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Bis(μ-ethyl pyridine-2,6-dicarboxylato)bis[diaquachlorocadmium(II)] dihydrate

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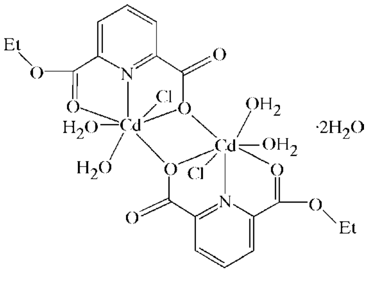
The reaction of cadmium chloride with pyridine-2,6-dicarboxylic acid (PDA) and 98% H_2SO_4 in ethanol led to the formation of the title compound, bis[μ-6-(ethoxycarbonyl)pyridine-2-carboxylato]-1:2$\kappa^4O^6,N,O^2:O^2$;1:2$\kappa^4O^2:O^2,N,O^6$-bis[diaquachlorocadmium(II)] dihydrate, $[Cd_2(C_9H_8NO_4)_2Cl_2(H_2O)_4]\cdot 2H_2O$. PDA is esterified to monoethyl pyridine-2,6-dicarboxylate (MEPD) by the catalysis of H_2SO_4 during the reaction. The dinuclear Cd^{II} complex lies about an inversion centre and the unique Cd atom has a pentagonal–bipyramidal geometry. The two Cd atoms are bridged by two carboxylate O atoms, forming a planar Cd_2O_2 unit. Stair-like chains are formed *via* O—H$\cdots$Cl hydrogen bonds and these are further arranged into two-dimensional layers *via* hydrogen bonds involving solvate water molecules.

Comment

Pyridine-2,6-dicarboxylate and diethyl pyridine-2,6-dicarboxylate (DEPD) are pentadentate ligands which generally act as tridentate meridional ligands, with their one amino and two carboxyl (or ester) groups acting as the chelating terminals. Many of their metal complexes have been reported (Kapoor *et al.*, 2002; MacDonald *et al.*, 2000; Yang *et al.*, 2002; Odoko *et al.*, 2002). However, a metal complex of monoethyl pyridine-2,6-dicarboxylate (MEPD) has not been reported to date. Cadmium has increasingly attracted research attention over the years due to its toxic manifestations in the environment and various animal or human organisms (Hammond & Foulkes, 1986). We report here the synthesis and crystal structure of the title Cd complex, (I), which is the first metal–MEPD complex.



(I)

Compound (I) was prepared by reaction of cadmium(II) chloride with pyridine-2,6-dicarboxylic acid and 98% H_2SO_4 in ethanol. The crystallographic analysis reveals that (I) is a dinuclear complex, *viz*. $[Cd_2(MEPD)_2Cl_2(H_2O)_4]\cdot 2H_2O$, in which MEPD is derived from the monoesterification of PDA *via* the catalysis of sulfuric acid. It is puzzling that we have not obtained PDA or DEPD complexes, but only the monoesterified MEPD product. At least two kinds of reactions exist in the synthetic system, namely esterification and self-assembly of the metal complex. MEPD is formed by the monoesterification of PDA or the monohydrolysis of DEPD, or by both reactions.

In the title complex, two Cd atoms are bridged by two carboxylate μ-O atoms from MEPD ligands, forming a centrosymmetric Cd_2O_2 parallelogram unit. Each Cd^{II} atom is coordinated by one N and three O atoms of MEPD ligands, as well as one Cl^- and two water O atoms, resulting in a distorted pentagonal–bipyramidal coordination with Cl1—Cd1—O2*W* in the axial direction (Fig. 1 and Table 1). The bond distances of Cd to the μ-O atoms [Cd1—O4 = 2.389 (3) Å and Cd1—O4^i = 2.370 (3) Å; symmetry code: (i) $1 - x, 1 - y, -z$] are apparently shorter than that of the carbonyl O atom on the ester side [Cd1—O1 = 2.573 (3) Å], and the bond distance to the central pyridine N atom (Cd1—N1) is 2.340 (3) Å, slightly shorter than these Cd1—O bonds.

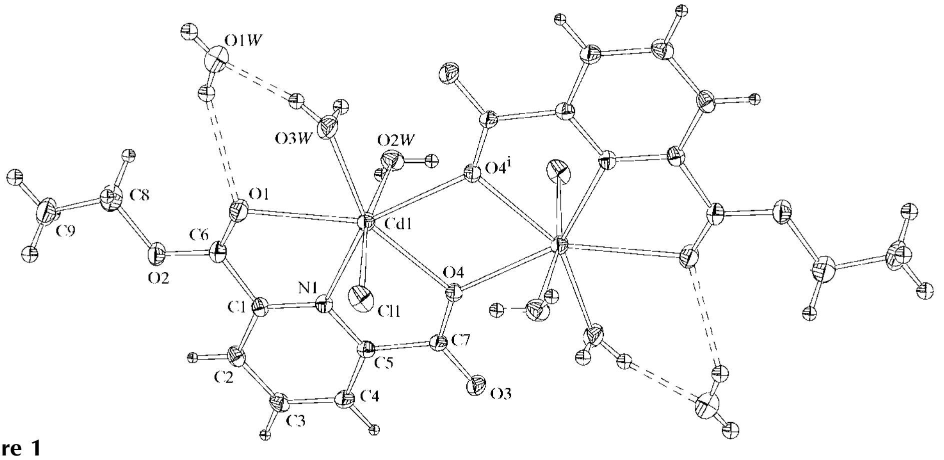


Figure 1
A view of (I) with the atom-labelling scheme, showing some of the intramolecular hydrogen bonds (dashed lines). Displacement ellipsoids are drawn at the 20% probability level. [Symmetry code: (i) $1 - x, 1 - y, -z$.]

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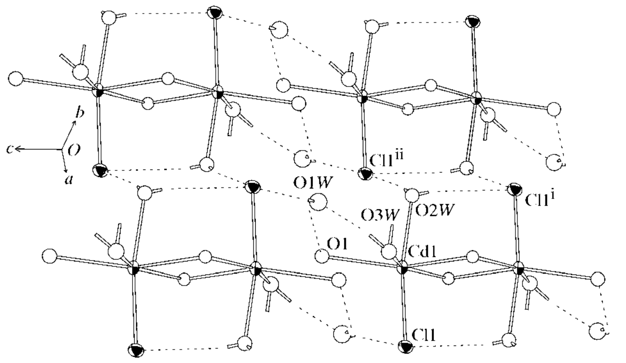

Figure 2
An illustration of the two-dimensional supramolecular layer (containing one-dimensional stairs) in the crystal structure of (I). The O—H···O and O—H···Cl interactions are indicated by dashed lines. [Symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $x - 1, y, z$.]

The investigation of hydrogen bonding is important for many practical applications, such as the design of antibiotics and the development of new materials with programmed properties (Bong *et al.*, 2001). A great variety of supramolecular assemblies owe their well defined structure to the existence of adjacent hydrogen-bond units of complementary constituent parts (MacDonald *et al.*, 2000). In (I), there is an intramolecular O2*W*—H2*WB*···$Cl1^{i}$ hydrogen bond, and intermolecular O—H···Cl and O—H···O hydrogen bonds (Table 2). The metal complexes are linked into one-dimensional stairs *via* an O2*W*—H2*WA*···$Cl1^{ii}$ hydrogen bond [Fig. 2; symmetry code: (ii) $x - 1, y, z$]. In other words, Cd_2O_2 and $Cl_2(H_2O)_2$ rings are arranged alternately along the extended direction of the Cd—Cl bond (Fig. 2). The Cd···Cd distance in the Cd_2O_2 parallelogram unit is 3.849 (5) Å, and the shortest Cd···Cd distance in the stairs is 6.841 (3) Å. The most interesting feature is that the solvate water molecule (O1*W*) acts as a junction to connect the one-dimensional stairs into two-dimensional layers *via* O—H···O and O—H···Cl hydrogen bonds.

Experimental

A mixture of 8-hydroxyquinoline (0.5 mmol), pyridine-2,6-dicarboxylic acid (0.5 mmol), $CdCl_2·2H_2O$ (0.5 mmol), dry ethanol (25 ml) and H_2SO_4 (98%, 1 ml) was stirred at *ca* 333 K for 2 h and then filtered. The filtrate was kept at room temperature for several days and produced pale-red crystals of the title compound (yield 8%).

Crystal data

$[Cd_2(C_9H_8NO_4)_2Cl_2(H_2O)_4]·2H_2O$
$M_r = 792.12$
Triclinic, $P\overline{1}$
$a = 6.8414 (6)$ Å
$b = 10.7408 (9)$ Å
$c = 10.7597 (9)$ Å
$\alpha = 64.042 (2)°$
$\beta = 77.298 (2)°$
$\gamma = 72.810 (2)°$
$V = 675.35 (10)$ Å^3
$Z = 1$
$D_x = 1.948$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 2630 reflections
$\theta = 2.1–25.1°$
$\mu = 1.84$ mm^{-1}
$T = 293 (2)$ K
Prism, pale red
0.60 × 0.28 × 0.26 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.416$, $T_{max} = 0.620$
3540 measured reflections

2371 independent reflections
2167 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25.1°$
$h = -6 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -11 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.089$
$S = 1.04$
2371 reflections
190 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2 + 0.9504P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 1.04$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—O3*W*	2.277 (4)	O1—C6	1.208 (6)
Cd1—N1	2.340 (3)	O2—C6	1.314 (5)
Cd1—$O4^{i}$	2.370 (3)	O2—C8	1.505 (6)
Cd1—O2*W*	2.381 (4)	O3—C7	1.228 (5)
Cd1—O4	2.389 (3)	O4—C7	1.259 (5)
Cd1—Cl1	2.5508 (13)	O4—$Cd1^{i}$	2.370 (3)
Cd1—O1	2.573 (3)		
O3*W*—Cd1—N1	138.56 (13)	N1—Cd1—Cl1	94.23 (9)
O3*W*—Cd1—$O4^{i}$	80.15 (12)	$O4^{i}$—Cd1—Cl1	92.37 (8)
N1—Cd1—$O4^{i}$	140.12 (11)	O2*W*—Cd1—Cl1	168.95 (10)
O3*W*—Cd1—O2*W*	93.61 (15)	O4—Cd1—Cl1	88.01 (8)
N1—Cd1—O2*W*	87.04 (12)	O3*W*—Cd1—O1	72.30 (12)
$O4^{i}$—Cd1—O2*W*	79.79 (12)	N1—Cd1—O1	66.27 (11)
O3*W*—Cd1—O4	152.23 (12)	$O4^{i}$—Cd1—O1	150.56 (10)
N1—Cd1—O4	68.90 (10)	O2*W*—Cd1—O1	91.60 (13)
$O4^{i}$—Cd1—O4	72.08 (11)	O4—Cd1—O1	134.99 (10)
O2*W*—Cd1—O4	82.20 (12)	Cl1—Cd1—O1	98.97 (9)
O3*W*—Cd1—Cl1	92.68 (12)	$Cd1^{i}$—O4—Cd1	107.92 (11)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2*W*—H2*WB*···$Cl1^{i}$	0.81 (2)	2.61 (2)	3.405 (4)	170 (6)
O2*W*—H2*WA*···$Cl1^{ii}$	0.81 (6)	2.43 (6)	3.227 (4)	168 (6)
O1*W*—H1*WB*···$Cl1^{iii}$	0.81 (6)	2.55 (7)	3.348 (5)	167 (8)
O1*W*—H1*WA*···O1	0.81 (7)	2.54 (6)	3.054 (6)	123 (7)
O3*W*—H3*WA*···O1*W*	0.84 (5)	1.96 (6)	2.757 (6)	158 (7)

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

H atoms bonded to C atoms were located geometrically, with C—H distances of 0.93 Å, and treated as riding atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). H atoms bonded to O atoms were located from difference density maps and refined with O—H bond distances restrained to 0.81–0.84 Å and with $U_{iso}(H) = 1.5U_{eq}(O)$. The highest residual peak is 1.02 Å from atom C8 and the deepest hole is 0.99 Å from atom Cd1.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART* and *SAINT* (Siemens, 1994); data reduction: *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1187). Services for accessing these data are described at the back of the journal.

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