

cis-Diaquabis[*(E)*-4-(2-hydroxybenzylideneamino)benzoato- κ^2 O,O']-cadmium(II): two-dimensional layers built from strong O—H...O hydrogen bonding in the coordination sphere

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Received 21 February 2006

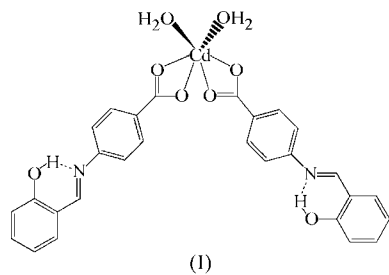
Accepted 15 March 2006

Online 13 April 2006

In the title compound, [Cd(C₁₄H₁₀NO₃)₂(H₂O)₂], which crystallizes with *Z* = 4 in the space group *C2c*, the Cd atom is located on a twofold rotation axis and coordinated by six O atoms from two water molecules and two carboxylate groups of two planar 4-(2-hydroxybenzylideneamino)benzoate ligands, with a dihedral angle of 85.6 (1)° between them. Strong O—H...O hydrogen bonding in the coordination sphere, together with π - π stacking interactions, assemble the molecules into two-dimensional layers.

Comment

Schiff base metal complexes have versatile functions, for example, Schiff base titanium(IV), cobalt(II), vanadium(III, IV, V) and copper(II) complexes can act as catalysts (Huang *et al.*, 2002; Niimi *et al.*, 2000; Liu & Anson, 2001; Bluhm *et al.*, 2003), Tb^{III} salen complexes have luminescent properties (Yang & Jones, 2005), non-linear absorption behaviour has been investigated in Schiff base zinc(II) and copper(I) complexes (Das *et al.*, 2006), and so on. All these properties



have attracted our interest. In one recent experiment, we synthesized 4-(2-hydroxybenzylideneamino)benzoic acid and intended to complex it with metal ions *via* the Schiff base

moiety, but instead, the title compound, (I), was obtained, with the carboxylate group coordinating to cadmium.

A perspective view of compound (I), with the atom-labelling scheme, is illustrated in Fig. 1. In (I), the Cd atom is located on a twofold rotation axis and is coordinated by six O atoms from two water molecules and two carboxyl groups of two 4-(2-hydroxybenzylideneamino)benzoic acid ligands. The two Cd—O(carboxyl) bond lengths are 2.232 (4) and 2.508 (4) Å, exhibiting an obvious difference. The two water

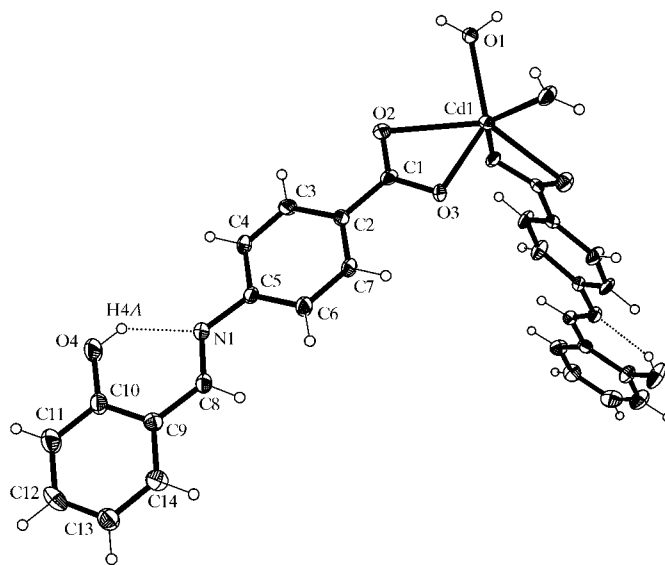


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dotted lines indicate hydrogen bonds. Unlabelled atoms are related to labelled atoms by the symmetry operator $(1-x, y, \frac{3}{2}-z)$.

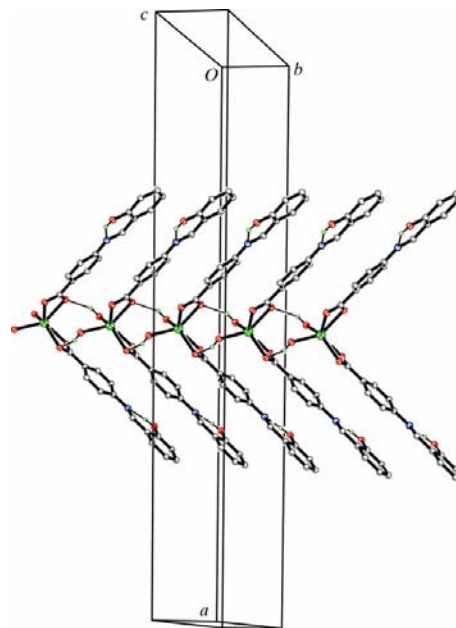


Figure 2

The one-dimensional penniform tape built from O—H...O hydrogen bonding (dotted lines) and π - π stacking between the planar ligands of (I). Cd atoms are cross-hatched, O atoms are hatched, N atoms have a central dot, C atoms are part shaded and H atoms are small open circles.

molecules are tightly coordinated to Cd, with a Cd—O(water) distance of 2.191 (4) Å. All these features are similar to those in the analogous complexes [Cd(C₇H₄NO₄)₂(H₂O)₂], [Cd-(C₇H₄ClO₂)₂(H₂O)₂] and [Cd(C₉H₇O₄)₂(H₂O)₂] (Rodesiler *et al.*, 1985; Vásquez-Árciga *et al.*, 2004). In the present compound, the ligand adopts a planar geometry, forming a large π -conjugation system. The two coordinated planar ligands form a dihedral angle of 85.6 (1)°, leading to an arrowhead shape for (I).

A noteworthy feature of this compound is that it is the carboxylate group and not the Schiff base moiety that coordinates to cadmium. The Schiff base moiety is only involved in an intramolecular hydrogen bond. To date, analogous coordination has only been reported for the crystal structures of Sn complexes (Yin *et al.*, 2005). This situation possibly implies that the coordination ability of the Schiff base moiety in this ligand is affected by the terminal carboxylate group, or that Cd and Sn have a greater preference for coordination by the two O atoms of the carboxylate group than do other metal ions. Indeed, there are many such Cd and Sn complexes in which Cd or Sn are coordinated by both O atoms of one carboxylate group (see, for example, Charles *et al.*, 1983; Rodesiler *et al.*, 1985; Ng *et al.*, 1990; Aletras *et al.*, 1997; Gao *et al.*, 2004; Zou *et al.*, 2004; Paz & Klinowski, 2004; Vásquez-Árciga *et al.*, 2004; Garbaskas *et al.*, 1991; Tiekink, 1991; Baul & Tiekink, 1996, 1999; Baul *et al.*, 2005; Yin *et al.*, 2005; Parvez *et al.*, 1997; Teoh *et al.*, 1997).

The hydrogen-bonding interactions in (I) are listed in Table 2 and illustrated in Figs. 2 and 3. It is interesting that in

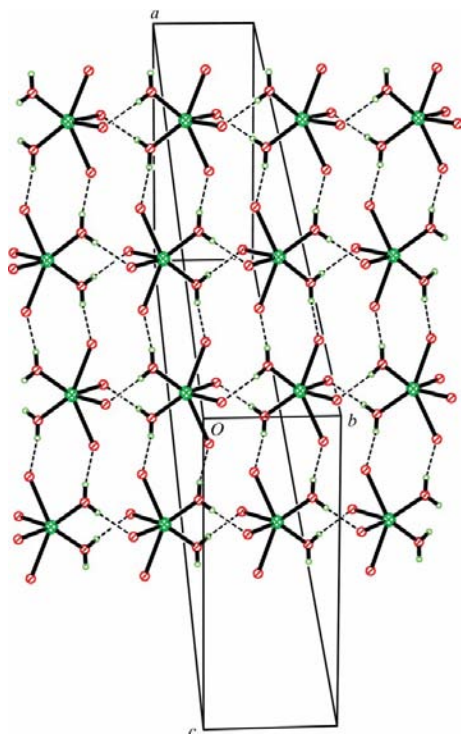


Figure 3
The two-dimensional sheet built from O—H...O hydrogen bonding (dotted lines) around the Cd coordination spheres. Cd atoms are cross-hatched, O atoms are hatched and H atoms are small open circles.

(I), the main intermolecular hydrogen bonds are formed by six coordinated O atoms, where four O atoms of two carboxyl groups act as hydrogen-bond acceptors and two water molecules as hydrogen-bond donors, forming four pairs of strong hydrogen bonds with O...O distances of only 2.686 (6) and 2.786 (5) Å. Two such pairs (O1—H1B...O3) link the molecules of (I) in an arrangement along the *b* axis, constructing a one-dimensional penniform tape with the arrowheads pointing in the same direction and the planes of the ligands partly overlapped in a parallel fashion (Fig. 2). In spite of the fact that the centroid-to-centroid distances between corresponding six-membered rings of the parallel ligands are more than 4.412 (4) Å, the perpendicular contacts are only about 3.4 Å. As the π -electron cloud is delocalized over the whole ligand, a π - π stacking interaction thus still exists between the parallel ligands, contributing to the stabilization of the one-dimensional tapes. A further two pairs of O1—H1A...O2 hydrogen bonds join the penniform tapes in an antiparallel fashion and, alternating with each other in the *c*-axis direction, organize the tapes into two-dimensional layers in which the coordination spheres are tightly hydrogen bonded as sheets (Fig. 3) in the middle.

Experimental

Compound (I) was synthesized by adding an ethanol (15 ml) solution of 4-(2-hydroxybenzylideneamino)benzoic acid (0.128 g) to an aqueous solution (5 ml) of CdSO₄·8H₂O (0.381 g). The mixed solution was refluxed at 333 K for 2 h after adjusting the pH to 7 with 0.1 M NaOH, then filtered after cooling to room temperature. Yellow crystals of (I) were obtained from the filtrate at room temperature over a period of 10 d.

Crystal data

[Cd(C₁₄H₁₀NO₃)₂(H₂O)₂]
M_r = 628.89
 Monoclinic, *C*2/*c*
a = 40.703 (6) Å
b = 5.0970 (8) Å
c = 12.2793 (18) Å
 β = 103.498 (3)°
V = 2477.1 (6) Å³
Z = 4

D_x = 1.686 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 1151 reflections
 θ = 3.1–21.2°
 μ = 0.94 mm⁻¹
T = 298 (2) K
 Rod, yellow
 0.37 × 0.08 × 0.06 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 2000)
T_{min} = 0.723, *T_{max}* = 0.946
 5875 measured reflections

2152 independent reflections
 1817 reflections with *I* > 2σ(*I*)
R_{int} = 0.050
 θ_{max} = 25.0°
h = -48 → 47
k = -5 → 6
l = -7 → 14

Table 1
Selected geometric parameters (Å, °).

Cd1—O1	2.191 (4)	Cd1—O2	2.508 (4)
Cd1—O3	2.232 (4)		
O1—Cd1—O1 ⁱ	91.9 (2)	O1—Cd1—O2 ⁱ	127.49 (16)
O1—Cd1—O3	136.46 (15)	O3—Cd1—O2 ⁱ	95.38 (14)
O1—Cd1—O3 ⁱ	100.12 (16)	O1—Cd1—O2	84.83 (14)
O3—Cd1—O3 ⁱ	99.3 (2)	O3—Cd1—O2	54.77 (13)

Symmetry code: (i) -*x* + 1, *y*, -*z* + $\frac{3}{2}$.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1B \cdots O3 ⁱⁱ	0.82	1.94	2.686 (6)	152
O1—H1A \cdots O2 ⁱⁱⁱ	0.82	1.98	2.786 (5)	167
O4—H4A \cdots N1	0.83	1.91	2.601 (6)	140

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

Refinement

Refinement on F^2

$$R[F^2 > 2\sigma(F^2)] = 0.056$$

$$wR(F^2) = 0.137$$

$$S = 1.14$$

2152 reflections

177 parameters

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0725P)^2]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} < 0.001$$

$$\Delta\rho_{\max} = 0.98 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.86 \text{ e } \text{Å}^{-3}$$

H atoms attached to C atoms were placed in geometrically idealized positions, with $Csp^2-H = 0.93 \text{ Å}$, and constrained to ride on their parent atoms, with $U_{\text{iso}}(H) = 1.2U_{\text{eq}}(C)$. H atoms attached to O atoms were located in difference Fourier maps and their global U_{iso} value was refined. The constrained O—H distances are in the range 0.82–0.83 Å.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXTL/PC*.

The authors acknowledge the National Natural Science Foundation of China (grant No. 20471033) and the Natural Science Foundation of Shanxi Province (grant No. 20051013) for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3003). Services for accessing these data are described at the back of the journal.

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