Hydrothermal Synthesis, Single-Crystal Structure, and Magnetic Properties of $VOSeO_3 \cdot H_2O$

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The layered compound $VOSeO_3 \cdot H_2O$ has been prepared by hydrothermal synthesis and characterized by single-crystal X-ray diffraction. The structure is triclinic, space group $P\bar{1}$ with $a = 5.969$ (2) Å, $b = 6.155$ (2) Å, $c = 6.349$ (2) Å, $\alpha = 92.00$ (3)°, $\beta = 101.88$ (2)°, $\gamma = 117.25$ (2)°, $Z = 2$, $D_{calc} = 3.506$ g/cm^3, $R = 0.0201$, and $R_w = 0.0292$ for 807 independent diffraction maxima. The structure is formed from layers of vanadium, oxygen, and selenium atoms with coordinated water molecules directed into the interlayer space, resulting in a layer repeat distance ($d_{1\bar{1}0}$) of 5.142 (2) Å. The layers contain pairs of $V^{4+}O_6$ octahedra connected through a shared edge, which in turn share corners with SeO_3 trigonal pyramids. The connectivity can be represented as $VO_{1/1}(H_2O)_{1/1}O_{2/2}O_{2/3}SeO_{2/2}O_{1/3}$. The magnetic properties are characteristic of antiferromagnetically coupled V^{4+}–V^{4+} dimers with a coupling constant of $J = -27.0$ cm^{-1}. The structure of the title compound is compared with those of $VOSeO_3$ and related vanadium phosphates.

Introduction

Vanadyl phosphonates $VORPO_3 \cdot xH_2O$, where R is an alkyl or an aryl group, form a class of layered compounds, some of which selectively intercalate alcohols.[1] In previous studies, we have found that the composition and structural features of these compounds are controlled by the size of the R group. When R is small, for example, CH_3, C_2H_5, and C_3H_7, x is 1.5 and the inorganic layers consist of face-sharing V_2O_9 dimers connected by RPO_3 groups through corners,[2] in an arrangement analogous to that found in $VO(HPO_4) \cdot 0.5H_2O$, where R = OH.[3] In contrast, the compound $VOC_6H_5PO_3 \cdot H_2O$, with a larger phenyl group[4] contains one-dimensional —V═O—V═O— chains connected by the tetrahedral RPO_3 groups through corners to form a two-dimensional layer with phenyl groups extending into the interlayer space. Further insight into the extent to which the organic group directs the structure of the inorganic layer can be obtained by examining the effect of substituting SeO_3^{2-} for RPO_3^{2-} in this series of compounds. The lone pair of electrons occupying the fourth coordination position in the pseudotetrahedral SeO_3^{2-} group has a very different steric requirement than the organic R group in tetrahedral RPO_3^{2-}. This article reports the synthesis, structure, and magnetic properties of the new V(IV) compound, $VOSeO_3 \cdot H_2O$, which is closely related to anhydrous $VOSeO_3$.[5]

Experimental Section

Synthesis. H_2SeO_3 (0.387 g, 3 mmol, Aldrich) and V_2O_5 (0.182 g, 1 mmol, Alfa) were transferred into a 23-mL Teflon-lined autoclave (Parr Instruments). Distilled water was added to fill ~60% of the total volume. The mixture was heated in an oven at 200 °C for ~48 h. Green plates and metallic needles were obtained as reaction products. They were filtered, washed several times with distilled water, and air-dried. The green plates were separated manually and were found to be $VSeO_6H_2$ by chemical analysis (Galbraith Laboratories, Inc.; observed H 1.01%, V 23.70%, Se 37.65%; calculated for H_2VSeO_6 H 0.95%, V 24.04%, Se 37.26%). The metallic needles were shown by powder X-ray diffraction to be elemental selenium.

Table I. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for $VOSeO_3 \bullet H_2O$

	x	y	z	U(eq)[a]
V	2759 (1)	2896 (1)	13097 (1)	10 (1)
Se	3415 (1)	1920 (1)	8401 (1)	10 (1)
O(1)	3897 (4)	1015 (4)	12978 (3)	19 (1)
O(2)	1352 (4)	5700 (4)	13174 (3)	19 (1)
O(3)	2033 (3)	3113 (3)	9881 (3)	14 (1)
O(4)	953 (4)	−723 (3)	7017 (3)	18 (1)
O(5)	3754 (4)	3858 (3)	6395 (3)	12 (1)
H(1)	1895 (87)	7061 (85)	14085 (61)	37 (11)
H(2)	458 (84)	5686 (77)	12277 (59)	29 (11)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Thermogravimetric analysis of $VOSeO_3 \cdot H_2O$ (10 °C/min in flowing He) shows a two-step weight loss. The first step, a loss of 8.1%, occurs from 240 to 280 °C and corresponds to the release of one lattice water molecule per formula unit. The second step, which is incompletely resolved from the first, results in the loss of an additional 51.5% corresponding to the loss of SeO_2, as observed previously in the thermal decomposition of anhydrous $VOSeO_3$.[5]

X-ray Crystallography. Crystal data: triclinic, $P\bar{1}$ (No. 2), $a = 5.969$ (2) Å, $b = 6.155$ (2) Å, $c = 6.349$ (2) Å, $\alpha = 92.00$ (3)°, $\beta = 101.88$ (3)°, $\gamma = 117.25$ (3)°, and D(calcd) = 3.506 g/cm^3. A Nicolet R3m/V diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator was used to collect 1652 diffraction maxima ($2\theta \leq 55°$) from a green plate of dimensions 0.02 × 0.2 × 0.3 mm at 298 K. Of these, 826 were unique, $R_{int} = 0.022$, and 807 observed ($F \geq 3\sigma(F)$). A semiempirical absorption correction was applied to the data ($\mu = 10.46$ mm^{-1}). The structure was solved by direct methods and refined by full-matrix least-squares methods; vanadium, selenium, and oxygen atoms were refined anisotropically to $R = 0.0201$, $R_w = 0.0292$, GOF = 1.10.

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Table II. Important Bond Lengths (Å) and Angles (deg) in $VOSeO_3 \cdot H_2O$

	Bond Lengths		
V-O(1)	1.594 (3)	Se-O(3)	1.711 (2)
V-O(2)	2.242 (3)	Se-O(4)	1.661 (2)
V-O(3A)	2.020 (2)	Se-O(5)	1.754 (2)
V-O(4A)	1.979 (2)	O(2)-H(1)	0.692 (43)
V-O(5A)	2.041 (2)	O(2)-H(2)	0.884 (43)
V-O(5B)	2.073 (2)		
	Bond Angles		
O(1)-V-O(2)	176.5 (1)	O(1)-V-O(3)	96.6 (1)
O(2)-V-O(3)	81.6 (1)	O(1)-V-O(4A)	103.6 (1)
O(2)-V-O(4A)	79.6 (1)	O(3)-V-O(4A)	93.3 (1)
O(1)-V-O(5A)	99.0 (1)	O(2)-V-O(5A)	82.3 (1)
O(3)-V-O(5A)	161.2 (1)	O(4A)-V-O(5A)	93.3 (1)
O(1)-V-O(5B)	97.6 (1)	O(2)-V-O(5B)	79.4 (1)
O(3)-V-O(5B)	89.7 (1)	O(4A)-V-O(5B)	158.1 (1)
O(5A)-V-O(5B)	77.8 (1)	O(3)-Se-O(4)	104.6 (1)
O(3)-Se-O(5)	97.1 (1)	O(4)-Se-O(5)	100.9 (1)

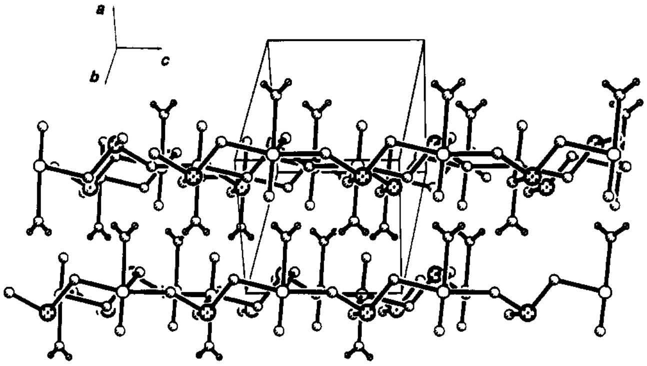

Figure 1. View of the layer stacking in $VOSeO_2 \cdot H_2O$.

Hydrogen atoms were located in a difference map and included in the refinement as riding on the oxygen atom to which they were attached. The highest peak on the final difference Fourier map was 0.74 e$^-$/Å^3. All computations were performed using SHELXTL PLUS (Nicolet) on a MicroVAX II.

Magnetic Measurements. The magnetic susceptibility of $VOSeO_3 \cdot H_2O$ was measured as a function of temperature by using a George Associates Faraday magnetometer with an applied magnetic field of 6.2 kG in the temperature range 6–400 K.

Results and Discussion

The atomic coordinates and important bond distances and angles for $VOSeO_3 \cdot H_2O$ are listed in Tables I and II. The structure consists of layers of corner-sharing VO_6 octahedra and SeO_3 trigonal pyramids stacked along the [1$\bar{1}$0] direction to give a layer repeat distance of 5.142 (2) Å, as shown in Figure 1. The water molecules coordinated to vanadium atoms project into the interlayer space and form hydrogen bonds with oxygen atoms from vanadyl groups (O(1)) and from selenite groups (O(3)) in the adjacent layer, holding the layers together. The layer can be viewed as made up from centrosymmetric edge-sharing V_2O_{10} dimers, each of which is connected to six SeO_3^{2-} groups through shared equatorial oxygen atoms as shown in Figure 2. The coordination sphere of the vanadium atom is a distorted octahedron typical of V^{4+}. The distance of the apical oxygen O(1) to V is 1.594 (3) Å, characteristic of a multiply bound vanadyl group. Oxygen O(2) from a water molecule is coordinated trans to O(1) at a vanadium–oxygen distance of 2.242 (3) Å. Of the four equatorial oxygens, two of them, O(5A) and O(5B), are shared with another vanadium atom within the dimer at bond distances of 2.073 (2) and 2.041 (2) Å, respectively. These two oxygen atoms are part of separate SeO_3^{2-} groups. The remaining two oxygen atoms, O(3) and O(4), are from two different SeO_3 groups, and their distances to V are 2.020 (2) and 1.979 (2) Å. Bond valence calculations[6] gave a total vanadium valence of 3.99. The Se atom is trigonal pyramidally coordinated by three oxygen atoms at distances of 1.711 (2), 1.661 (2), and 1.754 (2) Å, which is normal for Se(IV) with a lone pair of electrons.

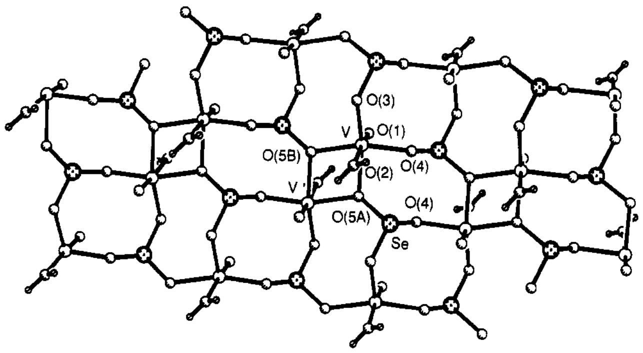

Figure 2. View of the in-layer arrangement of $VOSeO_2 \cdot H_2O$ illustrating the connectivity of the edge-sharing V_2O_{10} dimers and SeO_3 trigonal pyramids.

The structures of $VOSeO_3 \cdot H_2O$ and $VO(HPO_4) \cdot 0.5H_2O$ are similar.[3] Both contain vanadium dimers connected by bridging SeO_3^{2-} or $HOPO_3^{2-}$ groups. In $VO(HPO_4) \cdot 0.5H_2O$ the oxygen atom of the coordinated water molecule is shared between two vanadium atoms resulting in a face-shared dimer. The layers are held together in the *c* direction by strong hydrogen bonding between the coordinated water molecules and the P–OH groups of adjacent layers. The oxygen atom of the P–OH group acts as a hydrogen-bond acceptor to a hydrogen atom of the coordinated water molecule. Both hydrogen atoms of the water molecule are hydrogen bonded to different P–OH groups, resulting in an approximately tetrahedral coordination of the water molecule. Thus, the release of water molecules occurs at a remarkably high temperature, ~400 °C.[7] In contrast, each vanadium atom in $VOSeO_3 \cdot H_2O$ is coordinated by a water molecule, and the dimers are edge shared. The water molecules are coordinated to only one vanadium atom. The layers are held together by weak hydrogen bonds between coordinated water molecules and the vanadyl and selenite oxygen atoms. The oxygen-to-oxygen atom distances in the hydrogen bonds are 2.866 (3) Å for O(2)–O(3) and 2.929 (3) Å for O(2)–O(1) as shown in Figure 3a. The absence of the OH group, a good hydrogen-bond acceptor, results in a weaker interlayer hydrogen bonding network in $VOSeO_3 \cdot H_2O$ than found in the hydrogen phosphate, and this, along with the coordination of each water molecule to only one vanadium atom, leads to a lower water release temperature, ~250 °C, in $VOSeO_3 \cdot H_2O$.

The interlayer arrangement of $VOSeO_3 \cdot H_2O$ is almost identical with that of its dehydrated analogue $VOSeO_3$.[5] In the former compound the sixth coordination site of the vanadium atom is occupied by an oxygen atom from a water molecule, whereas in the latter compound, this coordination site is filled by a vanadyl oxygen atom from the adjacent layer. In $VOSeO_3$, the V═O groups from adjacent layers align perpendicular to the layers forming the -V═O···V═O interlayer connections with alternating vanadium–oxygen distances of 1.611 (2) and 2.409 (2) Å (see Figure 3b). In $VOSeO_3 \cdot H_2O$, in contrast, the position of the vanadium atom in one layer is shifted relative to those

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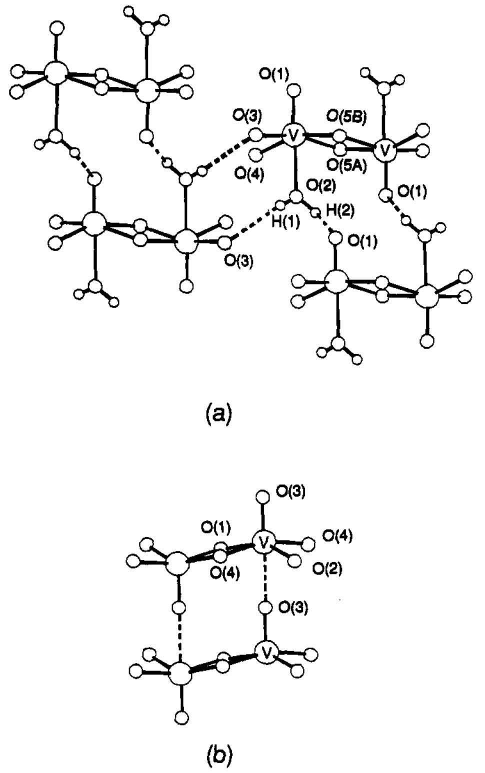

Figure 3. Interlayer connections (a) through hydrogen bonds in $VOSeO_3{\cdot}H_2O$ and (b) through —V=O···V=O in $VOSeO_3$.

in the layers above and below in order to form the interlayer hydrogen-bonding network described above. The relationship between $VOSeO_3{\cdot}H_2O$ and $VOSeO_3$ is analogous to that between $VO(HPO_4){\cdot}0.5H_2O$ and $(VO)_2P_2O_7$.[3,7]

In the compound $VOSeO_3{\cdot}H_2O$, the interatomic distance between the vanadium atoms in adjacent edge-sharing octahedra within one layer is 3.203 (3) Å, while all other V–V distances within the layer are 4.686 (3) Å or longer and the layer repeat distance is 5.142 (2) Å. The large difference between the nearest-neighbor and next-nearest-neighbor V–V distances suggests that the magnetic properties should exhibit the behavior expected for isolated V_2 dimers. Assuming that the exchange coupling within a V_2 dimer is isotropic, the magnetic susceptibility for an isolated dimer model containing two $S = {}^1/_2$ cations with isotropic **g** tensor is given by the Bleaney–Bowers equation[8]

$$\chi = \chi_0 + C_i/T + 4C_d/(T(3 + \exp(-2J/k_BT)))$$

where χ_0 is a temperature-independent contribution, C_i is the Curie-like contribution from isolated paramagnetic centers, C_d is the Curie constant associated with the V_2 dimers, and k_B is Boltzman's constant. A least-squares fit to the data over the entire temperature range as shown in Figure 4 gave values of $\chi_0 = -1.03 \times 10^{-6}$ g/cm^3, $C_d = 1.66 \times 10^{-3}$ g/cm^3·K, $C_i = 2.49 \times 10^{-5}$ g/cm^3·K, and $J = -27.0$ cm^{-1}. The μ_{eff} value calculated from C_d is 1.68 μ_B per vanadium, close to the spin-only value of 1.73 for one unpaired electron and consistent with the bond valence calculations.

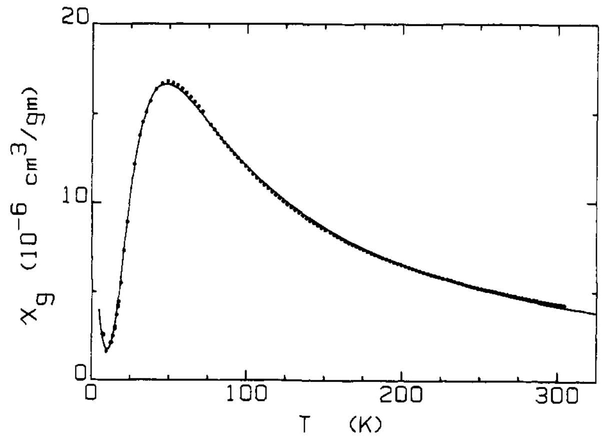

Figure 4. Magnetic susceptibility as a function of temperature for $VOSeO_3{\cdot}H_2O$: (●) experimental data; (—) best fit using the Bleaney–Bowers equation (see text).

The magnetic properties of $VOSeO_3{\cdot}H_2O$ are similar to those of $VO(HPO_4){\cdot}0.5H_2O$.[7] Both compounds contain V^{4+} dimers separated by distances of 3.203 (2) and 3.090 (3) Å and show comparable antiferromagnetic exchange constants of -27.0 and -30.6 cm^{-1}, respectively.

Conclusions

The layered vanadium(IV) compound $VOSeO_3{\cdot}H_2O$ has been prepared by hydrothermal synthesis and structurally characterized. The intralayer arrangement of vanadium–oxygen dimers and SeO_3 trigonal pyramids is similar to that found in $VOSeO_3$.[5] In $VOSeO_3{\cdot}H_2O$, the adjacent layers are held together through hydrogen bonds. The magnetic properties of $VOSeO_3{\cdot}H_2O$ are well described by antiferromagnetic coupling of V(IV) ions in isolated dimers. When the organic group in vanadyl organophosphonates of formula $VORPO_3{\cdot}nH_2O$ is formally substituted by a lone pair of electrons as is the case in $VOSeO_3{\cdot}H_2O$, a structure results that is similar to that of the structures of $VORPO_3$, where R is a small organic group such as methyl or ethyl, and to the structure of $VO(HPO_4){\cdot}0.5H_2O$, where R is a hydroxyl group.

Registry No. $VOSeO_3{\cdot}H_2O$, 133578-89-9; H_2SeO_3, 7783-00-8; V_2O_5, 1314-62-1; Se, 7782-49-2.

Supplementary Material Available: Tables of anisotropic thermal parameters and bond angles (1 page); table of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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