metal-organic papers

μ-Tetravanadato-bis[bis(2,2′-bipyridine)-cadmium(II)]

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The molecule of the title compound, $[\{Cd(bpy)_2\}_2V_4O_{12}]$ (bpy is 2,2′-bipyridine) or $[Cd_2V_4O_{12}(C_{10}H_8N_2)_4]$, has crystallographic twofold rotation symmetry. A $\{V_4O_{12}\}$ ring links through oxo groups of pairs of adjacent vanadium sites to two $\{Cd(bpy)_2\}$ moieties. The molecules are assembled into layers parallel to the *ab* plane by aromatic π–π stacking interactions involving the bpy ligands.

Comment

Polyoxometalate anions are a broad class of discrete metal–oxide compounds, $M_xO_y^{n-}$, which are of both fundamental and practical interest in a range of areas, including catalysis, biochemistry, medicine, magnetism and solid-state devices (Pope & Müller, 1991). The polyoxovanadates, a subset of the general family of polyoxometalates, have been studied extensively (Aschwanden *et al.*, 1993). The hydrothermal synthesis of organic–inorganic hybrid vanadium oxides and polyvanadate clusters is of great interest, due to their intriguing structural diversity and their potential application as microporous solids for molecular adsorption, ion exchange and heterogeneous catalysis (Lehn, 1995). To date, the study of vanadium clusters has largely focused on infinite chains and layer structures (Gu *et al.*, 2003). Only a few discrete vanadium clusters in bimetallic compounds have been reported.

(I)
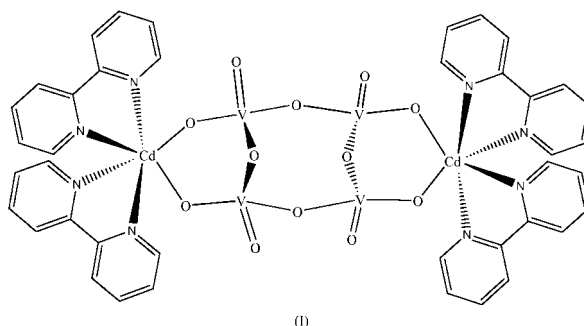
We report here the crystal structure of a new complex, $[\{Cd(bpy)_2\}_2V_4O_{12}]$ (bpy is 2,2′-bipyridine), (I). In (I), each Cd[II] atom is coordinated by four N atoms from two chelating bpy ligands and two O atoms from a bridging $\{V_4O_{12}\}$ unit, to give a highly distorted octahedral geometry. The terminal V—O bond distances are 1.621 (7) and 1.636 (7) Å (Table 1); those to O atoms bridging pairs of V atoms are 1.792 (3)–1.832 (7) Å, and those to O atoms coordinated to Cd are 1.676 (7) and 1.655 (7) Å, with each V atom in a slightly distorted tetrahedral environment. The $\{V_4O_{12}\}$ ring links through oxo groups of adjacent vanadium sites to two $\{Cd(bpy)_2\}$ moieties to give the complex molecule (Fig. 1). These molecules are assembled into layers parallel to the *ab*
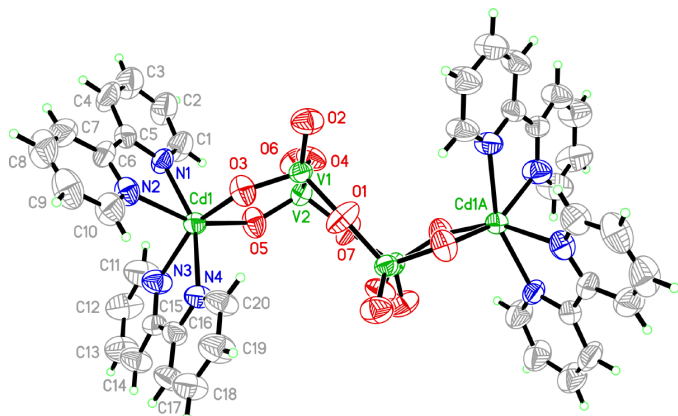
Figure 1
The molecular structure of (I), with 50% probability displacement ellipsoids. [Symmetry code: (A) $1 - x, \frac{1}{2} - y, z$.]
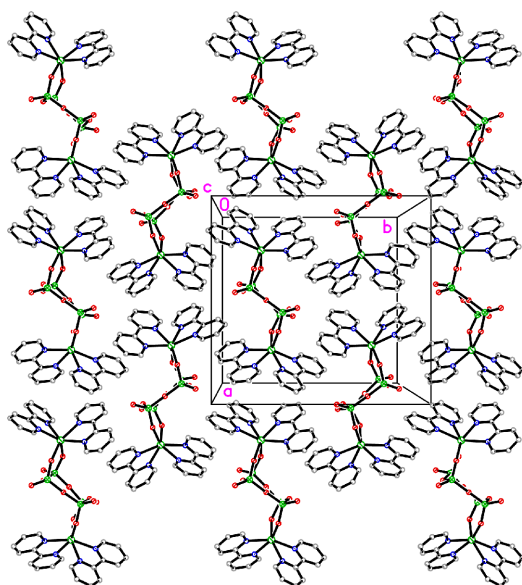

Figure 2
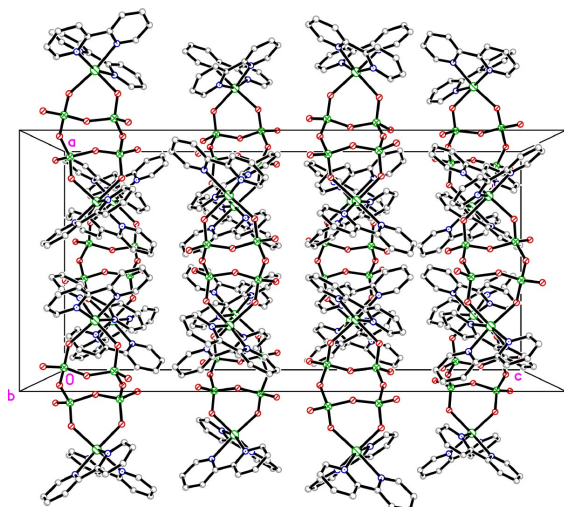Layers of the title complex, viewed along the *c* axis. H atoms have been omitted for clarity.

Figure 3
The molecular packing, viewed along the *b* axis. H atoms have been omitted for clarity.

plane by aromatic π–π stacking interactions (with distances *ca* 3.6 Å) involving the bpy ligands (Fig. 2). The layers are held together by van der Waals interactions (Fig. 3).

Experimental

A mixture of $Cd(OAc)_2 \cdot 2H_2O$ (0.25 mmol), 2,2′-bipyridine (0.5 mmol), NH_4VO_3 (0.5 mmol) and water (8 ml) was stirred for 15 min in air, then sealed in a 23 ml Teflon reactor, which was heated at 443 K for 5 d and then cooled to room temperature at a rate of 5 K h^{-1}. The resulting brown blocks were washed with deionized water and absolute ethanol (yield >60% based on Cd).

Crystal data

$[Cd_2V_4O_{12}(C_{10}H_8N_2)_4]$	Mo $K\alpha$ radiation
$M_r = 1245.30$	Cell parameters from 25
Orthorhombic, *Ibca*	reflections
$a = 16.287\ (7)$ Å	$\theta = 2$–$26°$
$b = 17.201\ (9)$ Å	$\mu = 1.69$ mm^{-1}
$c = 34.070\ (16)$ Å	$T = 293\ (2)$ K
$V = 9545\ (8)$ Å^3	Block, brown
$Z = 8$	$0.20 \times 0.18 \times 0.12$ mm
$D_x = 1.733$ Mg m^{-3}	

Data collection

Siemens *R3m* diffractometer	$R_{int} = 0.074$
ω scans	$\theta_{max} = 26.0°$
Absorption correction: ψ scan	$h = 0 \rightarrow 20$
(North *et al.*, 1968)	$k = 0 \rightarrow 21$
$T_{min} = 0.728$, $T_{max} = 0.823$	$l = -1 \rightarrow 42$
4865 measured reflections	2 standard reflections
4707 independent reflections	every 200 reflections
2729 reflections with $I > 2\sigma(I)$	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1212P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.071$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.210$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.01$	$\Delta\rho_{max} = 1.02$ e Å^{-3}
4707 reflections	$\Delta\rho_{min} = -0.95$ e Å^{-3}
300 parameters	Extinction correction: *SHELXL*97
H-atom parameters constrained	Extinction coefficient: 0.00085 (10)

Table 1
Selected geometric parameters (Å, °).

Cd1—O5	2.280 (6)	V1—O3	1.676 (7)
Cd1—O3	2.313 (7)	V1—O1	1.792 (3)
Cd1—N4	2.370 (8)	V1—O4	1.813 (7)
Cd1—N3	2.373 (9)	V2—O6	1.621 (7)
Cd1—N1	2.374 (7)	V2—O5	1.655 (7)
Cd1—N2	2.401 (8)	V2—O7	1.801 (3)
V1—O2	1.636 (7)	V2—O4	1.832 (7)
O5—Cd1—O3	91.7 (3)	O2—V1—O1	109.0 (4)
O5—Cd1—N4	107.7 (3)	O3—V1—O1	111.6 (3)
O3—Cd1—N4	86.4 (3)	O2—V1—O4	108.7 (3)
O5—Cd1—N3	91.9 (3)	O3—V1—O4	107.4 (3)
O3—Cd1—N3	156.4 (3)	O1—V1—O4	111.3 (4)
N4—Cd1—N3	70.3 (3)	O6—V2—O5	108.6 (4)
O5—Cd1—N1	88.7 (3)	O6—V2—O7	109.5 (4)
O3—Cd1—N1	106.8 (3)	O5—V2—O7	111.2 (3)
N4—Cd1—N1	158.9 (3)	O6—V2—O4	109.1 (4)
N3—Cd1—N1	96.7 (3)	O5—V2—O4	108.1 (3)
O5—Cd1—N2	156.9 (3)	O7—V2—O4	110.1 (4)
O3—Cd1—N2	85.7 (3)	V1—O1—V1^i	156.5 (8)
N4—Cd1—N2	95.1 (3)	V1—O3—Cd1	131.3 (4)
N3—Cd1—N2	99.7 (3)	V1—O4—V2	129.4 (4)
N1—Cd1—N2	70.2 (3)	V2—O5—Cd1	134.0 (4)
O2—V1—O3	108.7 (4)	V2—O7—V2^i	148.5 (6)

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

H atoms were positioned geometrically (C—H = 0.93 Å) and refined as riding on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. The largest peak in the final difference map lies 1.4 Å from the Cd atom.

Data collection: *R3m Software* (Siemens, 1990); cell refinement: *R3m Software*; data reduction: *R3m* Software; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1998); software used to prepare material for publication: *SHELXL*97.

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