

A new two-dimensional Cd^{II} coordination polymer constructed by pyrazine-2,3-dicarboxylate

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In the title compound, poly[μ_5 -pyrazine-2,3-dicarboxylato-cadmium(II)], [Cd(C₆H₂N₂O₄)_n or [Cd(pdc)]_n, where pdc is the pyrazine-2,3-dicarboxylate anion, the Cd^{II} atom is six-coordinated by five carboxylate O atoms and one N atom from five different pdc ligands in a distorted octahedral CdO₅N coordination geometry. Two Cd^{II} atoms are bridged by carboxylate groups of the pdc ligands to create a dimeric unit. The dimeric units are further connected by the pdc ligands to generate an interesting two-dimensional structure.

Comment

The field of metal-organic coordination polymers has undergone significant growth over the past decade, not only because of their intriguing structural diversity but also because of their tremendous potential applications as functional materials (Eddaoudi *et al.*, 2001; Shi *et al.*, 2004; Fang *et al.*, 2005; Fang, Zhu, Jin *et al.*, 2006). So far, most effort in this field has been focused on using either neutral ligands (*e.g.* 4,4'-bipyridine) or anionic ligands (*e.g.* carboxylates) (Tian *et al.*, 2006). However, in recent years, multifunctional ligands bearing both neutral

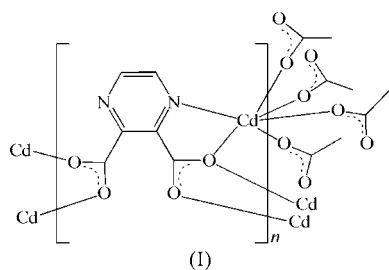
dimensional coordination polymer, [Cd(pdc)]_n, (I), composed of Cd²⁺ and pyrazine-2,3-dicarboxylate (pdc) with N- and O-donor atoms.

Selected bond lengths and angles for (I) are given in Table 1. Each Cd^{II} centre is hexacoordinated, residing in a distorted octahedral environment surrounded by five carboxylate O atoms and one N atom from five distinct pdc ligands (Fig. 1). Atoms N1, O1, O1ⁱ and O3ⁱⁱⁱ comprise the basal plane, while atoms O2ⁱⁱ and O4^{iv} occupy the axial positions (see Table 1 for symmetry codes). The axial O2ⁱⁱ—Cd1—O4^{iv} angle is 173.55 (7)° in the resulting polyhedron, indicating a slight octahedral distortion (Table 1). The coordination environment of the Cd^{II} centre in (I) is similar to those observed in the related three-dimensional pillared-layer coordination polymers {[Cd(pdc)(azpy)]·2H₂O}_n and {[Cd(pdc)(bpee)]·1.5H₂O}_n {azpy is 1,2-dipyridin-4-yl diazene and bpee is 4-[2-(pyridin-4-yl)-vinyl]pyridine} (Maji *et al.*, 2004). The Cd—O distances range from 2.224 (2) to 2.486 (2) Å, which are near to the values found in our previously reported three-dimensional coordination polymer [Cd₁₁(HCOO)₆(bpdc)₉]·9DMF·6H₂O (bpdc is 4,4'-biphenyldicarboxylate and DMF is *N,N*-dimethylformamide) (Fang, Zhu, Xue *et al.*, 2006).

An interesting aspect of the structure of (I) is that each pdc ligand bonds to five Cd^{II} centres. The number of coordination sites of the pdc unit of (I) is much higher than in other metal-pdc complexes (Li *et al.*, 2004; Tian *et al.*, 2003; Kitaura *et al.*, 2002). Notably, one pyrazine N atom coordinates to the Cd^{II} centre, while the remaining N atom does not associate with the Cd^{II} atom. This observation may be attributed to the steric hindrance of the pdc ligand, which reduces the coordination abilities of the N atoms.

The two Cd^{II} atoms are bridged by pdc ligands through their carboxylate groups to form a dimeric unit with a bond distance of 3.899 (4) Å. Such a Cd...Cd distance bridged by carboxylate groups has also been observed in another Cd^{II} complex formed with carboxylate ligands (Zang *et al.*, 2006). As a result, the dimers are further connected by pdc ligands to furnish an extended neutral two-dimensional layer.

Within this layer, each pyrazine ring is orientated in the same way and the dihedral angle between the pyrazine rings is



and anionic donor groups have attracted much attention because of their interesting structural features (Ghosh & Bharadwaj, 2006). The presence of different functional groups may allow diversity in the mode of coordination and may result in the interesting properties for the coordination polymers. Based on this consideration, we prepared the title two-

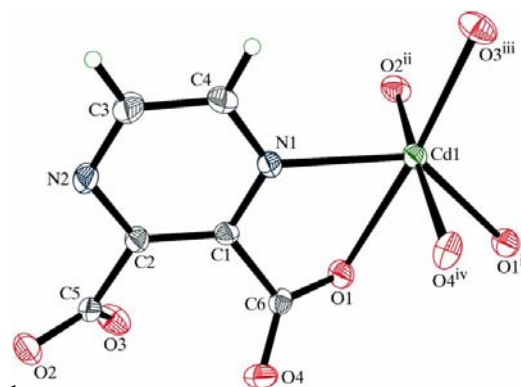


Figure 1
The structure of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (ii) $x, \frac{3}{2} - y, 1 - z$; (iii) $x, 1 + y, z$; (iv) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.]

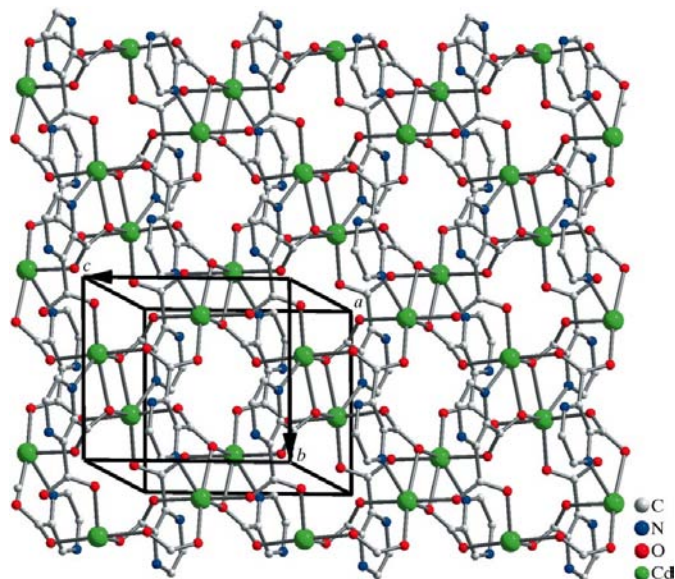


Figure 2
A view of the two-dimensional structure of (I). All H atoms have been omitted for clarity.

about 7.7°, owing to steric effects in the formation of the Cd^{II} coordination polymer. Such an arrangement of adjacent pyrazine rings has not been observed to date in metal complexes constructed by the pdc ligand (Li *et al.*, 2004; Tian *et al.*, 2003; Kitaura *et al.*, 2002). The carboxylate bond lengths C6—O1 and C6—O4 are different, suggesting localization of bonding in the carboxylate groups. It should be pointed out that compound (I) has the same Cd^{II}–pdc ratio (1:1) as both $[\text{Cd}(\text{pdc})(\text{azpy})] \cdot 2\text{H}_2\text{O}$ and $[\text{Cd}(\text{pdc})(\text{bpee})] \cdot 1.5\text{H}_2\text{O}$, prepared by solution methods at room temperature (Maji *et al.*, 2004), but without water content. This agrees with the fact that the hydrothermal reaction can create more condensed products with little or no water content (Zhu *et al.*, 2006). Therefore, there are no hydrogen-bonding interactions in the structure of (I).

Experimental

Colourless needle-shaped crystals of compound (I) were synthesized hydrothermally in a 23 ml Teflon-lined autoclave by heating a mixture of 2,3-H₂pdc (0.1 mmol) and Cd(NO₃)₂·2H₂O (0.1 mmol) in water (12 ml) at 413 K for 2 d (55% yield based on Cd).

Crystal data

$[\text{Cd}(\text{C}_6\text{H}_8\text{N}_2\text{O}_4)]$	$V = 675.7 (7) \text{ \AA}^3$
$M_r = 278.50$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 10.728 (6) \text{ \AA}$	$\mu = 3.21 \text{ mm}^{-1}$
$b = 7.731 (5) \text{ \AA}$	$T = 292 (2) \text{ K}$
$c = 8.674 (5) \text{ \AA}$	$0.31 \times 0.27 \times 0.24 \text{ mm}$
$\beta = 110.068 (5)^\circ$	

Data collection

Bruker APEX CCD area-detector diffractometer	3843 measured reflections
Absorption correction: multi-scan (SAINT; Bruker, 1998)	1568 independent reflections
$T_{\text{min}} = 0.355, T_{\text{max}} = 0.468$	1494 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.023$	119 parameters
$wR(F^2) = 0.054$	H-atom parameters constrained
$S = 1.15$	$\Delta\rho_{\text{max}} = 0.67 \text{ e \AA}^{-3}$
1568 reflections	$\Delta\rho_{\text{min}} = -0.90 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cd1—N1	2.342 (2)	Cd1—O2 ⁱⁱ	2.275 (2)
Cd1—O1	2.486 (2)	Cd1—O3 ⁱⁱⁱ	2.224 (2)
Cd1—O1 ⁱ	2.272 (2)	Cd1—O4 ^{iv}	2.332 (2)
O3 ⁱⁱⁱ —Cd1—O1 ⁱ	112.34 (7)	O2 ⁱⁱ —Cd1—N1	100.86 (7)
O3 ⁱⁱⁱ —Cd1—O2 ⁱⁱ	81.08 (6)	O4 ^{iv} —Cd1—N1	83.38 (7)
O1 ⁱ —Cd1—O2 ⁱⁱ	92.19 (8)	O3 ⁱⁱⁱ —Cd1—O1	170.69 (7)
O3 ⁱⁱⁱ —Cd1—O4 ^{iv}	102.10 (7)	O1 ⁱ —Cd1—O1	70.02 (7)
O1 ⁱ —Cd1—O4 ^{iv}	81.42 (8)	O2 ⁱⁱ —Cd1—O1	89.89 (6)
O2 ⁱⁱ —Cd1—O4 ^{iv}	173.55 (7)	O4 ^{iv} —Cd1—O1	87.11 (7)
O3 ⁱⁱⁱ —Cd1—N1	110.51 (8)	N1—Cd1—O1	68.82 (7)
O1 ⁱ —Cd1—N1	136.61 (7)		

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

All H atoms were positioned geometrically, with C—H = 0.93 Å, and refined as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1998); 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: AV3069). Services for accessing these data are described at the back of the journal.

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