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**$\mu$ -[N,N-Bis(2-pyridylmethyl-1 $\kappa$ N)-N',N'-bis(2-pyridylmethyl-2 $\kappa$ N)-1,3-diaminopropan-2-olato]-1 $\kappa$ N,2 $\kappa$ N',1:2 $\kappa^2$ O-bis(dioxovanadium)(1+) Iodide Dihydrate, [(VO<sub>2</sub>)<sub>2</sub>(TPHPN)]I<sub>2</sub>H<sub>2</sub>O**

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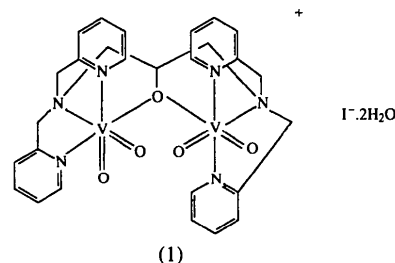
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## Abstract

In the binuclear [(VO<sub>2</sub>)<sub>2</sub>(TPHPN)]<sup>+</sup> cation of the title compound, [V<sub>2</sub>O<sub>4</sub>(C<sub>27</sub>H<sub>29</sub>N<sub>6</sub>O)]I<sub>2</sub>H<sub>2</sub>O, the two tridentate halves of the symmetrical TPHPN<sup>−</sup> ligand are arranged so that the three donor N atoms are *fac* at one pseudo-octahedral metal centre but *mer* at the other. The strong *trans* influence of the oxo ligand is apparent from trends in the  $\mu$ -V—O and V—N bond lengths.

## Comment

It is well established that vanadium has an important role in many biological processes (Rehder, 1991; Butler & Carrano, 1991). In the +5 oxidation state it has been postulated that the vanadate ion acts as a potent inhibitor of Na<sup>+</sup>, K<sup>+</sup> ATPase (Butler & Carrano, 1991). In order to gain more structural information about these complex systems, we synthesized and determined the crystal structure of a new binuclear vanadate complex with N and O donor ligands, (1). This is a continuation of our programme of research into the preparation and characterization of vanadium complexes with bioinorganic relevance (Neves, Ceccato, Erthal, Vencato, Nuber & Weiss, 1991; Neves, Ceccato, Vencato, Mascarenhas & Erasmus-Buhr, 1992; Neves, Ceccato, Erasmus-Buhr, Gehring, Haase, Paulus, Nascimento & Batista, 1993).



The title compound is built from discrete binuclear [(VO<sub>2</sub>)<sub>2</sub>(TPHPN)]<sup>+</sup> cations, uncoordinated I<sup>−</sup> anions and water molecules of crystallization. The V atoms in the cation of (1) are in pseudo-octahedral environments, bridged by the  $\mu$ -alkoxo O atom, with the VO<sub>2</sub> moieties in the expected *cis* configuration. The N donor atoms (from the two amine groups and the four pyridyl groups) of the symmetrical TPHPN<sup>−</sup> ligand complete the octahedral coordination spheres of the two vanadium(V) centers. The [(VO<sub>2</sub>)<sub>2</sub>(TPHPN)]<sup>+</sup> cation contains a (O<sub>2</sub>V<sup>V</sup>—OR—V<sup>V</sup>O<sub>2</sub>)<sup>+</sup> core, which, to the best of our knowledge, has not been crystallographically characterized previously, although a linear (O<sub>2</sub>V—O—VO<sub>2</sub>) unit in the complex [L<sub>2</sub>V<sub>2</sub>O<sub>4</sub>( $\mu$ -O)] (L = 1,4,7-trimethyl-1,4,7-triazacyclononane) has been reported recently (Knopp, Wieghardt, Nuber, Weiss & Sheldrick, 1990). Pertinent bridging features include the V<sup>V</sup>...V<sup>V</sup> distance of 3.690 (3) Å and the V(1)—O(5)—V(2) angle of 126.2 (1)°. Moreover, it is worth noting that the two tridentate halves (each with one amine and two pyridyl N donor atoms) of the symmetrical bridging ligand adopt distinct configurations around the vanadium centres: V(1) is coordinated in a meridional fashion whereas about V(2) the arrangement is facial.

The terminal V—O distances are short [average 1.620 (3) Å], indicating considerable multiple-bond character, and agree well with V=O distances in dimeric (Knopp *et al.*, 1990) and monomeric octahedral complexes containing *cis*-dioxovanadium units (Neves, Walz, Wieghardt, Nuber & Weiss, 1988; Neves, Hörner,

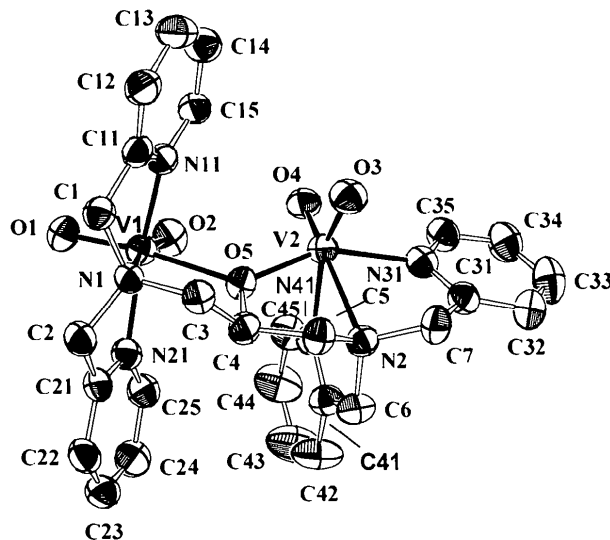


Fig. 1. A perspective view of the cation with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level for non-H atoms; H atoms have been omitted for clarity.

Fenner & Strähle, 1993). The vanadium– $\mu$ -alkoxo bond lengths differ significantly: the V(1)—O(5) distance is 0.264 (2) Å longer than the V(2)—O(5) distance, indicating that the *trans* influence of the terminal oxo group is much greater than that of the pyridyl group. The strong *trans* influence of the oxo group is also apparent from the V—N distances; the average V—N(*trans* to oxo) distance of 2.290 (3) Å is  $\sim$ 0.175 Å longer than the mean length of the V—N bonds *trans* to N(pyridyl) or O(alkoxo) donor atoms.

The structure also features two hydrogen bonds involving the two water molecules of crystallization O(W1) and O(W2) [O(W1)··O(4<sup>i</sup>) = 2.992 (9) and O(W2)··O(1<sup>ii</sup>) = 2.772 (14) Å; symmetry codes: (i)  $x, -\frac{1}{2}+y, -\frac{1}{2}+z$ ; (ii)  $-x+1, \frac{1}{2}+y, \frac{1}{2}-z$ ].

## Experimental

The title complex (1) was obtained by the reaction of VCl<sub>3</sub> and HTPHPN (2:1) (Chan & Armstrong, 1989) in a mixture of acetonitrile and tetrahydrofuran under reflux, whereby V<sup>III</sup> is oxidized to V<sup>V</sup> by air. Single crystals suitable for X-ray crystallography were obtained by recrystallization from a methanol solution.

### Crystal data

[V<sub>2</sub>O<sub>4</sub>(C<sub>27</sub>H<sub>29</sub>N<sub>6</sub>O)]I<sub>2</sub>·2H<sub>2</sub>O

*M<sub>r</sub>* = 782.38

Monoclinic

*P*2<sub>1</sub>/*c*

*a* = 15.369 (4) Å

*b* = 14.399 (7) Å

*c* = 13.772 (3) Å

$\beta$  = 90.88 (7)°

Mo *K* $\alpha$  radiation

$\lambda$  = 0.71073 Å

Cell parameters from 25 reflections

$\theta$  = 12.0–18.0°

$\mu$  = 1.65 mm<sup>-1</sup>

*T* = 293 K

Trapezoidal plate

*V* = 3047 (3) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.705 Mg m<sup>-3</sup>

0.30 × 0.20 × 0.15 mm

Clear yellow

### Data collection

Enraf–Nonius CAD-4 diffractometer

$\omega/2\theta$  scans

Absorption correction:

refined from  $\Delta F$

(*DIFABS*; Walker & Stuart, 1983)

*T<sub>min</sub>* = 0.62, *T<sub>max</sub>* = 0.78

5222 measured reflections

4380 independent reflections

4177 observed reflections

[*I* > 3.0 $\sigma$ (*I*)]

*R<sub>int</sub>* = 0.028

$\theta_{\max}$  = 24.0°

*h* = 0 → 15

*k* = 0 → 16

*l* = -17 → 17

2 standard reflections

frequency: 40 min

intensity variation: 0.6%

### Refinement

Refinement on *F*<sup>2</sup>

*R* = 0.0424

*wR* = 0.0516

*S* = 2.70

4177 reflections

389 parameters

H-atom parameters not refined

*w* = 1/ $\sigma^2$ (*F*)

( $\Delta/\sigma$ )<sub>max</sub> = 0.01

$\Delta\rho_{\max}$  = 0.74 e Å<sup>-3</sup>

$\Delta\rho_{\min}$  = -0.72 e Å<sup>-3</sup>

Extinction correction:

Zachariasen (1963)

Extinction coefficient:

4.657 (3) × 10<sup>-8</sup>

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV, Table

2.2A)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j.$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B<sub>eq</sub></i>
I	0.30242 (3)	0.38482 (4)	0.05607 (4)	4.26 (1)
V(1)	0.38539 (7)	-0.17838 (8)	0.20864 (8)	3.09 (2)
V(2)	0.15124 (7)	-0.23569 (7)	0.21657 (8)	3.04 (2)
O(1)	0.4903 (3)	-0.1761 (3)	0.1973 (3)	4.2 (1)
O(2)	0.3462 (3)	-0.2041 (3)	0.1027 (3)	4.2 (1)
O(3)	0.1438 (3)	-0.3117 (3)	0.3038 (3)	4.2 (1)
O(4)	0.1787 (3)	-0.2936 (3)	0.1216 (3)	3.8 (1)
O(5)	0.2514 (3)	-0.1647 (3)	0.2613 (3)	3.01 (8)
O(W1)	0.1333 (5)	-1.0111 (5)	0.6749 (9)	13.9 (3)
O(W2)	0.3625 (9)	0.3147 (8)	0.4161 (9)	16.5 (4)
N(1)	0.3992 (3)	-0.1398 (3)	0.3684 (4)	2.8 (1)
N(2)	0.0874 (3)	-0.1247 (4)	0.3102 (4)	3.2 (1)
N(11)	0.3864 (3)	-0.3063 (4)	0.2822 (4)	3.2 (1)
N(21)	0.3755 (3)	-0.0325 (4)	0.2088 (4)	3.3 (1)
N(31)	0.0147 (3)	-0.2484 (4)	0.1885 (4)	3.4 (1)
N(41)	0.1280 (3)	-0.1064 (4)	0.1200 (4)	3.4 (1)
C(1)	0.4534 (4)	-0.2149 (5)	0.4098 (5)	3.4 (1)
C(2)	0.4430 (4)	-0.0480 (5)	0.3684 (5)	3.6 (1)
C(3)	0.3131 (4)	-0.1366 (4)	0.4181 (4)	3.2 (1)
C(4)	0.2423 (4)	-0.1086 (5)	0.3460 (4)	3.3 (1)
C(5)	0.1536 (4)	-0.1203 (5)	0.3899 (4)	3.4 (1)
C(6)	0.0716 (5)	-0.0331 (5)	0.2637 (5)	4.1 (2)
C(7)	0.0046 (4)	-0.1683 (5)	0.3408 (5)	3.9 (1)
C(11)	0.4229 (4)	-0.3060 (4)	0.3716 (5)	3.1 (1)
C(12)	0.4344 (4)	-0.3881 (5)	0.4246 (5)	4.0 (1)
C(13)	0.4073 (5)	-0.4708 (5)	0.3823 (6)	4.6 (2)
C(14)	0.3681 (5)	-0.4692 (5)	0.2915 (5)	4.5 (2)
C(15)	0.3586 (4)	-0.3862 (5)	0.2435 (5)	3.6 (1)
C(21)	0.4071 (4)	0.0120 (5)	0.2883 (5)	3.4 (1)
C(22)	0.4046 (4)	0.1085 (5)	0.2939 (5)	3.9 (1)
C(23)	0.3689 (5)	0.1585 (5)	0.2193 (6)	4.4 (2)
C(24)	0.3354 (5)	0.1129 (5)	0.1397 (5)	4.6 (2)
C(25)	0.3401 (4)	0.0173 (5)	0.1366 (5)	3.9 (1)
C(31)	-0.0390 (4)	-0.2114 (5)	0.2534 (5)	3.6 (1)
C(32)	-0.1283 (5)	-0.2168 (6)	0.2416 (6)	4.7 (2)

C(33)	-0.1616 (5)	-0.2633 (7)	0.1615 (6)	5.6 (2)
C(34)	-0.1058 (5)	-0.3033 (6)	0.0953 (6)	4.9 (2)
C(35)	-0.0186 (4)	-0.2937 (5)	0.1122 (5)	3.9 (1)
C(41)	0.0975 (4)	-0.0288 (5)	0.1598 (5)	3.7 (1)
C(42)	0.0886 (7)	0.0516 (6)	0.1059 (6)	6.1 (2)
C(43)	0.1083 (8)	0.0524 (6)	0.0119 (7)	7.5 (3)
C(44)	0.1430 (7)	-0.0263 (6)	-0.0316 (6)	6.1 (2)
C(45)	0.1511 (5)	-0.1043 (5)	0.0252 (5)	4.4 (2)

Table 2. Selected geometric parameters (Å, °)

V(1)—O(1)	1.624 (3)	V(2)—O(4)	1.612 (3)
V(1)—O(2)	1.614 (3)	V(2)—O(5)	1.940 (2)
V(1)—O(5)	2.204 (2)	V(2)—N(2)	2.284 (3)
V(1)—N(1)	2.275 (4)	V(2)—N(31)	2.136 (3)
V(1)—N(11)	2.103 (3)	V(2)—N(41)	2.313 (3)
V(1)—N(21)	2.106 (3)	V(1)···V(2)	3.690 (3)
V(2)—O(3)	1.631 (3)		
O(1)—V(1)—O(2)	106.0 (1)	O(3)—V(2)—O(4)	105.8 (1)
O(1)—V(1)—O(5)	164.9 (1)	O(3)—V(2)—O(5)	100.7 (1)
O(1)—V(1)—N(1)	90.6 (1)	O(3)—V(2)—N(2)	91.1 (1)
O(1)—V(1)—N(11)	93.7 (1)	O(3)—V(2)—N(31)	89.8 (1)
O(1)—V(1)—N(21)	93.1 (1)	O(3)—V(2)—N(41)	162.2 (1)
O(2)—V(1)—O(5)	88.9 (1)	O(4)—V(2)—O(5)	108.3 (1)
O(2)—V(1)—N(1)	163.4 (1)	O(4)—V(2)—N(2)	160.1 (1)
O(2)—V(1)—N(11)	103.6 (1)	O(4)—V(2)—N(31)	94.5 (1)
O(2)—V(1)—N(21)	101.7 (1)	O(4)—V(2)—N(41)	89.4 (1)
O(5)—V(1)—N(1)	74.6 (1)	O(5)—V(2)—N(2)	78.3 (2)
O(5)—V(1)—N(11)	85.4 (2)	O(5)—V(2)—N(31)	151.1 (1)
O(5)—V(1)—N(21)	80.9 (1)	O(5)—V(2)—N(41)	82.7 (1)
N(1)—V(1)—N(11)	75.4 (1)	N(2)—V(2)—N(31)	74.5 (1)
N(1)—V(1)—N(21)	76.2 (1)	N(2)—V(2)—N(41)	72.4 (1)
N(11)—V(1)—N(21)	150.9 (1)	V(1)—O(5)—V(2)	126.2 (1)

H atoms were included at geometrically idealized positions; their coordinates were recalculated after each cycle. The H atoms of the two water molecules were not located.

Data collection, cell refinement and data reduction: *SDP* (Frenz, 1978). Program used to solve structure: *SHELXS86* (VMS version; Sheldrick, 1985). Program used to refine structure: *SDP*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SDP*. The calculations were performed on a VAX computer at the Universität Tübingen.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: MU1137). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Pentacarbonyl-1 $\kappa$ C,2 $\kappa$ <sup>4</sup>C-bis[1,1( $\eta$ <sup>5</sup>-cyclopentadienyl)(dimethylphenylphosphine-2 $\kappa$ P)- $\mu$ -dimethylphosphanido-niobiumtungsten

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## Abstract

The title complex, [NbW(C<sub>2</sub>H<sub>6</sub>P)(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>(CO)<sub>5</sub>-(C<sub>8</sub>H<sub>11</sub>P)], belongs to a small family of monophosphido-bridged transition metal complexes without both a metal–metal bond and any other bridges. The observed geometries of the Nb (distorted tetrahedral) and W (*cis*-octahedral) centers are as expected with a significantly enlarged Nb—P(1)—W angle of 124.9 (2)°. The methyl groups of the bridging phosphido ligand adopt an *endo* orientation towards the CO (Nb—CO) ligand which compels them to adopt symmetrical positions with respect to the (OC)NbP plane, bisecting that of the cyclopentadienyl rings. Consequently, the C(Nb—CO), Nb, P and W atoms are coplanar.

## Comment

During our studies on the reactivity of phosphido-bridged heterobimetallic compounds derived from bis( $\eta$ <sup>5</sup>-cyclopentadienyl)niobium and Group 6 metal (*M'*) carbonyls of the type [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Nb( $\mu$ -PR<sub>2</sub>CO)*M'*—