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Structural investigations of the hexavanadium core $\{V_6O_{19}\}$ in 'oxidized', mixed valence and 'reduced' clusters of the type $[V^{V}_{6-n}V^{IV}_{n}O_{13-n}(OH)_n\{(OCH_2)_3CR\}_2]^{2-}$, $n=0$, 3 and 6

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Abstract

The reactions of $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$ with the tris(hydroxymethyl)methane derived ligands $(HOCH_2)_3CR$ yield hexavanadate clusters of the type $[(n\text{-}C_4H_9)_4N]_2[V_6O_{13}\{(OCH_2)_3CR\}_2]$ ($R=-NHC(O)CHCH_2$ (**1**) and $-NO_2$ (**1a**)) and $[C_5H_5NH]_2[V_6O_{13}\{(OCH_2)_3CCH_3\}_2]\cdot 2Me_2NCOH$ (**2**). These V(V) clusters are readily reduced by organohydrazines to yield the mixed valence V(V)/V(IV) cluster $[(n\text{-}C_4H_9)_4N]_2[V^{V}_3V^{IV}_3O_{10}(OH)_3\{(OCH_2)_3CNO_2\}_2]\cdot 0.67CH_2Cl_2$ (**3**) and the reduced V(IV) cluster $[(n\text{-}C_4H_9)_4N]_2[V^{IV}_6O_7(OH)_6\{(OCH_2)_3CCH_3\}_2]\cdot 2HNPhNHPh$ (**4**). Complexes **1**–**4** share the common hexametalate core $\{M_6O_{19}\}$ which is, however, distorted from the regular octahedral symmetry adopted by $[Mo_6O_{19}]^{2-}$ and $[Nb_6O_{19}]^{8-}$ because of the substitution of doubly-bridging oxo groups of the parent structure type by alkoxy donor oxygens and as a consequence of the reduction of metal sites in **3** and **4**. Crystal data: **1**, space group $P2_1/c$, $a=10.602(3)$, $b=17.774(5)$, $c=16.451(6)$ Å, $\beta=95.42(2)°$, $V=3086(2)$ Å^3, $Z=2$, $D_{calc}=1.44$ g/cm^3; $R=0.060$ based on 2631 reflections. **2**, orthorhombic $Pbca$, $a=16.966(4)$, $b=20.235(4)$, $c=11.524(2)$ Å, $V=3956(2)$ Å^3, $Z=4$, $D_{calc}=1.77$ g/cm^3; $R=0.034$ based on 2729 reflections; **3**, triclinic $P\bar{1}$, $a=13.526(2)$, $b=27.032(5)$, $c=12.950(2)$ Å, $\alpha=100.70(1)$, $\beta=104.33(1)$, $\gamma=75.56(1)°$, $V=4403(2)$ Å^3, $Z=3$, $D_{calc}=1.52$ g/cm^3; $R=0.058$ based on 4494 reflections. **4**, monoclinic $P2_1/c$, $a=13.357(2)$, $b=14.416(2)$, $c=21.584(4)$ Å, $\beta=105.83(2)°$, $V=3998(2)$ Å^3, $Z=2$, $D_{calc}=1.33$ g/cm^3; $R=0.058$ based on 2972 reflections.

Introduction

While an extensive chemistry has been developed for both the polyoxoanions [1, 2] and transition metal alkoxides [3–6], the polyoxoalkoxo metalates represent an emerging structural variety. The prototypes for this structural class are $[Ti_7O_4(OEt)_{20}]$ [7] and $[Nb_8O_{18}(OEt)_{20}]$ [8], species whose structures are related to those of the polyoxoanions $[Mo_7O_{24}]^{6-}$ [9] and $[H_2W_{12}O_{42}]^{10-}$ [10], respectively. The chemistry of oxoalkoxide–titanium clusters has been extended recently with the description of the structures of $[Ti_8O_6(OCH_2C_6H_5)_{20}]$ and $[Ti_{10}O_8(OEt)_{24}]$ [11].

In contrast to these oxoalkoxide oligomers of Ti and Nb which exhibit d^0 metal centers, the molybdenum and vanadium oxoalkoxides may possess a variety of reduced and mixed valence metal cores [12–18] as well as the more common fully oxidized cluster types [19–23]. As part of our investigations of polyoxoalkoxovanadium species, we have described the structures of oxidized, mixed valence and reduced clusters of the type $[V_6O_{13-n}(OH)_n\{(OCH_2)_3CCH_3\}_2]^{2-}$, $n=0$, 2, 4 and 6 [24]. Here, we describe the structures of four members of this class of hexavanadium species $(TBA)_2$-$[V^{V}_6O_{13}\{(OCH_2)_3CNHC(O)CHCH_2\}_2]$ (**1**), $(HNC_5H_5)_2$-$[V^{V}_6O_{13}\{(OCH_2)_3CCH_3\}_2]\cdot 2Me_2NCOH$ (**2**), $(TBA)_2$-$[V^{V}_3V^{IV}_3VO_{10}(OH)_3\{(OCH_2)_3CNO_2\}_2]\cdot 0.67CH_2Cl_2$ (**3**) and $(TBA)_2[V^{IV}_6O_7(OH)_6\{(OCH_2)_3CCH_3\}_2]\cdot 2HN$-$(C_6H_5)NH(C_6H_5)$ (**4**) ($TBA=(n\text{-}C_4H_9)_4N^+$).

Experimental

All chemicals were obtained from either Aldrich, Alfa or Eastman. The precursor isopolyoxovanadate $[H_3V_{10}O_{28}]^{3-}$ was prepared by the literature method [25]. All manipulations were carried out under purified N_2 by using standard Schlenk techniques. Methanol and methylene chloride were dried over magnesium methoxide and CaH_2, respectively. Anhydrous ether was passed through activated alumina prior to use. Elemental analyses were performed by Desert Analytics, Tucson, AZ. The ligands $RC(CH_2OH)_3$ ($R=-CH_3$, $-CH_2CH_3$, $-NH_2$, $-NO_2$ and $NHC(O)CHCH_2$ were purchased from Aldrich Chemical Co.

The following instruments were used in this work: IR, Perkin-elmer 283B IR spectrophotometer; UV–Vis,

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Varian DMSO 90 UV–Vis spectrophotometer; X-ray crystallography, Siemens R3m/V diffractometer and Rigaku AFC5S diffractometer; electrochemistry, BAS100 electroanalytical system; NMR, Varian XL-300 spectrometer.

Cyclic voltammetric studies were carried out in acetonitrile or dimethylformamide solution 1.0×10^3 M in complex and 0.1 M in $(n\text{-}C_4H_9)_4NPF_6$ as supporting electrolyte. Platinum bead and platinum mesh working electrodes were used in the cyclic voltammetry. All potentials are referenced to the ferrocene/ferrocenium couple.

Preparation of $[(n\text{-}C_4H_9)_4N]_2[V_6O_{13}\{(OCH_2)_3CNHC(O)CHCH_2\}_2$ *(1)*

Tris(hydroxymethyl)methylacrylamide (0.53 g, 3.0 mmol) was added to a solution of $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$ (1.69 g, 1.0 mmol) in CH_3CN (50 ml) with stirring. The yellow–brown solution obtained upon refluxing for 24 h was cooled to room temperature and reduced in volume to 25 ml by rotary evaporation. Upon addition of 25 ml of diethyl ether, a reddish brown powder was obtained (1.25 g). Recrystallization from DMF/CH_3CN/diethyl ether (1:2:2 vol./vol./vol.) yielded red crystals in 45% yield. The crystalline product is indefinitely stable when exposed to the atmosphere, while solutions of the complex decompose over a period of days when exposed to the atmosphere at room temperature.*Anal.* Calc. for $C_{46}H_{92}N_4O_{21}V_6$: C, 41.1; H, 6.85; N, 4.17. Found: C. 40.9; H, 6.73; N, 4.06%. IR (KBr pellet, cm^{-1}): 3302(m), 2961(m), 2888(m), 1687(m), 1062(s), 956(s), 809(s), 723(s), 560(m).

The complex $[(n\text{-}C_4H_9)_4N]_2[V_6O_{13}\{(CH_2)_3CNO_2\}_2]$ (**1a**) was prepared in an analogous fashion from $(HOCH_2)_3CNO_2$ and $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$.

Preparation of $[C_5H_5NH]_2[V_6O_{13}\{(OCH_2)_3CCH_3\}_2]\cdot 2Me_2NCOH$ *(2)*

Tris(hydroxymethyl)ethane (0.36 g, 3.0 mmol) was added to a solution of $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$ (1.69 g, 1.0 mmol) in CH_3CN (50 ml) with stirring. After refluxing for 24 h, the yellow–brown solution obtained was treated with $(CH_3)_3SiCl$ (1 ml) in a pyridine–dimethyl formamide mixture (5 ml, 1:1 volume). Upon standing for 3 days, red crystals of **2** were obtained in 35% yield. *Anal.* Calc. for $C_{26}H_{42}N_4O_{21}V_6$: C, 30.00; H, 3.99; N, 5.32. Found: C, 29.8; H, 3.86; N, 5.03%. IR (KBr pellet, cm^{-1}): 2337(w), 1654(w), 1485(w), 1262(w), 1127(w), 1027(s), 958(s), 789(s), 704(s), 584(w).

Preparation of $[(n\text{-}C_4H_9)_4N]_2[V_6O_{10}(OH)_3\{(OCH_2)_3CNO_2\}_2]\cdot 0.69CH_2Cl_2$ *(3)*

Tris(hydroxymethyl)nitromethane (0.45 g, 3.0 mmol) was added to a solution of $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$ (1.69 g, 1.0 mmol) in CH_3CN (50 ml) with stirring. The yellow–brown solution obtained upon refluxing for 24 h was cooled to room temperature and reduced in volume to 25 ml by rotary evaporation. Upon addition of 25 ml of diethyl ether, a reddish brown powder of $[(n\text{-}C_4H_9)_4N]_2[V_6O_{13}\{(OCH_2)_3CNO_2\}_2]$ was obtained (1.25 g). A portion of the $[(n\text{-}C_4H_9)_4N]_2[V_6O_{13}\text{-}\{(OCH_2)_3CNO_2\}_2]$ (0.65 g, 0.5 mmol) was placed in a rigorously dried, argon-purged Schlenk flask. Upon dropwise addition with stirring of a solution of 1,1-methylphenylhydrazine (0.18 g, 1.5 mmol) in CH_2Cl_2 (30 ml), the red hexavanadate slowly dissolved to give a dark blue–green solution. After stirring for 5 h at room temperature under argon, the solution was concentrated to 15 ml and layered with 15 ml of anhydrous diethyl ether. After standing for 3 days at 4 °C, blue needles of **3** were collected in 30% yield. *Anal.* Calc. for $C_{40.67}H_{88.34}N_4O_{23}Cl_{1.34}V_6$: C, 40.0; H, 6.59; N, 4.13. Found: C, 39.8; H, 6.33; N, 4.01%. IR (KBr pellet, cm^{-1}: 2961(m), 2871(m), 1532(s), 1466(m), 1380(w), 1338(w), 1095(s), 950(s), 723(s), 577(m).

Preparation of $[(n\text{-}C_4H_9)_4N]_2[V_6O_7(OH)_6\{(OCH_2)_3CCH_3\}_2]\cdot 2PhNHNHPh$ *(4)*

Methylene chloride (30 ml) was added slowly with stirring to $[(n\text{-}C_4H_9)_4N]_2[V_6O_{13}\{(OCH_2)_3CCH_3\}_2]$ (0.61 g, 0.5 mmol), prepared as previously described [24], and 1,2-diphenylhydrazine (0.28 g, 1.5 mmol), resulting in a dark green solution. After 10 h stirring at room temperature, the solution turned dark brown, whereupon it was concentrated to 10 ml and layered with 15 ml of diethyl ether. After standing for 1 week at 4 °C, brown block-shaped crystals of $[(n\text{-}C_4H_9)_4N]_2[V_6O_{13}\{(OCH_2)_3CCH_3\}_2]\cdot 0.5PhNNPh\cdot 2CH_2Cl_2$ [24] were collected in 20% yield. The filtrate was stored at 4 °C for two months whereupon lustrous purple crystals of $[(n\text{-}C_4H_9)_4N]_2[V_6O_7(OH)_6\text{-}\{(OCH_2CCH_3)_3\}_2]\cdot 2PhNNHPh$ (**4**) were isolated in 40% yield. *Anal.* Calc. for $C_{68}H_{120}N_6O_{19}V_6$: C, 49.3; H, 7.47; N, 5.23. Found: C, 48.9; H, 7.68; N, 5.01%. IR (KBr pellet, cm^{-1}): 2960(m), 2873(w), 1602(s), 1495(s), 1381(w), 1241(w), 1139(m), 1055(s), 949(s), 693(m), 609(w), 567(s).

X-ray crystallographic studies

The details of the crystal data, data collection methods and refinement procedures are summarized in Table 1. In all cases, data were collected at −20 °C at scan speeds of 1 to 15° min^{-1}. The refinements proved unexceptional. Although some disorder of the terminal

TABLE 1. Summary of experimental details for the X-ray diffraction studies of $[(n\text{-}C_4H_9)_4N]_2[V_6O_{13}\{(OCH_2)_3CNHC(O)CHCH_2\}_2]$ (**1**, $[C_5H_5NH]_2[V_6O_{13}\{(OCH_2)_3CCH_3\}_2]\cdot 2Me_2NCOH$ (**2**), $[(n\text{-}C_4H_9)_4N]_2[V_6O_9(OH)_4\{(OCH_2)_3CNO_2\}_2]\cdot 0.67CH_2Cl_2$ (**3**) and $[(n\text{-}C_4H_9)_4N]_2[V_6O_7(OH)_6\{(OCH_2)_3CCH_3\}_2]\cdot 2PhNHNHPh$ (**4**)

	1	**2**	**3**	**4**
Cell parameters				
a (Å)	10.602(3)	16.966(4)	13.526(2)	13.357(2)
b (Å)	17.774(5)	20.235(4)	27.032(5)	14.416(2)
c (Å)	16.451(6)	11.524(2)	12.950(2)	21.584(4)
α (°)	90.00	90.00	100.70(1)	90.00
β (°)	95.42(2)	90.00	104.33(1)	105.83(2)
γ (°)	90.00	90.00	75.56(1)	90.00
V (Å^3)	3086(2)	3956(2)	4403(2)	3998(2)
Space group	$P2_1/c$	$Pbca$	$P\bar{1}$	$P2_1/c$
Z	2	4	3	2
D_{calc} (g/cm^3)	1.44	1.77	1.52	1.33
μ (cm^{-1})				
Measurement of intensity data				
Crystal shape	block	block	needle	needle
Crystal color	red	red	blue–green	purple
Crystal dimensions (mm)	0.35×0.27×0.32	0.31×0.30×0.35	0.26×0.44×0.21	0.19×0.37×0.22
Instrument	Rigaku AFC5S			
Radiation	Mo Kα (λ=0.71073 Å)			
Scan range (°)	$0 \leq 2\theta \leq 50$			
Scan mode	$\omega/2\theta$			
Standards	three taken every 200 reflections			
No. reflections collected	4479	3886	12792	5773
No. reflections used ($I_o \geq 3\sigma(I_o)$)	2631	2729	4494	2972
Reduction of intensity data and summary of structure solution and refinement				
Corrections	data treated for background, attenuators, Lorentz and polarization effects in the usual fashion			
Absorption correction	in all cases based on ψ scans for 5 reflections with χ angles near 90° or 270°			
Structure solution	direct methods			
Structure refinement	least-squares refinement; all non-hydrogen atoms anisotropically refined			
Atom scattering factors	neutral atomic scattering factors were used throughout			
Anomalous dispersion	applied to all non-hydrogen atoms			
Final discrepancy factors				
R	0.060	0.034	0.058	0.058
R_w	0.069	0.046	0.067	0.066
Goodness of fit	1.94	1.72	1.62	1.90

carbon atoms of the cations was apparent in the large parameters associated with these atoms, no further attempts to model the disorder were introduced.

Upon full-matrix least-squares refinement using anisotropic temperature factors for all non-hydrogen atoms of **1**, all hydrogen atom positions were clearly visible on the difference Fourier map. The ligand, solvent, hydrogen, and cation atoms were introduced as fixed contributors at idealized positions and several cycles of full-matrix least-squares refinement were performed to give an R of 0.037 upon convergence of this model.

For $[(n\text{-}C_4H_9)_4N]_2[V_6O_{10}(OH)_3\{(OCH_2)_3CNO_2\}_2\cdot 0.67CH_2Cl_2$ (**3**), the hydrogen positions of the cluster containing V(4)–V(9) were located from the difference Fourier maps. After full-matrix least-squares refinement cycles using anisotropic thermal parameters for all non-hydrogen atoms of the anion and the cation and fixed isotropic temperature factors for the hydrogen atoms of the cation (positioned at idealized C–H distances of 0.96 Å), a difference Fourier synthesis exhibited electron density maxima located at positions consistent with O2 and O6 as the protonation sites. The locations of the hydrogen atoms were confirmed by high-angle ($2\theta > 37°$) refinement of the non-hydrogen atoms followed by difference Fourier synthesis based on inner shell data. This procedure clearly revealed all but three hydrogen atoms of the cation and all hydrogen atoms of the anion. Hydrogen atoms bonded to O14, O15 and O18 were included in the structural model and refinement as independent isotropic atoms in the final least-squares cycles. In contrast, only the H atom bonded to O(3) of the cluster containing V(1)–V(3) and sitting on the center of symmetry could be unambiguously identified. Another H atom with a partial population of 0.4–0.5 appears to be associated with O(6) but could not be adequately refined.

The protonation sites on $[(n\text{-}C_4H_9)_4N]_2[V_6O_7(OH)_6\{(OCH_2)_3CCH_3\}_2]\cdot 2PhNHNHPh$ (**4**) were also apparent on the difference Fourier maps calculated based upon anisotropic refinement of all non-hydrogen atoms of the cation and anion. The hydrogen atom positions were again confirmed by high-angle refinement of non-hydrogen atoms, followed by difference Fourier synthesis of the inner shell data.

Results and discussion

Atomic positional parameters and isotropic thermal parameters, and selected bond lengths and angles are given in Tables 2 and 3, 4 and 5, 6 and 7, 8 and 9 for **1**, **2**, **3** and **4**, respectively.

TABLE 2. Atomic positional parameters and isotropic thermal parameters ($Å^2 \times 10^3$) for $[(n\text{-}C_4H_9)_4N]_2[V_6O_{13}\{(OCH_2)_3CNHC(O)CHCH_2\}_2$ (**1**)

Atom	x	y	z	B_{eq}
V(1)	0.1023(1)	0.01050(9)	1.12602(8)	3.38(7)
V(2)	−0.1708(1)	−0.02439(9)	1.06554(8)	3.34(7)
V(3)	−0.0207(1)	0.12509(8)	1.0057(1)	3.41(7)
O(1)	0.1870(5)	0.0108(3)	1.2111(3)	4.1(3)
O(2)	−0.0582(5)	−0.0137(3)	1.1543(3)	3.6(3)
O(3)	−0.1226(4)	−0.1208(3)	1.0464(3)	3.5(3)
O(4)	−0.3052(5)	−0.0359(3)	1.1028(3)	4.1(3)
O(5)	−0.0531(5)	0.2126(3)	1.0082(4)	4.2(3)
O(6)	0.0650(5)	0.1078(3)	1.1071(3)	3.6(3)
O(7)	0	0	1.0000	2.7(3)
O(8)	0.1225(4)	−0.1003(3)	1.1005(3)	3.1(3)
O(9)	0.1769(5)	−0.0868(3)	0.9460(3)	3.3(3)
O(10)	0.2433(4)	0.0201(3)	1.0537(3)	3.0(2)
O(11)	0.4119(6)	−0.2633(4)	1.0625(5)	6.8(4)
N(1)	0.4659(6)	−0.1404(4)	1.0790(4)	3.9(4)
C(1)	0.3374(7)	−0.1058(5)	1.0614(5)	3.8(4)
C(2)	0.2444(8)	−0.1371(5)	1.1186(5)	4.0(5)
C(3)	0.3583(7)	−0.0211(5)	1.0743(5)	3.7(4)
C(4)	0.2954(7)	−0.1237(5)	0.9713(6)	4.1(5)
C(5)	0.4915(9)	−0.2135(6)	1.0705(6)	4.4(5)
C(6)	0.6298(8)	−0.2304(6)	1.0743(6)	4.6(5)
C(7)	0.670(1)	−0.2987(7)	1.0705(7)	6.5(7)
N(2)	0.1410(7)	0.3326(4)	1.1833(4)	4.6(2)
C(11)	0.2137(9)	0.2715(6)	1.1435(6)	4.9(2)
C(12)	0.312(1)	0.2331(7)	1.1991(8)	8.3(3)
C(13)	0.405(1)	0.1857(8)	1.1593(8)	8.8(4)
C(14)	0.513(2)	0.160(2)	1.210(2)	11.6(7)
C(15)	0.2293(9)	0.3954(6)	1.2141(6)	5.1(2)
C(16)	0.297(1)	0.4366(7)	1.1507(7)	6.9(3)
C(17)	0.410(1)	0.4802(9)	1.192(1)	10.3(4)
C(18)	0.478(2)	0.523(1)	1.135(1)	14.0(6)
C(19)	0.043(1)	0.3594(6)	1.1172(6)	5.7(2)
C(20)	−0.041(1)	0.4243(7)	1.1431(7)	7.7(3)
C(21)	−0.145(1)	0.444(1)	1.073(1)	10.2(4)
C(22)	−0.247(2)	0.386(2)	1.068(2)	12.1(8)
C(23)	0.081(1)	0.3023(6)	1.2570(6)	5.2(2)
C(24)	−0.020(1)	0.2428(7)	1.2389(7)	6.5(3)
C(25)	−0.033(1)	0.1946(8)	1.3132(8)	8.3(3)
C(26)	−0.141(1)	0.142(1)	1.302(1)	11.3(5)

TABLE 3. Selected bond lengths (Å) and angles (°) for $[(n\text{-}C_4H_9)_4N]_2[V_6O_{13}\{(OCH_2)_3CNHC(O)CHCH_2\}_2]$ (**1**)

V1–O1	1.590(5)	N1–C5	1.34(1)
V1–O2	1.857(5)	C1–C2	1.53(1)
V1–O6	1.795(6)	C1–C3	1.53(1)
V1–O7	2.255(2)	C1–C4	1.54(1)
V1–O8	2.029(6)	C5–C6	1.49(1)
V1–O10	2.004(5)	C6–C7	1.29(1)
V2–O2	1.807(5)	N2–C11	1.52(1)
V2–O3	1.824(6)	N2–C15	1.51(1)
V2–O4	1.615(5)	N2–C19	1.51(1)
V2–O7	2.236(1)	N2–C23	1.52(1)
V2–O9	1.986(6)	C11–C12	1.48(1)
V2–O10	2.039(5)	C12–C13	1.50(2)
V3–O3	1.815(5)	C13–C14	1.42(3)
V3–O5	1.594(6)	C15–C16	1.51(1)
V3–O6	1.848(5)	C16–C17	1.53(2)
V3–O7	2.237(2)	C17–C18	1.45(2)
V3–O8	2.014(5)	C19–C20	1.54(1)
V3–O9	2.021(5)	C20–C21	1.56(2)
O8–C2	1.454(9)	C21–C22	1.49(3)
O9–C4	1.443(9)	C23–C24	1.52(1)
O10–C3	1.435(9)	C24–C25	1.51(2)
O11–C5	1.22(1)	C25–C26	1.48(2)
N1–C1	1.50(1)		
O1–V1–O2	103.6(2)	O4–V2–O10	96.0(2)
O1–V1–O6	104.3(3)	O7–V2–O9	77.4(1)
O1–V1–O7	172.9(2)	O7–V2–O10	77.2(1)
O1–V1–O8	97.1(3)	O9–V2–O10	82.2(2)
O1–V1–O10	97.6(2)	O3–V3–O5	104.2(3)
O2–V1–O6	94.3(2)	O3–V3–O6	93.3(2)
O2–V1–O7	80.7(2)	O3–V3–O7	81.3(2)
O2–V1–O8	86.8(2)	O3–V3–O8	89.1(2)
O2–V1–O10	157.1(2)	O3–V3–O9	157.6(3)
O6–V1–O7	80.9(2)	O5–V3–O6	103.2(3)
O6–V1–O8	157.7(2)	O5–V3–O7	173.2(2)
O6–V1–O10	88.8(2)	O5–V3–O8	97.8(3)
O7–V1–O8	77.3(1)	O5–V3–O9	97.5(3)
O7–V1–O10	77.4(1)	O6–V3–O7	80.3(2)
O8–V1–O10	82.0(2)	O6–V3–O8	157.6(2)
O2–V2–O3	93.7(2)	O6–V3–O9	86.6(2)
O2–V2–O4	104.2(3)	O7–V3–O8	78.0(2)
O2–V2–O7	82.3(2)	O7–V3–O9	76.7(2)
O2–V2–O9	89.2(2)	O8–V3–O9	82.8(2)
O2–V2–O10	159.0(2)	V1–O2–V2	111.9(3)
O3–V2–O4	102.6(3)	V2–O3–V3	112.5(3)
O3–V2–O7	81.1(2)	V1–O6–V3	113.5(3)
O3–V2–O9	157.7(2)	V1–O7–V1	180.00
O3–V2–O10	87.5(2)	V1–O7–V2	85.07(6)
O4–V2–O7	172.1(2)	V1–O7–V2	94.93(6)
O4–V2–O9	98.1(3)	V1–O7–V3	85.38(5)
V1–O7–V3	94.62(5)	C3–C1–C4	111.1(7)
V1–O7–V2	94.93(6)	O8–C2–C1	108.8(7)
V1–O7–V2	85.07(6)	O10–C3–C1	111.1(6)
V1–O7–V3	94.62(5)	O9–C4–C1	110.3(7)
V1–O7–V3	85.38(5)	O11–C5–N1	124.8(9)
V2–O7–V2	180.00	O11–C5–C6	122(1)
V2–O7–V3	94.90(5)	N1–C5–C6	113.5(9)
V2–O7–V3	85.10(5)	C5–C6–C7	121(1)
V2–O7–V3	85.10(5)	C11–N2–C15	110.4(7)
V2–O7–V3	94.90(5)	C11–N2–C19	105.0(7)
V3–O7–V3	180.00	C11–N2–C23	111.0(7)
V1–O8–V3	109.5(2)	C15–N2–C19	111.8(8)

(*continued*)

TABLE 3. (*continued*)

V1–O8–C2	120.3(5)	C15–N2–C23	106.6(7)
V3–O8–C2	118.2(5)	C19–N2–C23	112.1(7)
V2–O9–V3	110.6(2)	N2–C11–C12	114.8(9)
V2–O9–C4	120.0(5)	C11–C12–C13	116(1)
V3–O9–C4	117.2(5)	C12–C13–C14	117(2)
V1–O10–V2	109.9(2)	N2–C15–C16	116.5(8)
V1–O10–C3	118.8(4)	C15–C16–C17	110(1)
V2–O10–C3	118.7(4)	C16–C17–C18	113(1)
C1–N1–C5	124.7(7)	N2–C19–C20	114.4(9)
N1–C1–C2	111.0(7)	C19–C20–C21	110(1)
N1–C1–C3	105.1(7)	C20–C21–C22	110(2)
N1–C1–C4	106.0(7)	N2–C23–C24	115.5(8)
C2–C1–C3	111.4(7)	C23–C24–C25	111(1)
C2–C1–C4	111.8(7)	C24–C25–C26	113(1)

TABLE 4. Atomic positional parameters and isotropic temperature factors ($Å^2\times10^3$) for $[C_5H_5NH]_2[V_6O_{13}\{(OCH_2)_3CCH_3\}_2]\cdot 2Me_2NCOH$ (**2**)

Atom	*x*	*y*	*z*	B_{eq}
V(1)	0.40623(4)	0.04125(3)	0.61771(5)	1.92(3)
V(2)	0.53198(4)	0.10614(3)	0.46683(5)	1.93(3)
V(3)	0.57339(4)	−0.00852(3)	0.65983(5)	1.90(3)
O(1)	0.3310(2)	0.0670(1)	0.6893(2)	2.7(1)
O(2)	0.4498(2)	0.1205(1)	0.5600(2)	2.2(1)
O(3)	0.4686(1)	0.0893(1)	0.3368(2)	2.2(1)
O(4)	0.5665(2)	0.1783(1)	0.4389(2)	2.8(1)
O(5)	0.6330(2)	−0.0065(1)	0.7680(2)	2.7(1)
O(6)	0.4823(1)	0.0314(1)	0.7238(2)	2.0(1)
O(7)	1/2	0	1/2	1.5(1)
O(8)	0.3497(1)	0.0352(1)	0.4610(2)	1.9(1)
O(9)	0.3995(1)	−0.0853(1)	0.3973(2)	1.8(1)
O(10)	0.3831(1)	−0.0549(1)	0.6222(2)	1.9(1)
O(11)	0.2181(2)	0.2556(2)	0.2091(3)	5.4(2)
N(1)	0.1236(2)	0.3210(2)	0.0626(3)	3.6(2)
N(2)	0.3430(2)	0.2449(2)	0.2759(4)	4.2(2)
C(1)	0.2690(2)	−0.0655(2)	0.4888(3)	2.2(2)
C(2)	0.2705(2)	0.0081(2)	0.4593(3)	2.3(2)
C(3)	0.3020(2)	−0.0765(2)	0.6109(3)	2.2(2)
C(4)	0.3173(2)	−0.1039(2)	0.3998(3)	2.2(2)
C(5)	0.1832(2)	−0.0896(2)	0.4845(4)	3.0(2)
C(6)	0.1241(3)	0.3094(2)	−0.0513(5)	4.4(3)
C(7)	0.0852(3)	0.3496(3)	−0.1261(4)	4.3(2)
C(8)	0.0443(4)	0.4019(3)	−0.0819(4)	5.2(3)
C(9)	0.0427(3)	0.4123(3)	0.0375(4)	4.9(3)
C(10)	0.0832(3)	0.3711(2)	0.1078(4)	3.4(2)
C(11)	0.2893(4)	0.2723(2)	0.2112(4)	4.6(3)
C(12)	0.4241(4)	0.2673(4)	0.2790(7)	8.7(5)
C(13)	0.3233(4)	0.1906(4)	0.3513(7)	8.2(4)
H(1)	0.163(4)	0.295(4)	0.113(6)	10(2)

TABLE 5. Selected bond lengths (Å) and angles (°) for $[C_5H_5NH]_2[V_6O_{13}\{(OCH_2)_3CCH_3\}_2]\cdot 2Me_2NCOH$ (**2**)

V1–O1	1.607(3)
V1–O2	1.887(3)
V1–O6	1.788(2)
V1–O7	2.2511(7)
V1–O8	2.048(3)
V1–O10	1.986(3)
V2–O2	1.783(3)
V2–O3	1.876(3)
V2–O4	1.606(3)
V2–O7	2.2479(7)
V2–O9	1.995(2)
V2–O10	2.050(3)
V3–O3	1.784(3)
V3–O5	1.605(3)
V3–O6	1.894(3)
V3–O7	2.2299(7)
V3–O8	1.983(2)
V3–O9	2.061(3)
O8–C2	1.452(4)
O9–C4	1.446(4)
O10–C3	1.449(4)
O11–C11	1.254(6)
N1–C6	1.333(6)
N1–C10	1.331(6)
N2–C11	1.302(6)
N2–C12	1.450(7)
N2–C13	1.439(7)
C1–C2	1.526(6)
C1–C3	1.530(5)
C1–C4	1.525(5)
C1–C5	1.537(5)
C6–C7	1.357(7)
C7–C8	1.364(7)
C8–C9	1.392(7)
C9–C10	1.351(6)
O1–V1–O2	102.5(1)
O1–V1–O6	105.0(1)
O1–V1–O7	172.4(1)
O1–V1–O8	95.8(1)
O1–V1–O10	98.5(1)
O2–V1–O6	93.0(1)
O2–V1–O7	79.97(8)
O2–V1–O8	85.6(1)
O2–V1–O10	156.8(1)
O6–V1–O7	82.00(8)
O6–V1–O8	159.0(1)
O6–V1–O10	90.9(1)
O7–V1–O8	77.14(7)
O7–V1–O10	78.01(7)
O8–V1–O10	82.6(1)
O2–V2–O3	93.6(1)
O2–V2–O4	104.9(1)
O2–V2–O7	82.21(8)
O2–V2–O9	91.0(1)
O2–V2–O10	158.9(1)
O3–V2–O4	102.4(1)
O3–V2–O7	79.87(8)
O3–V2–O9	157.3(1)
O3–V2–O10	84.9(1)
O4–V2–O7	172.2(1)
O4–V2–O9	97.9(1)
O4–V2–O10	95.9(1)
O7–V2–O9	78.75(1)

(*continued*)

TABLE 5. (*continued*)

O7–V2–O10	76.82(7)
O9–V2–O10	82.9(1)
O3–V3–O5	104.9(1)
O3–V3–O6	93.3(1)
O3–V3–O7	82.29(8)
O3–V3–O8	91.6(1)
O3–V3–O9	160.1(1)
O5–V3–O6	101.6(1)
O5–V3–O7	172.3(1)
O5–V3–O8	97.9(1)
O5–V3–O9	94.8(1)
O6–V3–O7	80.37(7)
O6–V3–O8	157.9(1)
O6–V3–O9	85.0(1)
O7–V3–O8	78.94(7)
O7–V3–O9	77.84(7)
O8–V3–O9	83.1(1)
V1–O2–V2	112.3(1)
V2–O3–V3	112.2(1)
V1–O6–V3	111.7(1)
V1–O7–V1	180.00
V1–O7–V2	85.34(3)
V1–O7–V2	94.66(3)
V1–O7–V3	85.73(3)
V1–O7–V3	94.27(3)
V1–O7–V2	94.66(3)
V1–O7–V2	85.34(3)
V1–O7–V3	94.27(3)
V1–O7–V3	85.73(3)
V2–O7–V2	180.00
V2–O7–V3	94.56(2)
V2–O7–V3	85.44(2)
V2–O7–V3	85.44(2)
V2–O7–V3	94.56(2)
V3–O7–V3	180.00
V1–O8–V3	109.1(1)
V1–O8–C2	117.9(2)
V3–O8–C2	119.8(2)
V2–O9–V3	108.4(1)
V2–O9–C4	119.4(2)
V3–O9–C4	117.5(2)
V1–O10–V2	110.1(1)
V1–O10–C3	118.7(2)
V2–O10–C3	118.1(2)
C6–N1–C10	121.5(4)
C11–N2–C12	123.0(5)
C11–N2–C13	120.6(5)
C12–N2–C13	116.3(5)
C2–C1–C3	109.9(3)
C2–C1–C4	109.9(3)
C2–C1–C5	108.6(3)
C3–C1–C4	110.4(3)
C3–C1–C5	109.2(3)
C4–C1–C5	108.9(3)
O8–C2–C1	112.3(3)
O10–C3–C1	112.7(3)
O9–C4–C1	113.4(3)
N1–C6–C7	121.1(5)
C6–C7–C8	118.4(4)
C7–C8–C9	119.8(5)
C8–C9–C10	119.3(5)
N1–C10–C9	119.8(4)
O11–C11–N2	124.7(5)

TABLE 6. Atomic positional parameters and isotropic temperature factors ($Å^3 \times 10^3$) for $[(n\text{-}C_4H_9)_4N]_2[V_6O_{10}(OH)_3\{(OCH_2)_3CNO_2\}_2]$ (3)

Atom	*x*	*y*	*z*	B_{eq}
V(1)	1.1279(2)	−0.0531(1)	0.9170(2)	2.0(1)
V(2)	0.8871(2)	−0.0387(1)	0.8715(2)	2.0(1)
V(3)	1.0225(2)	−0.0604(1)	1.1131(2)	2.0(1)
V(4)	0.9448(2)	0.2591(1)	0.7698(2)	2.2(2)
V(5)	0.8529(2)	0.2418(1)	0.9641(2)	1.9(1)
V(6)	0.7832(2)	0.3525(1)	0.8684(2)	2.2(1)
V(7)	1.0160(2)	0.3635(1)	0.9221(2)	2.4(2)
V(8)	1.0913(2)	0.2524(1)	1.0171(2)	1.9(1)
V(9)	0.9323(2)	0.3422(1)	1.1115(2)	2.4(2)
O(1)	1.2251(8)	−0.0843(4)	0.8684(8)	2.4(2)
O(2)	1.0182(8)	−0.0739(4)	0.8325(8)	1.7(2)
O(3)	0.8886(8)	0.0171(4)	0.7985(8)	2.3(2)
O(4)	0.8038(8)	−0.0666(4)	0.7861(8)	2.3(2)
O(5)	1.0344(8)	−0.1051(4)	1.1842(8)	2.4(2)
O(6)	1.1337(8)	−0.0925(4)	1.0303(8)	1.6(2)
O(7)	1.0000	0	1.0000	1.4(3)
O(8)	1.0990(8)	0.0087(4)	0.8425(8)	2.2(2)
O(9)	1.0837(8)	0.0852(4)	1.0127(8)	1.8(2)
O(10)	1.2078(8)	−0.0095(4)	1.0409(8)	1.9(2)
O(11)	1.312(1)	0.0947(5)	0.846(1)	4.5(3)
O(12)	1.415(1)	0.0605(6)	0.978(1)	6.8(4)
O(13)	0.9602(8)	0.2320(4)	0.6531(9)	2.7(2)
O(14)	0.8774(8)	0.2125(4)	0.8148(8)	1.9(2)
O(15)	0.9999(8)	0.2079(4)	1.0217(8)	2.4(2)
O(16)	0.7945(8)	0.2014(4)	0.9849(9)	2.9(3)
O(17)	0.6720(8)	0.3873(4)	0.8247(9)	2.6(2)
O(18)	0.8109(8)	0.3050(4)	0.7415(8)	2.4(2)
O(19)	0.9346(9)	0.2992(4)	0.9390(9)	2.1(2)
O(20)	1.0814(8)	0.2235(4)	0.8591(8)	1.8(2)
O(21)	1.1385(8)	0.3094(4)	0.9772(8)	2.0(2)
O(22)	1.0183(8)	0.3167(4)	0.7800(8)	2.0(2)
O(23)	1.299(1)	0.2243(5)	0.687(1)	4.8(3)
O(24)	1.360(1)	0.2806(6)	0.804(1)	7.0(4)
O(25)	0.9204(9)	0.3717(4)	1.2273(9)	2.9(3)
O(26)	0.9938(8)	0.3862(4)	1.0584(9)	2.4(2)
O(27)	0.8751(8)	0.3913(4)	0.8569(9)	2.4(2)
O(28)	1.080(1)	0.4024(4)	0.905(1)	3.4(3)
O(29)	1.2039(8)	0.2199(4)	1.0602(8)	2.5(2)
O(30)	1.0559(8)	0.2941(4)	1.1387(8)	2.1(2)
O(31)	0.7943(9)	0.3789(4)	1.0248(9)	2.8(3)
O(32)	0.7303(8)	0.2937(4)	0.9002(8)	2.1(2)
O(33)	0.8529(8)	0.2883(4)	1.1052(9)	2.4(2)
O(34)	0.568(1)	0.3838(6)	1.184(1)	6.8(4)
O(35)	0.500(1)	0.3317(7)	1.068(1)	8.7(5)
N(1)	1.331(1)	0.0691(6)	0.919(1)	3.8(4)
N(2)	1.294(1)	0.2557(6)	0.762(1)	4.5(4)
N(3)	0.577(1)	0.3490(6)	1.114(1)	3.7(4)
N(4)	0.620(1)	0.1271(5)	0.699(1)	2.4(3)
N(5)	0.094(1)	0.2132(5)	0.364(1)	2.3(3)
N(6)	0.266(1)	0.4600(5)	0.194(1)	2.2(3)
C(1)	1.243(1)	0.0494(6)	0.942(1)	2.1(3)
C(2)	1.184(1)	0.0276(6)	0.833(1)	2.7(4)
C(3)	1.288(1)	0.0096(6)	1.019(1)	2.3(3)
C(4)	1.172(1)	0.0970(6)	0.991(1)	2.6(4)
C(5)	1.198(1)	0.2694(7)	0.813(1)	3.1(4)
C(6)	1.171(1)	0.2172(6)	0.817(1)	2.8(4)
C(7)	1.111(1)	0.3015(7)	0.739(1)	3.3(4)

(*continued*)

TABLE 6. (*continued*)

Atom	x	y	z	B_{eq}
C(8)	1.226(1)	0.2980(6)	0.927(1)	2.7(4)
C(9)	0.675(1)	0.3360(6)	1.063(1)	2.2(4)
C(10)	0.701(1)	0.3882(6)	1.065(1)	2.4(4)
C(11)	0.757(1)	0.3014(6)	1.140(1)	2.3(3)
C(12)	0.643(1)	0.3101(6)	0.950(1)	2.4(4)
C(21)	0.635(1)	0.1399(6)	0.820(1)	2.7(4)
C(22)	0.539(1)	0.1553(7)	0.866(1)	3.3(4)
C(23)	0.566(1)	0.1637(7)	0.988(2)	4.0(4)
C(24)	0.475(2)	0.185(1)	1.041(2)	7.2(7)
C(25)	0.563(1)	0.0836(6)	0.659(1)	2.9(4)
C(26)	0.620(1)	0.0330(7)	0.705(1)	3.9(4)
C(27)	0.560(1)	−0.0093(7)	0.661(1)	3.6(4)
C(28)	0.463(2)	0.0005(9)	0.699(2)	7.0(6)
C(29)	0.726(1)	0.1152(6)	0.672(1)	2.6(4)
C(30)	0.729(1)	0.1002(7)	0.556(2)	3.7(4)
C(31)	0.840(2)	0.0911(8)	0.538(2)	5.5(5)
C(32)	0.849(2)	0.073(1)	0.422(2)	7.2(7)
C(33)	0.546(1)	0.1725(7)	0.642(1)	3.2(4)
C(34)	0.585(1)	0.2226(7)	0.670(1)	3.8(4)
C(35)	0.514(1)	0.2607(7)	0.597(2)	4.2(4)
C(36)	0.537(2)	0.312(1)	0.621(2)	7.0(6)
C(37)	0.176(1)	0.1937(6)	0.294(1)	2.1(3)
C(38)	0.289(1)	0.1769(6)	0.353(1)	2.2(3)
C(39)	0.360(1)	0.1584(6)	0.273(1)	2.7(4)
C(40)	0.473(1)	0.1454(6)	0.321(1)	3.2(4)
C(41)	0.121(1)	0.1879(6)	0.465(1)	2.5(4)
C(42)	0.119(1)	0.1318(6)	0.444(1)	2.9(4)
C(43)	0.176(2)	0.106(1)	0.552(2)	6.3(6)
C(44)	0.179(2)	0.052(1)	0.531(2)	9.7(9)
C(45)	−0.010(1)	0.2019(6)	0.289(1)	2.4(3)
C(46)	−0.104(1)	0.2199(7)	0.341(1)	3.3(4)
C(47)	−0.188(2)	0.1911(7)	0.278(2)	4.2(5)
C(48)	−0.290(2)	0.2103(8)	0.319(2)	5.7(5)
C(49)	0.077(1)	0.2709(6)	0.394(1)	2.7(4)
C(50)	0.169(1)	0.2918(6)	0.457(1)	2.7(4)
C(51)	0.137(1)	0.3519(7)	0.484(1)	3.8(4)
C(52)	0.229(2)	0.3733(8)	0.548(2)	5.4(5)
C(53)	0.298(1)	0.4464(6)	0.087(1)	2.7(4)
C(54)	0.269(1)	0.4908(7)	0.023(2)	3.7(4)
C(55)	0.291(2)	0.4745(9)	−0.088(2)	6.2(6)
C(56)	0.402(3)	0.451(1)	−0.090(3)	8(1)
C(57)	0.146(1)	0.4743(7)	0.179(1)	3.6(4)
C(58)	0.102(2)	0.4757(7)	0.274(2)	3.8(4)
C(59)	−0.014(2)	0.4966(7)	0.254(2)	4.7(5)
C(60)	−0.065(2)	0.4966(8)	0.343(2)	5.4(5)
C(61)	0.309(1)	0.4117(6)	0.251(1)	2.5(4)
C(62)	0.272(1)	0.3627(7)	0.194(1)	3.5(4)
C(63)	0.305(2)	0.3203(8)	0.263(2)	5.4(5)
C(64)	0.421(2)	0.3021(8)	0.295(2)	5.6(5)
C(65)	0.313(1)	0.5040(6)	0.267(1)	3.0(4)
C(66)	0.430(2)	0.4964(7)	0.285(2)	4.5(5)
C(67)	0.470(2)	0.5379(7)	0.369(2)	3.9(4)
C(68)	0.585(2)	0.530(1)	0.396(2)	7.0(6)
Cl(1)	0.684(1)	0.3659(5)	0.425(1)	10.1(4)
Cl(2)	0.869(1)	0.3953(5)	0.564(1)	11.1(4)
C(20)	0.797(2)	0.357(1)	0.541(2)	9.4(8)
H(3)	0.9151	0.0027	0.7335	2.6
H(14)	0.8113	0.2107	0.7655	2.2
H(15)	1.0067	0.2032	1.0960	2.7
H(18)	0.8099	0.3249	0.6854	2.8

TABLE 7. Selected bond lengths (Å) and angles (°) for $[(n\text{-}C_4H_9)_4N]_2[V_6O_9(OH)_4\{(OCH_2)_3CNO_2\}]$ (**3**)

V1–O1	1.58(1)
V1–O2	1.76(1)
V1–O6	1.94(1)
V1–O7	2.305(3)
V1–O8	1.99(1)
V1–O10	2.05(1)
V2–O2	1.93(1)
V2–O3	1.93(1)
V2–O4	1.60(1)
V2–O7	2.256(3)
V2–O9	2.04(1)
V2–O10	1.99(1)
V3–O3	1.91(1)
V3–O5	1.61(1)
V3–O6	1.99(1)
V3–O7	2.307(3)
V3–O8	2.00(1)
V3–O9	2.02(1)
V4–O13	1.59(1)
V4–O14	1.97(1)
V4–O18	1.92(1)
V4–O19	2.28(1)
V4–O20	2.04(1)
V4–O22	2.01(1)
V5–O14	2.02(1)
V5–O15	1.99(1)
V5–O16	1.59(1)
V5–O19	2.23(1)
V5–O32	2.00(1)
V5–O33	2.02(1)
V6–O17	1.59(1)
V6–O18	1.94(1)
V6–O19	2.28(1)
V6–O27	1.86(1)
V6–O31	2.00(1)
V6–O32	2.04(1)
V7–O21	2.00(1)
V7–O22	2.03(1)
V7–O26	1.83(1)
V7–O27	1.91(1)
V7–O28	1.59(1)
V8–O15	1.95(1)
V8–O19	2.28(1)
V8–O20	2.03(1)
V8–O21	2.00(1)
V8–O29	1.58(1)
V8–O30	1.85(1)
V9–O19	2.32(1)
V9–O25	1.59(1)
V9–O26	1.91(1)
V9–O30	1.85(1)
V9–O31	2.04(1)
V9–O33	2.00(1)
O8–C2	1.42(2)
O9–C4	1.41(2)
O10–C3	1.42(2)
O11–N1	1.20(2)
O12–N1	1.20(2)
O20–C6	1.41(2)
O21–C8	1.43(2)
O22–C7	1.42(2)

(*continued*)

TABLE 7. (*continued*)

O23–N2	1.17(2)
O24–N2	1.21(2)
O31–C10	1.43(2)
O32–C12	1.42(2)
O33–C11	1.42(2)
O34–N3	1.19(2)
O35–N3	1.21(2)
N1–C1	1.53(2)
N2–C5	1.53(2)
N3–C9	1.55(2)
N4–C21	1.52(2)
N4–C25	1.52(2)
N4–C29	1.49(2)
N4–C33	1.55(2)
N5–C37	1.54(2)
N5–C41	1.51(2)
N5–C45	1.56(2)
N5–C49	1.51(2)
N6–C53	1.50(2)
N6–C57	1.54(2)
N6–C61	1.53(2)
N6–C65	1.53(2)
C1–C2	1.53(2)
C1–C3	1.51(2)
C1–C4	1.54(2)
C5–C6	1.56(2)
C5–C7	1.52(2)
C5–C8	1.54(2)
C9–C10	1.53(2)
C9–C11	1.54(2)
C9–C12	1.50(2)
C21–C22	1.49(2)
C22–C23	1.52(2)
C23–C24	1.50(3)
C25–C26	1.54(2)
C26–C27	1.51(2)
C27–C28	1.46(3)
C29–C30	1.49(2)
C30–C31	1.53(3)
C31–C32	1.52(3)
C33–C34	1.53(2)
C34–C35	1.52(2)
C35–C36	1.46(3)
C37–C38	1.53(2)
C38–C39	1.51(2)
C39–C40	1.48(2)
C41–C42	1.49(2)
C42–C43	1.61(3)
C43–C44	1.44(3)
C45–C46	1.52(2)
C46–C47	1.51(2)
C47–C48	1.53(3)
C49–C50	1.49(2)
C50–C51	1.57(2)
C51–C52	1.50(2)
C53–C54	1.50(2)
C54–C55	1.51(3)
C55–C56	1.48(4)
C57–C58	1.49(2)
C58–C59	1.50(2)
C59–C60	1.48(3)

(*continued*)

TABLE 7. (*continued*)

C61–C62	1.53(2)
C62–C63	1.50(2)
C63–C64	1.49(3)
C65–C66	1.51(2)
C66–C67	1.52(2)
C67–C68	1.47(3)
Cl1–C20	1.86(3)
Cl2–C20	1.53(3)
O1–V1–O2	106.1(5)
O1–V1–O6	102.2(5)
O1–V1–O7	172.4(4)
O1–V1–O8	97.1(5)
O1–V1–O10	96.9(5)
O2–V1–O6	94.1(4)
O2–V1–O7	81.2(3)
O2–V1–O8	91.5(4)
O2–V1–O10	156.9(5)
O6–V1–O7	79.3(3)
O6–V1–O8	157.6(4)
O6–V1–O10	82.9(4)
O7–V1–O8	80.1(3)
O7–V1–O10	75.8(3)
O8–V1–O10	83.5(4)
O2–V2–O3	87.9(4)
O2–V2–O4	103.2(5)
O2–V2–O7	79.1(3)
O2–V2–O9	89.6(4)
O2–V2–O10	157.1(4)
O3–V2–O4	101.7(5)
O3–V2–O7	81.0(3)
O3–V2–O9	161.2(4)
O3–V2–O10	90.1(4)
O4–V2–O7	176.5(4)
O4–V2–O9	97.0(5)
O4–V2–O10	99.5(5)
O7–V2–O9	80.3(3)
O7–V2–O10	78.1(3)
O9–V2–O10	85.0(4)
O3–V3–O5	104.1(5)
O3–V3–O6	89.2(4)
O3–V3–O7	80.0(3)
O3–V3–O8	88.1(4)
O3–V3–O9	159.2(4)
O5–V3–O6	100.4(5)
O5–V3–O7	175.8(4)
O5–V3–O8	101.3(5)
O5–V3–O9	96.6(5)
O6–V3–O7	78.3(3)
O6–V3–O8	158.2(4)
O6–V3–O9	89.2(4)
O7–V3–O8	79.9(3)
O7–V3–O9	79.4(3)
O8–V3–O9	85.8(4)
O13–V4–O14	102.8(5)
O13–V4–O18	103.2(5)
O13–V4–O19	175.8(5)
O13–V4–O20	99.3(5)
O13–V4–O22	97.4(5)
O14–V4–O18	88.2(4)
O14–V4–O19	80.4(4)
O14–V4–O20	87.0(4)

(*continued*)

TABLE 7. (*continued*)

O14–V4–O22	159.4(5)
O18–V4–O19	79.5(4)
O18–V4–O20	157.4(5)
O18–V4–O22	91.3(4)
O19–V4–O20	78.0(4)
O19–V4–O22	79.2(4)
O20–V4–O22	85.6(4)
O14–V5–O15	87.9(4)
O14–V5–O16	100.8(5)
O14–V5–O19	80.5(4)
O14–V5–O32	89.4(4)
O14–V5–O33	160.8(5)
O15–V5–O16	99.4(5)
O15–V5–O19	80.4(4)
O15–V5–O32	160.4(4)
O15–V5–O33	89.0(4)
O16–V5–O19	178.7(5)
O16–V5–O32	100.1(5)
O16–V5–O33	98.3(5)
O19–V5–O32	80.0(4)
O19–V5–O33	80.3(4)
O32–V5–O33	87.2(4)
O17–V6–O18	102.6(5)
O17–V6–O19	174.7(5)
O17–V6–O27	102.5(5)
O17–V6–O31	97.9(5)
O17–V6–O32	97.3(5)
O18–V6–O19	78.9(4)
O18–V6–O27	92.0(5)
O18–V6–O31	157.8(5)
O18–V6–O32	83.4(4)
O19–V6–O27	82.4(4)
O19–V6–O31	79.9(4)
O19–V6–O32	77.9(4)
O27–V6–O31	91.5(5)
O27–V6–O32	160.2(5)
O31–V6–O32	85.9(4)
O21–V7–O22	83.3(4)
O21–V7–O26	90.8(5)
O21–V7–O27	156.8(4)
O21–V7–O28	97.3(5)
O22–V7–O26	158.4(5)
O22–V7–O27	84.8(4)
O22–V7–O28	98.3(5)
O26–V7–O27	93.0(5)
O26–V7–O28	103.1(5)
O27–V7–O28	104.1(5)
O15–V8–O19	80.1(4)
O15–V8–O20	87.2(4)
O15–V8–O21	159.4(4)
O15–V8–O29	103.1(5)
O15–V8–O30	90.7(5)
O19–V8–O20	78.0(4)
O19–V8–O21	79.8(4)
O19–V8–O29	174.1(5)
O19–V8–O30	81.2(4)
O20–V8–O21	84.3(4)
O20–V8–O29	97.0(5)
O20–V8–O30	159.1(5)
O21–V8–O29	96.6(5)
O21–V8–O30	90.6(4)

(*continued*)

TABLE 7. (*continued*)

O29–V8–O30	103.7(5)
O19–V9–O25	175.1(5)
O19–V9–O26	80.2(4)
O19–V9–O30	80.0(4)
O19–V9–O31	78.0(4)
O19–V9–O33	78.4(4)
O25–V9–O26	102.7(5)
O25–V9–O30	103.6(5)
O25–V9–O31	98.2(5)
O25–V9–O33	98.2(5)
O26–V9–O30	93.3(5)
O26–V9–O31	85.0(5)
O26–V9–O33	157.5(5)
O30–V9–O31	157.9(5)
O30–V9–O33	89.8(5)
O31–V9–O33	83.8(4)
V1–O2–V2	114.1(5)
V2–O3–V3	111.1(5)
V1–O6–V3	112.0(5)
V1–O7–V1	180.00
V1–O7–V2	85.6(1)
V1–O7–V2	94.4(1)
V1–O7–V3	90.0(1)
V1–O7–V3	90.0(1)
V1–O7–V2	94.4(1)
V1–O7–V2	85.6(1)
V1–O7–V3	90.0(1)
V1–O7–V3	90.0(1)
V2–O7–V2	180.00
V2–O7–V3	92.1(1)
V2–O7–V3	87.9(1)
V2–O7–V3	87.9(1)
V2–O7–V3	92.1(1)
V3–O7–V3	180.00
V1–O8–V3	109.5(5)
V1–O8–C2	118.7(9)
V3–O8–C2	117.4(9)
V2–O9–V3	108.1(5)
V2–O9–C4	116.2(9)
V3–O9–C4	117.8(9)
V1–O10–V2	111.7(5)
V1–O10–C3	117.2(9)
V2–O10–C3	117.3(9)
V4–O14–V5	107.7(5)
V5–O15–V8	108.8(5)
V4–O18–V6	111.8(5)
V4–O19–V5	91.3(4)
V4–O19–V6	89.0(4)
V4–O19–V8	94.1(4)
V4–O19–V9	176.6(6)
V5–O19–V6	93.5(4)
V5–O19–V8	90.6(4)
V5–O19–V9	91.8(4)
V6–O19–V8	174.8(5)
V6–O19–V9	92.0(4)
V8–O19–V9	84.7(4)
V4–O20–V8	109.9(5)
V4–O20–C6	115.5(9)
V8–O20–C6	117.3(9)
V7–O21–V8	110.6(5)
V7–O21–C8	117.5(9)

(*continued*)

TABLE 7. (*continued*)

V8–O21–C8	120.0(9)
V4–O22–V7	111.0(5)
V4–O22–C7	114.3(9)
V7–O22–C7	120(1)
V7–O26–V9	114.0(5)
V6–O27–V7	112.3(5)
V8–O30–V9	114.0(5)
V6–O31–V9	109.9(5)
V6–O31–C10	116.4(9)
V9–O31–C10	120(1)
V5–O32–V6	108.7(5)
V5–O32–C12	118.9(9)
V6–O32–C12	114.2(9)
V5–O33–V9	109.2(5)
V5–O33–C11	115.2(9)
V9–O33–C11	120.6(9)

As the details of the synthesis and spectroscopy of polyoxoalkoxovanadium complexes have been presented elsewhere [24], only a brief discussion of these aspects will be developed. The reactions of $[(n\text{-}C_4H_9)_4N]_3[H_3V_{10}O_{28}]$ with the tris(hydroxymethyl)methane derivatives $(HOCH_2)_3CR$ (R = –NHC(O)CHCH$_2$ and –NO$_2$) in acetonitrile yield upon recrystallization the hexavanadate clusters $[(n\text{-}C_4H_9)_4N]_2[V_6O_{13}\{(OCH_2)_3CR\}_2]$. Under optimal conditions, the stoichiometry of the process conforms to the following:

$$2(TBA)_3[H_3V_{10}O_{28}] + 6(HOCH_2)_3CR \longrightarrow 3(TBA)_2[V_6O_{13}\{(OCH_2)_3CR\}_2] + 12H_2O + V_2O_5$$

An unusual feature of the reaction chemistry of tris(hydroxymethyl)methane derived ligands with $(TBA)_3[H_3V_{10}O_{28}]$ is the behavior of the tris(hydroxymethyl)aminomethane species, $(HOCH_2)_3CNH_2$, which acts as a reductant to give the mixed valence isopolyanion $(TBA)_4[V_{10}O_{26}]$ [26, 27] as the only vanadium containing product of the reaction. In contrast, derivatization of the amino group as in $(HOCH_2)_3CNHC(O)CHCH_2$ or $(HOCH_2)_3CNMe_2$ [24] results in isolation of the hexavanadate species $(TBA)_2[V_6O_{13}\{(OCH_2)_3CNRR'\}_2]$.

The hexanuclear V(V) clusters $(TBA)_2[V_6O_{13}\{(OCH_2)_3CR\}_2]$ are readily reduced both chemically and electrochemically [24]. Thus, addition of 2 equiv. of 1,1-methylphenylhydrazine to a deep red solution of $(TBA)_2[V_6O_{13}\{(OCH_2)_3CNO_2\}_2]$ (**1a**) in methylene chloride produces an immediate color change to deep blue–green. Addition of diethyl ether to this solution yields blue crystals of $(TBA)_2[V_6O_{10}(OH)_3\{(OCH_2)_3CNO_2\}_2]\cdot 0.67CH_2Cl_2$ (**3**). The hydrazine serves as both reductant and proton source in the process:

$$[V_6O_{13}\{(OCH_2)_3CNO_2\}_2]^{2-} + 3H_2NNMePh \longrightarrow [V_6O_9(OH)_4\{(OCH_2)_3CNO_2\}_2]^{2-} + 3HNMePh + 1.5N_2$$

TABLE 8. Atomic positional parameters and isotropic temperature factors (Å^2×10^3) for $[(n\text{-}C_4H_9)_4N]_2[VO_7(OH)_6\{(OCH_2)_3CCH_3\}_2]\cdot HNPhNHPh$ (**4**)

Atom	*x*	*y*	*z*	B_{eq}
V(1)	0.0617(1)	0.5591(1)	0.60413(7)	2.17(6)
V(2)	−0.1608(1)	0.4687(1)	0.51869(7)	2.12(6)
V(3)	0.0561(1)	0.3556(1)	0.53673(7)	2.19(6)
O(1)	0.1030(4)	0.6010(4)	0.6758(3)	3.1(3)
O(2)	−0.0832(4)	0.5212(4)	0.6050(2)	2.3(2)
O(3)	−0.1828(4)	0.6002(4)	0.4876(2)	2.3(2)
O(4)	−0.2715(4)	0.4439(4)	0.5292(3)	2.7(3)
O(5)	0.0964(4)	0.2532(4)	0.5622(3)	2.7(3)
O(6)	0.1032(4)	0.4262(4)	0.6195(2)	2.2(2)
O(7)	0	1/2	1/2	1.8(3)
O(8)	0.0044(4)	0.6757(4)	0.5567(2)	2.2(2)
O(9)	0.0871(4)	0.6511(4)	0.4516(2)	2.2(2)
O(10)	0.1886(4)	0.5777(4)	0.5728(2)	2.1(2)
N(1)	0.1286(5)	0.2702(5)	0.7820(3)	2.8(3)
N(2)	0.3236(6)	0.2800(6)	0.6230(4)	4.0(4)
N(3)	0.3309(6)	0.3736(6)	0.6410(4)	4.2(4)
C(1)	0.1699(7)	0.7457(6)	0.5476(4)	2.5(4)
C(2)	0.0707(7)	0.7551(6)	0.5690(4)	2.6(4)
C(3)	0.2357(6)	0.6669(7)	0.5831(4)	2.6(4)
C(4)	0.1439(6)	0.7328(6)	0.4741(4)	2.5(4)
C(5)	0.2305(7)	0.8369(7)	0.5646(5)	4.0(5)
C(11)	0.0187(7)	0.2824(7)	0.7866(4)	3.0(4)
C(12)	−0.0564(7)	0.3323(7)	0.7319(4)	3.5(5)
C(13)	−0.1658(8)	0.3306(7)	0.7412(5)	4.1(5)
C(14)	−0.2476(8)	0.3757(8)	0.6878(5)	5.4(6)
C(15)	0.1789(7)	0.3647(6)	0.7777(4)	3.1(4)
C(16)	0.1829(8)	0.4311(7)	0.8321(4)	4.1(5)
C(17)	0.2408(8)	0.5183(7)	0.8253(5)	4.8(5)
C(18)	0.243(1)	0.5889(9)	0.8771(7)	8.3(8)
C(19)	0.1883(7)	0.2178(6)	0.8421(4)	3.3(4)
C(20)	0.2978(7)	0.1895(7)	0.8440(5)	3.7(5)
C(21)	0.3459(7)	0.1339(7)	0.9041(4)	3.8(5)
C(22)	0.4524(8)	0.0972(9)	0.9055(6)	6.1(6)
C(23)	0.1292(7)	0.2177(6)	0.7201(4)	3.0(4)
C(24)	0.0843(8)	0.1213(7)	0.7163(5)	4.4(5)
C(25)	0.097(1)	0.0699(8)	0.6573(6)	6.1(7)
C(26)	0.207(1)	0.0515(9)	0.6608(8)	10(1)
H(2)	−0.0790	0.4754	0.6373	2.7
H(3)	−0.2417	0.6033	0.4511	2.8
H(6)	0.1768	0.4220	0.6355	2.6
C(31)	0.3832(6)	0.2481(5)	0.5834(3)	5.7(1)
C(32)	0.3499(5)	0.1679(5)	0.5475(4)	5.7(1)
C(33)	0.4087(6)	0.1312(4)	0.5090(3)	5.7(1)
C(34)	0.5008(6)	0.1746(5)	0.5063(3)	5.7(1)
C(35)	0.5341(5)	0.2548(5)	0.5422(4)	5.7(1)
C(36)	0.4753(6)	0.2915(4)	0.5807(3)	5.7(1)
C(37)	0.4005(5)	0.3985(5)	0.6981(3)	5.2(1)
C(38)	0.4491(6)	0.3329(4)	0.7440(4)	5.2(1)
C(39)	0.5131(5)	0.3618(5)	0.8033(3)	5.2(1)
C(40)	0.5285(5)	0.4562(5)	0.8167(3)	5.2(1)
C(41)	0.4799(6)	0.5217(4)	0.7708(4)	5.2(1)
C(42)	0.4159(5)	0.4929(5)	0.7115(3)	5.2(1)

TABLE 9. Selected bond lengths (Å) and angles (°) for $[(n\text{-}C_4H_9)_4N]_2[V_6O_7(OH)_6\{(OCH_2)_3\}_2]\cdot 2PhNHNHPh$ (4)

V1–O1	1.611(5)
V1–O2	2.016(6)
V1–O6	1.997(6)
V1–O7	2.334(1)
V1–O8	2.008(5)
V1–O10	2.007(6)
V2–O2	2.015(5)
V2–O3	2.005(6)
V2–O4	1.597(6)
V2–O7	2.335(2)
V2–O9	2.006(5)
V2–O10	2.021(5)
V3–O3	2.008(6)
V3–O5	1.616(6)
V3–O6	2.002(5)
V3–O7	2.280(2)
V3–O8	2.008(5)
V3–O9	1.998(6)
O8–C2	1.43(1)
O9–C4	1.41(1)
O10–C3	1.42(1)
N1–C11	1.51(1)
N1–C15	1.53(1)
N1–C19	1.52(1)
N1–C23	1.54(1)
N2–N3	1.40(1)
N2–C31	1.40(1)
N3–C37	1.373(9)
C1–C2	1.53(1)
C1–C3	1.51(1)
C1–C4	1.54(1)
C1–C5	1.53(1)
C11–C12	1.51(1)
C12–C13	1.53(2)
C13–C14	1.50(1)
C15–C16	1.50(1)
C16–C17	1.50(2)
C17–C18	1.50(2)
C19–C20	1.51(1)
C20–C21	1.51(1)
C21–C22	1.51(2)
C23–C24	1.51(1)
C24–C25	1.52(2)
C25–C26	1.47(2)
C31–C32	1.40(1)
C31–C36	1.40(1)
C32–C33	1.40(1)
C33–C34	1.40(1)
C34–C35	1.40(1)
C35–C36	1.40(1)
C37–C38	1.395(9)
C37–C42	1.40(1)
O1–V1–O2	99.9(3)
O1–V1–O6	101.2(3)
O1–V1–O7	179.2(2)
O1–V1–O8	99.1(3)
O1–V1–O10	100.0(3)
O2–V1–O6	87.8(2)
O2–V1–O7	79.7(1)
O2–V1–O8	89.9(2)
O2–V1–O10	160.1(2)
O6–V1–O7	79.6(1)
O6–V1–O8	159.7(2)
O6–V1–O10	87.9(2)
O7–V1–O8	80.2(2)
O7–V1–O10	80.4(1)
O8–V1–O10	87.5(2)
O2–V2–O3	86.9(2)
O2–V2–O4	102.5(3)
O2–V2–O7	79.7(2)
O2–V2–O9	86.8(2)
O2–V2–O10	159.8(2)
O3–V2–O4	101.6(3)
O3–V2–O7	79.5(2)
O3–V2–O9	159.4(2)
O3–V2–O10	90.9(2)
O4–V2–O7	177.5(2)
O4–V2–O9	98.9(3)
O4–V2–O10	97.7(3)
O7–V2–O9	80.0(2)
O7–V2–O10	80.1(2)
O9–V2–O10	88.3(2)
O3–V3–O5	98.8(3)
O3–V3–O6	89.5(2)
O3–V3–O7	80.8(2)
O3–V3–O8	86.9(2)
O3–V3–O9	162.3(2)
O5–V3–O6	99.6(2)
O5–V3–O7	179.5(2)
O5–V3–O8	98.1(3)
O5–V3–O9	98.9(3)
O6–V3–O7	80.8(2)
O6–V3–O8	162.3(2)
O6–V3–O9	89.5(2)
O7–V3–O8	81.5(2)
O7–V3–O9	81.6(2)
O8–V3–O9	88.8(2)
V1–O2–V2	110.3(3)
V2–O3–V3	109.2(3)
V1–O6–V3	109.5(2)
V1–O7–V1	180.00
V1–O7–V2	90.23(5)
V1–O7–V2	89.77(5)
V1–O7–V3	90.12(5)
V1–O7–V3	89.88(5)
V1–O7–V2	89.77(5)
V1–O7–V2	90.23(5)
V1–O7–V3	89.88(5)
V1–O7–V3	90.12(5)
V2–O7–V2	180.00
V2–O7–V3	89.67(5)
V2–O7–V3	90.33(5)
V2–O7–V3	90.33(5)
V2–O7–V3	89.67(5)
V3–O7–V3	180.00
V1–O8–V3	108.5(3)
V1–O8–C2	116.4(4)
V3–O8–C2	115.3(5)
V2–O9–V3	108.7(3)
V2–O9–C4	115.9(4)
V3–O9–C4	116.2(5)
V1–O10–V2	109.7(2)
V1–O10–C3	116.5(5)
V2–O10–C3	114.1(5)

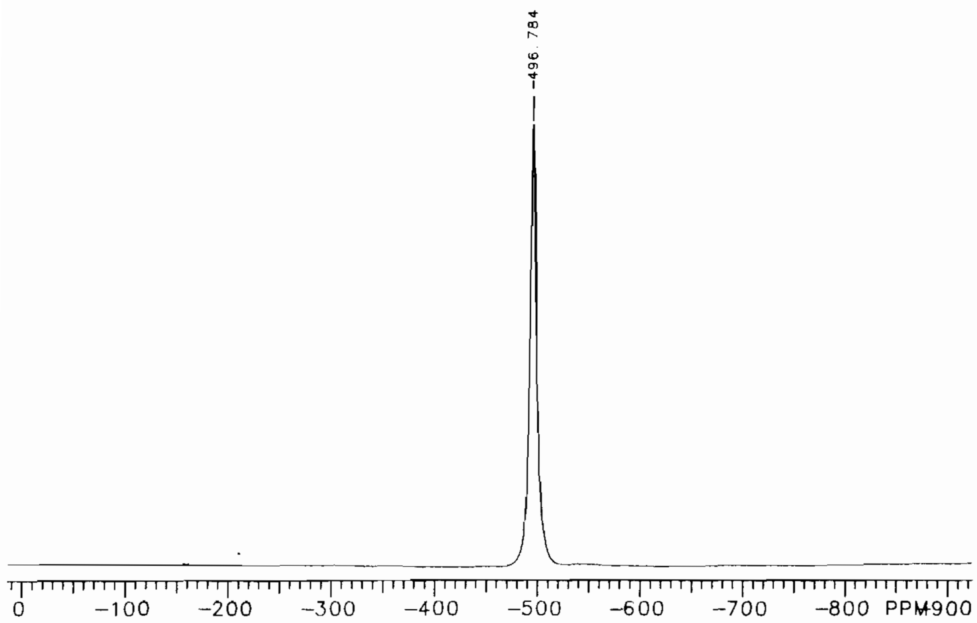

Fig. 1. ^{51}V NMR spectrum of $(C_5H_5NH)_2[V_6O_{13}\{(OCH_2)_3CCH_3\}_2]\cdot 2DMF$ (2).

Using an appropriate amount of 1,2-diphenylhydrazine complete reduction may be effected to give the V(IV) cluster $(TBA)_2[V_6O_7(OH)_6\{(OCH_2)_3CR\}_2]$.

$$[V_6O_{13}\{(OCH_2)_3CR\}_2]^{2-} + 3HNPhNHPh \longrightarrow [V_6O_7(OH)_6\{(OCH_2)_3CR\}_2]^{2-} + 3PhNNPh$$

In the presence of excess 1,2-diphenylhydrazine, purple crystals of $(TBA)_2[V_6O_7(OH)_6\{(OCH_2)_3CCH_3\}_2]\cdot 2HNPhNHPh$ (**4**) were isolated in good yield.

The V(V) clusters $(TBA)_2[V_6O_{13}\{(OCH_2)_3CR\}_2]$ (**1**) and $[C_5H_5NH]_2[V_6O_{13}\{(OCH_2)_3CCH_3\}_2]\cdot 2DMF$ (**2**) exhibit a single resonance in the ^{51}V NMR spectra, measured between 20 and 60 °C. At 20 °C, the chemical shifts are 497 (Fig. 1) and 500 ppm relative to $VOCl_3$ for **1** and **2**, respectively. At 60 °C, chemical shift values of 506 and 508 ppm are observed.

The IR spectra of the oxidized clusters **1** and **2** are characterized by a strong band in the 940–960 cm^{-1} region, attributed to $\nu(V{=}O)$ and several features in the 700–850 cm^{-1} range assigned to $\nu(V{-}O{-}V)$. The spectra of the mixed valence complex **3** and the reduced cluster **4** likewise exhibit a band in the 940–950 cm^{-1} region associated with $\nu(V{=}O)$. However, in complex **3** the pattern of bands in the 700–850 cm^{-1} region associated with $\nu(V{-}O{-}V)$ of the $[V_6O_{13}\{(OCH_2)_3CR\}_2]^{2-}$ oxidized cluster types is replaced by a single medium intensity feature at 723 cm^{-1}. The consequences of further reduction and protonation are apparent in the spectrum of **4** which contains no unprotonated [V–O–V] moieties and hence is featureless in the 700–850 cm^{-1} range.

The structures of the anions of **1**, **3** and **4** are illustrated in Figs. 2, 3 and 4, respectively. The structure of the anion of **1** consists of a hexavanadate core $\{V_6O_{19}\}$ in which six doubly-bridging oxo groups of the hexametalate framework [1] have been replaced by oxygen donors of the trisalkoxy ligands. As shown schemactically in Fig. 5, the alkoxy oxygens occupy the triangular faces of the tetrahedral cavities of the $\{M_6O_{19}\}$ core. While the cluster possesses eight cavities of this type, only two centrosymmetrically related about the core are occupied in the structure of **1**.

While the central core $\{V_6O_{19}\}$ is grossly analogous to the structures of $[Nb_6O_{19}]^{8-}$, $[Ta_6O_{19}]^{8-}$, $[Mo_6O_{19}]^{2-}$ and $[W_6O_{19}]^{2-}$ [1], the presence of both bridging oxo groups and bridging alkoxy groups results in considerable distortions from the regular geometries associated with the underivatized hexametalate cores. The $\{V_6O_{19}\}$ unit has been previously described only for the $(\eta^5\text{-}C_5Me_5)Rh(III)$ supported cluster $[(RhCp^*)_4V_6O_{19}]$ [28, 29].

The structure of **2** consists of an essentially identical anion core, differing only in the identity of the substituent R. However, an analysis of the V-bridging oxo and V-bridging alkoxo bond distances reveals a clear bond length alternation pattern which was not apparent in other structures of the type $[V_6O_{13}\{(OCH_2)_3CR\}_2]^{2-}$ [24].

This *trans* bond length alternation occurs in the eight-membered V_4O_4 rings, see schematic illustration in Fig. 6. Bond length alternation has also been reported for $[(C_5H_5)TiMo_5O_{18}]^{3-}$ [30], $[(Me_5C_5)RhNb_2W_4O_{19}]$ [31], $[(CO)_3Mn(Nb_2W_4O_{19})]$ [32],

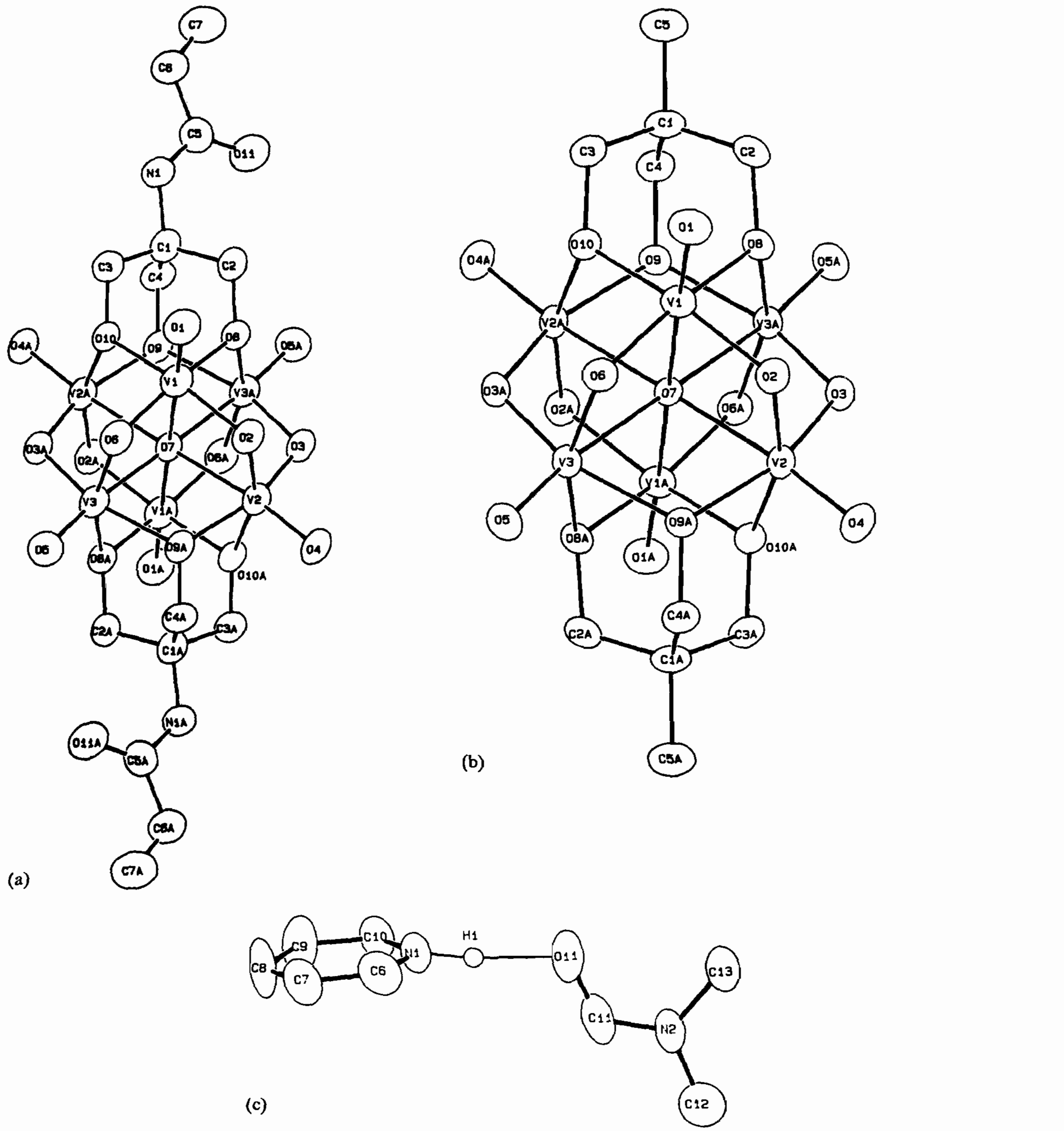

Fig. 2. ORTEP view of the structure of: (a) $[V_6O_{13}\{(OCH_2)_3CNHC(O)CHCH_2\}_2]^{2-}$; (b) $[V_6O_{13}\{(OCH_2)_3CCH_3\}_2]^{2-}$; (c) $(C_5H_5NH)^+ \cdot$ DMF unit of 2.

$[(C_5H_5)TiMo_5O_{18}MoO_2Cl]^{2-}$ [33], $[Mn(Nb_6O_{19})_2]^{12-}$ [34] and $[H_3V_{10}O_{28}]^{3-}$ [25], where the effect is related to the weakening of certain M–O (bridging) bonds relative to adjacent interactions as consequences of protonation, oxocyclic interactions with other metal centers or the introduction of heterometals into the ring.

However, the pattern of bond length alternations in **2** is quite distinct from those observed for these complexes and from that reported for $[Mo_6O_{19}]^{2-}$ [35]. The Mo–O (bridging) bond alternation in this case is rationalized in terms of classical off-center displacement of metals in a relatively rigid close-packed oxygen framework [36]. Thus, the *trans* bond alternation is a

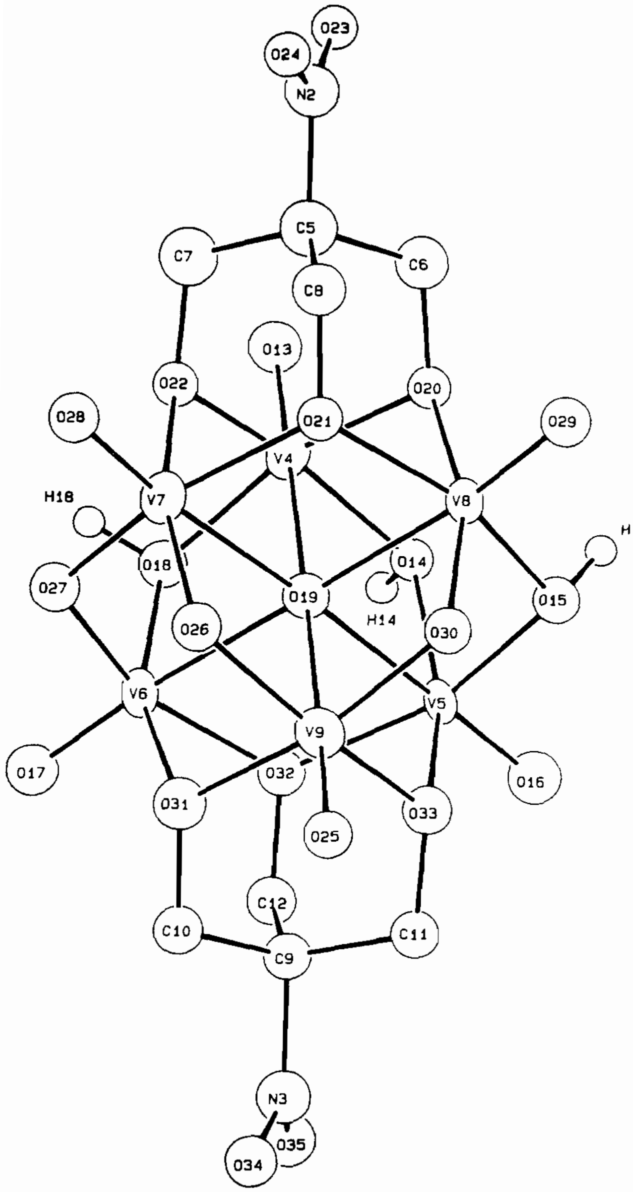

Fig. 3. ORTEP view of the structure of $[V_6O_{10}(OH)_3\{(OCH_2)_3CNO_2\}_2]^{2-}$.

consequence of the displacement of the metal toward one oxygen which concomitantly produces an equivalent displacement away from the *trans* oxygen. In the case of **2**, the bond length alternation reflects both off-center displacement of the metals and the presence of doubly-bridging alkoxy oxygens which distort the oxide framework.

The mixed valence cluster **3** retains the $\{V_6O_{19}\}$ structural core. The structural consequence of protonation of four doubly-bridging oxygens and reduction of four of six V sites are most apparent in the lengthening of V–OH(bridging) and V–O(bridging) distances, compared to those **1** and **2** (Table 10). Although the protonation sites in **3** were evident in the electron density mass, the identity of the protonation sites and the number of V(IV) sites was confirmed by valence sum calculations [37]. The results of these calculations are presented in Table 11. These clearly suggest that **3** is an example of a mixed oxidation state cluster 3V(V)/3V(IV) and quite distinct from the 2V(V)/4V(IV) cluster previously reported [24]. The magnetic properties of **3** are also quite different from those observed for the 2V(V)/4V(IV) cluster, $[(n\text{-}C_4H_9)_4N]_2[V_6O_9(OH)_4\{(OCH_2)_3CCH_3\}_2]$. While the latter exhibits a room temperature magnetic moment (μ_{eff}/molecule) of 3.50 μ_B (corresponding to 1.75 μ_B per V(IV) site), the room temperature moment of **3** is 2.98 μ_B/molecule (1.72 μ_B per V(IV) site). Further details of the magnetic properties of this class of hexavanadium clusters will be presented in a forthcoming publication [38].

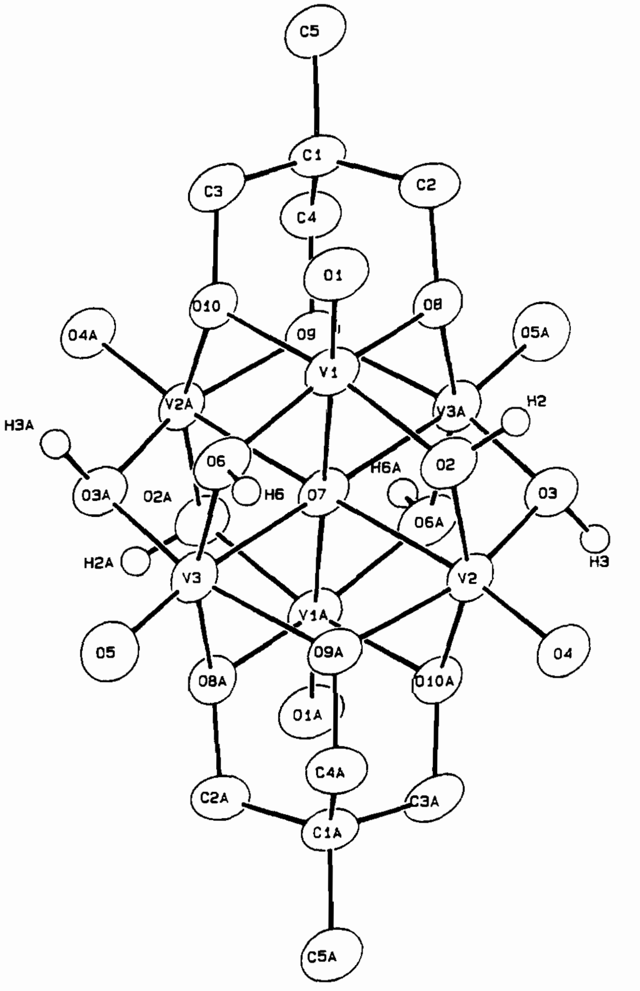

Fig. 4. ORTEP view of the structure of $[V_6O_7(OH)_6\{(OCH_2)_3CCH_3\}_2]^{2-}$.

The structural parameters associated with the fully reduced core of **4** are consistent with the presence of six protonated bridging oxo groups and six V(IV) centers. The metrical parameters for **4** are compared to those

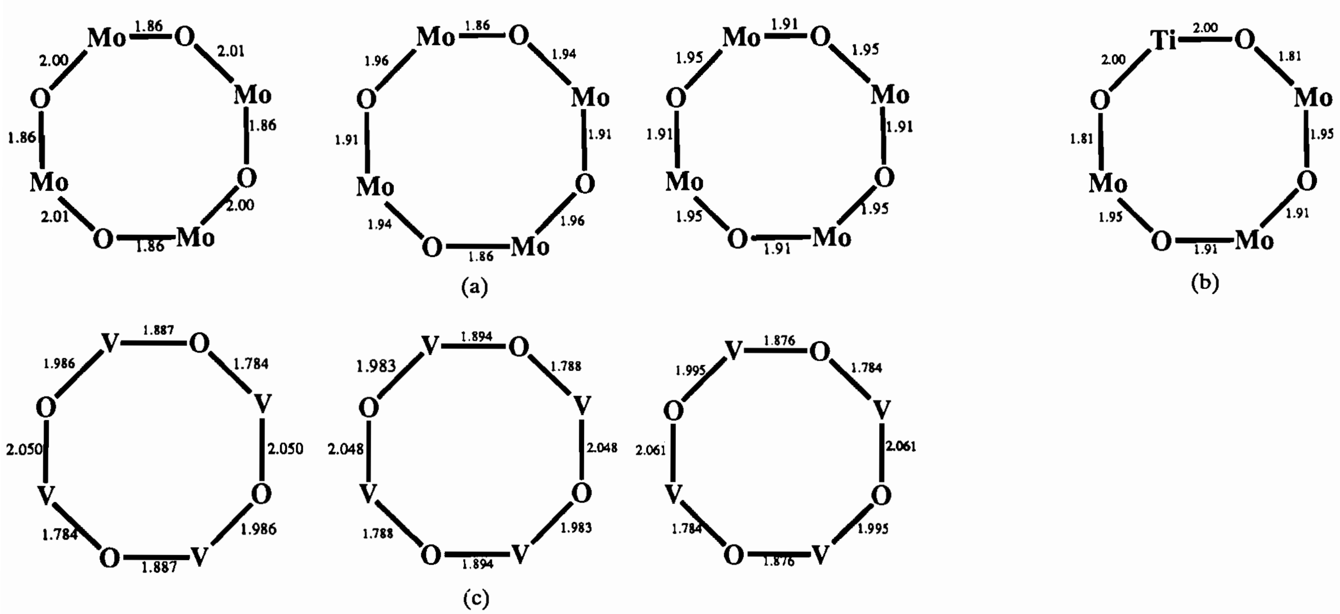

Fig. 5. Schematic representations of: (a) the Mo_4O_4 rings of $[Mo_6O_{19}]^{2-}$; (b) the $TiMo_3O_4$ ring of $[(C_5H_5)TiMo_5O_{18}]^{3-}$; (c) the V_4O_4 rings of **2**.

TABLE 10. Comparison of selected structural parameters for the structures **1**, **2**, **3** and **4**[a]

	1	2	3	4
V–O, bridging oxo	1.824(7)	1.886(4) 1.785(4)	1.86(1)	
V–O, bridging hydroxy			1.94(1)	2.007(8)
V–O, bridging alkoxy	2.016(7)	2.053(4) 1.988(4)	2.017(4)	2.008(9)
V–Oc[b]	2.243(4)	2.243(1)	2.28(1)	2.316(2)
V–O–V (oxo)[c]	112.6(6)	112.1(2)	114.0(7)	
V–O–V (hydroxy)[c]			110.6(8)	109.7(5)
V–O–V (alkoxy)[c]	110.0(6)	109.2(3)	109.8(8)	109.0(5)

[a] Bond lengths in Å, angles in °. [b] Oc = central oxo group. [c] Type of oxygen defined in parentheses.

for **1**, **2** and **3** in Table 10 and the results of valence sum calculations are presented in Table 11.

The structural changes which occur upon reduction and protonation of the $\{V_6O_{19}\}$ core are also manifested in an overall expansion of the core volume as reflected in an increase in the distances between planes of atoms in the structures. Figure 6 illustrates these effects by comparing the spacings between approximately planar layers of negatively-charged and close-packed oxygen atoms separated by layers of cationic vanadium centers. The plane containing the central oxo group and six doubly bridging oxo and/or hydroxy groups defines the reference plane from which the spacings to the other parallel layers have been calculated.

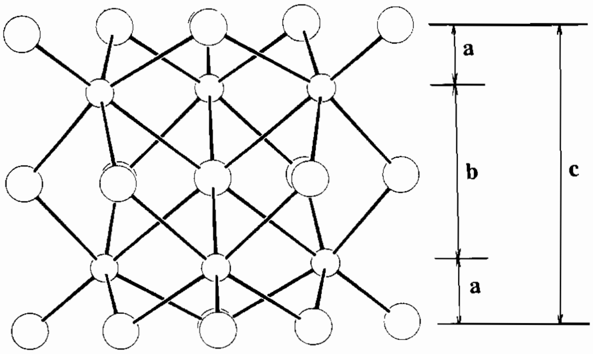

Fig. 6. Representation of the $\{V_6O_{19}\}$ core as approximate layers of oxygen atoms and layers of vanadium sites. The values of a, b and c are listed in Table 12.

TABLE 11. Bond valence sums for the vanadium sites of **1**, **2**, **3** and **4**

Complex	Σs_i (v.u.)[a]	Average vanadium oxidation state [b]
1 V1	5.01	5.00(4.98)
V2	4.99	
V3	4.93	
2 V1	5.02	5.00(4.98)
V2	4.98	
V3	4.96	
3 V1(I)[c]	4.86	4.50(4.51)
V2(I)	4.40	
V3(I)	4.27	
V4(II)[c]	4.37	4.50(4.48)
V5(II)	4.26	
V6(II)	4.45	
V7(II)	4.66	
V8(II)	4.63	
V9(II)	4.51	
4 V1	3.95	4.00(3.97)
V2	4.00	
V3	3.96	

[a] The valence sums in valence units (v.u.) for **1** and **2** are calculated according to $\Sigma_i(d(\text{V–O}_i)/1.791)^{-5.1}$ for V(V) centers. The valence sums for **4** are calculated to $\Sigma_i(d(\text{V–O}_i)/1.77)^{-5.2}$ for V(IV) centers. The valence sums for **3** are calculated using the averaged summation $\Sigma_i(d(\text{V–O}_i)/1.78)^{-5.15.}$ [b] Average of calculated values in parentheses; closest integral or half-integral value listed outside the parentheses. [c] Valence sums calculated for both clusters of the asymmetric unit of **3**. One cluster (I) is located with the central oxygen on the center of symmetry, while the second(II) occupies a general position in the cell.

TABLE 12. Comparison of distances between planes for **1**, **2**, **3** and **4**[a]

Complex	*a*	*b*	*c*
1	1.00	2.36	4.36
2	1.01	2.38	4.38
3	0.98	2.54	4.49
4	0.95	2.68	4.58

[a] *a*, *b* and *c* are defined in Fig. 6.

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