

A one-dimensional Cd^{II} coordination polymer: catena-poly[cadmium(II)-bis(μ -6-methylpicolinato)]

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In the title compound, [Cd(C₇H₆NO₂)₂]_n, the Cd^{II} ion has a distorted octahedral geometry. The 6-methylpyridine-2-carboxylate anions are perpendicular to one another and act as bidentate and bridging ligands. Two carboxylate O atoms bridge the Cd^{II} ions, forming centrosymmetric dinuclear units. These units are further connected *via* carboxylate O atoms into a one-dimensional polymeric chain which extends in the [100] direction.

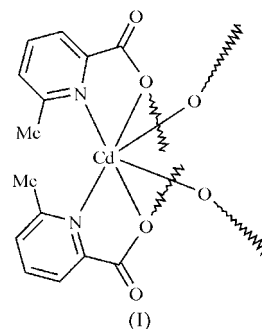
Comment

Several metal ions, such as Zn²⁺, Ca²⁺, Cu²⁺, Mn²⁺ and Mg²⁺, are commonly found in living organisms, acting as structure promoters or playing important roles in enzymatic activity. A systematic study of the coordination chemistry of metal ions in bioinorganic complexes is essential for obtaining a clear understanding of the role of these metals in biochemical processes (Lippert, 2000). The cadmium ion, a congener of zinc, has a similar size to both Zn²⁺ and Ca²⁺, and can therefore replace these ions in their complexes. This fact is utilized in using the cadmium ion as an NMR probe for elucidating the structure around the metal centres. It is also of interest in the identification of its preferred coordination sites, due to the improved control of the interactions in Zn, Cd or Hg homeostasis.

Metal complexes of picolinic acid have been widely investigated, as well as metal complexes of its derivatives containing electron-withdrawing substituents, such as 3- or 6-hydroxypicolinic acid. In contrast, less attention has been paid to complexes of derivatives of picolinic acid containing electron-donating substituents, such as 6-methylpicolinic acid (6-MepicH). To the best of our knowledge, only a few papers deal with this ligand. Three zinc(II) complexes with 6- and 3-methylpicolinic acid (3-MepicH) have been described to

date: [Zn(6-Mepic)₂(H₂O)]·H₂O, which exhibits *in vitro* insulinomimetic activity (Yoshikawa *et al.*, 2002; Pons *et al.*, 2004), and Zn(3-Mepic)₂ and Zn(6-Mepic)₂ (Yoshikawa *et al.*, 2002). Besides these three zinc complexes and the cadmium complex described in this report, only one other complex involving a group 12 element has been structurally described, namely one involving mercury(II) (González-Duarte *et al.*, 1998).

Hitherto, only two complexes of 6-MepicH with 3d block metals have been structurally characterized, namely a mononuclear Co^{II} complex (March *et al.*, 2003) and a heterobinuclear complex containing Cr^{III} (Xu *et al.*, 2006). Various silver salts react with 6-MepicH to give different complexes, but the structure of only one of them, Ag[(6-Mepic)-(6-MepicH)], has been reported to date (Leiva *et al.*, 1999). The only other complexes of 6-methylpicolinic acid with platinum group metals are two containing ruthenium (Rachford *et al.*, 2006) and palladium (Hoare *et al.*, 1996).



In the title complex, (I), the Cd^{II} ion is octahedrally coordinated by two 6-methylpicolinato ligands (Table 1 and Fig. 1) perpendicular to one another. Two carboxylate O atoms from another two symmetry-related ligand molecules are also coordinated to the Cd^{II} ion, expanding its coordination to a distorted octahedron. Each carboxylate O atom in (I) bridges Cd^{II} ions, forming centrosymmetric dinuclear units which are further connected *via* the same O atoms into a one-dimensional chain which extends in the [100] direction (Fig. 2). The bond angles around the Cd centre lie within the range 68–117° for the formally *cis* pairs of

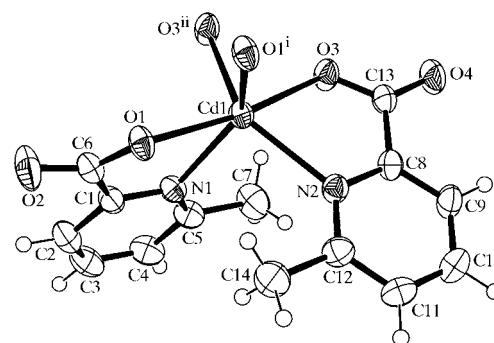


Figure 1

A view of the Cd^{II} coordination environment in the polymeric structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) 1 - x, 2 - y, 1 - z; (ii) -x, 2 - y, 1 - z.]

ligating atoms and 138–173° for the formally *trans* pairs, indicating the distortion of the octahedron (Table 1).

There are only three cadmium(II) coordination polymers found in the literature that are similar to (I). These are poly[bis(μ -pyridine-2-carboxylato)cadmium(II)] (Deloume & Loiseleur, 1974), poly[bis(μ -3-hydroxypyridine-2-carboxylato)cadmium(II)] (Kukovec *et al.*, 2007) and poly[[[bis-[methanolcadmium(II)]- μ_2 -aqua]-bis(μ_3 -pyridine-2,6-dicarboxylato)]] (Wu *et al.*, 2007). In the Cd^{II} complex with picolinic acid, both the coordination mode of the picolinic acid and the type of polymerization are the same as in (I). The Cd–N bond distances [2.35 (1) and 2.34 (2) Å] are comparable with Cd1–N2 in (I) but shorter than Cd1–N1. The Cd–O bond distances [2.35 (2) and 2.36 (2) Å] are slightly longer than in (I), while the other Cd–O bond distances [2.23 (2) and 2.25 (1) Å] (Deloume & Loiseleur, 1974) are shorter than the analogous ones in (I).

The Cd^{II} ion is seven-coordinate in the complex prepared by Wu and co-workers (Wu *et al.*, 2007). Cadmium(II) ions are bridged by pyridine-2,6-dicarboxylate ligands and water molecules into a one-dimensional chain similar to that in (I). Two cadmium(II) dimers with pyridine-2,6-dicarboxylic acid (Odoko *et al.*, 2002) and its ethyl ester (Yang *et al.*, 2004) have been reported. The coordination of Cd^{II} ions is pentagonal-bipyramidal in both dimers, while the Cd^{II} ions are bridged by carboxyl O atoms from the corresponding ligand. The Cd–N bond distances in the Cd^{II} complex with pyridine-2,6-dicarboxylic acid and its ethyl ester are 2.315 (4) (Odoko *et al.*, 2002) and 2.340 (3) Å (Yang *et al.*, 2004), respectively, which are slightly shorter than the corresponding distances in (I), while the Cd–O bond distances (where O is a bridging carboxylate O atom) are 2.396 (4) and 2.376 (3) Å (Odoko *et al.*, 2002), and 2.389 (3) and 2.370 (3) Å (Yang *et al.*, 2004), respectively, which are longer than the analogous values in (I).

The dihedral angle between the least-squares calculated planes through the atoms of the pyridine ring (N1/C1–C5) and the corresponding five-membered chelate ring (Cd1/N1/C1/

C6/O1) is 5.0 (1)°, while the analogous angle (between planes defined by atoms N2/C8–C12 and Cd1/N2/C8/C13/O3) is 4.8 (1)°. The O1–C6 and O3–C13 bond distances of the carboxylate group [1.280 (3) and 1.276 (3) Å, respectively] are longer than O2–C6 and O4–C13 [1.216 (3) and 1.221 (3) Å, respectively] due to the coordination of atoms O1 and O3 to the Cd^{II} atom. This deviation of carboxylate-group geometry was also found for the Pd complex with 6-methylpicolinic acid [1.280 (6) and 1.220 (6) Å; Hoare *et al.*, 1996].

Experimental

A solution of 6-methylpicolinic acid (0.1 g, 0.7 mmol) in water (15 ml) was added to a solution of cadmium(II) acetate dihydrate (0.1 g, 0.4 mmol) in water (5 ml); the pH of the resulting colourless solution was 5. The solution was left to stand for 5 d until the white product of (I) was formed. This was then filtered off, washed with water and dried in air (yield 0.08 g, 57.1%). IR (KBr pellet, ν , cm⁻¹): 2922 (*m*), 1657 (*s*), 1594 (*s*), 1570 (*m*), 1457 (*m*), 1404 (*m*), 1344 (*s*), 1244 (*m*), 791 (*m*), 779 (*m*), 679 (*m*). Colourless crystals of (I) suitable for X-ray analysis were obtained by slow evaporation at room temperature of the mother liquor which remained after removal by filtration of the white product.

Crystal data

[Cd(C ₇ H ₆ NO ₂) ₂]	<i>V</i> = 1350.13 (4) Å ³
<i>M_r</i> = 384.67	<i>Z</i> = 4
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Mo <i>K</i> α radiation
<i>a</i> = 6.8284 (1) Å	μ = 1.64 mm ⁻¹
<i>b</i> = 10.6888 (2) Å	<i>T</i> = 296 (2) K
<i>c</i> = 18.5505 (3) Å	0.13 × 0.10 × 0.02 mm
β = 94.305 (1)°	

Data collection

Oxford Diffraction Xcalibur2 diffractometer with Sapphire-3 CCD detector	33784 measured reflections 3929 independent reflections 2814 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2007)	<i>R_{int}</i> = 0.038
<i>T_{min}</i> = 0.879, <i>T_{max}</i> = 0.968	

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.027	192 parameters
<i>wR</i> (<i>F</i> ²) = 0.062	H-atom parameters constrained
<i>S</i> = 0.95	$\Delta\rho_{\max}$ = 1.44 e Å ⁻³
3929 reflections	$\Delta\rho_{\min}$ = -0.44 e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Cd1–O1 ⁱ	2.2724 (16)	Cd1–N1	2.3739 (18)
Cd1–O3 ⁱⁱ	2.2793 (16)	O1–C6	1.280 (3)
Cd1–O3	2.3247 (16)	O2–C6	1.216 (3)
Cd1–O1	2.3315 (15)	O3–C13	1.276 (3)
Cd1–N2	2.3418 (18)	O4–C13	1.221 (3)
O1–Cd1–O3	172.67 (6)	O1 ⁱ –Cd1–N2	102.29 (6)
O1 ⁱ –Cd1–N1	140.44 (6)	O3–Cd1–N2	70.67 (6)
O3 ⁱⁱ –Cd1–N2	138.53 (6)	O1–Cd1–N2	116.47 (6)
O1 ⁱ –Cd1–O3 ⁱⁱ	98.02 (7)	O3 ⁱⁱ –Cd1–N1	90.89 (6)
O1 ⁱ –Cd1–O3	107.49 (6)	O3–Cd1–N1	111.65 (6)
O3 ⁱⁱ –Cd1–O3	68.87 (6)	O1–Cd1–N1	70.34 (6)
O1 ⁱ –Cd1–O1	70.11 (6)	N2–Cd1–N1	95.75 (7)
O3 ⁱⁱ –Cd1–O1	104.32 (6)		

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $-x, -y + 2, -z + 1$.

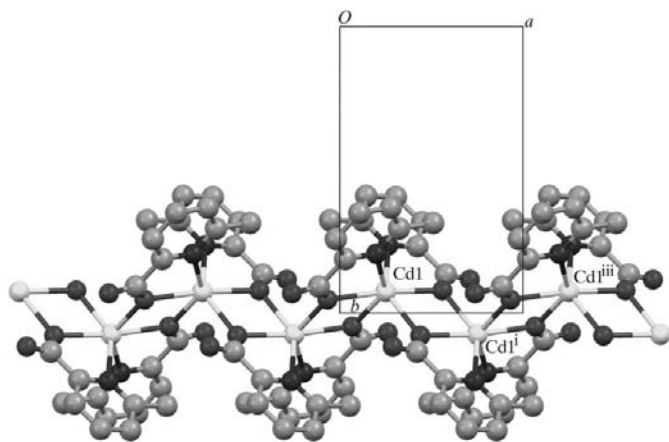


Figure 2

A view of the packing in the structure of (I). [Symmetry codes: (i) $1 - x, 2 - y, 1 - z$; (iii) $1 + x, y, z$.]

H atoms bonded to C atoms were introduced in calculated positions and refined using a riding model, with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic H atoms, and C–H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Version 1.4.2; Macrae *et al.*, 2006); 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: GD3123). Services for accessing these data are described at the back of the journal.

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