metal-organic compounds

Poly[[tetraaqua(μ_7-pyridine-2,3,5,6-tetracarboxylato)dicadmium(II)] monohydrate]

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The title compound, $\{[Cd_2(C_9HNO_8)(H_2O)_4] \cdot H_2O\}_n$, consists of two crystallographically independent Cd^{II} cations, one tetrabasic pyridine-2,3,5,6-tetracarboxylate (pdtc) anion, four coordinated water molecules and one solvent water molecule. The Cd^{II} cations have distorted square-antiprismatic (one pyridine N, six carboxylate O and one water O atom) and octahedral (three carboxylate O and three water O atoms) coordination environments. Each pdtc ligand employs its pyridine and carboxylate groups to chelate and bridge seven Cd^{II} cations. The square-antiprismatic coordinated Cd^{II} cations are linked by pdtc ligands into a lamellar framework structure, while the octahedral coordinated Cd^{II} cations are bridged by the μ_2-carboxylate O atoms and the pdtc ligands into a chain network that further joins neighbouring lamellae into a three-dimensional porous network. The cavities are filled with solvent water molecules that are linked to the host through complex hydrogen bonding.

Comment

In the past few years, crystal engineering of porous metal–organic coordination networks has attracted much attention because of their interesting structural patterns, with both aesthetic appeal and special functionalities for potential applications (Czaja *et al.*, 2009; Lee *et al.*, 2009; Li *et al.*, 2009; Ma *et al.*, 2009; Murray *et al.*, 2009; Tranchemontagne *et al.*, 2009; Wang & Cohen, 2009). It has been shown that judicious choice of organic bridging ligands and metal nodes is the key step towards the construction of interesting topological frameworks.

Pyridine-2,3,5,6-tetracarboxylic acid (H_4pdtc), which contains one pyridine and four carboxylate potential donor groups, should be an effective ligand for coordinating to transition metal cations to generate some interesting structural networks (Babu & Nangia, 2006). However, only two pdtc-ligand-coordinated compounds have been reported to date, a tetranuclear zinc(II) compound bridged by two pdtc

anions, and a mononuclear nickel(II) compound chelated by pdtc (Yang *et al.*, 2008). In the former case, because the additional coordination sites of the Zn^{II} cations are blocked by four chelating 1,10-phenanthroline molecules, the tetranuclear Zn unit cannot be further bridged by additional pdtc ligands to form a polymeric framework. In the latter case, as three water coordination sites of the Ni^{II} cation are not replaced by additional pdtc ligands, the pdtc ligand only chelates one Ni^{II} cation to form a mononuclear nickel(II) compound.

Because of the relatively large ionic radius of the Cd^{II} cation, its coordination numbers in *O*-donor complexes typically range from 6 to 8, which suggests that cadmium compounds should form some interesting three-dimensional frameworks (Wang *et al.*, 2007). In fact, there are several examples of three-dimensional frameworks of Cd^{II} cations bridged by pyridine carboxylates, such as pyridine-3,4-dicarboxylate (Xia *et al.*, 2004), pyridine-2,4-dicarboxylate (Bai *et al.*, 2008), pyridine-2,3-dicarboxylate (Zhang *et al.*, 2005; Han *et al.*, 2006) and pyridine-2,4,6-tricarboxylate (Wang *et al.*, 2007; Zou *et al.*, 2008). Attracted by the interesting structural motifs of these pyridine carboxylate-bridged cadmium compounds, we anticipated that pdtc would be an effective bridging ligand to generate a novel structural network. We report here the first three-dimensional porous polymeric framework compound based on the pdtc ligand, *viz.* the title compound, $[Cd_2(pdtc)(H_2O)_4] \cdot H_2O$, (I).

(I)
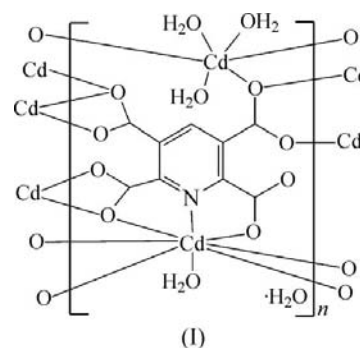
Compound (I) crystallizes in the triclinic $P\bar{1}$ space group with two Cd^{II} cations, one fully deprotonated pdtc anion, four aqua ligands and one solvent water molecule in the asymmetric unit (Fig. 1). Each pdtc ligand employs its pyridine group and carboxylate groups to chelate and bridge seven Cd^{II} cations. Atom Cd1 is chelated by the pyridine group and two neighbouring carboxylate O atoms from the first pdtc ligand, two O atoms of a carboxylate group from a second pdtc ligand, one carboxylate O atom from a third pdtc ligand, a μ_2-carboxylate O atom from a fourth pdtc ligand and one aqua ligand, in an octacoordinated distorted square-antiprismatic coordination environment (Table 1).

The pdtc ligands link the Cd1 cations into an interesting lamellar framework structure in the *ab* plane (Fig. 2). Atom Cd2 has a hexacoordinated octahedral geometry, chelated by two O atoms of one pdtc carboxylate group, one μ_2-carboxylate O atom of another pdtc ligand and three aqua ligands (Table 1). There is one additional interaction, Cd2—O8^v = 2.676 (4) Å [symmetry code: (v) $x, y, z - 1$], but this is outside
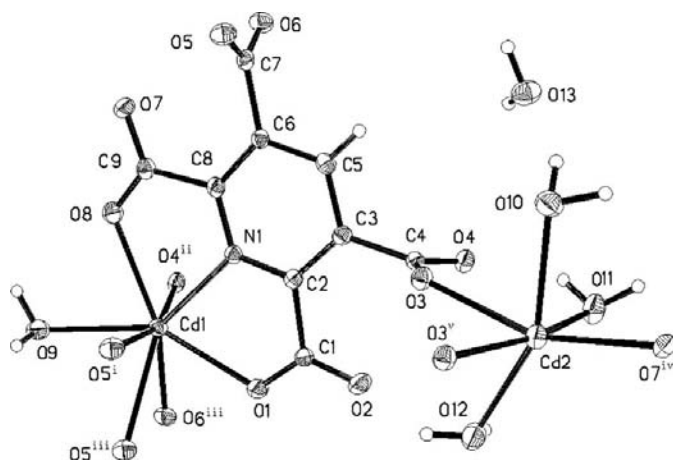
Figure 1
A perspective view of the locally expanded asymmetric unit for (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 25% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $2 - x, 1 - y, 2 - z$; (ii) $1 - x, 1 - y$, $2 - z$; (iii) $x, y - 1, z$; (iv) $x, y, z - 1$; (v) $2 - x, 1 - y, 1 - z$.]
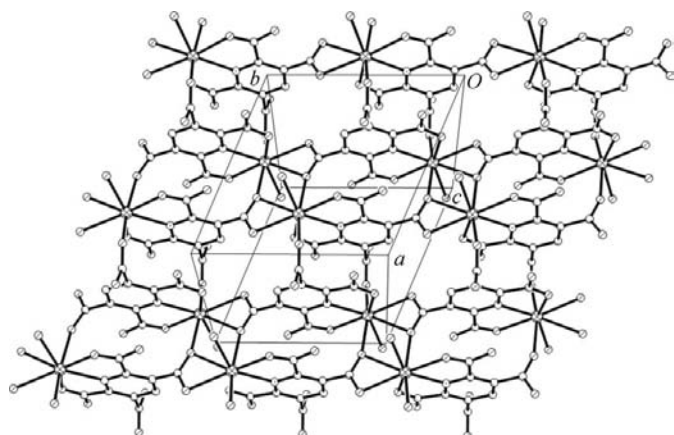

Figure 2
A view of the lamellar framework of Cd1 ions linked by pdtc ligands.

the typical range of 2.1–2.4 Å for Cd—O coordination. The μ_2-carboxylate O atom bridges two Cd2 sites into a binuclear unit, which is further doubly bridged by pdtc ligands into a chain network along the c direction (Fig. 3). As the alternating pdtc ligands along c are attributed to different layers of pdtc linking up Cd1 sites, the Cd2 sites serve to join neighbouring lamellar Cd1–pdtc frameworks into a three-dimensional porous network structure (Fig. 4). The cavities are filled with solvent water molecules that interact with the host framework through hydrogen bonding. The hydrogen-bond distances between solvent water molecules and carboxylate O atoms range from 2.728 (6) to 2.730 (6) Å, and those between solvent water molecules and aqua ligands from 2.707 (6) to 2.765 (6) Å. Finally, there are also extensive hydrogen bonds between aqua ligands and carboxylate O atoms [2.686 (6)–2.975 (6) Å] and between aqua ligands themselves [2.870 (6)–2.946 (6) Å].

The framework structure of (I) is quite different from previously reported three-dimensional Cd^{II} compounds
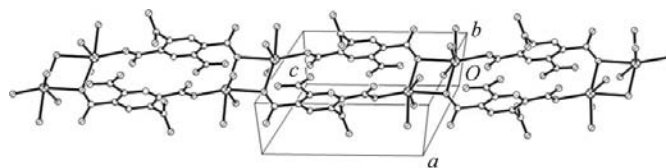

Figure 3
A view of the linear framework of Cd2 ions linked by pdtc ligands.
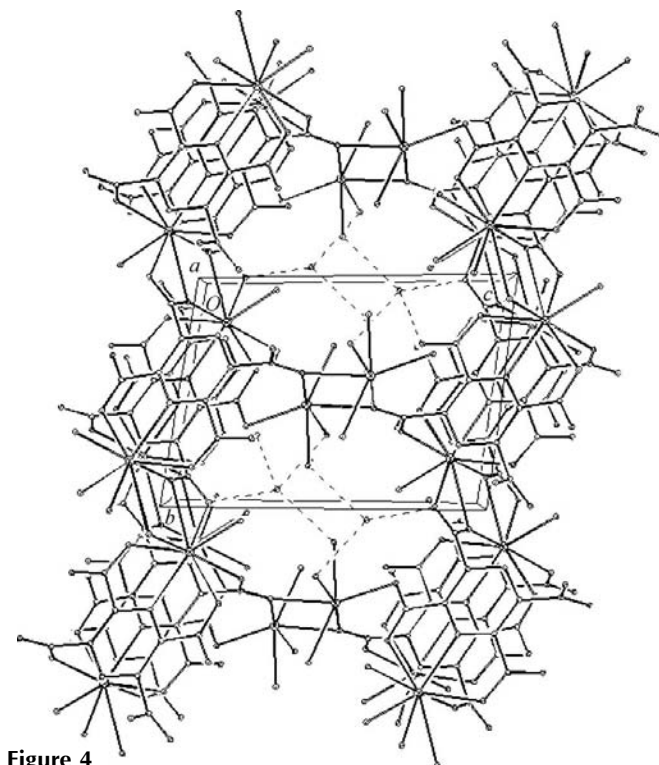

Figure 4
The packing of (I), viewed down the a axis, showing the hydrogen bonds involving the solvent water molecules as dashed lines. For clarity, H atoms have been omitted.

bridged by pyridine dicarboxylates. For example, pyridine-3,4-dicarboxylate acts a tetradentate ligand to link four octahedrally distorted Cd^{II} cations into a three-dimensional architecture with small square channels without guest molecules (Xia *et al.*, 2004). The pyridine-2,4-dicarboxylate ligand acts as a pentadentate ligand to link five octahedral Cd^{II} cations into a three-dimensional framework with large channels occupied by the pyridine groups of the ligands (Bai *et al.*, 2008), while pyridine-2,3-dicarboxylate, adopting two different coordination modes, bridges Cd^{II} tetramers into a three-dimensional network without guest molecules (Han *et al.*, 2006). The three-dimensional framework of pyridine-2,4,6-tricarboxylate-bridged Cd^{II} cations is similar to (I) in that there are two different types of Cd^{II} cations in distorted octahedral and pentagonal–bipyramidal coordination environments. Pyridine-2,4,6-tricarboxylate bridges the pentagonal–bipyramidal coordinated Cd^{II} cations into a two-dimensional layer structure, which is further extended into a three-dimensional network linked by the octahedrally coordinated Cd^{II} cations and carboxyl groups without guest molecules within the cavities thus formed (Wang *et al.*, 2007).

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Thermogravimetric analysis (TGA) of (I) indicates that a weight loss of 15.7% occurs between 303 and 433 K, corresponding to the loss of solvent water molecules and aqua ligands (expected 15.9%), without a distinct plateau in the curve. There is almost no further weight loss until 683 K, above which (I) began to lose the coordinated pdtc ligand and to decompose. After a sample of (I) was ground and heated at 368 K for 2 h, a powder X-ray diffraction (PXRD) profile of the resultant powder showed no sharp peaks in the PXRD pattern, and this material cannot be rehydrated and reverted to the original compound after being immersed in water, as confirmed by the PXRD pattern. These results indicate that both the solvent and ligand water molecules play important roles in the formation and stability of (I).

Experimental

Heating a mixture of $CdCl_2 \cdot 2.5H_2O$ (4.6 mg, 0.02 mmol) and H_4pdtc (2.6 mg, 0.01 mmol) in water (4.0 ml) at 368 K for 1 d afforded colourless crystals of (I), which were filtered off, washed with water, ethanol and diethyl ether, and dried at room temperature (yield 78%, based on H_4pdtc). IR (KBr pellet, v, cm^{-1}): 1616 (s), 1560 (s), 1453 (m), 1371 (s), 1334 (m), 1269 (w), 1159 (m), 837 (w).

Crystal data

$[Cd_2(C_9HNO_8)(H_2O)_4] \cdot H_2O$	$\gamma = 67.269 \ (4)°$
$M_r = 565.99$	$V = 701.48 \ (6) \ Å^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.3989 \ (5)$ Å	Mo $K\alpha$ radiation
$b = 8.5350 \ (3)$ Å	$\mu = 3.11 \ mm^{-1}$
$c = 11.4883 \ (5)$ Å	$T = 293$ K
$\alpha = 89.325 \ (4)°$	$0.18 \times 0.12 \times 0.09$ mm
$\beta = 69.014 \ (5)°$	

Data collection

Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector	4815 measured reflections
	2650 independent reflections
	2181 reflections with $I > 2\sigma(I)$
Absorption correction: analytical (CrysAlis Pro; Oxford Diffraction, 2010)	$R_{int} = 0.018$
$T_{min} = 0.645$, $T_{max} = 0.756$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	226 parameters
$wR(F^2) = 0.044$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{max} = 0.68$ e Å^{-3}
2650 reflections	$\Delta\rho_{min} = -0.87$ e Å^{-3}

H atoms on C atoms were positioned geometrically and included in the structure-factor calculations as riding atoms, with C—H = 0.93 Å. The H atoms of the water molecules were clearly visible in difference maps, and these were placed in the difference-map positions, then their positions were idealized and constrained to ride on their parent O atoms, with O—H = 0.82 Å. All H atoms were assigned fixed isotropic displacement parameters in the subsequent refinement, with $U_{iso}(H) = 1.2U_{eq}$(parent atom).

Data collection: CrysAlis Pro (Oxford Diffraction, 2010); cell refinement: CrysAlis Pro; data reduction: CrysAlis Pro; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXL97; software used to prepare material for publication: PLATON (Spek, 2009).

Table 1
Selected geometric parameters (Å, °).

Cd1—O5^i	2.345 (4)	Cd1—O5^{iii}	2.511 (4)
Cd1—N1	2.352 (5)	Cd2—O7^{iv}	2.238 (4)
Cd1—O4^{ii}	2.373 (4)	Cd2—O3^v	2.304 (4)
Cd1—O1	2.423 (4)	Cd2—O11	2.325 (4)
Cd1—O6^{iii}	2.446 (4)	Cd2—O12	2.325 (4)
Cd1—O9	2.447 (4)	Cd2—O10	2.344 (4)
Cd1—O8	2.460 (4)	Cd2—O3	2.389 (4)
O5^i—Cd1—N1	81.77 (14)	O6^{iii}—Cd1—O5^{iii}	52.58 (12)
N1—Cd1—O1	68.07 (14)	O9—Cd1—O5^{iii}	76.33 (13)
O4^{ii}—Cd1—O6^{iii}	72.44 (13)	O7^{iv}—Cd2—O11	84.78 (15)
O1—Cd1—O6^{iii}	78.83 (13)	O3^v—Cd2—O12	85.24 (14)
N1—Cd1—O8	67.71 (14)	O7^{iv}—Cd2—O10	82.08 (15)
O4^{ii}—Cd1—O8	76.64 (13)	O3^v—Cd2—O3	77.03 (14)
O9—Cd1—O8	71.03 (13)	O12—Cd2—O3	77.11 (14)
O5^i—Cd1—O5^{iii}	67.54 (15)	O10—Cd2—O3	77.03 (14)
O1—Cd1—O5^{iii}	71.84 (13)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O9—H9B···O12^{vi}	0.82	2.17	2.946 (6)	159
O9—H9A···O1^{vii}	0.82	2.06	2.872 (5)	170
O10—H10A···O9^{viii}	0.82	2.11	2.912 (6)	164
O10—H10B···O13	0.82	1.91	2.707 (6)	164
O11—H11A···O13^{ix}	0.82	2.00	2.765 (6)	154
O11—H11B···O4	0.82	1.94	2.686 (6)	151
O12—H12A···O10^v	0.82	2.14	2.892 (6)	152
O12—H12A···O2	0.82	2.48	2.975 (6)	120
O12—H12B···O11^x	0.82	2.12	2.870 (6)	152
O13—H13A···O6^{xi}	0.82	1.91	2.728 (6)	174
O13—H13B···O2^{xii}	0.82	1.93	2.730 (6)	168

Symmetry codes: (v) $-x + 2, -y + 1, -z + 1$; (vi) $x, y, z + 1$; (vii) $-x + 2, -y, -z + 2$; (viii) $x, y + 1, z - 1$; (ix) $-x + 1, -y + 2, -z + 1$; (x) $-x + 1, -y + 1, -z + 1$; (xi) $-x + 1, -y + 2, -z + 2$; (xii) $x, y + 1, z$.

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