

Poly[[aqua(μ_7 -ethylenediaminetetraacetato)dicadmium(II)] monohydrate]

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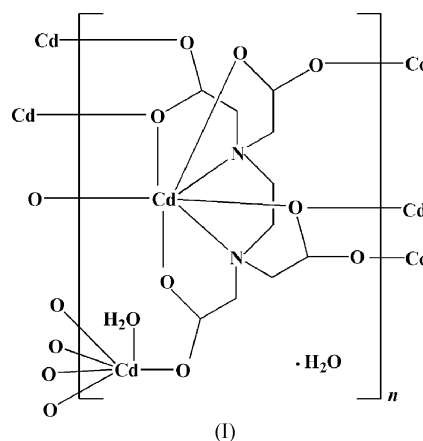
The title compound, $\{[\text{Cd}_2(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$, consists of two crystallographically independent Cd^{II} cations, one ethylenediaminetetraacetate (edta) tetraanion, one coordinated water molecule and one solvent water molecule. The coordination of one of the Cd atoms, Cd1, is composed of five O atoms and two N atoms from two tetraanionic edta ligands in a distorted pentagonal–bipyramidal coordination geometry. The other Cd atom, Cd2, is six-coordinated by five carboxylate O atoms from five edta ligands and one water molecule in a distorted octahedral geometry. Two neighbouring Cd1 atoms are bridged by a pair of carboxylate O atoms to form a centrosymmetric $[\text{Cd}_2(\text{edta})_2]^{4-}$ unit located on the inversion centre, which is further extended into a two-dimensional layered structure through Cd2–O bonds. There are hydrogen bonds between the coordinated water molecules and carboxylate O atoms within the layer. The solvent water molecules occupy the space between the layers and interact with the host layers through O–H...O and C–H...O interactions.

Comment

The construction of coordination polymers from multifunctional ligands with metal ions is one of the most active areas of materials research. The intense interest in these materials is driven by their intrinsic architectural beauty and aesthetically pleasing structures, as well as potential applications such as catalysis, molecular magnets, photoluminescence, adsorption and phase separation (Janiak, 2003; Kitagawa *et al.*, 2004; O'Keeffe *et al.*, 2000). The assembly of these coordination compounds allows for a wide choice of various parameters including diverse electronic properties and coordination geometries of the metal ions as well as versatile functions of organic ligands. To date, metal carboxylate frameworks have afforded the most diversity in this area because of their chemical stability and appropriate connectivity (Yaghi *et al.*, 1997; Chen *et al.*, 2009). Ethylenediaminetetraacetic acid (H_4edta), which has ten potential

donor atoms (eight O atoms and two N atoms), is an effective ligand for coordinating to metal cations to generate diverse structural networks (Luo & Xu, 2006; Mizuta *et al.*, 1995). H_4edta commonly acts as a chelating ligand to enclose a central metal ion, leaving some remaining sites available for coordination. Thus, some bimetallic compounds have been isolated successfully through this strategy (Brouca-Cabarrecq *et al.*, 1996; Yi *et al.*, 1998). In addition, some structurally defined peroxotitanate–edta coordination compounds can delineate certain cleavage reaction mechanisms (Zhou *et al.*, 2007). Although many compounds containing the H_4edta ligand have been reported, new coordination compounds with interesting structures based on the H_4edta ligand continue to be synthesized owing to the coordination versatility of the H_4edta ligand.

Because of the relatively large ionic radius of the Cd^{II} cation, its coordination numbers typically range from 6 to 8, which suggests that cadmium compounds should form some interesting frameworks (Liu *et al.*, 2006). The combination of the H_4edta ligand with cadmium(II) ions produced several complexes, such as the mononuclear $[\text{Cd}(\text{H}_2\text{edta})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$ (Polyakova *et al.*, 2001), the trinuclear $[\text{Cd}_3(\text{Hedta})_2(\text{H}_2\text{O})_6]\cdot\text{H}_2\text{O}$ (Solans *et al.*, 1987) and the polymeric bimetallic network $\{[\text{Na}_2\text{Cd}_3(\text{Hedta})_2(\text{H}_2\text{O})_6]\cdot 2\text{H}_2\text{O}\}_n$ (Wang *et al.*, 2008). However, all reported Cd^{II} compounds bridged by H_4edta ligands with polymeric structures are heterometallic compounds (Llyukhin & Davidovich, 1999; Solans *et al.*, 1985). We report here the cadmium compound $\{[\text{Cd}_2(\text{edta})(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}\}_n$ (I), which is the first homometallic two-dimensional layered framework compound based on the edta ligand and the cadmium ion. In addition, the edta ligand displays a novel heptadentate coordination mode in the compound.



The asymmetric unit of (I) consists of two Cd^{II} cations, one edta tetraanion, one coordinated water molecule and one solvent water molecule. As depicted in Fig. 1, atom Cd1 is seven-coordinated by four carboxylate O and two N atoms from an edta ligand and one carboxylate O atom [O5'; symmetry code: (i) $-x, -y, -z + 1$] from the other edta ligand in a pentagonal–bipyramidal coordination environment, with atoms O1 and O7 occupying the apical positions. Atom Cd2 is six-coordinated by three carboxylate O atoms from three edta

metal-organic compounds

ligands and one coordinated water molecule in a distorted square-planar geometry, and two carboxylate O atoms [O8ⁱⁱ and O3^v; symmetry codes: (ii) $x + 1, y, z + 1$; (v) $-x + 1, -y, -z + 1$] from another two edta ligands in the apical positions. The CdO₆ octahedron is distorted, with the O—Cd—O bond angles ranging from 79.47 (10) to 160.80 (9)° (Table 1). There is one additional interaction [Cd2—O4^v = 2.667 (3) Å], but this is outside the typical range of 2.10–2.45 Å for Cd—O coordination.

Each edta ligand employs its carboxylate groups and two N atoms to chelate and bridge seven Cd^{II} cations (Fig. 2). Two neighbouring Cd1 atoms are bridged by a pair of carboxylate O atoms (O5 and O5ⁱ) to form a centrosymmetric

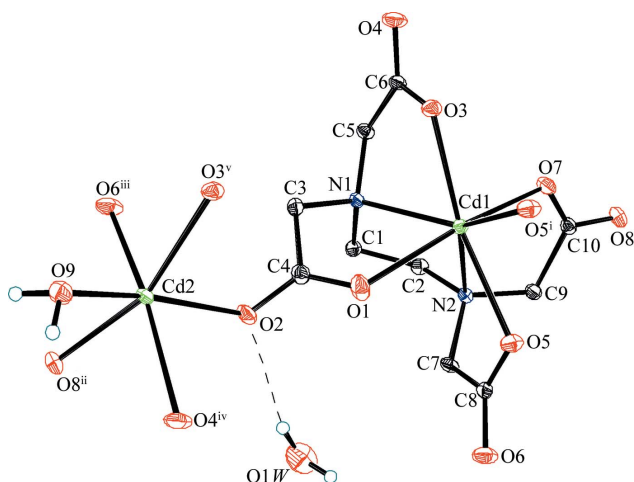


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. Water H atoms are shown as small spheres of arbitrary radii and methylene H atoms have been omitted for clarity. Dashed lines indicate hydrogen bonds. [Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $x + 1, y, z + 1$; (iii) $x + 1, y, z$; (iv) $x, y, z + 1$; (v) $-x + 1, -y, -z + 1$.]

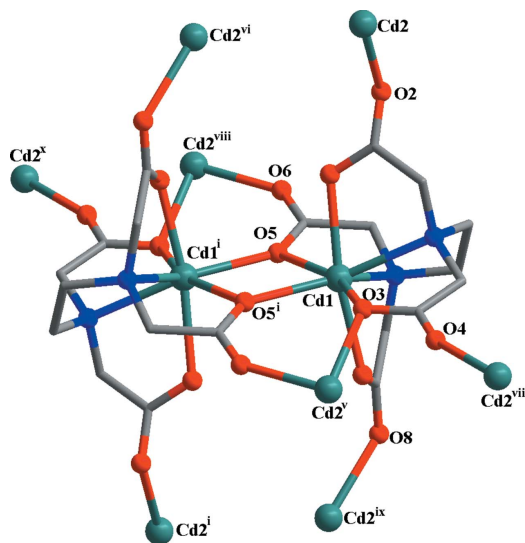


Figure 2
A view of the $[\text{Cd}_2(\text{edta})_2]^{4-}$ unit, surrounded by eight Cd2 atoms. [Symmetry codes: (i) $-x, -y, -z + 1$; (v) $-x + 1, -y, -z + 1$; (vi) $-x + 1, -y, -z + 2$; (vii) $x, y, z - 1$; (viii) $x - 1, y, z$; (ix) $x - 1, y, z - 1$; (x) $-x, -y, -z + 2$.]

$[\text{Cd}_2(\text{edta})_2]^{4-}$ unit containing a Cd₂O₂ core, located on the inversion centre, with a Cd···Cd separation of 3.7314 (5) Å. Each $[\text{Cd}_2(\text{edta})_2]^{4-}$ unit is surrounded by eight Cd2 atoms (Fig. 2). The $[\text{Cd}_2(\text{edta})_2]^{4-}$ units are linked by Cd2 atoms through Cd2^v—O3, Cd2^{vii}—O4 and Cd2^{viii}—O6 bonds [symmetry codes: (vii) $x, y, z - 1$; (viii) $x - 1, y, z$] to form a one-dimensional chain (Fig. 3). The one-dimensional chains are further linked by Cd2 atoms through Cd2—O2 and Cd2^{ix}—O8 bonds [symmetry code: (ix) $x - 1, y, z - 1$] to generate a two-dimensional layer in the *ac* plane (Fig. 3). Thus, the Cd2 sites serve to join neighbouring $[\text{Cd}_2(\text{edta})_2]^{4-}$ units into a two-dimensional layered structure. There are hydrogen bonds between aqua ligands and carboxylate O atoms within the layer (Table 2). The two-dimensional layers are stacked along the *b* direction (Fig. 4). The solvent water molecules occupy the space between the layers and interact with the host layers through O—H···O and C—H···O interactions (Table 2).

Several homometallic compounds with two-dimensional structures containing bridging edta ligands have been reported previously. However, the structure of (I) is quite different from those structures. For example, the $\{[\text{Ca}_2(\text{edta})(\text{H}_2\text{O})_2] \cdot (\text{H}_2\text{O})\}_n$ compound has a similar dinuclear $[\text{Ca}_2(\text{edta})_2(\text{H}_2\text{O})_2]^{4-}$ unit, which is extended into a two-dimensional layer through Ca—O bonds (Barnett & Uchtman, 1979). However, in this compound, each $[\text{Ca}_2(\text{edta})_2(\text{H}_2\text{O})_2]^{4-}$ unit is only surrounded by six Ca^{II} ions, and the edta ligand exhibits a hexadentate coordination mode, different from (I). The edta ligand chelates an Sn²⁺ ion and bridges four Sn²⁺ ions to generate a two-dimensional framework where the basic structural unit is the mononuclear $[\text{Sn}(\text{edta})]^{2-}$ (Van Remoortere *et al.*, 1971). This indicates that the structures of the final products are strongly influenced by the nature of the metal ions.

To examine the thermal stability of the compound and the structural variation as a function of temperature, thermo-

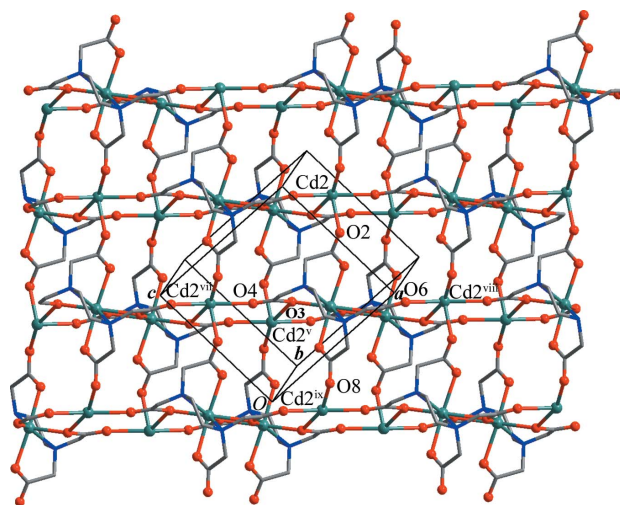
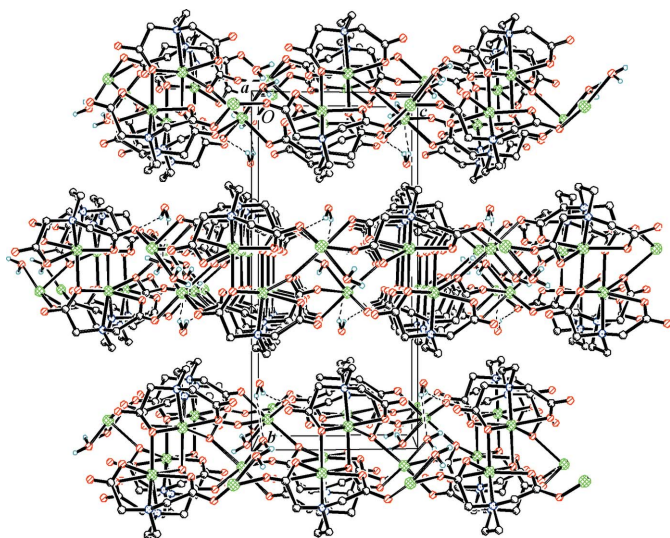


Figure 3
A perspective view of the two-dimensional layered structure constructed of one-dimensional chains. [Symmetry codes: (v) $-x + 1, -y, -z + 1$; (vii) $x, y, z - 1$; (viii) $x - 1, y, z$; (ix) $x - 1, y, z - 1$.]


Figure 4

A view of the packing for (I) down the *a* axis. H atoms not involved in hydrogen bonding have been omitted for clarity

gravimetric analysis (TGA) was performed on a single-phase polycrystalline sample of (I) (see Fig. S1 in the supplementary materials). TGA of (I) indicates that a weight loss of 6.4% occurs between 308 and 333 K, corresponding to the loss of the solvent water molecule and aqua ligand (expected 6.5%), with a distinct plateau in the curve. The second weight loss, in the temperature range 403–463 K, corresponds to the incomplete decomposition of the edta ligand. A sharp continual weight loss occurred at 508 K, which is attributed to further decomposition of the organic ligand.

Experimental

A mixture of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (154 mg, 0.5 mmol) and ethylenediaminetetraacetic acid (186 mg, 0.5 mmol) in a 1:1 molar ratio in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (14 ml, 3:4 v/v) was introduced into a Parr Teflon-lined stainless steel vessel (20 ml). The vessel was sealed and heated to 413 K. The temperature was held for 2 d and then the mixture was left to cool to room temperature to obtain colourless block-shaped crystals. The crystalline product was filtered off, washed with $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ and dried at ambient temperature [yield 43% based on $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$]. IR (KBr pellet, cm^{-1}): 3436, 3108, 3076, 1642, 1559, 1481, 1426, 1363, 1197, 1129, 1078, 1032, 996, 879, 862, 673, 628, 545.

Crystal data

$[\text{Cd}_2(\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8)(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$	$V = 1462.41 (18) \text{ \AA}^3$
$M_r = 549.07$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 8.4640 (6) \text{ \AA}$	$\mu = 2.97 \text{ mm}^{-1}$
$b = 19.2334 (14) \text{ \AA}$	$T = 296 \text{ K}$
$c = 9.0134 (6) \text{ \AA}$	$0.41 \times 0.21 \times 0.09 \text{ mm}$
$\beta = 94.680 (1)^\circ$	

Data collection

Bruker APEXII area-detector diffractometer	13303 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3590 independent reflections
$T_{\min} = 0.521$, $T_{\max} = 0.794$	3363 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.027$

Table 1

Selected geometric parameters (\AA , $^\circ$).

$\text{Cd1}-\text{O5}^i$	2.284 (2)	$\text{Cd2}-\text{O2}$	2.277 (3)
$\text{Cd1}-\text{O3}$	2.300 (2)	$\text{Cd2}-\text{O9}$	2.292 (3)
$\text{Cd1}-\text{O7}$	2.336 (3)	$\text{Cd2}-\text{O8}^{ii}$	2.297 (2)
$\text{Cd1}-\text{O1}$	2.365 (3)	$\text{Cd2}-\text{O6}^{iii}$	2.309 (3)
$\text{Cd1}-\text{N2}$	2.395 (3)	$\text{Cd2}-\text{O4}^{iv}$	2.349 (3)
$\text{Cd1}-\text{O5}$	2.423 (3)	$\text{Cd2}-\text{O3}^v$	2.370 (2)
$\text{Cd1}-\text{N1}$	2.437 (3)		
$\text{O5}^i-\text{Cd1}-\text{O3}$	83.75 (9)	$\text{N2}-\text{Cd1}-\text{N1}$	75.21 (9)
$\text{O5}^i-\text{Cd1}-\text{O7}$	93.88 (10)	$\text{O2}-\text{Cd2}-\text{O8}^{ii}$	105.87 (9)
$\text{O3}-\text{Cd1}-\text{O7}$	84.76 (9)	$\text{O9}-\text{Cd2}-\text{O8}^{ii}$	85.88 (10)
$\text{O5}^i-\text{Cd1}-\text{O1}$	97.39 (10)	$\text{O2}-\text{Cd2}-\text{O6}^{iii}$	90.53 (11)
$\text{O3}-\text{Cd1}-\text{O1}$	103.21 (10)	$\text{O9}-\text{Cd2}-\text{O6}^{iii}$	107.53 (11)
$\text{O7}-\text{Cd1}-\text{O1}$	166.82 (10)	$\text{O8}^{ii}-\text{Cd2}-\text{O6}^{iii}$	83.94 (10)
$\text{O7}-\text{Cd1}-\text{N2}$	71.06 (9)	$\text{O2}-\text{Cd2}-\text{O4}^{iv}$	79.78 (11)
$\text{O1}-\text{Cd1}-\text{N2}$	95.93 (10)	$\text{O9}-\text{Cd2}-\text{O4}^{iv}$	86.25 (10)
$\text{O5}^i-\text{Cd1}-\text{O5}$	75.17 (10)	$\text{O8}^{ii}-\text{Cd2}-\text{O4}^{iv}$	79.47 (10)
$\text{O7}-\text{Cd1}-\text{O5}$	98.08 (10)	$\text{O2}-\text{Cd2}-\text{O3}^v$	86.47 (9)
$\text{O1}-\text{Cd1}-\text{O5}$	78.34 (10)	$\text{O9}-\text{Cd2}-\text{O3}^v$	87.02 (9)
$\text{N2}-\text{Cd1}-\text{O5}$	68.34 (9)	$\text{O8}^{ii}-\text{Cd2}-\text{O3}^v$	160.80 (9)
$\text{O3}-\text{Cd1}-\text{N1}$	70.20 (9)	$\text{O6}^{iii}-\text{Cd2}-\text{O3}^v$	81.24 (9)
$\text{O7}-\text{Cd1}-\text{N1}$	103.02 (10)	$\text{O4}^{iv}-\text{Cd2}-\text{O3}^v$	117.83 (9)
$\text{O1}-\text{Cd1}-\text{N1}$	70.62 (9)		

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

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O9}-\text{H9C}\cdots\text{O7}^{ii}$	0.85	1.93	2.710 (4)	151
$\text{O9}-\text{H9D}\cdots\text{O1}^{vi}$	0.85	1.99	2.828 (4)	168
$\text{O1W}-\text{H1W}\cdots\text{O9}^{vi}$	0.85	2.53	3.081 (5)	122
$\text{O1W}-\text{H2W}\cdots\text{O2}$	0.85	2.26	3.038 (5)	151
$\text{C5}-\text{H5B}\cdots\text{O1W}^{vii}$	0.97	2.55	3.399 (5)	146

Symmetry codes: (ii) $x + 1, y, z + 1$; (vi) $-x + 1, -y, -z + 2$; (vii) $x, y, z - 1$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	217 parameters
$wR(F^2) = 0.073$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$
3590 reflections	$\Delta\rho_{\text{min}} = -1.20 \text{ e \AA}^{-3}$

Methylene H atoms were placed in calculated positions and treated using a riding-model approximation [$\text{C}-\text{H} = 0.97 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$]. H atoms bonded to O atoms were located in a difference map and were allowed to ride on their parent O atoms [$\text{O}-\text{H} = 0.85 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$].

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and DIAMOND (Brandenburg, 2005); software used to prepare material for publication: SHELXL97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3036). Services for accessing these data are described at the back of the journal.

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