

# First 12-tungstovanadate Keggin compound: synthesis and crystal structure of $[\text{Me}_4\text{N}]_7[\text{VW}_{12}\text{O}_{40}]\cdot 15\text{H}_2\text{O}$

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The hydrothermal reaction of  $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$  with finely powdered vanadium metal and tetramethylammonium chloride at 160 °C gave an orange solution which yielded the 12-tungstovanadate Keggin compound  $[\text{Me}_4\text{N}]_7[\text{VW}_{12}\text{O}_{40}]\cdot 15\text{H}_2\text{O}$  **1**. This novel compound has been characterized by the IR, UV-VIS and EPR spectroscopic methods, manganometric titration, and single crystal structure analysis. The crystal structure consists of discrete tetramethylammonium cations, lattice water molecules, and anions of the mixed-valence species  $[\text{VW}_{12}\text{O}_{40}]^{7-}$ . The anion cluster contains tungsten addenda atoms and a  $\{\text{V}^{\text{IV}}\text{O}_4\}$  group at its center which is responsible for the overall tetrahedral symmetry of the near spherical polyanion.

## Introduction

Interest in the chemistry of metal oxide clusters has grown significantly in recent years.<sup>1</sup> Ammonium phosphomolybdate,  $[\text{NH}_4]_3[\text{PMO}_{12}\text{O}_{40}]\cdot x\text{H}_2\text{O}$ , is one of the earliest metal oxide clusters synthesized by Berzelius.<sup>2</sup> The structure of its tungsten analog,  $[\text{H}_3\text{PW}_{12}\text{O}_{40}]\cdot 5\text{H}_2\text{O}$ , the Keggin compound, was determined by Keggin<sup>3</sup> by the X-ray diffraction method; 170 years after the discovery and 63 years after the first structure determination of the prototype, the Keggin compounds and their derivatives continue to have a prominent place at the forefront of the polyoxometalate field.<sup>1-5</sup> This is due to their robust structure, remarkable electron donor-acceptor attributes, unusual magnetic properties,<sup>1a-c</sup> potential medicinal, including antiviral and antibacterial values,<sup>1b,5j</sup> relevance in the design and development of new materials, proven roles in catalysis, and promise as catalysts for chemical transformations.<sup>1e</sup> Some of these compounds have been used for surface modifications by virtue of their  $\pi$ -acceptor ligand properties.<sup>5m</sup>

Among the known heteropolytungstate Keggin compounds of the type  $[\text{XW}_{12}\text{O}_{40}]^{n-}$  ( $\text{X} = \text{P}, \text{Si}, 2\text{H}, \text{etc.}$ )<sup>1a,b,3,4</sup> and their derivatives  $[\text{XM}_i\text{W}_{12-i}]^{m-}$  ( $\text{M} = \text{mixed-addenda atom, e.g. Ti, Cr, Mn, Sn, Ge, etc.}$ ),<sup>5a-i</sup> only few incorporating vanadium as addenda atom(s) and, with the exception of a poorly characterized  $[\text{VW}_{11}\text{VO}_{40}]^{4-}$  species,<sup>6a</sup> almost none containing the central tetrahedral  $\{\text{VO}_4\}$  group<sup>6b-e</sup> has been structurally characterized. Thus, while the mixed-metal addenda species  $[\text{VW}_{12-x}\text{V}_x]^{(3+x)-}$  ( $x = 2$  or  $3$ ), considered to be the derivatives of the 'Hypothetical' Keggin compound  $[\text{VW}_{12}\text{O}_{40}]^{3-}$ ,<sup>6b</sup> have been prepared by the acidification of solutions of  $[\text{V}_2\text{W}_4\text{O}_{19}]^{4-}$ ,<sup>6c</sup> to our knowledge the parent Keggin compound has neither been reported nor isolated and structurally characterized to date. We now report the synthesis and characterization of the first 12-tungstovanadate Keggin compound,  $[\text{Me}_4\text{N}]_7[\text{VW}_{12}\text{O}_{40}]\cdot 15\text{H}_2\text{O}$  **1**, composed of the mixed-valence tungsten addenda and reduced  $\{\text{V}^{\text{IV}}\text{O}_4\}$  group.

## Experimental

### Materials

All chemicals were of reagent grade as received from commercial sources (Aldrich or Cerac, Inc.).

## Methods

The IR spectra (KBr Pellet; 4000–400  $\text{cm}^{-1}$ ) were recorded on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer, UV-VIS spectrum of an aqueous solution of the compound on a Cary 300 spectrophotometer and the X-Band EPR spectrum on a crystalline solid sample at 77 K using a modified Varian 4-E instrument. The titration of reduced metal sites in compound **1** was performed on a Mettler Toledo DL12 Titrator using a dilute acidic solution and standardized  $\text{KMnO}_4$  solution.

### X-Ray diffraction analysis

The structure of compound **1** was determined from single crystal X-ray diffraction data collected on a Siemens P4/CCD diffractometer (graphite monochromatized Mo-K $\alpha$  radiation;  $\lambda = 0.71073$  Å). A brown opaque (prism-shaped) crystal ( $0.20 \times 0.15 \times 0.15$  mm) was mounted on a glass fiber and centered. The unit cell parameters were obtained at 133(2) K based on 6390 peaks ( $3 \leq \theta \leq 25^\circ$ ). A total of 19354 reflections ( $2.39 \leq \theta \leq 29.13^\circ$ ) were collected of which 9705 unique reflections were used for structural elucidation. The data collection nominally covered a hemisphere of reciprocal space using  $\phi$  rotation frames collected at  $0.4^\circ$  increments for 20 s per frame. The crystal-to-detector distance was 5.26 cm. Coverage of the unique data set is over 98.4% complete to at least  $25^\circ$  in  $\theta$ . Crystal decay was estimated by comparing common intensities at the start and end of data collection and found to be negligible.

All data were corrected for absorption<sup>7</sup> on the basis of  $\phi$ -scan profiles. The structure was solved in monoclinic space group  $P2_1/m$  (no. 11) by direct methods and refined on  $F^2$  by full-matrix least-squares techniques. At convergence,  $R1 = 0.0439$  and the goodness of fit on  $F^2$  was 1.066. Data collection,<sup>8</sup> reduction<sup>9</sup> and structure solution, refinement, and graphics<sup>10</sup> were done by use of the Siemens program packages. Neutral atom scattering factors were taken from ref. 11. A summary of the crystal data is given in Table 1.

CCDC reference number 186/1382.

See <http://www.rsc.org/suppdata/dt/1999/1651/> for crystallographic files in .cif format.

**Table 1** Summary of crystal structure determination for  $[\text{Me}_4\text{N}]_7[\text{VW}_{12}\text{O}_{40}] \cdot 15\text{H}_2\text{O}$  **1**

Empirical formula	$\text{C}_{28}\text{H}_{114}\text{N}_7\text{O}_{55}\text{VW}_{12}$
Formula weight	3686.40
Crystal symmetry	Monoclinic
Space group	$P2_1/m$ (no. 11)
$a/\text{\AA}$	12.9094(2)
$b/\text{\AA}$	20.8420(6)
$c/\text{\AA}$	15.1180(2)
$\beta/^\circ$	100.302(2)
$V/\text{\AA}^3$	4002.04(14)
$D_c/\text{Mg m}^{-3}$	3.059
$Z$	2
$\mu/\text{mm}^{-1}$	17.377
$R1(F_o)$	0.0439
$wR2(F_o^2)$	0.1271

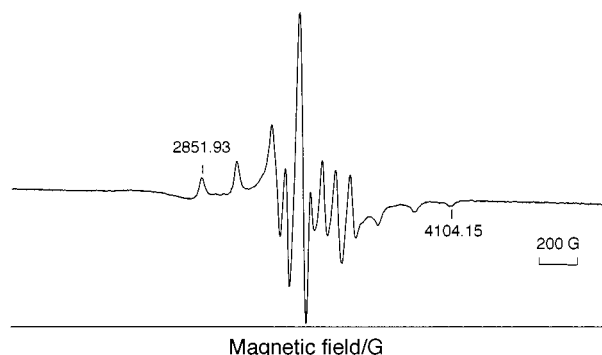
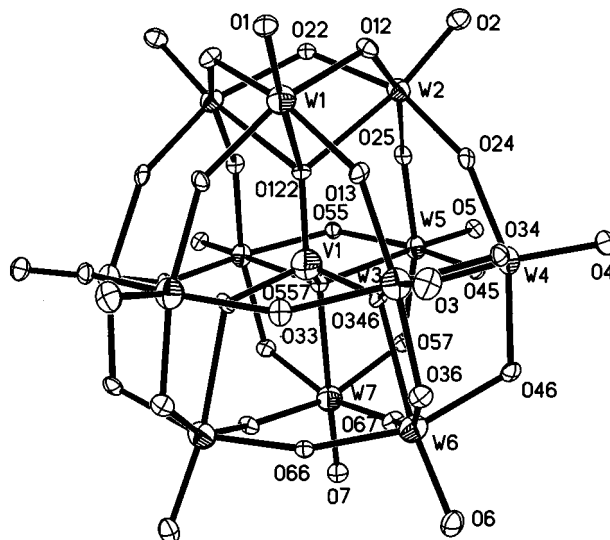
### Synthesis of $[\text{Me}_4\text{N}]_7[\text{VW}_{12}\text{O}_{40}] \cdot 15\text{H}_2\text{O}$ **1**

A mixture of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ , V(-325 mesh),  $\text{Me}_4\text{NCl}$ , and water in the molar ratio 3:2:4:333 was placed in a 23 mL Parr Teflon-lined autoclave which was subsequently heated for 90 h inside a programmable electric furnace maintained at 160 °C. After cooling the autoclave at room temperature for 4 h, the resultant solution was filtered and the orange-brown filtrate, contained in an open glass tube, was kept at room temperature for 150 d to give brown prism-shaped crystals of compound **1** in 8–10% yield along with an orange-yellow polycrystalline material that has not been fully characterized. The crystals were filtered from the mother-liquor, separated mechanically from the yellow impurity, and dried in air at ambient temperature. IR bands (1700–400  $\text{cm}^{-1}$  region): 1635s, 1489s, 998m, 949s, 901s, 887s, 781s and 545m.

### Results and discussion

The crystallization of compound **1** from the mother-liquor is accompanied by the precipitation of a polycrystalline yellow solid. The results of partial characterization of this material indicate it to be a different polyoxotungstate which probably is partly responsible for the reduction in the yield of **1**. Our attempts to increase the yield of **1** by changing the reaction conditions (stoichiometry, reaction temperature, time, etc.) have met with limited success. Reactions carried out by using different sources of tungsten and vanadium ( $\text{V}_2\text{O}_5$ ,  $\text{KVO}_3$ , etc.) in the presence of reducing agents at different temperatures and reaction times have either produced orange decavanadates, hexatungstates, or complex mixtures of amorphous solids that could not be characterized. However, the following alternative synthetic route reduces, to some extent, the preparation time of **1**: a mixture of  $\text{NaVO}_3$  (0.3 mmol),  $\text{NaCl}$  (5 mmol), and  $\text{Me}_4\text{NCl}$  (4 mmol) was added to a warm (60–70 °C) colorless solution obtained by dissolving  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{NH}_2\text{NH}_2 \cdot 2\text{HCl}$  in water (6 mL). The reaction mixture was refluxed for 24 h to give a brown solution which was transferred to an open mouthed glass tube and allowed to stay at room temperature. The brown crystals of **1**, that appeared in the bottom of the tube after 2 months were filtered off, mechanically separated from the minor yellow impurity, and dried at room temperature. The slow crystallization of **1** from the reaction mixtures appears to be reason that this compound remained elusive before this work.

The crystals of compound **1**, soluble in water and insoluble in common organic solvents, analyzed satisfactorily for the composition  $\text{C}_{28}\text{H}_{114}\text{N}_7\text{O}_{55}\text{VW}_{12}$ . The infrared spectrum exhibits features in the  $\nu(\text{W}=\text{O})$  region, a strong band at 887  $\text{cm}^{-1}$  assigned to  $\nu(\text{W}-\text{O}-\text{W})$ , and cation and water bands in their characteristic regions. The strong band at 781  $\text{cm}^{-1}$  is attributable to  $\nu(\text{VO}_4)$ . The UV-VIS spectrum of an aqueous solution of **1** exhibits a medium intensity (LMCT) charge

**Fig. 1** X-Band EPR spectrum of a solid sample of  $[\text{Me}_4\text{N}]_7[\text{VW}_{12}\text{O}_{40}] \cdot 15\text{H}_2\text{O}$  at 77 K.**Fig. 2** The structure of the Keggin anion  $[\text{VW}_{12}\text{O}_{40}]^{7-}$  in the crystal structure of  $[\text{Me}_4\text{N}]_7[\text{VW}_{12}\text{O}_{40}] \cdot 15\text{H}_2\text{O}$ . Displacement ellipsoids are drawn at the 50% probability level.

transfer band at 249 nm, a shoulder at 348 nm and another band at 368 nm with its tail extending to 500 nm.

The EPR spectrum recorded at low temperature (77 K) on a crystalline sample of compound **1** provides valuable information about the oxidation state of vanadium in the cluster. As shown in Fig. 1, the spectrum, characteristic for a vanadium(IV) center, exhibits hyperfine interaction  $[(2nI + 1)$  line multiplets where  $n = 1$ ] with the  $^{51}\text{V}$  nucleus ( $I = 7/2$ ) with  $g_{\parallel} = 1.897$ ,  $g_{\perp} = 1.923$ ,  $A_{\parallel} = 159.6 \times 10^{-4} \text{ cm}^{-1}$ , and  $A_{\perp} = 64.7 \times 10^{-4} \text{ cm}^{-1}$ .

The structure analysis performed on a crystal of compound **1** shows discrete  $[\text{VW}_{12}\text{O}_{40}]^{7-}$  anions, tetramethylammonium cations (seven per cluster anion) and lattice water molecules (fifteen per cluster). As shown in Fig. 2, the structure of the cluster anion may be viewed as a shell of  $\{\text{W}_{12}\text{O}_{36}\}$  encapsulating a  $\{\text{VO}_4\}$  moiety, present at its center and responsible for the local tetrahedral geometry. Each oxygen of the  $\{\text{VO}_4\}$  group, covalently bonded to three different tungsten centers of the shell, is in a  $\mu_4$ -bridging mode with  $\text{V}-\mu_4\text{-O}$  distances in the 1.625–1.630 Å range and  $\text{W}-\mu_4\text{-O}$  distances in the 2.311–2.344 Å range (Table 2). Alternatively, the cluster anion may be described as constructed from 12  $\{\text{WO}_6\}$  octahedra, present in the four groups of  $\{\text{W}_3\text{O}_{13}\}$  trioctahedra related with each other by a fourfold rotation axis. The 3  $\{\text{WO}_6\}$  octahedra in a  $\{\text{W}_3\text{O}_{13}\}$  unit are fused with each other by edge-sharing. Each  $\{\text{W}_3\text{O}_{13}\}$  unit is joined with the central  $\{\text{VO}_4\}$  group and with two other  $\{\text{W}_3\text{O}_{13}\}$  units through corner sharing. The seven independent tungsten centers in the cluster anion in **1** have essentially similar distorted octahedral environments defined by one terminal oxo-group with short  $\text{W}-\text{O}$  bond length (1.690–1.714 Å), four doubly bridging oxo-groups with intermediate

**Table 2** Selected bond lengths (Å) and angles (°) for compound **1**

W(1)–O(1)	1.708(9)	W(1)–O(13 <sup>1</sup> )	1.907(6)	W(5)–O(57)	1.906(6)	W(5)–O(25)	1.920(6)
W(1)–O(13)	1.907(6)	W(1)–O(12)	1.914(6)	W(5)–O(55)	1.937(4)	W(5)–O(557)	2.331(6)
W(1)–O(12 <sup>1</sup> )	1.914(6)	W(1)–O(122)	2.311(8)	W(6)–O(6)	1.712(7)	W(6)–O(66)	1.890(2)
W(2)–O(2)	1.712(7)	W(2)–O(24)	1.893(6)	W(6)–O(36)	1.897(6)	W(6)–O(67)	1.903(6)
W(2)–O(25)	1.900(6)	W(2)–O(12)	1.931(6)	W(6)–O(46)	1.952(6)	W(6)–O(346)	2.324(6)
W(2)–O(22)	1.936(4)	W(2)–O(122)	2.344(6)	W(7)–O(7)	1.690(9)	W(7)–O(67 <sup>1</sup> )	1.892(6)
W(3)–O(3)	1.710(7)	W(3)–O(33)	1.900(2)	W(7)–O(67)	1.892(6)	W(7)–O(57 <sup>1</sup> )	1.938(6)
W(3)–O(13)	1.902(6)	W(3)–O(34)	1.910(6)	W(7)–O(57)	1.938(6)	W(7)–O(557)	2.321(8)
W(3)–O(36)	1.919(6)	W(3)–O(346)	2.317(6)	V(1)–O(122)	1.625(9)	V(1)–O(557)	1.626(8)
W(4)–O(4)	1.708(7)	W(4)–O(24)	1.916(6)	V(1)–O(346)	1.630(6)	V(1)–O(346 <sup>1</sup> )	1.630(6)
W(4)–O(45)	1.918(6)	W(4)–O(34)	1.923(6)	O(22)–W(2 <sup>1</sup> )	1.936(4)	O(33)–W(3 <sup>1</sup> )	1.900(2)
W(4)–O(46)	1.935(6)	W(4)–O(346)	2.336(6)	O(55)–W(5 <sup>1</sup> )	1.937(4)	O(66)–W(6 <sup>1</sup> )	1.890(2)
W(5)–O(5)	1.714(6)	W(5)–O(45)	1.899(6)	O(122)–W(2 <sup>1</sup> )	2.344(6)	O(557)–W(5 <sup>1</sup> )	2.331(6)
O(1)–W(1)–O(13 <sup>1</sup> )	101.1(3)	O(1)–W(1)–O(13)	101.0(3)	O(45)–W(5)–O(25)	85.8(3)	O(57)–W(5)–O(25)	159.0(3)
O(13 <sup>1</sup> )–W(1)–O(13)	85.3(4)	O(1)–W(1)–O(12)	98.6(3)	O(5)–W(5)–O(55)	98.4(3)	O(45)–W(5)–O(55)	159.3(3)
O(13 <sup>1</sup> )–W(1)–O(12)	160.3(3)	O(13)–W(1)–O(12)	89.4(3)	O(57)–W(5)–O(55)	88.1(3)	O(25)–W(5)–O(55)	88.0(3)
O(1)–W(1)–O(12 <sup>1</sup> )	98.6(3)	O(13 <sup>1</sup> )–W(1)–O(12 <sup>1</sup> )	89.4(3)	O(5)–W(5)–O(557)	170.0(3)	O(45)–W(5)–O(557)	85.8(2)
O(13)–W(1)–O(12 <sup>1</sup> )	160.3(3)	O(12)–W(1)–O(12 <sup>1</sup> )	89.2(4)	O(57)–W(5)–O(557)	74.5(3)	O(25)–W(5)–O(557)	84.6(3)
O(1)–W(1)–O(122)	170.4(4)	O(13 <sup>1</sup> )–W(1)–O(122)	86.0(2)	O(55)–W(5)–O(557)	73.9(3)	O(6)–W(6)–O(66)	101.9(3)
O(13)–W(1)–O(122)	86.0(2)	O(12)–W(1)–O(122)	74.8(2)	O(6)–W(6)–O(36)	100.8(3)	O(66)–W(6)–O(36)	90.2(3)
O(12 <sup>1</sup> )–W(1)–O(122)	74.7(2)	O(2)–W(2)–O(24)	101.7(3)	O(6)–W(6)–O(67)	100.3(3)	O(66)–W(6)–O(67)	86.5(3)
O(2)–W(2)–O(25)	102.2(3)	O(24)–W(2)–O(25)	86.6(3)	O(36)–W(6)–O(67)	158.9(3)	O(6)–W(6)–O(46)	97.5(3)
O(2)–W(2)–O(12)	99.2(3)	O(24)–W(2)–O(12)	88.7(3)	O(66)–W(6)–O(46)	160.5(3)	O(36)–W(6)–O(46)	87.7(3)
O(25)–W(2)–O(12)	158.6(3)	O(2)–W(2)–O(22)	99.8(3)	O(67)–W(6)–O(46)	88.5(3)	O(6)–W(6)–O(346)	170.6(3)
O(24)–W(2)–O(22)	158.5(3)	O(25)–W(2)–O(22)	89.4(3)	O(66)–W(6)–O(346)	85.9(3)	O(36)–W(6)–O(346)	73.7(2)
O(12)–W(2)–O(22)	87.3(3)	O(2)–W(2)–O(122)	170.4(3)	O(67)–W(6)–O(346)	85.3(2)	O(46)–W(6)–O(346)	75.0(2)
O(24)–W(2)–O(122)	84.8(2)	O(25)–W(2)–O(122)	85.1(3)	O(7)–W(7)–O(67 <sup>1</sup> )	100.8(3)	O(7)–W(7)–O(67)	100.8(3)
O(12)–W(2)–O(122)	73.7(3)	O(22)–W(2)–O(122)	73.8(3)	O(67 <sup>1</sup> )–W(7)–O(67)	87.8(4)	O(7)–W(7)–O(57 <sup>1</sup> )	99.0(3)
O(3)–W(3)–O(33)	101.7(3)	O(3)–W(3)–O(13)	101.9(3)	O(67 <sup>1</sup> )–W(7)–O(57 <sup>1</sup> )	89.5(3)	O(67)–W(7)–O(57 <sup>1</sup> )	160.2(3)
O(33)–W(3)–O(13)	86.0(3)	O(3)–W(3)–O(34)	98.5(3)	O(7)–W(7)–O(57)	99.0(3)	O(67 <sup>1</sup> )–W(7)–O(57)	160.2(3)
O(33)–W(3)–O(34)	159.8(3)	O(13)–W(3)–O(34)	89.7(3)	O(67)–W(7)–O(57)	89.5(3)	O(57 <sup>1</sup> )–W(7)–O(57)	86.3(4)
O(3)–W(3)–O(36)	98.9(3)	O(33)–W(3)–O(36)	89.4(3)	O(7)–W(7)–O(557)	170.4(4)	O(67 <sup>1</sup> )–W(7)–O(557)	86.1(2)
O(13)–W(3)–O(36)	159.2(3)	O(34)–W(3)–O(36)	87.7(3)	O(67)–W(7)–O(557)	86.1(2)	O(57 <sup>1</sup> )–W(7)–O(557)	74.2(2)
O(3)–W(3)–O(346)	169.6(3)	O(33)–W(3)–O(346)	85.5(3)	O(57)–W(7)–O(557)	74.2(2)	O(122)–V(1)–O(557)	109.1(5)
O(13)–W(3)–O(346)	85.9(2)	O(34)–W(3)–O(346)	74.5(2)	O(122)–V(1)–O(346)	109.4(3)	O(557)–V(1)–O(346)	109.8(3)
O(36)–W(3)–O(346)	73.5(2)	O(4)–W(4)–O(24)	101.6(3)	O(122)–V(1)–O(346 <sup>1</sup> )	109.4(3)	O(557)–V(1)–O(346 <sup>1</sup> )	109.8(3)
O(4)–W(4)–O(45)	101.9(3)	O(24)–W(4)–O(45)	85.2(3)	O(346)–V(1)–O(346 <sup>1</sup> )	109.4(5)	W(1)–O(12)–W(2)	120.1(3)
O(4)–W(4)–O(34)	99.3(3)	O(24)–W(4)–O(34)	89.2(3)	W(3)–O(13)–W(1)	150.4(4)	W(2)–O(22)–W(2 <sup>1</sup> )	120.7(4)
O(45)–W(4)–O(34)	158.7(3)	O(4)–W(4)–O(46)	99.2(3)	W(2)–O(24)–W(4)	151.5(3)	W(2)–O(25)–W(5)	150.3(4)
O(24)–W(4)–O(46)	159.2(3)	O(45)–W(4)–O(46)	89.4(3)	W(3)–O(33)–W(3 <sup>1</sup> )	150.5(5)	W(3)–O(34)–W(4)	120.5(3)
O(34)–W(4)–O(46)	88.6(3)	O(4)–W(4)–O(346)	170.8(3)	W(6)–O(36)–W(3)	121.2(3)	W(5)–O(45)–W(4)	151.4(4)
O(24)–W(4)–O(346)	84.6(2)	O(45)–W(4)–O(346)	85.3(2)	W(4)–O(46)–W(6)	118.5(3)	W(5 <sup>1</sup> )–O(55)–W(5)	120.0(5)
O(34)–W(4)–O(346)	73.8(2)	O(46)–W(4)–O(346)	75.0(2)	W(5)–O(57)–W(7)	120.0(3)	W(6 <sup>1</sup> )–O(66)–W(6)	151.1(5)
O(5)–W(5)–O(45)	102.2(3)	O(5)–W(5)–O(57)	99.2(3)	W(7)–O(67)–W(6)	149.2(4)	V(1)–O(122)–W(1)	124.5(5)
O(45)–W(5)–O(57)	90.7(3)	O(5)–W(5)–O(25)	101.8(3)	V(1)–O(122)–W(2)	124.0(3)	W(1)–O(122)–W(2)	91.4(2)
				V(1)–O(122)–W(2 <sup>1</sup> )	124.0(3)	W(1)–O(122)–W(2 <sup>1</sup> )	91.4(2)
				W(2)–O(122)–W(2 <sup>1</sup> )	91.7(3)	V(1)–O(346)–W(3)	124.2(3)
				V(1)–O(346)–W(6)	123.9(3)	W(3)–O(346)–W(6)	91.5(2)
				V(1)–O(346)–W(4)	124.5(3)	W(3)–O(346)–W(4)	91.3(2)
				W(6)–O(346)–W(4)	91.6(2)	V(1)–O(557)–W(7)	123.0(5)
				V(1)–O(557)–W(5 <sup>1</sup> )	124.7(3)	W(7)–O(557)–W(5 <sup>1</sup> )	91.4(2)
				V(1)–O(557)–W(5)	124.7(3)	W(7)–O(557)–W(5)	91.4(2)
				W(5 <sup>1</sup> )–O(557)–W(5)	92.1(3)		

Symmetry transformation used to generate equivalent atoms:  $1-x, -y + \frac{1}{2}, z$ .

W–μ–O bond lengths (1.890–1.938 Å), and one μ<sub>4</sub>-oxygen, also bonded to V, with long W–μ<sub>4</sub>-O distances (2.311–2.344 Å). The tungsten centers lie slightly above the plane defined by the four μ-oxygens.

The O–V–O bond angles [109.1(5)–109.8(4)°] in {VO<sub>4</sub>} represent almost ideal tetrahedral geometry around vanadium. The average V–O distance [1.628(7) Å] is longer than the corresponding bond distance [1.538(10) Å] in the fully oxidized Keggin-like isopolyvanadate [V<sub>15</sub>O<sub>42</sub>]<sup>9–6e</sup> indicating a reduced vanadium(IV) in {VO<sub>4</sub>} in **1** which corroborates the EPR spectral results. The presence of the reduced {V<sup>IV</sup>O<sub>4</sub>} group at the center of such a Keggin ion is unprecedented. Interestingly, the average V–O distance in **1** is comparable with the corresponding bond length in [H<sub>6</sub>Mn<sub>3</sub>V<sup>IV</sup><sub>15</sub>V<sup>V</sup><sub>3</sub>(V<sup>V</sup>O<sub>4</sub>)O<sub>42</sub>(H<sub>2</sub>O)<sub>12</sub>].30H<sub>2</sub>O (V<sup>V</sup>–O 1.661 Å) which could possibly be due to the larger size of the {V<sub>18</sub>O<sub>42</sub>} ‘container’ and its interaction with the central {VO<sub>4</sub>} group in the latter compound.<sup>12</sup> The W–O distances are comparable to the corresponding distances in [H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub>] (1.62–1.77; 1.76–2.00, 1.91–2.47 Å),<sup>5f</sup> [Pr<sub>4</sub>N]<sub>3</sub>[H<sub>3</sub>W<sub>12</sub>O<sub>40</sub>].2H<sub>2</sub>O

(1.68–1.71, 1.88–1.95, 2.26–2.30 Å),<sup>13a</sup> and [Me<sub>4</sub>N]<sub>6</sub>[H<sub>2</sub>W<sub>12</sub>O<sub>40</sub>].2H<sub>2</sub>O (1.71, 1.91–1.96, 2.22 Å).<sup>13b</sup>

The anion cluster, three of the cations (N3, N4, and N5) and one water molecule (O5S) of crystallization sit on a crystallographic mirror plane. The B and C hydrogens for the three water molecules (O6S, O7S, and O8S) have 50% occupancy. All tetramethylammonium cations are unambiguously identified in the crystal structure of compound **1**. Charge balance considerations require seven units of negative charge on each cluster anion. The bond valence sum (BVS)<sup>14</sup> values of the terminal as well as the doubly bridging oxygens in the cluster anion fall within the 1.73–2.05 range, normal for oxo groups. The final Fourier difference map does not exhibit any electron density attributable to hydroxy hydrogen. These results rule out any protonation sites associated with the cluster oxygens. The unambiguous identification of the V<sup>IV</sup> and the result of the manganometric titration of **1** indicate the presence of three W<sup>V</sup> per anion cluster. The BVS values of the tungsten centers and W–O distances, however, do not clearly identify the reduced

tungsten(v) sites. This is due to the possible delocalization of the d electrons of the reduced tungsten centers over the polyanion framework involving all W as found in heteropolyblues,<sup>1b,5h,15</sup> reduced hexamolybdate<sup>16</sup> and hexatungstates.<sup>17</sup>

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