

SYNTHESIS AND CHARACTERIZATION OF MATERIALS CONTAINING ARRAYS OF DECAVANADATE CLUSTERS

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1. ABSTRACT

The synthesis and characterization by single crystal x-ray structure analysis, manganometric titration, valence sum calculations, thermogravimetric analysis, and IR spectroscopic studies of $(\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH})_2(\text{Na}(\text{H}_2\text{O})_2)(\text{HV}_{10}\text{O}_{28}) \cdot 2\text{H}_2\text{O}$ (1) and $(\text{H}_3\text{N}-4-\text{C}_5\text{H}_4\text{N})_2(\text{NH}_4)_4(\text{V}_{10}\text{O}_{28}) \cdot x\text{H}_2\text{O}$ (2) has been described. The structure of 1 consists of alternating layers composed of two-dimensional arrays of decavanadate clusters $(\text{HV}_{10}\text{O}_{28})^{5-}$ interlinked by the $\{\text{Na}(\text{H}_2\text{O})_2\text{O}_4\}$ moieties, separated by the doubly protonated DABCO cations-- $(\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH})^{2+}$. The structure exhibits a fascinating network of hydrogen bonds between cations, solvate water molecules and anion clusters. The crystal structure of 2 contains three-dimensional arrays of $(\text{V}_{10}\text{O}_{28})^{6-}$ cluster anions, protonated 4-aminopyridinium groups, ammonium ions, and water molecules. Crystal data for 1: $\text{C}_{12}\text{H}_{37}\text{N}_4\text{Na}_2\text{O}_{32}\text{V}_{10}$, Monoclinic space group C2/m, $a = 20.4242(8)$, $b = 8.4550(3)$, $c = 11.9255(5)\text{\AA}$, $\beta = 122.0500(10)^\circ$, Volume = $1745.49(12)(\text{\AA}^3)$, $Z = 2$, $D_{\text{calc}} = 2.439 \text{ Mg/m}^3$. Crystal data for 2: Triclinic space group $P\bar{1}$, $a = 14.911(2)$, $b = 16.928(2)$, $c = 39.714(5)\text{\AA}$, $\alpha = 84.454(2)$, $\beta = 84.895(2)$, $\gamma = 79.603(2)^\circ$, Volume = $9787.4(13) \text{ \AA}^3$, $Z = 8$.

2. INTRODUCTION

Polyoxometalates are an important and fast emerging class of compounds which exhibit many remarkable properties (1-6). Their actual and potential applications span a number of fields, including medicine and clinical analysis, catalysis, solid-state technology, chemical analysis, coatings, processing radioactive waste, separations, sorbents of gases, sensors, electrooptics, cation exchangers, selective and high-capacity oxidants and reductants, and food chemistry (7-8). Polyoxometalates have some properties that make them especially attractive

for applications in medicine (3,9-16). Particular attention is being focused on their potential use in antiviral and antitumoral chemotherapy. The size (up to several nanometer diameter), charge-density, high stability, and high solubility of polyoxoanions seem important to their potential activity as medicinal agents (9).

The ability of certain vanadium compounds to induce a number of important biological responses, such as insulin-mimetic activity and cardiovascular effects (17-19), has resulted in considerable interest in the aqueous chemistry and biochemistry of vanadium. Consequently, polyoxovanadates have attracted considerable attention in recent years (10-16). In particular, decavanadate has been shown to be an inhibitor of catalysis by bovine pancreatic ribonuclease A (RNase A) (Messmore). Furthermore, decavanadates have shown a high affinity for selected kinases, phosphorylase, and reverse transcriptase, are useful in facilitating protein crystallization, and provide model compounds for understanding polyoxometalates-protein interactions (20). Decavanadates inhibit some kinases and phosphorylases, as well as the glycolytic enzyme aldolase (12).

The decavanadate anion cluster, $(\text{V}_{10}\text{O}_{28})^{6-}$ (1,21-24), that has also been found in several minerals (1, 21), is a prominent member of a well-characterized polyvanadate (1-5) series: $(\text{V}_4\text{O}_{12})^{4-}$ (25) $(\text{V}_5\text{O}_{14})^{3-}$ (26), $(\text{V}_{12}\text{O}_{32})^{4-}$ (27), $(\text{V}_{13}\text{O}_{34})^{3-}$ (28), and $(\text{V}_{15}\text{O}_{42})^{9-}$ (29). The interest in this species is reflected by the numerous compounds containing the $(\text{V}_{10}\text{O}_{28})^{n-}$ anion cluster and its derivatives with a variety of cations that have been prepared and characterized. Mixed-metal derivatives (30), a new form of mixed-valence decavanadate, $(\text{V}_{10}\text{O}_{30})^{11-}$ (31), and reduced decavanadates incorporating varying numbers of organic ligands have also been reported in recent years (32-35).

We have been studying the potential of polyvanadate clusters as structural motifs for the preparation of metal oxide based extended structure systems and composites (36-43). During the course of our investigation we have prepared new systems containing arrays of decavanadates networked by extensive hydrogen bonding with cyclic nitrogen bases. In this report, we describe the synthesis and characterization of $(\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH})_2(\text{Na}(\text{H}_2\text{O})_2)(\text{HV}_{10}\text{O}_{28})\cdot 2\text{H}_2\text{O}$ (**1**) and $(\text{H}_3\text{N}-4-\text{C}_5\text{H}_4\text{N})_2(\text{NH}_4)_4(\text{V}_{10}\text{O}_{28})\cdot x\text{H}_2\text{O}$ (**2**) by single crystal x-ray structure analyses, manganometric titration, valence sum calculations, thermogravimetric analysis, and IR spectroscopic studies.

3. MATERIALS AND METHODS

3.1. Materials

All the chemicals used during this work were of reagent grade. They were used as received from commercial sources (Aldrich, ACROS, and Fisher) without any further purification.

3.2. Methods

IR spectra (KBr pellets; 4000-400 cm^{-1}) were recorded on either a Thermo Nicolet Nexus 470 Spectrometer or a Perkin Elmer Paragon 1000 FT-IR Spectrophotometer. Manganometric titration of the compounds were performed on a Mettler Toledo DL12 Titrator using dilute sulfuric solutions of the compounds against standardized KMnO_4 solution. The pH measurements were carried out with an Accumet pH meter (model 910), following calibration with standard buffer solutions. Thermogravimetric analysis data were obtained by using a Mettler-Toledo STAR System. Typically 10-20 mg of sample was placed in a quartz bucket and heated in argon flow of 50 mL/min with a heating rate of $5^\circ/\text{min}$. The residues from TGA experiments were examined by IR spectroscopy.

3.3. Single Crystal X – Ray Diffraction.

An x-ray quality crystal of each compound was selected. After the crystal was mounted on a thin glass fiber with Paratone oil, it was mounted on a Siemens/Bruker SMART-CCD diffractometer (44), equipped with graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The x-ray data were collected at 183(2) K. The data were processed with SAINT (45), software and empirical absorption corrections were carried out with SADABS (46). All calculations were performed using SHELXTL package (47). The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques.

3.4. Synthesis of $(\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH})_2(\text{Na}(\text{H}_2\text{O})_2)(\text{HV}_{10}\text{O}_{28})\cdot 2\text{H}_2\text{O}$ (**1**)

A colorless solution of N_3VO_4 (2.14 g, 11.66 mmol) in water (15 mL), contained in a round-bottomed flask at room temperature, was acidified with 3N HCl (8 mL) to give an orange solution of pH 4.5. 4.6 mL of this solution, 0.2 mmol of 1,4-diazabicyclo(2.2.2)octane (DABCO) ($\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}$) and 0.2 mmol of tripentaerythritol ($(\text{HOH}_2\text{C})_3\text{C}(\text{CH}_2)\text{O}(\text{CH}_2)\text{C}(\text{CH}_2\text{OH})_3$) (TPE) were placed in a 23-ml Teflon-lined Parr autoclave.

This mixture was stirred for few minutes and subsequently heated in an electric furnace, maintained at 70°C , for 24 hours. The furnace was then turned off and the autoclave was allowed to cool down slowly to room temperature. The orange cubic crystals of **1** were filtered from the yellow mother liquor. The crystals were washed thoroughly with deionized water and dried at room temperature. Yield: 25% (based on vanadium). Prominent IR bands (KBr pellet, 4000–400 cm^{-1}): 3021(m), 1635(w), 1476(m), 1386(m), 987(s), 969(s), 955(s), 851(m), 811(w), 742(s), 585(s).

The compound can also be prepared, in lower yield, without using tripentaerythritol by the following modified synthetic method: A colorless solution of N_3VO_4 (2.14 g, 11.66 mmol) in water (15 mL), contained in a round-bottomed flask at room temperature, is acidified with 3N HCl (8 mL) to give an orange solution of pH 4.5. After adding DABCO (1 mmol) to this solution, the reaction mixture was refluxed for 24 hours at 70°C . The resultant orange mother liquor was left in a closed vessel at room temperature. The orange crystals, that separated over a period of several weeks, were filtered, washed with water, and dried in air at room temperature. Yield 15% (based on vanadium).

3.5. Synthesis of $(\text{H}_3\text{N}-4-\text{C}_5\text{H}_4\text{N})_2(\text{NH}_4)_4(\text{V}_{10}\text{O}_{28})\cdot x\text{H}_2\text{O}$ (**2**)

To a stirred light yellow colored solution of NH_4VO_3 (0.146 g, 1.25 mmol) in water (15 mL), contained in a round bottomed flask and maintained at $82-84^\circ\text{C}$, was added $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (0.525g, 1.87 mmol). After the complete dissolution of $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ in few minutes, the stirring of the solution was continued for another few minutes followed by the addition of 4-aminopyridine ($\text{H}_2\text{N}-4-\text{C}_5\text{H}_4\text{N}$) (0.176 g, 1.87 mmol) in the reaction mixture. The mixture was refluxed at 82°C for 24 hours. After cooling the reaction vessel to the room temperature, the orange crystals were filtered from the light pink mother liquor. The crystals were mechanically separated from the yellow amorphous impurity and dried at room temperature. Yield: 40% (based on vanadium). Prominent IR bands (KBr pellet 4000–400 cm^{-1}): 1648(s), 1526(s), 1199(s), 948(s), 817(s), 745(m), 523(m).

4. RESULTS AND DISCUSSION

Compounds 1-2 are readily prepared by the synthetic procedures described in the experimental section. The preparation reactions are, however, pH sensitive as the decavanadate cluster is formed only in the acidic medium. As expected, the crystals of 1-2 are stable in air at room temperature. The crystals of **1** are insoluble in cold and hot water, DMSO, DMF, and other common organic solvents. The results of the manganometric redox titrations show no reduced vanadium(IV) sites in either compound. This is consistent with the orange -- the characteristic color of the oxidized decavanadate cores -- colors of the crystals.

The infrared spectrum of **1** exhibits very strong bands in the 980-950 cm^{-1} region characteristic of $\nu(\text{V}=\text{O})$, and multiple medium intensity bands in the region characteristic of the bridging $\{\text{V}-\text{O}-\text{V}\}$ groups. The

Table 1. Crystallographic Data for 1

Compound	(HN(CH ₂ CH ₂) ₃ NH) ₂ (Na(H ₂ O) ₂)(HV ₁₀ O ₂₈)·2H ₂ O (1)
Empirical Formula	C ₁₂ H ₃₇ N ₄ NaO ₃₂ V ₁₀
Formula Weight	1281.85
Space Group	C2/m
Crystal System	Monoclinic
Temperature (K)	183(2)
λ (Å)	0.71073
a (Å)	20.4242(8)
b (Å)	8.4550(3)
c (Å)	11.9255(5)
α (°)	90
β (°)	122.0500(10)
γ (°)	90
Volume (Å ³)	1745.49(12)
Z	2
Density (Calculated)	2.439 Mg/m ³
μ (mm ⁻¹)	2.681
R ₁ (F _o) ^a (all data)	0.0238
WR ₂ (F _o ²) ^b (all data)	0.0647

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o| \quad ^b WR_2 = ((\sum w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)))^{1/2}$$

Table 2. Atomic Coordinates (x 10⁴) and Equivalent Isotropic Displacement Parameters (Å² x 10³) for 1. U(eq) is Defined as One Third of the Trace of the Orthogonalized Uij Tensor

	x	y	z	U(eq)
V(1)	0	-1935(1)	0	9(1)
V(2)	-1373(1)	0	-2323(1)	10(1)
V(3)	-1197(1)	0	357(1)	12(1)
V(4)	203(1)	-1816(1)	2748(1)	11(1)
Na(1)	-5000	0	-5000	11(1)
O(1)	82(1)	0	1182(2)	11(1)
O(2)	-83(1)	-3116(1)	-1218(1)	14(1)
O(3)	-1084(1)	-1469(1)	-833(1)	11(1)
O(4)	-1224(1)	1566(1)	-3228(1)	11(1)
O(5)	-2302(1)	0	-3027(2)	14(1)
O(6)	-896(1)	1594(2)	1593(1)	16(1)
O(7)	-2121(1)	0	-341(2)	16(1)
O(8)	245(1)	0	3616(2)	13(1)
O(9)	263(1)	-3183(2)	3729(1)	17(1)
O(10)	-3739(1)	0	-3201(2)	23(1)
O(11)	-1176(1)	-5000	860(2)	22(1)
N(1)	2223(1)	-5000	1766(2)	13(1)
N(2)	3146(1)	-5000	4196(2)	15(1)
C(1)	1777(1)	-5000	2438(2)	16(1)
C(2)	2713(1)	-6458(2)	2142(2)	14(1)
C(3)	2346(2)	-5000	3911(3)	49(1)
C(4)	3279(2)	-6432(3)	3630(2)	45(1)

spectrum also contains several bands of protonated-DABCO cation (HN(CH₂CH₂)₃NH)²⁺ in the 1700-1000 cm⁻¹ and 3500-3400 cm⁻¹ regions. It also shows the characteristic water absorption bands in the usual range.

The IR spectrum of 2 contains a very strong band at 948 cm⁻¹ assigned to ν (V=O) and medium intensity bands in the 750-600 cm⁻¹ region due to the bridging {V-O-V} groups. The spectrum also exhibits very strong bands due to 4-aminopyridine and ammonium ions in the 1650-1000 cm⁻¹ and 3400-3200 cm⁻¹ regions.

The thermogravimetric analysis of 1 indicates an initial weight loss of 1.7% at around 100°C, which corresponds to the removal of one molecule of water (calculated 1.4%). This is followed by a significant weight loss (24.65%) in the temperature range 168-405°C due to the removal of the remaining three water molecules and the decomposition of protonated DABCO cations-(HN(CH₂CH₂)₃NH)²⁺. The other 13.6% weight loss in the 405-596 °C region could possibly be attributed to the release of (six) oxygen molecules. The infrared spectrum of the shining black residue, left after the heating, exhibits only a few weak bands (985 cm⁻¹, 631 cm⁻¹, and 548 cm⁻¹) below 1000 cm⁻¹. None of these corresponds to the characteristic bands of the decavanadate cluster. This indicates that the removal of water and (HN(CH₂CH₂)₃NH)²⁺ leads to the decomposition of the cluster core (leading to release of the oxygen). The residue is likely to be a reduced metal oxide phase and has not been characterized further.

Table 1 contains the x-ray crystallographic data for 1. Atomic coordinates are given in Table 2. Selected bond lengths and bond angles are listed in Table 3. The hydrogen coordinates are given in Table 4. The x-ray crystal structure of 1 contains layers composed of 2-dimensional arrays of decavanadate clusters. Organic cations and solvated water molecules occupy the interlayer regions. Figure 1 is a packing drawing, projected down the c-axis, showing the contents of three unit cells in the crystals of 1. The unit cell contains two {V₁₀O₂₈}-based anion clusters, four (HN(CH₂CH₂)₃NH)²⁺ (doubly protonated DABCO cations), two sodium cations, and eight water molecules. The structure consists of alternating layers perpendicular to the a-axis. The anionic layers containing decavanadate clusters, sodium cations, and water molecules are separated by doubly protonated DABCO groups. The environment of each Na⁺ ion in the layer consists of four terminal oxygen atoms (O9) from four different cluster anions at 2.41Å and the oxygen atoms (O10) of two water molecules at 2.32Å. Thus, the anionic layers may be viewed as composed of arrays of decavanadate clusters interlinked by the {Na(H₂O)₂O₄} moieties.

A view of the decavanadate cluster showing the atom numbering is given in Figure 2. The structure of the cluster is essentially similar to those reported earlier (21-23). The anion cluster, which exhibits 2/m crystallographic symmetry, is composed of ten edge-sharing {VO₆} octahedra generated from a highly condensed arrangement of 10 vanadium and 28 oxygen atoms. Eight terminal, 14 μ_2 -, 4 μ_3 -, and 2 μ_6 -oxygen atoms define the distorted octahedral geometries around the ten vanadium atoms in the cluster. Eight (V2-, V3-, and V4- type) vanadium centers have one short (1.60-1.62Å), four intermediate (1.83-2.03Å), and one very long (2.24-2.33Å) V-O bonds.

Table 3. Selected Bond Lengths (Å) and Angles (°) for 1

V(1)-O(2)	1.6946(12)	O(2)-V(1)-O(3)	96.50(5)
V(1)-O(3)	1.9255(12)	O(2)-V(1)-O(1)	165.19(6)
V(1)-O(1)	2.1077(11)	O(3)-V(1)-O(1)	81.24(6)
V(1)-V(4)	3.0783(3)	O(2)-V(1)-V(4)	145.77(4)
V(2)-O(5)	1.6168(17)	O(3)-V(1)-V(4)	90.63(3)
V(2)-O(4)	1.8331(12)	O(1)-V(1)-V(4)	49.04(3)
V(2)-O(3)	1.9839(12)	O(5)-V(2)-O(4)	102.13(6)
V(2)-O(1)#2	2.2358(16)	O(5)-V(2)-O(3)	100.08(6)
V(2)-V(3)	3.0197(5)	O(4)-V(2)-O(3)	156.36(6)
V(2)-V(4)#2	3.0998(4)	O(5)-V(2)-V(3)	89.89(6)
V(3)-O(7)	1.6087(18)	O(4)-V(2)-V(3)	131.24(4)
V(3)-O(6)	1.8455(13)	O(3)-V(2)-V(3)	40.59(3)
V(3)-O(3)	1.9888(12)	O(7)-V(3)-O(6)	102.41(6)
V(3)-O(1)	2.2490(16)	O(7)-V(3)-O(3)	100.33(6)
V(4)-O(9)	1.6030(12)	O(6)-V(3)-O(3)	155.57(6)
V(4)-O(8)	1.8287(9)	O(7)-V(3)-O(1)	175.79(8)
V(4)-O(4)#2	1.8577(12)	O(6)-V(3)-O(1)	80.40(5)
V(4)-O(6)#3	1.9206(12)	O(3)-V(3)-O(1)	76.43(5)
V(4)-O(2)#1	2.0305(12)	O(7)-V(3)-V(2)	90.25(6)
V(4)-O(1)	2.3263(12)	O(6)-V(3)-V(2)	130.36(4)
V(4)-V(4)#3	3.0707(6)	O(3)-V(3)-V(2)	40.47(3)
Na(1)-O(10)	2.3179(18)	O(1)-V(3)-V(2)	85.54(4)
Na(1)-O(9)#5	2.4103(12)	O(9)-V(4)-O(8)	103.25(6)
N(1)-C(1)	1.498(3)	O(9)-V(4)-O(1)	175.03(6)
N(1)-C(2)#10	1.4983(19)	O(8)-V(4)-O(1)	81.57(5)
N(1)-C(2)	1.4983(19)	O(9)-V(4)-V(1)	131.97(5)
N(2)-C(4)	1.479(2)	O(8)-V(4)-V(1)	124.74(4)
N(2)-C(4)#10	1.479(2)	O(1)-V(4)-V(1)	43.17(3)
N(2)-C(3)	1.481(4)	V(1)-O(1)-V(3)	92.62(5)
C(1)-C(3)	1.506(4)	V(1)-O(1)-V(4)	87.788(13)
C(2)-C(4)	1.520(3)	V(3)-O(1)-V(4)	87.47(5)
		V(1)-O(3)-V(2)	107.73(6)
		V(1)-O(3)-V(3)	107.24(5)
		V(2)-O(3)-V(3)	98.95(5)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y,-z #2 -x,-y,-z #3 x,-y,z #4 -x-1,-y,-z-1 #5 x-1/2,-y-1/2,z-1 #6 -x-1/2,y+1/2,-z #7 x-1/2,y+1/2,z-1 #8 -x-1/2,-y-1/2,-z #9 x+1/2,y-1/2,z+1 #10 x,-y-1,z

The remaining two (V1-type) vanadium atoms have two short (1.69Å), two intermediate (1.93Å), and two long (2.11Å) V-O bonds. These bond distances are in the expected range. The charge balance requires the presence of two additional units of positive charge in the unit cell. On the basis of bond valence sum calculations (48) and hydrogen bonding considerations, we believe that each polyoxovanadate cluster is singly protonated with the proton disordered over the four equivalent doubly bridging O6 atoms. A weak difference map peak near O6 is consistent with this interpretation.

The structure of 1 exhibits a network of hydrogen bonds, many of which are shown by the dotted lines in Figure 1. The water molecules, present in the environment

of the sodium ion, are involved in hydrogen bonding with the axial terminal oxygen atom (O5) (O10---O5 = 2.83Å) of the anion cluster and the solvate water molecule -- O11 (O10---O11 = 2.89Å). The solvate water molecule has additional interactions involving the equatorial bridging groups O2 (O11---O2 = 2.86Å) and O6 (O11---O6 = 2.97Å) and one of the protonated nitrogen atoms -- N1 (O11---N1 = 2.70Å) of the (HN(CH₂CH₂)₃NH)²⁺ ion. The other nitrogen atom (N2) of the cyclic cation forms an apparent four-center hydrogen bond to three bridging oxygen atoms (two O4 (N2---O4 = 2.94 Å) and the O8 atom (N2---O8 = 2.92Å)) of the anion.

Crystals of 2 were of marginal quality and yielded only a very weak data set. Although its structure was not as clearly resolved as that of 1, its overall features are clear. A view of a portion of the crystal structure is shown in Figure 3. The asymmetric unit of the triclinic unit cell contains four {V₁₀O₂₈}-based cluster anions and 22 4-aminopyridine groups. The (V₁₀O₂₈)⁶⁻ anions have the same overall configuration as those in 1 and crystallize with the 4-aminopyridine groups in a complicated three-dimensional array. In addition, the unit cell contains a number of isolated atoms that could be either water oxygen atoms or the nitrogen atoms of ammonium ions (49). Extensive hydrogen bonding clearly is present here also, but the details cannot be resolved.

A recent report describes the significance of hydrogen bonding found in the structurally characterized decavanadate-dipeptide glycylglycine (Gly-Gly) complex: (NH₄)₆(Gly-Gly)₂(V₁₀O₂₈).4H₂O (50). Here, the dipeptide acts as bridge between the decavanadate cluster anions by forming hydrogen bonds. These non-covalent interactions involving decavanadate may have relevance in understanding the potent inhibition of phosphofructokinase (51) by decavanadate and its role in facilitating protein crystallization (52).

5. SUPPORTING INFORMATION AVAILABLE

Further details of the crystallographic structure determination are available on request (deposition number CCDC 199278) from the Director of the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK.

6. ACKNOWLEDGMENT

This work was supported by grants (to M.I.K.) from the American Chemical Society's Petroleum Research Fund (ACS-PRF#35591-AC5) and the National Science Foundation (CHE-0210354).

7. REFERENCES

1. M T Pope: Heteropoly and Isopoly Oxometalates. Springer-Verlag, New York (1983)
2. M T Pope & A Müller, Eds: Polyoxometalate Chemistry. From Topology Via Self-Assembly To Applications. Kluwer Academic, Dordrecht (2001)

Table 4. Hydrogen Coordinates ($\times 10^4$) and Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for 1

	x	y	z	U(eq)
H(6A)	-1154	2437	1259	19
H(10A)	-3308	0	-2980	28
H(10B)	-3675	0	-2420	28
H(11A)	-699	-5000	1090	26
H(11B)	-1095	-4013	1114	26
H(1)	1887	-5000	885	16
H(2)	3479	-5000	5078	18
H(1A)	1451	-5931	2182	19
H(1B)	1451	-4069	2182	19
H(2A)	2991	-6478	1689	17
H(2B)	2390	-7394	1891	17
H(3A)	2266	-4071	4300	58
H(3B)	2266	-5929	4300	58
H(4A)	3209	-7369	4025	54
H(4B)	3804	-6431	3824	54

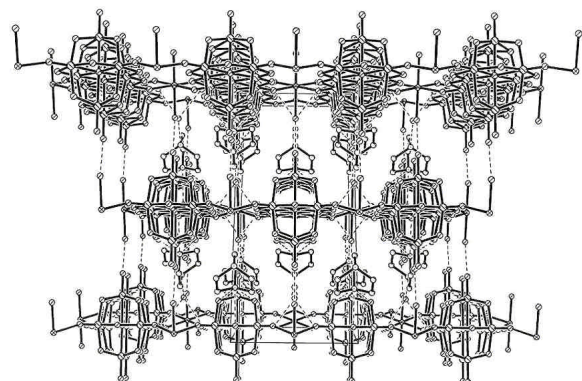


Figure 1. Packing Drawing, Projected Down the C-Axis, Showing the Contents of Three Unit Cells in the Crystals of $(\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH}_2)(\text{Na}(\text{H}_2\text{O})_2)(\text{HV}_{10}\text{O}_{28}) \cdot 2\text{H}_2\text{O}$ (1). Many of the Hydrogen Bonds are Shown by the Dotted Lines.

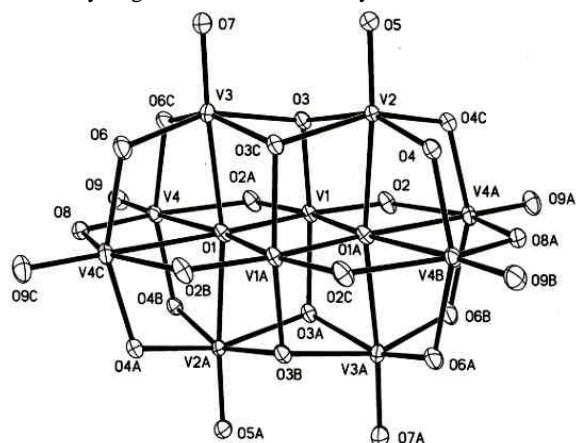


Figure 2. A View of the Decavanadate Cluster, Showing the Atom Numbering Scheme, in the Crystal Structure of $(\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH}_2)(\text{Na}(\text{H}_2\text{O})_2)(\text{HV}_{10}\text{O}_{28}) \cdot 2\text{H}_2\text{O}$ (1). The Hydroxy Proton is Not Shown.

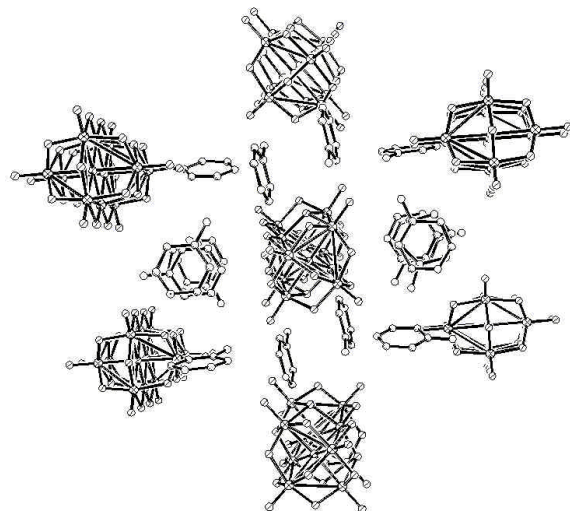


Figure 3. A view of a Portion of the Crystal Structure of $(\text{H}_3\text{N}-4-\text{C}_5\text{H}_4\text{N})_2(\text{NH}_4)_4(\text{V}_{10}\text{O}_{28}) \cdot x\text{H}_2\text{O}$ (2). The Oxygen Atoms of Water Molecules and the Nitrogen Atoms of Ammonium Ions are Not Shown.

3. M T Pope & A Müller, Eds: *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*. Kluwer Academic Publishers, Dordrecht, The Netherlands (1994)

4. Pope M T & A Müller: *Polyoxometalate Chemistry: An Old Field with New Dimensions in Several Disciplines*. *Angew. Chem. Int. Ed. Engl* 30, 34-48 (1991)

5. T Yamase & M T Pope, Eds: *Polyoxometalate Chemistry for Nano-Composite Design*. Kluwer Academic, New York, 27-28 (2002)

6. Jolivet, Jean-Pierre: *Metal Oxide Chemistry and Synthesis: From Solution to Solid State*. John Wiley & Sons, Chichester, England (2000)

7. 600 refereed publications and over 120 patents on chemistry and technology related to polyoxometalates in one year. See, Katsoulis D E: *A Survey of Applications of Polyoxometalates*. *Chem. Rev* 98, 359-388 (1998) and references therein

8. See a special edition on *Polyoxometalates*, Guest Ed., Hill C L: *Introduction: Polyoxometalates-Multicomponent Molecular Vehicles To Probe Fundamental Issues and Practical Problems*. *Chem. Rev* 98, 1-390 (1998)

9. Rhule J T, C L Hill & D A Judd: *Polyoxometalates in Medicine*. *Chem. Rev* 98, 327-357 (1998)

10. Crans D C, A D Keramidas, M Mahroof-Tahir, O P Anderson & M M Miller: *Factors Affecting Solution Properties of Vanadium (V) Compounds: X-ray Structure of β -cis-NH₄(VO₂(EDDA))*. *Inorg. Chem* 35, 3599-3606 (1996)

11. Elvingson K, A D Keramidas, D C Crans & L Pettersson: *Speciation in Vanadium Bioinorganic Systems*.

Arrays Of Decavanadate Clusters

5. Interaction between Vanadate, Uridine, and Imidazole—An Aqueous Potentiometric, ^{51}V , ^{17}O , and ^{13}C NMR Study. *Inorg. Chem* 37, 6153-6160 (1998)
12. Crans D C: Aqueous Chemistry of Labile Oxovanadates: Relevance to Biological Studies. Comments *Inorg. Chem* 16, 1-33 (1994)
13. Crans D C, F Jiang, J, Chen, O P Anderson & M M Miller: Syntheses, X-ray Structures, and Solution properties of $(\text{V}_4\text{O}_4\{\text{OCH}_2\}_3\text{CCH}_3\}_3(\text{OC}_2\text{H}_5)_3)$ and $(\text{V}_4\text{O}_4\{\text{OCH}_2\}_3\text{CCH}_3\}_2(\text{OCH}_3)_6)$: Examples of New Ligand Coordination modes. *Inorg Chem* 36, 1038-1047 (1997)
14. Crans D C, H Chen, O P Anderson & M M Miller: Vanadium (V)—Protein Model Studies: Solid-State and Solution Structure. *J. Am. Chem. Soc* 115, 6769-6776 (1993)
15. Crans D C & P K Shin: Characterization of Vanadium (V) Complexes in Aqueous Solutions: Ethanolamine- and Glycine-Derived Complexes. *J. Am. Chem. Soc* 116, 1305-1315 (1994)
16. Crans D C, R A Felty, H Chen, H Eckert & N Das: Oxovanadium (V) Alkoxide Derivatives of 1,2-Diols: Synthesis and Solid-State ^{51}V NMR Characterization. *Inorg Chem* 33, 2427-2438 (1994)
17. H Sigel & A Sigel, Eds.: Vanadium and Its Role in Life; Metal ions in Biological Systems 31, Marcel Dekker, New York, 1995
18. N D Chasteen: Vanadium in biological Systems. Ed: Chasteen N D, Kluwer Academic Publishers, Boston, 1990
19. Shechter Y, J Meyerovitch, Z Farfel, J Sack, R Bruck, S BarMeir, S Amir, H Degani & S J D Karlish: Vanadium in Biological Systems: Physiology and Biochemistry. Ed: Chasteen N D, Kluwer Academic Publishers, Boston, MA (1990)
20. Crans D C, M M Tahir, O P Anderson, & M M Miller: X-ray Structure of $(\text{NH}_4)_6(\text{Gly-Gly})_2\text{V}_{10}\text{O}_{28}\cdot 4\text{H}_2\text{O}$: Model Studies for Polyoxometalate-Protein Interactions. *Inorg Chem* 33, 5586-5590 (1994) and references therein.
21. Evans H T Jr.: The Molecular Structure of the Isopoly Complex Ion, Decavanadate ($\text{V}_{10}\text{O}_{28}^{6-}$). *Inorg Chem* 5, 967-977 (1966)
22. Swallow A G, F R Ahmed, & W H Barnes: The crystal structure of pascoite, $\text{Ca}_3\text{V}_{10}\text{O}_{28}\cdot 16\text{H}_2\text{O}$. *Acta Cryst* 21, 397-405 (1966)
23. Day V W, W G Klemperer, & D J Maltbie: Where are the protons in $(\text{H}_3\text{V}_{10}\text{O}_{28})^{3-}$. *J. Am. Chem. Soc* 109, 2991-3002 (1987)
24. Durif P A, M T Everbuch-Pouchot & J. C. Guitel: Structure d'un décavanadate d'hexasodium hydrate. *Acta Cryst* B36, 680-682 (1980)
25. J Fuchs, S Mahjour, & J Pickard: Structure of the "True" Metavanadate Ion. *Angew. Chem. Int. Ed. Engl* 15, 374 (1976)
26. Day V W, W G Klemperer & O M Yaghi: A new structure type in polyoxoanion chemistry: synthesis and structure of the $\text{V}_5\text{O}_{14}^{3-}$ anion. *J. Am. Chem. Soc* 111, 4518-4519 (1989).
27. Day V W, W G Klemperer & O M Yaghi: Synthesis and characterization of a soluble oxide inclusion complex, $(\text{CH}_3\text{CN})_{\text{cndnd}}(\text{V}_{12}\text{O}_{32}^{4-})$. *J. Am. Chem. Soc* 111, 5959-5961 (1989).
28. Hou D, K S Hagen & C L Hill: Tridecavanadate, $(\text{V}_{13}\text{O}_{34})^{3-}$, a new high-potential isopolyvanadate. *J. Am. Chem. Soc* 114, 5864-5866 (1992).
29. Hou D, K S Hagen & C L Hill: Pentadecavanadate, $\text{V}_{15}\text{O}_{42}^{9-}$, a New Highly Condensed Fully Oxidized Isopolyvanadate with Kinetic Stability in Water. *J. Chem. Soc Chem. Commun* 426 (1993)
30. Strukan N, M Cindric & B Kamenar: Synthesis and structure of $((\text{CH}_3)_4\text{N})_4(\text{H}_2\text{MoV}_9\text{O}_{28})\text{Cl}\cdot 6\text{H}_2\text{O}$. *Polyhedron* 16, 629-634 (1997).
31. Y. Zhang, R. C. Haushalter, and J. Zubietta, *Inorg. Chim. Acta* 277, 263 (1998)
32. Khan M I & J Zubietta, In Prog. *Inorg. Chem* 43, 1; K D Carlin (Ed), John Wiley & Sons: New York, 1996.
33. Khan M I, Q Chen, D P Goshorn & J Zubietta: Polyoxo alkoxide clusters of vanadium: structural characterization of the decavanadate core in the "fully reduced" vanadium(IV) species $(\text{V}_{10}\text{O}_{16}\{(\text{OCH}_2)_3\text{CCH}_2\text{CH}_3\}_4)^{4-}$ and $(\text{V}_{10}\text{O}_{14}(\text{OH})_2\{(\text{OCH}_2)_3\text{CCH}_2\text{OH}\}_4)^{2-}$ and in the mixed-valence clusters $(\text{V}^{\text{IV}}_8\text{V}^{\text{V}}_2\text{O}_{16}\{(\text{OCH}_2)_3\text{CR}\}_4)^{2-}$ ($\text{R} = -\text{CH}_2\text{CH}_3, -\text{CH}_3$). *Inorg. Chem* 32, 672 (1993)
34. Khan M I, Y-D Chang, Q Chen, S Parkin, H Hope, D P Goshorn & J Zubietta: (Organoarsonato)polyoxovanadium Clusters: Properties and Structures of the V^{V} Cluster $(\text{V}_{10}\text{O}_{42}(\text{O}_3\text{AsC}_6\text{H}_4\text{-4-NH}_2)_3)^{4-}$ and the $\text{V}^{\text{IV/V}}$ Cluster $(\text{H}_2\{\text{V}_6\text{O}_{10}(\text{O}_3\text{AsC}_6\text{H}_5)_6\})^{2-}$. *Angew. Chem. Int. Ed. Engl* 31, 1197 (1992).
35. Khan M I, Q Chen, D P Goshorn, H Hope, S Parkin & J Zubietta: Polyoxo alkoxides of vanadium: the structures of the decanuclear vanadium(IV) clusters $(\text{V}_{10}\text{O}_{16}\{\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{O})_3\}_4)^{4-}$ and $(\text{V}_{10}\text{O}_{13}\{\text{CH}_3\text{CH}_2\text{C}(\text{CH}_2\text{O})_3\}_5)^{3-}$. *J. Am. Chem. Soc* 114, 3341-3346 (1992)
36. Khan M I, S Cevik, & R J Doedens: Inorganic-Organic Hybrids Derived From Oxovanadium Sulfate Motifs: synthesis and characterization of $(\text{V}^{\text{IV}}\text{O}(\mu_3\text{-SO}_4)(2,2'\text{-bpy}))_{\infty}$. *Chem. Commun* 1930 (2001)
37. Khan M I: Novel Extended Solids Composed of Transition Metal Oxide Cluster. *J. Solid State Chem* 152, 105 (2000)

38. Khan M I, E Yohannes & D Powell: Synthesis and Characterization of a new mixed-metal oxide framework material composed of vanadium oxide clusters: X-ray crystal structure of $(\text{N}_2\text{H}_5)_2(\text{Zn}_3\text{V}^{\text{IV}}_{12}\text{V}^{\text{V}}_6\text{O}_{42}(\text{SO}_4)(\text{H}_2\text{O})_{12})\cdot 24\text{H}_2\text{O}$. *J. Chem Soc Chem Com* 23 (1999)

39. Khan M I, E Yohannes & D Powell: Metal Oxide Clusters as Building Blocks for the Synthesis of Metal Oxide Surfaces and Framework Materials: Synthesis and X-Ray Crystal Structure of $(\text{Mn}_3\text{V}_{19}\text{H}_6\text{O}_{46}(\text{H}_2\text{O})_{12})\cdot 30\text{H}_2\text{O}$. *Inorg. Chem* 38, 212 (1999).

40. Khan M I, E Yohannes & R J Doedens: Metal Oxide Based Framework Materials Composed of Polyoxovanadate Clusters: Synthesis and X-Ray Crystal Structures of $(\text{M}_3\text{V}_{18}\text{O}_{42}(\text{H}_2\text{O})_{12}(\text{XO}_4))\cdot 24\text{H}_2\text{O}$ (M = Fe, Co; X = V, S). *Angew. Chemie. Int. Ed. Engl* 38, 1292 (1999).

41. Khan M I, T Hope, S Cevik, C Zheng & D Powell: Organically Templated Vanadium Oxide Phases: Synthesis and Structures of $(\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3)(\text{V}_2\text{O}_6)$ and $(\text{HN}(\text{CH}_2\text{CH}_2)_3\text{NH})(\text{V}^{\text{V}}_2\text{V}^{\text{IV}}_4\text{O}_{14})\cdot \text{H}_2\text{O}$. *J. Cluster Sci* 11, 433 (2000).

42. Khan M I, S Tabussum & Robert J Doedens: A novel cationic heteropolyoxovanadium(IV) cluster functionalized with organic ligands: synthesis and characterization of the fully reduced species $(\text{Mn}^{\text{II}}\text{V}^{\text{IV}}_6\text{O}_6\{(\text{OCH}_2\text{CH}_2)_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})\}_6)\cdot \text{Cl}_2$. *Chem. Commun* 2002 (submitted).

43. Khan M I, S Cevik & R J Doedens: Composite Materials Derived From Oxovanadium Sulfates. In: *Polyoxometalate Chemistry for Nano-Composite Design*. Eds: Yamase T & M T Pope, Kluwer Academic, New York, 27-38 (2002)

44. SMART, Version 4.210, Siemens Analytical X-Ray Systems, Madison, WI, (1997)

45. SAINT, Version 4.050, Siemens Analytical X-Ray Systems, Madison, WI, (1995)

46. Sheldrick G M, *SADABS*, University of Göttingen, Germany (1997)

47. Sheldrick G M, *SHELXTL* Version 5.1, Siemens Industrial Automation, Inc., Madison, WI, (1995)

48. Brown I D, In: *Structure and Bonding in Crystals*. Eds: O'Keefe M & A Navrotsky, Academic Press, New York, Vol. II, 1 (1981)

49. Spectroscopic and analytical data indicate the presence of at least some ammonium ions. On the assumptions that the $\{\text{V}_{10}\text{O}_{28}\}$ anions have their usual -6 charge and that all of the 4-aminopyridine groups are singly protonated, charge balance would require two NH_4^+ ions per asymmetric unit. Microanalytical data, IR, TGA, and determination of the number of V^{IV} sites are consistent with this formulation. Because the data did not permit

distinction of oxygen from nitrogen atoms, all 10 of the isolated atoms included in the final refinement were treated as oxygens. Additional disordered water molecules are probably also present. Crystal data for **2**: Triclinic space group $P\bar{1}$, $a = 14.911(2)$, $b = 16.928(2)$, $c = 39.714(5)\text{\AA}$, $\alpha = 84.454(2)^\circ$, $\beta = 84.895(2)^\circ$, $\gamma = 79.603(2)^\circ$, Volume = $9787.4(13)\text{\AA}^3$, $Z = 8$.

50. Crans D C, M M Tahir, O P Anderson, and M M Miller, *Inorg. Chem.*, 33, 5586 (1994) and references therein.

51. (a) Boyd D W, K Kustin, & M Niwa, *Biochim. Biophys. Acta*, 827, 472 (1985). (b) Soman G, Y C Chang & D J Graves: Effect of oxanions of the early transition metals on rabbit skeletal muscle phosphorylase. *Biochem* 22, 4994-5000 (1983).

52. (a) Pai E F, W Sachsenheimer, R H Schirmer, & G E Schulz: *J. Mol. Biol* 114, 27 (1977). (b) Csermely P, A Mortonosi, G. C. Levy & A. J. Ejchart, *Biochem. J* 230, 807 (1985)

Key Words: Decavanadates, Layered structures, x-ray, Crystal Structure, Polyoxovanadates, Clusters, Hydrogen Bonding

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