metal-organic compounds

Tetrapiperidinium di-μ-methoxy-di-μ5-oxo-tetra-μ3-oxo-dodeca-μ2-oxo-octaoxodecavanadate

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The structure of the title compound, $(C_5H_{12}N)_4[V_{10}O_{26}(CH_3O)_2]$, reveals the presence of four protonated piperidinium cations and a $[\{V_{10}O_{26}\}(OCH_3)_2]^{4-}$ polyanion having an embedded centre of inversion. The compound is distinguished by presenting, in contrast with other anionic decavanadates, two methoxy groups bridging the outermost V atoms, and it becomes the first example of this type among reported decavanadates.

Comment

Polyoxometallates have received increasing attention in recent years, since they have been used successfully as drugs with antiviral activity, for example, against herpes or HIV (Rhule *et al.*, 1998). In many other fields, such as catalysis, biology and materials science, the possible applications of polyoxometallates also attract much attention (Müller *et al.*, 1998; Oyaizu & Tsuchida, 1998; Pope & Müller, 1991). In particular, the polyoxovanadate clusters, an important class of polyoxometallates, have been studied extensively because of their fascinating structure and potential applications (Zhang & Chen, 2003). Recently, some interesting studies have been
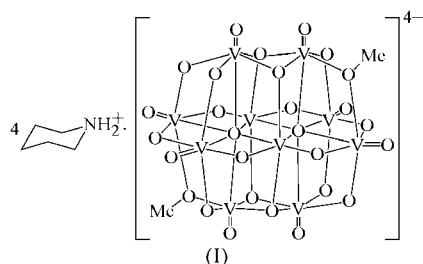
carried out to investigate the interactions of polyoxovanadate with organic ligands (Khan *et al.*, 1993, 1992). Taking into account the above facts, the synthesis of new poly-oxovanadates is of considerable interest in order to gain insight into the nature of this kind of complex. In this paper,

the title new decavanadate compound with the piperidinium cation, formulated as $[(C_5H_{12}N)_4][V_{10}O_{26}(OCH_3)_2]$, (I), has been synthesized and characterized by single-crystal X-ray diffraction and the results are presented here.

Compound (I) contains a $[V_{10}O_{26}(OCH_3)_2]^{4-}$ polyanion and four protonated piperidinium cations. As shown in Fig. 1, its structure consists of a centrosymmetric framework of ten V atoms disposed as two almost regular V_6 octahedra with a common edge, V5–V5[i] [symmetry code: (i) $-x + 1$, $-y$, $-z + 1$], the V···V distances ranging from 3.0169 (9) (V1···V5) to 3.2730 (12) Å (V5···V5[i]). Each V atom coordinates to six O atoms to form ten small VO_6 octahedra occupying the framework vertexes. The ten V atoms can be distinguished into three categories, namely V_a = atoms V5 and V5[i], V_b = atoms V2, V4, V2[i] and V4[i], and V_c = atoms V1, V3, V1[i] and V3[i]. V_a atoms form the common edge, as mentioned above, V_b atoms form two tetrahedra and V_c atoms form quadrangles with V_a atoms. In the polyanion, four different modes for bonding of the oxo ligands are present. Eight terminal O atoms, O1–O4 and O1[i]–O4[i], are simply η^1-bonded to V_b and V_c atoms, with short V—O distances from 1.598 (2) (V2—O2) to 1.603 (2) Å (V4—O4), which indicate substantial V=O character (Table 1). Atoms O5, O5[i], O7–O11 and O7[i]–O11[i] are μ_2-bonded to the corresponding V—V edges of the framework. Two short distances [V5—O5 = 1.689 (2) Å and V5—O9 = 1.684 (2) Å] are observed and result in the two long V—O distances V1—O9 [2.033 (2) Å] and V3[i]—O5 [2.033 (2) Å]. For other μ_2-bridging oxo ligands, the V—O distances are in the range 1.755 (2)–1.904 (2) Å (V2—O10 and V3—O10, respectively). Atoms O12, O13, O12[i] and O13[i] are μ_3-bridging O atoms which form similar V—O interactions in the range 1.903 (2)–2.051 (2) Å (V5—O13 and V2—O13). Finally, both atoms O14 and O14[i] are in the centre of a V_6 octahedron and coordinate to six V atoms with long V—O distances, ranging from 2.072 (2) (V5—O14) to 2.337 (2) Å (V3—O14), which obviously correlate with the short V—O distances discussed above.
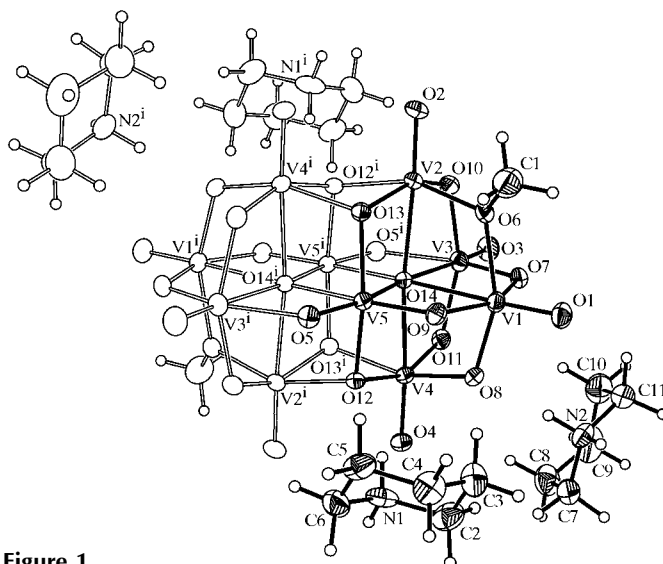

Figure 1
The molecular structure of (I), shown with 30% probability displacement ellipsoids. [Symmetry code: (i) $-x + 1$, $-y$, $-z + 1$.]

An interesting feature of the structure of (I) is the geometry of the μ_2-bridging methoxy ligands. This is the first example of such a group acting as a component of a decavanadium cluster, although it has previously been observed in other vanadium complexes (Chen & Zubieta, 1993; Hitchcock *et al.*, 1997; Hughes *et al.*, 1994; Mikuriya *et al.*, 1993; Jiang *et al.*, 1998; Herron *et al.*, 1997). The O atom of the methoxy ligand (O6) is μ_2-bonded to atoms V1 and V2, with bond lengths of 1.952 (2) and 2.007 (2) Å, respectively, which are more similar to the distances between the V atoms and the μ_3-bridging oxo ligands than to the μ_2-bridging ones. The displacement of atom O6 from the V1/V2/C1 plane is 0.2507 (33) Å. The angles C1—O6—V1 and C1—O6—V2 are 122.0 (2) and 121.0 (2)°, respectively. These features imply that the μ_2-bridging atom O6 bonds to V1 and V2 with sp^2 hybrid orbitals.

In the crystal structure of (I), the six-membered piperidine rings occur in chair conformations. The puckering parameters (Cremer & Pople, 1975) are σ = 2.8 (4)°, φ = 172 (9)° and Q = 0.551 (5) Å for the N1-containing ring, and σ = 6.1 (5)°, φ = −174 (5)° and Q = 0.553 (5) Å for the N2-containing ring. Each piperidinium cation interacts with two [V10O26(OCH3)2]4− anions *via* N—H···O hydrogen bonds (Table 2), which results in a three-dimensional hydrogen-bonding structure, with the N2 H atoms joining decavanadate units along the (101) plane and the N1 H atoms binding along the [100] direction (Fig. 2).
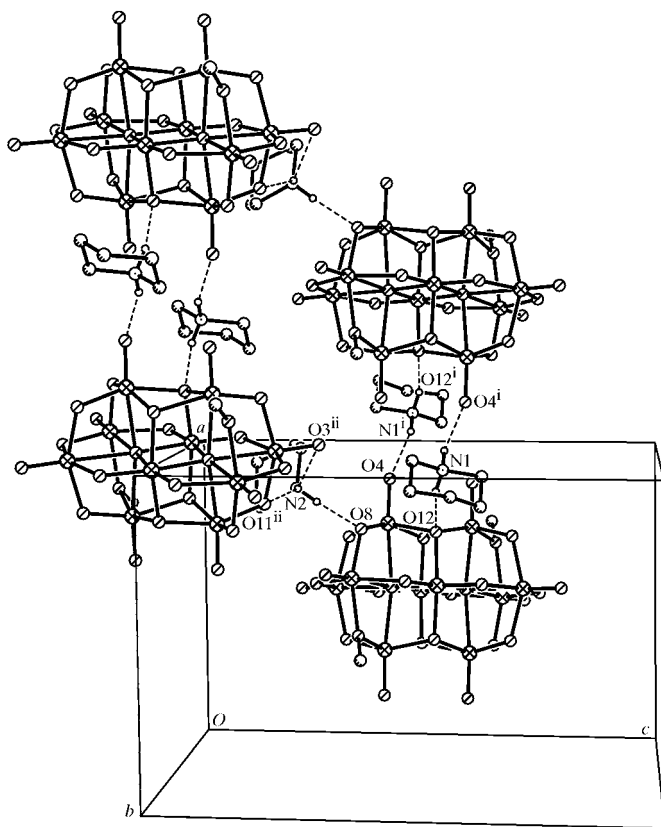

Figure 2
A view of the three-dimensional hydrogen-bonding structure of (I). N2 H atoms join decavanadate units along the (101) plane and N1 H atoms bind along the [100] direction. Dotted lines indicate hydrogen bonds. [Symmetry codes: (i) −x + 2, −y, −z + 1; (ii) −x + 3/2, y + 1/2, −z + 1/2.]

Experimental

Although the initial scope of this work was to prepare a polynuclear complex of oxovanadium(IV) bridged by pyromellitic acid, during the synthetic process a pentavalent species was obtained. It was also found that the decavanadate was easily generated under the experimental pH conditions used, a fact already mentioned in some earlier reports (Pope, 1983; Duraisamy *et al.*, 2000). Thus, the serendipitous presence of pyromellitic acid became important to the formation of the title compound, which was obtained as follows. Pyromellitic acid (0.0254 g, 0.1 mmol) was dissolved in methanol (5 ml) containing piperidine (0.034 g, 0.4 mmol). VO(acac)2 (0.053 g, 0.2 mmol) dissolved in methanol (5 ml) was then added dropwise to the solution. The mixture was heated under reflux with stirring for 7 h. The reaction solution was filtered and concentrated by slow evaporation at room temperature for several days, and orange crystals of the title compound of suitable size for X-ray analysis were obtained from the mixed solution.

Crystal data

(C5H12N)4[V10(CH3O)2O26]	D_x = 2.021 Mg m^{-3}
M_r = 1332.09	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 5269
a = 10.546 (2) Å	reflections
b = 12.950 (3) Å	θ = 2.3–23.3°
c = 16.033 (3) Å	μ = 2.13 mm^{-1}
β = 90.58 (3)°	T = 296 (2) K
V = 2189.5 (8) Å^3	Block, orange
Z = 2	0.22 × 0.18 × 0.14 mm

Data collection

Bruker APEX area-detector diffractometer	3957 independent reflections
	3226 reflections with $I > 2\sigma(I)$
φ and ω scans	R_{int} = 0.021
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	θ_{max} = 25.2°
	h = −12 → 12
T_{min} = 0.639, T_{max} = 0.734	k = −10 → 15
11580 measured reflections	l = −19 → 19

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 2.2417P]$
$R[F^2 > 2\sigma(F^2)]$ = 0.031	
$wR(F^2)$ = 0.093	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.01	$(\Delta/\sigma)_{max}$ = 0.001
3957 reflections	$\Delta\rho_{max}$ = 0.73 e Å^{-3}
290 parameters	$\Delta\rho_{min}$ = −0.45 e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

V1—O1	1.600 (2)	V3—O10	1.904 (2)
V1—O6	2.007 (2)	V3—O11	1.893 (2)
V1—O7	1.836 (2)	V3—O14	2.337 (2)
V1—O8	1.810 (2)	V4—O4	1.603 (2)
V1—O9	2.033 (2)	V4—O8	1.893 (2)
V1—O14	2.271 (2)	V4—O11	1.784 (2)
V2—O2	1.598 (2)	V4—O12	2.036 (2)
V2—O6	1.952 (2)	V4—O13^i	1.936 (2)
V2—O10	1.755 (2)	V4—O14	2.288 (2)
V2—O12^i	1.942 (2)	V5—O5	1.689 (2)
V2—O13	2.051 (2)	V5—O9	1.684 (2)
V2—O14	2.242 (2)	V5—O12	1.956 (2)
V3—O3	1.600 (2)	V5—O13	1.903 (2)
V3—O5^i	2.033 (2)	V5—O14	2.072 (2)
V3—O7	1.807 (2)	V5—O14^i	2.163 (2)
C1—O6—V1	122.0 (2)	C1—O6—V2	121.0 (2)

Symmetry code: (i) −x + 1, −y, −z + 1.

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1$D\cdots$O4[ii]	0.90	2.04	2.887 (4)	157
N1—H1$E\cdots$O12	0.90	1.90	2.774 (4)	162
N2—H2$C\cdots$O3[iii]	0.90	2.53	3.276 (4)	140
N2—H2$C\cdots$O11[iii]	0.90	2.34	3.134 (4)	146
N2—H2$D\cdots$O8	0.90	1.90	2.795 (4)	174

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

All H atoms were positioned geometrically, with C—H distances of 0.97 (CH$_2$) or 0.96 Å (CH$_3$) and N—H distances of 0.90 Å, and they were then treated in riding mode, with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}$(methyl C); the torsion angles of the methyl groups were refined.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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