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

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Abstract

The reactions of $[(n-C_4H_9)_4N]_3[H_3V_{10}O_{28}]$ with the tris(hydroxymethyl)methane derived ligands (HOCH₂)_3CR yield hexavanadate clusters of the type $[(n-C_4H_9)_4N]_2[V_6O_{13}\{(OCH_2)_3CR\}_2]$ (R = -NHC(O)CHCH₂ (1) and -NO₂ (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 $[(n-C_4H_9)_4N]_2[V_3^VV_3^VO_{10}(OH)_3\{(OCH_2)_3-CNO_2\}_2] \cdot 0.67CH_2Cl_2$ (3) and the reduced V(IV) cluster $[(n-C_4H_9)_4N]_2[V_6^{VO}(OH)_6\{(OCH_2)_3-CCH_3\}_2] \cdot 2HNPhNHPh$ (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, $\beta = 95.42(2)^\circ$, V = 3086(2) Å³, Z = 2, $D_{calc} = 1.44$ g/cm³; 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) Å³, Z = 4, $D_{calc} = 1.77$ g/cm³; R = 0.034 based on 2729 reflections; 3, triclinic P1, a = 13.526(2), b = 27.032(5), c = 12.950(2) Å, $\alpha = 100.70(1)$, $\beta = 104.33(1)$, $\gamma = 75.56(1)^\circ$, V = 4403(2) Å³, Z = 3, $D_{calc} = 1.52$ g/cm³; 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, $\beta = 105.83(2)^\circ$, V = 3998(2) Å³, Z = 2, $D_{calc} = 1.33$ g/cm³; 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 [Nb₈O₁₈(OEt)₂₀] [8], species whose structures are related to those of the polyoxoanions [Mo₇O₂₄]⁶⁻ [9] and $[H_2W_{12}O_{42}]^{10-}$ [10], respectively. The chemistry of oxoalkoxide-titanium clusters has been extended recently description of the structures with the 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 d⁰ 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 $(TBA)_2$ - $[V_6^VO_{13}\{(OCH_2)_3CNHC(O)CHCH_2\}_2]$ (1), $(HNC_5H_5)_2$ - $[V_6^VO_{13}\{(OCH_2)_3CCH_3\}_2] \cdot 2Me_2NCOH$ (2), $(TBA)_2$ - $[V_3^VV_3^{IV}VO_{10}(OH)_3\{(OCH_2)_3CNO_2\}_2] \cdot 0.67CH_2Cl_2$ (3) and $(TBA)_2[V_6^{IV}O_7(OH)_6\{(OCH_2)_3CCH_3\}_2] \cdot 2HN (C_6H_5)NH(C_6H_5)$ (4) $(TBA = (n-C_4H_5)_4N^+).$

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 N₂ by using standard Schlenk techniques. Methanol and methylene chloride were dried over magnesium methoxide and CaH₂, respectively. Anhydrous ether was passed through activated alumina prior to use. Elemental analyses were performed by Desert Analytics, Tucson, AZ. The ligands RC(CH₂OH)₃ (R = - CH₃, - CH₂CH₃, -NH₂, -NO₂ and NHC(O)CHCH₂ 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 $(n-C_4H_9)_4NPF_6$ 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

$[(\hat{n}-C_{4}H_{9})_{4}N]_{2}[V_{6}O_{13}\{(OCH_{2})_{3}CNHC(O)CHCH_{2}\}_{2}$ (1)

Tris(hydroxymethyl)methylacrylamide (0.53 g, 3.0 mmol) was added to a solution of [(n- $C_4H_9_4N_3[H_3V_{10}O_{28}]$ (1.69 g, 1.0 mmol) in CH₃CN (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/CH₃CN/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 C46H92N4O21V6: 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 $[(n-C_4H_9)_4N]_2[V_6O_{13}\{(CH_2)_3CNO_2\}_2]$ (1a) was prepared in an analogous fashion from $(HOCH_2)_3CNO_2$ and $[(n-C_4H_9)_4N]_3[H_3V_{10}O_{28}]$.

Preparation of

$[C_{5}H_{5}NH]_{2}[V_{6}O_{13}\{(OCH_{2})_{3}CCH_{3}\}_{2}] \cdot 2Me_{2}NCOH$ (2)

Tris(hydroxymethyl)ethane (0.36 g, 3.0 mmol) was added to a solution of $[(n-C_4H_9)_4N]_3[H_3V_{10}O_{28}]$ (1.69 g, 1.0 mmol) in CH₃CN (50 ml) with stirring. After refluxing for 24 h, the yellow-brown solution obtained was treated with (CH₃)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 C₂₆H₄₂N₄O₂₁V₆: 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

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

Tris(hydroxymethyl)nitromethane (0.45 g, 3.0 mmol) was added to a solution of $[(n-C_4H_9)_4N]_3[H_3V_{10}O_{28}]$ (1.69 g, 1.0 mmol) in CH₃CN (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 $[(n-C_4H_9)_4N]_2[V_6O_{13}\{(OCH_2)_3CNO_2\}_2]$ was obtained (1.25 g). A portion of the $[(n-C_4H_9)_4N]_2[V_6O_{13} \{(OCH_2)_3CNO_2\}_2\}$ (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 1,1methylphenylhydrazine (0.18 g, 1.5 mmol) in CH₂Cl₂ (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}N₄O₂₃Cl_{1.34}V₆: 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

$[(n-C_4H_9)_4N]_2[V_6O_7(OH)_6\{(OCH_2)_3CCH_3\}_2]$ · 2PhNHNHPh (4)

Methylene chloride (30 ml) was added slowly with stirring to $[(n-C_4H_9)_4N]_2[V_6O_{13}{(OCH_2)_3CCH_3}_2]$ (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 $[(n-C_4H_9)_4N]_2[V_6O_{13}{(OCH_2)_3CCH_3}_2] \cdot 0.5PhNNPh \cdot$ 2CH₂Cl₂ [24] were collected in 20% yield. The filtrate was stored at 4 °C for two months whereupon lustrous $[(n-C_4H_9)_4N]_2[V_6O_7(OH)_6$ purple crystals of $\{(OCH_2CCH_3)_3\}_2$ · 2PhNNHPh (4) were isolated in 40% yield. Anal. Calc. for C₆₈H₁₂₀N₆O₁₉V₆: 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 $[(n-C_4H_9)_4N]_2[V_6O_{13}\{(OCH_2)_3CNHC(O)CHCH_2\}_2]$ (1, $[C_5H_5NH]_2[V_6O_{13}\{(OCH_2)_3CCH_3\}_2] \cdot 2Me_2NCOH$ (2), $[(n-C_4H_9)_4N]_2[V_6O_9(OH)_4\{(OCH_2)_3CNO_2\}_2] \cdot 0.67CH_2Cl_2$ (3) and $[(n-C_4H_9)_4N]_2[V_6O_7(OH)_6\{(OCH_2)_3CCH_3\}_2] \cdot 2PhNHNHPh$ (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	$P\bar{1}$	$P2_1/c$
ż	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)	$0.35 \times 0.27 \times 0.32$	$0.31 \times 0.30 \times 0.35$	$0.26 \times 0.44 \times 0.21$	0.19×0.37×0.22
Instrument		Rigaku	AFC5S	
Radiation		Μο Κα (λ	=0.71073 Å)	
Scan range (°)		0≤2	2θ≤50	
Scan mode		ω	$\sqrt{2\theta}$	
Standards		three taken eve	ry 200 reflections	
No. reflections collected	4479	3886	12792	5773
No. reflections used $(I_o \ge 3\sigma(I_o))$	2631	2729	4494	2972
Reduction of intensity data and	d summary of structure solu	ution and refinement		
Corrections	data treated for back	kground, attenuators, Lore	ntz and polarization effect	s in the usual fashion
Absorption correction	in all cases	based on ψ scans for 5 re	flections with χ angles near	ar 90° or 270°
Structure solution		direct	methods	
Structure refinement	least-squa	ares refinement; all non-hy	drogen atoms anisotropica	lly refined
Atom scattering factors	1	neutral atomic scattering fa	actors were used throughout	ut
Anomalous dispersion		applied to all no	on-hydrogen atoms	
Final discremance factors				

Goodness of fit	1.94	1.72	1.62	1.90
R_{w}	0.069	0.046	0.067	0.066
R	0.060	0.034	0.058	0.058
That discrepancy factors				

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 $[(n-C_4H_9)_4N]_2[V_6O_{10}(OH)_3\{(OCH_2)_3CNO_2\}_2$.

 $0.67 CH_2 Cl_2$ (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 nonhydrogen 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 $(2\theta > 37^{\circ})$ 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 $[(n-C_4H_9)_4N]_2$ -[V₆O₇(OH)₆{(OCH₂)₃CCH₃}₂]·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 $[(n-C_4H_9)_4N]_2[V_6O_{13}\{(OCH_2)_3-CNHC(O)CHCH_2\}_2$ (1)

Atom	r	v	7	B	010-000
Atom	*	y	<u> </u>	Deq	N1 C1
V(1)	0.1023(1)	0.01050(9)	1,12602(8)	3.38(7)	141-C1
V(2)	-0.1708(1)	-0.02439(9)	1.06554(8)	3.34(7)	O1V1O2
V(3)	-0.0207(1)	0.12509(8)	1.0057(1)	3.41(7)	O1-V1-O6
O(1)	0.1870(5)	0.0108(3)	1.2111(3)	4.1(3)	O1–V1–O7
O(2)	-0.0582(5)	-0.0137(3)	1,1543(3)	3.6(3)	O1–V1–O8
O(3)	-0.1226(4)	-0.1208(3)	1.0464(3)	3.5(3)	O1-V1-O10
O(4)	-0.3052(5)	-0.0359(3)	1.1028(3)	4.1(3)	O2-V1-O6
O(5)	-0.0531(5)	0.2126(3)	1.0082(4)	4.2(3)	O2V1O7
0(6)	0.0650(5)	0.1078(3)	1.1071(3)	3.6(3)	O2-V1-O8
0(7)	0	0	1.0000	2.7(3)	O2-V1-O10
0(8)	0.1225(4)	-0.1003(3)	1,1005(3)	3.1(3)	O6–V1–O7
0(9)	0.1769(5)	-0.0868(3)	0.9460(3)	3.3(3)	O6–V1–O8
O(10)	0.2433(4)	0.0201(3)	1.0537(3)	3.0(2)	O6-V1-O10
O(11)	0.4119(6)	-0.2633(4)	1.0625(5)	6.8(4)	O7–V1–O8
N(1)	0.4659(6)	-0.1404(4)	1.0790(4)	3.9(4)	O7-V1-O10
C(1)	0.3374(7)	-0.1058(5)	1.0614(5)	3.8(4)	O8-V1-O10
C(2)	0.2444(8)	-0.1371(5)	1.1186(5)	4.0(5)	O2V2O3
C(3)	0.3583(7)	-0.0211(5)	1.0743(5)	3.7(4)	O2-V2-O4
C(4)	0.2954(7)	-0.1237(5)	0.9713(6)	4.1(5)	O2–V2–O7
C(5)	0.4915(9)	-0.2135(6)	1.0705(6)	4.4(5)	O2–V2–O9
C(6)	0.6298(8)	-0.2304(6)	1.0743(6)	4.6(5)	O2–V2–O10
C(7)	0.670(1)	-0.2987(7)	1.0705(7)	6.5(7)	O3–V2–O4
N(2)	0.1410(7)	0.3326(4)	1.1833(4)	4.6(2)	O3V2O7
C(11)	0.2137(9)	0.2715(6)	1.1435(6)	4.9(2)	O3-V2-O9
C(12)	0.312(1)	0.2331(7)	1.1991(8)	8.3(3)	O3–V2–O10
C(13)	0.405(1)	0.1857(8)	1.1593(8)	8.8(4)	O4–V2–O7
C(14)	0.513(2)	0.160(2)	1.210(2)	11.6(7)	O4-V2-O9
C(15)	0.2293(9)	0.3954(6)	1.2141(6)	5.1(2)	V1-07-V3
C(16)	0.297(1)	0.4366(7)	1.1507(7)	6.9(3)	V107V2
C(17)	0.410(1)	0.4802(9)	1.192(1)	10.3(4)	V1-07-V2
C(18)	0.478(2)	0.523(1)	1.135(1)	14.0(6)	V1-07-V3
C(19)	0.043(1)	0.3594(6)	1.1172(6)	5.7(2)	V1-07-V3
C(20)	-0.041(1)	0.4243(7)	1.1431(7)	7.7(3)	V2-07-V2
C(21)	-0.145(1)	0.444(1)	1.073(1)	10.2(4)	V2-07-V3
C(22)	-0.247(2)	0.386(2)	1.068(2)	12.1(8)	V2-07-V3
C(23)	0.081(1)	0.3023(6)	1.2570(6)	5.2(2)	$v_2 = 07 = v_3$
C(24)	-0.020(1)	0.2428(7)	1.2389(7)	6.5(3)	V2-07-V3
C(25)	-0.033(1)	0.1946(8)	1.3132(8)	8.3(3)	V1 09 V2
C(26)	-0.141(1)	0.142(1)	1.302(1)	11.3(5)	v1-08- v3

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

	V1-01	1 590(5)	N1-C5	1.34(1)
l	V1_01	1.550(5)	C1 C2	1.54(1)
l	V1-02	1.657(5)	CI-C2	1.55(1)
	V1-O6	1.795(6)	C1C3	1.53(1)
	V1-07	2.255(2)	C1–C4	1.54(1)
•	V1-08	2.029(6)	C5-C6	1.49(1)
	V1_010	2.004(5)	C6-C7	1 20(1)
	V1-010	2.004(5)	C0-C7	1.29(1)
	v2-02	1.807(5)	N2-C11	1.52(1)
	V2-O3	1.824(6)	N2C15	1.51(1)
	V2-O4	1.615(5)	N2-C19	1.51(1)
	V2-07	2.236(1)	N2-C23	1.52(1)
	V2-09	1 986(6)	C_{11} C_{12}	1 48(1)
	V2-09	1.900(0)	C11-C12	1.40(1)
	V2-010	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)
	V3-07	2 237(2)	C17 - C18	1.45(2)
	V2 08	2.237(2)	C_{10} C_{20}	1.45(2)
	V3-08	2.014(5)	C19 - C20	1.54(1)
	V3-09	2.021(5)	C20–C21	1.56(2)
	O8–C2	1.454(9)	C21C22	1.49(3)
	O9–C4	1.443(9)	C23-C24	1.52(1)
-	O10-C3	1.435(9)	C24-C25	1.51(2)
	011 C5	1.33(2)	$C_{24} C_{25} C_{26}$	1.31(2) 1.48(2)
_	VI CI	1.22(1)	C2J-C20	1.40(2)
	NI-CI	1.50(1)		
	01 - V1 - 02	103 6(2)	04 - V2 - 010	96.0(2)
	01 V1 02	103.0(2)	07 V2 010	77.4(1)
	01 - v1 - 00	104.5(5)	07-72-09	77.4(1)
	01-V1-0/	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)
	02-V1-07	80 7(2)	03-V3-07	813(2)
	02 - 1 - 07	9(.7(2))	03 - V3 - 07	31.3(2)
	02-01-08	80.8(2)	03-V3-08	89.1(2)
	O2-V1-O10	157.1(2)	O3–V3–O9	157.6(3)
	O6–V1–O7	80.9(2)	O5V3O6	103.2(3)
	O6-V1-O8	157.7(2)	O5V3O7	173.2(2)
	O6-V1-O10	88 8(2)	05-V3-08	97 8(3)
	07 - V1 - 08	77.3(1)	05 V3 00	07.5(3)
	07 V = 00	77.3(1)	03 - V3 - 09	97.5(5)
	0/-v1-010	77.4(1)	06-73-07	80.3(2)
	O8-V1-O10	82.0(2)	O6–V3–O8	157.6(2)
	O2V2O3	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)	07V309	767(2)
	$02 V_{2} 00$	80 2(2)	O_{8} V3 O_{9}	82.8(2)
	02 - V2 = 03	150.0(2)	V1 02 V2	02.0(2)
	02 - V2 - 010	159.0(2)	V1-02-V2	111.9(3)
	03-02-04	102.6(3)	V2-O3-V3	112.5(3)
	O3V2O7	81.1(2)	V1O6V3	113.5(3)
	O3-V2-O9	157.7(2)	V1-07-V1	180.00
	O3-V2-O10	87.5(2)	V1-07-V2	85 07(6)
	04 - V2 - 07	1721(2)	$V_{1} = 07 + V_{2}$	04.03(6)
	0 + 12 - 07	172.1(2)	V1-07-V2	94.93(0)
	04-72-09	98.1(3)	V1-0/-V3	85.38(5)
	V1-07-V3	94.62(5)	C3C1C4	111.1(7)
	V1O7V2	94.93(6)	O8C2C1	108.8(7)
	V1O7V2	85.07(6)	O10-C3-C1	111.1(6)
	V107V3	94.62(5)	09C4C1	110.3(7)
	V1-07-V3	85 38(5)	011-C5-N1	124 8(0)
	V2_07_V2	180.00	011 05 06	127.0(5)
	V2-07-V2	100.00		122(1)
	v2-07-V3	94.90(5)	N1-C5-C6	113.5(9)
	V2-07-V3	85.10(5)	C5-C6-C7	121(1)
	V207V3	85.10(5)	C11-N2-C15	110.4(7)
	V207V3	94.90(5)	C11-N2-C19	105.0(7)
	V307V3	180.00	C11-N2-C23	111.0(7)
	V1_08_V3	109 5(2)	$C15_N2_C10$	111 9(9)
	1-00-45	109.3(2)	015-142-019	111.0(0)
				(continued)

TABLE 3. (continued)

V108C2	120.3(5)	C15-N2-C23	106.6(7)	
V3O8C2	118.2(5)	C19-N2-C23	112.1(7)	
V2O9V3	110.6(2)	N2-C11-C12	114.8(9)	
V209C4	120.0(5)	C11-C12-C13	116(1)	
V3O9C4	117.2(5)	C12C13C14	117(2)	
V1O10V2	109.9(2)	N2-C15-C16	116.5(8)	
V1010C3	118.8(4)	C15-C16-C17	110(1)	
V2O10C3	118.7(4)	C16-C17-C18	113(1)	
C1N1C5	124.7(7)	N2-C19-C20	114.4(9)	
N1C1C2	111.0(7)	C19-C20-C21	110(1)	
N1C1C3	105.1(7)	C20-C21-C22	110(2)	
N1C1C4	106.0(7)	N2-C23-C24	115.5(8)	
C2C1C3	111.4(7)	C23-C24-C25	111(1)	
C2C1C4	111.8(7)	C24-C25-C26	113(1)	

TABLE 4. Atomic positional parameters and isotropic temperature factors $(A^2 \times 10^3)$ for $[C_5H_5NH]_2[V_6O_{13}\{(OCH_2)_3-CCH_3\}_2] \cdot 2Me_2NCOH$ (2)

Atom	x	У	<i>z</i>	Beq
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(4̀)	0.113(ć)	10(2)

TABLE	5.	Selected	bond	lengths	(Å)	and	angles	(°)	for
[C ₅ H ₅ NH	I]2[\	/ ₆ O ₁₃ {(OC	$(H_2)_3CO$	$[H_3]_2] \cdot 21$	Me ₂ N	СОН	(2)		

V1-01	1,607(3)
V1-O2	1.887(3)
V1–O6	1.788(2)

(continued)

TABLE 5. (continued)

V1_07	2 2511(7)
V1-08	2.048(3)
V1-010	1.986(3)
V2-02	1.783(3)
V2-03	1.876(3)
V2-04	1.606(3)
V2-07	2 2479(7)
V2-07	2.2475(7)
V2-09	2.050(2)
V2-010	2.000(3)
V3-05	1.704(3)
V3-05	1.005(5)
V3-00	1.694(3)
V3-07	2.2299(7)
V3-08	1.983(2)
V3-09	2.001(3)
08-02	1.452(4)
09-04	1.440(4)
010-C3	1.449(4)
UII-CII	1.254(6)
NI-Co	1.333(6)
N1-C10	1.331(6)
N2-C11	1.302(6)
N2-C12	1.450(7)
N2-C13	1.439(7)
C1C2	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)
O1V1O7	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)
O2V2-O7	82.21(8)
O2V2O9	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)

TABLE 5. (continued)

07 - V2 - 010	76 82(7)	{(OCH ₂	$(11)_{3}$ (11)		
$O_{-V_{2}-O_{10}}$	82 9(1)				
03-V3-05	104.9(1)	Atom	r	v	7
O3-V3-O6	93.3(1)	- Hom	~	<i>y</i>	2
O3-V3-O7	82.29(8)	V(1)	1.1279(2)	-0.0531(1)	0.9170(2)
O3V3O8	91.6(1)	V(2)	0.8871(2)	-0.0387(1)	0.8715(2)
O3-V3-O9	160.1(1)	V(3)	1.0225(2)	-0.0604(1)	1.1131(2)
O5-V3-O6	101.6(1)	V(4)	0.9448(2)	0.2591(1)	0.7698(2)
O5V3O7	172.3(1)	V(5)	0.8529(2)	0.2418(1)	0.9641(2)
O5–V3–O8	97.9(1)	V(6)	0.7832(2)	0.3525(1)	0.8684(2)
O5–V3–O9	94.8(1)	V(7)	1.0160(2)	0.3635(1)	0.9221(2)
O6–V3–O7	80.37(7)	V(8)	1.0913(2)	0.2524(1)	1.0171(2)
O6-V3-O8	157.9(1)	V(9)	0.9323(2)	0.3422(1)	1.1115(2)
O6-V3-O9	85.0(1)	O(1)	1.2251(8)	-0.0843(4)	0.8684(8)
07–V3–O8	78.94(7)	O(2)	1.0182(8)	-0.0739(4)	0.8325(8)
07-V3-09	77.84(7)	O(3)	0.8886(8)	0.0171(4)	0.7985(8)
08-V3-09	83.1(1)	O(4)	0.8038(8)	-0.0666(4)	0.7861(8)
V1-O2-V2	112.3(1)	O(5)	1.0344(8)	-0.1051(4)	1.1842(8)
V203V3	112.2(1)	O(6)	1.1337(8)	-0.0925(4)	1.0303(8)
V1-O6-V3	111./(1)	O(7)	1.0000	0	1.0000
VI-0/-VI	180.00	O(8)	1.0990(8)	0.0087(4)	0.8425(8)
V1-07-V2	83.34(3)	O(9)	1.0837(8)	0.0852(4)	1.0127(8)
V1-07-V2 V1 07 V2	94.00(3)	O(10)	1.20/8(8)	-0.0095(4)	1.0409(8)
V1-07-V3	03.73(3) 04.27(3)	O(11)	1.312(1)	0.094/(5)	0.846(1)
V1-07-V2	94.27(3)	O(12)	1.415(1)	0.0605(6)	0.978(1)
V1-07-V2	85 34(3)	O(13)	0.9002(8)	0.2320(4)	0.0531(9)
V1_07_V3	94 27(3)	O(14)	0.07/4(0)	0.2123(4) 0.2079(4)	0.0146(0)
V1-07-V3	85 73(3)	O(15)	0.9999(8)	0.2079(4)	0.0840(0)
V207V2	180.00	O(10)	0.7943(8)	0.2014(4) 0.3873(4)	0.9049(9)
V2-07-V3	94.56(2)	O(17)	0.8109(8)	0.3050(4)	0.0247(9) 0.7415(8)
V2-07-V3	85.44(2)	O(19)	0.9346(9)	0.2992(4)	0.9390(9)
V2-07-V3	85.44(2)	O(20)	1.0814(8)	0.2235(4)	0.8591(8)
V2-O7-V3	94.56(2)	O(21)	1.1385(8)	0.3094(4)	0.9772(8)
V3-O7-V3	180.00	O(22)	1.0183(8)	0.3167(4)	0.7800(8)
V1-O8-V3	109.1(1)	O(23)	1.299(1)	0.2243(5)	0.687(1)
V1O8C2	117.9(2)	O(24)	1.360(1)	0.2806(6)	0.804(1)
V3O8C2	119.8(2)	O(25)	0.9204(9)	0.3717(4)	1.2273(9)
V209V3	108.4(1)	O(26)	0.9938(8)	0.3862(4)	1.0584(9)
V2-O9-C4	119.4(2)	O(27)	0.8751(8)	0.3913(4)	0.8569(9)
V3-09-C4	117.5(2)	O(28)	1.080(1)	0.4024(4)	0.905(1)
V1-O10-V2	110.1(1)	O(29)	1.2039(8)	0.2199(4)	1.0602(8)
V1-010-C3	118.7(2)	O(30)	1.0559(8)	0.2941(4)	1.1387(8)
V2-010-03	118.1(2) 121 5(4)	O(31)	0.7943(9)	0.3789(4)	1.0248(9)
$C_{11} N_{2} C_{12}$	121.3(4)	O(32)	0.7303(8)	0.2937(4)	0.9002(8)
C11 - N2 - C12 C11 - N2 - C13	120.6(5)	O(33)	0.8529(8)	0.2883(4)	1.1052(9)
C12 - N2 - C13	116 3(5)	0(34)	0.506(1)	0.3838(0) 0.3317(7)	1.184(1)
$C_{2}-C_{1}-C_{3}$	109 9(3)	N(1)	1.300(1)	0.3317(7)	1.008(1)
C2-C1-C4	109.9(3)	N(2)	1.331(1) 1 294(1)	0.0091(0) 0.2557(6)	0.919(1) 0.762(1)
C2-C1-C5	108.6(3)	N(2)	0.577(1)	0.3490(6)	1114(1)
C3C1C4	110.4(3)	N(4)	0.620(1)	0.1271(5)	0.699(1)
C3C1C5	109.2(3)	N(5)	0.020(1)	0.2132(5)	0.364(1)
C4C1C5	108.9(3)	N(6)	0.266(1)	0.4600(5)	0.194(1)
O8-C2-C1	112.3(3)	C(1)	1.243(1)	0.0494(6)	0.942(1)
O10-C3-C1	112.7(3)	C(2)	1.184(1)	0.0276(6)	0.833(1)
09-C4-C1	113.4(3)	C(3)	1.288(1)	0.0096(6)	1.019(1)
N1C6C7	121.1(5)	C(4)	1.172(1)	0.0970(6)	0.991(1)
C6-C7-C8	118.4(4)	C(5)	1.198(1)	0.2694(7)	0.813(1)
C7-C8-C9	119.8(5)	C(6)	1.171(1)	0.2172(6)	0.817(1)
C8-C9-C10	119.3(5)	C(7)	1.111(1)	0.3015(7)	0.739(1)
N1-C10-C9	119.8(4)				
011–C11–N2	124.7(5)				

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

 B_{eq}

2.0(1)

2.0(1)

2.0(1)

2.2(2)

1.9(1)

2.2(1) 2.4(2)

1.9(1)

2.4(2) 2.4(2)

1.7(2)

2.3(2)

2.3(2)

2.4(2)

1.6(2) 1.4(3)

2.2(2)

1.8(2)

1.9(2)

4.5(3)

6.8(4)

2.7(2)

1.9(2)

2.4(2)

2.9(3)

2.6(2)

2.4(2)

2.1(2)

1.8(2)

2.0(2) 2.0(2)

4.8(3) 7.0(4)

2.9(3)

2.4(2)

2.4(2)

3.4(3)

2.5(2)

2.1(2)

2.8(3)

2.1(2)

2.4(2)

6.8(4)

8.7(5)

3.8(4)

4.5(4)

3.7(4)

2.4(3)

2.3(3)

2.2(3)

2.1(3) 2.7(4)

2.3(3)

2.6(4)

3.1(4)

(*continued*)

TABLE 6. (continued)

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)

Atom	x	У	z	B_{eq}		
C(8)	1 226(1)	0.2980(6)	0.927(1)	27(4)	V101	1.58(1)
C(0)	1.220(1)	0.2360(0)	1.927(1)	2.7(4)	V1-02	1.76(1)
C(10)	0.073(1)	0.3500(0)	1.005(1) 1.065(1)	2.2(4)	V1-06 V1-07	1.94(1)
C(10)	0.757(1)	0.3002(0) 0.3014(6)	1.005(1) 1 140(1)	2.4(4)	V1-07	2.305(3)
C(12)	0.737(1) 0.643(1)	0.3014(0)	0.950(1)	2.3(3) 2 4(4)	V1-08 V1 010	1.99(1)
C(21)	0.635(1)	0.3101(0) 0.1300(6)	0.930(1) 0.820(1)	2.7(4)	V1-010 V2-02	2.05(1)
C(21)	0.035(1)	0.1559(0) 0.1553(7)	0.820(1)	2.7(4)	V2-02	1.93(1)
C(22)	0.559(1)	0.1555(7) 0.1637(7)	0.800(1)	3.3(4)	V2-03	1.93(1)
C(24)	0.300(1) 0.475(2)	0.1057(7)	1.041(2)	7.0(7)	V204 V207	1.60(1)
C(25)	0.473(2)	0.0836(6)	0.659(1)	29(4)	V2-07	2.230(3)
C(26)	0.505(1)	0.0000(0)	0.055(1)	2.9(4)	V2-09 V2-010	2.04(1)
C(27)	0.560(1)	-0.0093(7)	0.765(1)	3.6(4)	V2-010 V3-02	1.99(1)
C(28)	0.566(1)	0.0005(9)	0.601(1)	7.0(6)	V3-05	1.91(1)
C(29)	0.726(1)	0.1152(6)	0.672(1)	2.6(4)	V3-06	1.01(1)
C(30)	0.729(1)	0.1002(7)	0.556(2)	3.7(4)	V3-07	1.99(1) 2 307(3)
C(31)	0.840(2)	0.0911(8)	0.538(2)	5.5(5)	V3-08	2.307(3) 2.00(1)
C(32)	0.849(2)	0.073(1)	0.422(2)	7.2(7)	V3-09	2.00(1) 2.02(1)
C(33)	0.546(1)	0.1725(7)	0.642(1)	3.2(4)	V4-013	2.02(1) 1 59(1)
C(34)	0.585(1)	0.2226(7)	0.670(1)	3.8(4)	V4-014	1.07(1)
C(35)	0.514(1)	0.2607(7)	0.597(2)	4.2(4)	V4-018	1.97(1) 1.92(1)
C(36)	0.537(2)	0.312(1)	0.621(2)	7.0(6)	V4-019	2.28(1)
C(37)	0.176(1)	0.1937(6)	0.294(1)	2.1(3)	V4-020	2.04(1)
C(38)	0.289(1)	0.1769(6)	0.353(1)	2.2(3)	V4-022	2.01(1)
C(39)	0.360(1)	0.1584(6)	0.273(1)	2.7(4)	V5-014	2.02(1)
C(40)	0.473(1)	0.1454(6)	0.321(1)	3.2(4)	V5015	1.99(1)
C(41)	0.121(1)	0.1879(6)	0.465(1)	2.5(4)	V5016	1.59(1)
C(42)	0.119(1)	0.1318(6)	0.444(1)	2.9(4)	V5-O19	2.23(1)
C(43)	0.176(2)	0.106(1)	0.552(2)	6.3(6)	V5-O32	2.00(1)
C(44)	0.179(2)	0.052(1)	0.531(2)	9.7(9)	V5-O33	2.02(1)
C(45)	-0.010(1)	0.2019(6)	0.289(1)	2.4(3)	V6017	1.59(1)
C(46)	-0.104(1)	0.2199(7)	0.341(1)	3.3(4)	V6–O18	1.94(1)
C(47)	-0.188(2)	0.1911(7)	0.278(2)	4.2(5)	V6019	2.28(1)
C(48)	-0.290(2)	0.2103(8)	0.319(2)	5.7(5)	V6O27	1.86(1)
C(49)	0.077(1)	0.2709(6)	0.394(1)	2.7(4)	V6-O31	2.00(1)
C(50)	0.169(1)	0.2918(6)	0.457(1)	2.7(4)	V6-O32	2.04(1)
C(51)	0.137(1)	0.3519(7)	0.484(1)	3.8(4)	V7–O21	2.00(1)
C(52)	0.229(2)	0.3733(8)	0.548(2)	5.4(5)	V7O22	2.03(1)
C(53)	0.298(1)	0.4464(6)	0.087(1)	2.7(4)	V7–O26	1.83(1)
C(54)	0.269(1)	0.4908(7)	0.023(2)	3.7(4)	V7–O27	1.91(1)
C(55)	0.291(2)	0.4745(9)	-0.088(2)	6.2(6)	V7-O28	1.59(1)
C(50)	0.402(3)	0.451(1)	-0.090(3)	8(1)	V8-015	1.95(1)
C(57)	0.146(1)	0.4743(7)	0.179(1)	3.6(4)	V8019	2.28(1)
C(50)	0.102(2)	0.4757(7)	0.274(2)	3.8(4)	V8-O20	2.03(1)
C(59)	-0.014(2)	0.4966(7)	0.234(2) 0.343(2)	4.7(5)	V8-021	2.00(1)
C(00)	-0.003(2)	0.4900(8)	0.343(2) 0.251(1)	2.4(3)	V8-029	1.58(1)
C(61)	0.309(1) 0.272(1)	0.4117(0) 0.3627(7)	0.251(1) 0.194(1)	2.5(4)	V8-030	1.85(1)
C(62)	0.272(1) 0.305(2)	0.3027(7)	0.194(1) 0.263(2)	5.3(4)	V9-019	2.52(1)
C(64)	0.303(2)	0.3021(8)	0.205(2)	5.6(5)	V9-025	1.09(1)
C(65)	0.313(1)	0.5040(6)	0.267(1)	3.0(3)	V9-020	1.91(1)
C(66)	0.430(2)	0.4964(7)	0.285(2)	4.5(5)	V9-031	2.04(1)
C(67)	0.470(2)	0.5379(7)	0.369(2)	3.9(4)	V9-033	2.04(1)
C(68)	0.585(2)	0.530(1)	0.396(2)	7.0(6)	08-C2	1 42(2)
CI(1)	0.684(1)	0.3659(5)	0.425(1)	10.1(4)	09-C4	1.41(2)
Cl(2)	0.869(1)	0.3953(5)	0.564(1)	11.1(4)	010-C3	1.41(2) 1.42(2)
C(20)	0.797(2)	0.357(1)	0.541(2)	9.4(8)	011-N1	1.20(2)
H(3)	0.9151	0.0027	0.7335	2.6	O12-N1	1.20(2)
H(14)	0.8113	0.2107	0.7655	2.2	O20-C6	1.41(2)
H(15)	1.0067	0.2032	1.0960	2.7	O21-C8	1.43(2)
H(18)	0.8099	0.3249	0.6854	2.8	O22–C7	1.42(2)

(continued)

TABLE 7. (continued)

TABLE 7. (continued)

O23–N2	1.17(2)	C61-C62	1.53(2)
O24–N2	1.21(2)	C62–C63	1.50(2)
O31C10	1.43(2)	C63–C64	1.49(3)
O32C12	1.42(2)	C65-C66	1.51(2)
O33-C11	1.42(2)	C66–C67	1.52(2)
O34-N3	1.19(2)	C67-C68	1.47(3)
O35-N3	1.21(2)	Cl1-C20	1.86(3)
N1C1	1.53(2)	Cl2-C20	1.53(3)
N2C5	1.53(2)	O1–V1–O2	106.1(5)
N3C9	1.55(2)	O1–V1–O6	102.2(5)
N4-C21	1.52(2)	O1V1O7	172.4(4)
N4-C25	1.52(2)	O1–V1–O8	97.1(5)
N4-C29	1.49(2)	O1–V1–O10	96.9(5)
N4-C33	1.55(2)	O2–V1–O6	94.1(4)
N5C37	1.54(2)	O2-V1-O7	81.2(3)
N5-C41	1.51(2)	O2–V1–O8	91.5(4)
N5-C45	1.56(2)	O2-V1-O10	156.9(5)
N5-C49	1.51(2)	O6–V1–O7	79.3(3)
N6-C53	1.50(2)	O6-V1-O8	157.6(4)
N6-C57	1.54(2)	O6-V1-O10	82.9(4)
N6-C61	1.53(2)	O7V1O8	80.1(3)
N6-C65	1.53(2)	O7-V1-O10	75.8(3)
C1C2	1.53(2)	O8-V1-O10	83.5(4)
C1–C3	1.51(2)	O2V2O3	87.9(4)
C1-C4	1.54(2)	O2V2O4	103.2(5)
C5-C6	1.56(2)	O2-V2-O7	79.1(3)
C5-C7	1.52(2)	O2-V2-O9	89.6(4)
C5–C8	1.54(2)	O2-V2-O10	157.1(4)
C9-C10	1.53(2)	O3–V2–O4	101.7(5)
C9–C11	1.54(2)	O3–V2–O7	81.0(3)
C9–C12	1.50(2)	O3-V2-O9	161.2(4)
C21C22	1.49(2)	O3-V2-O10	90.1(4)
C22-C23	1.52(2)	O4–V2–O7	176.5(4)
C23-C24	1.50(3)	O4-V2-O9	97.0(5)
C25-C26	1.54(2)	O4–V2–O10	99.5(5)
C26-C27	1.51(2)	O7–V2–O9	80.3(3)
C27-C28	1.46(3)	O7-V2-O10	78.1(3)
C29-C30	1.49(2)	09-V2-010	85.0(4)
C30-C31	1.53(3)	O3-V3-O5	104.1(5)
C31-C32	1.52(3)	03-V3-06	89.2(4)
C33-C34	1.53(2)	03-V3-07	80.0(3)
C34-C35	1.52(2)	03V308	88.1(4)
C35-C36	1.40(3)	03-V3-09	159.2(4)
$C_{3}/-C_{3}$	1.53(2)	05-V3-06	100.4(5)
C30-C39	1.51(2)	05-V3-07	175.8(4)
C39-C40 C41 C42	1.46(2)	$05 - \sqrt{3} - 08$	101.3(5)
C41 = C42	1.49(2)	$05 - \sqrt{3} - 09$	96.6(5)
C42-C45	1.01(3)	$06 - \sqrt{3} - 07$	78.3(3)
C45-C44	1.44(3)	$06 - \sqrt{3} - 08$	158.2(4)
C45-C40	1.52(2)	$00 = \sqrt{3} = 09$	89.2(4) 70.0(2)
C47-C48	1.51(2)	07-V3-09	79.9(3)
C49-C50	1.33(3) 1.49(2)	08-1/3-09	79.4(<i>3</i>) 85.8(<i>A</i>)
C50-C51	1 57(2)	$013 V_{-} V_{-} 014$	03.0(4)
C51-C52	1.50(2)	013_V4_014	102.0(3)
C53-C54	1.50(2)	012-V4-019	175 8(5)
C54-C55	1.51(3)	013-V4-020	90 3(5)
C55-C56	1.48(4)	013-V4-022	97 4(5)
C57-C58	1.49(2)	014-V4-018	88 2(4)
C58-C59	1.50(2)	014-V4-019	80 4(4)
C59-C60	1.48(3)	O14-V4-O20	87.0(4)

(continued)

(continued)

TABLE 7. (continued)

014-V4-022 159,4(5) 020-V9-036 110,7(5) 018-V4-020 157,4(5) 019-V9-026 80,2(4) 018-V4-020 75,4(4) 019-V9-026 80,0(4) 019-V4-022 79,2(4) 019-V9-030 80,0(4) 019-V4-022 79,2(4) 019-V9-031 78,4(4) 020-V4-022 85,5(4) 025-V9-030 105,5(5) 014-V5-015 87,7(4) 025-V9-031 98,2(5) 014-V5-016 100,8(5) 025-V9-031 98,2(5) 014-V5-032 89,4(4) 026-V9-031 157,5(5) 015-V5-016 99,4(5) 026-V9-033 88,8(5) 015-V5-016 99,4(4) 030-V9-033 88,8(5) 016-V5-032 100,1(5) V2-03-V3 111,1(5) 016-V5-033 88,4(4) 014-V2-033 88,8(5) 016-V5-033 88,3(5) 015-V5-033 88,8(6) 016-V5-032 100,1(5) V2-03-V3 111,1(5) 016-V5-033 88,3(5) 016-V5-033 88,8(6) 016-V5-033				
$\begin{array}{c} 018-V4-019 & 79.5(4) & 019-V9-025 & 17.1(5) \\ 018-V4-020 & 157.4(5) & 019-V9-026 & 88.2(4) \\ 018-V4-022 & 91.3(4) & 019-V9-03 & 80.0(4) \\ 019-V4-022 & 72.2(4) & 019-V9-03 & 78.0(4) \\ 019-V4-022 & 72.2(4) & 019-V9-03 & 78.0(4) \\ 019-V4-022 & 85.6(4) & 025-V9-03 & 103.5(5) \\ 014-V5-015 & 87.9(4) & 025-V9-03 & 98.2(5) \\ 014-V5-015 & 87.9(4) & 025-V9-03 & 98.2(5) \\ 014-V5-016 & 100.8(5) & 025-V9-03 & 98.2(5) \\ 014-V5-016 & 99.4(5) & 025-V9-03 & 98.2(5) \\ 014-V5-033 & 160.8(5) & 026-V9-03 & 95.3(5) \\ 014-V5-033 & 160.8(5) & 026-V9-03 & 95.3(5) \\ 014-V5-033 & 160.8(5) & 026-V9-03 & 95.3(5) \\ 015-V5-019 & 80.4(4) & 030-V9-03 & 85.8(6) \\ 015-V5-019 & 80.4(4) & 030-V9-03 & 85.8(6) \\ 016-V5-033 & 85.1(5) & 021-033 & 85.8(6) \\ 016-V5-033 & 85.1(5) & 021-033 & 85.8(6) \\ 016-V5-033 & 85.1(5) & V1-07-V3 & 111.1(6) \\ 016-V5-033 & 85.1(5) & V1-07-V1 & 118.000 \\ 019-V5-033 & 85.1(5) & V1-07-V2 & 94.4(1) \\ 017-V6-018 & 102.6(5) & V1-07-V2 & 94.4(1) \\ 017-V6-027 & 92.0(5) & V2-07-V3 & 97.9(1) \\ 018-V6-027 & 92.0(5) & V2-07-V3 & 97.9(1) \\ 018-V6-027 & 92.0(5) & V2-07-V3 & 97.9(1) \\ 018-V6-032 & 85.4(4) & V2-07-V3 & 87.9(1) \\ 018-V6-032 & 85.4(4) & V2-07-V3 & 92.1(1) \\ 018-V6-032 & 85.4(4) & V2-07-V3 & 92.1(1) \\ 018-V6-032 & 85.4(4) & V2-07-V3 & 92.1(1) \\ 018-V6-032 & 93.3(5) & V1-01-C3 & 117.7(9) \\ 022-V7-026 & 193.8(5) & V1-01-C3 & 117.7(9) \\ 022-V7-026 & 193.8(5) & V2-01-C3 & 117.7(9) \\ 022-V7-026 & 193.8(4) & V2-01-V3 & 193.8(6) \\ 015-V8-021 & 73.8(4) & V2-01-V3 & 193.8(6) \\ 015-V8-021 & 73.8(4) & V2-01-V3 & 193.8(6) \\ 015-V8-021 & 73.$	O14-V4-O22	159.4(5)	Q29-V8-Q30	103 7(5)
OTB-VI-020 1574(2) OTB-VI-026 B80(4) OTB-VI-022 91.3(4) OTB-VI-030 B80(4) OTB-VI-022 78.0(4) OTB-VI-030 B80(4) OTB-VI-022 78.0(4) OTB-VI-030 B80(4) OTB-VI-022 85.6(4) OZS-VI-033 185.4(4) OZB-VI-022 85.6(4) OZS-VI-030 103.6(5) OTH-VI-015 87.9(4) OZS-VI-030 93.3(5) OTH-VI-023 89.4(4) OZS-VI-031 85.2(5) OTH-VI-033 160.8(5) OZE-VI-033 185.0(5) OTS-VI-019 89.4(4) O30-VI-033 89.8(5) OTS-VI-019 89.4(4) O30-VI-033 89.8(5) OTS-VI-019 178.7(5) VI-02-V2 114.1(5) OTS-VI-019 178.7(5) VI-02-V2 114.1(5) OTS-VI-019 183.9(4) VI-07-V2 85.6(1) OTS-VI-019 178.7(5) VI-07-V2 85.6(1) OTS-VI-019 178.7(5) VI-07-V2 85.6(1) OTS-VI-020 <t< td=""><td>O18-V4-O19</td><td>79.5(4)</td><td>019 - V9 - 025</td><td>105.7(5)</td></t<>	O18-V4-O19	79.5(4)	019 - V9 - 025	105.7(5)
018-V4-022 97.2(4) 019-V9-030 80.0(4) 019-V4-022 72.2(4) 019-V9-031 78.0(4) 019-V4-022 72.2(4) 019-V9-031 78.0(4) 019-V4-022 85.6(4) 025-V9-026 1102.7(5) 014-V5-015 87.9(4) 025-V9-031 198.2(5) 014-V5-015 87.9(4) 025-V9-031 98.2(5) 014-V5-019 80.5(4) 025-V9-031 98.2(5) 014-V5-015 99.4(5) 026-V9-031 98.2(5) 014-V5-033 160.8(5) 026-V9-031 157.5(5) 015-V5-015 89.4(4) 030-V9-031 157.5(5) 015-V5-019 80.4(4) 030-V9-031 88.8(4) 015-V5-019 178.7(5) V1-02-V2 114.1(5) 016-V5-032 100.1(5) V2-03-3 88.8(4) 016-V5-032 100.1(5) V2-03-3 88.8(4) 016-V5-032 100.1(5) V2-03-3 88.8(4) 016-V5-032 100.1(5) V2-03-3 88.8(4) 016-V5-032 80.0(4) V1-07-V2 85.6(1) 016-V5-033 88.3(5) V1-06-V3 112.0(5) 019-V5-033 88.3(4) V1-07-V2 85.6(1) 017-V6-019 178.7(5) V1-07-V3 90.0(1) 017-V6-019 178.7(5) V1-07-V3 90.0(1) 017-V6-021 97.8(4) V2-07-V3 87.9(1) 018-V6-027 92.0(5) V2-07-V2 180.00 018-V6-027 92.0(5) V2-07-V3 87.9(1) 018-V6-027 92.0(5) V2-07-V3 92.1(1) 018-V6-021 75.8(4) V2-07-V3 87.9(1) 018-V6-021 77.8(4) V4-019-V5 98.8(4) 02-V7-028 98.8(5) V2-016-C3 117.2(9) 02-V7-028 98.8(5) V2-016-C3 117.2(9) 02-V7-028 98.8(5) V2-016-C3 117.2(9) 02-V7-028 98.8(5) V2-016-C3 117.2(9) 02-V7-028 99.8(5) V2-016-C3 117.2(9) 02-V7-028 99.8(5) V2-016-C3 117.2(9)	O18-V4-O20	157.4(5)	O19-V9-O26	80.2(4)
019-V4-020 78.0(4) 019-V9-031 78.0(4) 019-V4-022 79.2(4) 019-V9-033 78.4(4) 020-V4-022 85.6(4) 025-V9-026 102.7(5) 014-V5-015 87.9(4) 025-V9-030 103.6(5) 014-V5-016 109.8(5) 025-V9-031 98.2(5) 014-V5-032 89.4(4) 026-V9-031 185.0(5) 015-V5-016 99.4(5) 026-V9-031 185.0(5) 015-V5-016 99.4(4) 030-V9-031 185.0(5) 015-V5-016 99.4(4) 030-V9-031 185.0(5) 015-V5-032 160.4(4) 030-V9-033 88.8(4) 016-V5-032 160.4(4) 030-V9-033 88.8(4) 016-V5-033 89.0(4) 031-V9-033 88.8(4) 016-V5-033 89.0(4) V1-07-V1 180.00 016-V5-033 89.3(5) V1-06-V3 111.1(5) 016-V5-033 89.3(5) V1-06-V3 112.0(6) 016-V5-033 89.3(5) V1-07-V3 12.0(6) 016-V5-033 89.3(5) V1-07-V2 85.6(1) 017-V6-018 102.6(5) V1-07-V2 85.6(1) 017-V6-018 102.6(5) V1-07-V2 85.6(1) 017-V6-018 102.6(5) V1-07-V2 85.6(1) 017-V6-027 102.5(5) V1-07-V2 85.6(1) 017-V6-031 97.9(5) V1-07-V3 90.0(1) 017-V6-032 97.3(5) V1-07-V3 90.0(1) 017-V6-031 97.9(5) V1-07-V3 90.0(1) 017-V6-031 97.9(5) V1-07-V3 90.0(1) 018-V6-032 83.4(4) V2-07-V3 87.9(1) 018-V6-032 83.4(4) V2-07-V3 87.9(1) 018-V6-031 179.9(4) V2-07-V3 87.9(1) 018-V6-031 179.9(4) V2-07-V3 87.9(1) 018-V6-031 97.9(5) V1-07-V3 199.5(5) 019-V6-032 83.4(4) V2-07-V3 87.9(1) 018-V6-031 97.9(5) V1-07-V3 199.5(5) 019-V6-032 83.4(4) V2-07-V3 87.9(1) 018-V6-031 97.9(5) V1-07-V3 199.5(5) 019-V6-032 83.4(4) V2-07-V3 87.9(1) 018-V6-031 97.9(5) V1-07-V3 199.5(5) 019-V6-032 83.9(4) V3-07-V3 180.00 027-V6-031 97.9(5) V1-08-V3 118.7(9) 021-V7-022 83.8(4) V2-07-V3 87.9(1) 018-V6-031 97.9(5) V1-08-V3 199.5(5) 021-V7-023 97.3(5) V1-014-V2 111.7(5) 022-V7-023 97.3(5) V1-014-V2 111.7(9) 022-V7-023 97.3(5) V1-014-V2 111.7(9) 022-V7-023 97.3(5) V1-014-V2 111.7(9) 022-V7-024 97.9(4) V2-01-V3 198.4(4) 021-V7-025 97.3(5) V1-014-V2 111.7(9) 022-V7-026 97.9(4) V4-019-V9 98.4(1) 015-V8-020 77.9(4) V4-019-V9 99.8(4) 015-V8-020 77.9(4) V4-	O18-V4-O22	91.3(4)	O19-V9-O30	80.0(4)
019-V4-022 72(4) 019-V9-033 78.4(4) 019-V4-022 85.6(4) 025-V9-026 102.7(5) 014-V5-015 87.9(4) 025-V9-030 103.6(5) 014-V5-019 80.5(4) 025-V9-031 88.2(5) 014-V5-023 89.4(4) 025-V9-031 85.0(5) 014-V5-033 160.8(5) 026-V9-031 157.5(5) 015-V5-016 99.4(5) 026-V9-033 88.8(4) 015-V5-019 80.4(4) 030-V9-033 88.8(4) 015-V5-033 89.0(4) 031-V9-033 88.8(4) 015-V5-033 89.0(4) 031-V9-033 88.8(4) 016-V5-032 100.1(5) V2-03-V2 114.1(5) 016-V5-033 98.3(5) V1-02-V2 114.1(5) 016-V5-033 89.3(4) V1-02-V2 144.1(5) 016-V5-033 89.3(4) V1-07-V2 85.6(1) 019-V5-033 80.3(4) V1-07-V2 85.6(1) 019-V5-033 80.3(4) V1-07-V2 85.6(1) 017-V6-019 174.7(5) V1-07-V2 85.6(1) 017-V6-019 174.7(5) V1-07-V2 85.6(1) 017-V6-019 174.7(5) V1-07-V2 85.6(1) 017-V6-019 174.7(5) V1-07-V3 90.0(1) 017-V6-027 102.5(5) V1-07-V3 90.0(1) 017-V6-031 97.9(5) V1-07-V3 90.0(1) 017-V6-031 97.9(5) V1-07-V3 80.0(1) 017-V6-031 97.9(5) V1-07-V3 90.0(1) 017-V6-031 97.9(5) V1-07-V3 90.0(1) 018-V6-031 97.9(5) V1-07-V3 90.0(1) 018-V6-031 97.9(5) V1-07-V3 80.0(1) 018-V6-027 92.0(5) V2-07-V3 87.79(1) 018-V6-027 82.4(4) V2-07-V3 87.79(1) 018-V6-021 77.9(4) V2-07-V3 89.9(4) 015-V8-020 87.2(4) V4-019-V9 87.79(4) 022-V7-028 99.8(5) V2-010-C3 117.2(9) 022-V7-028 99.8(5) V2-010-C3 117.2(9) 022-V7-028 99.8(5) V2-010-	O19-V4-O20	78.0(4)	O19-V9-O31	78.0(4)
C26-V4-C22 85.6(4) C25-V9-C26 102.7(5) Ol4-V5-O15 57.9(4) C25-V9-O31 98.2(5) Ol4-V5-O16 100.8(5) C25-V9-O31 98.2(5) Ol4-V5-O32 89.4(4) C26-V9-O30 99.3(5) Ol4-V5-O32 89.4(4) C26-V9-O31 85.0(5) Ol5-V5-O16 99.4(4) C30-V9-O31 85.0(5) O15-V5-O32 160.4(4) C30-V9-O33 83.8(4) O15-V5-O32 160.4(4) C30-V9-O33 83.8(4) O15-V5-O33 89.0(4) C1-O2-V2 114.1(5) O16-V5-O33 89.3(5) V1-O6-V3 112.0(5) O16-V5-O33 80.3(4) V1-O7-V1 18.00 O15-V5-O33 80.3(4) V1-O7-V2 94.4(1) O17-V6-O18 102.6(5) V1-O7-V2 94.4(1) O17-V6-O18 102.5(5) V1-O7-V2 94.4(1) O17-V6-O27 102.5(5) V1-O7-V2 85.6(1) O17-V6-O31 97.9(5) V1-O7-V3 90.0(1) O18-V6-O32 97.3	O19-V4-O22	79.2(4)	O19-V9-O33	78.4(4)
014-VS-015 879(4) 025-V9-030 193,6(5) 014-VS-019 80,5(4) 025-V9-031 98,2(5) 014-VS-033 160,8(5) 026-V9-031 98,3(5) 014-VS-033 160,8(5) 026-V9-031 157,5(5) 015-VS-016 99,4(5) 026-V9-033 157,5(5) 015-VS-019 80,4(4) 030-V9-033 88,8(5) 015-VS-033 89,0(4) 031-V9-033 88,8(6) 015-VS-032 160,4(4) 030-V9-033 88,8(6) 015-VS-032 160,4(4) 030-V9-033 88,8(6) 015-VS-032 106,1(5) V2-03-V2 114,1(5) 016-VS-032 106,1(5) V2-03-V3 111,0(5) 016-VS-032 80,0(4) V1-07-V1 180,00 016-VS-033 89,3(5) V1-06-V3 112,0(5) 015-VS-033 89,3(6) V1-07-V2 85,6(1) 015-VS-033 87,2(4) V1-07-V2 85,6(1) 017-V6-018 102,6(5) V1-07-V2 85,6(1) 017-V6-019 174,7(5) V1-07-V2 85,6(1) 017-V6-019 174,7(5) V1-07-V2 85,6(1) 017-V6-019 174,7(5) V1-07-V2 85,6(1) 017-V6-011 97,9(5) V1-07-V2 85,6(1) 017-V6-031 97,9(5) V1-07-V2 85,6(1) 017-V6-031 97,9(5) V1-07-V3 90,0(1) 017-V6-031 97,9(5) V1-07-V3 90,0(1) 018-V6-031 175,8(5) V2-07-V3 90,0(1) 018-V6-031 175,8(5) V2-07-V3 87,9(1) 018-V6-031 175,8(5) V2-07-V3 87,9(1) 018-V6-031 175,8(5) V2-07-V3 87,9(1) 018-V6-032 77,9(4) V2-07-V3 87,9(1) 018-V6-032 117,9(9) 022-V7-027 83,8(6) V1-018-V3 117,8(9) 021-V7-028 93,3(6) V2-09-V3 116,1(5) 021-V7-028 93,3(6) V2-09-V3 116,1(5) 022-V7-027 84,8(4) V2-09-V3 116,1(5) 022-V7-028 103,1(6) V4-018-V5 91,3(4) 015-V8-030 90,7(5) V5-018-V8 90,6(4) 015-V8-030 90,7(5) V5-018-V8 90,6(4) 015-V8-030 90,7(5) V5-018-V8 90,6(4) 015-V8-020 78,0(4) V5-018-V9 90,7(4) 022-V7-027 84,8(4) V4-018-V5 90,8(4) 015-V8-020	O20-V4-O22	85.6(4)	O25-V9-O26	102.7(5)
014-V5-016 100.8(5) 025-V9-031 98.2(5) 014-V5-032 89.4(4) 025-V9-033 98.2(5) 014-V5-032 100.8(5) 026-V9-033 157.9(5) 015-V5-016 99.4(5) 026-V9-031 157.9(5) 015-V5-032 100.1(5) 026-V9-031 157.9(5) 015-V5-033 89.0(4) 031-V9-033 89.8(5) 015-V5-033 89.0(4) 031-V9-033 89.8(5) 015-V5-032 100.1(5) V7-02-V2 114.1(5) 016-V5-032 80.0(4) V1-07-V2 112.0(5) 015-V5-033 80.3(6) V1-06-V3 111.1(5) 016-V5-033 80.3(6) V1-07-V2 85.6(1) 016-V5-033 80.3(6) V1-07-V2 85.6(1) 016-V5-033 80.3(6) V1-07-V2 85.6(1) 017-V6-018 102.6(5) V1-07-V3 90.0(1) 017-V6-019 174.7(5) V1-07-V2 94.4(1) 017-V6-019 174.7(5) V1-07-V2 85.6(1) 017-V6-019 174.7(5) V1-07-V3 90.0(1) 017-V6-019 174.7(5) V1-07-V3 90.0(1) 017-V6-019 174.7(5) V1-07-V3 90.0(1) 017-V6-031 97.9(5) V1-07-V3 90.0(1) 018-V6-032 87.4(4) V2-07-V3 85.6(1) 018-V6-032 87.4(4) V2-07-V3 87.9(1) 018-V6-031 157.8(5) V2-07-V3 87.9(1) 018-V6-031 157.8(5) V2-07-V3 87.9(1) 018-V6-031 157.8(5) V2-07-V3 87.9(1) 018-V6-031 157.9(4) V2-07-V3 87.9(1) 018-V6-031 157.9(4) V2-07-V3 87.9(1) 018-V6-032 83.4(4) V2-07-V3 87.9(1) 018-V6-031 157.9(5) V1-08-V3 109.5(5) 027-V6-031 157.9(5) V1-08-V3 109.5(5) 027-V6-031 157.9(5) V1-08-V3 109.5(5) 027-V6-031 157.9(5) V1-08-V3 109.5(5) 027-V6-031 157.9(6) V2-07-V3 87.9(1) 019-V6-031 79.9(4) V2-07-V3 87.9(1) 019-V6-031 79.9(4) V2-07-V3 87.9(1) 019-V6-031 79.9(4) V2-07-V3 87.9(1) 019-V6-031 173.9(6) V1-08-V3 109.5(5) 027-V7-032 83.3(4) V2-09-V3 108.5(5) 027-V7-032 83.9(4) V3-08-C2 117.4(9) 022-V7-026 138.4(6) V2-09-V3 108.5(5) 027-V7-032 83.9(4) V3-08-C2 117.4(9) 022-V7-027 84.8(4) V2-09-V3 108.5(5) 027-V7-038 97.3(5) V1-010-C3 117.3(9) 022-V7-028 98.3(5) V4-010-V3 111.7(8) 022-V7-028 98.3(5) V4-010-V3 111.7(8) 022-V7-028 98.3(5) V4-010-V3 111.7(8) 022-V7-028 103.1(5) V4-019-V8 99.8(4) 015-V8-021 75.9(4) V4-019-V9 91.8(4) 015-V8-021 75.9(5) V4-020-C6 115.1(6) 020-V7-028 99.6(O14-V5-O15	87.9(4)	O25-V9-O30	103.6(5)
014-V5-019 80.5(4) 025-V9-033 98.2(5) 014-V5-032 89.4(4) 026-V9-030 93.3(5) 015-V5-016 99.4(5) 026-V9-031 157.5(5) 015-V5-019 80.4(4) 030-V9-033 89.8(5) 015-V5-033 89.0(4) 030-V9-033 89.8(5) 015-V5-033 89.0(4) 031-V9-033 89.8(5) 015-V5-032 100.1(5) V2-03-V3 111.1(5) 016-V5-032 100.1(5) V2-03-V3 111.0(5) 016-V5-032 80.0(4) V1-07-V1 180.00 016-V5-033 89.3(5) V1-06-V3 112.0(5) 019-V5-033 89.3(5) V1-06-V3 112.0(5) 019-V5-033 80.3(4) V1-07-V2 85.6(1) 032-V5-033 80.3(4) V1-07-V2 85.6(1) 032-V5-033 80.3(4) V1-07-V2 85.6(1) 032-V5-033 80.3(4) V1-07-V3 90.0(1) 017-V6-018 102.6(5) V1-07-V3 90.0(1) 017-V6-019 174.7(5) V1-07-V3 90.0(1) 017-V6-019 79.5(5) V1-07-V3 90.0(1) 017-V6-031 97.9(5) V1-07-V3 90.0(1) 017-V6-031 97.9(5) V1-07-V3 90.0(1) 018-V6-071 102.5(5) V1-07-V3 90.0(1) 018-V6-071 125.5(5) V1-07-V3 90.0(1) 018-V6-071 125.5(5) V1-07-V3 90.0(1) 018-V6-071 82.4(4) V2-07-V3 82.1(1) 018-V6-071 82.4(4) V2-07-V3 87.9(1) 018-V6-071 82.4(4) V2-07-V3 87.9(1) 018-V6-071 82.4(4) V2-07-V3 87.9(1) 018-V6-071 82.4(4) V2-07-V3 87.9(1) 018-V6-071 82.4(4) V2-07-V3 87.9(1) 018-V6-072 83.8(4) V2-09-V3 108.1(5) 022-V7-022 83.8(4) V2-09-V3 108.1(5) 022-V7-022 83.8(4) V2-09-V3 108.1(5) 022-V7-022 83.8(4) V2-09-V3 108.1(5) 022-V7-024 97.3(5) V1-08-V2 117.8(9) 022-V7-025 156.8(6) V1-01-023 117.2(9) 022-V7-026 158.4(6) V1-010-C3 117.2(9) 022-V7-027 84.8(4) V2-09-V3 108.1(5) 022-V7-028 97.3(5) V4-018-V6 111.8(5) 022-V7-027 84.8(4) V2-019-V3 99.8(4) 021-V7-028 97.3(5) V4-018-V6 99.8(4) 021-V7-028 97.3(5) V4-018-V6 99.8(4) 021-V7-028 97.3(5) V4-018-V6 99.8(4) 021-V7-028 98.3(6) V4-019-V9 99.8(4) 021-V7-028 99.8(5) V7-021-V8 99.8(4) 021-V7-028 99.8(5) V7-021-V8 99.8(4) 021-V8-020 78.0(4) V4-019-V9 99.8(4) 021-V8-020 78.0(4	O14-V5-O16	100.8(5)	O25-V9-O31	98.2(5)
014-V5-032 89.4(4) 026-V9-031 85.0(5) 015-V5-016 99.4(5) 026-V9-031 157.5(5) 015-V5-018 80.4(4) 030-V9-031 157.5(5) 015-V5-032 160.4(4) 030-V9-033 85.8(4) 016-V5-033 89.0(4) 01-V9-033 85.8(4) 016-V5-032 100.1(5) V2-03-V3 111.1(5) 016-V5-033 98.3(5) V1-02-V2 114.1(5) 016-V5-033 98.3(6) V1-07-V1 180.00 019-V5-033 80.3(4) V1-07-V1 88.0(1) 019-V5-033 80.3(4) V1-07-V2 85.6(1) 017-V6-018 102.6(5) V1-07-V2 85.6(1) 017-V6-018 102.6(5) V1-07-V2 85.6(1) 017-V6-018 102.6(5) V1-07-V3 90.0(1) 017-V6-018 102.6(5) V1-07-V3 90.0(1) 017-V6-019 174.7(5) V1-07-V3 90.0(1) 017-V6-031 97.5(5) V1-07-V2 85.6(1) 017-V6-032 97.3(5) V1-07-V3 90.0(1) 017-V6-031 97.5(5) V1-07-V3 90.0(1) 018-V6-032 97.3(5) V1-07-V3 90.0(1) 018-V6-031 97.8(4) V2-07-V3 87.9(1) 018-V6-031 157.8(5) V2-07-V3 87.9(1) 018-V6-032 83.4(4) V2-07-V3 87.9(1) 018-V6-031 157.8(5) V1-08-V3 100.00 018-V6-031 97.9(4) V2-07-V3 87.9(1) 019-V6-031 97.9(4) V2-07-V3 87.9(1) 019-V6-031 97.9(4) V2-07-V3 87.9(1) 019-V6-031 99.8(5) V1-08-V2 118.7(9) 018-V6-032 85.9(4) V3-07-V3 108.1(5) 027-V6-032 90.8(5) V1-08-V2 117.7(9) 021-V7-022 85.3(4) V2-09-V3 108.1(5) 021-V7-022 85.3(4) V3-09-C4 115.2(9) 021-V7-022 85.3(4) V3-09-C4 115.2(9) 021-V7-023 99.8(5) V3-09-C4 115.2(9) 022-V7-026 198.4(6) V3-010-C3 117.3(9) 022-V7-028 99.8(5) V3-09-C4 115.8(9) 021-V7-028 99.8(5) V3-09-C4 115.8(9) 021-V7-028 99.8(5) V3-09-C4 115.8(9) 021-V7-028 99.8(5) V3-09-C4 115.8(9) 022-V7-028 99.8(5) V3-09-C4 115.8(9) 022-V7-028 99.8(5) V3-09-C4 115.8(9) 022-V7-028 99.8(5) V3-010-C3 117.3(9) 022-V7-028 99.8(5) V3-010-C3 117.3(9) 022-V7-028 99.8(5) V3-010-V3 99.8(4) 015-V8-029 103.1(5) V4-019-V9 98.9(4) 015-V8-020 78.8(4) V4-019-V9 98.9(4) 015-V8-021 78.8(4) V4-019-V9 98.9(4) 015-V8-021 78.8(4) V4-019-V9 98.9(4) 015-V8-021 78.8(4) V4-019-V9 98.9	O14-V5-O19	80.5(4)	O25–V9–O33	98.2(5)
014-VS-033 108.8(5) 026-V9-031 157.9(5) 015-VS-019 80.4(4) 030-V9-031 157.9(5) 015-VS-023 189.4(4) 031-V9-033 88.8(5) 015-VS-033 89.8(5) 015-VS-033 89.4(4) 031-V9-033 88.8(4) 016-VS-019 178.7(5) V1-02-V2 114.1(5) 016-VS-032 100.1(5) V2-03-V3 112.0(5) 016-VS-033 80.3(4) V1-07-V1 180.00 019-VS-033 80.3(4) V1-07-V2 85.6(1) 019-VS-033 80.3(4) V1-07-V2 85.6(1) 015-VS-033 80.3(4) V1-07-V2 94.4(1) 017-V6-018 102.6(5) V1-07-V3 90.0(1) 017-V6-019 174.7(5) V1-07-V3 90.0(1) 017-V6-019 174.7(5) V1-07-V2 85.6(1) 017-V6-019 174.7(5) V1-07-V2 85.6(1) 017-V6-019 174.7(5) V1-07-V3 90.0(1) 017-V6-019 97.8(4) V1-07-V3 90.0(1) 018-V6-031 97.8(5) V1-07-V3 90.0(1) 018-V6-031 97.8(5) V2-07-V3 92.1(1) 018-V6-031 157.8(5) V2-07-V3 92.1(1) 018-V6-031 157.8(5) V2-07-V3 87.9(1) 018-V6-031 157.8(5) V2-07-V3 87.9(1) 018-V6-031 157.8(5) V2-07-V3 87.9(1) 018-V6-031 195.9(4) V3-07-V3 180.00 027-V6-031 97.9(4) V3-07-V3 180.00 027-V6-031 97.9(4) V3-07-V3 180.00 027-V6-031 99.9(4) V3-07-V3 180.00 027-V6-031 99.9(4) V3-08-C2 117.4(9) 021-V7-022 83.3(4) V3-08-C2 117.4(9) 021-V7-022 83.3(4) V3-09-V3 180.00 027-V6-031 99.5(5) V3-09-V3 180.00 027-V7-028 98.5(5) V3-09-V3 180.00 027-V7-028 98.5(5) V3-09-V3 180.00 027-V7-028 98.5(5) V3-09-V3 180.00 021-V7-027 84.8(4) V3-010-V3 117.2(9) 022-V7-028 98.5(5) V3-09-V3 180.00 022-V7-028 98.5(5) V3-019-V8 98.4(4) 015-V8-029 103.1(5) V4-019-V9 89.5(4) 015-V8-020 87.2(4) V4-019-V9 89.5(4) 015-V8-020 87.2(4) V4-019-V9 89.5(4) 015-V8-020 87.2(4) V4-019-V9 80.7(4) 019-V8-021 99.8(4	O14-V5-O32	89.4(4)	O26-V9-O30	93.3(5)
015-V5-016 99.4(5) 026-V9-033 157.5(5) 015-V5-019 80.4(4) 030-V9-033 858.(5) 015-V5-032 160.4(4) 030-V9-033 858.(5) 015-V5-033 89.0(4) 021-V9-033 858.(4) 016-V5-033 98.3(5) V1-02-V2 114.1(5) 016-V5-033 98.3(5) V1-06-V3 112.0(5) 015-V5-033 80.3(4) V1-07-V1 180.00 015-V5-033 80.3(4) V1-07-V2 85.6(1) 015-V5-033 80.3(4) V1-07-V2 85.6(1) 017-V6-018 102.6(5) V1-07-V2 94.4(1) 017-V6-019 174.7(5) V1-07-V2 94.4(1) 017-V6-019 174.7(5) V1-07-V2 94.4(1) 017-V6-019 178.9(4) V1-07-V3 90.0(1) 018-V6-027 92.0(5) V2-07-V3 90.0(1) 018-V6-021 157.8(5) V1-07-V3 90.0(1) 018-V6-031 179.9(4) V2-07-V3 87.9(1) 018-V6-031 179.9(4) </td <td>O14-V5-O33</td> <td>160.8(5)</td> <td>O26-V9-O31</td> <td>85.0(5)</td>	O14-V5-O33	160.8(5)	O26-V9-O31	85.0(5)
015-V5-019 80.4(4) 030-V9-031 157.9(5) 015-V5-032 160.4(4) 030-V9-033 88.8(5) 015-V5-033 89.0(4) 031-V9-033 88.8(5) 016-V5-019 178.7(5) V1-02-V2 114.1(5) 016-V5-032 100.1(5) V2-03-V3 111.0(5) 016-V5-032 80.0(4) V1-07-V1 180.00 019-V5-033 80.3(4) V1-07-V2 85.6(1) 032-V5-033 87.2(4) V1-07-V2 85.6(1) 017-V6-018 102.6(5) V1-07-V2 85.6(1) 017-V6-019 174.7(5) V1-07-V2 85.6(1) 017-V6-019 174.7(5) V1-07-V2 85.6(1) 017-V6-019 78.8(4) V1-07-V3 90.0(1) 018-V6-027 92.0(5) V2-07-V3 92.1(1) 018-V6-031 157.8(5) V2-07-V3 87.9(1) 018-V6-031 79.9(4) V2-07-V3 87.9(1) 018-V6-031 79.9(4) V2-07-V3 87.9(1) 018-V6-031 79.9(4)	O15V5O16	99.4(5)	O26-V9-O33	157.5(5)
O15-V5-032 160.4(4) O30-V9-033 89.8(5) O15-V5-033 89.0(4) O31-V9-033 83.8(4) O16-V5-019 178.7(5) V1-02-V2 114.1(5) O16-V5-033 98.3(5) V1-06-V3 112.0(5) O16-V5-033 80.0(4) V1-07-V1 180.00 O19-V5-033 80.3(4) V1-07-V2 85.6(1) O17-V6-018 102.6(5) V1-07-V3 90.0(1) O17-V6-018 102.6(5) V1-07-V2 94.4(1) O17-V6-018 102.6(5) V1-07-V3 90.0(1) O17-V6-018 102.6(5) V1-07-V2 94.4(1) O17-V6-021 102.5(5) V1-07-V3 90.0(1) O18-V6-031 97.9(5) V1-07-V3 90.0(1) O18-V6-032 83.4(4) V2-07-V3 87.9(1) O18-V6-031 175.8(5) V2-07-V3 87.9(1) O18-V6-032 79.4(4) V2-07-V3 87.9(1) O18-V6-031 91.9(5) V1-08-V2 118.7(9) O2-V7-022 83.4(4)	O15-V5-O19	80.4(4)	O30-V9-O31	157.9(5)
Ols-VS-033 858(4) Ols-VS-033 858(4) Ols-VS-032 100.1(5) V2-03-V3 111.1(5) Ols-VS-032 100.1(5) V2-03-V3 112.0(5) Ols-VS-033 853(5) V1-06-V3 112.0(5) Ols-VS-033 80.3(4) V1-07-V2 85.6(1) Ols-VS-033 87.2(4) V1-07-V2 94.4(1) Ol7-V6-018 102.6(5) V1-07-V3 90.0(1) Ol7-V6-019 174.7(5) V1-07-V2 85.6(1) Ol7-V6-019 174.7(5) V1-07-V3 90.0(1) Ol7-V6-019 79.5(5) V1-07-V3 90.0(1) Ol8-V6-027 92.0(5) V2-07-V3 92.1(1) Ol8-V6-031 157.8(5) V2-07-V3 92.1(1) Ol8-V6-031 157.8(5) V2-07-V3 92.1(1) Ol8-V6-031 79.9(4) V2-07-V3 92.1(1) Ol8-V6-031 79.9(4) V2-07-V3 92.1(1) Ol9-V6-031 79.9(4) V2-07-V3 92.1(1) Ol9-V6-031 99.5(5)	015-V5-032	160.4(4)	O30-V9-O33	89.8(5)
$\begin{array}{c} 0.16-V5-0.19 & 17.8.7(5) & V1-02-V2 & 114.1(5) \\ 0.16-V5-0.32 & 100.1(5) & V2-03-V3 & 111.1(5) \\ 0.16-V5-0.33 & 98.3(5) & V1-06-V3 & 112.0(5) \\ 0.19-V5-0.33 & 80.3(4) & V1-07-V2 & 85.6(1) \\ 0.32-V5-0.33 & 87.2(4) & V1-07-V2 & 94.4(1) \\ 0.17-V6-0.18 & 102.6(5) & V1-07-V3 & 90.0(1) \\ 0.17-V6-0.18 & 102.6(5) & V1-07-V2 & 94.4(1) \\ 0.17-V6-0.18 & 102.5(5) & V1-07-V2 & 94.4(1) \\ 0.17-V6-0.11 & 97.9(5) & V1-07-V2 & 94.4(1) \\ 0.17-V6-0.22 & 97.3(5) & V1-07-V2 & 94.4(1) \\ 0.17-V6-0.32 & 97.3(5) & V1-07-V3 & 90.0(1) \\ 0.18-V6-0.12 & 97.9(5) & V2-07-V3 & 90.0(1) \\ 0.18-V6-0.12 & 92.0(5) & V2-07-V3 & 90.0(1) \\ 0.18-V6-0.22 & 83.4(4) & V2-07-V3 & 87.9(1) \\ 0.18-V6-0.22 & 83.4(4) & V2-07-V3 & 87.9(1) \\ 0.19-V6-0.22 & 83.4(4) & V2-07-V3 & 87.9(1) \\ 0.19-V6-0.32 & 10.2(5) & V1-08-V3 & 100.00 \\ 0.27-V6-0.31 & 97.9(4) & V2-07-V3 & 100.00 \\ 0.27-V6-0.32 & 160.2(5) & V1-08-V3 & 109.5(5) \\ 0.27-V6-0.32 & 160.2(5) & V1-08-V3 & 109.5(5) \\ 0.21-V7-0.22 & 83.3(4) & V2-09-V3 & 108.1(6) \\ 0.21-V7-0.22 & 83.3(4) & V2-09-V3 & 108.1(5) \\ 0.21-V7-0.25 & 90.8(5) & V2-09-V4 & 116.2(9) \\ 0.21-V7-0.26 & 90.8(5) & V2-09-V4 & 116.2(9) \\ 0.21-V7-0.26 & 19.8(5) & V1-010-V2 & 117.4(9) \\ 0.22-V7-0.26 & 19.8(5) & V1-010-V3 & 107.7(5) \\ 0.22-V7-0.28 & 97.3(5) & V1-010-V3 & 107.7(5) \\ 0.22-V7-0.28 & 97.3(5) & V1-010-V3 & 107.7(5) \\ 0.22-V7-0.28 & 10.1(5) & V4-018-V6 & 110.8(5) \\ 0.22-V7-0.28 & 10.3.1(5) & V4-018-V6 & 111.8(5) \\ 0.22-V7-0.28 & 10.3.1(5) & V4-018-V6 & 111.8(5) \\ 0.22-V7-0.28 & 10.3.1(5) & V4-018-V6 & 113.8(5) \\ 0.22-V7-0.28 & 10.3.1(5) & V4-018-V6 & 10.18.4(5) \\ 0.22-V7-0.28 & 10.3.1(5) & V3-019-V3 & 90.6(4) \\ 0.15-V8-0.20 & 87.2(4) & V4-019-V3 & 91.3(4) \\ 0.15-V8-0.20 & 87.2(4) & V4-019-V3 & 91.3(4) \\ 0.15-V8-0.20 & 87.2(4) & V4-019-V3 & 90.6(4) \\ 0.15-V8-0.20 & 87.2(4) & V4-019-V3 & 90.6(4) \\ 0.15-V8-0.20 & 77.0(5) & V3-019-V3 & 90.6(4) \\ 0.15-V$	015-V5-033	89.0(4)	031-V9-033	83.8(4)
$\begin{array}{c} 0.16 \times 3-0.52 & 100.1(5) & V-2.03 \times 3 & 111.1(5) \\ 0.16 \times 3-0.52 & 100.1(5) & V-2.05 \times 3 & 112.0(5) \\ 0.19 \times 5-0.33 & 80.3(4) & V1-07 \times V1 & 180.00 \\ 0.19 \times 5-0.33 & 80.3(4) & V1-07 \times V2 & 85.6(1) \\ 0.32 \times 5-0.33 & 87.2(4) & V1-07 \times V2 & 94.4(1) \\ 0.17 \times 6-0.19 & 112.6(5) & V1-07 \times V3 & 90.0(1) \\ 0.17 \times 6-0.19 & 112.5(5) & V1-07 - V2 & 85.6(1) \\ 0.17 - V6-0.27 & 102.5(5) & V1-07 - V2 & 85.6(1) \\ 0.17 - V6-0.31 & 97.9(5) & V1-07 - V3 & 90.0(1) \\ 0.18 - V6-0.19 & 78.9(4) & V1-07 - V3 & 90.0(1) \\ 0.18 - V6-0.19 & 78.9(4) & V1-07 - V3 & 90.0(1) \\ 0.18 - V6-0.19 & 78.9(4) & V1-07 - V3 & 90.0(1) \\ 0.18 - V6-0.11 & 15.78(5) & V2-07 - V3 & 87.9(1) \\ 0.18 - V6-0.27 & 92.0(5) & V2-07 - V3 & 87.9(1) \\ 0.18 - V6-0.31 & 15.78(5) & V2-07 - V3 & 87.9(1) \\ 0.19 - V6-0.31 & 79.9(4) & V2-07 - V3 & 87.9(1) \\ 0.19 - V6-0.31 & 79.9(4) & V2-07 - V3 & 180.00 \\ 0.27 - V6-0.31 & 99.9(4) & V2-07 - V3 & 180.00 \\ 0.27 - V6-0.31 & 99.9(4) & V3-07 - V3 & 180.00 \\ 0.27 - V6-0.31 & 99.8(5) & V1-08 - C2 & 118.7(9) \\ 0.21 - V7-0.22 & 83.3(4) & V2-09 - V3 & 108.1(5) \\ 0.21 - V7-0.22 & 83.3(4) & V2-09 - V3 & 108.1(5) \\ 0.21 - V7-0.25 & 19.8(5) & V1-010 - V2 & 117.2(9) \\ 0.21 - V7-0.26 & 99.8(5) & V1-010 - V2 & 117.8(9) \\ 0.21 - V7-0.26 & 19.8(5) & V1-010 - V2 & 117.8(9) \\ 0.22 - V7-0.26 & 19.8(5) & V1-010 - V3 & 107.7(5) \\ 0.22 - V7-0.26 & 19.8(5) & V1-010 - V3 & 107.7(5) \\ 0.22 - V7-0.28 & 19.3.1(5) & V4-019 - V8 & 99.0(4) \\ 0.5 - V8-0.29 & 103.1(5) & V4-019 - V8 & 99.0(4) \\ 0.5 - V8-0.21 & 159.4(4) & V4-019 - V8 & 99.0(4) \\ 0.5 - V8-0.21 & 159.4(4) & V4-019 - V8 & 99.0(4) \\ 0.5 - V8-0.21 & 159.4(4) & V4-019 - V8 & 99.0(4) \\ 0.5 - V8-0.21 & 159.4(4) & V4-019 - V8 & 99.0(4) \\ 0.5 - V8-0.21 & 159.4(4) & V4-019 - V8 & 99.0(4) \\ 0.5 - V8-0.21 & 159.4(4) & V4-019 - V8 & 99.0(4) \\ 0.5 - V8-0.21 & 159.4(4) & V4-019 - V8 & 109.8(5) \\ 0.2 - V7-0.28 & 103.1(5) & V5-019 - V8 & 104.8(5) \\ 0.15 - V8-0.20 & 77.0(5) & V3-019 - V8 & 104.8(5) \\ 0.15 - V8-0.21 & 79.8(4) & V4-019 - V8 & 109.9(5) \\ 0.15 - V8-0.21 & 79.8(4) & V4-019 - V8 & 109.9(5) \\ 0.2 - V8$	016-03-019	1/8./(5)	V1-02-V2	114.1(5)
$\begin{array}{c} 0.16 \times 1-0.33 & 95.3(.3) & V1-06 \times 3 & 112.0(.9) \\ 0.19 \times 1-0.32 & 80.0(.4) & V1-07 - V1 & 180.00 \\ 0.19 \times 1-0.32 & 85.5(.1) & 0.10 \\ 0.19 \times 1-0.33 & 87.2(.4) & V1-07 - V2 & 85.6(.1) \\ 0.17 \times 1-0.19 & 114.7(.5) & V1-07 - V3 & 90.0(.1) \\ 0.17 - V6-019 & 114.7(.5) & V1-07 - V2 & 94.4(.1) \\ 0.17 - V6-019 & 114.7(.5) & V1-07 - V2 & 94.4(.1) \\ 0.17 - V6-019 & 114.7(.5) & V1-07 - V2 & 85.6(.1) \\ 0.17 - V6-032 & 97.3(.5) & V1-07 - V3 & 90.0(.1) \\ 0.18 - V6-032 & 97.3(.5) & V1-07 - V3 & 90.0(.1) \\ 0.18 - V6-031 & 157.8(.5) & V2-07 - V3 & 90.0(.1) \\ 0.18 - V6-032 & 83.4(.4) & V2-07 - V3 & 87.9(.1) \\ 0.18 - V6-032 & 83.4(.4) & V2-07 - V3 & 87.9(.1) \\ 0.18 - V6-031 & 79.9(.4) & V2-07 - V3 & 87.9(.1) \\ 0.19 - V6-032 & 83.4(.4) & V2-07 - V3 & 180.00 \\ 0.27 - V6-031 & 91.5(.5) & V1-08 - V2 & 118.7(.9) \\ 0.31 - V6-032 & 150.2(.5) & V1-08 - V2 & 117.4(.9) \\ 0.21 - V7-022 & 83.3(.4) & V2-09 - V3 & 108.1(.5) \\ 0.21 - V7-022 & 83.3(.4) & V2-09 - V3 & 108.1(.5) \\ 0.21 - V7-022 & 83.3(.4) & V2-09 - C4 & 117.8(.9) \\ 0.21 - V7-022 & 83.3(.4) & V2-09 - C4 & 117.8(.9) \\ 0.21 - V7-022 & 97.3(.5) & V1-010 - V2 & 111.7(.5) \\ 0.21 - V7-023 & 97.3(.5) & V1-010 - V2 & 117.3(.9) \\ 0.22 - V7-024 & 97.3(.5) & V1-010 - V2 & 117.3(.9) \\ 0.22 - V7-025 & 90.8(.5) & V2-09 - C4 & 117.8(.9) \\ 0.22 - V7-025 & 91.3(.5) & V4-018 - V6 & 111.8(.5) \\ 0.22 - V7-025 & 91.3(.5) & V4-018 - V6 & 111.8(.5) \\ 0.22 - V7-026 & 97.3(.5) & V1-010 - V2 & 117.3(.9) \\ 0.22 - V7-027 & 94.8(.4) & V4-019 - V8 & 94.1(.4) \\ 0.15 - V8 - 021 & 159.4(.4) & V4-019 - V8 & 94.1(.4) \\ 0.15 - V8 - 021 & 159.4(.4) & V4-019 - V8 & 94.1(.4) \\ 0.15 - V8 - 021 & 159.4(.4) & V4-019 - V8 & 94.1(.4) \\ 0.15 - V8 - 021 & 159.4(.4) & V4-019 - V8 & 94.1(.4) \\ 0.15 - V8 - 021 & 79.8(.4) & V4-019 - V8 & 94.1(.4) \\ 0.15 - V8 - 021 & 79.8(.4) & V4-019 - V8 & 94.1(.4) \\ 0.15 - V8 - 021 & 78.0(.4) & V5-019 - V8 & 94.1(.4) \\ 0.15 - V8 - 021 & 78.0(.4) & V5-019 - V8 & 94.1(.4) \\ 0.15 - V8 - 021 & 78.0(.4) & V4-019 - V8 & 94.1(.4) \\ 0.15 - V8 - 021 & 78.0(.4) & V4-019 - V8 & 94.1(.4) \\ 0.15 - V8 -$	016 - V5 - 032	100.1(5)	V2-03-V3	111.1(5)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$010 - \sqrt{3} - 033$	98.3(3)	V1-00-V3	112.0(5)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$019 - \sqrt{3} - 032$	80.3(4)	V1-07-V1	180.00
$\begin{array}{c} 0.22-V5-0.23 & 0.12(4) & V1-07-V3 & 90.0(1) \\ 0.17-V6-018 & 102.6(5) & V1-07-V3 & 90.0(1) \\ 0.17-V6-027 & 102.5(5) & V1-07-V2 & 94.4(1) \\ 0.17-V6-031 & 97.9(5) & V1-07-V2 & 94.4(1) \\ 0.17-V6-032 & 97.3(5) & V1-07-V3 & 90.0(1) \\ 0.18-V6-019 & 78.9(4) & V1-07-V3 & 90.0(1) \\ 0.18-V6-027 & 92.0(5) & V2-07-V3 & 90.0(1) \\ 0.18-V6-031 & 157.8(5) & V2-07-V3 & 97.9(1) \\ 0.18-V6-032 & 83.4(4) & V2-07-V3 & 87.9(1) \\ 0.19-V6-032 & 83.4(4) & V2-07-V3 & 87.9(1) \\ 0.19-V6-032 & 77.9(4) & V2-07-V3 & 92.1(1) \\ 0.19-V6-031 & 79.9(4) & V2-07-V3 & 92.1(1) \\ 0.19-V6-032 & 17.9(4) & V2-07-V3 & 180.00 \\ 0.27-V6-031 & 91.5(5) & V1-08-V3 & 109.5(5) \\ 0.27-V6-032 & 160.2(5) & V1-08-V3 & 109.5(5) \\ 0.27-V6-032 & 160.2(5) & V1-08-C2 & 117.4(9) \\ 0.21-V7-022 & 83.3(4) & V2-09-V3 & 108.1(5) \\ 0.21-V7-026 & 90.8(5) & V2-09-C4 & 117.8(9) \\ 0.21-V7-027 & 15.68(4) & V2-09-C4 & 117.8(9) \\ 0.22-V7-026 & 158.4(5) & V1-010-V2 & 111.7(5) \\ 0.22-V7-027 & 84.8(4) & V2-010-C3 & 117.2(9) \\ 0.22-V7-028 & 97.3(5) & V1-010-V2 & 111.7(5) \\ 0.22-V7-028 & 98.3(5) & V4-014-V5 & 107.7(5) \\ 0.22-V7-028 & 108.1(5) & V4-019-V5 & 91.3(4) \\ 0.15-V8-019 & 80.1(4) & V4-019-V5 & 91.3(4) \\ 0.15-V8-020 & 87.2(4) & V4-019-V8 & 94.1(4) \\ 0.15-V8-020 & 97.0(5) & V4-020-C6 & 115.5(9) \\ 0.20-V8-020 & 97.0(5) & V4-020-C6 & 115.5(9) \\ 0.20-V8-020 & 97.0(5) & V4-020-C6 & 115.5(9) \\ 0.20-V8-020 & 97.0(5) & V4-020-C6 & 117.3(9) \\ 0.20-V8-020 & 96.6(5) & V7-021-V8 & 110.6(5) \\ 0.20-V8-020$	019-V5-033	87 2(4)	V1-07 V2	94.4(1)
$\begin{array}{cccc} 0.1 \times 0.2 & 0.0 & 0.1 \times 0.1 \times 0.1 \times 0.1 \times 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0.0 & 0 & $	017-V6-018	102 6(5)	V1-07-V3	90.0(1)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	017-V6-019	174.7(5)	V1-07-V3	90.0(1)
017-v6-031 973(5) V1-07-V2 85.6(1) 017-v6-032 973(5) V1-07-V3 90.0(1) 018-V6-019 78.9(4) V1-07-V3 90.0(1) 018-V6-027 92.0(5) V2-07-V2 180.00 018-V6-031 157.8(5) V2-07-V3 92.1(1) 018-V6-032 83.4(4) V2-07-V3 87.9(1) 019-V6-032 83.4(4) V2-07-V3 92.1(1) 019-V6-031 79.9(4) V2-07-V3 92.1(1) 019-V6-032 87.9(1) V2-07-V3 92.1(1) 019-V6-032 91.5(5) V1-08-V3 109.5(5) 027-V6-031 91.5(5) V1-08-V3 109.5(5) 021-V7-022 83.3(4) V2-09-V3 108.1(5) 021-V7-022 83.3(4) V2-09-V3 108.1(5) 021-V7-024 97.3(5) V1-010-V2 111.7(5) 021-V7-027 156.8(4) V3-09-C4 116.2(9) 021-V7-028 97.3(5) V1-010-C3 117.3(9) 022-V7-028 98.3(5)	017-V6-027	102.5(5)	V1-07-V2	94.4(1)
017-V6-032 97,3(5) V1-07-V3 90,0(1) 018-V6-019 78.9(4) V1-07-V3 90,0(1) 018-V6-027 92,0(5) V2-07-V2 180,00 018-V6-031 157.8(5) V2-07-V2 180,00 018-V6-032 83,4(4) V2-07-V3 87,9(1) 019-V6-031 79,9(4) V2-07-V3 87,9(1) 019-V6-032 77,9(4) V2-07-V3 180,00 027-V6-032 160,2(5) V1-08-V3 109,5(5) 027-V6-032 160,2(5) V1-08-C2 1118,7(9) 031-V6-032 85,9(4) V3-08-C2 117,4(9) 021-V7-022 83,3(4) V2-09-V3 108,1(5) 021-V7-026 90,8(5) V2-09-C4 116,2(9) 021-V7-027 156,8(4) V3-09-C4 117,8(9) 021-V7-027 156,8(4) V3-09-C4 117,8(9) 021-V7-027 156,8(4) V3-09-C4 117,8(9) 021-V7-027 156,8(4) V2-09-C3 117,2(9) 022-V7-027 19,3(5) V1-010-C3 117,2(9) 022-V7-027 19,3(5) V4-014-V5 107,7(5) 022-V7-028 103,1(5) V4-018-V6 111,8(5) 026-V7-028 103,1(5) V4-019-V5 91,3(4) 015-V8-019 80,1(4) V4-019-V6 89,0(4) 015-V8-020 87,2(4) V4-019-V6 93,5(4) 015-V8-020 87,2(4) V4-019-V6 93,5(4) 015-V8-020 79,13,1(5) V5-019-V8 117,6(6) 015-V8-029 103,1(5) V5-019-V8 117,6(6) 015-V8-029 103,1(5) V5-019-V8 117,8(9) 015-V8-020 79,8(4) V4-019-V9 91,8(4) 015-V8-020 79,8(4) V4-019-V9 91,8(4) 015-V8-020 78,0(4) V4-020-V8 109,9(5) 020-V8-021 79,8(4) V4-020-V8 109,9(5) 020-V8-021 79,8(4) V4-020-V8 109,9(5) 020-V8-021 79,8(4) V4-020-V8 109,9(5) 020-V8-020 99,0(6) V7-021-C8 115,5(9) 021-V8-030 155,1(5) V7-021-C8 115,5(9) 021-V8-030 155,1(5) V7-021-C8 117,5(9) (continued)	O17-V6-O31	97.9(5)	V1-07-V2	85.6(1)
OIB-V6-O19 78.9(4) V1-O7-V3 90.0(1) OIB-V6-O27 92.0(5) V2-O7-V2 180.00 OIB-V6-O31 157.8(5) V2-O7-V3 92.1(1) OIB-V6-O32 83.4(4) V2-O7-V3 87.9(1) OIP-V6-O31 79.9(4) V2-O7-V3 87.9(1) OIP-V6-O32 77.9(4) V3-O7-V3 180.00 O27-V6-O31 91.5(5) V1-O8-V3 109.5(5) O27-V6-O32 160.2(5) V1-O8-C2 118.7(9) O31-V6-O32 85.9(4) V3-O9-V3 108.1(5) O21-V7-O22 83.3(4) V2-O9-V3 108.1(5) O21-V7-O26 90.8(5) V2-O9-C4 117.4(9) O21-V7-O27 156.8(4) V3-O9-C4 117.8(9) O21-V7-O28 97.3(5) V1-O10-C3 117.3(9) O22-V7-O26 158.4(5) V1-O10-C3 117.3(9) O22-V7-O27 84.8(4) V2-O10-C3 117.3(9) O22-V7-O28 103.1(5) V4-O14-V5 107.7(5) O26-V7-O27 93.0(5) <td>O17-V6-O32</td> <td>97.3(5)</td> <td>V1-07-V3</td> <td>90.0(1)</td>	O17-V6-O32	97.3(5)	V1-07-V3	90.0(1)
OIB-V6-027 92.0(5) V2-07-V2 180.00 018-V6-031 157.8(5) V2-07-V3 92.1(1) 019-V6-032 83.4(4) V2-07-V3 87.9(1) 019-V6-031 79.9(4) V2-07-V3 87.9(1) 019-V6-032 77.9(4) V2-07-V3 180.00 027-V6-031 91.5(5) V1-08-V3 109.5(5) 027-V6-032 160.2(5) V1-08-C2 118.7(9) 031-V6-032 85.9(4) V3-08-C2 117.4(9) 021-V7-022 83.3(4) V2-09-V3 108.1(5) 021-V7-026 90.8(5) V1-00-V2 117.8(9) 021-V7-027 156.8(4) V3-09-C4 117.8(9) 021-V7-028 97.3(5) V1-010-V2 111.7(5) 022-V7-027 156.8(4) V2-010-C3 117.3(9) 022-V7-028 98.3(5) V4-014-V5 107.7(5) 022-V7-028 98.3(5) V4-014-V5 117.3(9) 022-V7-028 103.1(5) V4-019-V5 91.3(4) 025-V7-028 103.1(5)<	O18-V6-O19	78.9(4)	V1-07-V3	90.0(1)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	O18-V6-O27	92.0(5)	V2-07-V2	180.00
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	O18-V6-O31	157.8(5)	V207V3	92.1(1)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	O18-V6-O32	83.4(4)	V2-07-V3	87.9(1)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	O19-V6-O27	82.4(4)	V2-O7-V3	87.9(1)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	O19-V6-O31	79.9(4)	V2-O7-V3	92.1(1)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	019-V6-032	77.9(4)	V3-07-V3	180.00
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	027-V6-031	91.5(5)	V1-08-V3	109.5(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$02/-v_0-032$	100.2(5)	V1-08-C2	118.7(9)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$031 - v_0 - 032$ $021 - v_7 - 022$	83 3(4)	V2-00-V3	117.4(9)
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$021 - \sqrt{7 - 022}$ $021 - \sqrt{7 - 026}$	90.8(5)	V2-09-04	116 2(9)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	021 - V7 - 023	156 8(4)	V3-09-C4	117.8(9)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O21-V7-O28	97.3(5)	V1-010-V2	111.7(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O22-V7-O26	158.4(5)	V1-010-C3	117.2(9)
022-V7-028 $98.3(5)$ $V4-014-V5$ $107.7(5)$ $026-V7-027$ $93.0(5)$ $V5-015-V8$ $108.8(5)$ $026-V7-028$ $103.1(5)$ $V4-018-V6$ $111.8(5)$ $027-V7-028$ $104.1(5)$ $V4-019-V5$ $91.3(4)$ $015-V8-019$ $80.1(4)$ $V4-019-V6$ $89.0(4)$ $015-V8-020$ $87.2(4)$ $V4-019-V8$ $94.1(4)$ $015-V8-021$ $159.4(4)$ $V4-019-V9$ $176.6(6)$ $015-V8-029$ $103.1(5)$ $V5-019-V6$ $93.5(4)$ $015-V8-020$ $78.0(4)$ $V5-019-V8$ $90.6(4)$ $015-V8-020$ $78.0(4)$ $V5-019-V8$ $90.6(4)$ $019-V8-020$ $78.0(4)$ $V5-019-V9$ $91.8(4)$ $019-V8-020$ $78.0(4)$ $V6-019-V8$ $174.8(5)$ $019-V8-021$ $79.8(4)$ $V6-019-V9$ $92.0(4)$ $019-V8-029$ $174.1(5)$ $V6-019-V9$ $92.0(4)$ $019-V8-029$ $97.0(5)$ $V4-020-V8$ $109.9(5)$ $020-V8-021$ $84.3(4)$ $V4-020-V8$ $109.9(5)$ $020-V8-021$ $84.3(4)$ $V4-020-V8$ $109.9(5)$ $020-V8-020$ $95.1(5)$ $V8-020-C6$ $117.3(9)$ $021-V8-029$ $96.6(5)$ $V7-021-C8$ $117.5(9)$ $021-V8-030$ $90.6(4)$ $V7-021-C8$ $117.5(9)$	O22-V7-O27	84.8(4)	V2-O10-C3	117.3(9)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O22-V7-O28	98.3(5)	V4014V5	107.7(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O26-V7-O27	93.0(5)	V5-O15-V8	108.8(5)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O26-V7-O28	103.1(5)	V4O18V6	111.8(5)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O27-V7-O28	104.1(5)	V4O19V5	91.3(4)
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	O15-V8-O19	80.1(4)	V4O19V6	89.0(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O15V8O20	87.2(4)	V4-O19-V8	94.1(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O15-V8-O21	159.4(4)	V4019V9	176.6(6)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	O15-V8-O29	103.1(5)	V5-019-V6	93.5(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$015 - \sqrt{8} - 030$	90.7(5)	V5-019-V8	90.0(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	019 - V8 - 020	78.0(4)	V5-019-V9 V6 010 V8	91.0(4)
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	019-00-021	77.0(4) 174 1(5)	V6_019-V8 V6_010_V0	92 0(4)
O20-V8-O21 84.3(4) V4-O20-V8 109.9(5) O20-V8-O29 97.0(5) V4-O20-C6 115.5(9) O20-V8-O30 159.1(5) V8-O20-C6 117.3(9) O21-V8-O29 96.6(5) V7-O21-V8 110.6(5) O21-V8-O30 90.6(4) V7-O21-C8 117.5(9)	019-029	81 2(4)	V8-019-V9	84.7(4)
O20-V8-O29 97.0(5) V4-O20-C6 115.5(9) O20-V8-O30 159.1(5) V8-O20-C6 117.3(9) O21-V8-O29 96.6(5) V7-O21-V8 110.6(5) O21-V8-O30 90.6(4) V7-O21-C8 117.5(9)	O20-V8-O21	84.3(4)	V4-020-V8	109.9(5)
O20-V8-O30 159.1(5) V8-O20-C6 117.3(9) O21-V8-O29 96.6(5) V7-O21-V8 110.6(5) O21-V8-O30 90.6(4) V7-O21-C8 117.5(9) (continued)	O20-V8-O29	97.0(5)	V4O20C6	115.5(9)
O21-V8-O29 96.6(5) V7-O21-V8 110.6(5) O21-V8-O30 90.6(4) V7-O21-C8 117.5(9) (continued) (continued) (continued)	O20-V8-O30	159.1(5)	V8-020-C6	117.3(9)
O21-V8-O30 90.6(4) V7-O21-C8 117.5(9) (continued) (continu	O21-V8-O29	96.6(5)	V7-O21-V8	110.6(5)
(continued) (continued)	O21-V8-O30	90.6(4)	V7-O21-C8	117.5(9)
······································		((continued)	(continue)

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ed)

TABLE 7. (continued)

 V8–O21–C8	120.0(9)
V4O22V7	111.0(5)
V4022C7	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-O31V9	109.9(5)
V6-O31-C10	116.4(9)
V9-O31-C10	120(1)
V5-O32-V6	108.7(5)
V5O32C12	118.9(9)
V6-O32-C12	114.2(9)
V5-O33-V9	109.2(5)
V5-033-C11	115.2(9)
V9O33C11	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 $[(n-C_4H_9)_4N]_3$ - $[H_3V_{10}O_{28}]$ with the tris(hydroxymethyl)methane derivatives (HOCH₂)₃CR (R=-NHC(O)CHCH₂ and -NO₂) in acetonitrile yield upon recrystallization the hexavanadate clusters $[(n-C_4H_9)_4N]_2[V_6O_{13}-{(OCH_2)_3CR}_2]$. Under optimal conditions, the stoichiometry of the process conforms to the following:

 $2(TBA)_3[H_3V_{10}O_{28}] + 6(HOCH_2)_3CR \longrightarrow$

 $3(TBA)_{2}[V_{6}O_{13}{(OCH_{2})_{3}CR}_{2}] + 12H_{2}O + V_{2}O_{5}$

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, $(HOCH_2)_3$ -CNH₂, 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 $(HOCH_2)_3$ CNHC(O)CHCH₂ or $(HOCH_2)_3$ CNMe₂ [24] results in isolation of the hexavanadate species $(TBA)_2[V_6O_{13}{(OCH_2)_3}CNRR']_2]$.

hexanuclear The clusters (TBA)2-V(V) $[V_6O_{13}{(OCH_2)_3CR}_2]$ 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 $(TBA)_{2}$ of $[V_6O_{10}(OH)_3\{(OCH_2)_3CNO_2\}_2] \cdot 0.67CH_2Cl_2$ (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 $(Å^2 \times 10^3)$ for $[(n-C_4H_9)_4N]_2[VO_7(OH)_6-{(OCH_2)_3CCH_3}_2]$ ·HNPhNHPh (4)

Atom	x	у	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)
0(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)
0(6)	0.1032(4)	0.4262(4)	0.6195(2)	2.2(2)
O(7)	0	1/2	1/2	1.8(3)
0(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)	0.0071(1) 0.1886(4)	0.5777(4)	0.5728(2)	2.2(2) 2.1(2)
N(1)	0.1000(1) 0.1286(5)	0.2702(5)	0.3720(2) 0.7820(3)	2.1(2) 2.8(3)
N(2)	0.3236(6)	0.2800(6)	0.7620(3) 0.6230(4)	4.0(3)
N(3)	0.3309(6)	0.2000(0)	0.6230(4) 0.6410(4)	4.0(4)
C(1)	0.5505(0) 0.1699(7)	0.3750(0) 0.7457(6)	0.5476(4)	7.2(7)
C(2)	0.1077(7)	0.7551(6)	0.5470(4)	2.5(4)
C(3)	0.2357(6)	0.7551(0)	0.5050(4)	2.0(4)
C(3)	0.2337(0) 0.1430(6)	0.0009(7)	0.3031(4)	2.0(4)
C(4)	0.1455(0) 0.2305(7)	0.7320(0)	0.4741(4)	2.3(4)
C(3)	0.2303(7) 0.0187(7)	0.8309(7)	0.3040(3)	4.0(3)
C(11)	-0.0564(7)	0.2624(7)	0.7800(4)	3.0(4)
C(12)	-0.0304(7)	0.3323(7)	0.7319(4) 0.7412(5)	5.5(5)
C(13)	-0.1036(8)	0.3300(7)	0.7412(3)	4.1(3)
C(14)	-0.2470(8)	0.3737(6)	0.0676(3)	5.4(b) 2.1(4)
C(15)	0.1709(7)	0.3047(0)	0.777(4)	5.1(4)
C(10)	0.1029(0)	0.4311(7)	0.0521(4)	4.1(5)
C(17)	0.2406(6) 0.242(1)	0.5185(7)	0.8233(3)	4.8(5)
C(10)	0.243(1)	0.3889(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)	0.3439(7)	0.1339(7)	0.9041(4)	3.8(5)
C(22)	0.4524(8)	0.0972(9)	0.9055(6)	0.1(0)
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)	0.65/3(6)	6.1(7)
U(20)	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(0)	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)	0.4 (59(5))	0.4929(5)	0.7115(3)	5.2(1)

TABLE 9. Selected bond lengths (Å) and angles (°) for TABLE 9. (continued)

$[(n-C_4H_9)_4N]_2[V_6O_7(OH)]_3$	$_{6}$ {(OCH ₂) ₃ } ₂]·2PhNHNHPh (4)		
		O6-V1-O7	79.6(1)
V1-01	1.611(5)	O6-V1-O8	159.7(2)
V1-O2	2.016(6)	O6-V1-O10	87.9(2)
V1-06	1.997(6)	O7–V1–O8	80.2(2)
VI-07	2.334(1)	O7-V1-O10	80.4(1)
VI-08	2.008(5)	O8-V1-O10	87.5(2)
V1-010 V2-02	2.007(6)	O2–V2–O3	86.9(2)
V2-02	2.015(5)	O2–V2–O4	102.5(3)
V2-03	2.005(0)	O2–V2–O7	79.7(2)
V2-04 V2-07	2 335(2)	O2V2O9	86.8(2)
V2-07	2.006(5)	O2-V2-O10	159.8(2)
V2-010	2.000(5)	O3–V2–O4	101.6(3)
V2-010 V3-03	2.0021(5)	O3V2O7	79.5(2)
V3-05	1.616(6)	O3-V2-O9	159.4(2)
V3-O6	2.002(5)	O3-V2-O10	90.9(2)
V3-07	2.280(2)	04-V2-07	177.5(2)
V3-O8	2.008(5)	04-V2-09	98.9(3)
V309	1.998(6)	$04 - \sqrt{2} - 010$	97.7(3)
O8C2	1.43(1)	$07 - \sqrt{2} - 09$	80.0(2)
O9–C4	1.41(1)	$07 - \sqrt{2} - 010$	88 2(2)
O10-C3	1.42(1)	$O_{3} = \sqrt{2} - O_{10}$	08 8(3)
N1-C11	1.51(1)	$03 - \sqrt{3} - 05$	89 5(2)
N1-C15	1.53(1)	03-V3-07	80 8(2)
N1-C19	1.52(1)	03-V3-08	86.9(2)
N1-C23	1.54(1)	03 - V3 - 09	162.3(2)
N2-N3	1.40(1)	O5-V3-O6	99.6(2)
N2C31	1.40(1)	O5-V3-O7	179.5(2)
N3-C37	1.373(9)	O5-V3-O8	98.1(3)
C1-C2	1.53(1)	O5V3O9	98.9(3)
C1-C3	1.51(1)	O6-V3-O7	80.8(2)
C1-C4	1.54(1)	O6-V3-O8	162.3(2)
	1.53(1)	O6-V3-O9	89.5(2)
C11-C12	1.51(1)	O7–V3–O8	81.5(2)
C12 - C13 C13 - C14	1.55(2)	O7–V3–O9	81.6(2)
C15-C16	1.50(1)	O8–V3–O9	88.8(2)
C16-C17	1 50(2)	V1-O2-V2	110.3(3)
C17-C18	1.50(2)	V2O3V3	109.2(3)
$C_{19}-C_{20}$	1.51(1)	V1-O6-V3	109.5(2)
C20–C21	1.51(1)	V1-07-V1	180.00
C21-C22	1.51(2)	V1-07-V2	90.23(3)
C23-C24	1.51(1)	V1 - 07 - V2	09.77(3) 00.12(5)
C24-C25	1.52(2)	V1 - 07 - V3	89.88(5)
C25-C26	1.47(2)	V1_07_V2	89.77(5)
C31–C32	1.40(1)	V1-07-V2	90.23(5)
C31–C36	1.40(1)	V1-07-V3	89.88(5)
C32–C33	1.40(1)	V1-07-V3	90.12(5)
C33–C34	1.40(1)	V2-07-V2	180.00
C34-C35	1.40(1)	V2-07-V3	89.67(5)
C35-C36	1.40(1)	V2-07-V3	90.33(5)
C37-C38	1.395(9)	V207V3	90.33(5)
C37-C42	1.40(1)	V207V3	89.67(5)
01-V1-02	99-9(3)	V3O7V3	180.00
01-V1-06	101.2(3)	V1-O8-V3	108.5(3)
01-V1-07	179.2(2)	V108C2	116.4(4)
O1-V1-O8	99.1(3)	V3-O8-C2	115.3(5)
O1-V1-O10	100.0(3)	V2-O9-V3	108.7(3)
O2V1O6	87.8(2)	V209C4	115.9(4)
O2-V1-O7	79.7(1)	V309C4	116.2(5)
O2-V1-O8	89.9(2)	V1-010-V2	109.7(2)
O2-V1-O10	160.1(2)	VI-010-C3	110.5(5)
	(continu	$(v_2 - 010 - 0.3)$	114.1(3)
	\	r	



Fig. 1. ⁵¹V 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 $(TBA)_2[V_6O_7(OH)_6\{(OCH_2)_3CCH_3\}_2]$. 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 ⁵¹V NMR spectra, measured between 20 and 60 °C. At 20 °C, the chemical shifts are 497 (Fig. 1) and 500 ppm relative to VOCl₃ 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 ν (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 ν (V=O). However, in complex 3 the pattern of bands in the 700-850 cm^{-1} region ν (V–O–V) $[V_6O_{13}$ associated with of the $\{(OCH_2)_3CR\}_2]^{2-}$ 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 $(\eta^5 C_5Me_5)Rh(III)$ 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 doublybridging 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



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

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, $[(n-C_4H_9)_4N]_2$ - $[V_6O_9(OH)_4\{(OCH_2)_3CCH_3\}_2]$. While the latter exhibits a room temperature magnetic moment (μ_{eff} /molecule) of 3.50 $\mu_{\rm B}$ (corresponding to 1.75 $\mu_{\rm B}$ per V(IV) site), the room temperature moment of 3 is 2.98 $\mu_{\rm B}$ /molecule $(1.72 \,\mu_{\rm B} \, {\rm per} \, {\rm V(IV)} \, {\rm site})$. Further details of the magnetic properties of this class of hexavanadium clusters will be presented in a forthcoming publication [38].

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 Mo₄O₄ rings of $[Mo_6O_{19}]^{2-}$; (b) the TiMo₃O₄ ring of $[(C_5H_5)TiMo_5O_{18}]^{3-}$; (c) the V₄O₄ 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)	1.86(1)	
V–O, bridging hydroxy		1,705(4)	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)

"Bond lengths in Å, angles in °. bOc=central oxo group. "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.

С	omplex	$\Sigma s_i (v.u.)^a$	Average vanadium oxidation state ^b
1	V 1	5.01	5.00(4.98)
	V2	4.99	
	V 3	4.93	
2	\mathbf{V}_1	5.02	5.00(4.98)
	V 2	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	V 1	3.95	4.00(3.97)
	V2	4.00	
	V3	3.96	

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

^aThe valence sums in valence units (v.u.) for 1 and 2 are calculated according to $\Sigma_i (d(V-O_i)/1.791)^{-5.1}$ for V(V) centers. The valence sums for 4 are calculated to $\Sigma_i (d(V-O_i)/1.77)^{-5.2}$ for V(IV) centers. The valence sums for 3 are calculated using the averaged summation $\Sigma_i (d(V-O_i)/1.78)^{-5.15}$. ^bAverage of calculated values in parentheses; closest integral or half-integral value listed outside the parentheses. ^cValence 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	а	ь	с
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, b and c are defined in Fig. 6.

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