metal-organic papers

Diaqua(2,2'-bipyridyl)(2,2'-dihydroxy-[1,1']-binaphthalene-3,3'-dicarboxylato)cadmium(II) N,N-dimethylformamide solvate

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The title compound, [Cd(C$_{22}$H$_{12}$O$_6$)(C$_{10}$H$_8$N$_2$)(H$_2$O)$_2$]·-·C$_3$H$_7$NO, is a mononuclear cadmium(II) complex, which is coordinated by two water molecules, two N atoms from a bipyridyl ligand and one carboxyl O atom from the binaphthalene ligand, forming a trigonal–bipyramidal geometry. A molecule of N,N-dimethylformamide solvent is also present in the asymmetric unit. The crystal structure is stabilized by hydrogen bonds, forming a three-dimensional network.

Comment

The non-linear optical activities of d^{10} transition metal complexes, especially those of cadmium(II) (Ayyappan *et al.*, 2002; Evans & Lin, 2001*a,b*), have received considerable attention recently. The d^{10} configuration of the metal center and the π* orbitals of the ligands are combined to produce low-lying metal-to-ligand charge-transfer and intra-ligand transitions, which significantly affect the emission behavior of these systems. Our interest in the non-linear optical activity of cadmium complexes has led us to the title complex, (I), a new mononuclear cadmium complex. As a part of the study, we have analysed its crystal structure.

(I)
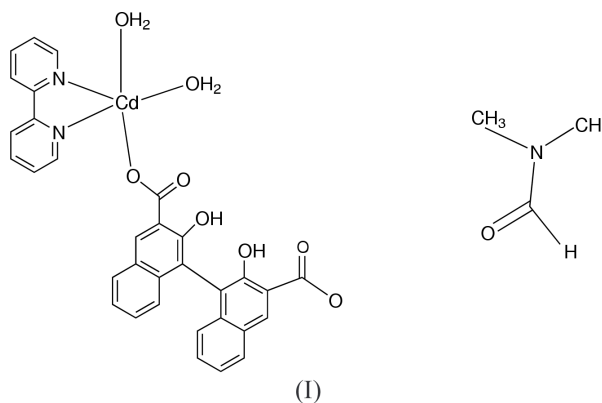
(I) is a new, five-coordinate, complex of the bna ligand (bna = 2,2'-dihydroxy[1,1']binaphthalene-3,3'-dicarboxylate), in which two N atoms are from 2,2'-bipyridyl, one O atom is from the bna ligand, and the other O atoms are from the water molecules. As shown in Fig. 1, it has a trigonal–bipyramidal geometry. The average Cd—N distance is 2.357 (3) Å. The distances between Cd1 and the two water molecules are 2.250 (4) and 2.385 (3) Å. The Cd1—O1 bond [2.290 (3) Å] is shorter than those in a similar bna–Cd^{II} complex (Zheng *et al.*, 2004). In addition, the bna ligand is in the monodentate coordination mode, in contrast to the modes described by Zheng *et al.* (2004) for the other complex.

All the O atoms of the aqua ligands and the other O atoms from the bna ligand and *N,N*-dimethylformamide contribute to intermolecular hydrogen bonds, forming a three-dimensional network (Fig. 2).

Experimental

An (Me)₂NCHO/H₂O [1:5 (*v/v*), 10 ml] solution containing Cd(NO₃)₂·4H₂O (0.154 g, 0.5 mmol), 2,2′-bipyridyl (0.039 g, 0.25 mmol) and H₂bna (0.187 g, 0.5 mmol) was stirred for 1 h in air, and then placed in an 18 ml Parr Teflon-lined stainless-steel vessel). The vessel was sealed and heated at 423 K for 48 h, cooled to 373 K at a rate of 281 K h⁻¹, and held for 10 h, followed by further cooling to room temperature. Yellow crystals of (I) were collected, washed with water, and dried in a vacuum using CaCl₂ (yield 49.6%). Elemental analysis: found C: 56.32; H, 4.22; N, 5.51%. calc. for CdC₃₅H₃₁N₃O₉: C, 56.05; H, 4.17; N, 5.60%.

Crystal data

[Cd(C$_{22}$H$_{12}$O$_6$)(C$_{10}$H$_8$N$_2$)-(H$_2$O)$_2$]·C$_3$H$_7$NO	$D_x = 1.480$ Mg m^{-3}
$M_r = 750.03$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3369
$a = 14.376$ (6) Å	reflections
$b = 20.576$ (8) Å	$\theta = 5{-}28°$
$c = 11.383$ (4) Å	$\mu = 0.71$ mm^{-1}
$\beta = 90.301$ (7)°	$T = 293$ (2) K
$V = 3367$ (2) Å^3	Block, yellow
$Z = 4$	$0.28 \times 0.22 \times 0.16$ mm

Data collection

Bruker SMART CCD area-detector diffractometer	7134 independent reflections
φ and ω scans	3369 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	$R_{int} = 0.067$
$T_{min} = 0.827$, $T_{max} = 0.895$	$\theta_{max} = 27.0°$
19183 measured reflections	$h = -18 \rightarrow 18$
	$k = -26 \rightarrow 18$
	$l = -13 \rightarrow 14$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.02P)^2]$
$wR(F^2) = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.96$	$(\Delta/\sigma)_{max} = 0.002$
7134 reflections	$\Delta\rho_{max} = 0.63$ e Å^{-3}
433 parameters	$\Delta\rho_{min} = -0.54$ e Å^{-3}

Table 1
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^i	0.86	2.37	3.225 (5)	170
O1W—H1$WB\cdots$O4^{ii}	0.86	2.00	2.792 (4)	153
O2W—H2$WB\cdots$O5^{ii}	0.87	2.37	3.052 (4)	135
O2W—H2$WB\cdots$O4^{ii}	0.87	2.56	3.372 (4)	156
O3—H3$A\cdots$O2	0.87	1.90	2.588 (4)	135
O6—H6$B\cdots$O5	0.87	1.86	2.553 (4)	135

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

All H atoms were located in Fourier maps and refined as riding, with C—H distances in the range 0.96–1.00 Å and O—H distances in the range 0.85–0.88 Å, and with U_{iso}(H) = 1.2U_{eq}(C, O) or 1.5U_{eq}(C) (C33 and C34).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve
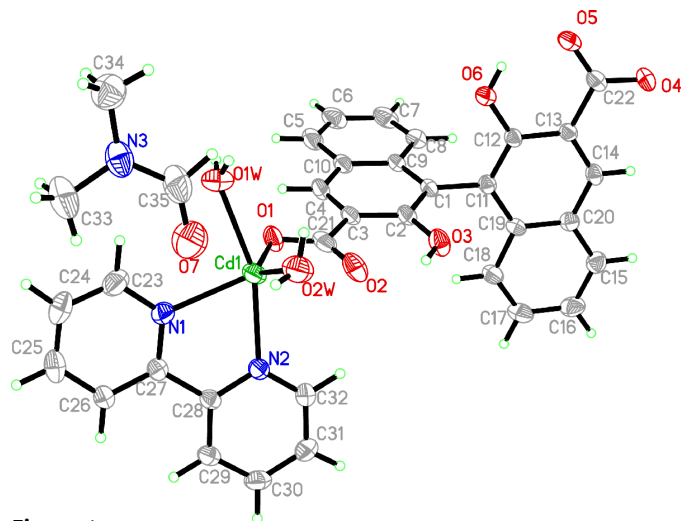

Figure 1
The structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.
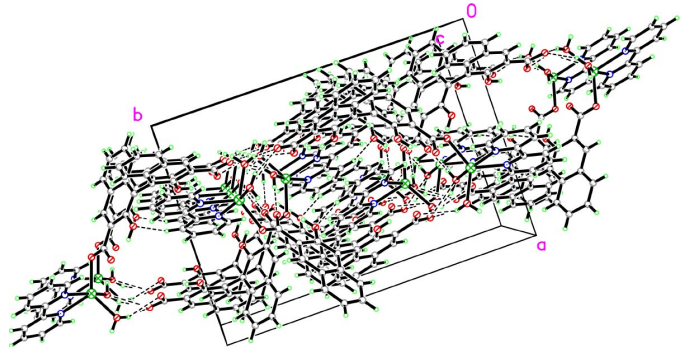

Figure 2
The crystal packing of (I), showing the O—H$\cdots$O hydrogen-bonding interactions as dashed lines.

structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

References

Ayyappan, P., Evans, O. R., Cui, Y., Wheeler, K. A., & Lin, W. (2002). *Inorg. Chem.* **41**, 4978–4980.
Evans, O. R. & Lin, W. (2001*a*). *Chem. Mater.* **13**, 2705–2712.
Evans, O. R. & Lin, W. (2001*b*). *Chem. Mater.* **13**, 3009–3017.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*a*). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Zheng, S.-L., Yang, J.-H., Yu, X.-L., Chen, X.-M. & Huang, W.-T. (2004). *Inorg. Chem.* **43**, 830–838.