

Poly[(μ_3 -benzene-1,4-diacetato)[μ_2 -1,4-bis(1,2,4-triazol-1-yl)butane]-cadmium(II)]: self assembly into a three-dimensional supramolecular framework based on [Cd(μ_3 -benzene-1,4-diacetate)] double chains

Jun Wang,* Jian-Qing Tao and Xiao-Juan Xu

Department of Chemistry, Yancheng Teachers' College, Yancheng 224002, People's Republic of China

Correspondence e-mail: wjyctu@gmail.com

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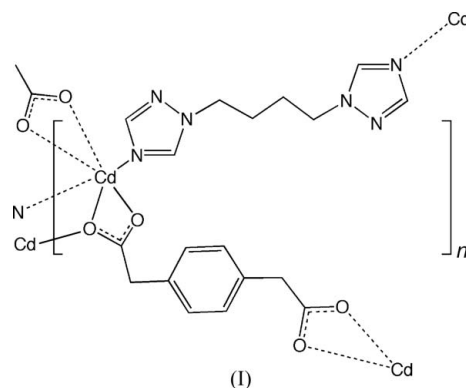
The title compound, [Cd(C₁₀H₈O₄)(C₈H₁₂N₆)_n], crystallizes with an asymmetric unit comprising a divalent Cd^{II} atom, a benzene-1,4-diacetate (PBEA²⁻) ligand and a complete 1,4-bis(1,2,4-triazol-1-yl)butane (BTB) ligand. [Cd(PBEA)]_n double chains, arranged parallel to the *c* axis, are formed through an *exo*-tridentate binding mode of the PBEA²⁻ ligands. These [Cd(PBEA)]_n double chains are pillared by tethering BTB ligands, in which the BTB shows a *trans-trans-trans* conformation, to establish [Cd(PBEA)(BTB)]_n two-dimensional coordination polymer (4,4)-layer slab patterns. The three-dimensional supramolecular architecture is formed by C—H...O hydrogen bonds and C—H... π interactions.

Comment

The design and synthesis of coordination polymers is an attractive area of research, not only due to their diverse topology and intriguing structures but also owing to their potential applications in many fields (Eddaoudi *et al.*, 2001; Kitagawa *et al.*, 2004; Ferey *et al.*, 2005; Roy *et al.*, 2009). The mainstream method of constructing such coordination polymers is to utilize dicarboxylate ligands, since carboxylate groups have an excellent coordination capability and flexible coordination patterns (Farnum *et al.*, 2011). The disposition of the donor groups around the periphery of the dicarboxylate ligands, their metal coordination modes, and the different types and flexibility of such ligands act synergistically to provide access to vast numbers of structural topologies.

Owing to the increased flexibility of its two carboxylate groups, benzene-1,4-diacetic acid (H₂PBEA) may show a variety of coordination modes and conformations (Pan *et al.*, 2003; Chen *et al.*, 2006; Braverman & LaDuca, 2007; Wang, Yang *et al.*, 2008). Meanwhile, on the basis of the relative

orientations of its CH₂ groups, 1,4-bis(1,2,4-triazol-1-yl)butane (BTB) can adopt different conformations compared with the corresponding 1,2,4-triazole ligand (Zhou *et al.*, 2006; Wang, Zhang *et al.*, 2008; Liang *et al.*, 2009; Zhu *et al.*, 2009). We have selected H₂PBEA and BTB as organic linkers, generating the title new Cd^{II} coordination polymer, [Cd(PBEA)(BTB)]_n, (I), the crystal structure of which we now report. We recently also reported the structure of a polymorph of (I) (Wang *et al.*, 2011).



Compound (I) crystallizes in the centrosymmetric triclinic space group $P\bar{1}$ with an asymmetric unit comprising a divalent Cd^{II} cation, a dianionic PBEA²⁻ ligand and a complete BTB

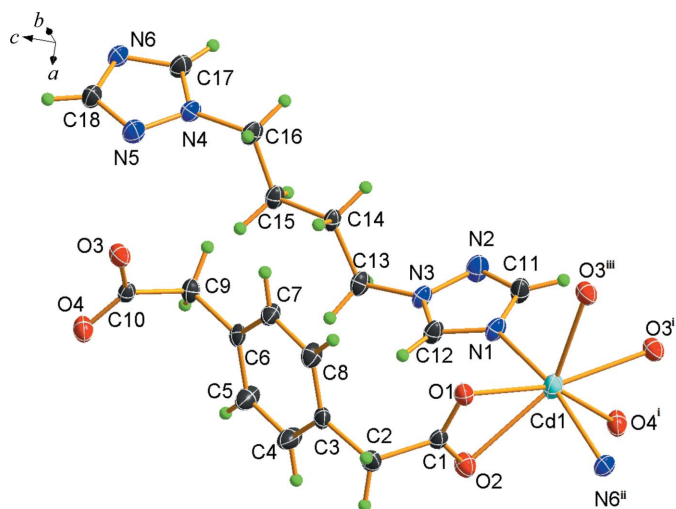


Figure 1
A view of the local coordination of the Cd^{II} cations in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $x, y, z - 1$; (ii) $x + 1, y, z - 1$; (iii) $-x + 2, -y + 1, -z$.]

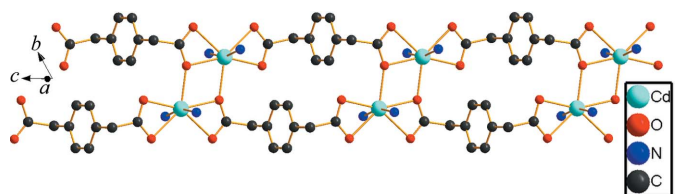


Figure 2
A single [Cd(PBEA)]_n chain in (I), highlighting the presence of {Cd₂O₂} rhomboid dimers.

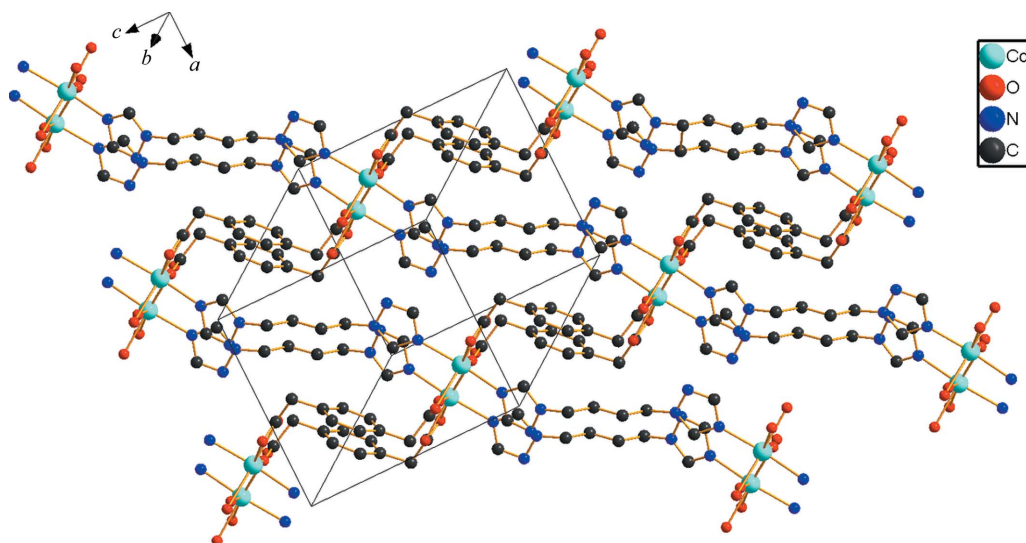


Figure 3
A view of the two-dimensional framework in (I).

ligand (Fig. 1). The coordination environment at the Cd^{II} centre is best considered as a distorted {CdN₂O₅} pentagonal bipyramid, with the axial positions occupied by *trans* N donor atoms [N1 and N6ⁱⁱ; symmetry code: (ii) $x + 1, y, z - 1$] from two BTB ligands. The equatorial sites are filled by four O-atom donors [O1, O2, O3ⁱ and O4ⁱ; symmetry code: (i) $x, y, z - 1$] from two chelating carboxylate termini from two different PBEA²⁻ ligands and a single O-atom donor [O3ⁱⁱⁱ; symmetry code: (iii) $-x + 2, -y + 1, -z$] from a third PBEA²⁻ unit. The Cd1–N1 and Cd1–N6 bond lengths are 2.348 (4) and 2.326 (4) Å, respectively, while the Cd–O bond lengths vary from 2.317 (4) to 2.551 (4) Å. The average Cd–O and Cd–N distances in (I) are comparable with those in previously reported Cd-based compounds (Liu *et al.*, 2008) and in the polymorph of (I) (Wang *et al.*, 2011), in which a very similar coordination geometry about the Cd atom is found.

[Cd(PBEA)]_n double chains (Fig. 2), arranged parallel to the *c* axis, are formed through an *exo*-tridentate binding mode of the PBEA²⁻ ligands. Within these chains are embedded {Cd₂O₂} rhomboid subunits constructed by the chelating/bridging carboxylate end groups of the PBEA²⁻ ligands. The Cd···Cd and O···O through-space distances across the dinuclear core measure 3.909 (2) and 2.687 (8) Å, respectively. These rhomboid subunits are noticeably pinched, with Cd–O–Cd and O–Cd–O angles of 111.0 (2) and 69.00 (17)°, respectively. They are linked by the PBEA²⁻ ligands giving a Cd···Cd distance of 11.2737 (14) Å, which corresponds to the *c* lattice parameter. The one-dimensional double chains can be considered as being formed by the edge-sharing of {Cd₂O₂} rhomboids with 22-membered {CdOC₈O}₂ rings. These [Cd(PBEA)]_n double chains are pillared by tethering BTB ligands, in which the BTB shows a *trans–trans–trans* conformation, with a Cd···Cd separation of 14.6624 (14) Å. This establishes [Cd(PBEA)(BTB)]_n two-dimensional coordination polymer slab patterns that are arranged parallel to the (010) crystal plane (Fig. 3). If the centroids of the {Cd₂O₂} rhomboids are considered as connecting nodes, the slab

pattern of (I) can be represented as a (4,4) rectangular grid motif. As determined by through-space Cd···Cd distances, the apertures within the grid measure 11.27 × 14.66 Å. Adjacent [Cd(PBEA)(BTB)]_n slabs stack in a simple AA pattern along the *b* axis.

There are two types of weak hydrogen bond in the structure of (I) (Fig. 4 and Table 1), namely two C–H···O intralayer hydrogen bonds involving carboxylate atom O1 and two C–H···O interlayer hydrogen bonds involving carboxylate atom O2. In addition, an intralayer C–H···π interaction (Fig. 4) is observed between C12–H12 and the centroid (C_g) of the C3–C8 ring, with C12···C_g = 3.752 (7) Å, H12···C_g = 2.88 Å

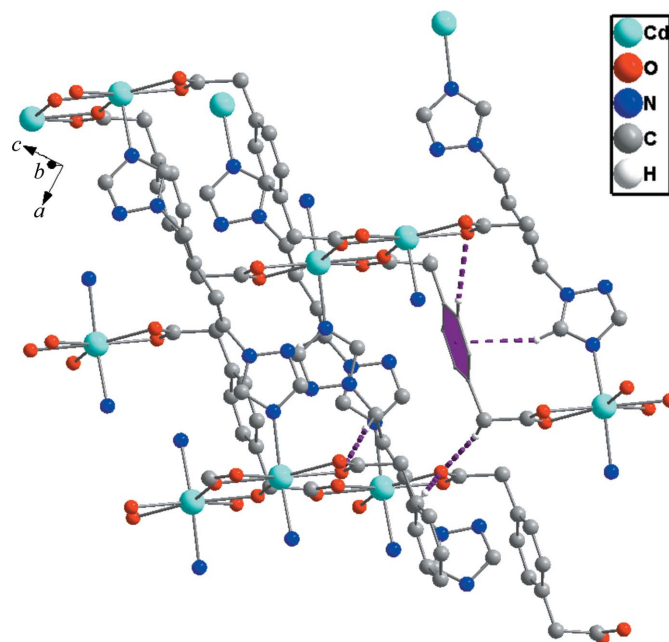


Figure 4
A perspective view of the three-dimensional supramolecular structure of (I), incorporating C–H···O hydrogen bonds and C–H···π interactions (dashed lines).

and C12—H12...Cg = 156°. On comparing the structure of complex (I) with that of the previously reported polymorph of (I) [(II); Wang *et al.*, 2011], it can be seen that the two complexes have a similar connectivity within their two-dimensional layered structures, but that the supramolecular interactions are different, being more plentiful in (I). Not only are there more C—H...O interactions, but also C—H... π interactions exist in complex (I). It might be possible that the differences in conditions during the syntheses, such as pH value and temperature [433 K for (I) and 413 K for (II)] are responsible for the differences between the two complexes.

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 KOH (11.2 mg, 0.2 mmol) in H₂O (10 ml) was sealed in a 16 ml Teflon-lined stainless steel container and heated at 433 K for 72 h. After cooling to room temperature, colourless block-shaped crystals of (I) were collected by filtration and washed several times with water and ethanol (yield 41.7%, based on BTB). Elemental analysis for C₁₈H₂₀CdN₆O₄: C 43.52, H 4.06, N 16.92%; found: 43.49, H 4.04, N 16.90%.

Crystal data

[Cd(C ₁₀ H ₈ O ₄)(C ₈ H ₁₂ N ₆)]	γ = 69.418 (2)°
M_r = 496.81	V = 948.7 (2) Å ³
Triclinic, $P\bar{1}$	Z = 2
a = 9.7900 (13) Å	Mo $K\alpha$ radiation
b = 10.1129 (13) Å	μ = 1.19 mm ⁻¹
c = 11.2737 (14) Å	T = 291 K
α = 66.198 (2)°	0.21 × 0.20 × 0.19 mm
β = 87.935 (1)°	

Data collection

Bruker SMART CCD area-detector diffractometer	4728 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2000)	3337 independent reflections
T_{\min} = 0.779, T_{\max} = 0.798	3089 reflections with $I > 2\sigma(I)$
	R_{int} = 0.075

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039	262 parameters
$wR(F^2)$ = 0.122	H-atom parameters constrained
S = 1.22	$\Delta\rho_{\text{max}}$ = 1.10 e Å ⁻³
3265 reflections	$\Delta\rho_{\text{min}}$ = -0.81 e Å ⁻³

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

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

Table 1

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
C16—H16A...O1 ⁱ	0.97	2.60	3.563 (8)	175
C13—H13B...O2 ⁱⁱ	0.97	2.34	3.288 (7)	165
C7—H7...O1 ⁱ	0.93	2.55	3.380 (7)	149
C2—H2A...O2 ⁱⁱⁱ	0.97	2.59	3.552 (8)	169

Symmetry codes: (i) $-x + 2, -y + 1, -z$; (ii) $-x + 2, -y, -z$; (iii) $-x + 3, -y, -z$.

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: WQ3002). Services for accessing these data are described at the back of the journal.

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