metal-organic papers

catena-Poly[[diaquapyridinecadmium(II)]-μ-terephthalato]

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The title compound, $[Cd(C_8H_4O_4)(C_5H_5N)(H_2O)_2]_n$, is a one-dimensional spiral polymer in which the organic species act in bis-monodentate and bis-bidentate coordination modes. The two crystallographically independent terephthalate ligands lie on centers of symmetry. The Cd^{2+} cation is hexacoordinated in a distorted octahedral geometry by five O atoms [Cd—O = 2.2370 (16)–2.4928 (17) Å] and one N atom [Cd—N = 2.316 (2) Å]. The water molecules and carboxylate O atoms are involved in O—H···O hydrogen bonds, which link adjacent polymeric chains into a three-dimensional supramolecular network.

Comment

Multifunctional ligands with two or more chelating atoms play an important role in the construction of metal-organic coordination polymers (Janiak, 2003, and references therein). Hydrogen bonding has also been demonstrated to exert additional control over the coordination geometry of metal ions and over the generation of supramolecular polymers. Terephthalate, with versatile modes of coordination, is a suitable ligand for the design and construction of metal-organic coordination polymers which exhibit various topological structures (Kitagawa *et al.*, 2004). We report here the crystal structure of the one-dimensional polymeric compound, $[Cd(terephthalate)(pyridine)(H_2O)_2]_n$, (I), in which hydrogen-bonding interactions link the polymeric chains into a three-dimensional supramolecular architecture.

(I)
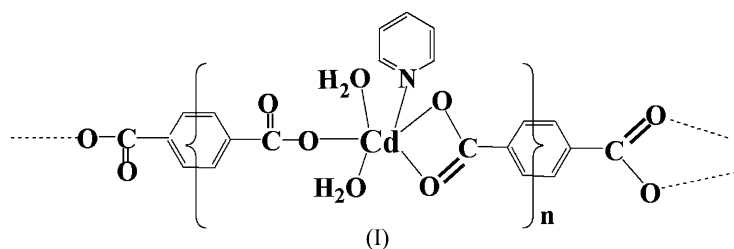
In (I) (Fig. 1), two crystallographically different terephthalate (thp) ligands each lie on an inversion center. The thp ligands adopt two coordination modes, *viz*. bis-bidentate and bis-monodentate (Tao *et al.*, 2000). Each ligand links two metal centers and each Cd^{2+} links one bis-bidentate thp and one bis-monodentate thp into infinite polymeric spirals. The coordination of Cd^{2+} is distorted octahedral (Table 1). The Cd1—N1 distance of 2.316 (2) Å indicates a typical Cd—N bond length (2.32–2.39 Å; Fujita *et al.*, 1994), while the Cd—O distances of 2.2370 (16)–2.4928 (17) Å are close to normal Cd—
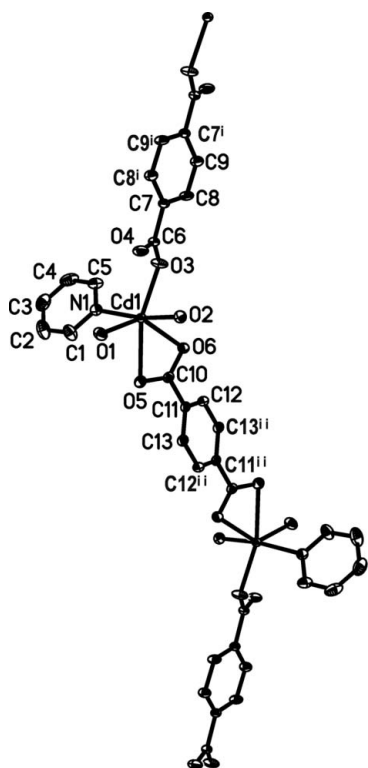
Figure 1
Part of the polymeric structure of (I), showing 30% displacement ellipsoids and the atomic labeling [symmetry codes: (i) $1 - x, -1 - y, -z$; (ii) $-x, 1 - y, -z$]. H atoms have been omitted.
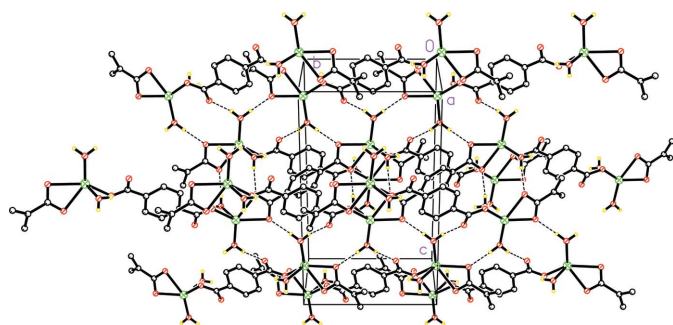
Figure 2
The crystal packing of (I), showing the O—H···O hydrogen bonds as dashed lines. Pyridyl rings and C-bound H atoms have been omitted for clarity.

O(carboxylate) distances (2.251–2.879 Å; Clegg *et al.*, 1995). The two O atoms from the bis-bidentate thp ligand asymmetrically coordinate the Cd atom [Cd1—O5 = 2.4928 (17) Å and Cd1—O6 = 2.3323 (16) Å]. The Cd1—O4 distance of 2.951 (2) Å suggests a non-negligible interaction with the uncoordinated oxygen of the bis-monodentate thp ligand, which may be described as a semi-chelating coordination mode. Thus, the geometry of the Cd center in (I) may also be described as a pentagonal.

The two water molecules are engaged in hydrogen-bonding interactions with carboxylate O atoms (Table 2). These O—H···O hydrogen bonds link adjacent polymeric chains into a three-dimensional supramolecular network (Fig. 2).

Experimental

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.154 g, 0.5 mmol), terephthalic acid (0.083 g, 0.5 mmol), pyridine (3 ml) and H_2O (7 ml) was placed in a 15 ml Teflon-lined stainless steel autoclave. The autoclave was sealed, heated to 433 K under autogenous pressure for 3 d, and then cooled to room temperature at a rate of 5 K h^{-1}. Colourless block-shaped crystals suitable for X-ray diffraction measurement were obtained.

Crystal data

$[Cd(C_8H_4O_4)(C_5H_5N)(H_2O)_2]$	$Z = 4$
$M_r = 391.64$	$D_x = 1.872$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 8.639$ (2) Å	$\mu = 1.60$ mm^{-1}
$b = 9.617$ (3) Å	$T = 293$ (2) K
$c = 16.951$ (4) Å	Block, colorless
$\beta = 99.324$ (5)°	$0.42 \times 0.31 \times 0.28$ mm
$V = 1389.6$ (6) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	7409 measured reflections
	3034 independent reflections
ω scans	2326 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)	$R_{int} = 0.019$
	$\theta_{max} = 27.0°$
$T_{min} = 0.549$, $T_{max} = 0.639$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 0.1996P]$
$R[F^2 > 2\sigma(F^2)] = 0.022$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.059$	$(\Delta/\sigma)_{max} = 0.045$
$S = 1.05$	$\Delta\rho_{max} = 0.31$ e Å^{-3}
3034 reflections	$\Delta\rho_{min} = -0.70$ e Å^{-3}
206 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cd1—O3	2.2370 (16)	Cd1—O6	2.3323 (16)
Cd1—O1	2.2600 (19)	Cd1—O2	2.339 (2)
Cd1—N1	2.316 (2)	Cd1—O5	2.4928 (17)
O3—Cd1—O1	126.26 (7)	O1—Cd1—O2	82.24 (8)
O3—Cd1—N1	88.55 (7)	N1—Cd1—O2	165.69 (8)
O1—Cd1—N1	89.38 (7)	O6—Cd1—O2	89.60 (7)
O3—Cd1—O6	97.77 (6)	O1—Cd1—O5	83.84 (7)
O1—Cd1—O6	134.40 (7)	N1—Cd1—O5	88.65 (6)
N1—Cd1—O6	104.51 (7)	O6—Cd1—O5	54.03 (5)
O3—Cd1—O2	87.11 (7)	O2—Cd1—O5	101.88 (7)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H21···O4	0.81 (4)	2.19 (4)	2.845 (3)	138 (3)
O2—H22···O6^i	0.75 (4)	1.99 (4)	2.741 (3)	173 (4)
O1—H12···O4^{ii}	0.89 (3)	1.87 (3)	2.742 (3)	168 (3)
O1—H11···O5^{iii}	0.86 (3)	1.91 (3)	2.774 (3)	176 (3)

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

The C-bound H atoms were positioned geometrically (C—H = 0.96 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. The aqua H atoms were located in a difference Fourier map and refined isotropically.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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