

A three-dimensional pyrazine-2,5-dicarboxylate Cd^{II} coordination framework with new (4,4,4)-connected three-nodal topology

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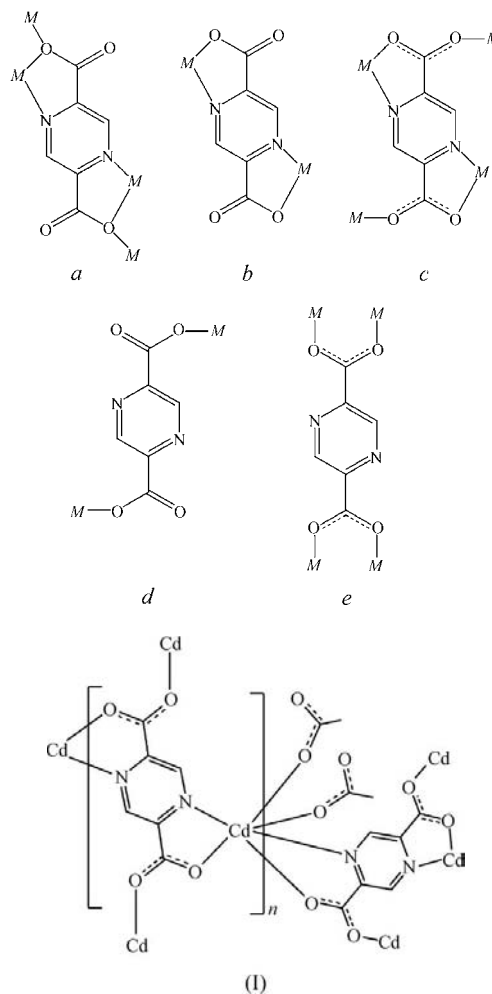
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Poly[(μ_4 -pyrazine-2,5-dicarboxylato)cadmium(II)], [Cd(C₆H₂N₂O₄)_n] or [Cd(pzdc)]_n (pzdc is the pyrazine-2,5-dicarboxylate dianion), has been synthesized hydrothermally. The asymmetric unit consists of a Cd^{II} atom and two independent halves of pzdc ligands that can be expanded *via* inversion through the centres of the ligands so that each ligand binds to four Cd^{II} atoms with the same binding mode using six donor atoms. The Cd^{II} centre is in a distorted octahedral coordination geometry with four O- and two N-atom donors from four pzdc ligands. The infinite linkage of the metal atoms and ligands forms a three-dimensional framework with a rectangular channel which is so narrow that there is no measurable void space in the overall structure. This coordination polymer represents the first example of (4,4,4)-connected three-nodal framework.

Comment

There has been significant growth in recent years in the field of metal-organic frameworks (MOFs), because of their intriguing structural diversity and wide range of potential applications as functional materials (Tranchemontagne *et al.*, 2008; Banerjee *et al.*, 2008; Zhang & Kitagawa, 2008; Zheng *et al.*, 2008). Bridging ligands are essential in constructing MOFs. Among the many kinds of bridging ligands, N-heterocyclic multicarboxylic acids have been used frequently (Evans & Lin, 2002; Blake *et al.*, 1999; Moulton & Zaworotko, 2001). These ligands combine the advantages of both carboxyl and aromatic N-heterocyclic components and are able to connect various metal ions *via* a variety of coordination modes. The dianionic pyrazine-2,5-dicarboxylate (pzdc) ligand, derived from deprotonation of pyrazine-2,5-dicarboxylic acid, displays five bridging modes, *a–e* (see scheme), in its coordination polymers with some metal ions, including the alkaline earth metal Sr^{II} (Ptasiewicz-Bak & Leciejewicz, 1998), the transition metals Mn^{II} (Xu *et al.*, 2003; Beobide *et al.*, 2003, 2006), Fe^{II}, Zn^{II} and Cu^{II} (Beobide *et al.*, 2006), and the rare earth metals

La^{III} (Zheng & Jin, 2005), Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III} and Gd^{III} (Yang *et al.*, 2008). The metal centres have a large impact on the crystal structure, including the binding modes of the ligand and the molecular packing. For example, in {[Ln(pzdc)_{1.5}(H₂O)₃·0.5H₂O]_n} (Ln = Pr, Nd, Sm, Eu or Gd), we found that pzdc binding modes *b*, *c* and *d* exist simultaneously and there is an ultramicroporous channel (Yang *et al.*, 2008), while in [La(pzdc)_{1.5}(H₂O)]_n, binding modes *c* and *e* are observed and there is no channel (Zheng & Jin, 2005). The second-row transition metal Cd^{II} has been used to construct coordination polymers with some other pyrazinecarboxylates, such as pyrazine-2-carboxylate (Ciurtin *et al.*, 2002, 2003*a,b*), pyrazine-2,3-dicarboxylate (Yin & Liu, 2007; Mao *et al.*, 1996; Maji *et al.*, 2004, 2005; Ma *et al.*, 2006; Liu *et al.*, 2007) and pyrazine-2,3,5,6-tetracarboxylate (Wang *et al.*, 2007; Ghosh & Bharadwaj, 2006), and exhibits ligand-dependent coordination numbers of 6, 7 and 8 (Wang *et al.*, 2007). However, there has been no report to date on the bonding between Cd^{II} and pyrazine-2,5-dicarboxylate. We report here the preparation of the title compound, [Cd(pzdc)]_n, (I), and its crystal structure.



Complex (I) was obtained by the hydrothermal method. In a hydrothermal reaction, water molecules are easily introduced into the crystal structure as a binding ligand or lattice component. However, (I) has no water in the crystal structure. Double deprotonation of pyrazine-2,5-dicarboxylic acid was

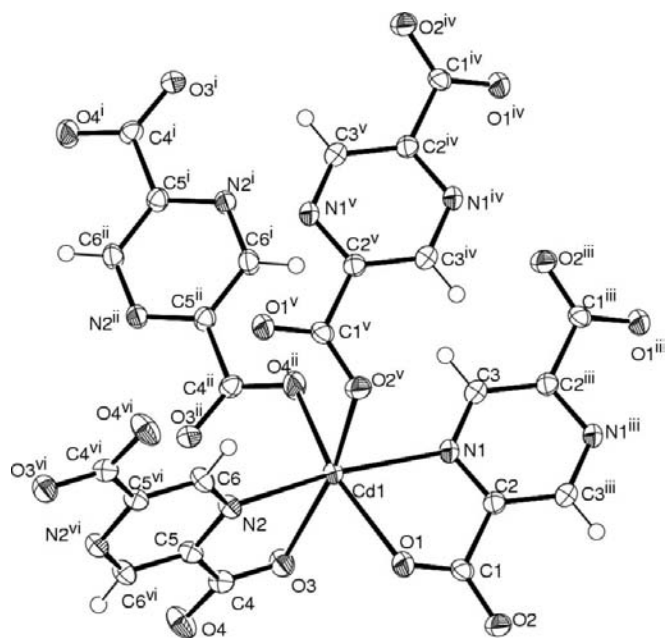


Figure 1

The coordination environment of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $x, -\frac{1}{2} - y, -\frac{1}{2} + z$; (ii) $2 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (iii) $1 - x, 1 - y, -z$; (iv) $1 - x, -y, -z$; (v) $x, -1 + y, z$; (vi) $2 - x, -y, 1 - z$.]

accomplished without adding bases such as sodium hydroxide, as occasionally applied (Xu *et al.*, 2003; Zheng & Jin, 2005).

Selected bond lengths and angles for (I) are given in Table 1. The Cd—O and Cd—N distances fall into the common ranges. The asymmetric unit of (I) consists of one Cd^{II} atom and two independent halves of pzdc ligands. Each pzdc ligand sits about an inversion centre. Expansion of the structure through the symmetry elements of the space group $P2_1/c$ generates four pzdc ligands bound to each Cd^{II} centre. The coordination environment around the Cd^{II} centre is shown in Fig. 1. The Cd^{II} atom resides in a distorted octahedral environment surrounded by four carboxylate O atoms and two pyrazine N atoms from four different pzdc ligands. Two *cis*-related ligands coordinate to the Cd^{II} atom through a single carboxylate O atom, while the other two ligands have bidentate coordination to the Cd^{II} atom through adjacent (N and O) sites. It is noteworthy that atom O3 is 3.225 (2) Å from the same Cd atom to which atom O4 is bonded. This is only slightly longer than the sum of the van der Waals radii (3.10 Å), so atom O3 has some bridging function between two Cd^{II} atoms.

The angle between the N2/C4/C5/C6 and C4/C5/O3/O4 least-squares planes is 2.2 (3)°, implying that the N2-containing ligand is almost planar, as would be expected. In contrast, the corresponding dihedral angle for the N1-containing ligand (between the N1/C1/C2/C3 and C1/C2/O1/O2 planes) is 23.0 (3)°, almost an order of magnitude larger. This large angle leads to the somewhat long C1—C2 distance [1.530 (4) Å] and a puckered five-membered chelate ring (atoms N1, C2, C1, O1 and Cd1). The dihedral angle between the two least-squares planes through the N1- and N2-containing ligands is 68.92 (13)°.

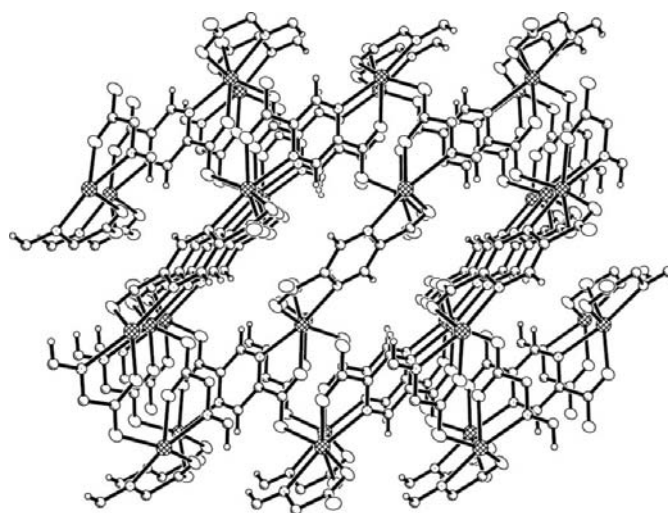


Figure 2

A perspective view of the packing of (I) down the *b* axis, showing the narrow rectangular channel.

The pzdc ligands in (I) display only one type of hexadentate binding mode (mode *c* as defined in the first scheme) and bind four symmetry-related Cd^{II} atoms. This binding mode makes each pzdc a four-connected linker. Along the $[1\bar{1}1]$ and $[111]$ directions the Cd atoms are connected by N atoms *via* the pyrazine rings. The other two directions, *viz.* $[010]$ and $[110]$, are dominated by CdOCOCd... chains bridged *via* a single carboxylate group, *viz.* O1/C1/O2 or O3/C4/O4, respectively, from different pzdc ligands. This expansion of the coordination environment leads to a three-dimensional network. In the $[010]$ direction, a rectangular channel seems to exist, as illustrated in Fig. 2. However, the width of the 'channel' is so narrow (around 2.2 Å) that the space-filling model of the crystal structure implies that the atoms around it compact quite closely and there are no significant voids, as confirmed by PLATON (Spek, 2003). This could be the reason that there are no solvent molecules inside the framework.

Topological analysis of the coordination net reveals that (I) is a three-nodal net with one four-connected Cd node and two distinct four-connected ligand nodes, as shown in Fig. 3. The Schläfli symbol is $\{4^1 6^3 8^2\}_2 \{4^2 6^2 8^2\} \{6^2 8^4\}$, which has not been

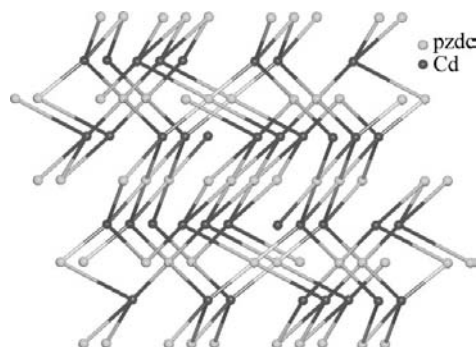


Figure 3

A topological representation of the coordination framework of (I).

reported previously and which therefore represents a new topological type (Blatov, 2006).

Experimental

Colourless plate-shaped crystals of (I) were synthesized hydrothermally in a 23 ml Teflon-lined autoclave by heating a mixture of pzdcH_2 (0.5 mmol) and CdCl_2 (0.5 mmol) in water (10 ml) at 413 K for 3 d.

Crystal data

$[\text{Cd}(\text{C}_6\text{H}_2\text{N}_2\text{O}_4)]$	$V = 674.80 (6) \text{ \AA}^3$
$M_r = 278.50$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.4704 (5) \text{ \AA}$	$\mu = 3.21 \text{ mm}^{-1}$
$b = 5.4606 (3) \text{ \AA}$	$T = 298 (2) \text{ K}$
$c = 12.2847 (6) \text{ \AA}$	$0.20 \times 0.15 \times 0.05 \text{ mm}$
$\beta = 106.107 (3)^\circ$	

Data collection

Bruker APEXII CCD area-detector diffractometer	8845 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2002)	1595 independent reflections
$T_{\min} = 0.566$, $T_{\max} = 0.856$	1369 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	118 parameters
$wR(F^2) = 0.054$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$
1595 reflections	$\Delta\rho_{\text{min}} = -0.54 \text{ e \AA}^{-3}$

All H atoms were located in a difference map and then treated as riding in geometrically idealized positions, with $\text{C-H} = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: APEX2 (Bruker, 2004); cell refinement: APEX2; data reduction: APEX2; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 (Farrugia, 1999); software used to prepare material for publication: PLATON (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3119). Services for accessing these data are described at the back of the journal.

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Table 1

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

Cd1-O4^i	2.249 (2)	Cd1-O3	2.311 (2)
Cd1-O1	2.277 (2)	Cd1-N2	2.334 (2)
Cd1-O2^{ii}	2.310 (2)	Cd1-N1	2.371 (2)
$\text{O4}^i\text{-Cd1-O1}$	157.16 (8)	$\text{O2}^{ii}\text{-Cd1-N2}$	92.41 (8)
$\text{O4}^i\text{-Cd1-O2}^{ii}$	87.17 (8)	O3-Cd1-N2	71.96 (8)
O1-Cd1-O2^{ii}	102.59 (8)	$\text{O4}^i\text{-Cd1-N1}$	88.81 (8)
$\text{O4}^i\text{-Cd1-O3}$	96.02 (8)	O1-Cd1-N1	71.79 (8)
O1-Cd1-O3	80.17 (8)	$\text{O2}^{ii}\text{-Cd1-N1}$	85.08 (8)
$\text{O2}^{ii}\text{-Cd1-O3}$	164.36 (7)	O3-Cd1-N1	110.24 (8)
$\text{O4}^i\text{-Cd1-N2}$	101.78 (8)	N2-Cd1-N1	169.00 (8)
O1-Cd1-N2	98.42 (8)		

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

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