

Polymeric hexa- μ -nicotinato-
tricadmium(II) tetrahydrate

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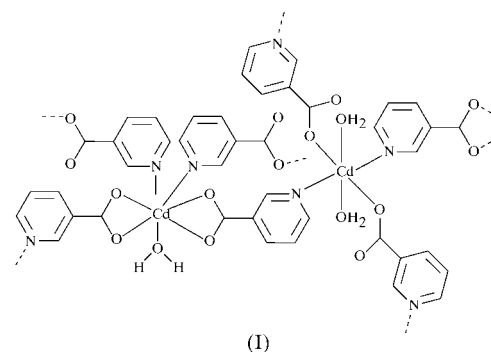
The title polymeric complex, poly[tetraaquatricadmium(II)-hexa- μ -nicotinato], $[\text{Cd}_3(\text{C}_6\text{H}_4\text{NO}_2)_6(\text{H}_2\text{O})_4]_n$, exhibits two types of metal centers, *i.e.* a seven-coordinated Cd atom and a six-coordinated Cd atom located on an inversion center. The seven-coordinated Cd atoms are linked by κ^3N,O,O' -nicotinate bridges into one-dimensional chains that are further linked by κ^2N,O -nicotinate–Cd2– κ^2N,O -nicotinate bridges into a two-dimensional network which is parallel to the *xy* plane and which contains large 24- and 36-membered rings.

Comment

In recent years, the *m*-pyridinecarboxylate (nicotinate) group has been used as a bi/tridentate ligand to build coordination polymers for exploring non-linear optical and magnetic materials (Lin *et al.*, 2000; Chen *et al.*, 2001; Evans & Lin, 2001). In these reported coordination polymers, the metal atoms exhibit different types of coordination geometry, *viz.* pentagonal bipyramidal in poly[aquacadmium-bis(η -nicotinato)] (Clegg *et al.*, 1995), octahedral in poly[manganese-bis(η -nicotinato)] (Wang *et al.*, 2002) and distorted square pyramidal in two three-dimensional coordination polymers built from a nicotinate group and binuclear copper(II)/cadmium(II), namely poly[copper(II)/cadmium(II)-bis(η -nicotinato)] (Lu & Babb, 2001; Lu & Kohler, 2002). Only one type of metal center is found in all of the coordination polymers mentioned above.

In this work, we report a new two-dimensional Cd^{II} coordination polymer, *viz.* poly[tetraaquatricadmium(II)-hexa- μ -nicotinato], (I), featuring a binuclear Cd^{II} unit with both seven- and six-coordination geometries. The seven-coordinated Cd1 atom in (I) occupies a very distorted pentagonal bipyramidal coordination environment. Four O atoms of two nicotinate groups [Cd1–O1 = 2.348 (4) Å, Cd1–O2 = 2.539 (5) Å, Cd1–O3ⁱ = 2.483 (4) Å and Cd1–O4ⁱ = 2.367 (4) Å; symmetry code: (i) *x*, 1 + *y*, *z*; Fig. 1 and Table 1] and a nicotinate N atom [Cd1–N2 = 2.396 (4) Å] are located at the equatorial positions, and an O atom of a coordinated water molecule [Cd1–O1W = 2.292 (4) Å] and an N atom of another nicotinate group [Cd1–N3ⁱⁱ = 2.422 (4) Å; symmetry

code: (ii) 1 – *x*, –*y*, 1 – *z*] are at the apical positions. At the equatorial positions, the coordinating O and N atoms are almost coplanar, and atom Cd1 is 0.288 Å above the plane; however, the alignment of the N and O atoms at the



apical positions deviates from 180° [N3ⁱⁱ–Cd1–O1W = 163.72 (13)°]. On the other hand, the coordination environment of atom Cd2, located on an inversion centre, is distorted octahedral. Atom Cd2 is coordinated by two N atoms from two nicotinate groups [Cd2–N1 = 2.325 (5) Å] and two O atoms from another two nicotinate groups [Cd2–O5 = 2.268 (4) Å] at the equatorial positions, and by two water molecules [Cd2–O2W = 2.377 (4) Å] at the apical positions.

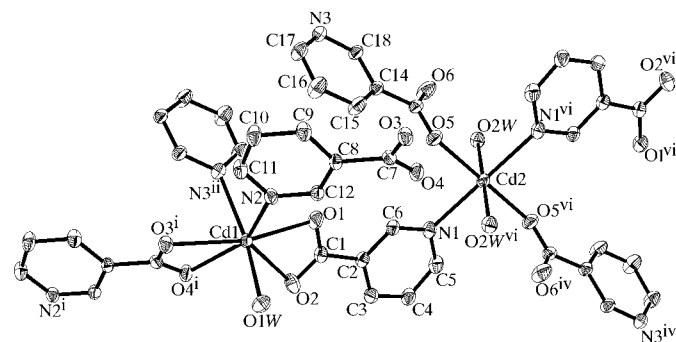


Figure 1

The coordination environment in (I), showing displacement ellipsoids at the 30% probability level. [Symmetry codes: (i) *x*, 1 + *y*, *z*; (ii) 1 – *x*, –*y*, 1 – *z*; (vi) –*x*, –1 – *y*, 1 – *z*.]

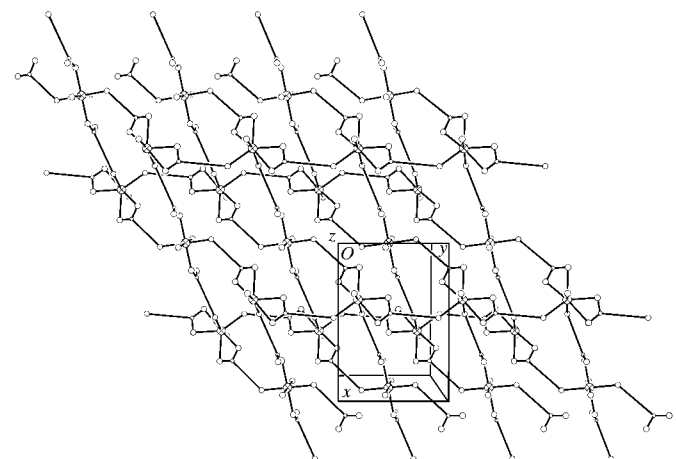


Figure 2

A view of the three-dimensional framework of (I). The nicotinate groups are represented by Y-shaped sticks for clarity.

Adjacent Cd1 ions are connected by $\kappa^3N:OO'$ -nicotinate bridges, thus forming infinite one-dimensional chains. These chains are linked by κ^2N,O -nicotinate–Cd2– κ^2N,O -nicotinate bridges into two-dimensional zigzag sheets. In these sheets, large 36-membered rings, with *ca* 17.82 × 8.20 Å internal dimensions, are formed. Two zigzag sheets are then connected by common Cd1 atoms *via* covalent bonds, thus forming double-layered sheets containing 24-membered rings (Fig. 2). The 36- and 24-membered rings in (I) are larger than the 24- and eight-membered rings in poly[copper(II)/cadmium(II)-bis(η -nicotinato)] (Lu & Babb, 2001; Lu & Kohler, 2002). Finally, the two-dimensional double-layered sheets are further linked by hydrogen bonds between O atoms from both lattice water molecules and the coordinated nicotinate groups into a three-dimensional network (see Table 2 for details).

Experimental

An aqueous solution (9 ml) of Cd(NO₃)₂ (0.5 mmol) and nicotinic acid (1.0 mmol) was placed in a Teflon-lined stainless steel Parr vessel (23 ml). The pH of the solution was adjusted to ~8.0 with an aqueous solution (0.2 M) of sodium hydrate. The vessel was sealed, heated at 423 K for 24 h, cooled at a rate of 5 K h⁻¹ to 353 K, maintained at this temperature for 10 h and then cooled slowly to room temperature. Pale yellow crystals suitable for X-ray diffraction were obtained [yield 39% based on Cd(NO₃)₂]. Analysis calculated for C₃₆H₃₂-Cd₃N₆O₁₆: C 37.87, H 2.82, N 7.36%; found: C 37.93, H 2.91, N 7.19%. IR (cm⁻¹): 3265 (*s*), 1611 (*s*), 1566 (*s*), 1387 (*vs*), 1050 (*m*), 842 (*m*), 765 (*m*), 699 (*m*).

Crystal data

[Cd ₃ (C ₆ H ₄ NO ₂) ₆ (H ₂ O) ₄]	$D_x = 1.955 \text{ Mg m}^{-3}$
$M_r = 1141.88$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 reflections
$a = 11.825 (11) \text{ \AA}$	$\theta = 6.5\text{--}15.0^\circ$
$b = 8.195 (8) \text{ \AA}$	$\mu = 1.71 \text{ mm}^{-1}$
$c = 20.097 (11) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 95.160 (3)^\circ$	Prism, yellow
$V = 1940 (3) \text{ \AA}^3$	$0.32 \times 0.30 \times 0.26 \text{ mm}$
$Z = 2$	

Data collection

Siemens R3m diffractometer	$R_{\text{int}} = 0.100$
ω scans	$\theta_{\text{max}} = 28.0^\circ$
Absorption correction: ψ scan (Kopfmán & Huber, 1968)	$h = 0 \rightarrow 14$
$T_{\text{min}} = 0.569$, $T_{\text{max}} = 0.641$	$k = 0 \rightarrow 10$
4705 measured reflections	$l = -26 \rightarrow 26$
4489 independent reflections	2 standard reflections every 200 reflections
4063 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0881P)^2 + 3.6257P]$
$R[F^2 > 2\sigma(F_o^2)] = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F_o^2) = 0.135$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.09$	$\Delta\rho_{\text{max}} = 2.63 \text{ e \AA}^{-3}$
4489 reflections	$\Delta\rho_{\text{min}} = -1.05 \text{ e \AA}^{-3}$
278 parameters	
H-atom parameters constrained	

H atoms of the nicotinate group were placed in calculated positions, with fixed isotropic displacement parameters, and were allowed to ride on their respective parent atoms.

Data collection: *SHELXTL-Plus* (Siemens, 1990); cell refinement: *SHELXTL-Plus*; data reduction: *SHELXTL-Plus*; program(s) used

Table 1

Selected geometric parameters (Å, °).

N1—Cd2	2.325 (5)	O1W—Cd1	2.292 (4)
N2—Cd1	2.396 (4)	O2W—Cd2	2.377 (4)
O1—Cd1	2.348 (4)	Cd1—O4 ⁱ	2.367 (4)
O2—Cd1	2.539 (5)	Cd1—N3 ⁱⁱ	2.422 (4)
O5—Cd2	2.269 (4)	Cd1—O3 ⁱ	2.483 (4)
O1W—Cd1—O1	104.77 (14)	O4 ⁱ —Cd1—O3 ⁱ	54.29 (11)
O1W—Cd1—O4 ⁱ	95.16 (13)	N2—Cd1—O3 ⁱ	91.71 (13)
O1—Cd1—O4 ⁱ	128.46 (13)	N3 ⁱⁱ —Cd1—O3 ⁱ	80.14 (13)
O1W—Cd1—N2	84.47 (13)	O1W—Cd1—O2	81.87 (13)
O1—Cd1—N2	83.92 (14)	O1—Cd1—O2	53.33 (13)
O4 ⁱ —Cd1—N2	145.90 (12)	O4 ⁱ —Cd1—O2	84.28 (11)
O1W—Cd1—N3 ⁱⁱ	163.72 (13)	N2—Cd1—O2	129.07 (13)
O1—Cd1—N3 ⁱⁱ	87.28 (14)	N3 ⁱⁱ —Cd1—O2	114.34 (14)
O4 ⁱ —Cd1—N3 ⁱⁱ	85.41 (13)	O3 ⁱ —Cd1—O2	135.87 (11)
N2—Cd1—N3 ⁱⁱ	86.00 (14)	O5—Cd2—N1	88.46 (14)
O1W—Cd1—O3 ⁱ	86.97 (13)	O5—Cd2—O2W	91.58 (13)
O1—Cd1—O3 ⁱ	166.95 (12)	N1—Cd2—O2W	101.49 (13)

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

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1W—H1WA \cdots O4 ⁱⁱⁱ	0.85	1.92	2.751 (5)	165
O2W—H2WA \cdots O6	0.85	1.94	2.677 (6)	145
O1W—H1WB \cdots O2W ^{iv}	0.89	2.01	2.847 (5)	154
O2W—H2WB \cdots O2 ^v	0.82	1.93	2.712 (6)	158

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

to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1659). Services for accessing these data are described at the back of the journal.

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