Poly[aqua(μ2-benzene-1,4-dicarboxylato)(μ2-4,4′-bipyridine N,N′-dioxide)cadmium(II)], a threefold interpenetrating diamond net

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In the title compound, $[Cd(C_8H_4O_4)(C_{10}H_8N_2O_2)(H_2O)]_n$, (I), each Cd^{II} atom is seven-coordinated in a distorted mono-capped trigonal prismatic coordination geometry, surrounded by four carboxylate O atoms from two different benzene-1,4-dicarboxylate (1,4-bdc) anions, two O atoms from two distinct 4,4′-bipyridine N,N′-dioxide (bpdo) ligands and one water O atom. The Cd^{II} atom and the water O atom are on a twofold rotation axis. The bpdo and 1,4-bdc ligands are on centers of inversion. Each crystallographically unique Cd^{II} center is bridged by the 1,4-bdc dianions and bpdo ligands to give a three-dimensional diamond framework containing large adamantanoid cages. Three identical such nets are interlocked with each other, thus directly leading to the formation of a threefold interpenetrated three-dimensional diamond architecture. To the best of our knowledge, (I) is the first example of a threefold interpenetrating diamond net based on both bpdo and carboxylate ligands. There are strong linear O—H⋯O hydrogen bonds between the water molecules and carboxylate O atoms within different diamond nets. Each diamond net is hydrogen bonded to its two neighbors through these hydrogen bonds, which further consolidates the threefold interpenetrating diamond framework.

Comment

The synthesis of metal–organic frameworks (MOFs) has attracted much attention, not only because of the tremendous number of potential applications of MOFs in nonlinear optics, catalysis, gas absorption, luminescence, magnetism, ion exchange and zeolite-like materials for molecular selection, but also because of the intriguing variety of architectures and topologies (Abrahams *et al.*, 1999; Noro *et al.*, 2000; Spencer *et al.*, 2006). The topologies of MOFs can often be controlled and modified by selecting the coordination geometry preferred by the metal ion and the chemical structure of the organic ligand

chosen. It is well known that careful selection of a suitable organic ligand with certain features is helpful for constructing MOFs with desirable properties (Wang *et al.*, 2006). Recently, it has been demonstrated that 4,4′-bipyridine N,N′-dioxide (bpdo) and its derivatives show some unique features in the construction of MOFs (Hill *et al.*, 2005; Manna *et al.*, 2007) and they have been shown to have extremely versatile coordination modes compared with 4,4′-bipyridine and its derivatives (Xu *et al.*, 2005). To date, a number of MOFs based on bpdo ligands have been reported, including one-dimensional chain or ladder, two-dimensional layer, and unusual five-, six-, seven- and eight-connected frameworks (Hill *et al.*, 2005). However, only a few MOFs based on both bpdo and carboxylate ligands have been documented (Manna *et al.*, 2006, 2007; Fabelo *et al.*, 2007). In the new structure reported here, bpdo assembles with cadmium benzene-1,4-dicarboxylate (1,4-bdc) to furnish a 1:1 adduct, *viz.* $[Cd(1,4-bdc)(bpdo)(H_2O)]_n$, (I), which exists as an unusual threefold interpenetrating diamond framework.

(I)
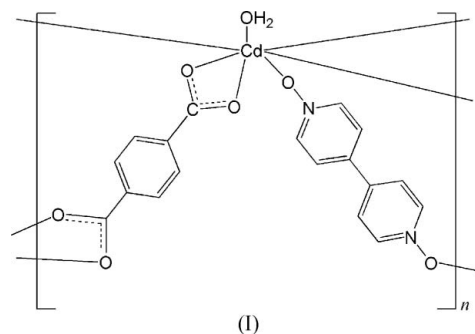
The asymmetric unit of (I) contains half a Cd^{II} atom, half a bpdo ligand, half a 1,4-bdc anion and half a coordination water molecule (Fig. 1). The Cd^{II} atom and the water O atom rest on a twofold rotation axis. The bpdo and 1,4-bdc ligands are on centers of inversion that occur at the mid-point of the C7—C7^{ii} bond of bpdo [symmetry code: (ii) $-x$, $-y$, $-z$] and the centroid of the arene ring of 1,4-bdc. Each Cd^{II} atom is seven-coordinated in a distorted monocapped trigonal prismatic coordination geometry, surrounded by four carboxylate O atoms from two different 1,4-bdc anions [O2, O3, O2^{iii} and O3^{iii}; symmetry code: (iii) $1 - x$, y, $\frac{1}{2} - z$], two O atoms from two distinct bpdo ligands (O1 and O1^{iii}) and one water O atom (O1W). The Cd—O$_{carboxylate}$ distances (Table 1) are comparable to those observed for $[Cd_4(bpea)_4(1,4-bix)_4]\cdot4H_2O$ [1,4-bix is 1,4-bis(imidazol-1-ylmethyl)benzene and H$_2$bpea is 4,4′-ethylenedibenzoic acid] (Yang *et al.*, 2008). Each crystallographically unique Cd^{II} center is bridged by the 1,4-bdc dianions and bpdo ligands to give a three-dimensional framework (Fig. 2). A better insight into the structure of (I) can be achieved by the application of a topological approach, that is, reducing multidimensional structures to simple node-and-linker nets (Batten & Robson, 1998). According to the simplification principle, the Cd^{II} center is defined as a four-connected node, while the 1,4-bdc and bpdo ligands serve as linkers. Therefore, on the basis of this concept of chemical topology, the overall structure is a diamond framework
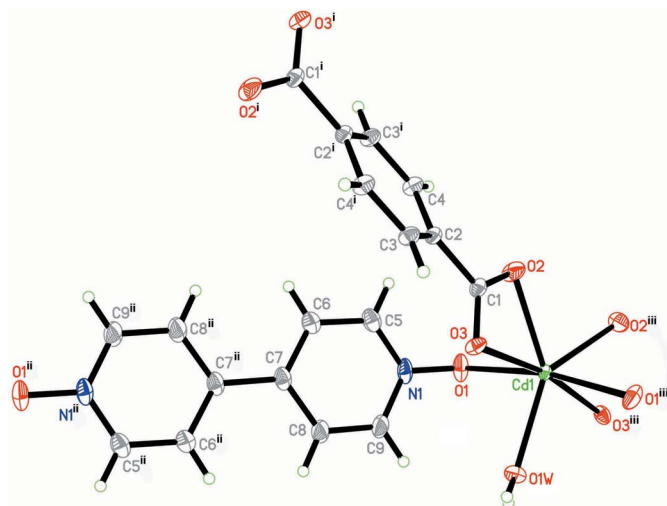
Figure 1
A view of the local coordination of the Cd^{II} atom in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $-x, -y, -z$; (iii) $1 - x, y, \frac{1}{2} - z$.]

Figure 2
A view of the diamond framework of (I) (the central Cd^{II} atom and its four neighbors are shown in pink in the electronic version of the paper).

Figure 3
A view of the threefold interpenetrating three-dimensional diamond net of (I) (the hydrogen-bonding interactions are shown as dashed lines).

containing large adamantanoid cages (Fig. 2). As can be seen, each distorted rectangular ring has six Cd^{II} centers, leading to the formation of a hexagon which is the shortest circuit here. In the adamantanoid cage, the Cd···Cd distances bridged by bpdo and 1,4-bdc are 12.624 (5) and 11.245 (4) Å, respectively.

It is well known that diamond networks tend to interpenetrate to fill the voids within a single net. Of particular interest, the most striking feature of (I) is that three identical three-dimensional single nets are interlocked with each other, thus directly leading to the formation of a threefold interpenetrated three-dimensional diamond architecture (Fig. 3). In addition, there are strong linear O—H···O hydrogen bonds between the water molecules and carboxylate O atoms within different diamond nets (Fig. 3). Each diamond net is hydrogen bonded to its two neighbors through these hydrogen bonds, which further consolidates the threefold interpenetrating diamond framework (Table 2).

Although many diamond-related nets displaying various interpenetration modes ranging from twofold to 11-fold have been reported, threefold interpenetrating MOFs in the presence of mixed organic ligands with different lengths is relatively rare (Batten, 2001; O'Keeffe et al., 2008; Carlucci et al., 2003). So far, only a few threefold interpenetrating MOFs, including [Co(D-cam)(TMDPy)]·2H$_2$O (D-H$_2$Cam is D-camphoric acid and TMDPy is 4,4'-trimethylenedipyridine; Zhang et al., 2008), [Cu$_2$(bpy)$_2$(Hbpy)(H$_2$O)][PW$_{12}$O$_{40}$] (bpy is 4,4'-bipyridine; Yang et al., 2009), [Tb(NO$_3$)$_3$(bpdo)(CH$_3$OH)] (Long et al., 2002) and [Cu(3,4'-bpdc)(H$_2$O)]·DMF·2H$_2$O (3,4'-bpdc is biphenyl-3,4'-dicarboxylate and DMF is dimethylformamide) (Feng et al., 2009), have been reported. The structure of (I) is entirely different from that of the related structure [Cu$_2$(bpy)$_2$(Hbpy)(H$_2$O)][PW$_{12}$O$_{40}$], which shows an unprecedented threefold interpenetrating diamond-like network in polyoxometalate chemistry. The structure of (I) is also different from those of the polymers [Tb(bpdo)-
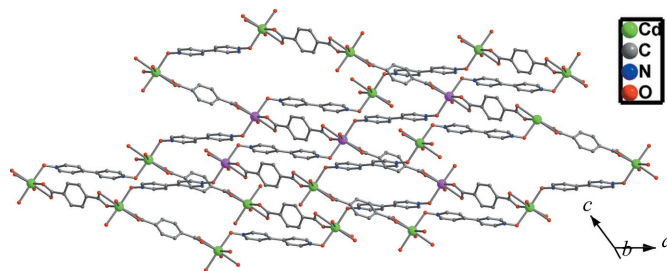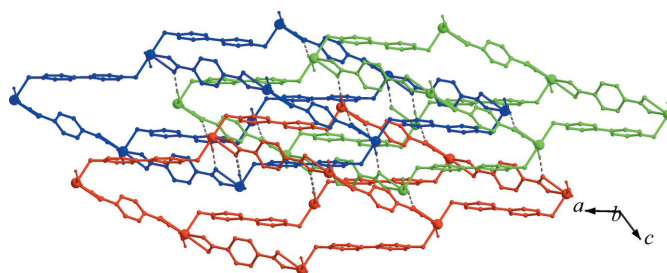
(CH$_3$OH)(NO$_3$)$_3$] and [Cu(3,4'-bpdc)(H$_2$O)]·DMF·2H$_2$O, whose threefold interpenetrating diamond nets only contain single organic ligands. In particular, [Tb(NO$_3$)$_3$(bpdo)(CH$_3$OH)] adopts a zigzag chain structure, which forms threefold interpenetrating diamond frameworks through interchain hydrogen bonding between coordinated methanol and a nitrate group on an adjacent chain. Although the reported compound Co(D-cam)(TMDPy)·2H$_2$O is constructed by mixed organic ligands, it exhibits a homochiral threefold interpenetrating diamond topology. Notably, there are only a few previously reported examples of MOFs based on bpdo–carboxylate mixed ligand systems (Manna et al., 2006, 2007; Fabelo et al., 2007). The related compounds [Co(H$_2$O)$_6$]-(H$_2$bta)·bpdo·4H$_2$O and {[Co$_2$(bpdo)(H$_2$O)$_4$]$_2$(bta)}·4H$_2$O are discrete molecular complexes (H$_4$bta is benzene-1,2,4,5-tetracarboxylic acid; Fabelo et al., 2007). The structure of [Co(H$_2$bta)(bpdo)$_2$(H$_2$O)$_2$]$_n$ is constituted by uniform chains of Co^{II} ions bridged by the dianionic H$_2$bta^{2-} species (Fabelo et al., 2007). The related compounds [Co(bta)$_{1/2}$(bpdo)-(H$_2$O)$_3$]$_n$, {[Co(ox)(bpdo)]}$_n$ and [Mn(ox)(bpdo)]$_n$ display two-dimensional layer structures (ox is the oxalate dianion; Manna et al., 2006, 2007; Fabelo et al., 2007).

Experimental

A mixture of CdCl$_2$·2.5H$_2$O (0.5 mmol), 1,4-H$_2$bdc (0.5 mmol) and bpdo (0.5 mmol) was dissolved in N,N-dimethylformamide (10 ml). The resulting solution was stirred for about 1 h at room temperature, sealed in a 23 ml Teflon-lined stainless steel autoclave and heated at 393 K for 1 d under autogenous pressure. The reaction system was then cooled slowly to room temperature. Block-shaped crystals of (I)

suitable for single-crystal X-ray diffraction analysis were collected from the final reaction system by filtration, washed several times with distilled water and dried in air at ambient temperature (yield: 38%, based on Cd^{II}).

Crystal data

$[Cd(C_8H_4O_4)(C_{10}H_8N_2O_2)(H_2O)]$	$V = 1683.0\ (3)\ \text{Å}^3$
$M_r = 482.71$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 14.1052\ (15)\ \text{Å}$	$\mu = 1.35\ \text{mm}^{-1}$
$b = 16.8934\ (18)\ \text{Å}$	$T = 293\ \text{K}$
$c = 8.8967\ (10)\ \text{Å}$	$0.22 \times 0.18 \times 0.15\ \text{mm}$
$\beta = 127.451\ (1)^\circ$	

Data collection

Bruker APEX diffractometer	4629 measured reflections
Absorption correction: multi-scan	1658 independent reflections
($SADABS$; Sheldrick, 1996)	1623 reflections with $I > 2\sigma(I)$
$T_{min} = 0.64,\ T_{max} = 0.85$	$R_{int} = 0.064$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of
$wR(F^2) = 0.073$	independent and constrained
$S = 1.07$	refinement
1658 reflections	$\Delta\rho_{max} = 1.07\ \text{e}\ \text{Å}^{-3}$
132 parameters	$\Delta\rho_{min} = -0.83\ \text{e}\ \text{Å}^{-3}$

Table 1
Selected geometric parameters (Å, °).

Cd1—O1W	2.258 (3)	Cd1—O1	2.316 (2)
Cd1—O2	2.314 (2)	Cd1—O3	2.520 (2)
O1W—Cd1—O2	137.26 (5)	O1W—Cd1—O3	84.99 (4)
O2—Cd1—O2^i	85.48 (10)	O2—Cd1—O3	53.95 (6)
O1W—Cd1—O1	84.84 (6)	O2^i—Cd1—O3	135.79 (7)
O2—Cd1—O1	84.98 (9)	O1^i—Cd1—O3	87.57 (8)
O2^i—Cd1—O1	102.69 (8)	O1—Cd1—O3	91.53 (8)
O1^i—Cd1—O1	169.67 (12)	O3^i—Cd1—O3	169.98 (9)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1W$\cdots$O3^{ii}	0.81 (3)	1.95 (3)	2.755 (2)	172 (4)

Symmetry code: (ii) $-x + 1, -y, -z + 1$.

Carbon-bound H atoms were positioned geometrically (C—H = 0.93 Å) and refined as riding, with $U_{iso}(H)$ values fixed at $1.2U_{eq}(C)$. The water H atom was located in a difference Fourier map and refined freely.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); 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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