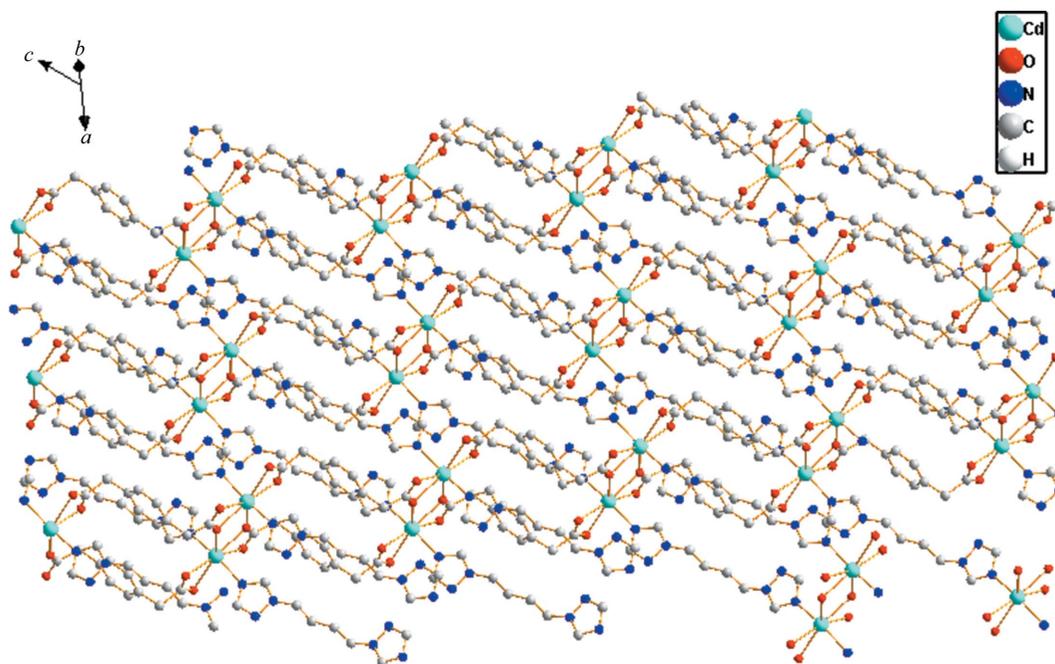


Figure 2
A view of the two-dimensional framework of (I).

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C3-H3B\cdots O3^i$	0.97	2.29	3.220 (3)	160

Symmetry code: (i) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$.**Crystal data**

$[Cd(C_{10}H_8O_4)(C_8H_{12}N_6)]$	$V = 1892.68 (17) \text{ \AA}^3$
$M_r = 496.81$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.8072 (5) \text{ \AA}$	$\mu = 1.19 \text{ mm}^{-1}$
$b = 17.1235 (9) \text{ \AA}$	$T = 290 \text{ K}$
$c = 14.6837 (6) \text{ \AA}$	$0.25 \times 0.21 \times 0.17 \text{ mm}$
$\beta = 129.866 (2)^\circ$	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	9517 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2000)	3380 independent reflections
$T_{\min} = 0.75, T_{\max} = 0.816$	2930 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	266 parameters
$wR(F^2) = 0.060$	H-atom parameters constrained
$S = 0.90$	$\Delta\rho_{\max} = 0.66 \text{ e \AA}^{-3}$
3380 reflections	$\Delta\rho_{\min} = -0.69 \text{ e \AA}^{-3}$

H atoms were placed in calculated positions and refined using a riding model, with C–H = 0.93 (triazole) or 0.97 Å (methylene), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Sheldrick, 2008); program(s) used to refine structure: SHELXTL; molecular graphics: DIAMOND (Brandenburg, 1999); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: QS3003). Services for accessing these data are described at the back of the journal.

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