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Poly[[tetraaquabis(μ_2-2-nitroterephthalato-κ^3O^1:O^4,$O^{4'}$)(μ_2-piperazine-κ^3N:N')dicadmium(II)] dihydrate]

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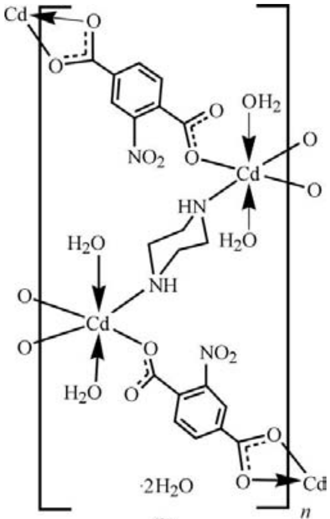
In the title complex, $\{[Cd_2(C_8H_3NO_6)_2(C_4H_{10}N_2)(H_2O)_4]\cdot 2H_2O\}_n$, the Cd^{II} atoms show distorted octahedral coordination. The two carboxylate groups of the dianionic 2-nitroterephthalate ligand adopt monodentate and 1,2-bridging modes. The piperazine molecule is in a chair conformation and lies on a crystallographic inversion centre. The Cd^{II} atoms are connected *via* three O atoms from two carboxylate groups and two N atoms from piperazine molecules to form a two-dimensional macro-ring layer structure. These layers are further aggregated to form a three-dimensional structure *via* rich intra- and interlayer hydrogen-bonding networks. This study illustrates that, by using the labile Cd^{II} salt and a combination of 2-nitroterephthalate and piperazine as ligands, it is possible to generate interesting metal–organic frameworks with rich intra- and interlayer O—H$\cdots$O hydrogen-bonding networks.

Comment

An important objective in crystal engineering is the control and manipulation of either coordination bonds or weak intermolecular interactions in order to tune the properties of metal–organic frameworks (Guilera & Steed, 1999; Burrows *et al.*, 2000; Guo *et al.*, 2008). Such studies depend on the coordination habits and geometric preferences of both metal ions and bridging ligands, as well as on the influence of hydrogen bonding, van der Waals interactions, *etc.* (Baca *et al.*, 2003). The vast majority of current work centres around the controlled assembly of donor and acceptor building blocks. Amongst the more labile metal ions are Cu$^+$, Cu^{2+}, Ag$^+$, Cd^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} (James, 2003). The terephthalate dianion has often been used as a bridging ligand in such a self-assembly approach, *e.g.* in poly[[[μ_2-1,3-bis(1*H*-benzimidazol-2-yl)benzene-κ^2N^3:$N^{3'}$](μ_2-terephthalato-κ^2O:O')zinc(II)] ethanol solvate] (Meng *et al.*, 2007), *catena*-poly[[diaqua-pyridinecadmium(II)]-μ-terephthalato] (Ni *et al.*, 2006), poly[aqua(μ_2-1,4-benzenedicarboxylato)dipyridinecopper(II) 0.25-hydrate] (Wang *et al.*, 2007), *catena*-poly[[bis(1*H*-benzimidazole-κN^3)cobalt(II)]-μ-terephthalato-κ^3O^1,$O^{1'}$:O^4] (Pan *et al.*, 2005), $[Ni(bdc)(2,2'\text{-bipyridine})(H_2O)_2]_n$ (bdc = benzene-1,4-dicarboxylate) (Go *et al.*, 2004), and so on. However, in spite of this wealth of possibilities, only a few complexes of metal–nitroterephthalate systems have been reported to date. We have used reactions of divalent metal cations with 2-nitroterephthalate dianions in the expectation of generating some interesting metal–organic frameworks. We have recently reported the crystal structure of *catena*-poly[[[triaqua-zinc(II)]-μ-2-nitroterephthalato-$\kappa O^{1'}$:κ^2O^4,$O^{4'}$] monohydrate] (Guo & Guo, 2007), and further, using piperazine as second ligand, have obtained the novel title six-coordinated 2-nitroterephthalate–Cd complex, (I). We describe here the structure of this two-dimensional macro-ring metal–nitroterephthalate coordination polymer, with rich intra- and interlayer O—H$\cdots$O hydrogen-bonding networks.



(I)

The asymmetric unit in the structure of (I) comprises one Cd atom, half of a piperazine molecule, one complete 2-nitroterephthalate dianion and three non-equivalent water molecules, and is shown in Fig. 1 in a symmetry-expanded view which displays the full coordination of the Cd atom. Selected geometric parameters are given in Table 1.

The Cd atom in (I) is surrounded by an O$_5$N donor set in octahedral geometry. The four equatorial sites are occupied by one N atom of piperazine and three O atoms from a monodentate (O1) and a bidentate carboxylate group [O3^i and O4^i; symmetry code: (i) $-x + 2$, $y - \frac{1}{2}$, $-z + \frac{1}{2}$]. Atoms O7 and O8 from two coordinated water molecules occupy the opposing apices of the octahedron. The Cd—O/N distances are in the range 2.190 (5)–2.409 (5) Å and are shorter than the corresponding distances in *catena*-poly[[diaquabis(2-methoxymethyl-1*H*-benzimidazole-κN^3)cadmium(II)]-μ-terephthalato-κ^2O:O'] (Zu *et al.*, 2007) and *catena*-poly[[diaqua-pyridinecadmium(II)]-μ-terephthalato] (Ni *et al.*, 2006). The *cis* O—Cd1—O/N angles range from 54.87 (17) to 107.0 (2)°, while the *trans* O—Cd—O/N angles span the range 153.37 (19)–172.1 (2)°. Thus, the coordination octahedron around the Cd atom is significantly distorted.

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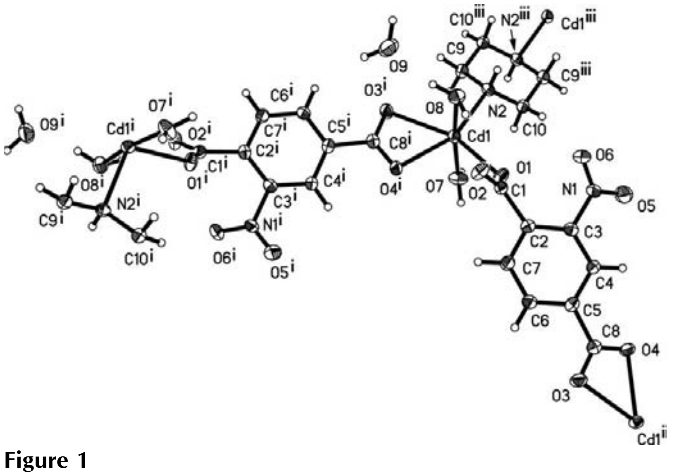

Figure 1
A view of the structure of (I), showing the atom-numbering scheme and the coordination polyhedra for the Cd atoms. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x + 2, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + 2, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x + 1, -y, -z - 1$.]

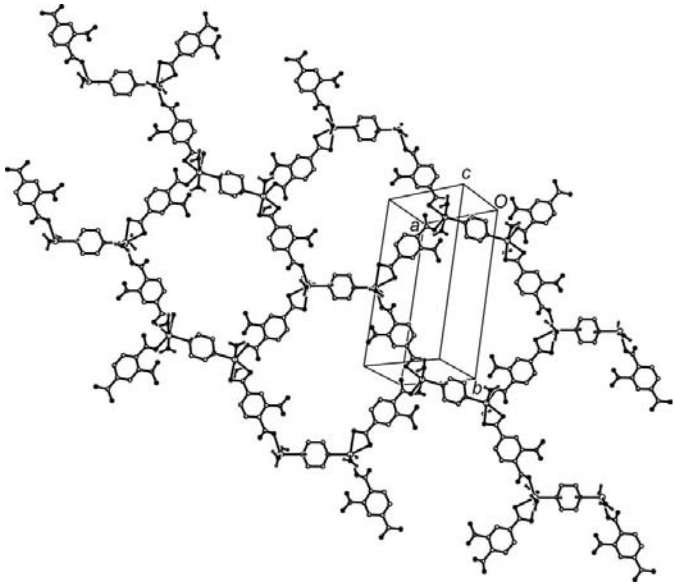

Figure 2
A packing diagram for (I), viewed along the nearest [30$\overline{2}$] direction, showing the two-dimensional macro-ring layer of Cd atoms and ligands.

In the present structure, the O—C—O angle for the O1/C1/O2 carboxylate group is 127.1 (7)°, larger than the value of 121.2 (6)° for the O3/C8/O4 carboxylate group. The mean planes of the O1/C1/O2 group and the benzene ring make a dihedral angle of 60.3 (10)°, and the dihedral angle for the O3/C8/O4 group is 17.3 (9)°. The carboxylate C—O bond distances (Table 1) indicate that the mesomeric effect for the bidentate 1,2-chelating carboxylate group is somewhat greater than that of the monodentate carboxylate group. It is worth noting that these C—O bond distances are shorter than those in six-coordinate *catena*-poly[[[triaquazinc(II)]-μ-2-nitroterephthalato-$\kappa O^{1'}$:$\kappa^2 O^4,O^{4'}$] monohydrate] (Guo & Guo, 2007).

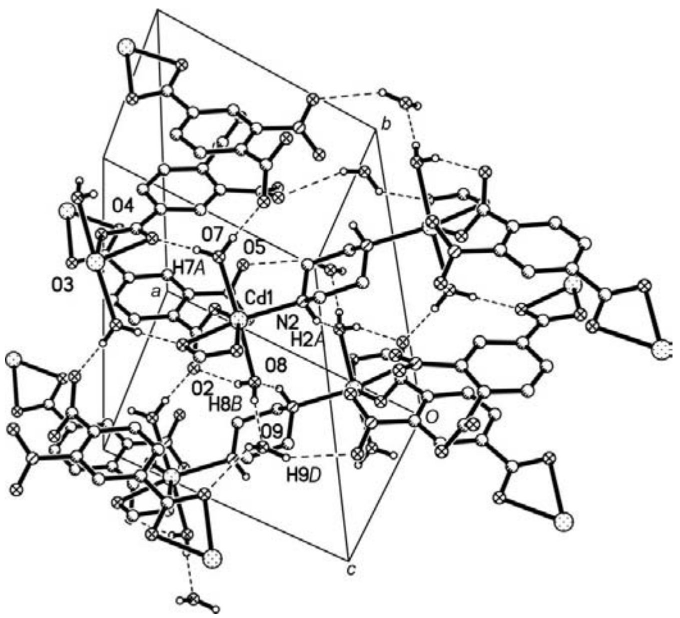

Figure 3
A packing diagram of (I). Hydrogen-bonding interactions between neighbouring layers are shown as dashed lines.

The Cd atoms of (I) are linked together *via* the dianionic 2-nitroterephthalate ligand into a one-dimensional chain. The piperazine molecules are in a chair conformation and lie on a crystallographic inversion centre. They coordinate two Cd atoms, thus leading to the connection of two chains *via* their two N atoms. These result in Cd$\cdots$Cd^{i} and Cd$\cdots$Cd^{iii} separations of 10.793 (3) and 7.113 (2) Å, respectively, and a Cd$^{i}\cdots$Cd$\cdots$Cd^{iii} angle of 134.38 (1)° (see Fig. 1 for symmetry codes). The other two angles, *viz.* Cd$^{i}\cdots$Cd$\cdots$Cd^{ii} and Cd$^{ii}\cdots$Cd$\cdots$Cd^{iii}, are 110.62 (1) and 114.57 (1)°, respectively. In this way, six Cd atoms are associated into a 46-membered macro-ring approximately parallel to (30$\overline{2}$) *via* four dianionic 2-nitroterephthalate ligands and two piperazine molecules. Each group of six Cd atoms build up a polygon, in which the three diagonal distances are 17.952 (7), 20.234 (2) and 19.312 (6) Å, respectively. These macro-rings are further joined into a honeycomb two-dimensional layer structure (Fig. 2). The resulting layers are stacked parallel to the (30$\overline{2}$) plane.

The H atoms of two of the coordinated water molecules are involved in the formation of some strong intra- and intermolecular hydrogen bonds (Brown, 1976). The other water ligand, the piperazine ligand and the nitro group (O5/N1/O6) are also engaged in distinct hydrogen-bonded interactions (Table 2). Hydrogen bonding plays an important role in the manipulation of the two-dimensional macro-ring structure. There are at least the following hydrogen-bonded graph sets (Bernstein *et al.*, 1995): (*a*) a 22-membered $R^4_4(22)$ motif *via* O8—H8*A*$\cdots$O9 and O9—H9*D*$\cdots$O5^{iv}; (*b*) a six-membered ring *S*(6) motif *via* O8—H8*B*$\cdots$O2; (*c*) a 17-membered $R^4_4(17)$ motif *via* O8—H8*A*$\cdots$O9 and O9—H9*C*$\cdots$O3^{v}; (*d*) an eight-membered $R^2_2(8)$ motif *via* O7—H7*A*$\cdots$O4^{vii}; (*e*) an 18-membered $R^3_3(18)$ motif *via* O7—H7*B*$\cdots$O2^{vi}; (*f*) an eight-membered $R^2_2(8)$ motif *via* N2—H2*A*$\cdots$O8^{iv}; (*g*) an 11-membered $R^3_2(11)$ motif *via* N2—H2*A*$\cdots$O8^{iv} and the piperazine ring. Neighbouring layers are linked together *via* these hydrogen-bonded interactions, except for the six-membered $S(6)$ motif (Fig. 3). Thus, the three-dimensional connection of the structure is achieved.

Experimental

The title complex was prepared under continuous stirring with successive addition of $CdSO_4\cdot 8H_2O$ (0.40 g, 0.52 mmol), 2-nitroterephthalic acid (0.50 g, 2.4 mmol) and piperazine (0.20 g, 2.3 mol) to distilled water (25 ml) at room temperature. After filtration, slow evaporation over a period of 2 weeks at room temperature provided colourless needle-like crystals of (I).

Crystal data

$[Cd_2(C_8H_3NO_6)_2(C_4H_{10}N_2)(H_2O)_4]\cdot 2H_2O$
$M_r = 837.26$
Monoclinic, $P2_1/c$
$a = 10.572$ (3) Å
$b = 17.755$ (5) Å
$c = 7.390$ (2) Å
$\beta = 105.374$ (5)°
$V = 1337.5$ (6) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 1.69$ mm^{-1}
$T = 294$ (2) K
0.20 × 0.16 × 0.12 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.734$, $T_{max} = 0.819$
6702 measured reflections
2331 independent reflections
2019 reflections with $I > 2\sigma(I)$
$R_{int} = 0.059$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.129$
$S = 1.15$
2331 reflections
199 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 1.35$ e Å^{-3}
$\Delta\rho_{min} = -1.06$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—O1	2.190 (5)	O1—C1	1.225 (9)
Cd1—N2	2.226 (5)	O2—C1	1.238 (8)
Cd1—O3^{i}	2.409 (5)	O3—C8	1.234 (9)
O4—Cd1^{ii}	2.244 (5)	O4—C8	1.232 (9)
Cd1—O7	2.256 (5)	C9—C10^{iii}	1.487 (10)
Cd1—O8	2.307 (5)		
O1—Cd1—N2	107.0 (2)	O7—Cd1—O8	172.1 (2)
O1—Cd1—O4^{i}	99.5 (2)	O1—Cd1—O3^{i}	153.37 (19)
N2—Cd1—O4^{i}	153.4 (2)	N2—Cd1—O3^{i}	98.83 (19)
O1—Cd1—O7	86.6 (2)	O4^{i}—Cd1—O3^{i}	54.87 (17)
N2—Cd1—O7	91.1 (2)	O7—Cd1—O3^{i}	99.3 (2)
O4^{i}—Cd1—O7	89.9 (2)	O8—Cd1—O3^{i}	87.7 (2)
O1—Cd1—O8	85.49 (19)	O1—C1—O2	127.1 (7)
N2—Cd1—O8	91.5 (2)	O4—C8—O3	121.2 (6)
O4^{i}—Cd1—O8	91.1 (2)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O9—H9$D\cdots$O5^{iv}	0.85	2.45	3.198 (10)	148
O9—H9$C\cdots$O3^{v}	0.85	2.21	2.820 (9)	129
N2—H2$A\cdots$O8^{iv}	0.91	2.65	3.344 (8)	133
O8—H8$B\cdots$O2	0.85	1.90	2.683 (7)	154
O8—H8$A\cdots$O9	0.85	1.86	2.690 (8)	165
O7—H7$B\cdots$O2^{vi}	0.85	1.81	2.660 (8)	173
O7—H7$A\cdots$O4^{vii}	0.85	1.81	2.660 (7)	174

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

All water H atoms were found in difference Fourier maps. However, during refinement they were fixed at O—H distances of 0.85 Å, with $U_{iso}(H) = 1.2U_{eq}(O)$. N- and C-bound H atoms were treated as riding, with N—H = 0.91 Å and C—H = 0.93–0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}$(N or C).

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: AV3159). Services for accessing these data are described at the back of the journal.

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