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A New Layered Vanadium Selenium Oxide with a Structure Related to Hexagonal Tungsten Oxide: $NH_4(VO_2)_3(SeO_3)_2$

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The compound $NH_4(VO_2)_3(SeO_3)_2$ has been prepared by hydrothermal synthesis at 200 °C from V_2O_5, SeO_2, and NH_4Cl. The crystal structure was determined by single-crystal X-ray diffraction. Crystal data: $NH_4(VO_2)_3(SeO_3)_2$, $M_r = 410.79$; hexagonal, space group $P6_3$ (No. 173); cell parameters $a = 7.137(3)$ Å, $c = 11.462(4)$ Å, $V = 505.7(4)$ Å^3, $Z = 2$; $R(F) = 0.0416$ and $R_w(F^2) = 0.1041$ (515 reflections). The structure consists of hexagonal layers of corner-sharing VO_6 octahedra. The apical oxygen atoms of the VO_6 octahedral are capped by Se atoms that form SeO_3^{2-} groups; the ammonium ions are located between adjacent layers. The structure contains the first example of a hexagonal tungsten bronze type layer where the octahedral cation is vanadium. Redox intercalation reactions similar to those reported for $VOPO_4 \cdot H_2O$ were studied but are complicated by the ease of reduction of the SeO_3^{2-} group to selenium metal accompanied by decomposition of the vanadium–oxygen layers and the formation of V_2O_5.

Introduction

A large number of oxide structures can be derived from the hexagonal network of corner-sharing MO_6 octahedra shown in Figure 1a. Examples of structures based on this network include hexagonal WO_3[1-3] and the alkali metal tungsten bronzes A_xWO_3 (A = K, Rb, Cs).[4] In these structures, the apical oxygen atoms of the WO_6 octahedra are shared between adjacent layers to give a three-dimensional framework with three- and six-sided tunnels in a direction perpendicular to the layers. The structures of $WO_3 \cdot {}^1/_3H_2O$ and $MoO_3 \cdot {}^1/_3H_2O$ have similar hexagonal layers that are translated relative to each other so that only two-thirds of the apical oxygen atoms are shared between adjacent layers.[5,6] The remaining one-third of the octahedra have one unshared water molecule coordinated *trans* to an apical oxygen atom. The overall stoichiometry can be written $2(WO_{6/2})(WO_{4/2}O_{1/1}H_2O)$ or $WO_3 \cdot {}^1/_3H_2O$. The pyrochlore structure may also be considered to be derived from this building unit. In the ideal pyrochlore composition $A_2B_2O_7$, the B_2O_6 octahedral network consists of hexagonal sheets connected by metal atoms in octahedral sites between layers. The interlayer octahedral sites are made up from the apical oxygens from two triangular octahedral units from adjacent layers.[7] Tungsten trioxide, $W_2O_6 \cdot H_2O$, is one oxide that can be synthesized with the pyrochlore octahedral framework without the A_2O sublattice.[8-10]

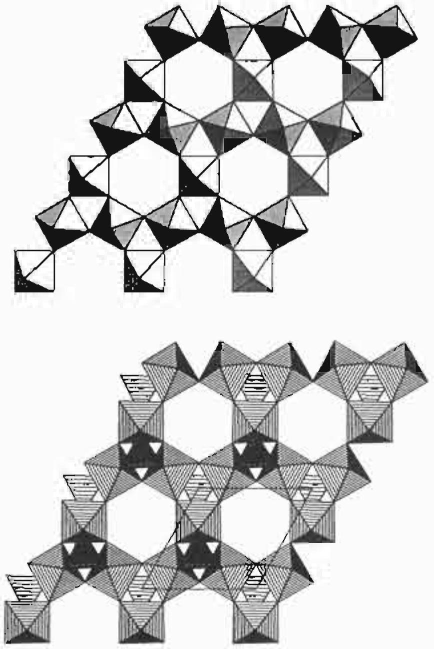

Figure 1. (a) Top: A single hexagonal layer of corner-sharing MO_6 octahedra with the composition $MO_4(MO_{4/2}O_{2/1})$. (b) Bottom: A single hexagonal layer of corner-sharing SbO_6 octahedra "capped" by phosphate tetrahedra.

All of the above structures are three-dimensionally connected. A smaller number of compounds are known with layered structures based on the hexagonal network of corner-sharing MO_6 octahedra. For example, the compounds $K_3(SbO_2)_3(XO_4)_2$ (X = P, As) are built up from a single hexagonal layer of corner-sharing SbO_6 octahedra.[11,12] The apical oxygen atoms are not shared between layers but are "capped" by phosphate or arsenate groups (see Figure 1b). The potassium ions and any water molecules occupy interlayer sites. These compounds show ion exchange and interlayer hydration chemistry similar to that of other layered oxides. The phases $M'[M(OH)_2]_3(SO_4)_2$ ($M' = K^+$ or other monovalent cation; M = Al (alunite), Fe (jarosite),

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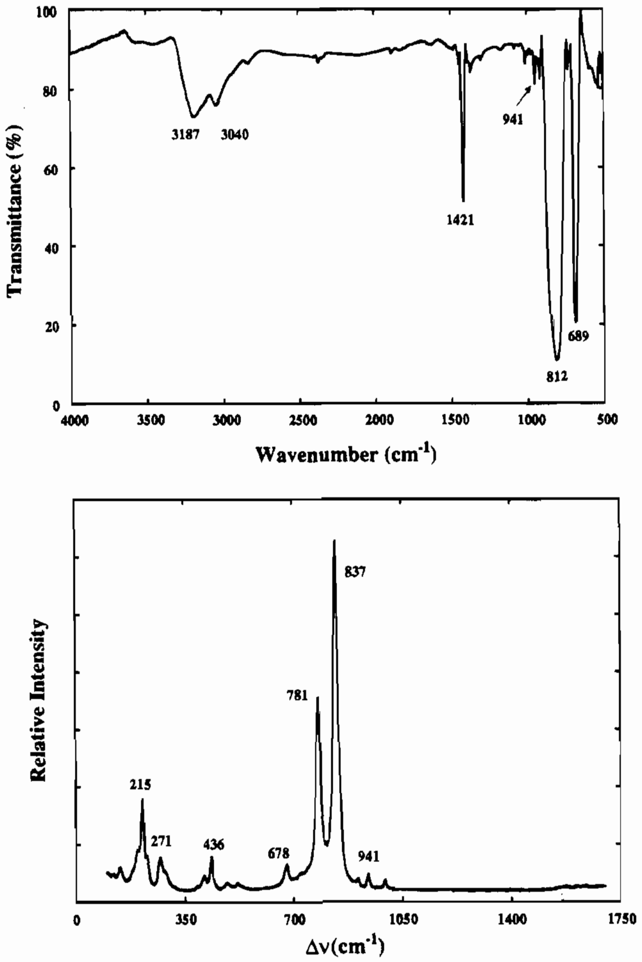

Figure 2. (a) Top: Infrared spectrum of $NH_4(VO_2)_3(SeO_3)_2$. (b) Bottom: Raman spectrum of $NH_4(VO_2)_3(SeO_3)_2$.

and Ga) have similar structures with the sulfate group as the "capping" unit.[13–15] The recently synthesized phase $Cs_3(SbO_2)_3(Ge_2O_7)$ is closely related to the layered antimony phosphate and arsenate structures, but the hexagonal SbO_6 layers are cross-linked by Ge_2O_7 groups.[16]

In this paper we report the synthesis, structure, and reactivity of a new member of this general class of oxides. The compound, $NH_4(VO_2)_3(SeO_3)_2$, is the first example of a layered hexagonal tungsten bronze (HTB) related structure based on vanadium(V) oxygen octahedra. The apical oxygen atoms in the octahedral sheets are capped by selenium atoms forming selenite (SeO_3^{2-}) anions, and the remaining charge is compensated by interlayer ammonium cations.

Experimental Section

Synthesis. Single crystals of $NH_4(VO_2)_3(SeO_3)_2$ were isolated from the reaction of 0.6 g of V_2O_5 (3.3 mmol, Aldrich, 99.9%), 1.0 g of SeO_2 (9.0 mmol, Aldrich, 99.99%), and 1.0 g of NH_4Cl (Aldrich, 99.9%). The pH was adjusted to ≈5.0 by addition of a 50% solution of NH_4OH and the container 75% filled with distilled water. The mixture was heated in a 23-mL Parr bomb at 200 °C for 4 days and cooled to room temperature over a 2-day period. Large yellow rodlike crystals of the title compound were isolated with a small number of bright orange single crystals identified by powder X-ray diffraction as $(NH_4)_2V_6O_{16}$.[17] Single-phase mustard yellow powder samples of $NH_4(VO_2)_3(SeO_3)_2$ were isolated using the same synthetic procedure, except for the addition of more SeO_2 (1.2 g) to suppress the formation of the ammonium vanadate, $(NH_4)_2V_6O_{16}$.

Table 1. X-ray Powder Data for $NH_4(VO_2)_3(SeO_3)_2$: Hexagonal; $a = 7.115(2)$ Å, $c = 11.440(2)$ Å, $V = 501.5(2)$ Å^3

hkl	d_{obs} (Å)	d_{calc} (Å)	Δd^a (Å)	$I_{obs}{}^b$
100	6.156	6.162	−0.006	27
002	5.714	5.720	−0.006	4
101	5.421	5.425	−0.004	72
102	4.192	4.192	0.000	16
110	3.557	3.557	0.000	12
111	3.397	3.397	0.000	9
103	3.243	3.243	0.001	10
200	3.080	3.081	−0.001	3
112	3.022	3.021	0.001	100
201	2.975	2.975	0.001	31
004	2.861	2.860	0.001	23
202	2.713	2.712	0.000	12
104	2.596	2.594	0.002	25
203	2.396	2.396	0.000	2
120	2.330	2.329	0.001	2
211	2.283	2.282	0.001	2
114	2.230	2.229	0.001	3
212	2.157	2.157	0.000	6
105	2.144	2.145	−0.001	6
301	2.021	2.022	0.000	4
123	1.987	1.988	0.000	6
302	1.933	1.933	0.000	20
006	1.906	1.907	0.000	3
205	1.837	1.837	0.000	4
106	1.821	1.821	−0.001	2
124	1.806	1.806	0.000	3
220	1.779	1.779	0.000	20
130	1.709	1.709	0.000	3
311	1.690	1.690	0.000	6
116	1.681	1.680	0.000	7
304	1.668	1.668	0.000	3
206	1.621	1.621	0.000	8
313	1.559	1.559	0.000	4

^{a} $d_{obs} - d_{calc}$. ^{b} $100I/I_{max}$.

Characterization. Thermogravimetric analysis was carried out using a DuPont 9900 thermogravimetric analyzer. Samples were heated at a rate of 5 °C/min from room temperature to 500 °C in an oxygen atmosphere. The sample lost 45.1(1)% of its weight in three overlapping steps at 337, 359, and 379 °C. The calculated weight loss for the composition $NH_4(VO_2)_3(SeO_3)_2$ is 47.6% after loss of SeO_2 by sublimation and decomposition of the ammonium cation to ammonia and water. The sole product isolated after the decomposition was identified by powder X-ray diffraction methods as V_2O_5.

Elemental analysis was carried out by Galbraith Laboratories, Knoxville, TN. The experimental weight percents of vanadium and selenium were 29.7% and 30.4%, respectively, versus values of 29.3% V and 30.3% Se calculated for the composition $NH_4(VO_2)_3(SeO_3)_2$. The infrared spectrum of $NH_4(VO_2)_3(SeO_3)_2$ was recorded at ambient temperature on a Galaxy FTIR 5000 series spectrometer in the range 500–4000 cm^{-1} using the KBr pellet method. A Raman spectrum was obtained with a Coherent K-2 Kr^+ ion laser excited at 406.7 nm. The Raman instrument was equipped with a Spex 1403 double monochromator and a Hamamatsu 928 photomultiplier. The sample was mounted as a KCl pellet. The Raman data were collected at 1-s intervals for every wave number in the range 100–1700 cm^{-1} at ambient temperature using a Spex DM 3000 computer system. The infrared and Raman spectra are shown in Figure 2.

The powder X-ray diffraction pattern of $NH_4(VO_2)_3(SeO_3)_2$ was recorded on a Scintag XDS2000 automated powder diffractometer with Cu Kα radiation. An indexed powder pattern is given in Table 1.

Single-Crystal Structure Determination. The crystal structure of $NH_4(VO_2)_3(SeO_3)_2$ was determined from single-crystal X-ray diffraction data. A yellow hexagonal prism (dimensions ≈ 0.15 × 0.15 × 0.12

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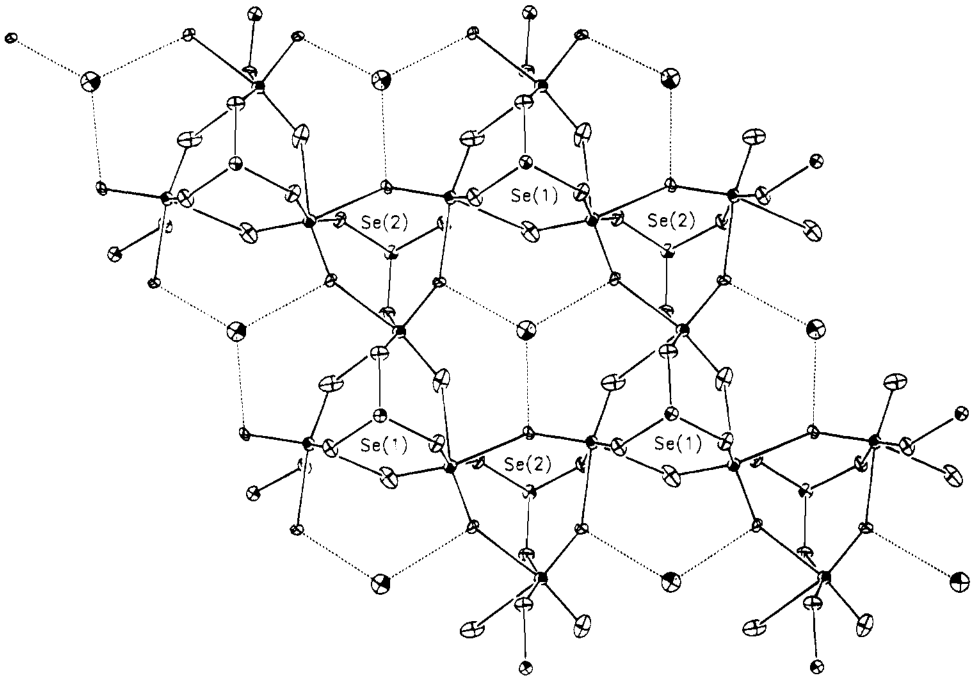

Figure 3. Structure of $NH_4(VO_2)_3(SeO_3)_2$ viewed perpendicular to the layers down [001] showing the vanadium–oxygen octahedra and the Se atoms capping the apical oxygen atoms. NH_4- - -O contacts are indicated by the dotted lines.

mm^3) was mounted on a thin glass fiber with epoxy, and room-temperature (25(2) °C) intensity data were collected on a Nicolet/Siemens automated four-circle diffractometer (graphite-monochromated Mo Kα radiation, $\lambda = 0.710\,73$ Å).

After location and centering of 27 reflections ($20° < 2\theta < 30°$), the unit cell constants were optimized by a least-squares refinement, resulting in hexagonal lattice parameters of $a = 7.137(3)$ Å and $c = 11.462(4)$ Å (esd's in parentheses). Intensity data were collected in the $\omega-2\theta$ mode, with standard reflections monitored for intensity changes throughout the experiment ($<\pm2\%$ variation observed). The scan speed varied from 1.5 to 15.0°/min, for a total of 1639 data collected ($-10 \le h \le 8$, $0 \le k \le 10$, $0 \le l \le 16$; $4° < 2\theta < 60°$). The systematic absence condition ($00l$, $l \ne 2n$) in the reduced data indicated space groups $P6_3$, $P6_3/m$, and $P6_322$. Test data merges ($R_{int} = 4.31\%$) indicated that Laue class $6/m$ was probably the correct one.

The crystal structure model of $NH_4(VO_2)_3(SeO_3)_2$ was developed in space group $P6_3$, with the atom positions (V, Se, O) located by using the direct-methods program SHELXS-86.[18] No reasonable starting atomic model could be established in space group $P6_3/m$, and $P6_3$ was assumed for the remainder of the crystallographic analysis. The least-squares refinement was carried out with the program SHELXL-93,[19] with the weighted refinements optimized against F^2 data. Complex, neutral-atom scattering factors were obtained from ref 20. The nitrogen atom position was located from Fourier difference maps, and the refinement converged without problems. The final cycles of the full-matrix least-squares refinement included anisotropic thermal factors, a Larson-type[21] secondary extinction correction, and the Flack polarity parameter[22] to determine the absolute configuration of the structure which is set out below. Without a secondary extinction correction, strong low-angle reflections (especially 004 (the strongest reflection) and $\bar{2}40$) showed $F_o{}^2 < F_c{}^2$. No hydrogen atoms could be located from the Fourier difference maps, and attempts at geometrical placement were ambiguous. Crystallographic data for $NH_4(VO_2)_3(SeO_3)_2$ are summarized in Tables 2 (crystal data), 3 (atomic positional/thermal parameters), and 4 (geometrical data).

Discussion

The compound $NH_4(VO_2)_3(SeO_3)_2$ is formed hydrothermally but only over a narrow range of synthesis conditions. Control of the pH of the reaction mixture is particularly important to prevent the reduction of SeO_2 to selenium metal. According to the Pourbaix diagram for selenium,[23] the redox stability range for the $HSeO_3{}^-$ and $SeO_3{}^{2-}$ anions that are present in solution in the pH range 2.5–6.5 is very narrow. Reduction to selenium metal and oxidation to $SeO_4{}^{2-}$ occur at lower and higher potentials, respectively. Addition of excess SeO_2 is required to prevent the formation of $(NH_4)_2V_6O_{16}$.[17] Single-phase polycrystalline samples of $NH_4(VO_2)_3(SeO_3)_2$ can be prepared, but the conditions we used to grow crystals always resulted in the formation of some $(NH_4)_2V_6O_{16}$. Attempts to synthesize analogous phases with the same layer structure but with the interlayer ammonium cation replaced by other alkali metal cations were unsuccessful. The products were selenium metal and the corresponding alkali metal phase, $M_2V_6O_{16}$. The successful synthesis of the ammonium compound may be a result of a pH buffering effect. With cations other than ammonium, the pH falls during the reaction, favoring reduction to selenium metal. The layer structure imposes no strong steric requirements on the interlayer cation, and consequently it may be possible to obtain the other alkali metal phases by further modification of the reaction conditions.

The Raman spectrum of $NH_4(VO_2)_3(SeO_3)_2$ has strong bands due to the symmetric stretching modes of the VO_6 and SeO_3 groups; the asymmetric stretching modes are weaker. The strong bands at 837 and 781 cm^{-1} are assigned to symmetric stretching modes of the VO_6 and SeO_3 groups, respectively. In the infrared spectrum, absorptions at 3187, 3040, and 1421 cm^{-1} and a weak band at 2800 cm^{-1} are due to the ammonium cation. Absorptions at 812 and 689 cm^{-1} are most likely assigned to the symmetric and asymmetric stretching modes of the VO_6 octahedra, but the $SeO_3{}^{2-}$ anion is also expected to have absorptions in the same region. The weak band at 941 cm^{-1},

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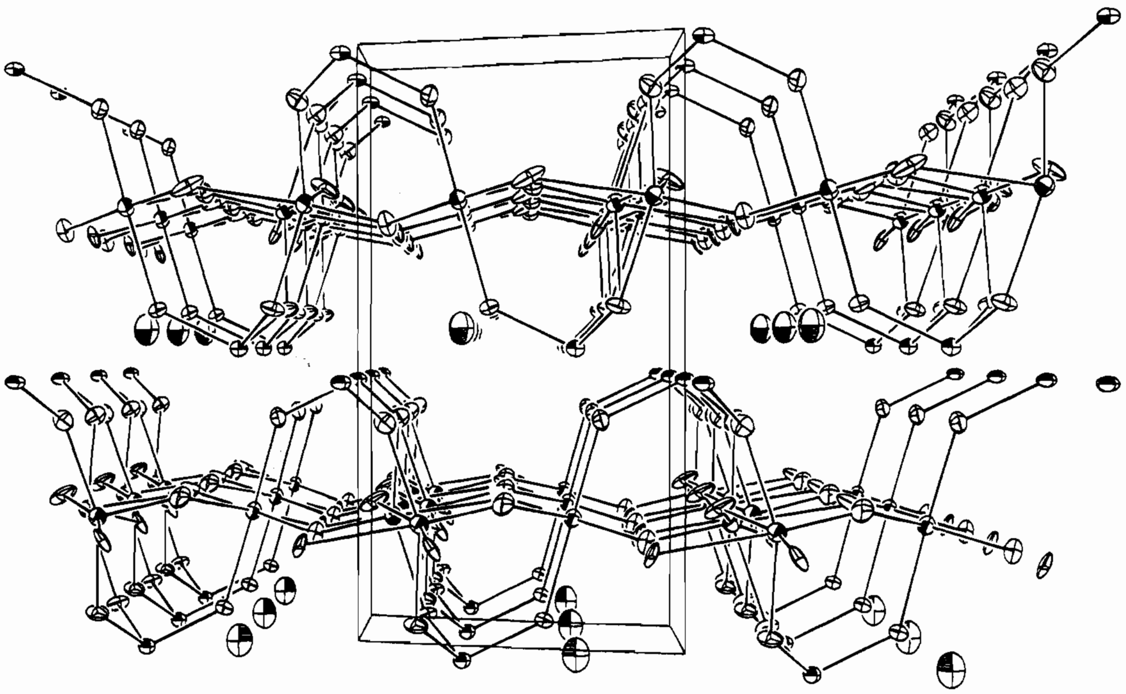

Figure 4. Structure of $NH_4(VO_2)_3(SeO_3)_2$ viewed in a [110] direction parallel to the layers (50% thermal ellipsoids). The ammonium ions occupy interlayer sites.

Table 2. Crystallographic Parameters for $NH_4(VO_2)_3(SeO_3)_2$

empirical formula	$Se_2V_3NO_{12}H_4$	T (°C)	25(2)
a (Å)	7.137(3)	λ(Mo Kα) (Å)	0.710 73
b (Å)	7.137(3)	ϱ_{calc} (g/cm^3)	3.42
c (Å)	11.462(4)	μ(Mo Kα) (mm^{-1})	9.84
V (Å^3)	505.7(4)	$R(F)^a$ (%)	4.64
Z	2	$R_w(F^2)^b$ (%)	10.41
fw	520.78	S (goodness of fit)	1.153
space group	$P6_3$ (No. 173)		

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F^2) = [\sum w(|F_o^2| - |F_c^2|)^2/\sum w|F_o^2|^2]^{1/2}$ with $w = 1/[\sigma^2(F_o^2) + (0.0001P)^2 + 11.049P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Table 3. Atomic Positional Parameters for $NH_4(VO_2)_3(SeO_3)_2$

atom	x	y	z	$U_{eq}{}^a$
N(1)	$^1/_3$	$^2/_3$	−0.0249(23)	0.028(5)
V(1)	0.7864(3)	0.1199(3)	−0.2180(2)	0.0114(4)
Se(1)	$^1/_3$	$^2/_3$	0.50764(15)	0.0106(4)
Se(2)	0	0	0.0594(2)	0.0117(4)
O(1)	0.7990(15)	0.2193(14)	−0.0558(7)	0.015(2)
O(2)	0.8837(13)	0.1349(14)	−0.3763(8)	0.015(2)
O(3)	0.7452(13)	−0.1233(12)	−0.1860(9)	0.013(2)
O(4)	0.5419(16)	0.0726(18)	−0.2471(8)	0.024(2)

[a] U_{eq} (Å^2) = $(U_1U_2U_3)^{1/3}$.

observed in both the infrared and Raman spectra, is associated with the SeO_3^{2-} anion.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $NH_4(VO_2)_3(SeO_3)_2$

N(1)—O(2) × 3	3.08(2)	N(1)—O(3) × 3	3.14(2)
V(1)—O(4)	1.637(10)	V(1)—O(3)	1.650(8)
V(1)—O(2)	1.927(9)	V(1)—O(1)	1.975(8)
V(1)—O(3)′	2.181(8)	V(1)—O(4)′	2.198(11)
Se(1)—O(1) × 3	1.689(9)	Se(2)—O(2) × 3	1.720(8)
O(4)—V(1)—O(3)	102.5(4)	O(4)—V(1)—O(2)	97.9(4)
O(3)—V(1)—O(2)	97.9(4)	O(4)—V(1)—O(1)	96.8(4)
O(3)—V(1)—O(1)	97.0(4)	O(2)—V(1)—O(1)	156.3(4)
O(4)—V(1)—O(3)′	167.7(5)	O(3)—V(1)—O(3)′	89.7(5)
O(2)—V(1)—O(3)′	80.6(4)	O(1)—V(1)—O(3)′	81.1(4)
O(4)—V(1)—O(4)′	92.2(7)	O(3)—V(1)—O(4)′	165.2(4)
O(2)—V(1)—O(4)′	81.2(3)	O(1)—V(1)—O(4)′	79.8(4)
O(3)′—V(1)—O(4)′	75.5(3)		
O(1)—Se(1)—O(1) × 3	102.8(4)	O(2)—Se(2)—O(2) × 3	103.0(4)
Se(1)—O(1)—V(1)	130.0(5)	Se(2)—O(2)—V(1)	129.3(5)
V(1)—O(3)—V(1)	141.1(5)	V(1)—O(4)—V(1)	140.3(6)

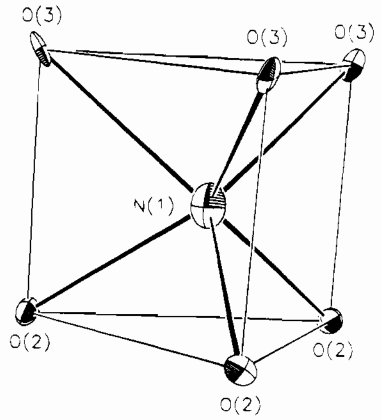

Figure 5. Local environment of the ammonium ion nitrogen atom (50% thermal ellipsoids).

The structure of $NH_4(VO_2)_3(SeO_3)_2$ can be described as a layered hexagonal net of distorted VO_6 octahedra of the type shown in Figure 1. Each vanadium oxygen octahedron shares four corners with adjacent octahedra. The apical oxygen atoms are coordinated to selenium atoms above and below the hexagonal sheet. The ammonium ions are located between the layers below the centers of the six rings of oxygen atoms in the layer. The structure is shown in Figures 3 and 4 in directions perpendicular and parallel to the layers. The ammonium ion coordination and vanadium and selenium/oxygen atom coordinations are shown in Figures 5 and 6. The vanadium atom occupies a position inside a nearly regular octahedron of oxygen atoms (the average O—O distance is 2.695 ± 0.052 Å) but is displaced off center approximately along a local 110 direction (Figure 7). The displacement results in two short *cis* V—O bonds *trans* to two longer distances in the basal plane of the octahedron. The direction of the vanadium atom displacement results in a geometry intermediate between octahedral and

Table 5. Comparison of Bond Lengths (Å) for Vanadium Oxide Phases

	$(NH_4)_2V_6O_{16}$		V_2O_5	α-$VOPO_4$	β-$VOPO_4$	$(NH_4)(VO_2)_3(SeO_3)_2$	MoO_3
	1.594	1.589	1.585	1.580	1.566	1.637	1.671
	1.728	1.836 × 2	1.780	1.858 × 4	1.849	1.650	1.735
	1.868		1.878 × 2		1.886 × 2	1.927	1.948 × 2
	1.961	1.974 × 2				1.975	
	1.988		2.021		1.902	2.181	2.251
	2.919	2.287	2.785	2.853	2.591	2.198	2.332
ref	17		25	24	30	this work	26

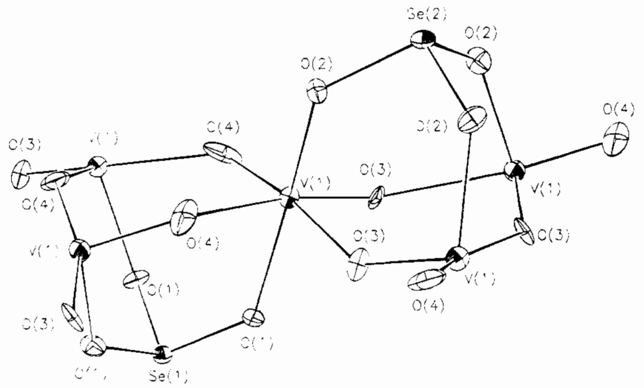

Figure 6. Isolated segment of the structure showing the vanadium–oxygen and selenium–oxygen coordination (50% thermal ellipsoids).

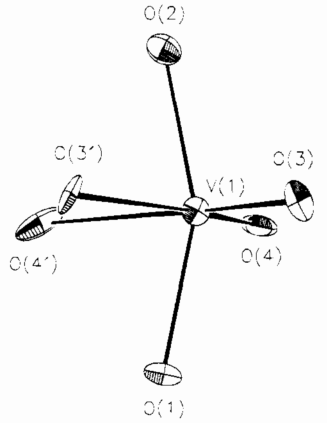

Figure 7. Local environment of a vanadium atom indicating the local 110 distortion toward tetrahedral geometry (50% thermal ellipsoids).

tetrahedral and is different from the displacement directions that are usually observed. In most simple vanadium(V) oxides, the direction of the vanadium atom displacement is predominantly toward one oxygen atom (e.g. along [001] in α-$VOPO_4$).[24] One very short distance, typically <1.6 Å, *trans* to one longer distance results. Some examples are given in Table 5. The displacements are not always exactly along [100], and an additional short bond length is present in several examples (e.g. 1.780 Å in V_2O_5).[25] The present structure is the only V(V) oxide structure that we have noted with the [110] displacement direction although it is also observed in MoO_3[26] (see Table 5). Bond valence sum calculations were carried out for the vanadium cation.[27] A value of 5.13 was obtained as expected, even though the coordination geometry is unusual.

To our knowledge, the structure of $NH_4(VO_2)_3(SeO_3)_2$ is the only example of a layer structure based on a hexagonal arrangement of VO_6 octahedra. Two examples of $M_2V_2O_7$ (A = Cd, Hg) compounds with the pyrochlore structure have been reported, but these phases can be synthesized only at high pressure.[7]

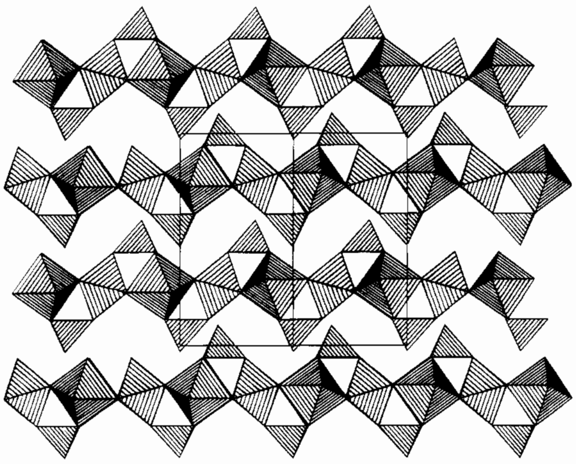

Figure 8. Polyhedral representation[31] of the structure viewed parallel to the layers. In this representation the coordination of the selenium atom is represented as a tetrahedron with the lone pair of electrons at one vertex. This representation emphasizes the close similarity to the structure of $K_3(SbO_2)_3(PO_4)_2$.

The structure of $NH_4(VO_2)_3(SeO_3)_2$ can be directly compared with the structures of $K_3(SbO_2)_3(XO_4)_2$ (X = P, As). The potassium antimony phosphate and arsenate structures are also based on HTB layers of corner-sharing (SbO_6) octahedra. The apical oxygen atoms of the antimony octahedra are "capped" by phosphate groups, and three potassium cations occupy interlayer sites for charge balance. The potassium ions interact weakly with the layers and can be replaced by protons by ion exchange in aqueous acid. The $NH_4(VO_2)_3(SeO_3)_2$ structure is closely related to these phases. The SeO_3^{2-} and the $P(As)O_4^{3-}$ groups have the same structural role in relation to the hexagonal octahedral layers. The relationship is illustrated in Figure 8. Due to the charge difference between PO_4^{3-} and SeO_3^{2-}, only one interlayer cation is required in the selenite compound. This type of structural relationship between selenites and phosphates has been observed for other compounds, for example, $VOSeO_3{\cdot}H_2O$ and $VO(PO_3OH){\cdot}{}^1/_2H_2O$.[28] The SeO_3^{2-} group has a lone pair of electrons occupying the fourth coordination position of a pseudotetrahedron and behaves structurally like a $[PO_3OH]^{2-}$ unit.

In contrast to the layered vanadium(V) compound $VOPO_4{\cdot}2H_2O$, the selenite $NH_4(VO_2)_3(SeO_3)_2$ does not demonstrate a wide variety of redox intercalation reactions. Reactions of $VOPO_4{\cdot}2H_2O$ with metal iodide salts result in the reduction of V(V) in the layers and the intercalation of the corresponding metal cation into interlayer sites.[29] In NH_4-

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$(VO_2)_3(SeO_3)_2$, the redox chemistry of the selenite group interfers with redox intercalation associated with vanadium cation reduction. Powder X-ray diffraction shows some evidence for intercalation, but X-ray analysis studies of reaction products indicate that the reduction process is nonselective. Reductions of both the vanadium(V) cations and the selenite anions to selenium metal occur at the same time. Even at low iodide concentrations, both reduction reactions are observed and we have not been able to devise conditions that would selectively reduce one species. Electrochemical methods that would provide greater control cannot be straightforwardly used because of the insulating nature of the compound. Other types of interlayer reactions have been studied. In contrast to $VOPO_4{\cdot}2H_2O$, $NH_4(VO_2)_3(SeO_3)_2$ does not oxidize alcohol under refluxing conditions. Attempts to oxidize the SeO_3^{2-} group to a selenate SeO_4^{2-} group with chemical oxidants such as $K_2S_2O_8$ also proved unsuccessful. Simple ion exchange reactions, for example in 2 M KCl, resulted in decomposition with the formation of V_2O_5.

In summary, we have synthesized and structurally characterized a new layered ammonium vanadium(V) selenite, $NH_4(VO_2)_3(SeO_3)_2$. The compound is a member of a family of compounds that have structures based on a hexagonal layer of corner-shared octahedra of the type found in the hexagonal tungsten bronze phases. Reactivity studies with aqueous metal iodides show evidence for redox intercalation similar to that observed in other layered vanadium oxides, but in the present case, the reactions are complicated by the reduction of the selenite anion to selenium metal with associated decomposition of the octahedral layers. Further studies of related molybdenum and tungsten selenite phases are in progress and will be reported elsewhere.

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Supplementary Material Available: A table of anisotropic thermal parameters (1 page). Ordering information is given on any current masthead page.

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