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

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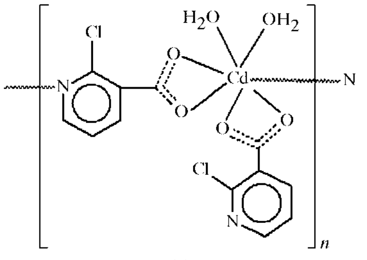
In the title neutral coordination polymer, $[Cd(C_6H_3ClNO_2)_2(H_2O)_2]_n$, each Cd^{II} ion is coordinated by one N and four O atoms from three 2-chloronicotinate ligands and by two aqua ligands, defining a distorted monocapped octahedral coordination geometry. Adjacent Cd atoms are linked by the pyridyl N atom and the bidentate carboxylate functional group of a 2-chloronicotinate ligand, forming a one-dimensional infinite chain along the *b* axis. The Cd···Cd distance is 8.112 (3) Å. These chains are linked by O—H···O and O—H···N hydrogen bonds into a three-dimensional network structure.

Comment

Nicotinic acid and its derivatives, which have good biological activities and versatile bonding modes, have been studied extensively over the past decade. The structures of many of the complexes that have been reported (Moore *et al.*, 1972; Lu & Kohler, 2002; Prout *et al.*, 1985; Clegg *et al.*, 1995; Premkumar & Govindarajan, 2003) show nicotinic acid and its derivatives acting as bridging ligands through the carboxylate group and pyridyl N atom. In order to investigate the steric effect of its *ortho* configuration, we synthesized 2-chloronicotinic acid, which is an important pharmaceutical synthesis intermediate and a potential multifunctional ligand. However, little is known about the structures of its metal complexes (Moncol *et al.*, 2002). In the case of the mononuclear copper complex $[Cu\{2\text{-Cl(nicotinate)}\}_2(Et_2nia)_2(H_2O)_2]$ (where Et_2nia is *N*,*N*′-diethylnicotinamide), the 2-chloronicotinate group adopts a monodentate mode and the Cu^{II} atom has an elongated tetragonal bipyramidal geometry. We report here the synthesis and structure of the title coordination polymer, *viz*. $[Cd\{2\text{-Cl(niconinate)}\}_2(H_2O)_2]_n$, (I).



(I)

As illustrated in Fig. 1, the asymmetric unit of (I) is composed of a Cd^{II} ion, two independent 2-chloronicotinate groups and two coordinated water molecules, the carboxylate groups being bonded to the Cd^{II} ion in a chelating fashion. The Cd^{II} ion is coordinated by four O atoms from two different carboxylate groups, pyridyl atom $N2^{i}$ [symmetry code: (i) *x*, 1 + *y*, *z*] and two aqua ligands. The coordination geometry can best be described as distorted monocapped octahedral. The equatorial plane of the complex is defined by atoms O3, O4, $N2^{i}$ and O2*W* [the r.m.s. deviation for the four ligating atoms is 0.12 (3) Å and the deviation of atom Cd1 from the mean plane is 0.14 (3) Å]. Atoms O1 and O1*W* occupy the apical sites, with a bond angle of 167.71 (8)°. The capping atom, O2, lies 1.768 Å out of the O1/O2*W*/$N2^{i}$ plane. The Cd1—O2 distance [2.654 (3) Å; Table 1] lies within the range of the corresponding bond distances [2.639 (2) and 2.879 (2) Å] reported for the related Cd^{II} two-dimensional coordination polymer $[Cd(nicotinate)_2(H_2O)]_n$, (II) (Clegg *et al.*, 1995). In (I), the axial Cd1—O1*W* bond length [2.315 (2) Å] is longer than the Cd1—O2*W* distance [2.258 (2) Å]. The Cd1—O(carboxylate) distances range from 2.304 (2) to 2.470 (2) Å, except for the Cd1—O2 distance, which is considerably longer. The dihedral angle formed by the two independent pyridyl ring planes is 75.0 (3)°. The dihedral angles between the carboxyl groups and the attached pyridyl rings of the 2-chloronicotinate ligands are 32.5 (3) and 50.5 (3)° in (I), whereas the corre-

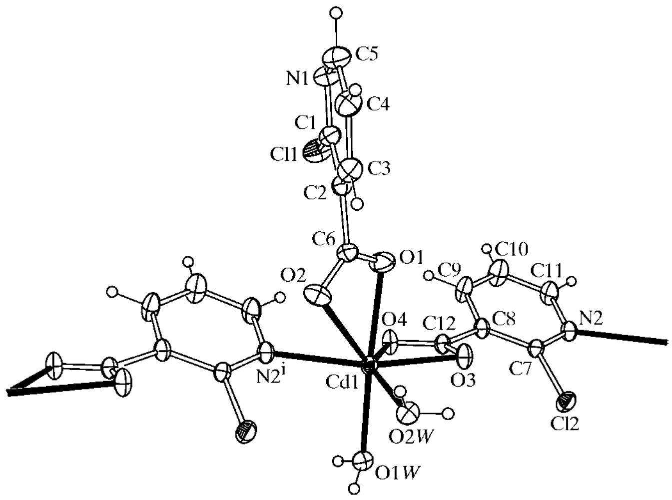


Figure 1
A view of the chain structure of (I), showing 30% probability displacement ellipsoids. [Symmetry code: (i) *x*, 1 + *y*, *z*.]

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sponding dihedral angles for the nicotinate ligands in (II) are 4.6 and 17.4°.

In (II), each Cd^{II} ion forms an approximate pentagonal bipyramidal coordination geometry, with the carboxylate O atoms and one N atom in the equatorial plane (the r.m.s. deviation for the five ligating atoms is $\sim$0.10 Å), and with the second N atom and the aqua ligand in axial positions. The two nicotinate ligands exhibit tridentate modes, binding to the metal atoms through their N atoms and chelating carboxylate functional groups. In (I), one of 2-chloronicotinate ligands has the same coordination mode as the ligands in (II), while the other 2-chloronicotinate ligand exhibits only a chelating mode through its carboxylate group; pyridine atom N1 is not involved in binding to the metal atom. This difference can be attributed to the steric effect of the *ortho* configuration of the ligand, leading to the formation of the distorted monocapped octahedral geometry in (I), which differs from the geometry in (II).

Adjacent Cd atoms are linked by the pyridyl N atom and bidentate carboxylate functional group of one 2-chloronicotinate ligand, forming a one-dimensional infinite chain propagating along the *b* direction. The Cd$\cdots$Cd separation in the chain is 8.112 (3) Å. In addition, chains are connected through intermolecular hydrogen bonds (Table 2) involving the 2-chloronicotinate groups and aqua ligands, with O$\cdots$O/O$\cdots$N distances of 2.700 (3)–2.867 (3) Å and O—H$\cdots$O/O—H$\cdots$N angles of 167 (3)–177 (3)°, thus giving rise to a three-dimensional network structure.

Experimental

2-Chloronicotinic acid was prepared by the reaction of oxidized nicotinic acid and trichlorodeoxyphosphorus (Richter & Vegyeszeti, 1982). Cadmium dinitrate tetrahydrate (6.16 g, 20 mmol) and 2-chloronicotinic acid (3.17 g, 20 mmol) were dissolved separately in water (25 ml) and the two solutions were mixed slowly with stirring at room temperature. The pH was adjusted to 6 with 0.1 *M* sodium hydroxide. Colorless crystals of (I) separated from the filtered solution after several days (yield *ca* 49%). Analysis calculated for $C_{12}H_{10}CdCl_2N_2O_6$: C 31.23, H 2.18, N 6.07%; found: C 31.01, H 2.39, N 5.99%.

Crystal data

$[Cd(C_6H_3ClNO_2)_2(H_2O)_2]$
$M_r = 461.53$
Monoclinic, $P2_1/n$
$a = 10.577$ (2) Å
$b = 8.112$ (2) Å
$c = 19.661$ (4) Å
$\beta = 105.60$ (3)°
$V = 1624.8$ (6) Å^3
$Z = 4$
$D_x = 1.887$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 13 628 reflections
$\theta = 3.2$–27.4°
$\mu = 1.70$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.42 × 0.23 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.535$, $T_{max} = 0.749$
14 573 measured reflections
3725 independent reflections
3444 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -10 \rightarrow 9$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.078$
$S = 1.06$
3725 reflections
220 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 1.7742P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.91$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—O1	2.304 (2)	Cd1—O1*W*	2.315 (2)
Cd1—O2	2.654 (3)	Cd1—O2*W*	2.258 (2)
Cd1—O3	2.356 (2)	Cd1—N2^{i}	2.374 (2)
Cd1—O4	2.470 (2)		
O1—Cd1—O3	82.91 (8)	O2—Cd1—O2*W*	78.26 (8)
O1—Cd1—O4	86.14 (9)	O2—Cd1—N2^{i}	70.8 (9)
O1—Cd1—O1*W*	167.71 (8)	O1*W*—Cd1—O3	89.17 (7)
O1—Cd1—N2^{i}	92.08 (9)	O1*W*—Cd1—O4	81.60 (7)
O3—Cd1—O4	54.26 (6)	O1*W*—Cd1—N2^{i}	88.60 (8)
O3—Cd1—N2^{i}	143.05 (7)	O2*W*—Cd1—O1	104.07 (9)
O2—Cd1—O1	51.80 (9)	O2*W*—Cd1—O3	92.63 (7)
O2—Cd1—O3	128.36 (8)	O2*W*—Cd1—O4	144.37 (7)
O2—Cd1—O4	130.72 (7)	O2*W*—Cd1—O1*W*	85.61 (8)
O2—Cd1—O1*W*	139.23 (7)	O2*W*—Cd1—N2^{i}	123.93 (8)

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

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
O1*W*—H1*W*1$\cdots$O4^{ii}	0.85 (2)	1.91 (2)	2.755 (3)	175 (3)
O1*W*—H1*W*2$\cdots$N1^{iii}	0.85 (3)	2.03 (3)	2.863 (3)	167 (3)
O2*W*—H2*W*1$\cdots$O2^{iv}	0.85 (3)	1.85 (3)	2.700 (3)	177 (3)
O2*W*—H2*W*2$\cdots$O3^{v}	0.85 (3)	2.03 (3)	2.867 (3)	168 (3)

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

The final difference Fourier map had a peak 2.5 Å from atom H4. This peak exists in a solvent-accessible void of 31 Å^3, as suggested by *PLATON* (Spek, 2003). The magnitude of the peak could be decreased by lowering the σ threshold to $2\theta = 50°$; refining this peak as a water O atom did not lead to a meaningful outcome. As the spreading of the electron density by the *SQUEEZE* option (van der Sluis & Spek, 1990) in *PLATON* led to a peak of 0.72 e Å^{-3} near atom Cd1, the peak could not be due to an O atom; the elemental analysis also supported the above results. H atoms were placed in calculated positions [C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$] and were treated in the riding-model approximation. H atoms of water molecules were located in difference-density maps and included in the refinement with O—H and H$\cdots$H distance restraints of 0.85 (1) and 1.39 (1) Å, respectively, and with U_{iso}(H) values of $1.2U_{eq}$(O).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1179). Services for accessing these data are described at the back of the journal.

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