Synthesis and characterization of a reduced heteropoly-tungstovanadate: $(NH_4)_7[\,V^VO_4W_{10}^{VI}V_2^{IV}O_{36}]\cdot ca.\ 22H_2O$

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Abstract. The compound $(NH_4)_7[\,V^VO_4W_{10}^{VI}V_2^{IV}O_{36}]\cdot ca.22H_2O$ (**1**) has been synthesized from an aqueous ammonium acetate buffer (*p*H 4) containing sodium vanadate, sodium tungstate and sodium dithionite. Compound (**1**) crystallizes in a cubic space group $Fm\overline{3}$, with $a = 22\cdot2001(6)$ Å and $Z = 8$. The anion $[\,V^VO_4W_{10}^{VI}V_2^{IV}O_{36}]^{7-}$ is a typical Keggin type structure with V^VO_4 as the central tetrahedron. (**1**) has further been characterized by elemental analyses, redox titration, IR, EPR, and electronic spectroscopy and room temperature magnetic moment measurement.

Keywords. Heteropolytungstovanadate; crystal structure; Keggin type anion; reduction; spectral characterization.

1. Introduction

The chemistry of the early transition elements, particularly vanadium, molybdenum and tungsten, in aqueous solution is dominated by the formation of polyoxoanions which constitute a class of metal-oxygen cluster containing compounds, called poly-oxometalates[1]. Heteropolyanions with general formula $XM_{12}O_{40}^{n-}$ (where $X = P^V$, Si^{IV}, B^{III}, V^V, etc. as central tetrahedrally coordinated atoms and $M = Mo^{VI}$, W^{VI}, etc.), known as Keggin anions, constitute a special class of polyoxometalates[2]. Some of these Keggin compounds have applications in catalysis, medicine and chemical analysis[3]. The characterization of 'substituted' heteropoly Keggin anions, $XZ_yM_{12-y}O_{40}^{n-}$, where X is the central tetrahedrally coordinated atom, M is molybdenum or tungsten, and Z is a second heteroatom (e.g., vanadium), was first reported by Baker *et al*[4]. Numerous examples of such 'mixed-addenda' compounds have since been described[1,3]. When a solution of orthotungstate (WO_4^{2-}) and metavanadate (VO_3^-) salts is acidified, heteropolytungsto-vanadate complexes are precipitated. Pope and Flynn reported a series of such compounds of the general formula $V^tV_nW_{12-n}O_{40}^{(n+3)-}$ (where V^t is the vanadium in the center of the tertrahedron, $n = 2, 3, 4$)[5,6]. The synthesis and characterization of these heteropolytungstovanadates have been described many years ago, but the reduced analogue of any of these in the series has yet to be reported. There is considerable current interest in reduced heteropolyanions with respect to electron transfer and thereby its application in catalysis[3]. We report here the two-electron reduced compound of the

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heteropolytungstovanadate with $n = 2$ of this series. The synthesis and characterization, including crystal structure analysis of $(NH_4)_7[V^VO_4W_{10}^{VI}V_2^{IV}O_{36}]\cdot ca.22H_2O$ (**1**) are described.

2. Experimental

Infrared spectra were obtained as KBr pellets using a JASCO FT/IR-5300 spectrometer. UV-visible spectra were recorded using a 3101 Phillips spectrophotometer. The solid powder of **1** was spread over grease on a glass plate and the diffuse reflectance spectra obtained were then Kubelka-Munk corrected with grease (on a glass plate) background. ESR spectra (crystals of **1** were ground with KBr) were recorded on a Bruker ECS 106 spectrometer at 65 K. The degree of reduction (the number of V^{IV} centres) of **1** was determined by potentiometric titraton with 0·1 N KMnO$_4$ with a memotitrator Mettler DL 40 (Pt-/calomel-electrode). The vanadium values (three vanadiums per formula unit of **1**) were obtained using the literature method [7].

2.1   *Preparation of stock buffer solution*

250 ml of CH$_3$COOH was mixed with 250 ml of water in 1 L Erlenmeyer flask and 25% ammonia solution was added into it with stirring untill pH of this ammonium acetate solution reached to 4·0.

2.2   *Synthesis of $(NH_4)_7[V^VO_4W_{10}^{VI}V_2^{IV}O_{36}]\cdot ca. 22H_2O$*

40 ml of this stock buffer solution (pH 4·0) was diluted with 40 ml of water in a 100 ml conical flask, into which Na$_2$WO$_4\cdot$2H$_2$O (2·0 g, 6·06 mmol) was dissolved by stirring. This was treated with Na$_2$S$_2$O$_4$ (0·6 g, 3·45 mmol) and stirred for 15 min. NaVO$_3$ (1·5 g, 12·29 mmol) was subsequently added into this and stirred for another half an hour. Na$_2$SO$_3$ (1·1 g, 8·73 mmol) was added and stirred for one hour. The reaction mixture was filtered and the filtrate was kept at 20°C in a closed flask for 15 days. Deep green block-shaped crystals appeared during this time with some amorphous material. Decanting the amorphous substance with water separated the crystals of $(NH_4)_7[V^VO_4W_{10}^{VI}V_2^{IV}O_{36}]\cdot ca$ 22H$_2$O. Yield: 0·15 g (8% based on W). Analysis: H$_{72}$N$_7$O$_{62}$V$_3$W$_{10}$ requires H = 2·30, N = 3·11, V = 4·84%, Found: H = 2·39, N = 3·23, V = 4·70%. Room temperature effective magnetic moment (μ_{eff}) value for (**1**) = 1·56 BM.

2.3   *Single crystal X-ray structure analysis*

The structure of $(NH_4)_7[V^VO_4W_{10}^{VI}V_2^{IV}O_{36}]\cdot ca$ 22H$_2$O (**1**) was determined by single crystal X-ray method. A suitable crystal of dimensions $0·18 \times 0·18 \times 0·18$ mm was mounted on a X-ray diffractometer using MoKα radiation. The absorption correction was based on symmetry equivalent reflections using the SADABS programs [8]. A total of 22546 reflections ($1·59 < \theta < 29·94^o$) were collected of which 1439 unique reflections ($R_{int} = 0·0586$) were used. The structure was solved using SHELXS-97 [9] and refined using SHELXL-97 [10] to $R = 0·0370$ for 1138 reflections with $I > 2\sigma(I)$. The relevant details of the single crystal structure determination of (**1**) are summarized in table 1. The final atomic coordinates along with the thermal parameters are presented in table 2.

Table 1. Crystallographic data for **1**.

Empirical formula	$H_{72}N_7O_{62}V_3W_{10}$
Formula weight (M)	3153·87
Temperature (K)	183
Wavelength	0·71073
Crystal system	cubic
Space group	$Fm\overline{3}$
a (Å)	22·2001(6)
V (Å³)	10941·2 (5)
Z	8
D_{calcd} (g/cm³)	3·829
Absorption coefficient (mm^{-1})	21·54
$F(000)$	11408
Crystal size (mm)	$0·18 \times 0·18 \times 0·18$
Theta range for data collection (°)	1·59 to 29·94
Reflections collected	22546
Unique reflections	1439 [R_{int} = 0·0586)
Final R indices	[$I > 2\sigma(I)$] $R1 = 0.0370$, $wR2 = 0.1110$
R indices (all data)	$R1 = 0.0525$, $wR2 = 0.1207$

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å² $\times 10^3$) for **1**.

Atom	x	y	z	U(eq)^a
M^b	2555(1)	1374(1)	1374(1)	29(1)
V	2500	2500	2500	29(1)
Oa^c	2953(3)	2047(3)	2047(3)	21(2)
Ob	2003(3)	2005(3)	1169(3)	28(2)
Oc	3185(3)	950(3)	1814(3)	31(2)
Od	2397(3)	840(3)	841(3)	38(2)
O(1)	2905(9)	0	0	50(4)
O(2)	3768(8)	0	1236(8)	79(5)
O(3)	2500	0	2500	76(7)
O(4)	1437(12)	0	1431(11)	49(6)
O(5)	− 748(8)	− 762(9)	0	35(4)
O(6)	0	− 1250(40)	0	120(30)
O(7)	0	0	0	260(70)
O(8)	4535(10)	465(10)	465(10)	78(11)
O(9)	5000	0	0	150(70)

$^a U$(eq) is defined as one-third of the trace of the orthogonalized Uij tensor
^{b}M = (2V + 10W)/12, see text
^{c}The Evans classification of oxygen atoms in the Keggin structure (see text) [11]
O(1)–O(9) are the located oxygen atoms of lattice water molecules

3 Results and discussion

3.1 *Synthesis*

It is well known that when a solution of orthotungstate (WO_4^{2-}) and metavanadate (VO_3^-) are mixed and acidified polyvanadotungstate compounds are formed. These polyvanadotungstate anions are of two types: $V_n W_{6-n} O_{19}^{(n+2)-}$ ($n = 1$, 2) and

$V^t V_n W_{12-n} O_{40}^{(n+3)-}$ (where V^t is the vanadium in the centre of the tetrahedron, $n = 2, 3, 4$)[5-7]. In the present work we deal with one compound of the latter series, but under reducing condition. We have used sodium dithionite as reducing agent and we could isolate the 2-electron reduced Keggin type compound **1**. Ammonium acetate buffer (*p*H 4) was used, whereby the compound **1** was isolated as the ammonium salt.

3.2 *Description of crystal structure*

As shown in figure 1, this is a typical Keggin type polyanion, $VM_{12}O_{40}^{7-}$, where V represents the central vanadium atom of the $V^V O_4$ tetrahedron and where M_{12} means 2
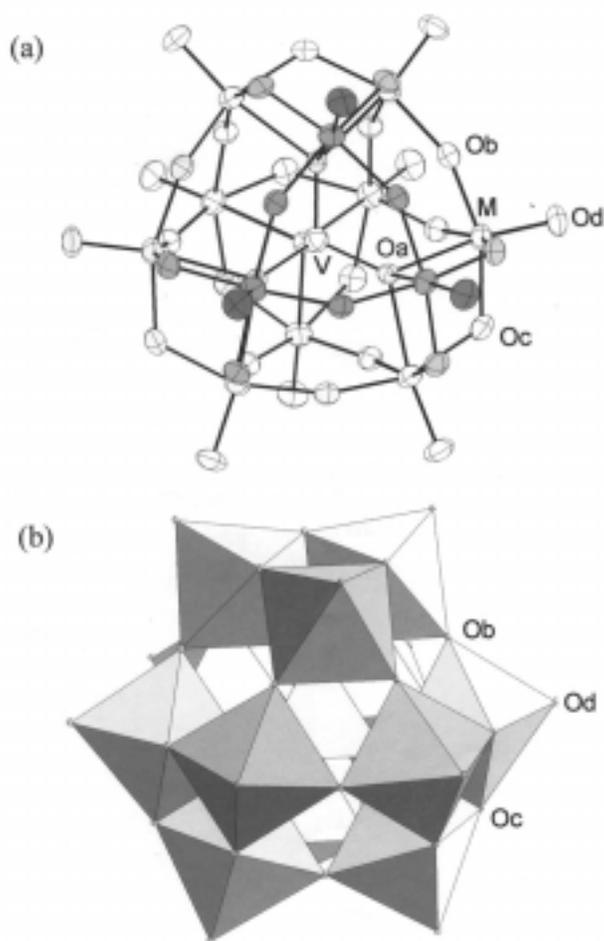
Figure 1. The structure of Keggin type anion $[V^V O_4 W_{10}^{VI} V_2^{IV} O_{36}]^{7-}$, where the vanadium atom is located at the centre and the other twelve metal (M) positions are occupied by ten tungsten atoms and two vanadium atoms with a $10:2$ probability: thermal ellipsoid (50% probability) plot (**a**), the polyhedral representation (**b**).

V^{IV} and 10 W^{VI} atoms randomly mixed. The space-group symmetry requires that twelve metal positions are crystallographically equivalent and it is not possible to locate two vanadium(IV) positions in the crystal structure. The structure of $VM_{12}O_{40}^{7-}$ (figure 1) is constructed as follows: Three MO_6 octahedra link together by sharing edges to form a M_3O_{13} unit with a trigonal symmetry (figure 1b). Four such M_3O_{13} units arrange in a tetrahedral symmetry with a central vanadium atom by sharing corners to build the

Table 3. Selected bond lengths [Å] and angles [°] for **1**.

Bond lengths

M–Oa	2·291(5)		M–Ob	1·915(7)
M–Oc	1·948(6)		M–Od	1·712(6)
		V–Oa		1·740(10)

Bond angles

Oc–M–Oa	73·2(2)		Ob–M–Oc	158·6(3)
Od–M–Oa	169·1(3)		Ob–M–Oa	85·7(2)
Od–M–Ob	102·2(3)		Od–M–Oc	99·1(3)
		V–Oa–M		122·0(2)
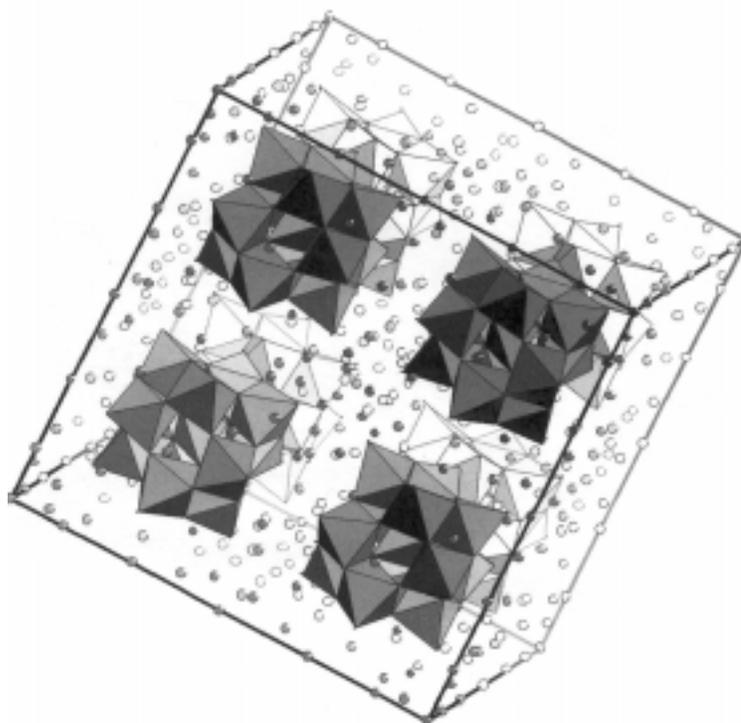
Figure 2. Unit cell packing of **1**. One unit cell contains eight Keggin type anions (shown in polyhedral representation). The circles are oxygen atoms of water molecules.

structure known as Keggin anion. Oxygen atoms in the polyanion can be classified[11] into four groups – Oa, Ob, Oc, and Od, as shown in figure 1. Oa is the oxygen atom shared by three MO_6 octahedra and the central VO_4 tetrahedron. Ob is linked to two different M atoms of different M_3O_{13} units. Oc is bound to two different M atoms in the same M_3O_{13} unit. Od is the terminal unshared oxygen atom. The MO_6 octahedra are distorted. Selected bond distances and angles are presented in table 3. The M–O distances in table 3 are the weighted average of the W^{VI}–O and V^{IV}–O distances, since the M in each position
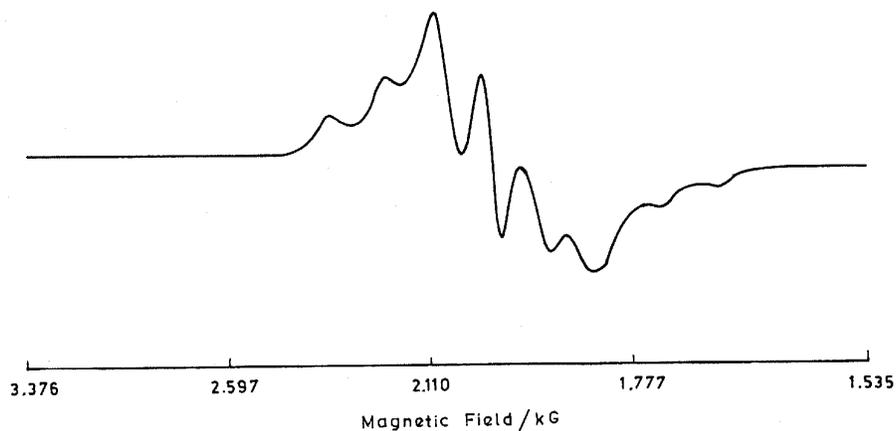
Figure 3. ESR spectrum of solid sample of **1**, ground with KBr, at 65 K.
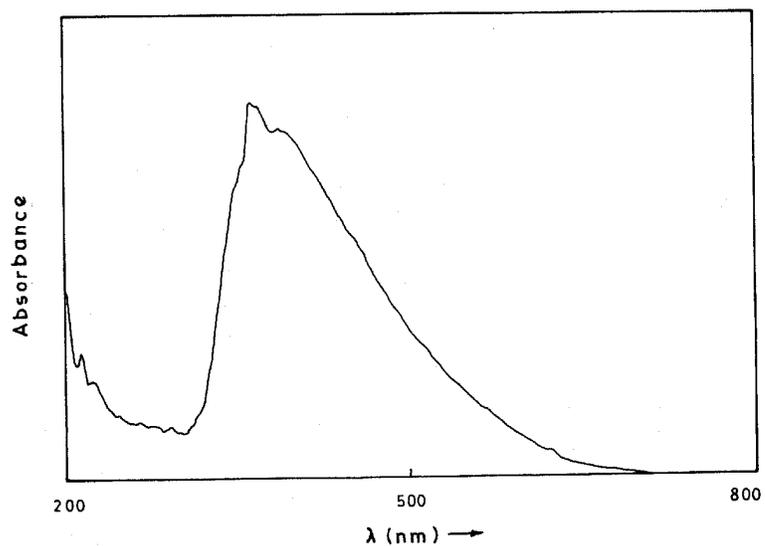
Figure 4. Diffuse reflectance spectrum of **1**.

is occupied by the randomly distributed W and V atoms with 10:2 probability. One unit cell contains eight $VM_{12}O_{40}^{7-}$ Keggin type anions (figure 2). The NH_4^+ cations could not be located in the crystal structure of (**1**), but elemental analyses are consistent with the presence of seven ammonium cations (see Experimental section). The V–O distance of the central VO_4 tetrahedron is 1·74 Å, which is in good agreement with that in the crystal structure of $K_7V_5W_8O_{40}\cdot12H_2O$ [12]. This justifies the +5 oxidation state of central vanadium atom.

3.3 *Analysis and spectroscopy*

The crystal structure analysis of (**1**) tells us that the anionic part of this compound is a typical Keggin type of structure, but it does not say much about its vanadium content and anything about its degree of reduction. The vanadium content has been estimated from vanadium analysis (three vanadium per formula unit) and this is consistent with the EDAX analysis, which gives the ratio of tungsten to vanadium as 10:3. The central tetrahedral atom is V^V, which is confirmed from the crystal structure data and the rest vanadium atoms are two of the 12 metal positions. The degree of reduction was obtained by redox titration, which gave two electrons per formula unit. The two electrons are likely to belong to the two vanadiums (W^{VI} ion is, in general, difficult to reduce). The vanadium reduction is further corroborated by the eight-line (I value of $^{51}V = 7/2$) EPR spectrum of (**1**) (figure 3). There are two unpaired electrons located on two vanadium atoms (per formula unit) and these will make the resultant spin quantum number $S = 1$ with three orientations represented three M_s values +1, 0 and –1. In the cubic (octahedral) crystal field, two expected transitions (namely $M_s = 0 \rightarrow M_s = +1$ and $M_s = -1 \rightarrow M_s = 0$) should have equal energy, and hence, effectively we observe a single transition in the EPR spectrum (figure 3) at low temperature. The absorption bands at around 400 nm in the optical (diffuse reflectance) spectrum (figure 4) of (**1**) that are responsible for the intense green color of the compound can be assigned as heteronuclear intervalence charge-transfer (IVCT) transitions [13], $V(IV) \rightarrow W(VI)$. The FTIR spectrum of (**1**) is
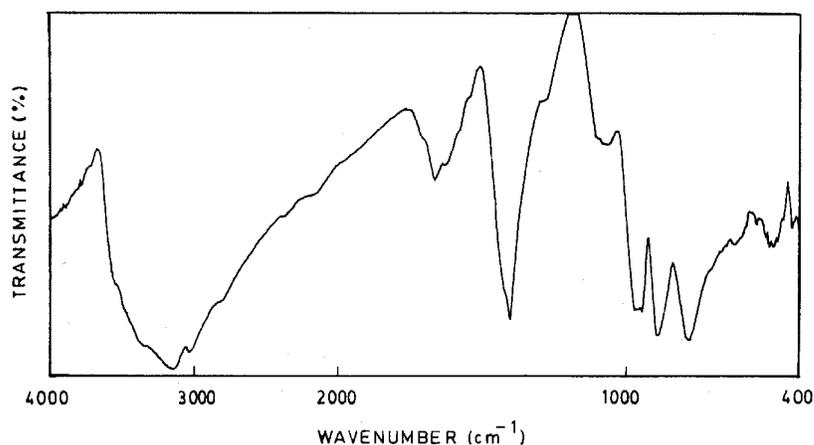
Figure 5. FTIR spectrum of **1**.

shown in figure 5. The IR absorption features of the central VO_4 tetrahedron and MO_6 octahedra in (**1**) are quite similar to those of the oxidized analogue compound[5] $K_5[V^VO_4W_{10}^{VI}V_2^{IV}O_{36}]\cdot20H_2O$.

4. Conclusions

We have synthesized a reduced heteropolytungstovanadate polyanion containing compound in a one-pot synthesis. The anion $[V^VO_4W_{10}^{VI}V_2^{IV}O_{36}]^{7-}$ has typical Keggin type of structure. Whereas the central vanadium ion (V^{5+}) is established, the other two vanadiums are not located in the crystal structure. The vanadium content and the degree of reduction are established by elemental analysis, spectroscopic characterization and magnetic moment data.

Acknowledgement

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