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Synthesis and characterization of a polyvanadate polyester involving a monodentate alcohol, $[(n\text{-}C_4H_9)_4N][V_6O_{12}(OCH_3)_7]$*

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Abstract

Polyvanadates are of interest in conjunction with new materials and catalysis, sensor technology, and enzymology. We report here the preparation, X-ray structure and other properties of the new compound, heptamethoxyhexavanadate, $[V_6O_{12}(OCH_3)_7]^-$ (**1**). Crystalline $(n\text{-}Bu_4N)[V_6O_{12}(OCH_3)_7]$ ($a=10.184(4)$, $b=12.742(4)$, $c=17.148(5)$ Å, $\alpha=72.62(3)$, $\beta=73.42(3)$, $\gamma=70.92(3)°$, $Z=2$, space group $=P\bar{1}$) contains a total of seven μ_2-(OCH_3) groups with one of the OCH_3 groups having two-fold disorder in the solid state. NMR on three nuclei (^1H, ^{13}C and ^{51}V) confirm that **1** retains the solid state structure in anhydrous acetonitrile solution at 25 °C. **1** has a quite positive potential: $E^f=E_{pc}+E_{pa}/2=-0.344$ V versus Fc^+/Fc ($E_{pc}-E_{pa}=78$ mV; $n=1$ electron).

Introduction

Polyvanadates are of interest in conjunction with new materials and catalysis [1–3], sensor technology [4], and enzymology [5, 6]. It is now clear, particularly from the profusion of reports from several groups over the last few years [7–10], that the number of structurally diverse polyvanadates is substantial. One subset of these new polyvanadates are the (trisalkoxy)polyvanadates which have been prepared and structurally characterized by Zubieta and co-workers [11]. The latter complexes are effectively triesters of polyvanadate acids. The purpose of this work was to determine if alkoxy of polyalkoxy polyvanadates could be prepared of unidentate alcohols (versus chelating triols) and whether polyalkoxy polyvanadates exhibit simultaneously high solubilities in a range of non-aqueous media and extensive and reversible redox chemistry. Such complexes could have applications as oxidation catalysts, including garments composed of fiber-immobilized redox active clusters for catalytic decontamination, as sensor components, and as precursors to various materials of current interest. We report here the preparation, X-ray structure and other properties of the title compound, a tetra-n-butylammonium (Q) salt of a polyanion complex with seven monodentate ester groups, the heptamethoxyhexavanadate, $[V_6O_{12}(OCH_3)_7]^-$ (**1**).

Experimental

Synthesis of $[(n\text{-}C_4H_9)_4N][V_6O_{12}(OCH_3)_7]$ *(Q1)*

In a typical reaction, a yellow–orange solution was immediately formed by dissolving 2.0 g, (1.19 mmol) $Q_3H_3V_{10}O_{28}$ in 30 ml of rapidly stirred CH_3OH at ambient temperature. After 48 h of refluxing, a red–orange solution was obtained. This was cooled to ambient temperature and then concentrated to one half the original volume. The solution was stored at −25 °C for 3 days resulting in the formation of red–orange microcrystals. Maintaining the mother liquor at −25 °C produced additional product for a combined yield of 0.401 g of Q**1** (~21% yield based on vanadium). The cyclic voltammetry (CV) of Q**1** was conducted at room temperature under Ar using 1.0 mM complex and 0.1 M QPF_6 supporting electrolyte in CH_3CN, a glassy carbon disk as working electrode, an $Ag/AgNO_3$ reference electrode (note values cited relative to Fc^+/Fc, however) and a scan rate of 200 mV/s. An X-ray quality crystal was grown by slow diffusion of anhydrous diethyl ether into a CH_3CN solution of Q**1**. IR (KBr pellet, 400–1050 cm^{-1}): 1030 (ν(O–Me), vs), 965 ($\nu(V\text{–}O_t)$, vs) 765 and 663 ($\nu(V\text{–}O_b)$, s), 625 ($\nu(V\text{–}O_{bm})$, m), 445 ($\nu(V\text{–}O_c)$, m), 410 ($\delta(O_b\text{–}V\text{–}O_t)$, m). These tentative assignments are based on the normal-coordinate analyses and IR studies of the (M_6O_{19}) structures [12]. ^1H NMR of the **1** polyanion (300 MHz, CD_3CN): 4.88 (s, 6H), 4.70 (s, 6H), 4.61 (s, 9H) ppm. The final peak of 9H represents two largely overlapping resonances, one of two symmetry equivalent methyl groups and one of a symmetry unique methyl group. ^{13}C NMR of the **1** polyanion (75.48 MHz, CD_3CN): 70.08, 70.31, 71.27, 72.94 ppm. ^{51}V NMR of the **1** polyanion (52.6 MHz; δ relative to external neat $VOCl_3$): −453.2 (1V), −465.0 (2V), −472.3 (2V), −478.3 (1V) ppm. *Anal.* Calc. for $C_{23}H_{57}NO_{19}V_6$: C, 28.85; H, 5.96; N, 1.46; O,

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31.78; V, 31.96. Found: C, 28.95; H, 5.77; N, 1.56; O, 32.35 (by difference); V, 31.37%.

X-ray structure determination

An X-ray quality crystal was grown by slow diffusion of anhydrous diethyl ether into a ~0.37 mM CH_3CN solution of **Q1** at −25 °C. The single crystal was mounted on the end of a glass fiber. Intensity data were collected on a Siemens R3m/V diffractometer by using graphite monochromatized Mo Kα (0.71073 Å) radiation with θ–2θ step-scan techniques. Throughout the data collection the intensities of three standard reflections were checked every 100 reflections to monitor crystal and instrumental stability. The structure was solved by direct methods (Siemens SHELXTL PLUS) and all vanadium, oxygen and nitrogen atoms were refined anisotropically by using a weighted full-matrix least-squares technique. All hydrogen atoms were fixed with an idealized C–H bond length of 0.96 Å. Azimuthal scans and a small absorption coefficient indicated that the data did not require correction for absorption. One of the bridging (μ_2) methyl groups exhibited a two-fold positional disorder. Details concerning crystal characteristics for **Q1** are summarized in Table 1.

Results and discussion

The X-ray structural analysis of **Q1** revealed the presence of discrete $[(n\text{-}C_4H_9)_4N]^+$(Q) cations and $[V_6O_{12}(OCH_3)_7]^-$ anions. All of the vanadium atoms in **1** are in the +5 (d^0) oxidation state. Complex **1** displays the classic hexametalate core structure, $M_6O_{19}{}^{x-}$, a structure known for isopolyanions of four elements, M = Nb^V, Ta^V, (x = 8), Mo^{VI} and W^{VI} (x = 2). Although at present this binary hexametalate structure is unknown for M = V, it has been previously observed in the hexavanadate complexes containing organic [11c] and organometallic moieties [13]. Unlike the former compounds, **1** is a heptaalkoxy compound, or effectively, a heptamethyl ester of the, as yet, unknown hexavanadic acid (Fig. 1).

TABLE 1. Summary of crystal data and experimental conditions for the X-ray analysis of $[(n\text{-}C_4H_9)_4N][V_6O_{12}(OCH_3)_7]$

Empirical formula	$C_{23}H_{57}NO_{19}V_6$
Formula weight	956.46
Space group	$P\bar{1}$
a (Å)	10.184(4)
b (Å)	12.742(4)
c (Å)	17.148(5)
α (°)	72.62(3)
β (°)	73.42(3)
γ (°)	70.92(3)
Volume (Å^3)	1963(1.1)
D_{calc}/D_{obs}[a] (g/cm^3)	1.62/1.62
Z	2
Temperature (°C)	23
Total data	4395
Unique data ($I > 3\sigma(I)$)	2473
Number of parameters refined	331
Weighting scheme	$w^{-1} = r^2(F) + 0.0010F^2$
Data-to-parameter ratio	7.5:1
Final R indices (obs. data) (%)	$R = 5.68$, $R_w = 6.38$
R indices (all data) (%)	$R = 7.69$, $R_w = 7.69$
Goodness of fit[b]	1.769

[a] Measured by flotation method in $CCl_4/1,2\text{-}C_2H_4Br_2$. [b] Goodness of fit = $[\Sigma w(|F_o| - |F_c|)^2/(n_o - n_v)]^{1/2}$, where n_o and n_v denote the number of data and variables, respectively.

Complex **1** contains a total of seven μ_2-(OCH_3) groups with one of the OCH_3 groups having two-fold disorder in the solid state between doubly bridging oxygen atoms on O3 to O6. This disorder obscures, to some extent, visualization of the effective molecular C_s symmetry of **1**. The mirror plane is defined by the atoms O3, O1, O10, O15, O17, V2 and V4, when O3 is a methoxy and O6 is an oxo. Table 2 summarizes the principle bond distances for the major structurally characterized hexametalates, (M_6O_{19}), including **1**. Based upon X-ray structure analysis for **1**, the bond lengths of the six terminal V···O_t(terminal oxygen) do not vary appreciably, ranging from 1.583(7) to 1.602(7) Å. However, the average V···O_b(doubly bridging oxygen) distance of 1.826(7) Å is significantly shorter than those of V···O_{bm}(methoxy bridging oxygen) which average

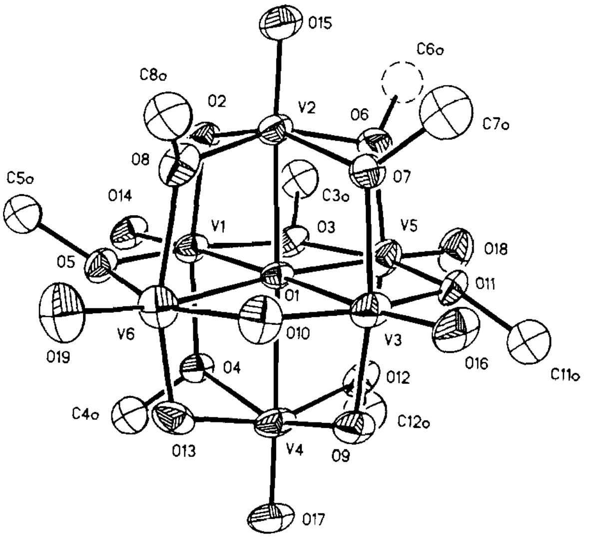

Fig. 1. Side-view ORTEP illustration of $[V_6O_{12}(OCH_3)_7]^-$ with 25% thermal ellipsoids, showing the full atom-labeling scheme. C3a and C3b represented by dotted circles are two-fold disordered between the O3 and O6 doubly bridging oxygens. Selected bond lengths (Å) and angles (°): V···V, 3.045(3) (av.); V···O_c(1): 2.212(6) (av.); V···O_b (2,9,10,13): 1.826(7) (av.); V···O_{bm} (3,4,5,6,7,8,11,12): 1.974(7) (av.); V···O_t (14,15,16,17,18,19): 1.591(7) (av.); C···O, 1.443(15) (av.); *fac*-V···V···V: 60.5(1) (av.); *cis*-V···O_c···V: 90.0(2) (av.); *trans*-V···O_c···V: 176.4(3) (av.); V···O_b···V: 112.6(3) (av.); V···O_{bm}···V: 110.7(3) (av.).

TABLE 2. Principle interatomic distances (Å) in the representative M_6O_{19} cores

	M–O$_c$	M–O$_b$	M–O$_t$	Ref.
1	2.20–2.30	1.83(av.) (1.97)[a]	1.58–1.60	
$[V_6O_{13}\{RC(CH_2O)_3\}_2]^{2-}$	2.24(av.)	1.82(av.) (2.03)[a]	1.60(av.)	11a
$[(RhCp)_4V_6O_{19}]$	2.25–2.27	1.91–1.93	1.60–1.64	13
$Mo_6O_{19}{}^{2-}$	2.30–2.33	1.90–1.94	1.67–1.68	14
$W_6O_{19}{}^{2-}$	2.32–2.33	1.89–1.95	1.67–1.71	15
$Nb_6O_{19}{}^{8-}$	2.37–2.39	1.97–2.06	1.75–1.78	16
$Ta_6O_{19}{}^{8-}$	2.38	1.99	1.80	17a
$OFe_6[(O_3CH_2)_3CCH_3]_6{}^{2-}$	2.23–2.27	1.99–2.03	1.86–1.89	18
$[OFe_6(OCH_3)_{18}]^{2-}$	2.25–2.30	1.95–2.03	1.85–1.88	19

[a] Number inside parentheses is the average bond distances of M–O(alkoxy).

1.974(7) Å. A similar contraction has also been observed in the structure of $[V_6O_{13}\{RC(CH_2O)_3\}_2]^{2-}$ [11c]. A typical V···O$_b$···V angle is approximately 113°. This is slightly longer than the V···O$_{bm}$···V angles which range between 110 and 111°. As expected, the distance of V···O$_c$(central oxygen) ranges from 2.202(6) to 2.300(6) Å. The bond distance of C···O$_{bm}$ varies greatly from 1.407(14) Å for C7–O7 to 1.444(12) Å for C4–O4 with the C···O$_{bm}$ distances of the disordered methoxy groups being substantially longer (1.526(25) Å for C3a–O3 and 1.499(26) Å for C3b–O6). The presence of the methoxy ligands induces a marked distortion of the octahedral (V_6O_{19}) core of **1**: *cis*-V–O$_c$–V angles are not close to the idealized value of 90° but range from 83 to 94° and the typical *trans*-V–O$_c$–V angle is 175° instead of 180°.

NMR on three nuclei (^{1}H, ^{13}C and ^{51}V) confirm that **1** retains effective C_s symmetry in anhydrous acetonitrile solution at 25 °C consistent with the solid state structure in Fig. 1 and the fact that inversion at methoxide as well as rotation about the carbon–oxygen bonds of the methoxy groups is far faster than the requisite NMR timescales. Upon consideration of the electronic and steric factors [20] as well as the different populations of V(4), C(4) and CH_3 (3) groups based on their NMR spectra, only one isomer of **1** is likely to be present in solution. A trace amount of water in solution would result in the slow hydrolysis of methoxy groups in **1** over a period of time. The electronic absorption spectrum of **1** (~0.90 mM in acetonitrile; 25 °C) has two discernible charge transfer features, a maximum at 212 nm ($\epsilon = 2380$ M^{-1} cm^{-1}) and a shoulder at 233 nm ($\epsilon = 2370$ M^{-1} cm^{-1}). Beyond 233 nm, only a monotonically decreasing absorption tail is observed (ϵ at 298 nm $= 571$ M^{-1} cm^{-1}). Like other hexametalate species, **1** has well-behaved redox chemistry in acetonitrile [11]. Not surprisingly, given the lower charge density, **1** has a quite positive potential: $E^f = E_{pc} + E_{pa}/2 = -0.344$ V versus Fc$^+$/Fc($E_{pc} - E_{pa} = 78$ mV; $n = 1$ electron) as compared to $E^f = -0.52$, -0.643 and $+0.228$ V versus Fc$^+$/Fc for the polyvanadates, $[H_3V_{10}O_{28}]^{3-}$, $[CH_3CN \cdot (V_{12}O_{32}{}^{4-})]$ and $[V_{13}O_{34}]^{3-}$, respectively [7].

Treatment of Q1 with ethanol, 2-propanol or phenol in refluxing acetonitrile under N_2 for times much shorter than that used in the synthesis of Q1 (48 h) did not lead to the corresponding heptaalkoxy homologues of Q1 by transesterification, eqn. (1). Consistent with the redox potential of Q1, the alcohols were oxidized, the vanadium(V) was reduced and complex mixtures of unidentified partially reduced polyvanadates and V_2O_5 were obtained in all cases.

$$[V_6O_{12}(OCH_3)_7]^{1-} + n\mathrm{ROH} \nrightarrow [V_6O_{12}(OCH_3)_{7-n}(OR)_n]^{(8-n)-} + n\mathrm{CH_3OH} \quad (1)$$

Supplementary material

Further data (atomic fractional coordinates, etc.) can be obtained on request from the Director of the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

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