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The Polymeric Structure of Aquacadmium Bisnicotinate

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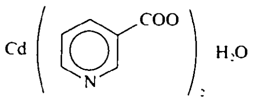
Abstract

The title compound, poly[aquacadmium-bis(μ-nicotinato-κN:κO,$\kappa O'$)], [Cd($C_6H_4NO_2$)$_2$(H_2O)], consists of a polymeric network in which each nicotinate acts as a bidentate chelating ligand towards one Cd atom through its carboxylate group while simultaneously binding to a second Cd atom through its pyridine N atom. Cd has approximate pentagonal bipyramidal coordination geometry. Water acts as a ligand; it is also involved in hydrogen bonding to nearby carboxylate O atoms, contributing further to the polymeric network interactions.

Comment

The structure of the title compound, (I), was determined as part of an investigation of the structural chemistry of carboxylate complexes of Group 12 metals. It is polymeric, with the nicotinate ligands binding through their N atoms and carboxylate functional groups. Each Cd atom is coordinated by four different nicotinate ligands, two through their N atoms and two in a chelating fashion through their carboxylate groups. Both these carboxylates are bound asymmetrically, with one Cd—O bond considerably longer than the other. The presence of one water ligand makes each Cd atom seven-coordinate. The coordination geometry can best be described as approximately pentagonal bipyramidal, with the carboxylates and one N atom in the equatorial plane (r.m.s. deviation for the five ligating atoms = 0.101 Å; deviation of Cd from the mean plane = 0.163 Å), and with the second N atom and the water ligand in axial positions.



(I)

The two crystallographically independent nicotinate ligands both show deviations from planarity, consisting mainly of a twist in the carboxylate group about the C—C bond out of the aromatic ring plane. The dihedral angles between the carboxylate group and the mean ring plane for the two ligands are 17.4 and 4.6°, so one ligand is markedly more non-planar than the other. This is presumably a consequence of the bridging nature of the ligands, with effective coordination to the metals being of primary importance. Nicotinic acid itself shows a degree of non-planarity in the crystalline state similar to the less distorted of the two ligands here, with a dihedral angle of 4.4° (Kutoglu & Scheringer, 1983).

Both H atoms of the water ligand engage in hydrogen bonding to a carboxylate O atom in an adjacent asymmetric unit. The O$\cdots$O distances for these hydrogen bonds are O5$\cdots$O1$^{\text{v}}$ 2.891 and O5$\cdots$O4$^{\text{vi}}$ 2.839 Å [symmetry code: (v) $-x+1, -y+1, -z+1$; (vi) = $-x+\frac{1}{2}, y-\frac{1}{2}, z$]. The hydrogen bonding reinforces the polymeric framework, which is created primarily by the linking of Cd-atom centres through the bridging nicotinate ligands.

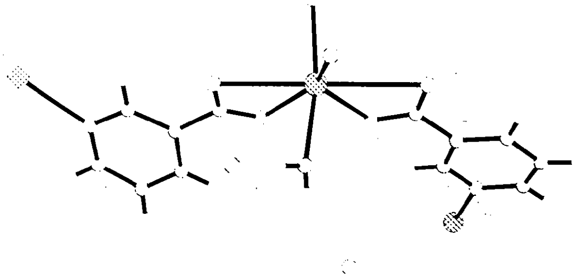


Fig. 1. The asymmetric unit of the structure together with atoms in adjacent units to which it is bonded. Symmetry operators are: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (iv) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+1$; (v) $-x+1, -y+1, -z+1$; (vi) $-x+\frac{1}{2}, y-\frac{1}{2}, z$.

A number of hydrated metal nicotinate structures have been reported. In the case of lanthanide complexes (with La, Pr, Sm, Ho or Tm) these are dinuclear, with both chelating and bridging nicotinate ligands (Moore, Glick & Baker, 1972; Aslanov, Abdul'minev & Porai-Koshits, 1972; Prout, Marín & Hutchinson, 1985), except for a polymeric lanthanum complex containing only bridging nicotinates (Kay, Moore & Glick, 1972); the N atom of the ligand is not involved in binding to the metals. Complexes of Cr, Co and Zn are mononuclear, and involve binding only to the N atom, with no coordination by the carboxylate group (Cotton, Falvello, Ohlhausen, Murillo & Quesada, 1991; Anagnostopoulos, Drew & Walton, 1969). The trihydrated calcium complex is polymeric, with coordination to carboxylate groups (simultaneously chelating and bridging) but not by N atoms, while magnesium forms a salt structure containing discrete [Mg(OH_2)$_6$]$^{2+}$ and nicotinate ions (Cole & Holt, 1985). The present cadmium complex is unique in this set of structures in showing coordination by both the functional groups of the nicotinate anion.

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Experimental

The compound was prepared by refluxing cadmium carbonate and nicotinic acid in water, and crystals were obtained by slow evaporation of the resulting solution.

Crystal data

$[Cd(C_6H_4NO_2)_2(H_2O)]$
$M_r = 374.62$
Orthorhombic
Pbca
$a = 11.453$ (2) Å
$b = 12.119$ (2) Å
$c = 17.444$ (4) Å
$V = 2421.2$ (8) Å^3
$Z = 8$
$D_x = 2.055$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 32 reflections
$\theta = 10.92$–$12.23°$
$\mu = 1.826$ mm^{-1}
$T = 295$ (2) K
Block
0.29 × 0.23 × 0.19 mm
Colourless

Data collection

Stoe Siemens diffractometer
ω/θ scans with on-line profile fitting (Clegg, 1981)
Absorption correction: empirical
$T_{\min} = 0.480$, $T_{\max} = 0.549$
3851 measured reflections
2125 independent reflections

1829 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.0225$
$\theta_{\max} = 24.98°$
$h = -8 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -20 \rightarrow 20$
5 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0207$
$wR(F^2) = 0.0609$
$S = 1.096$
2120 reflections
190 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 1.8122P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$

$\Delta\rho_{\max} = 0.372$ e Å^{-3}
$\Delta\rho_{\min} = -0.364$ e Å^{-3}
Extinction correction: *SHELXL* (Sheldrick, 1993)
Extinction coefficient: 0.00091 (13)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cd	0.36188 (2)	0.600424 (15)	0.386553 (10)	0.02182 (10)
O1	0.5341 (2)	0.5126 (2)	0.36372 (13)	0.0393 (5)
O2	0.3926 (2)	0.4133 (2)	0.31187 (14)	0.0404 (5)
N1	0.6522 (2)	0.1916 (2)	0.23220 (13)	0.0263 (5)
C1	0.4958 (3)	0.4266 (2)	0.3305 (2)	0.0289 (6)
C2	0.5857 (2)	0.3391 (2)	0.31315 (15)	0.0245 (6)
C3	0.5715 (2)	0.2666 (2)	0.2525 (2)	0.0247 (6)
C4	0.7472 (2)	0.1829 (2)	0.2765 (2)	0.0299 (6)
C5	0.7668 (2)	0.2484 (2)	0.3396 (2)	0.0302 (6)
C6	0.6867 (3)	0.3300 (2)	0.3568 (2)	0.0282 (6)
O3	0.4822 (2)	0.7108 (2)	0.45393 (13)	0.0405 (5)
O4	0.3163 (2)	0.7998 (2)	0.47115 (13)	0.0385 (5)
N2	0.6616 (2)	0.9129 (2)	0.60310 (13)	0.0245 (5)
C7	0.4217 (2)	0.7849 (2)	0.4850 (2)	0.0265 (6)
C8	0.4825 (2)	0.8584 (2)	0.54206 (14)	0.0227 (6)
C9	0.6016 (2)	0.8478 (2)	0.5546 (2)	0.0238 (6)
C10	0.6018 (3)	0.9906 (2)	0.6415 (2)	0.0278 (6)
C11	0.4838 (3)	1.0040 (2)	0.6342 (2)	0.0288 (6)
C12	0.4228 (2)	0.9383 (2)	0.5833 (2)	0.0270 (6)
O5	0.3413 (2)	0.4781 (2)	0.49228 (15)	0.0394 (6)

Table 2. *Selected geometric parameters* (Å, °)

Cd—O3	2.251 (2)	Cd—O5	2.378 (2)
Cd—O1	2.276 (2)	Cd—O2	2.639 (2)
Cd—N2^{i}	2.307 (3)	Cd—O4	2.879 (2)
Cd—N1^{ii}	2.353 (2)		
O3—Cd—O1	80.73 (7)	O1—Cd—O2	52.87 (7)
O3—Cd—N2^{i}	127.54 (8)	N2^{i}—Cd—O2	96.37 (7)
O1—Cd—N2^{i}	147.42 (8)	N1^{ii}—Cd—O2	88.75 (8)
O3—Cd—N1^{ii}	102.86 (8)	O5—Cd—O2	81.97 (8)
O1—Cd—N1^{ii}	97.18 (8)	O3—Cd—O4	49.06 (7)
N2^{i}—Cd—N1^{ii}	91.91 (8)	O1—Cd—O4	129.74 (7)
O3—Cd—O5	91.50 (9)	N2^{i}—Cd—O4	80.69 (7)
O1—Cd—O5	86.00 (8)	N1^{ii}—Cd—O4	92.56 (7)
N2^{i}—Cd—O5	78.29 (9)	O5—Cd—O4	96.18 (8)
N1^{ii}—Cd—O5	165.60 (9)	O2—Cd—O4	176.82 (7)
O3—Cd—O2	133.38 (7)		

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

H atoms were placed at expected positions, riding, with $U = 1.2U_{\rm eq}$(C), except those of water, which were refined freely.

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL*93 and local programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HR1037). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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