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catena-Poly[[[(benzene-1,3,5-tricarboxylic acid)(1,10-phenanthroline)-cadmium(II)]-μ-oxalato] 1*H*-benzotriazole solvate monohydrate]

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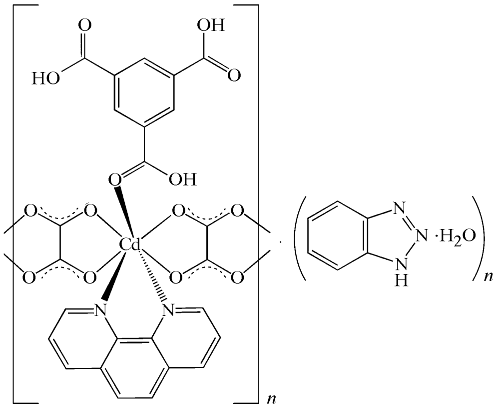
In the title compound, $[Cd(C_2O_4)(C_{12}H_8N_2)(C_9H_6O_6)]\cdot C_6H_5N_3\cdot H_2O$, the Cd^{II} atom has a distorted pentagonal–bipyramidal geometry, defined by two N atoms and five O atoms from bidentate 1,10-phenanthroline ligands, oxalate ligands and benzene-1,3,5-tricarboxylic acid ligands. The oxalate ligands in the asymmetric unit possess inversion symmetry. The triazole molecule is not coordinated to the Cd atom. The structure of the title compound features a one-dimensional chain running along the crystallographic *a* axis, and a three-dimensional supramolecular network is formed *via* aromatic π–π interactions and hydrogen-bonding interactions.

Comment

Rational design and synthesis of metal–organic polymers is of current interest in the field of supramolecular chemistry and crystal engineering. Benzene-1,3,5-tricarboxylic acid (H_3BTC), as a popular organic ligand, has been investigated in the construction of metal–organic frameworks. As a multi-carboxylate ligand, H_3BTC exhibits versatile binding modes in the construction of polymeric complexes. It can act as H_2BTC^- (Ying & Mao, 2004), $HBTC^{2-}$(Shi *et al.*, 2004) and BTC^{3-} (Almeida Paz & Kilnowski, 2004) anions and serve as a μ_2 (Cheng *et al.*, 2004), μ_3 (Zheng *et al.*, 2004), μ_4 (Shi *et al.*, 2003), μ_5 (Wang *et al.*, 2003) and μ_6 (Serre *et al.*, 2004) linker. So far, some structures of metal–organic polymers containing H_3BTC and 1,10-phenanthroline have been reported, examples being *catena*-[bis(μ_3-benzenecarboxylic acid-3,5-dicarboxylato)bis(1,10-phenanthroline)dicadmium(II) (μ_2-benzenecarboxylic acid-3,5-dicarboxylato)bis(1,10-phenanthroline)-cadmium(II)] (Shi *et al.*, 2004), *catena*-[(μ_3-1,3,5-benzenetricarboxylato)(1,10-phenanthroline)indium] (Gomez-Lor *et al.*, 2005), *catena*-[(μ_2-1,3-dicarboxybenzene-5-carboxylato)-diaqua(1,10-phenanthroline)manganese(II) 1,3-dicarboxybenzene-5-carboxylate monohydrate] (Majumder *et al.*, 2005), *catena*-[(μ_2-benzene-1,3-dicarboxylato-5-carboxylic acid)-aqua(1,10-phenanthroline)cobalt(II)] (Plater *et al.*, 2001) and bis[diaquabis(1,10-phenathroline)manganese(II)] hexaaqua-copper(II) bis(1,3,5-benzenetricarboxylate) docosahydrate clathrate (Qiu *et al.*, 2005). We report here the structure of the title compound, (I), which contains four different organic ligands.



(I)

As shown in Fig. 1, the asymmetric unit contains one Cd atom, one H_3BTC ligand, one 1,10-phenanthroline ligand, two half oxalate ligands, one uncoordinated benzotriazole molecule and one solvent water molecule. The Cd^{II} ion is coordinated by five O atoms of one H_3BTC ligand and two oxalate ligands, and two N atoms from the 1,10-phenanthroline ligand, showing a distorted pentagonal–bipyramidal geometry. The two half oxalate ligands in the asymmetric unit possess inversion symmetry. The Cd—O bond distances range from 2.287 (3) to 2.525 (4) Å, and the Cd—N bond distances are 2.334 (4) and 2.351 (4) Å (Fig. 1). Adjacent Cd atoms are linked by oxalate ligands, forming one-dimensional chains running along the crystallographic *a* axis (Fig. 2). The dihedral

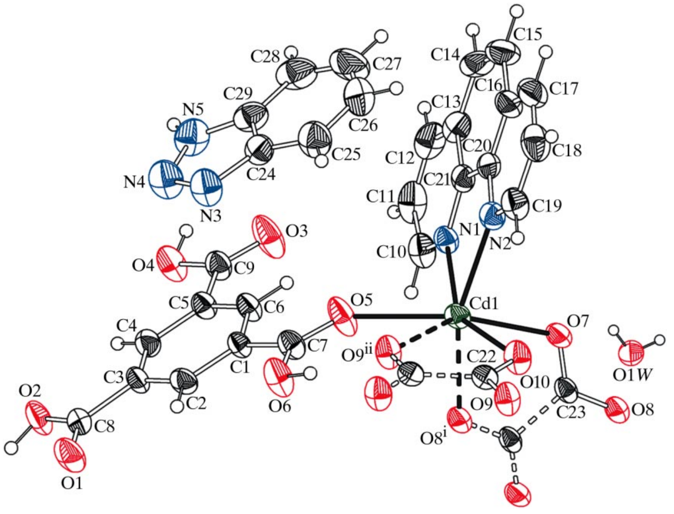


Figure 1
The molecular structure of the title compound, shown with 50% probability displacement ellipsoids. [Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $-x, -y, -z + 1$.]

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angles between the oxalate and 1,10-phenanthroline ligands are 72.790 (14) and 82.139 (12)°. The chains of (I) are linked by O—H···O hydrogen bonds involving the hydroxy groups of H_3BTC ligands and the carboxylate groups of oxalate ligands (O2—H1···O8^{v} and O6—H3···O9^{ii}; all symmetry codes as in Table 1), resulting in two-dimensional layers (Fig. 3). Although the benzotriazole ligands are not coordinated to the Cd atom, they take part in the construction of the three-dimensional hydrogen-bond network. These sheets are further linked into a three-dimensional supramolecular network *via* O —H···N, N—H···O and O—H···O hydrogen bonds (O4—H2···N3, N5—H5*A*···O1*W*^{iv}, O1*W*—H4···O1^{iii} and O1*W*—H5···O10; Fig. 3), and details are given in Table 1. Meanwhile, the three-dimensional network is stabilized by strong π–π stacking interactions between the 1,10-phenanthroline ligands and H_3BTC ligands. As shown in Fig. 3, the face-to-face distance between adjacent 1,10-phenanthroline ligands is 3.324 (3) Å, and that between the H_3BTC ligands and the benzotriazole system is 3.414 (3) Å. These strong π–π stacking and hydrogen-bonding interactions play important roles in forming the resulting three-dimensional supramolecular network.

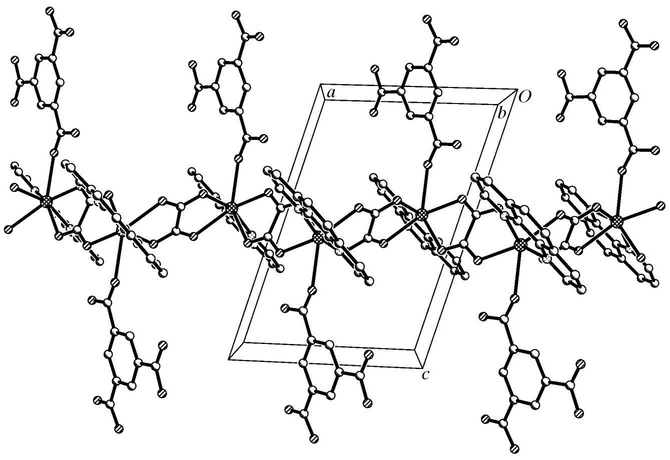

Figure 2
A view of the one-dimensional zigzag chain running along the *a* axis.

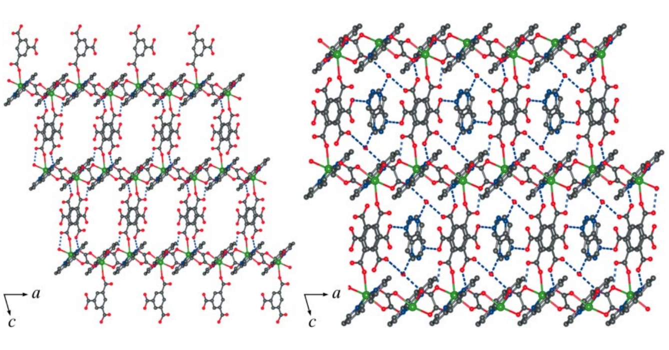

Figure 3
Perspective views of the two- (left) and three-dimensional (right) supramolecular networks along the *b* axis.

Experimental

The title compound was prepared by hydrothermal methods. A mixture of $Cd(NO_3)_2\cdot6H_2O$ (0.17 g, 0.5 mmol), H_3BTC (0.13 g, 0.6 mmol), 1,10-phenanthroline (0.1 g, 0.6 mmol), oxalic acid (0.027 g, 0.3 mmol), benzotriazole (0.06 g, 0.5 mmol) and water (10 ml) was stirred for 20 min in air. The mixture was then transferred to a 23 ml Teflon reactor and kept at 433 K for 72 h under autogenous pressure. Crystals suitable for X-ray analysis were obtained after the mixture was cooled to room temperature.

Crystal data

$[Cd(C_2O_4)(C_9H_6O_6)(C_{12}H_8N_2)]\cdot C_6H_5N_3\cdot H_2O$
$M_r = 727.91$
Triclinic, $P\bar{1}$
$a = 9.4531$ (19) Å
$b = 10.869$ (2) Å
$c = 14.100$ (3) Å
$\alpha = 87.86$ (3)°
$\beta = 73.28$ (3)°
$\gamma = 84.63$ (3)°
$V = 1381.3$ (5) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.87$ mm^{-1}
$T = 298$ (2) K
0.26 × 0.25 × 0.16 mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.806$, $T_{max} = 0.874$
13575 measured reflections
6247 independent reflections
4186 reflections with $I > 2\sigma(I)$
$R_{int} = 0.073$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.119$
$S = 1.03$
6247 reflections
415 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max} = 0.77$ e Å^{-3}
$\Delta\rho_{min} = -1.12$ e Å^{-3}

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H4···O1^{iii}	0.85	1.99	2.824 (5)	165
N5—H5*A*···O1*W*^{iv}	0.86	1.93	2.775 (6)	166
O6—H3···O9^{ii}	0.85	1.83	2.659 (5)	163
O2—H1···O8^{v}	0.85	1.79	2.636 (5)	172
O4—H2···N3	0.85	1.94	2.711 (6)	150
O1*W*—H5···O10	0.85	2.12	2.942 (5)	164

Symmetry codes: (ii) $-x, -y, -z+1$; (iii) $x, y, z+1$; (iv) $x+1, y+1, z-1$; (v) $x, y, z-1$.

All H atoms were initially located in a difference Fourier map. H atoms of hydroxy groups and water molecules were then constrained to an ideal geometry, with O—H distances of 0.85 Å and U_{iso}(H) values of $1.5U_{eq}$(O). All other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93 Å, an N—H distance of 0.86 Å and U_{iso}(H) values of $1.2U_{eq}$(C,N).

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 2005); software used to prepare material for publication: *SHELXTL* (Bruker, 2001).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3065). Services for accessing these data are described at the back of the journal.

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