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catena-Poly[[diaqua(nicotinato-κ^2O,O')cadmium(II)]-μ-nicotinato-$\kappa^3N:O,O'$]

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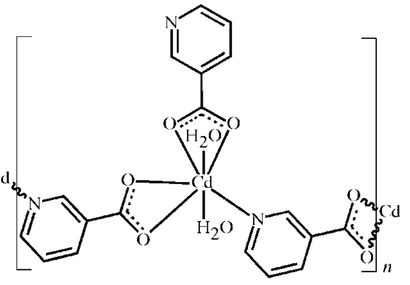
The title compound, $[Cd(C_6H_4NO_2)_2(H_2O)_2]_n$, forms a one-dimensional chain structure based on a Cd atom with approximate pentagonal bipyramidal coordination geometry and two nicotinate ligands in different coordination modes. One acts as a tridentate ligand, chelating one Cd atom through the carboxylate group while simultaneously binding to a second symmetry-related Cd atom through the pyridine N atom; the other acts only as a bidentate ligand through its carboxylate group. Hydrogen bonds utilizing the coordinated water molecules, uncoordinated nitrogen and carboxylate O atoms as acceptors link the chains.

Comment

There has been considerable recent interest in the design and synthesis of supramolecular complexes because of their novel structural architectures and favorable properties, which allow applications such as ion exchange, adsorption, non-linear optics and magnetism (Noro *et al.*, 2000; Yaghi *et al.*, 1998). Some organic nitrogen donors, such as bipyridine or related species, are often chosen to fabricate these various species (Hagman *et al.*, 1999). The pyridinecarboxylate ligand is also an attractive choice because of its multifunctional linking groups (Evans & Lin, 2002). Furthermore, polynuclear cadmium complexes are of interest not only for their novel structures but also for their photoluminescence properties (Tong *et al.*, 1999). There are several polymers built from the nicotinate group and Cd^{II} centers, and these polymers exhibit different types of topology, *viz.* a discrete structure in tetra-aqua-*trans*-bis(nicotinato-κN)cadmium(II) (Zhou *et al.*, 2003), a two-dimensional structure in poly[aquacadmium-bis(μ-nicotinato-$\kappa N{:}\kappa O,\kappa O'$)] (Clegg *et al.*, 1995) and poly[tetra-aquatricadmium(II)-hexa-μ-nicotinato] (Chen, 2003), and a three-dimensional structure in *catena*-[(μ_3-nicotinato)(μ_2-nicotinato)cadmium(II)] (Evans & Lin, 2001; Lu & Kohler, 2002). In this paper, we report the first example of a one-dimensional coordination polymer, *catena*-poly[[diaqua(nicotinato-κ^2O,O')cadmium(II)]-μ-nicotinato-$\kappa^3N:O,O'$], (I).



(I)

The structure of (I) consists of one-dimensional zigzag chains. The seven-coordinate Cd atoms exhibit a distorted pentagonal bipyramidal geometry, involving one N-donor and four O-donors of the two nicotinate ligands (one symmetry-related) lying almost in the equatorial plane, and two coordinated water molecules at the apex sites, as shown in Figs. 1 and 2; the deviation of the Cd atom from the mean plane is 0.124 (2) Å. The bond angles around the Cd1 atom range from 51.26 (14) to 174.42 (18)°. The Cd1—O distances range from 2.255 (4) to 2.724 (5) Å, while the Cd1—N distance is 2.278 (4) Å (Table 1); all are in agreement with the values reported in other Cd–nicotinate complexes, *e.g.* poly[aquacadmium-bis(μ-nicotinato-$\kappa N{:}\kappa O,\kappa O'$)] (Clegg *et al.*, 1995). The two carboxylate groups are bound asymmetrically, with one Cd—O bond considerably longer than the other. There are two crystallographically independent nicotinate ligands, having two different coordination modes (Fig. 2). One acts as a tridentate ligand, chelating one Cd atom through the carboxylate group while simultaneously binding to a second symmetry-related Cd atom through the pyridine N atom. The other acts as a simple bidentate ligand through its carboxylate group. The dihedral angles between the carboxylate group and the main ring plane are 10.48 (2)° in the tridentate ligand and 2.97 (2)° in the bidentate ligand, so the tridentate ligand is markedly less planar than the bidentate ligand. This difference is presumably a consequence of the bridging nature of the ligand, with effective coordination to the metal atoms being of primary importance.

A number of hydrated metal–nicotinate structures have been reported. Only some dinuclear lanthanide complexes (with La, Pr, Sm, Ho or Tm) have both chelating and bridging

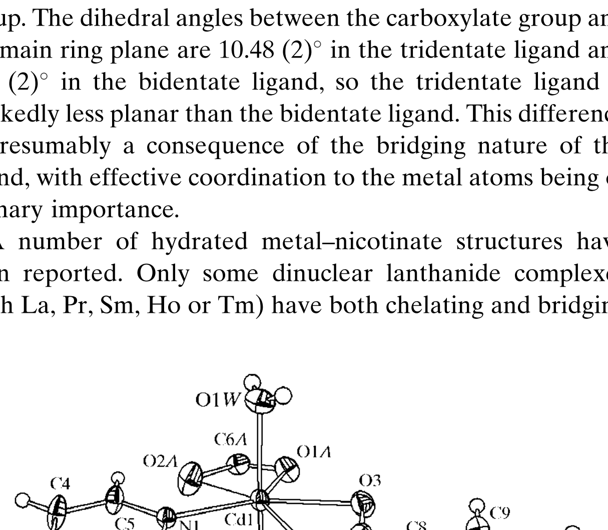


Figure 1
A view of (I), with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. Atoms labeled with the suffix *A* are at the symmetry position ($x - 1$, y, z).

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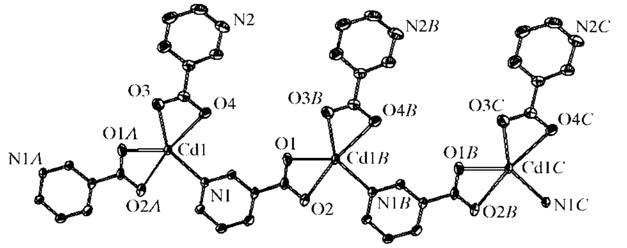

Figure 2

The one-dimensional chain structure of (I), showing the two different coordination modes of the nicotinate ligand. H atoms and water molecules have been omitted for clarity. Atoms labeled with the suffixes *A*, *B* or *C* are at the symmetry positions ($x - 1$, y, z), ($x + 1$, y, z) and ($x + 2$, y, z).

nicotinate ligands (Moore *et al.*, 1972; Prout *et al.*, 1985), but the N atoms of the ligands are not involved in binding to the metals. To our knowledge, complex (I) is the first example of two such coordination modes co-existing in one crystal.

Each bridging nicotinate ligand connects two Cd^{II} ions into a one-dimensional structure in a head-to-tail manner. The chain propagates along the *a* axis, but adjacent chains are antiparallel, and hence there is a center of symmetry in the structure. As shown in Table 2, all H atoms of the bound water molecules engage in hydrogen bonds to the carboxylate O or uncoordinated N atoms of the pyridine rings in adjacent asymmetric units. The O···O distances range from 2.831 (6) to 3.082 (8) Å, and the O···N distance is 2.822 (8) Å. An extensive network of intermolecular hydrogen bonds links the one-dimensional chains to complete a three-dimensional framework.

Experimental

For the preparation of the title compound, $Cd(CH_3COO)_2$ (0.23 g, 1.0 mmol), *m*-pyridinecarboxylic acid (0.124 g, 1.0 mmol) and $Na_2B_4O_7{\cdot}10H_2O$ (0.19 g, 0.5 mmol) in a 2:2:1 molar ratio and water (10 ml) were placed in a Parr Teflon-lined stainless steel vessel (25 ml). The vessel was sealed, heated to 433 K and maintained at that temperature for 3 d. The reaction was cooled at a rate of 0.5 K min^{-1}, leading to the formation of colorless crystals of (I) (yield: 63%, based on Cd).

Crystal data

$[Cd(C_6H_4NO_2)_2(H_2O)_2]$
$M_r = 392.64$
Monoclinic, $P2_1/n$
$a = 7.8620$ (3) Å
$b = 12.6448$ (5) Å
$c = 14.0134$ (2) Å
$\beta = 97.755$ (2)°
$V = 1380.38$ (8) Å^3
$Z = 4$
$D_x = 1.889$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2215 reflections
$\theta = 2.2$–25.1°
$\mu = 1.61$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.60 × 0.22 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.576$, $T_{max} = 0.725$
4182 measured reflections
2438 independent reflections
1825 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 25.1°$
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 15$
$l = -12 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.118$
$S = 1.04$
2438 reflections
202 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0595P)^2 + 3.9106P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.006$
$\Delta\rho_{max} = 0.84$ e Å^{-3}
$\Delta\rho_{min} = -1.17$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Cd1—O1^i	2.255 (4)	Cd1—O1*W*	2.366 (5)
Cd1—N1	2.278 (4)	Cd1—O4	2.573 (4)
Cd1—O3	2.295 (4)	Cd1—O2^i	2.724 (5)
Cd1—O2*W*	2.335 (5)		
N1—Cd1—O3	139.86 (16)	O2*W*—Cd1—O1*W*	174.42 (18)
N1—Cd1—O2*W*	91.75 (15)	N1—Cd1—O4	87.31 (14)
O3—Cd1—O2*W*	89.91 (16)	O3—Cd1—O4	53.20 (15)
N1—Cd1—O1*W*	88.13 (17)	O2*W*—Cd1—O4	82.38 (17)
O3—Cd1—O1*W*	86.61 (18)	O1*W*—Cd1—O4	92.04 (16)

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

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*W*—H2*WA*···O4^i	0.82 (5)	2.02 (6)	2.831 (6)	170 (8)
O1*W*—H1*WB*···N2^{ii}	0.82 (7)	2.13 (6)	2.822 (8)	143 (9)
O1*W*—H1*WA*···O2^{iii}	0.82 (5)	2.27 (3)	3.082 (8)	170 (9)
O2*W*—H2*WB*···O1^i	0.82 (6)	2.18 (5)	2.870 (6)	142 (7)

Symmetry codes: (i) $-x, -y, 2 - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{5}{2} - z$.

C-bound H atoms were positioned geometrically and refined using a riding model [C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$]. The water H atoms were located from difference maps and refined isotropically [$U_{iso}(H) = 1.5U_{eq}(O)$]. In the final difference map, the deepest hole is 0.94 Å from atom Cd1 and the highest peak is 1.03 Å from atom C10.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *SAINT* and *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; 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: GA1055). Services for accessing these data are described at the back of the journal.

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