

An unusual polycatenating network self-assembled by the 2D → 2D parallel → 3D parallel interpenetration of coordinative and hydrogen-bonded (6,3) motifs

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In the title coordination compound, *catena*-poly[[[bis[*diaqua*-cadmium(II)- μ_2 -*trans*-1,2-bis(4-pyridyl)ethene]bis[μ_2 -2,2'-[(5-carboxymethoxy-*m*-phenylene)dioxy]diacetate]] *trans*-1,2-bis(4-pyridyl)ethene solvate dihydrate], {[Cd₂(C₁₂H₁₀O₉)₂(C₁₂H₁₀N₂)(H₂O)₄·C₁₂H₁₀N₂·2H₂O]}_n, (I), each Cd^{II} centre adopts a pentagonal-bipyramidal coordination geometry. The incompletely deprotonated 2,2'-[(5-carboxymethoxy-*m*-phenylene)dioxy]diacetate (TCMB) ligands and *trans*-1,2-bis(4-pyridyl)ethene (bpe) ligands both act as bidentate bridges, linking the Cd^{II} centres into one-dimensional ladders, which are connected into an undulating two-dimensional (6,3) layer through O—H...N hydrogen bonds between the carboxylate groups of the TCMB ligands and the N atoms of the uncoordinated bpe ligands. Each undulating layer polycatenates two other identical layers, exhibiting the unusual combination of both 2D → 2D parallel and 2D → 3D parallel interpenetration (2D and 3D are two- and three-dimensional, respectively).

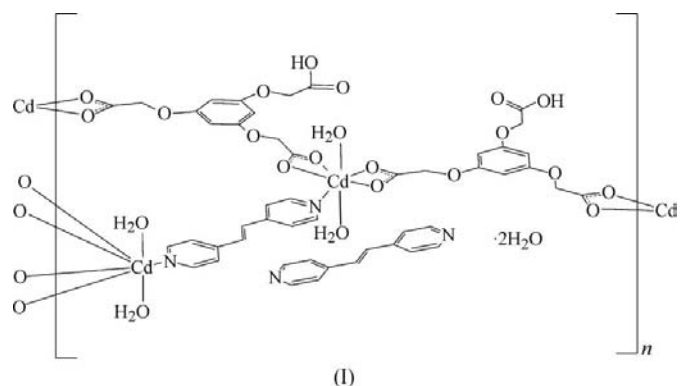
Comment

Recent years have witnessed the rapid development of the construction of metal-organic assemblies, not only for their potential applications but also for their fascinating architectures and topologies (Moulton & Zaworotko, 2001; Kitagawa *et al.*, 2004; Ferey *et al.*, 2005; Murray *et al.*, 2009). Of great interest are interpenetration motifs, which have been classified into more complex types of entanglement involving polycatenation, polythreading and polyknotting, as well as Borromean links, and these have been reviewed by Batten, Robson and Ciani (Batten & Robson, 1998; Batten, 2001; Carlucci *et al.*, 2003). Polycatenation indicates that entanglement of the lower-dimensional polymeric motifs can generate a structure of overall higher dimensionality, such as 1D → 2D,

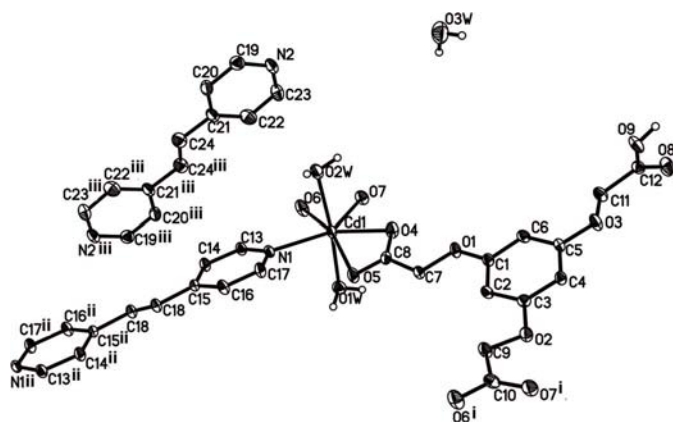
1D → 3D and 2D → 3D (1D, 2D and 3D are one-, two- and three-dimensional, respectively).

An increase in dimensionality from a 2D layer to a 3D entanglement has been observed for systems interpenetrating in a parallel/inclined fashion. Reports of such examples are still relatively rare (Blatov *et al.*, 2004; Baburin *et al.*, 2005; Chen *et al.*, 2006) following the first 2D → 3D parallel interpenetration was reported by Liu & Tilley (1997). It is even unusual to observe 2D → 2D parallel → 3D parallel interpenetration, *i.e.* both 2D → 2D and 2D → 3D parallel interpenetration occurring within the same structure. To the best of our knowledge, there are only a few examples in the literature of organic nets (Bényei *et al.*, 1998) and coordination polymers (Banfi *et al.*, 2004; Guo *et al.*, 2009).

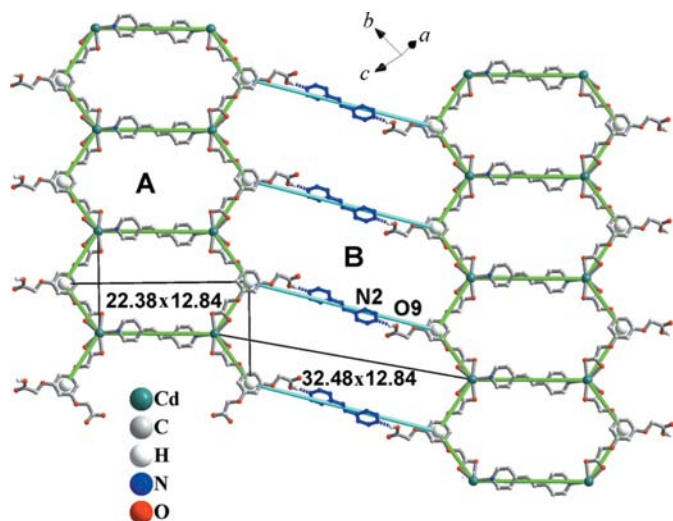
Meanwhile, (6,3) nets, one of the most common topologies in 2D coordination polymers, easily interpenetrate with each other when large six-membered rings are formed or the net shows undulating features. Many layers of this type are interlocked into *n*-fold interpenetrating sheets or polycatenated 2D → 3D systems (Tong *et al.*, 1999; Jung *et al.*, 2002). Very recently, Su and co-workers reported a very rare 3D coordination polymer with 11-fold interpenetration and fivefold catenation, which may represent the highest degree of interpenetration yet observed for the (6,3) net (Yang *et al.*, 2009). We report here the title coordination compound, {[Cd₂(TCMB)₂(bpe)(H₂O)₄·bpe·2H₂O]}_n, (I) {TCMB is 2,2'-[(5-carboxymethoxy-*m*-phenylene)dioxy]diacetate and bpe is *trans*-1,2-bis(4-pyridyl)ethene}, which features an unusual 3D combination of both 2D → 2D parallel and 2D → 3D parallel interpenetration self-assembled from both coordinative and hydrogen-bonded 2D (6,3) layer motifs.



As shown in Fig. 1, the asymmetric unit of complex (I) is composed of one Cd^{II} centre, one TCMB ligand, half a coordinated bpe ligand, two water molecules, half a free bpe ligand and one solvent water molecule. The Cd^{II} centre adopts a pentagonal-bipyramidal coordination geometry, with four carboxylate O atoms from two carboxylate groups of different TCMB ligands and one N atom from the bpe ligand in the equatorial plane, and two water O atoms occupying the axial positions. The TCMB ligand is incompletely deprotonated and adopts a bis(chelating bidentate) mode, linking two Cd^{II} centres. The two coordinated carboxylate groups (C8 and C10) are almost coplanar with the central benzene ring, with small dihedral angles between the individual groups and the


Figure 1

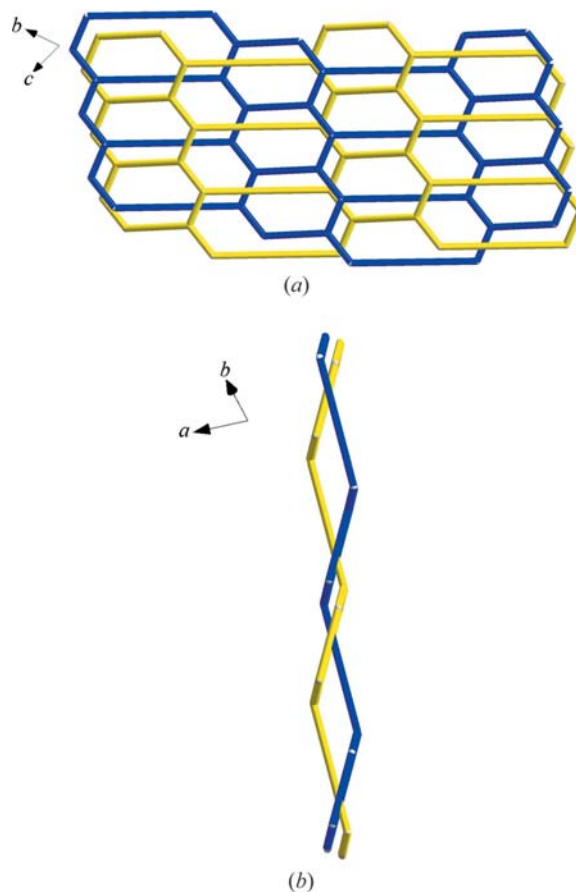
The local coordination environment of the Cd^{II} centre in (I). All H atoms have been omitted for clarity, except for the carboxy H atom and those of the solvent water molecule, and displacement ellipsoids are drawn at the 30% probability level. Selected bond parameters are listed in Table 1. [Symmetry codes: (i) $x, 1 + y, -1 + z$; (ii) $2 - x, -y, -z$; (iii) $2 - x, -y, 1 - z$.]


Figure 2

The two different kinds of hexagon formed within and between the ladders of (I). O—H...O hydrogen bonds are represented by dotted lines. The water ligands and most H atoms have been omitted for clarity and the dimensions of the hexagons are given in Å.

benzene ring of 3.7 (2) and 15.0 (3)°, respectively, while the carboxyl group (C12) forms a large dihedral angle of 76.2 (2)° with the benzene ring.

The Cd^{II} centres of (I) are linked by TCMB ligands and bpe ligands into a ladder structure. These ladders are interlinked through O—H...N hydrogen bonds between the hydroxy groups (O9—H9) of the TCMB ligands and the N2 atoms of the uncoordinated bpe ligands (Fig. 2). As a result, a 2D undulating layer is formed in the *bc* plane. Within this layer, there are two kinds of hexagonal ring, A and B. Ring A is situated within the ladder, with four Cd^{II} ions and the benzene rings of two TCMB ligands located at its vertices, and four carboxylate groups of two TCMB ligands and two coordinated bpe ligands along its edges. Ring B is formed by hydrogen bonds between the free bpe ligands and two adjacent ladders,


Figure 3

(a) Top and (b) side views of the 2D → 2D parallel interpenetration of pairs of (6,3) nets in the structure of (I) (twofold layer).

the vertices being composed of two Cd^{II} ions and four benzene rings from different TCMB ligands. The longest opposite sides are situated with two free bpe ligands connected to the carboxyl groups of the ladders through hydrogen bonds. The large hexagonal meshes have dimensions of 22.38 (1) × 12.84 (2) Å for ring A and 32.48 (2) × 12.84 (2) Å for ring B, based on the opposite metal–metal or *Cg*...*Cg* (*Cg* is the centre of the benzene ring) distances. If the metal centres and benzene rings of the TCMB ligands are considered as nodes and the hydrogen bonds as actual bonds, the whole layer can be regarded as a (6,3) network.

As expected, the large dimensions and corrugated nature of these layers allow them to interpenetrate in an extensive and unusual fashion. Firstly, pairs of layers interpenetrate in a 2D → 2D parallel fashion and their mean planes are parallel and coincident (Fig. 3). It should be noted that for the doubly interpenetrating layers, each ring A in one layer penetrates a ring B in the other: the two layers are translationally equivalent and are generated by a unique interpenetration vector (Carlucci *et al.*, 2002) $T_i = a + 2b$, with a relative displacement distance of 22.10 (2) Å. Secondly, the resulting twofold layers interpenetrate further with neighbouring doubly interpenetrating layers that are parallel but offset, in a 2D → 3D parallel fashion. Thus, each individual sheet interpenetrates two others, one in the same layer, the other from the layer

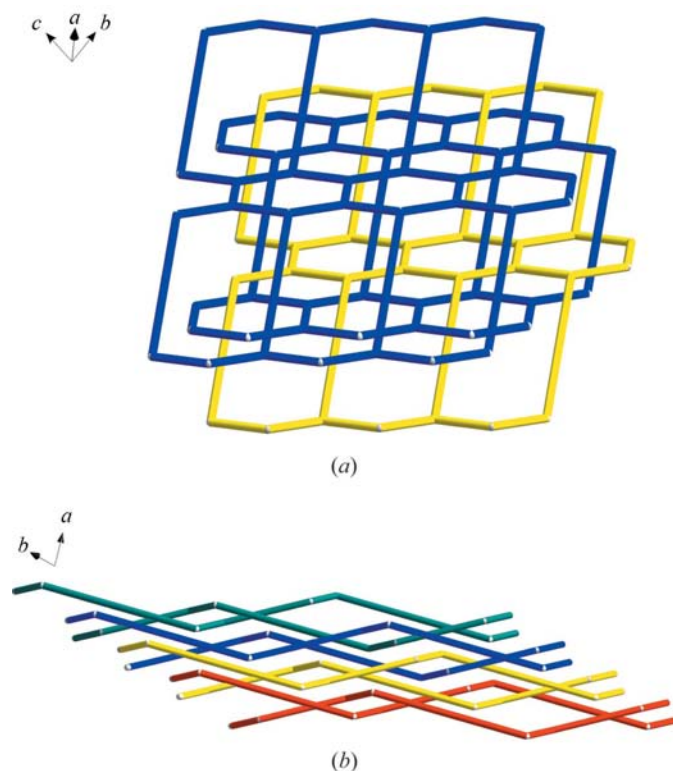


Figure 4
 (a) Top and (b) side views of the 2D \rightarrow 3D parallel interpenetration of adjacent layers of interpenetrating sheets of (I). Different twofold layers are represented in different colours. For clarity, only three adjacent layers are shown in (a).

above or below (Fig. 4). Repeating this interpenetration in a parallel fashion leads to an overall 2D \rightarrow 3D increase in dimensionality. Therefore, the generation of the 3D framework in this complex can be considered to occur through interpenetration of the nets *via* an unusual 2×3 parallel polycatenating mode.

To the best of our knowledge, there are only a few examples of this mode in the field of coordination polymers. The first example, *viz.* [Ag{1,3,5-tris(4-cyanophenoxymethyl)-2,4,6-trimethylbenzene}(CF₃SO₃)₂] \cdot 0.5H₂O, was reported by Banfi *et al.* (2004) and exhibits similar entanglement to complex (I). However, in that compound, the undulating (6,3) layer is interlocked with three others, one on the same average plane plus one of the two layers interpenetrated above and one of the two layers interpenetrated below. In another example, [Zn(MFDA)(bpp)] [H₂MFDA is 9,9-dimethylfluorene-2,7-dicarboxylic acid and bpp is 1,3-bis(4-pyridyl)propane], each individual (4,4) sheet interpenetrates five others, one in the same layer, two from the layer above and two from the layer below (Guo *et al.*, 2009). The particular arrangement of the hexagons in the case of (I) may explain the unusual polycatenation. On the one hand, the undulating (6,3) layer containing two different kinds of large hexagon is unique; in previous examples, both the (6,3) and (4,4) nets have only one kind of polygon. On the other hand, the coordinated water molecules (O1W and O2W) can form O—H \cdots O hydrogen bonds with the carboxylate O atoms between adjacent layers

(Table 2), which may further stabilize the overall packing mode.

Additionally, due to such complex interpenetration, the voids within any single independent 2D network are almost completely occupied. Only small 1D channels running along the *b* axis are observed and these contain the guest water molecules (O3W) *via* hydrogen-bonding interactions with the carboxylate O6 atoms. Calculations using *PLATON* (SOLV routine; Spek, 2009) reveal that these channels occupy 3.4% of the unit-cell volume.

In summary, we have prepared a novel 3D polycatenating motif generated by the 2D \rightarrow 2D parallel \rightarrow 3D parallel interpenetration of coordinative and hydrogen-bonded (6,3) layers. The appropriate choice of ligands may lead to more fascinating structures and may further contribute to understanding assembly processes in coordination chemistry and crystal engineering.

Experimental

A mixture of Cd(OAc)₂ \cdot 2H₂O (0.026 g, 0.1 mmol), TCMB (0.030 g, 0.1 mmol), bpe (0.018 g, 0.1 mmol), ethanol (5 ml) and H₂O (5 ml) was placed in a Teflon reactor and heated at 353 K for 50 h. After cooling to room temperature, colourless crystals of (I) were obtained (yield 42%, based on TCMB). Elemental analysis for C₂₄H₂₆CdN₂O₁₂ (*M_r* = 646.87): C 44.56, H 4.05, N 4.33%; found: 44.20, H 4.63, N 4.05%. FT-IR (KBr pellet, ν , cm⁻¹): 3422 (*s, br*), 2928 (*w*), 1605 (*s*), 1426 (*m*), 1337 (*w*), 1165 (*m*), 1083 (*w*), 843 (*w*).

Crystal data

[Cd ₂ (C ₁₂ H ₁₀ O ₉) ₂ (C ₁₂ H ₁₀ N ₂) \cdot (H ₂ O) ₄] \cdot C ₁₂ H ₁₀ N ₂ \cdot 2H ₂ O	β = 79.777 (2) $^\circ$
<i>M_r</i> = 1293.74	γ = 74.451 (1) $^\circ$
Triclinic, <i>P</i> $\bar{1}$	<i>V</i> = 1241.35 (19) Å ³
<i>a</i> = 10.8627 (9) Å	<i>Z</i> = 1
<i>b</i> = 11.1883 (9) Å	Mo <i>K</i> α radiation
<i>c</i> = 11.3773 (11) Å	μ = 0.95 mm ⁻¹
α = 69.362 (1) $^\circ$	<i>T</i> = 298 K
	0.32 \times 0.28 \times 0.26 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	6314 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 1996)	4315 independent reflections
<i>T_{min}</i> = 0.744, <i>T_{max}</i> = 0.785	3814 reflections with <i>I</i> > 2 σ (<i>I</i>)
	<i>R_{int}</i> = 0.057

Refinement

<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)] = 0.032	2 restraints
<i>wR</i> (<i>F</i> ²) = 0.078	H-atom parameters constrained
<i>S</i> = 1.00	$\Delta\rho_{\max}$ = 0.59 e Å ⁻³
4315 reflections	$\Delta\rho_{\min}$ = -0.60 e Å ⁻³
353 parameters	

The H atom on O9 was located from a circular difference Fourier synthesis and thereafter refined as part of a rigid rotating group, with O—H = 0.82 Å and *U_{iso}*(H) = 1.5*U_{eq}*(O). In addition, the H atoms of the water ligands and solvent water molecule were also determined from a circular difference Fourier synthesis and thereafter treated as riding on their parent atoms, with O—H = 0.85 Å and *U_{iso}*(H) = 1.2*U_{eq}*(O). All other H atoms were placed geometrically and treated as riding on their parent atoms, with C—H = 0.93 (aromatic) or 0.97 (methylene) Å, and with *U_{iso}*(H) = 1.2*U_{eq}*(C).

Table 1

Selected geometric parameters (Å, °).

Cd1—N1	2.338 (2)	Cd1—O7	2.415 (2)
Cd1—O4	2.315 (2)	Cd1—O1W	2.322 (2)
Cd1—O5	2.535 (2)	Cd1—O2W	2.293 (2)
Cd1—O6	2.482 (2)		
O2W—Cd1—O4	89.90 (9)	N1—Cd1—O6	86.53 (8)
O2W—Cd1—O1W	170.89 (8)	O7—Cd1—O6	53.33 (8)
O4—Cd1—O1W	98.45 (9)	O4—Cd1—O5	53.75 (7)
O4—Cd1—O7	85.92 (8)	N1—Cd1—O5	83.14 (8)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O9—H9...N2 ⁱ	0.82	1.81	2.619 (4)	169
O1W—H1WB...O9 ⁱⁱ	0.85	1.93	2.763 (3)	167
O1W—H1WC...O5 ⁱⁱⁱ	0.85	1.97	2.815 (3)	172
O2W—H2WB...O8 ^{iv}	0.85	2.05	2.763 (4)	141
O2W—H2WC...O7 ^v	0.85	1.96	2.799 (3)	170
O3W—H3WC...O6 ^{vi}	0.85	2.02	2.862 (4)	174
O3W—H3WD...O6 ^v	0.85	2.36	3.207 (4)	174

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM3089). Services for accessing these data are described at the back of the journal.

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