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An aquacadmium(II) complex of 1,10-phenanthroline with a fumarate counter-ion

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Key indicators

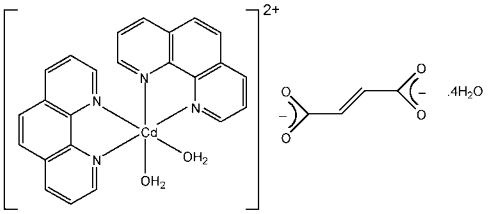
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.032
wR factor = 0.107
Data-to-parameter ratio = 15.6

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

In the title compound, diaquabis(1,10-phenanthroline-κ^2N,N')cadmium(II) fumarate tetrahydrate, $[Cd(phen)_2(H_2O)_2]L\cdot 4H_2O$ where phen is 1,10-phenanthroline ($C_{12}H_8N_2$) and L^{2-} is the fumarate anion ($C_4H_2O_4^{2-}$), the cadmium(II) cation is six-coordinated by two water molecules and four N atoms derived from two phen molecules. Each of the two independent L^{2-} anions is located about an inversion centre and they do not coordinate to cadmium(II), acting rather as counter-ions. The water molecules and L^{2-} anions are linked through a complex hydrogen-bonding network to form a three-dimensional structure.

Comment

In recent years, studies on metal carboxylate complexes with aromatic N-donor chelating ligands have attracted special attention owing to their interesting structural and chemical properties (Cariati *et al.*, 1983; Hammershoi *et al.*, 1984; Robl, 1992). In their reported X-ray structures, the anion derived from fumaric acid has been found to be a versatile ligand, so that the coordination mode can be tailored by introducing different neutral ligands to the complex (Young *et al.*, 1998). Here, we present the crystal structure of (I), which is isomorphous with the recently reported zinc(II) structure (Yang *et al.*, 2003).



(I)

The structure of (I) reveals that the coordination environment of the cadmium(II) cation is defined by two water molecules and four N atoms, derived from two phen molecules (Fig. 1 and Table 1). Two independent fumarate ions, each disposed about a centre of inversion, provide the charge balance. There are four non-coordinating water molecules in the asymmetric unit.

The carboxylate groups of the L^{2-} anions do not coordinate to the cadmium(II) cation; a similar situation pertains in $[Zn(phen)_2(H_2O)_2]L\cdot 4H_2O$ (Yang *et al.*, 2003). The presence of uncoordinated L^{2-} anions is somewhat unexpected, because the carboxylate group is generally considered to be a better coordinating group than water for cadmium(II). In the related compound, $[Cu_2(C_4H_2O_4)(C_{14}H_{33}N_3)_2](ClO_4)_2$ (Char-

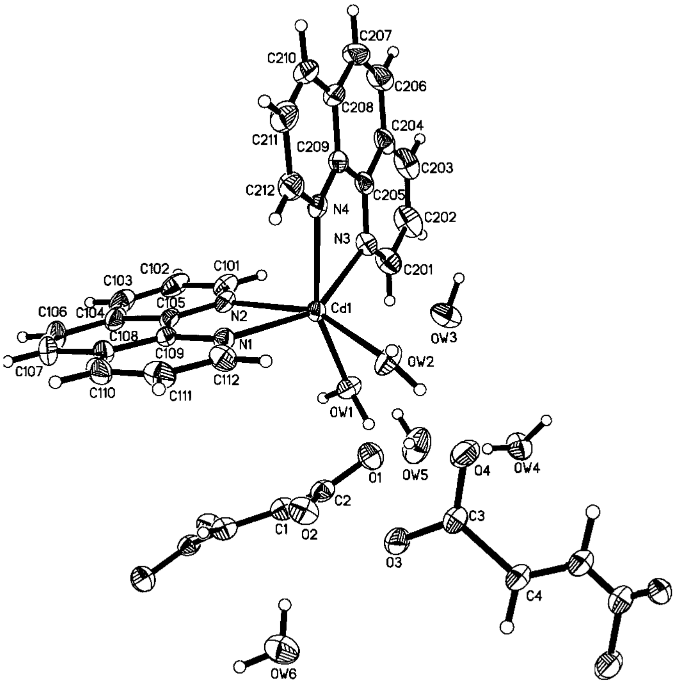


Figure 1

View of the cation, two centrosymmetric anions and two water molecules of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level (Sheldrick, 1990).

pin *et al.*, 1987), the carboxylate O atoms coordinate to copper(II) to form a dimer.

In the crystal structure of (I), water molecules and L^{2-} anions are linked through hydrogen bonds to form a complex three-dimensional network. All 12 acidic H atoms participate in hydrogen-bonding interactions (Table 2). The water molecules function as both acceptors and donors, while the carboxylate O atoms are only acceptors, consistent with their anionic status.

Experimental

A mixture of fumaric acid (0.116 g, 1 mmol) and NaOH (0.080 g, 2 mmol) in water (10 ml) was stirred at room temperature, then $CdCl_2 \cdot 2.5H_2O$ (0.228 g, 1 mmol) was then added with constant stirring. 1,10-Phenanthroline (0.198 g, 1 mmol) was then added to the resulting suspension. Colourless crystals of (I) were obtained after allowing the solution to stand at room temperature for several days. Yield: 73% (based on Cd). Analysis calculated for $[Cd(phen)_2(H_2O)_2]L \cdot 4H_2O$: C 48.35, H 4.32, N 8.06%; found: C 48.51, H 4.44, N 7.91%.

Crystal data

$[Cd(C_{12}H_8N_2)_2(H_2O)_2]$-
$(C_4H_2O_4) \cdot 4H_2O$
$M_r = 694.96$
Triclinic, $P\overline{1}$
$a = 10.619$ (2) Å
$b = 10.630$ (2) Å
$c = 13.586$ (3) Å
$\alpha = 95.19$ (3)°
$\beta = 95.56$ (3)°
$\gamma = 104.94$ (3)°
$V = 1464.1$ (6) Å^3

$Z = 2$
$D_x = 1.576$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6009 reflections
$\theta = 1.5$–27.4°
$\mu = 0.81$ mm^{-1}
$T = 293$ (2) K
Block, colorless
0.28 × 0.24 × 0.17 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.791$, $T_{max} = 0.874$
14103 measured reflections

6613 independent reflections
5875 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 27.4°$
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 13$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.107$
$S = 1.09$
6613 reflections
424 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0739P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -1.06$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Cd1—OW1	2.252 (2)	Cd1—N2	2.383 (2)
Cd1—OW2	2.259 (2)	Cd1—N3	2.338 (2)
Cd1—N1	2.340 (2)	Cd1—N4	2.365 (2)
OW1—Cd1—OW2	82.59 (8)	OW2—Cd1—N4	96.85 (9)
OW1—Cd1—N1	113.70 (8)	N1—Cd1—N2	70.94 (8)
OW1—Cd1—N2	89.55 (8)	N1—Cd1—N3	150.62 (9)
OW1—Cd1—N3	87.18 (9)	N1—Cd1—N4	89.84 (8)
OW1—Cd1—N4	156.45 (8)	N2—Cd1—N3	89.70 (9)
OW2—Cd1—N1	91.67 (8)	N2—Cd1—N4	99.17 (8)
OW2—Cd1—N2	156.18 (9)	N3—Cd1—N4	71.15 (9)
OW2—Cd1—N3	112.20 (9)		

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
OW2—H21···O4	0.92 (4)	1.80 (2)	2.718 (3)	178 (4)
OW2—H22···OW4^{i}	0.92 (4)	1.77 (2)	2.680 (3)	171 (4)
OW1—H12···O2	0.91 (4)	1.71 (2)	2.618 (3)	176 (5)
OW1—H11···O3	0.93 (4)	1.78 (2)	2.700 (3)	171 (4)
OW3—H31···O3^{ii}	0.92 (4)	1.89 (2)	2.800 (3)	174 (4)
OW3—H32···OW6^{ii}	0.90 (4)	1.95 (2)	2.832 (4)	168 (4)
OW4—H42···O4^{iii}	0.90 (4)	1.85 (2)	2.746 (3)	170 (4)
OW4—H41···OW5	0.90 (4)	1.83 (2)	2.721 (4)	171 (4)
OW5—H51···OW3	0.91 (4)	1.96 (2)	2.835 (4)	162 (4)
OW5—H52···O1	0.91 (4)	1.89 (2)	2.762 (4)	162 (4)
OW6—H61···O2	0.90 (4)	1.93 (2)	2.816 (3)	172 (4)
OW6—H62···OW3^{iv}	0.90 (4)	2.03 (2)	2.913 (4)	173 (4)

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

All H atoms on C atoms were positioned geometrically and refined in the riding model approximation, with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atoms of water molecules were located from a difference Fourier map and were refined with restrained O—H distances of 0.93 (4) Å and $U_{iso}(H) = 1.5U_{eq}(O)$.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

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