

# Poly[[ $\mu$ -1,1'-(butane-1,4-diyl)diimidazole- $\kappa^2$ N:N']( $\mu$ -cyclohexane-1,4-dicarboxylato- $\kappa^4$ O<sup>1</sup>,O<sup>1'</sup>:O<sup>4</sup>,O<sup>4'</sup>)-cadmium(II)] hemihydrate]: a parallel interpenetrating two-dimensional (4,4) network

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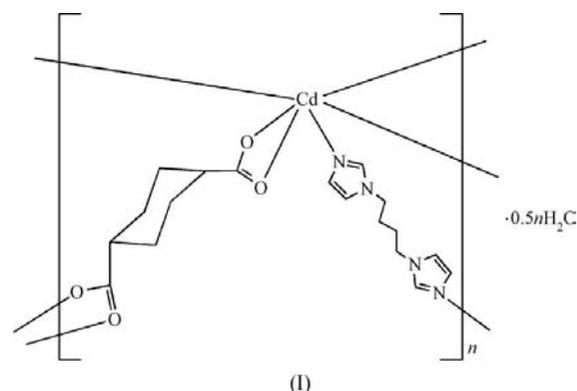
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In the title coordination compound,  $\{[\text{Cd}(\text{C}_8\text{H}_{10}\text{O}_4)(\text{C}_{10}\text{H}_{14}\text{N}_4)]\cdot 0.5\text{H}_2\text{O}\}_n$ , the 1,1'-(butane-1,4-diyl)diimidazole ligand and the cyclohexane-1,4-dicarboxylate dianion both function in a bridging mode to link adjacent cadmium(II) centers into a two-dimensional four-connected (4,4) network. The networks are parallel to the (001) plane. Two (4,4) networks are interpenetrated in an unusual parallel mode. The compound is the first two-dimensional parallel interpenetrating (4,4) network structure based on a flexible dicarboxylate and a long bidentate *N*-donor ligand. The interpenetrating nets are further consolidated by water-carboxylate  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds.

## Comment

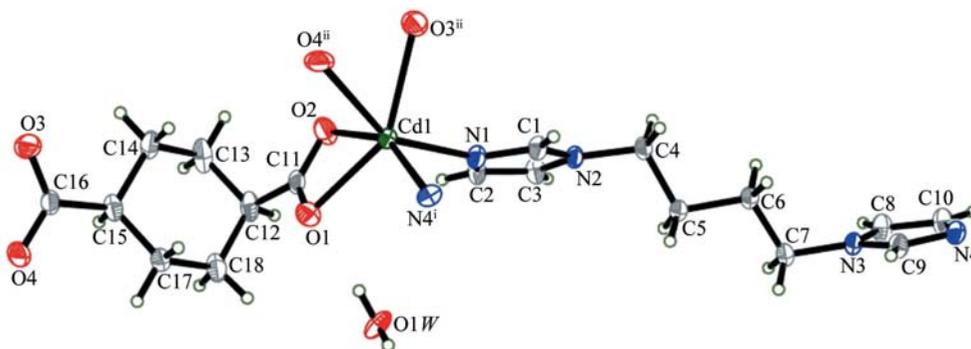
The design and synthesis of coordination polymers with infinite two- and three-dimensional networks have been an area of rapid growth in recent years because of the potential of these polymers in various applications, such as catalysis, electrical conductivity, host-guest chemistry and magnetism (Eddaoudi *et al.*, 2001; Moulton *et al.*, 2003). Generally, the topology of a coordination polymer can often be controlled and modified by taking into account the coordination geometry preferred by the metal ion and the chemical structure of the chosen organic ligand (Carlucci *et al.*, 2003; Hsu *et al.*, 2008). It is well known that long ligands will lead to larger voids that may result in interpenetrated structures (Yang *et al.*, 2008). Therefore, flexible dicarboxylate and long bidentate *N*-donor ligands with these characteristics are excellent candidates for the construction of interpenetrating networks (Batten, 2001). The cyclohexane-1,4-dicarboxylate dianion ( $\text{chdc}^{2-}$ ) is an example of a dianion with a flexible conformation (Yang *et al.*, 2007).  $\text{H}_2\text{chdc}$  has three possible conformations,

namely *a,a-trans*-, *e,e-trans*- and *e,a-cis*- $\text{H}_2\text{chdc}$ . Usually, the *e,e-trans* form is thermodynamically more stable than the *e,a-cis* form because of the presence of two equatorial substituents in the latter, and the *a,a-trans* form is the least stable owing to 1,3-diaxial hindrance. So far, the reported coordination polymers resulting from adduct formation with a rigid bidentate *N*-donor ligand, such as, for example, 2,5-di-pyridyl-1,3,4-oxadiazole, have adopted layer structures, as observed for the copper adduct (Du *et al.*, 2005). On the other hand, flexible bidentate *N*-donor ligands in place of rigid spacers have been known to yield three-dimensional network structures, particularly if the spacer ligands are both flexible and long (Ockwig *et al.*, 2005). In the present study, 1,1'-(butane-1,4-diyl)diimidazole (bis) assembles with cadmium cyclohexane-1,4-dicarboxylate ( $\text{chdc}^{2-}$ ) to furnish a 1:1 adduct,  $[\text{Cd}(\text{cis-chdc})(\text{bis})]\cdot 0.5\text{H}_2\text{O}$ , (I), which exists as an unusual twofold interpenetrating (4,4) network.

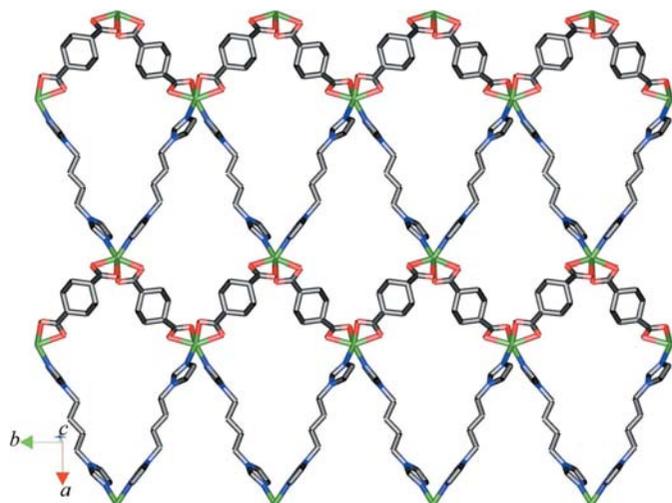


Selected bond lengths and angles for (I) are given in Table 1. As shown in Fig. 1, the asymmetric unit of (I) contains one  $\text{Cd}^{\text{II}}$  atom, one *cis*- $\text{chdc}^{2-}$  anion, one bis ligand and half a free water molecule. Each  $\text{Cd}^{\text{II}}$  atom lies on a center of symmetry and is six-coordinated in a distorted octahedral environment surrounded by four carboxylate O atoms from two different  $\text{chdc}^{2-}$  anions and two N atoms from two distinct bis ligands. The average Cd—O and Cd—N distances in (I) (Table 1) are comparable to those observed for  $[\text{Cd}_4(\text{bpea})_4(1,4\text{-bix})_4]\cdot 4\text{H}_2\text{O}$  [1,4-bix is 1,4-bis(imidazol-1-ylmethyl)benzene and  $\text{H}_2\text{bpea}$  is biphenylethene-4,4'-dicarboxylic acid; Yang *et al.*, 2008]. As depicted in Fig. 2, each  $\text{Cd}^{\text{II}}$  center in (I) is bridged by the  $\text{chdc}^{2-}$  dianions and bis ligands to give a two-dimensional four-connected (4,4) network (Ma, Liu, Liu *et al.*, 2000). The networks are parallel to the (001) plane. Two (4,4) networks are further interpenetrated in an unusual parallel mode (Fig. 3). The driving force for the formation of this unusual topology becomes apparent when the structure of (I) is examined in detail. The  $\text{O}1\text{W}$  molecule, as the donor, forms a hydrogen bond with carboxylate atom  $\text{O}3^{\text{iii}}$  [symmetry code: (iii)  $x + 1, y, z$ ; Table 2]. The water-carboxylate  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds observed in the network consolidate the interpenetrating nets of (I).

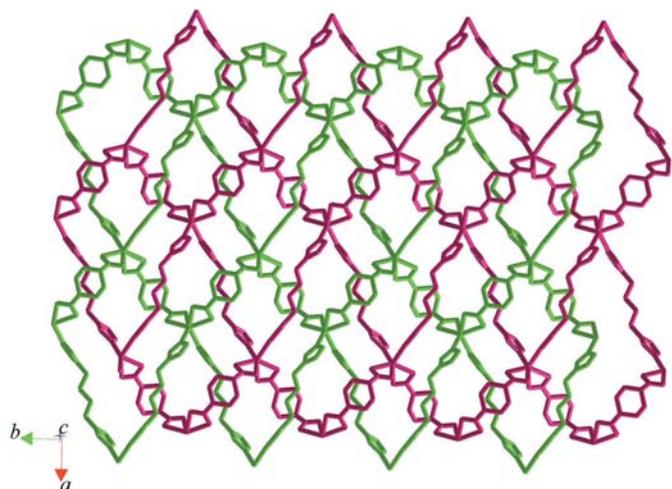
It is noteworthy that the structure of (I) is entirely different from that of the related structure  $[\text{Mn}(\text{BF}_4)_2(\text{bis})]$  (Duncan *et*



**Figure 1**  
A displacement ellipsoid plot of (I) at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i)  $-x + 3, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ .]



**Figure 2**  
A view of the two-dimensional (4,4) network of (I) [the network is parallel to the (001) plane].



**Figure 3**  
A view of the parallel interpenetrating (4,4) networks of (I) [the networks are parallel to the (001) plane].

*al.*, 1996), which is composed of two equivalent mutually interpenetrating three-dimensional networks. The structure of (I) is also entirely different from that of the related polymer

[Zn(SO<sub>4</sub>)(bis)<sub>1.5</sub>(H<sub>2</sub>O)]·6H<sub>2</sub>O (Ma, Liu, Xing *et al.*, 2000), where the networks are interpenetrated in an inclined mode by symmetry-related identical networks to give an interlocked three-dimensional structure.

Over the past decade, interpenetrating structures have received much attention in coordination chemistry and materials chemistry because of their importance in advanced materials (Batten & Robson, 1998). Consequently, many interpenetrating structures have been generated by self-assembly processes. To the best of our knowledge, the reported (4,4) networks interpenetrated in parallel mode are usually constructed by only one type of ligand. Compound (I) is the first two-dimensional parallel interpenetrating (4,4) network structure based on flexible dicarboxylate and long bidentate *N*-donor ligands.

## Experimental

For the synthesis of bis, a mixture of imidazole (3.4 g, 50 mmol) and NaOH (2.0 g, 50 mmol) in dimethyl sulfoxide (10 ml) was stirred at 333 K for 1 h, then 1,4-dichlorobutane (3.2 g, 25 mmol) was added. The mixture was cooled to room temperature after stirring at 333 K for 2 h, then poured into water (200 ml). A white solid formed immediately, which weighed 3.6 g after drying in air. For the synthesis of (I), a mixture of CdCl<sub>2</sub>·2.5H<sub>2</sub>O (0.114 g, 0.5 mmol), H<sub>2</sub>chdc (0.086 g, 0.5 mmol) and bis (0.095, 0.5 mmol) was dissolved in distilled water (12 ml), and then triethylamine was added until the pH value of the system was adjusted to about 5.5. 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 425 K for 3 d under autogenous pressure. The reaction system was subsequently cooled slowly to room temperature. Colorless 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 57%, based on Cd<sup>II</sup>).

## Crystal data

[Cd(C <sub>8</sub> H <sub>10</sub> O <sub>4</sub> )(C <sub>10</sub> H <sub>14</sub> N <sub>4</sub> )]·0.5H <sub>2</sub> O	$V = 2061.8 (15) \text{ \AA}^3$
$M_r = 481.82$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 9.468 (4) \text{ \AA}$	$\mu = 1.09 \text{ mm}^{-1}$
$b = 12.339 (5) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 17.817 (8) \text{ \AA}$	$0.25 \times 0.21 \times 0.18 \text{ mm}$
$\beta = 97.864 (6)^\circ$	

## Data collection

Bruker APEX diffractometer  
Absorption correction: multi-scan  
(SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.755$ ,  $T_{\max} = 0.821$

11154 measured reflections  
3999 independent reflections  
3391 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.026$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$   
 $wR(F^2) = 0.081$   
 $S = 1.04$   
3999 reflections  
259 parameters  
4 restraints

H atoms treated by a mixture of  
independent and constrained  
refinement  
 $\Delta\rho_{\text{max}} = 0.57 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{\AA}^{-3}$

Table 1

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

Cd1—N1	2.265 (2)	Cd1—O2	2.414 (3)
Cd1—N4 <sup>i</sup>	2.272 (3)	Cd1—O4 <sup>ii</sup>	2.325 (3)
Cd1—O1	2.325 (2)	Cd1—O3 <sup>ii</sup>	2.382 (3)
N1—Cd1—N4 <sup>i</sup>	93.72 (10)	O4 <sup>ii</sup> —Cd1—O3 <sup>ii</sup>	54.48 (9)
N1—Cd1—O4 <sup>ii</sup>	149.02 (9)	O1—Cd1—O3 <sup>ii</sup>	147.59 (9)
N4 <sup>i</sup> —Cd1—O4 <sup>ii</sup>	96.15 (11)	N1—Cd1—O2	89.38 (9)
N1—Cd1—O1	107.38 (9)	N4 <sup>i</sup> —Cd1—O2	153.55 (9)
N4 <sup>i</sup> —Cd1—O1	99.10 (9)	O4 <sup>ii</sup> —Cd1—O2	94.55 (12)
O4 <sup>ii</sup> —Cd1—O1	99.95 (9)	O1—Cd1—O2	55.14 (8)
N1—Cd1—O3 <sup>ii</sup>	94.69 (9)	O3 <sup>ii</sup> —Cd1—O2	103.00 (9)
N4 <sup>i</sup> —Cd1—O3 <sup>ii</sup>	102.91 (10)		

Symmetry codes: (i)  $-x + 3, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ .

Table 2

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—HW11 $\cdots$ O3 <sup>iii</sup>	0.838 (10)	1.982 (18)	2.803 (5)	166 (6)
O1W—HW12 $\cdots$ O1	0.837 (8)	2.001 (9)	2.835 (5)	173 (6)

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

C-bound H atoms were positioned geometrically ( $C-H = 0.93$  and  $0.97 \text{ \AA}$ ) and refined as riding, with  $U_{\text{iso}}(\text{H})$  values fixed at  $1.2U_{\text{eq}}(\text{C})$ . The water H atoms were located in a difference Fourier map and were refined with  $O-H$  and  $H\cdots H$  distance restraints of  $0.82$  (3) and  $1.36$  (3)  $\text{\AA}$ , respectively; their displacement parameters were tied to those of the parent atoms by a factor of 1.5. During the refinement,

atom O1W exhibited very large atomic displacement parameters; the occupancy of this atom was fixed at 0.50.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; 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: *publCIF* (Westrip, 2009).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3286). Services for accessing these data are described at the back of the journal.

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