metal-organic compounds

Bis[μ-1,2-bis(2-pyridyl)ethyne-$\kappa^2 N$:N']-bis[aquadinitratocadmium(II)]

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Two twisted 1,2-bis(2-pyridyl)ethyne ligands bridge two Cd^{2+} centers in the C_2-symmetric title complex, [$Cd_2(NO_3)_4(\mu$-$C_{12}H_8N_2)_2(H_2O)_2$]. The bridging ligands arch across one another creating a 'zigzag loop' molecular geometry. Two nitrate ions and a water molecule complete the irregular seven-coordinate Cd-atom environment. The dihedral angles between the equivalent pyridyl ring planes of the two independent ligands are 67.2 (1)°. O_{water}—H···$O_{nitrate}$ hydrogen bonding creates two-dimensional layers parallel to the ab plane.

Comment

Dipyridylacetylene ligands have been used by several groups for the construction of structurally diverse coordination networks (Bosch & Barnes, 2001; Carlucci *et al.*, 1998, 1999*a*,*b*; Dong, Layland, Pschirer *et al.*, 1999; Dong, Layland, Smith *et al.*, 1999) and as supramolecular synthons (Zaman *et al.*, 2000). Most efforts have employed the 4,4'-dipyridyl species, with comparatively fewer 3,3'- and 2,2'-dipyridyl studies. As part of an exploration of the structural effect of the 2,2'-, 3,3'- and 4,4'-positional orientation of the N atoms in dipyridylacetylene ligands, we report here the structure of [Cd(NO₃)₂-(2,2'-dpa)(H₂O)]₂, (I), the product of the reaction of 2,2'-dipyridylacetylene [systematic name: 1,2-bis(2-pyridyl)ethyne, hereafter 2,2'-dpa] with Cd(NO₃)₂·4H₂O.

Slow evaporation of a Cd(NO₃)₂·4H₂O/2,2'-dpa (1:1) mixture from a methylene chloride/methanol (1:1) solvent system deposited plentiful block-shaped yellow crystals of (I) after 2 d. The asymmetric unit of the dinuclear title complex consists of half of two independent 2,2'-dpa ligands, two nitrate ions and a coordinated water molecule. The hepta-coordinate Cd environment is irregular but can be described as a distorted trigonal bipyramid (Fig. 1) with two additional long Cd—O bonds. The equatorial sites contain a pyridyl N atom from each of the two 2,2'-dpa ligands and atom O2, with the axial sites occupied by the coordinated water molecule and atom O5. Atoms O1 and O4 complete the coordination sphere

at distances greater than 2.5 Å. The nitrate anions are thus intermediate between monodentate and bidentate (the distances and angles around the Cd atom are given in Table 1).

(I)
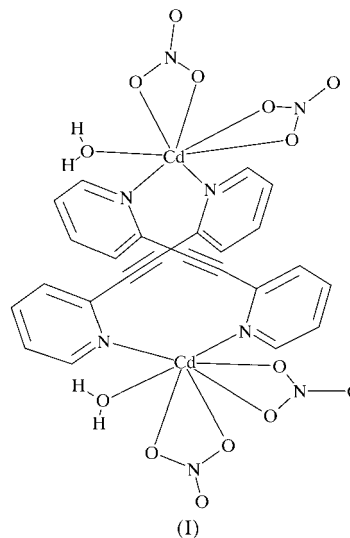
The complex molecule lies on a C_2 axis passing through the mid-point of the acetylene units of both ligands [C6—C6^i and C12—C12^i; symmetry code: (i) $1 - x, y, \frac{1}{2} - z$]. Each 2,2'-dpa ligand bridges two equivalent cadmium centers [Cd···Cd = 6.1045 (6) Å], and the ligands arch across one another to create an infinite 'zigzag cycle' molecular geometry (Fig. 1). The ligands crisscross each other in projection along [010], with interligand $C_{acetylene}$—$C_{acetylene}$ distances of 3.422 (2) (C6—C12) and 3.280 (2) Å (C6—C12^i), the latter indicating a possible alkyne–alkyne interaction (C···C van der Waals radius sum = 3.40 Å).

Both independent ligands in (I) are significantly distorted as a result of the geometric requirements of bridging two metal centers into a cyclic system. The acetylene units of the ligands show a more pronounced deviation from linearity [C11—C12—C12^i = 175.85 (11)° and C5—C6—C6^i = 170.74 (11)°] than observed previously (Neenan *et al.*, 1996). Additionally, the pyridyl rings in each independent ligand are rotated with respect to one another by identical values [67.2 (1)°], whereas in all other published accounts, this ligand tends strongly toward planarity, with maximum dihedral angles between pyridyl ring planes of less than 5° (Neenan *et al.*, 1996; Zaman *et al.*, 2000).

Intermolecular O—H···O hydrogen bonding (Table 2) between water atoms H1W and H2W and uncoordinated nitrate atoms O6 and O3, respectively, serves to link the complexes into sheets parallel to the crystallographic ab plane (Fig. 2). All available hydrogen-bonding donor and acceptor atoms are utilized in the crystal, either in coordination to the Cd atom or in the O—H···O network. The hydrogen-bonded layers then stack along [001], with no obvious interactions except for those of the van der Waals type.

An unusually short C···O contact of 2.861 (2) Å, involving atom C11 of a pyridyl ring (adjacent to N2) and the nitrate donor O6^{ii} [symmetry code: (ii) $x, y - 1, z$] from a neighboring molecule, is present in the crystal structure. Although quite
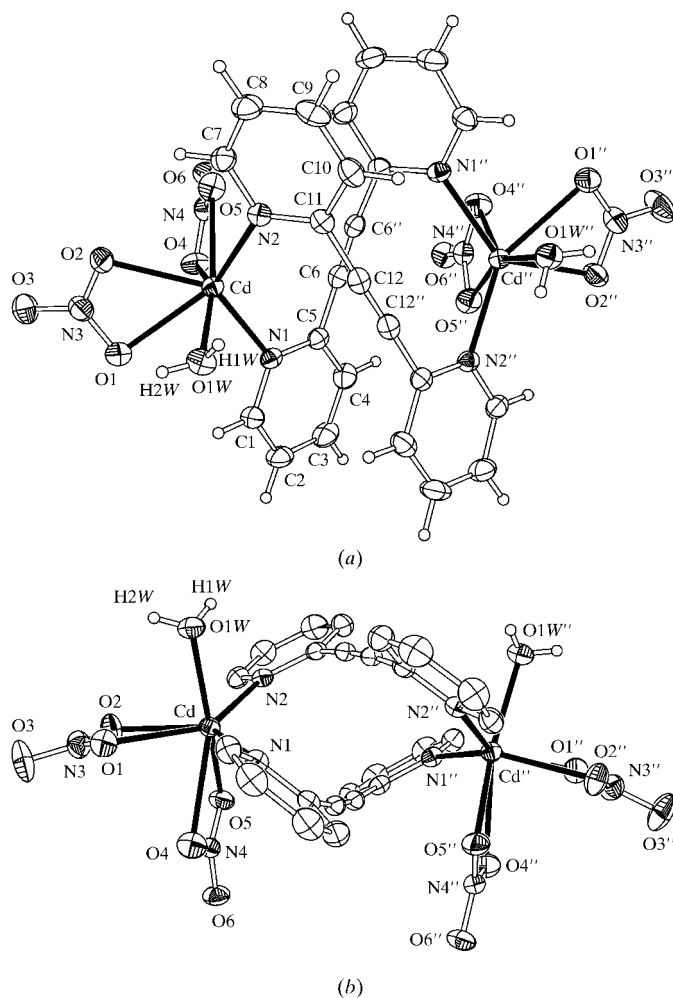
Figure 1
(a) A view of (I), slightly off the C_2 axis. (b) A view of (I), perpendicular to the above. In both cases, displacement ellipsoids are shown at the 50% probability level. [Symmetry code: ($''$) $1 - x, y, \frac{1}{2} - z$.]
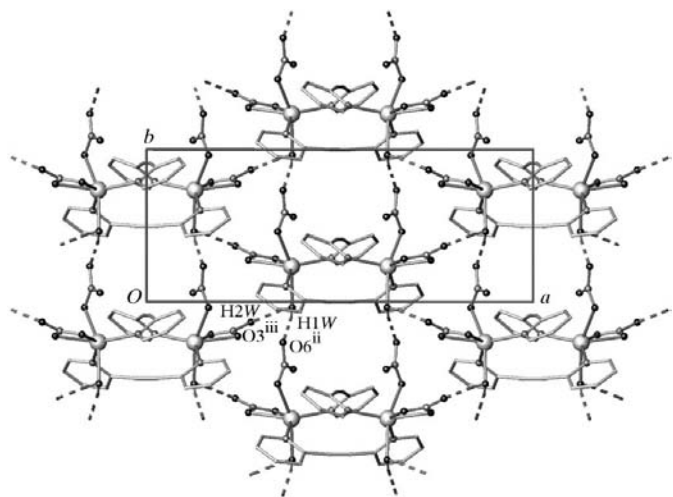

Figure 2
[001] view perpendicular to one layer of the extended two-dimensional hydrogen-bonding network. [Symmetry codes: (ii) $x, y - 1, z$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, z$.]

short ($C\cdots O$ van der Waals radius sum = 3.3 Å), this interaction is most likely to be a by-product of the strong $O1W$—$H1W\cdots O6^{ii}$ hydrogen bond mentioned above.

The 'zigzag loop' geometry of the title complex represents the third distinct structural motif obtained from the $M(NO_3)_2$–2,2′-dpa system (M = transition metal), after the unusual non-cyclic $[Cu_2(NO_3)_2(\mu$-2,2′-dpa$)(2,2′$-dpa$)_2]$ zigzag complex and the infinite one-dimensional $[Co(NO_3)_2(2,2′$-dpa$)]$ polymer zigzag chain, both reported by Neenan *et al.* (1996). Besides demonstrating the structural unpredictability of this ligand, these results show how the 2,2′-position of the pyridyl N atoms necessarily results in zigzag motifs rather than systems that are more orthogonal. For example, the reported 4,4′-dpa coordination network structures tend to adopt ladder, brick-wall, 'parquet' and more complex structural motifs, with N—M—N angles near 90°. Also, there is increased steric difficulty in coordinating more than two 2,2′-dpa ligands around a metal center because of the 'bending back' of the ligand toward the metal and therefore toward any other coordinated ligands, instead of stretching outward, as with 4,4′-dpa. However, higher 2,2′-dpa ligand coordination and increased structure dimensionality might be more likely with a non-coordinating anion.

Experimental

The 1,2-bis(2-pyridyl)ethyne ligand was prepared according to the method described by Teitei *et al.* (1972). A methanol solution (5 ml) of $Cd(NO_3)_2\cdot 4H_2O$ (30.8 mg, 0.1 mmol) was added slowly to a methylene chloride (5 ml) solution of 2,2′-dpa (18.2 mg, 0.1 mmol). After one week, the yellow–orange solution was evaporated slowly (at room temperature over a period of two weeks) to saturation. Large block-like yellow crystals grew at the bottom of the test tube after 2 d.

Crystal data

$[Cd_2(NO_3)_4(C_{12}H_8N_2)_2(H_2O)_2]$	Mo $K\alpha$ radiation
$M_r = 869.28$	Cell parameters from 5750
Orthorhombic, *Pbcn*	reflections
$a = 19.910\ (3)$ Å	$\theta = 2.6$–26.4°
$b = 7.8559\ (8)$ Å	$\mu = 1.50$ mm^{-1}
$c = 19.263\ (2)$ Å	$T = 173\ (2)$ K
$V = 3013.0\ (6)$ Å^3	Block, yellow
$Z = 4$	$0.48 \times 0.44 \times 0.32$ mm
$D_x = 1.916$ Mg m^{-3}	

Data collection

Bruker SMART APEX CCD	3074 independent reflections
diffractometer	2697 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.019$
Absorption correction: multi-scan	$\theta_{max} = 26.4°$
(*SADABS*; Bruker, 1999)	$h = -24 \rightarrow 14$
$T_{min} = 0.515$, $T_{max} = 0.647$	$k = -8 \rightarrow 9$
14 574 measured reflections	$l = -21 \rightarrow 24$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.019$	$+ 0.0456P]$
$wR(F^2) = 0.052$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
3074 reflections	$\Delta\rho_{max} = 0.40$ e Å^{-3}
234 parameters	$\Delta\rho_{min} = -0.43$ e Å^{-3}
H atoms treated by a mixture of	Extinction correction: *SHELXL*97
independent and constrained	Extinction coefficient: 0.00294 (13)
refinement	

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Table 1
Selected geometric parameters (Å, °).

Cd—N1	2.2852 (15)	Cd—O1	2.5364 (14)
Cd—N2	2.3052 (15)	Cd—O4	2.5848 (16)
Cd—O1W	2.3102 (14)	C6—C12^i	3.280 (2)
Cd—O2	2.3429 (15)	C6—C12	3.422 (2)
Cd—O5	2.4162 (14)		
N1—Cd—N2	122.27 (5)	N2—Cd—O1	148.65 (5)
N1—Cd—O1W	90.36 (5)	O1W—Cd—O1	77.69 (5)
N2—Cd—O1W	85.94 (5)	O5—Cd—O1	110.66 (4)
N1—Cd—O2	135.39 (6)	N1—Cd—O4	74.15 (5)
N2—Cd—O2	102.31 (5)	N2—Cd—O4	125.71 (5)
O1W—Cd—O2	91.31 (5)	O1W—Cd—O4	148.34 (5)
N1—Cd—O5	111.14 (5)	O2—Cd—O4	81.63 (5)
N2—Cd—O5	76.34 (5)	O1—Cd—O4	73.60 (5)
O1W—Cd—O5	157.20 (5)	C6^i—C6—C5	170.74 (11)
O2—Cd—O5	78.82 (5)	C12^i—C12—C11	175.85 (11)
N1—Cd—O1	84.77 (5)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1W$\cdots$O6^{ii}	0.81 (3)	2.01 (3)	2.817 (2)	172 (3)
O1W—H2W$\cdots$O3^{iii}	0.81 (3)	2.06 (3)	2.856 (2)	172 (3)

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

H atoms attached to C atoms were idealized and treated as riding [C—H = 0.95 Å and U_{iso}(H) = 1.2 U_{iso}(C)]. Water H atoms were located in a difference Fourier map and refined freely.

Data collection: *SMART–NT* (Bruker, 1999); cell refinement: *SAINT-Plus–NT* (Bruker, 1999); data reduction: *SAINT-Plus–NT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *ATOMS* (Dowty, 2001) and *SHELXTL* (Shel-

drick, 1997b); software used to prepare material for publication: *SHELXTL*.

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