

**Bis[tris(2,2'-bipyridyl- κ^2N,N')iron(II)]
cyclo-tetranavanadate decahydrate****Ming-Hua Huang, Li-Hua Bi and
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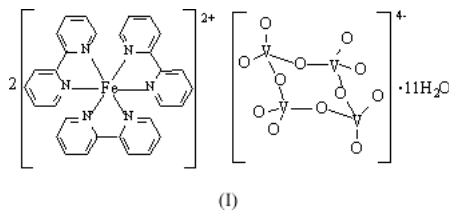
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Key indicatorsSingle-crystal X-ray study
 $T = 293$ K
Mean $\sigma(C-C) = 0.010$ Å
H-atom completeness 71%
Disorder in solvent or counterion
 R factor = 0.074
 wR factor = 0.211
Data-to-parameter ratio = 15.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The hydrothermal reactions of metavanadate and divalent iron salts in the presence of nitrogen-donor chelating ligands yield the complex $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]_2[\text{V}_4\text{O}_{12}] \cdot 10\text{H}_2\text{O}$, which consists of one centrosymmetric eight-membered ring $[\text{V}_4\text{O}_{12}]^{4-}$ anion cluster, formed by four VO_4 tetrahedra sharing vertices, two discrete octahedral $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]^{2+}$ cations, formed by three 2,2'-bipyridyl ligands coordinated to Fe^{II} , and ten water molecules of solvation. The anion and coordination cations are isolated and form anion and cation layers, respectively. In the anion layers, these anions and water molecules of solvation are linked to each other, in a two-dimensional motif, through hydrogen-bonding interactions.

Comment

Considerable efforts have been devoted to the hydrothermal synthesis of vanadium(V) solid-state inorganic-organic species based on discrete clusters, infinite chains and layer structures, such as $[\text{Cu}(\text{bipy})][\text{V}_2\text{O}_6]$, $[\text{Cu}(\text{bipy})_2][\text{V}_2\text{O}_6]$ (DeBord *et al.*, 1996), $\text{Zn}(\text{phen})_2[\text{V}_4\text{O}_{12}] \cdot \text{H}_2\text{O}$, $[\text{Zn}(\text{bipy})_3]_2[\text{V}_4\text{O}_{12}] \cdot 11\text{H}_2\text{O}$ (Zhang *et al.*, 1997), $[\text{Ni}(\text{bipy})_3]_2[\text{V}_4\text{O}_{12}] \cdot 11\text{H}_2\text{O}$ (Yang *et al.*, 1998), $[\text{Mn}(\text{phen})_2]_2[\text{V}_4\text{O}_{12}] \cdot 0.5\text{H}_2\text{O}$ (Lu *et al.*, 2002), and $[\text{Co}(\text{phen})_2]_2[\text{V}_4\text{O}_{12}] \cdot \text{H}_2\text{O}$ (Kucsera *et al.*, 2002), because of their diverse topologies and fascinating physical properties. As an extension to these synthetic and structural approaches, we have investigated the inorganic-organic hybrid compound containing the $[\text{V}_4\text{O}_{12}]^{4-}$ anion cluster and transition metal cations coordinated by 2,2'-bipyridyl. Here we present a new compound, $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]_2[\text{V}_4\text{O}_{12}] \cdot 10\text{H}_2\text{O}$, (I), possessing an eight-membered ring $[\text{V}_4\text{O}_{12}]^{4-}$ anion cluster, discrete octahedral $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]^{2+}$ cations and crystallization water molecules of solvation (Fig. 1). In the compound, the $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3]^{2+}$ cation acts as a space-filling and charge-compensating unit, while the $[\text{V}_4\text{O}_{12}]^{4-}$ anion clusters are isolated and do not covalently bond to each other.



The discrete $[\text{V}_4\text{O}_{12}]^{4-}$ anion cluster exhibits a centrosymmetric eight-membered ring structure, constructed from four distorted VO_4 tetrahedra sharing vertices, with two terminal oxo groups $[\text{V}-\text{O}_t$ ranging from 1.625 (6) to 1.656 (6) Å] and with two bridging oxo groups $[\text{V}-\text{O}_b$ ranging from 1.765 (5)

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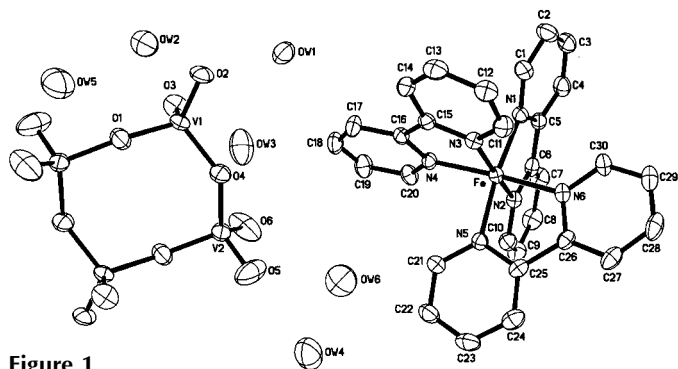


Figure 1
The asymmetric unit (and centrosymmetrically related half of the anion) of the title compound, with atom numbering and displacement ellipsoids at the 30% probability level. H atoms have been omitted.

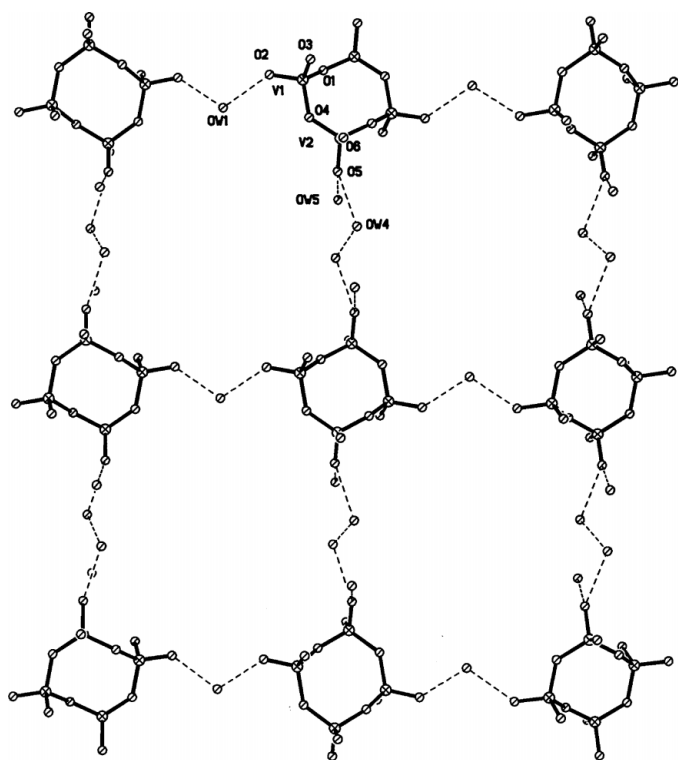


Figure 2
Two-dimensional layers of $[V_4O_{12}]^{4-}$ anions and solvent water oxygen hydrogen-bonding interactions in compound (I).

to 1.799 (5) Å]. The coordination environment and mode are identical to those in the reported compounds $[Zn(bipy)_3]_2 \cdot [V_4O_{12}] \cdot 11H_2O$ (Zhang *et al.*, 1997) and $[Ni(bipy)_3]_2 \cdot [V_4O_{12}] \cdot 11H_2O$ (Yang *et al.*, 1998).

As shown in Fig. 2, the anion clusters and solvent water molecules are connected to each other, in two-dimensional planar layers, through hydrogen-bonding interactions. The Fe^{II} center exhibits slightly distorted octahedral coordination geometry, defined by six N atoms from three 2,2'-bipy ligands (Fig. 1). As depicted in Fig. 3, the $[V_4O_{12}]^{4-}$ anion layers are separated by an interlamellar region occupied by the $[Fe(C_{10}H_8N_2)_3]^{2+}$ cations.

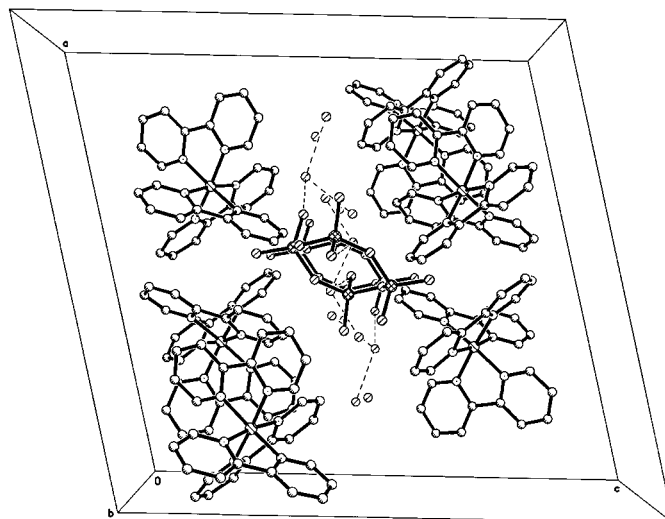


Figure 3
Packing diagram, showing the structure of compound (I) viewed along the *b* axis.

Experimental

The title compound was prepared hydrothermally from a mixture of $Na_3VO_4 \cdot 12H_2O$, $FeCl_2 \cdot 4H_2O$, 2,2'-bipy, H_2O (molar ratio 1:1:2:555) with 8 M H_3PO_4 , adjusting the solution pH to *ca* 8.7 in a 18 ml polyfluoroethylene-lined stainless steel bomb heated to 443 K for 5 d. The black-red crystals were collected from a solution cooled to room temperature.

Crystal data

$[Fe(C_{10}H_8N_2)_3]_2[V_4O_{12}] \cdot 10H_2O$
 $M_r = 1624.72$
 Monoclinic, *C2/c*
 $a = 21.619$ (3) Å
 $b = 13.656$ (3) Å
 $c = 23.517$ (4) Å
 $\beta = 103.296$ (14)°
 $V = 6757$ (2) Å³
 $Z = 4$

$D_x = 1.597$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 28 reflections
 $\theta = 5.2$ – 11.2 °
 $\mu = 1.03$ mm⁻¹
 $T = 293$ (2) K
 Block, black-red
 $0.48 \times 0.32 \times 0.18$ mm

Data collection

Siemens *P4* diffractometer
 ω scans
 Absorption correction: ψ scan
 (SHELXTL; Siemens, 1994)
 $T_{min} = 0.622$, $T_{max} = 0.830$
 7943 measured reflections
 6634 independent reflections
 4004 reflections with $I > 2\sigma(I)$

$R_{int} = 0.030$
 $\theta_{max} = 26.0$ °
 $h = -1 \rightarrow 26$
 $k = -1 \rightarrow 16$
 $l = -29 \rightarrow 28$
 3 standard reflections
 every 197 reflections
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.074$
 $wR(F^2) = 0.211$
 $S = 1.07$
 6634 reflections
 439 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 1.55$ e Å⁻³
 $\Delta\rho_{min} = -1.37$ e Å⁻³

All H atoms of bipyridyl were placed in idealized positions using a riding model, with C–H distances of 0.93 Å. U_{iso} values were set equal to U_{eq} of the carrier atom. The H atoms of water molecules

were not located in difference Fourier maps, due to limitations of the data. Water atom OW6 was refined at half occupancy.

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *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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