

catena-Poly[[aqua(2,2'-bipyridine- κ^2N,N')cadmium(II)]- μ -4-carboxylatophenoxyacetato- $\kappa^3O:O^4,O^4'$]

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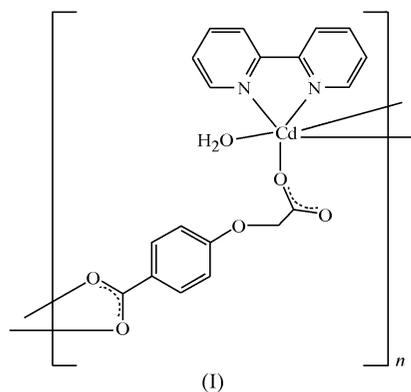
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In the title compound, [Cd(C₉H₆O₅)(C₁₀H₈N₂)(H₂O)]_n, the Cd^{II} atom is coordinated in a distorted octahedral fashion by two carboxylate groups (one in a monodentate and one in a bidentate fashion) from two 4-carboxylatophenoxyacetate anions, two N atoms from a 2,2'-bipyridine ligand and one aqua ligand. The structure is a helix with a long pitch of 16.441 (5) Å. A three-dimensional supramolecular network is further constructed through π - π stacking and hydrogen-bonding interactions between the helices.

Comment

It has been noted that employment of flexible or V-shaped exobidentate organic bridges can improve the helicity of polymeric chains (Ye *et al.*, 2005). Therefore, we assumed that



the 4-carboxylatophenoxyacetate (cpoa²⁻) anion, as a multi-dentate ligand with two different carboxylate groups, one at a flexible site, may be useful in the formation of single-stranded helical chains in the presence of aromatic chelate ligands, such as 2,2'-bipyridine (2,2'-bipy) and 1,10-phenanthroline (phen). These ligands are important in maintaining the one-dimen-

sionality and may provide potential supramolecular recognition sites for π - π stacking interactions (Chen *et al.*, 2002; Zhang *et al.*, 2004) to form multi-stranded helices. Using 4-carboxyphenoxyacetic acid (H₂cpoa) and 2,2'-bipy, we have hydrothermally prepared the title compound, [Cd(cpoa)-(2,2'-bipy)(H₂O)]_n, (I), which is a new neutral infinite Cd^{II}-dicarboxylate helical coordination polymer. The structure is reported in this paper.

The asymmetric unit of (I) contains one Cd^{II} atom, one cpoa²⁻ ligand, one 2,2'-bipy ligand and one aqua ligand (Fig. 1). The Cd atom is coordinated by three O atoms from one monodentate and one bidentate carboxylate group of two cpoa²⁻ ligands, the aqua ligand, and two N atoms from the 2,2'-bipy ligand to furnish a distorted octahedral geometry. The Cd1—O3ⁱ and Cd1—O4ⁱ bonds are longer than the Cd1—O1 bond (see Table 1 for distances and symmetry codes). Each pair of adjacent Cd^{II} atoms are bridged by cpoa²⁻ ligands to form a chiral helical chain running along the 2₁ axis in the *c* direction with a pitch of 16.441 (5) Å; this is longer than the pitch of 11.25 (1) Å in [Cu(ipa)(2,2'-bipy)]_n·2nH₂O (H₂ipa is isophthalic acid; Chen *et al.*, 2002) because the cpoa²⁻ dianion is larger than the ipa²⁻ dianion. These chains are decorated with 2,2'-bipy ligands, positioned alternately on two sides and pointing outwards, as depicted in Fig. 2. The benzene rings of the cpoa²⁻ ions at each side of the helix are arranged in a

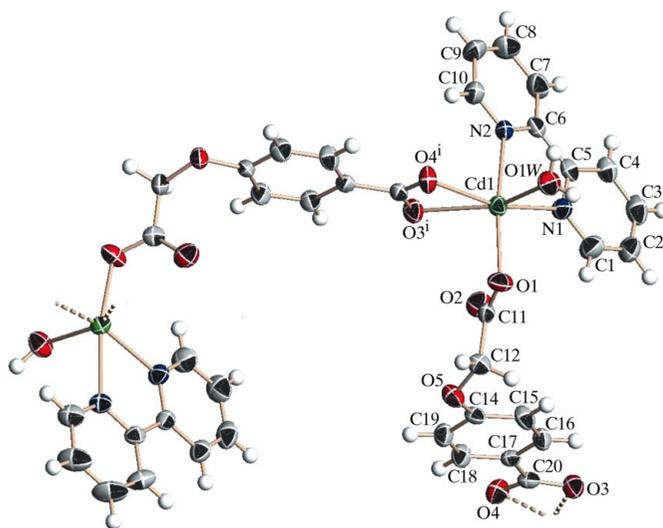


Figure 1
A view of (I), shown with 30% probability displacement ellipsoids. [Symmetry code: (i) $-x + \frac{1}{2}, -y + 1, z - \frac{1}{2}$]

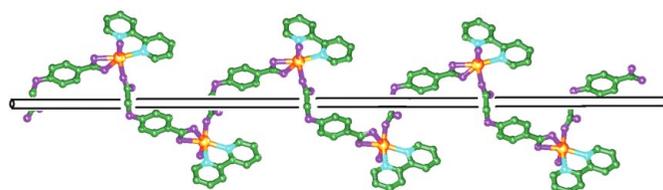


Figure 2
The chiral helical chain of (I).

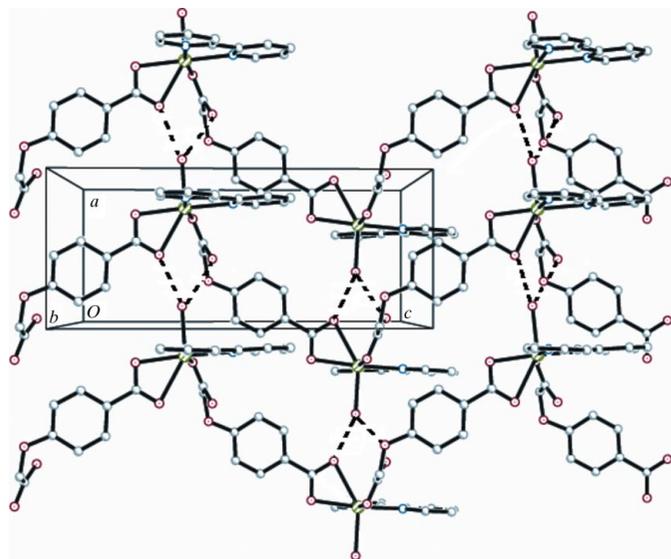


Figure 3
The two-dimensional layer of (I), formed through hydrogen bonds (dashed lines). H atoms have been omitted.

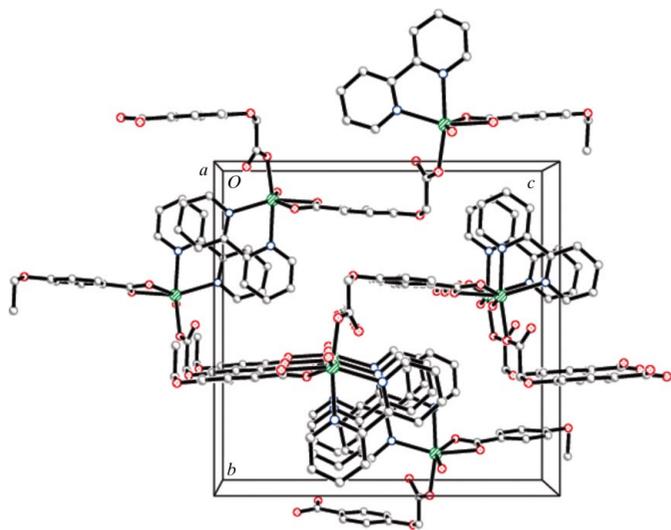


Figure 4
The three-dimensional network of (I), formed through hydrogen bonds and π - π stacking. H atoms have been omitted.

parallel fashion, with a vertical inter-ring distance of 5.04 (1) Å; adjacent chiral helices are connected into a two-dimensional network through hydrogen bonds involving aqua ligands (Table 2 and Fig. 3). The two-dimensional network is extended into a three-dimensional supramolecular network by π - π stacking through intercalation of the 2,2'-bipy rings [the face-to-face distance is 3.42 (1) Å; Fig. 4].

Experimental

2,2'-Bipyridine (0.157 g, 1 mmol) and cadmium nitrate (0.308 g, 1 mmol) were dissolved in a hot aqueous solution of 4-carboxyphenoxyacetic acid (0.196 g, 1 mmol) and the pH of the solution was

adjusted to 6 with triethylamine. The solution was sealed in a 15 ml Teflon-lined stainless steel bomb and held at 413 K for 96 h. The bomb was then allowed to cool naturally to room temperature. Colorless prismatic crystals were filtered off, washed with water and dried at room temperature (yield 58%).

Crystal data

$[\text{Cd}(\text{C}_9\text{H}_6\text{O}_5)(\text{C}_{10}\text{H}_8\text{N}_2)(\text{H}_2\text{O})]$	$Z = 4$
$M_r = 480.74$	$D_x = 1.804 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 6.799$ (2) Å	$\mu = 1.27 \text{ mm}^{-1}$
$b = 15.834$ (5) Å	$T = 293$ (2) K
$c = 16.441$ (5) Å	Prism, colorless
$V = 1769.9$ (9) Å ³	$0.37 \times 0.21 \times 0.17 \text{ mm}$

Data collection

Bruker APEX area-detector diffractometer	10675 measured reflections
φ and ω scans	3866 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	3417 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.650$, $T_{\max} = 0.812$	$R_{\text{int}} = 0.028$
	$\theta_{\max} = 27.1^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0231P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.050$	$(\Delta/\sigma)_{\max} = 0.001$
$S = 1.06$	$\Delta\rho_{\max} = 0.56 \text{ e \AA}^{-3}$
3866 reflections	$\Delta\rho_{\min} = -0.27 \text{ e \AA}^{-3}$
262 parameters	Absolute structure: Flack (1983),
H atoms treated by a mixture of independent and constrained refinement	1617 Friedel pairs
	Flack parameter: 0.36 (2)

Table 1

Selected geometric parameters (Å, °).

Cd1—O1	2.206 (2)	Cd1—O1W	2.336 (3)
Cd1—O4 ⁱ	2.295 (2)	Cd1—N2	2.342 (2)
Cd1—N1	2.328 (2)	Cd1—O3 ⁱ	2.513 (2)
O1—Cd1—O4 ⁱ	99.5 (1)	N1—Cd1—N2	70.25 (9)
O1—Cd1—N1	99.8 (1)	O1W—Cd1—N2	94.43 (9)
O4 ⁱ —Cd1—N1	159.4 (1)	O1—Cd1—O3 ⁱ	96.09 (8)
O1—Cd1—O1W	88.7 (1)	O4 ⁱ —Cd1—O3 ⁱ	54.03 (7)
O4 ⁱ —Cd1—O1W	94.7 (1)	N1—Cd1—O3 ⁱ	116.52 (9)
N1—Cd1—O1W	92.86 (10)	O1W—Cd1—O3 ⁱ	148.72 (9)
O1—Cd1—N2	169.70 (9)	N2—Cd1—O3 ⁱ	86.33 (8)
O4 ⁱ —Cd1—N2	90.05 (8)		

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1A ⁱ ⋯O3 ⁱⁱ	0.89 (4)	1.92 (4)	2.773 (3)	161 (3)
O1W—H1B ⁱ ⋯O2 ⁱⁱⁱ	0.76 (4)	2.09 (4)	2.787 (4)	154 (4)

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

The water H atoms were located in difference Fourier maps and refined freely. All other H atoms were positioned geometrically and refined using a riding model, with C—H distances of 0.97 (CH₂) or 0.93 Å (aromatic) and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB3012). Services for accessing these data are described at the back of the journal.

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