

Poly[(μ_3 -benzene-1,4-dicarboxylato)-di- μ -chlorido-(triethanolamine)di-cadmium(II)]: a cadmium–halide coordination polymer with a hydrogen-bonded three-dimensional framework

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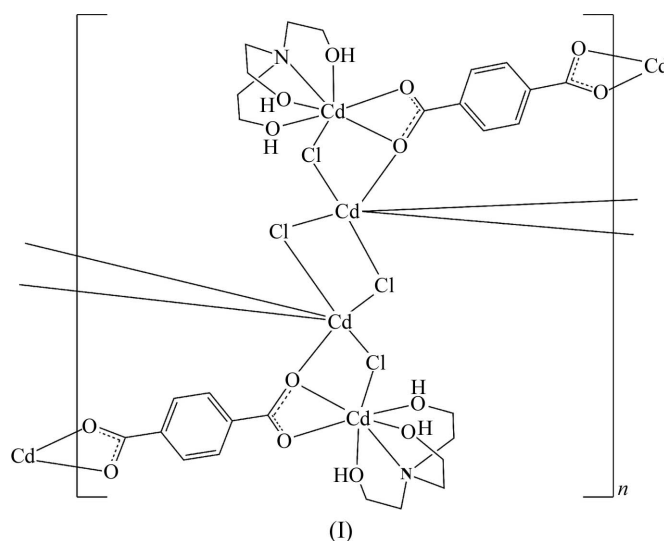
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The structure of the title compound, $[\text{Cd}_2(\text{C}_8\text{H}_4\text{O}_4)\text{Cl}_2(\text{C}_6\text{H}_{15}\text{NO}_3)]_n$, consists of one-dimensional chains in which each centrosymmetric tetranuclear $\text{Cd}_4\text{Cl}_4\text{O}_2$ cluster is terminated by two chelating triethanolamine (teaH₃) ligands but linked to two adjacent clusters through four bridging benzene-1,4-dicarboxylate (bdc) ligands. The tetranuclear $\text{Cd}_4\text{Cl}_4\text{O}_2$ clusters are held together *via* bridging Cl and O atoms. Three directional hydrogen bonds from the multi-podal hydroxy groups of the teaH₃ ligand stabilize and extend the one-dimensional chains into a three-dimensional framework. All three hydroxy groups of the teaH₃ ligand form hydrogen bonds, illustrating the fact that the teaH₃ ligand can serve as an excellent hydrogen-bond donor.

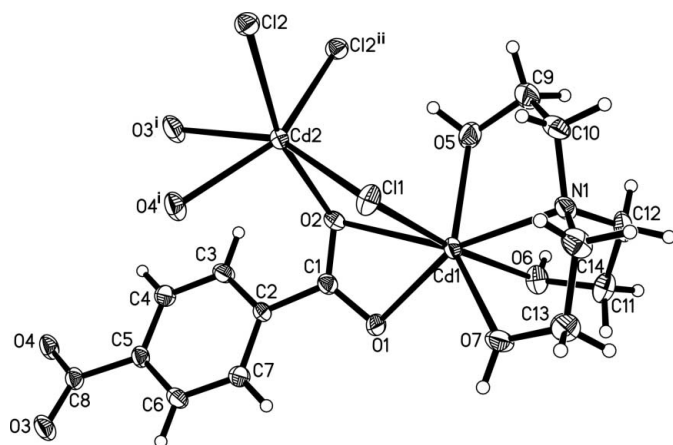
Comment

Recent advances in supramolecular assembly of coordination polymers have led to many organic–inorganic hybrid materials with interesting structures and desirable functions (Desiraju, 2007). It is now well established that the combination of coordination bonds and hydrogen bonds presents an ideal synthetic paradigm for the crystal engineering of crystalline materials (MacDonald *et al.*, 2000). Triethanolamine (teaH₃) is a member of the alkoxide family containing both amine and alcohol groups, and can serve as a versatile ligand that readily forms coordination complexes with almost all metal ions (Sen & Dotson, 1970). The multi-podal capabilities of the three ethanolic arms suggest that the teaH₃ molecule is indeed an excellent candidate for hydrogen-bond donation, endowing the resultant complexes with great potential in supramolecular chemistry (Chen *et al.*, 2009). Alternatively, the hydroxy H atoms of the teaH₃ molecule may be deprotonated to give the

triethanolamine anion, which can act as both a bridging and a chelating ligand for synthesizing polynuclear species (Liu *et al.*, 2008). The teaH₃ molecule can also behave as an *N,O,O'*-tridentate or *N,O,O',O''*-tetradentate neutral ligand to chelate one metal ion, especially for metal ions with large ionic radii. It is known that the ability of the Cd^{II} ion to extend its coordination number to 7 enables the synthesis of seven-coordinated Cd^{II} complexes of teaH₃ (Andac *et al.*, 2001). Among Cd-containing complexes, polynuclear cadmium halides have been found to exhibit interesting photoluminescent properties (Dai *et al.*, 2002) and to form a wide range of coordination complexes with variations promoted not only by the ligand characteristics, but also by the variable coordination number of the Cd^{II} centres. However, the successful incorporation of two types of ligand into such cadmium halides is rare (Liu *et al.*, 2010, 2007). Analogous complexes based on the collaborative use of linear terephthalic acid (bdcH₂) and multi-podal triethanolamine (teaH₃) have not hitherto received any attention. Here, we have chosen the bdcH₂ molecule as a bridging ligand and teaH₃ as a terminal ligand to explore the crystal structure of the novel title coordination polymer, $[\text{Cd}_2(\text{bdc})\text{Cl}_2(\text{teaH}_3)]_n$, (I), with an unusual hydrogen-bonded three-dimensional framework.



Single-crystal X-ray diffraction reveals that two independent Cd^{II} cations and Cl[−] anions, one teaH₃ molecule and one bdc dianion are present in the asymmetric unit of (I). As shown in Figs. 1 and 2, the structure of (I) consists of a one-dimensional chain in which each tetranuclear $\text{Cd}_4\text{Cl}_4\text{O}_2$ cluster is terminated by two chelating teaH₃ molecules but linked to two adjacent clusters through four bridging bdc dianions. The tetranuclear $\text{Cd}_4\text{Cl}_4\text{O}_2$ entity has an inversion centre and is held together *via* bridging Cl and O atoms. The Cd^{II} cations in the tetranuclear $\text{Cd}_4\text{Cl}_4\text{O}_2$ cluster can be of two types. Each Cd1 centre [and its symmetry-related Cd1ⁱⁱ centre; symmetry code: (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$] is seven-coordinate with a distorted pentagonal bipyramidal coordination geometry, surrounded by three O atoms and one N atom from one teaH₃ molecule, two O atoms from one carboxylate group and one μ -Cl[−] ion, while each Cd2 centre (and its symmetry-related


Figure 1

A view of the local coordination environment of the Cd^{II} ions in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.]

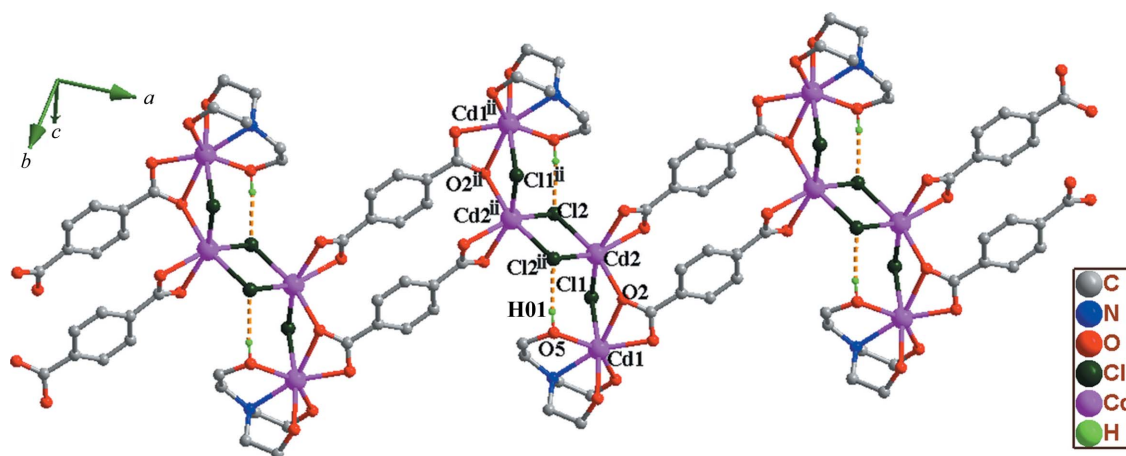
equivalent) is bonded to three O atoms from two bdc dianions and three μ_2 -Cl⁻ anions, displaying a distorted octahedral configuration. In the Cd1 coordination polyhedron, three coordinated atoms of the teaH₃ ligand and two carboxylate O atoms form the equatorial plane (O1/O2/O5/N1/O7) of the Cd1 centre, while hydroxy atom O6 and the Cl1 anion are located in axial positions. For the Cd2 centre, atoms Cl2, Cl2ⁱⁱ and O2 are meridional, as are three other atoms [Cl1, O3ⁱ and O4ⁱ; symmetry code: (i) $-x + 1, -y, -z$].

The Cd–O bond lengths (Table 1) are comparable with those observed for [Cd(bdc)(bpdo)(H₂O)]_n (bpdo is 4,4'-bipyridine *N,N'*-dioxide; Xu & Xie, 2010). It should be noted that the Cd–O2 bond lengths [2.4045 (16) and 2.5792 (16) Å] involved in the μ_2 -O bridging interactions are somewhat longer than the other Cd–O bonds. The Cd–Cl bond lengths (Table 1) range from 2.5343 (8) to 2.6726 (13) Å and are in the normal range for cadmium halide complexes (Zhou *et al.*, 2004). The deviations of the Cl_{ax}–Cd–O_{ax} angles (ax is axial) from linearity (Table 1) indicate that the two Cd^{II} centres have

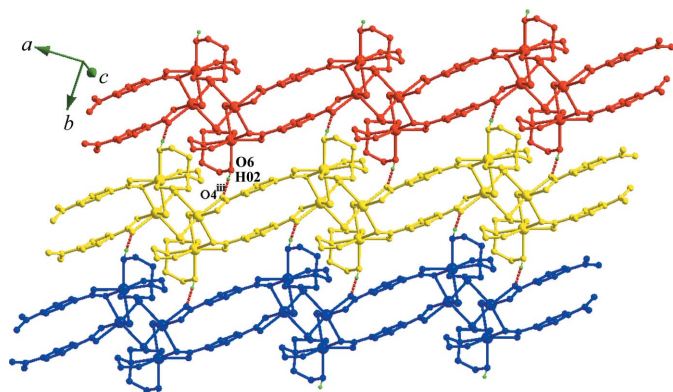
significantly distorted coordination geometries [Cl1–Cd1–O6 = 169.31 (4)° and Cl2–Cd2–O2 = 165.31 (4)°]. The closest Cd···Cd contact of 3.815 (2) Å between the two Cd2 atoms of the Cd₂Cl₂ grouping is much longer than in the metal (2.98 Å; Amirouche & Erkoç, 2005).

The overall binding mode of the bdc ligand in (I) can be assigned as unsymmetrical μ_3 - $\eta^2\eta^1$ connections to three metal centres. One carboxylate end is chelated to one metal centre in a bidentate chelating mode but the other end is coordinated to two Cd^{II} cations in a chelating–bridging manner. Two inversion-related bdc dianions are antiparallel and link adjacent tetranuclear Cd₄Cl₄O₂ clusters into a one-dimensional chain. It is noteworthy that the interplanar distance [3.4740 (9) Å] between parallel benzene rings suggests the presence of a π – π interaction between each pair of bdc ligands, although the ring centroids are quite offset with a distance between them of 4.383 (3) Å. This particular arrangement necessitates a bent conformation of the bdc linkers (mean deviation from the C1–C8 plane = 0.041 Å) and a significant rotation of the two –COO⁻ groups [dihedral angles between the –COO⁻ groups and benzene planes in the bdc ligand = 27.9 (2) and 15.1 (3)°].

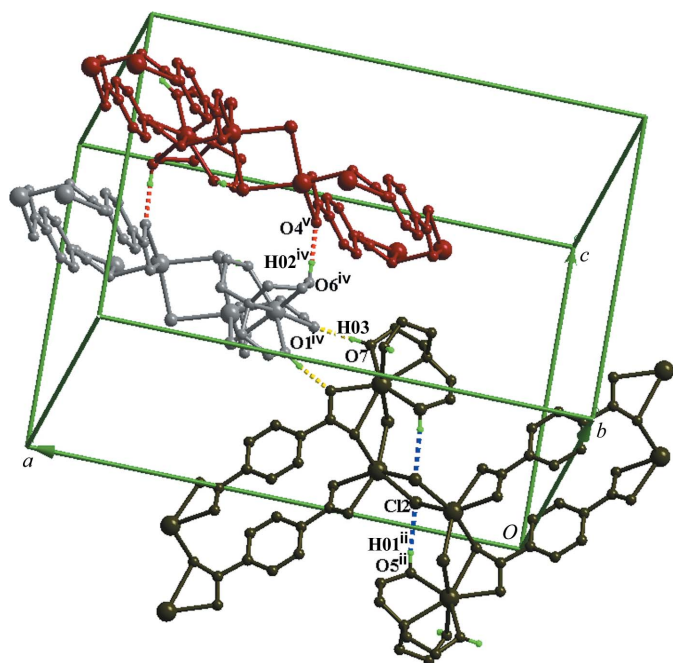
The most interesting structural feature of (I) is the hydrogen-bonding rôle of the three ethanolic arms of teaH₃ in stabilizing the open three-dimensional framework. Although the teaH₃ molecules serve as *N,O,O',O''*-tetradentate neutral ligands in the *endo* conformation, all the hydroxy groups of the teaH₃ ligands are involved in the formation of classical hydrogen bonds. One hydroxy group of the teaH₃ ligand forms a strong intrachain hydrogen bond with an adjacent chloride ligand (O5···Cl2ⁱⁱ; distances and symmetry codes are given in Table 2), which further consolidates the tetranuclear Cd₄Cl₄O₂ cluster (Fig. 2). A second hydrogen bond between one of the outer hydroxy groups and a carboxylate O atom (O6···O4ⁱⁱⁱ) extends the one-dimensional chains into two-dimensional layers (Fig. 3). Finally, the third hydroxy group is engaged in interlayer hydrogen bonding with another carboxylate O atom (O7···O1^{iv}), linking each such layer into an open three-dimensional framework in a crossed manner (Fig. 4). It is interesting that, viewed down the crystallographic *a* axis, the


Figure 2

A view of the one-dimensional chain of (I), showing the strong intrachain O–H···Cl interactions (dashed lines) consolidating the tetranuclear Cd₄Cl₄O₂ clusters. Uninvolved H atoms have been omitted for clarity. [Symmetry code: (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.]

**Figure 3**

The two-dimensional layer of (I) formed by strong interchain O—H...O interactions (dashed lines). Uninvolved H atoms have been omitted for clarity. [Symmetry code: (iii) $-x + 1, -y + 1, -z$.]

**Figure 4**

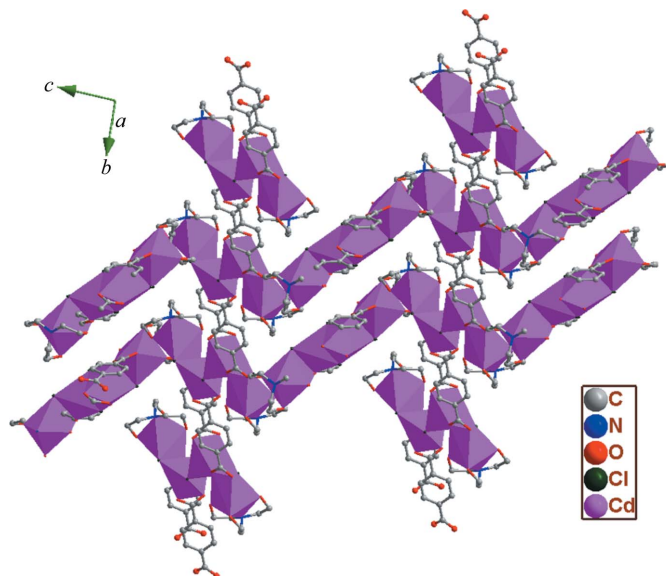
A packing diagram for (I), showing the three-dimensional framework formed *via* strong O—H...O interactions (dashed lines) between crossed layers. (In the electronic version of the paper, three colours are used to show the different hydrogen bonds: blue for intrachain, red for interchain and yellow for interlayer.) Uninvolved H atoms have been omitted for clarity. [Symmetry codes: (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (iv) $-x + 1, y, -z + \frac{1}{2}$; (v) $x, -y + 1, z + \frac{1}{2}$.]

alternate packing of one-dimensional chains displays beautiful sinusoidal ruffles with a period of 38.4 Å ($= 2c$) (Fig. 5).

The crystal structure of (I) thus clearly illustrates the important role of the teaH₃ ligand in directing supramolecular assembly *via* directional hydrogen bonds from its multi-podal hydroxy groups.

Experimental

A mixture of CdCl₂·2.5H₂O (0.0297 g, 0.13 mmol) and bdcH₂ (0.0221 g, 0.13 mmol) in methanol (10 ml) was stirred for 10 min, and then teaH₃ (4 drops) was added to the mixture with further stirring for 20 min. The resulting solution was transferred to a 17 ml Teflon-

**Figure 5**

A packing diagram for (I) showing the arrangement of the coordination polyhedra.

lined stainless steel container and heated at 393 K for 24 h. After cooling to room temperature, yellow block-shaped crystals of (I) were collected in 86.5% yield, based on the initial quantity of CdCl₂·2.5H₂O.

Crystal data

[Cd₂(C₈H₄O₄)Cl₂(C₆H₁₅NO₃)]
M_r = 609.00
 Monoclinic, *C2/c*
a = 23.251 (5) Å
b = 8.907 (5) Å
c = 19.233 (5) Å
 β = 101.221 (5)°

V = 3907 (3) Å³
Z = 8
 Mo *K*α radiation
 μ = 2.49 mm⁻¹
T = 293 K
 0.40 × 0.40 × 0.20 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
*T*_{min} = 0.436, *T*_{max} = 0.636

13547 measured reflections
 4821 independent reflections
 4261 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.047$
S = 1.03
 4821 reflections
 244 parameters
 3 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.31 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.62 \text{ e } \text{Å}^{-3}$

All C-bound H atoms were refined using a riding model, with C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C) for aromatic H atoms, and with C—H = 0.97 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C) for CH₂ groups. The hydroxy H atoms were located in a difference Fourier map and their positions were refined under the application of an O—H bond-length restraint of 0.90 (1) Å, with *U*_{iso}(H) = 1.5*U*_{eq}(O).

Data collection: APEX2 (Bruker, 2005); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics:

Table 1

Selected geometric parameters (Å, °).

N1—Cd1	2.3686 (17)	O7—Cd1	2.3273 (16)
O1—Cd1	2.2691 (15)	Cl1—Cd2	2.5343 (8)
O2—Cd2	2.4045 (16)	Cl1—Cd1	2.6726 (13)
O2—Cd1	2.5792 (16)	Cl2—Cd2 ⁱⁱ	2.5460 (8)
O3—Cd2 ⁱ	2.3657 (17)	Cl2—Cd2	2.6473 (8)
O4—Cd2 ⁱ	2.3237 (18)	Cd2—O4 ⁱ	2.3236 (18)
O5—Cd1	2.3280 (17)	Cd2—O3 ⁱ	2.3657 (17)
O6—Cd1	2.361 (2)	Cd2—Cl2 ⁱⁱ	2.5460 (8)
O1—Cd1—O7	89.14 (6)	O6—Cd1—Cl1	169.31 (4)
O1—Cd1—O5	126.22 (6)	N1—Cd1—Cl1	94.72 (6)
O7—Cd1—O5	144.29 (6)	O2—Cd1—Cl1	74.56 (4)
O1—Cd1—O6	92.44 (6)	O4 ⁱ —Cd2—O3 ⁱ	55.79 (6)
O7—Cd1—O6	87.32 (6)	O4 ⁱ —Cd2—O2	97.68 (6)
O5—Cd1—O6	86.40 (7)	O3 ⁱ —Cd2—O2	97.87 (6)
O1—Cd1—N1	156.62 (6)	O4 ⁱ —Cd2—Cl1	98.75 (4)
O7—Cd1—N1	71.19 (6)	O3 ⁱ —Cd2—Cl1	154.21 (4)
O5—Cd1—N1	73.25 (6)	O2—Cd2—Cl1	80.18 (4)
O6—Cd1—N1	74.61 (6)	O4 ⁱ —Cd2—Cl2 ⁱⁱ	147.67 (4)
O1—Cd1—O2	53.49 (5)	O3 ⁱ —Cd2—Cl2 ⁱⁱ	91.89 (5)
O7—Cd1—O2	135.00 (6)	O2—Cd2—Cl2 ⁱⁱ	85.20 (5)
O5—Cd1—O2	78.70 (6)	Cl1—Cd2—Cl2 ⁱⁱ	113.42 (3)
O6—Cd1—O2	115.06 (5)	O4 ⁱ —Cd2—Cl2	96.27 (5)
N1—Cd1—O2	149.75 (5)	O3 ⁱ —Cd2—Cl2	93.76 (5)
O1—Cd1—Cl1	97.34 (5)	O2—Cd2—Cl2	165.31 (4)
O7—Cd1—Cl1	88.54 (5)	Cl1—Cd2—Cl2	93.18 (2)
O5—Cd1—Cl1	91.24 (5)	Cl2 ⁱⁱ —Cd2—Cl2	85.48 (3)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—HO1 ⁱⁱ ···Cl2 ⁱⁱ	0.89 (1)	2.21 (1)	3.096 (2)	174 (2)
O6—HO2 ⁱⁱⁱ ···O4 ⁱⁱⁱ	0.89 (1)	1.78 (1)	2.666 (2)	178 (3)
O7—HO3 ^{iv} ···O1 ^{iv}	0.89 (1)	1.78 (1)	2.667 (2)	175 (2)

 Symmetry codes: (ii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x + 1, y, -z + \frac{1}{2}$.

SHELXTL-Plus (Sheldrick, 2008); 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: SF3169). Services for accessing these data are described at the back of the journal.

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