metal-organic compounds

A novel one-dimensional coordination polymer with Cd^{2+} and diethylenetriaminepentaacetic acid

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catena-Poly[[[bis[diaqua(4,4′-bipyridine)cadmium(II)]-bis[μ-(N″-carboxymethyldiethylenetriamine-N,N,N′,N″-tetraacetato)cadmium(II)]]-μ-4,4′-bipyridine] tetradecahydrate], [Cd$_4$(C$_{14}$H$_{19}$N$_3$O$_{10}$)$_2$(C$_{10}$H$_8$N$_2$)$_3$(H$_2$O)$_4$]·14H$_2$O or [Cd$_4$(HDTPA)$_2$(BPY)$_3$(H$_2$O)$_4$]·14H$_2$O, where BPY is 4,4′-bipyridine and HDTPA^{4-} is N″-carboxymethyldiethylenetriamine-N,N,-N′,N″-tetraacetate, consists of a one-dimensional coordination polymer formed from a secondary building unit which comprises four Cd centres. The chain structure of the title compound was obtained by the use of a multidentate organic ligand, N,N,N′,N″,N″-diethylenetriaminepentaacetic acid (H$_5$DTPA), which forms multiple chelate rings with the Cd metal centres. An extended network is formed *via* hydrogen bonds.

Comment

Crystal engineering of *n*-dimensional coordination polymers is an active field of research, exemplified by several recent reports of novel compounds with interesting architectures and a variety of promising applications (Chui *et al.*, 1999; Kagan *et al.*, 1999; Seo *et al.*, 2000; Tabellion *et al.*, 2001). 4,4′-Bipyridine (BPY) has been repeatedly and successfully employed in the syntheses of one-, two- and three-dimensional coordination polymers (Tao *et al.*, 2000; Batten & Robson, 1998; Janiak, 1997; Zaworotko, 2001). HDTPA^{4-} is a flexible organic ligand with several donor atoms able to coordinate to one or more metal centres [see, for example, Seccombe *et al.* (1975) and Finnen *et al.* (1991)]. The formation of chelate complexes of HDTPA^{4-} leads both to stable structures and to the elimination of available metal coordination sites. HDTPA^{4-} appears, therefore, to be a good ligand for controlling the dimensionality of coordination polymers. We believe the title compound, (I), to be the first example of such a material, in which HDTPA^{4-} directs the formation of a one-dimensional coordination polymer, with BPY acting as a spacer between the metal centres.

The crystal structure of (I) contains two crystallographically independent heptacoordinated Cd centres in distorted pentagonal–bipyramidal geometries (Fig. 1 and Table 1). The coordination sphere of atom Cd1 is completely occupied by the donor atoms (N and O) of one HDTPA^{4-} ligand, which forms six five-membered chelate rings. The C31 carboxylate group establishes a bridge between atoms Cd1 and Cd2 [Cd1···Cd2 = 4.6757 (3) Å]. Atom Cd2 has two BPY ligands *trans*-coordinated in the axial sites and two water molecules (O21 and O22) in equatorial positions.

(I)
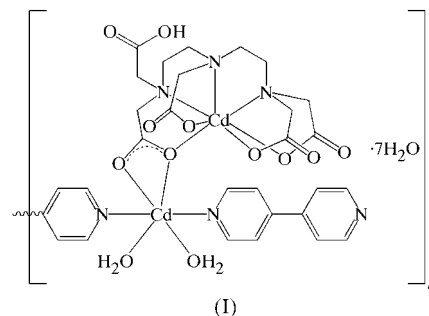
Compound (I) can be considered to arise from self-assembly of a tetrametallic secondary building unit (SBU) into a metal–organic chain along the crystallographic *b* direction (Fig. 2). The SBUs are connected by BPY molecules which adopt two different coordination modes. A bridging bidentate BPY molecule (N51/C51–C55) establishes a coordinative connection between two Cd2 metal centres across a centre of symmetry [Cd2···Cd2^i = 11.6715 (4) Å; symmetry code: (i) 1 − *x*,
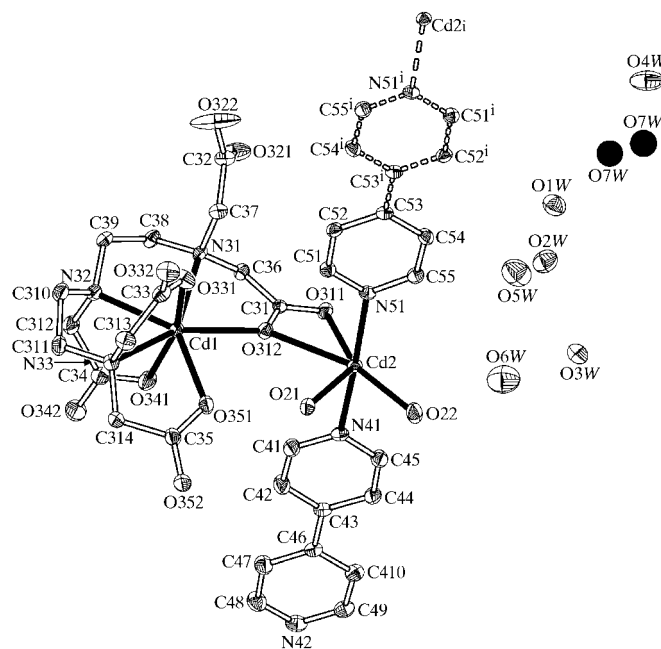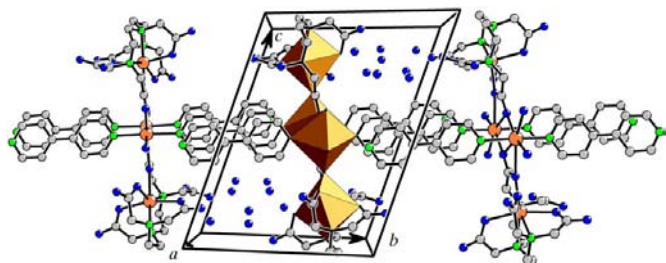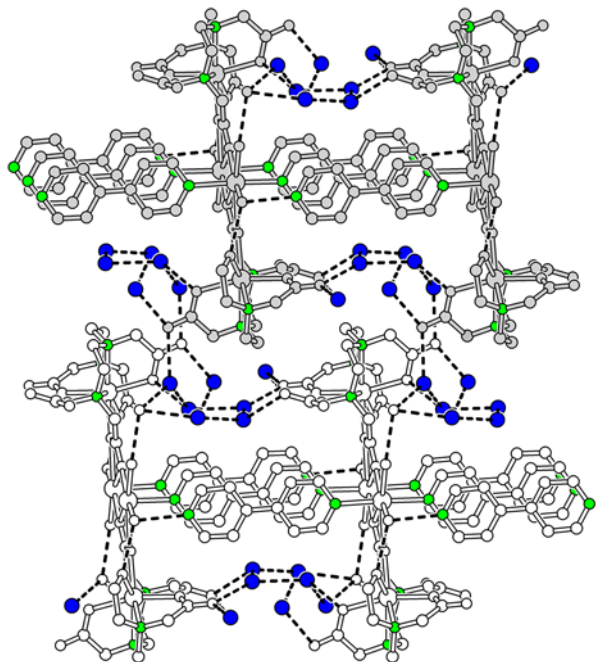

Figure 1
A view of the asymmetric unit of (I), showing displacement ellipsoids at the 50% probability level. The symmetry-generated parts of one BPY unit are also shown [symmetry code: (i) 1 − *x*, −*y*, 1 − *z*]. H atoms have been omitted for clarity.

Figure 2
A perspective view of the one-dimensional coordination polymer of (I), made up from repetition of the tetrametallic secondary building unit along the b direction. H atoms have been omitted for clarity.

$-y$, $1 - z$], and a monodentate BPY molecule has its uncoordinated 4-pyridyl group (N42) hydrogen bonded to the coordinated water molecule (O22) of an adjacent SBU (Table 2).

The steric influence of two HDTPA^{4-} ligands in the external part of the Cd1 SBU appears to direct the growth of the coordination polymer only through the core of the same

Figure 3
The hydrogen-bond network between two adjacent one-dimensional polymers in (I).

SBU (BPY being coordinated only to atom Cd2). Furthermore, the occupation of all the coordination sites around Cd1 by the HDTPA^{4-} ligand prevents coordinative bridging between adjacent chains. Bridges between chains are established by an extensive hydrogen-bond network *via* seven water molecules included within the lattice (Fig. 3 and Table 2).

Experimental

All chemicals were obtained from commercial sources and used as received. To a solution of Cd(NO$_3$)$_2$·4H$_2$O (0.325 g, Aldrich) in distilled water (6.15 g), 4,4'-bipyridyl (0.160 g, Aldrich), *N,N,N'*,*N'',N''*-diethylenetriaminepentaacetic acid (0.399 g, Aldrich) and

triethylamine (0.416 g, Avocado) were added, and the resulting mixture stirred for 1 h at ambient temperature. The suspension was transferred to a Parr stainless steel Teflon-lined autoclave (21 ml) and placed inside a preheated oven at 418 K for a period of 24 h. The autoclave was then cooled slowly to 298 K at a rate of 5 K h^{-1} before being opened. The resulting colourless solution was allowed to evaporate slowly at ambient temperature over a period of one week, yielding colourless crystals of the title compound.

Crystal data

[Cd$_4$(C$_{14}$H$_{19}$N$_3$O$_{10}$)$_2$(C$_{10}$H$_8$N$_2$)$_3$-(H$_2$O)$_4$]·14H$_2$O	$Z = 1$
$M_r = 2021.12$	$D_x = 1.724$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.2785$ (2) Å	Cell parameters from 10 839
$b = 12.6674$ (3) Å	reflections
$c = 16.2495$ (5) Å	$\theta = 1.0$–$27.5°$
$\alpha = 71.693$ (2)°	$\mu = 1.18$ mm^{-1}
$\beta = 89.362$ (2)°	$T = 180$ (2) K
$\gamma = 76.317$ (2)°	Block, colourless
$V = 1947.05$ (9) Å^3	$0.28 \times 0.23 \times 0.18$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	8787 independent reflections
Thin-slice ω and φ scans	7885 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	$R_{int} = 0.035$
$T_{min} = 0.731$, $T_{max} = 0.809$	$\theta_{max} = 27.5°$
19 997 measured reflections	$h = -13 \rightarrow 13$
	$k = -15 \rightarrow 16$
	$l = -18 \rightarrow 21$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0279P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$+ 1.7516P]$
$wR(F^2) = 0.072$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
8787 reflections	$\Delta\rho_{max} = 0.74$ e Å^{-3}
565 parameters	$\Delta\rho_{min} = -0.98$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cd1—O331	2.2571 (17)	Cd2—N41	2.2822 (19)
Cd1—O341	2.2720 (17)	Cd2—N51	2.2896 (18)
Cd1—O312	2.3363 (16)	Cd2—O21	2.3530 (15)
Cd1—O351	2.3679 (17)	Cd2—O22	2.3561 (18)
Cd1—N32	2.432 (2)	Cd2—O311^i	2.3822 (15)
Cd1—N33	2.4650 (19)	Cd2—O312	2.5221 (16)
Cd1—N31	2.4940 (18)	Cd2—O311	2.5363 (16)
O331—Cd1—O312	96.41 (6)	N41—Cd2—O21	91.04 (6)
O341—Cd1—O312	98.42 (6)	N51—Cd2—O21	92.44 (6)
O331—Cd1—O351	93.32 (7)	N41—Cd2—O22	93.31 (7)
O341—Cd1—O351	89.70 (6)	N51—Cd2—O22	91.56 (7)
O312—Cd1—O351	77.66 (5)	O21—Cd2—O22	72.32 (6)
O331—Cd1—N32	94.37 (7)	N41—Cd2—O311^i	89.23 (6)
O341—Cd1—N32	73.91 (6)	N51—Cd2—O311^i	88.88 (6)
O331—Cd1—N33	74.30 (6)	O22—Cd2—O311^i	87.53 (6)
O341—Cd1—N33	93.47 (7)	N41—Cd2—O312	90.19 (6)
O351—Cd1—N33	68.11 (6)	N51—Cd2—O312	86.48 (6)
N32—Cd1—N33	74.37 (6)	O21—Cd2—O312	80.03 (5)
O331—Cd1—N31	88.64 (6)	N41—Cd2—O311	84.44 (6)
O341—Cd1—N31	96.67 (6)	N51—Cd2—O311	90.26 (6)
O312—Cd1—N31	69.55 (6)	O311^i—Cd2—O311	68.94 (6)
N32—Cd1—N31	74.41 (6)	O312—Cd2—O311	51.46 (5)

Symmetry code: (i) $1 - x$, $-1 - y$, $1 - z$.

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O21—H21$A$$\cdots$N42[i]	0.85 (1)	1.93 (1)	2.772 (3)	178 (3)
O21—H21$B$$\cdots$O351	0.85 (1)	1.82 (1)	2.663 (2)	178 (2)
O22—H22$A$$\cdots$O352[ii]	0.85 (1)	1.92 (1)	2.749 (3)	167 (3)
O22—H22$B$$\cdots$O21[ii]	0.83 (1)	2.12 (2)	2.893 (2)	155 (3)
O322—H322$\cdots$O4W	0.84	1.63	2.448 (3)	163
O1W—H1$A$$\cdots$O332	0.84 (3)	1.94 (3)	2.777 (3)	172 (4)
O1W—H1$B$$\cdots$O2$W$	0.84 (3)	1.96 (2)	2.755 (3)	158 (3)
O2W—H2$A$$\cdots$O3$W$	0.83 (3)	1.92 (3)	2.744 (3)	175 (4)
O2W—H2$B$$\cdots$O341[i]	0.84 (3)	2.12 (2)	2.916 (3)	159 (3)
O3W—H3$A$$\cdots$O352[iii]	0.85 (3)	1.90 (3)	2.734 (3)	167 (3)
O3W—H3$B$$\cdots$O342[iv]	0.844 (10)	1.91 (2)	2.745 (3)	170 (3)
O4W—H4$A$$\cdots$O332[v]	0.85 (3)	1.75 (3)	2.599 (3)	175 (4)
O4W—H4$B$$\cdots$O7$W$	0.85 (3)	1.78 (2)	2.611 (5)	167 (4)
O4W—H4$B$$\cdots$O7$W'$	0.85 (3)	1.82 (3)	2.555 (8)	145 (4)
O5W—H5$A$$\cdots$O322	0.84 (4)	1.98 (4)	2.811 (4)	169 (4)
O5W—H5$B$$\cdots$O1$W$	0.85 (3)	1.93 (3)	2.768 (3)	175 (5)
O6W—H6$A$$\cdots$O5$W$	0.85 (4)	2.00 (2)	2.784 (4)	153 (4)
O6W—H6$B$$\cdots$O352[iii]	0.84 (3)	2.14 (3)	2.983 (3)	174 (4)
O7W—H7$A$$\cdots$O6$W$	0.84 (1)	2.01 (4)	2.691 (5)	137 (5)
O7W—H7$B$$\cdots$O342[iii]	0.85 (1)	2.16 (5)	2.840 (4)	138 (6)
O7W'—H7$A'$$\cdots$O6$W$	0.84 (1)	2.21 (9)	2.853 (9)	133 (11)
O7W'—H7$B'$$\cdots$O342[iii]	0.84 (1)	1.84 (2)	2.677 (8)	174 (13)

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

Anisotropic refinement of water molecule O7W in a single position resulted in a large prolate displacement ellipsoid, so it was modelled in two positions, O7W and O7W', with respective site-occupancy factors of 0.65 and 0.35. Both O7W and O7W' were refined with an isotropic displacement parameter. H atoms bound to C atoms were placed in calculated positions and allowed to ride during subsequent refinement, with U_{iso}(H) = $1.2U_{eq}$(C). Atom H322, associated with the uncoordinated carboxyl group, was placed so as to give the best hydrogen-bond geometry to O4W (*HFIX* 83 in *SHELXTL*; Bruker, 2001). The H atoms of the water molecules were located in difference Fourier maps, and were refined with O—H distances restrained to 0.84 (1) Å and H$\cdots$H distances restrained to 1.37 (1) Å; these restraints ensure a reasonable geometry for the water molecules. All H atoms bound to O atoms were refined with U_{iso}(H) = $1.5U_{eq}$(O).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL* *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

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