Bis(1,10-phenanthroline)(pyridine-2,6-dicarboxyl-ato)cadmium(II)–pyridine–2,6-dicarboxylic acid–water (1/1/4)

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Key indicators

Single-crystal X-ray study

T = 173 K

Mean σ(C–C) = 0.003 Å

H-atom completeness 91%

Disorder in solvent or counterion

R factor = 0.027

wR factor = 0.070

Data-to-parameter ratio = 17.4

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

The mixed-ligand title complex, [Cd(C$_7$H$_3$NO$_4$)(C$_{12}$H$_8$N$_2$)$_2$]·C$_7$H$_5$NO$_4$·4H$_2$O, contains a seven-coordinate Cd atom with a distorted pentagonal bipyramidal geometry. The asymmetric unit also contains an uncoordinated pyridine-2,6-dicarboxylic acid molecule and four water molecules. The units are linked via O—H···O and O—H···N hydrogen bonds, forming a three-dimensional network.

Comment

The title compound, (I), is the first cadmium complex to incorporate both 1,10-phenanthroline and pyridine-2,6-di-carboxyate ligands. It was prepared from cadmium chloride and an adduct of the two ligands.

(I)
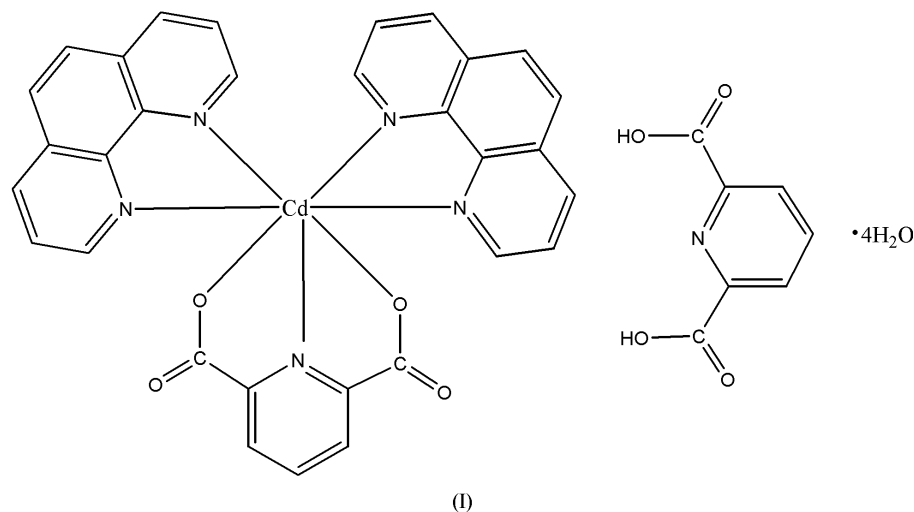
The molecular structure of (I) is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The central Cd atom is coordinated by four N atoms from two bidentate 1,10-phenanthroline molecules, with an average Cd—N bond length of 2.368 (1) Å. This is similar to the values for other Cd–1,10-phenanthroline complexes reported previously (Aragoni *et al.*, 2002; Chen *et al.*, 2003; Yang *et al.*, 2003). Atom Cd1 is also coordinated by one N and two O atoms from the tridentate pyridine-2,6-dicarboxylate ligand. The shortest Cd—N bond is Cd1—N5 [2.3080 (14) Å]. This is in agreement with the values reported previously for seven-coordinate cadmium complexes containing pyridine-2,6-di-carboxylate as a ligand (Ranjbar *et al.*, 2002; Odoko *et al.*, 2002).

The geometry of the complex is distorted pentagonal bipyramidal with two N atoms, N1 and N4 (one from each 1,10-phenanthroline ligand), in axial sites. The equatorial
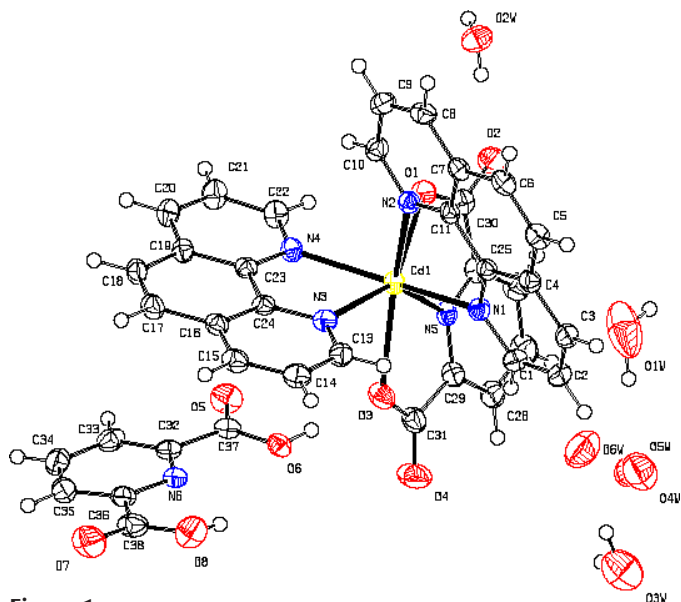
Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level (arbitrary spheres for the H atoms).
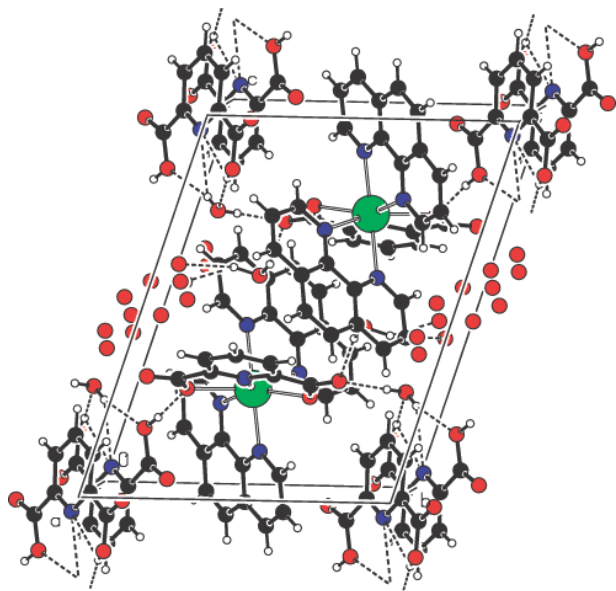

Figure 2
The crystal packing in (I), viewed approximately down the *a* axis; hydrogen bonds are indicated by dashed lines.

PLATON (Spek, 2003) analysis of (I), although their chemical significance is uncertain.

Experimental

In order to prepare an adduct of the two ligands, an aqueous solution of pyridine-2,6-dicarboxylic acid (pydcH₂) and 1,10-phenanthroline (phen) in a 1:2 molar ratio was refluxed for an hour. Slow concentration of the solution at room temperature gave an adduct of the two ligands in a 1:2 molar ratio. The melting point of the adduct is different from those of the starting materials. IR and NMR characterization suggested that proton transfer had occurred from pydcH₂ to phen. The complex was synthesized by the reaction of the adduct and cadmium(II) chloride monohydrate in a 2:1 molar ratio in water. Colourless rod-like crystals of (I) were obtained by slow evaporation of the solvent at room temperature. The block-like crystal used for data collection was cut from a rod.

Crystal data

$[Cd(C_7H_3NO_4)(C_{12}H_8N_2)_2]\cdot$ $C_7H_5NO_4\cdot4H_2O$	$Z = 2$ $D_x = 1.620$ Mg m^{-3}
$M_r = 877.10$	Mo $K\alpha$ radiation
Triclinic, $P\bar{1}$	Cell parameters from 29056
$a = 10.9455$ (7) Å	reflections
$b = 12.1212$ (8) Å	$\theta = 1.9–29.6°$
$c = 15.5145$ (11) Å	$\mu = 0.68$ mm^{-1}
$\alpha = 67.355$ (5)°	$T = 173$ (2) K
$\beta = 74.854$ (5)°	Block, colourless
$\gamma = 74.044$ (5)°	$0.35 \times 0.30 \times 0.22$ mm
$V = 1798.2$ (2) Å^3	

Data collection

Stoe IPDS-2 Image Plate diffractometer	8530 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.029$
Absorption correction: none	$\theta_{max} = 29.2°$
26165 measured reflections	$h = -14 \rightarrow 14$
9657 independent reflections	$k = -16 \rightarrow 16$
	$l = -21 \rightarrow 21$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0435P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.027$	$+ 0.2854P]$
$wR(F^2) = 0.070$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.014$
9657 reflections	$\Delta\rho_{max} = 0.76$ e Å^{-3}
554 parameters	$\Delta\rho_{min} = -0.65$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

Cd1—N5	2.3080 (14)	Cd1—N3	2.4262 (14)
Cd1—N4	2.3356 (14)	Cd1—O1	2.4313 (12)
Cd1—N2	2.3528 (15)	Cd1—O3	2.4700 (13)
Cd1—N1	2.4162 (15)		
N5—Cd1—N4	112.20 (5)	N4—Cd1—O1	84.32 (5)
N5—Cd1—N2	134.15 (5)	N2—Cd1—O1	76.11 (5)
N4—Cd1—N2	91.68 (5)	N1—Cd1—O1	109.30 (5)
N5—Cd1—N1	95.06 (5)	N3—Cd1—O1	145.06 (5)
N4—Cd1—N1	152.60 (5)	N5—Cd1—O3	67.63 (5)
N2—Cd1—N1	69.84 (5)	N4—Cd1—O3	99.04 (5)
N5—Cd1—N3	143.10 (5)	N2—Cd1—O3	148.90 (5)
N4—Cd1—N3	70.38 (5)	N1—Cd1—O3	88.55 (5)
N2—Cd1—N3	80.83 (5)	N3—Cd1—O3	75.57 (4)
N1—Cd1—N3	86.37 (5)	O1—Cd1—O3	133.73 (4)
N5—Cd1—O1	68.51 (5)		

positions are occupied by atoms N2 and N3 of the 1,10-phenanthroline ligands, and atoms O1, N5 and O3 of the pyridine-2,6-dicarboxylate ligand. The angle N4···Cd1···N1 is 152.60 (5)°. With respect to the angles in the equatorial plane, the largest and smallest deviations from the ideal value of 72° are observed for N2—Cd1—N3 [80.83 (5)°] and N3—Cd1—O3 [75.57 (4)°], respectively.

The crystal packing in (I) involves many O—H···O and O—H···N hydrogen bonds (Table 2), with H···*A* distances ranging from 1.77 (3) to 2.54 (3) Å. This leads to the formation of a three-dimensional network, as shown in Fig. 2. A number of C—H···O interactions (Table 2) were identified in a

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1$WA\cdots$O2$^{\text{i}}$	0.91 (7)	1.95 (6)	2.797 (4)	155 (6)
O1W—H1$WB\cdots$O4W	0.99 (4)	2.51 (5)	3.357 (7)	144 (5)
O1W—H1$WB\cdots$O6W	0.99 (4)	1.89 (3)	2.738 (7)	143 (5)
O2W—H2$WA\cdots$O6$^{\text{ii}}$	0.74 (3)	2.16 (3)	2.880 (2)	166 (3)
O2W—H2$WA\cdots$N6$^{\text{ii}}$	0.74 (3)	2.54 (3)	3.013 (2)	124 (3)
O2W—H2$WB\cdots$O2	0.79 (4)	1.98 (4)	2.762 (2)	179 (4)
O3W—H3$WA\cdots$O5W	0.90	2.22	2.916 (8)	134
O6—H6$\cdots$O3	0.81 (3)	1.77 (3)	2.575 (2)	173 (3)
O8—H8$\cdots$O2W^{iii}	0.83 (3)	1.93 (3)	2.741 (3)	165 (3)
O8—H8$\cdots$N6	0.83 (3)	2.35 (3)	2.696 (2)	105 (2)
C2—H2$A\cdots$O4$^{\text{iv}}$	0.95	2.45	3.337 (3)	155
C8—H8$A\cdots$O1W^{v}	0.95	2.36	3.251 (4)	155
C13—H13$A\cdots$O3W^{iv}	0.95	2.56	3.220 (6)	127
C15—H15$A\cdots$O7$^{\text{vi}}$	0.95	2.49	3.346 (3)	151
C17—H17$A\cdots$O7$^{\text{vi}}$	0.95	2.59	3.427 (3)	147
C22—H22$A\cdots$O1	0.95	2.59	3.193 (2)	122
C33—H33$A\cdots$O2$^{\text{vii}}$	0.95	2.59	3.373 (3)	140

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x, 1+y, z$; (iii) $x, y-1, z$; (iv) $1-x, -y, 1-z$; (v) $-x, 1-y, 1-z$; (vi) $-x, -y, -z$; (vii) $1-x, 1-y, -z$.

Some of the water H atoms could be located in Fourier difference maps. In the final refinement cycles they were either refined with an O—H distance restraint of 0.90 (2) Å or as riding on their carrier O atom. The constraint U_{iso}(H) = $1.5U_{\text{eq}}$(O) was applied in all cases. The other H atoms were included in calculated positions and treated as riding atoms using *SHELXL*97 (Sheldrick, 1997) default parameters; C—H = 0.95 Å and U_{iso}(H) = $1.2U_{\text{eq}}$(parent C atom). Atoms O3W, O4W, O5W, and O6W are disordered with occupancies of 0.5. The H atoms attached to O4W, O5W, and O6W were not found.

Data collection: *X-AREA* (Stoe, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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