

Hexaaquabis(μ -pyridine-2,6-dicarboxylato-*O,N,O':O*)-dicadmium(II)-pyridine-2,6-dicarboxylic acid (1/2)

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Key indicators

Single-crystal X-ray study

 $T = 296$ KMean $\sigma(\text{C}-\text{C}) = 0.007$ Å R factor = 0.037 wR factor = 0.124

Data-to-parameter ratio = 10.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the structure of the title compound, $[\text{Cd}_2(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_6] \cdot 2\text{C}_7\text{H}_5\text{NO}_4$, a centrosymmetric dinuclear Cd^{II} complex and free pyridine-2,6-dicarboxylic acid are present in a 1:2 ratio. Within the dinuclear complex, two Cd^{2+} ions are bridged by two carboxylate O atoms. Each Cd^{2+} ion is coordinated by one N and three O atoms of the pyridine-2,6-dicarboxylato ligands and three water O atoms, resulting in a distorted pentagonal bipyramidal coordination. The crystal structure is stabilized by hydrogen bonds involving all the H atoms of the water ligands.

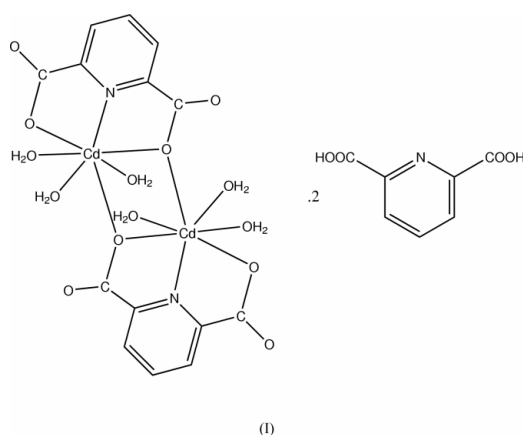
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Comment

Pyridine-2,6-dicarboxylic acid (dipicolinic acid) is present in large amounts in bacterial spores (Powell, 1953; Church & Halvorson, 1959). It has been considered that it contributes to the high heat resistance of bacterial spores, in which it forms a metal complex with divalent metal ions, especially with the Ca^{2+} ion. Many crystal structures of chelate compounds of pyridine-2,6-dicarboxylic acid with divalent ions, such as Ca^{2+} (Strahs & Dickerson, 1968), Ag^{2+} (Drew *et al.*, 1970), Ti^{2+} (Schwarzenbach, 1970), Sr^{2+} (Palmer *et al.*, 1972), Ni^{2+} (Quagliari *et al.*, 1972), Fe^{2+} (Lainé *et al.*, 1995; Lainé *et al.*, 1995), Cu^{2+} , Zn^{2+} (Okabe & Oya, 2000*a*) and Mn^{2+} (Okabe & Oya, 2000*b*) have been determined. In order to clarify the coordination mode of chelate compounds of pyridine-2,6-dicarboxylic acid with divalent metal ions, we have analysed the crystal structure of the title compound, (I).



Crystals of (I) were obtained as a 1:2 mixture of the dinuclear metal complex and free pyridine-2,6-dicarboxylic acid. The Cd^{2+} ions are related by a center of symmetry to each other. Each Cd^{2+} ion is coordinated by two O atoms and one N atom of one ligand molecule, by one carboxylate O atom of the second ligand molecule and by three water O

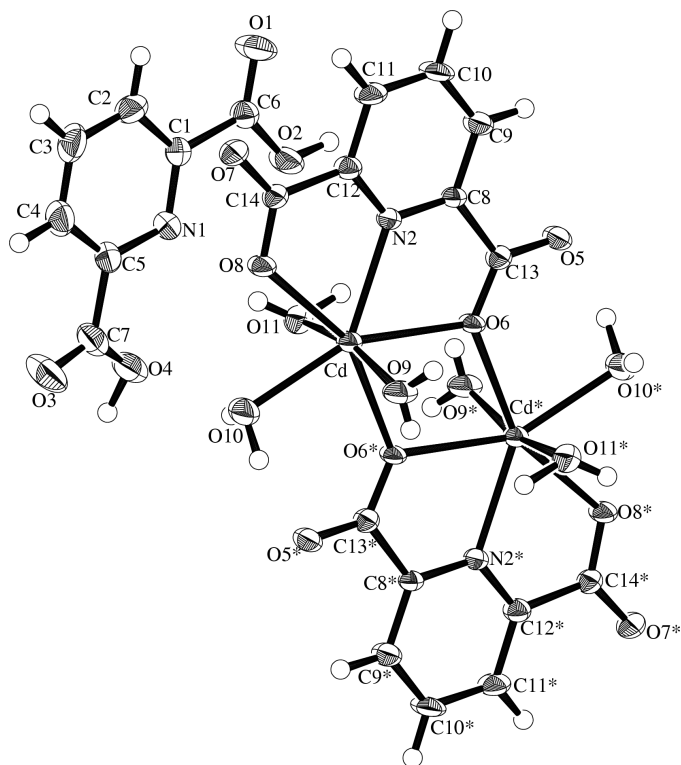


Figure 1
ORTEP (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability.

atoms. In the dinuclear complex, the carboxylate group and the N atom form a five-membered chelate ring with the Cd^{2+} ion (N2/C12/C14/O8/Cd and N2/C8/C13/O6/Cd), and the two Cd^{2+} ions are bridged by two bifurcated coordination bonds of two carboxylate O atoms [O6 and O6ⁱ; symmetry code: (i) $-x, -y, 1-z$]. Each Cd^{2+} ion is seven-coordinate, forming a distorted pentagonal bipyramid, in which the atoms N2, O6, O6ⁱ, O10 and O8 form the distorted pentagonal plane. The pentagonal bipyramidal coordination of the d^2sp^3 -hybridized Cd^{2+} ion seems to be rare; it usually forms an octahedral d^2sp^3 hybridization with six coordination bonds. The planar conformation of the free ligand molecules co-crystallized with the chelate complex in (I) resembles the crystal structure of pyridine-2,6-dicarboxylic acid itself (Takusagawa *et al.*, 1973).

Until now, many crystal structure of chelate compounds of pyridine-2,6-dicarboxylic acid with various metal ions have been determined. In the crystal structures of Ag^{2+} (Drew *et al.*, 1970), Sr^{2+} (Palmer *et al.*, 1972), Ni^{2+} (Quaglieri *et al.*, 1972), Cu^{2+} and Zn^{2+} ions (Okabe & Oya, 2000a), the pyridine-2,6-dicarboxylic acid ligand is coordinated to a mononuclear metal ion and acts as a terdentate ligand, with the central metal ion bonded to two N and four O atoms of two ligand molecules. But the Ti^{2+} , Fe^{2+} , Ca^{2+} and Mn^{2+} complexes are dinuclear, and the Sr^{2+} complex is polynuclear. Among these, the structures of the Fe^{2+} (Lainé *et al.*, 1995) and Mn^{2+} (Okabe & Oya, 2000b) complexes are isomorphous with the Cd^{2+} complex, which are composed of the dinuclear metal complex

and free ligand molecules in a 1:2 ratio. Not only do these structures have the same geometry, but they also have the same space group and similar cell constants. Each metal has three bonds to one ligand molecule, one to the second ligand molecule and three to water molecules. In the crystal structure of the title compound, the complex molecules and free ligand molecules are connected by hydrogen bonds involving all the H atoms of the water ligands.

Experimental

Colorless plate-shaped crystals of (I) were obtained by slow evaporation from a 70% methanol-water solution of pyridine-2,6-dicarboxylic acid and cadmium chloride in a 1:4 molar ratio at room temperature.

Crystal data

$[\text{Cd}_2(\text{C}_7\text{H}_3\text{NO}_4)_2(\text{H}_2\text{O})_6] \cdot 2\text{C}_7\text{H}_5\text{NO}_4$
 $M_r = 997.36$
 Monoclinic, $P2_1/c$
 $a = 9.222(3) \text{ \AA}$
 $b = 14.768(3) \text{ \AA}$
 $c = 12.239(3) \text{ \AA}$
 $\beta = 97.70(2)^\circ$
 $V = 1651.8(7) \text{ \AA}^3$
 $Z = 2$

$D_x = 2.005 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 14.6\text{--}15.0^\circ$
 $\mu = 1.39 \text{ mm}^{-1}$
 $T = 296.2 \text{ K}$
 Plate, colorless
 $0.20 \times 0.20 \times 0.05 \text{ mm}$

Data collection

Rigaku AFC-5R diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.784$, $T_{\max} = 0.933$
 4175 measured reflections
 3788 independent reflections
 2684 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = 0 \rightarrow 11$
 $k = 0 \rightarrow 19$
 $l = -15 \rightarrow 15$
 3 standard reflections
 every 150 reflections
 intensity decay: 1.4%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.124$
 $S = 1.08$
 2684 reflections
 253 parameters

H-atom parameters not refined
 $w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.84 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.39 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Cd—O6	2.396 (4)	Cd—O10	2.271 (4)
Cd—O6 ⁱ	2.376 (3)	Cd—O11	2.434 (3)
Cd—O8	2.478 (4)	Cd—N2	2.315 (4)
Cd—O9	2.310 (4)		
O6—Cd—O6 ⁱ	69.7 (1)	O8—Cd—O11	100.8 (1)
O6—Cd—O8	135.7 (1)	O8—Cd—N2	67.0 (1)
O6—Cd—O9	91.3 (1)	O9—Cd—O10	90.2 (1)
O6—Cd—O10	151.1 (1)	O9—Cd—O11	165.9 (1)
O6—Cd—O11	87.7 (1)	O9—Cd—N2	98.5 (1)
O6—Cd—N2	69.1 (1)	O10—Cd—O11	84.0 (1)
O8—Cd—O9	89.7 (1)	O10—Cd—N2	139.1 (1)
O8—Cd—O10	73.2 (1)	O11—Cd—N2	94.2 (1)

Symmetry codes: (i) $-x, -y, 2-z$.

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H4 \cdots O8 ⁱ	0.99	1.54	2.515 (6)	165
O4—H5 \cdots O11 ⁱⁱ	1.05	1.88	2.821 (5)	166
O9—H9 \cdots O3 ⁱⁱⁱ	0.78	1.98	2.752 (6)	172
O9—H10 \cdots O7 ^{iv}	0.70	2.02	2.713 (5)	177
O10—H11 \cdots O5 ^v	0.96	1.94	2.638 (5)	128
O10—H12 \cdots O4	1.10	2.42	3.117 (5)	133
O11—H13 \cdots O4	0.81	2.57	2.956 (5)	127
O11—H14 \cdots O7 ⁱ	1.01	1.95	2.956 (6)	179

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

H atoms were located from difference Fourier maps and not refined.

Data collection: *MSC/AFSC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFSC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN*.

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