A New Three-Dimensional Vanadium Selenite, $(VO)_2(SeO_3)_3$, with Isolated and Edge-Shared VO_6 Octahedra

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Single crystals of $(VO)_2(SeO_3)_3$ have been prepared from SeO_2 and V_2O_5. The crystal structure has been determined by single-crystal X-ray diffraction. Crystal data: $(VO)_2(SeO_3)_3$, $M_r = 514.75$; monoclinic, space group $P2_1/a$ (No. 14); cell parameters $a = 9.151(1)$ Å, $b = 6.353(1)$ Å, $c = 14.992(1)$Å, $\beta = 93.538(5)°$, and Z = 4. The structure consists of VO_6 octahedra and SeO_3 groups. The vanadium octahedra either are edge-sharing and form $[V_2O_{6.66}]^{3.33-}$ groups or are corner-linked through an $[SeO_{3/2}]^+$ cation. The structure may be rationalized in terms of connecting layers of $\{2[SeO_{2/2}O_{1/3}]^{4/3+}[VO_{1/1}O_{4/2}O_{1/3}]^{5/3-}\}^+$ cations and $\{[SeO_{3/2}]^+[VO_{1/1}O_{5/2}]^{2-}\}^-$ anions.

Introduction

Although it is well established that macroscopic noncentrosymmetry[1] must occur for second-order nonlinear optical (NLO) behavior, the *a-priori* synthesis of new NLO materials remains elusive. For inorganic materials, this macroscopic acentricity is usually manifested microscopically through the metal cations distorting from the center of their coordination polyhedra. *It is emphasized that these distortions are a necessary but not sufficient condition for acentricity*. In other words, the material can and often does crystallize such that the distortions occur in an antiparallel manner, thus producing macroscopic centricity.

From a crystal chemical perspective, "distortable" metal cations are found for two groups of elements, d^0 transition metals (Ti^{4+}, Nb^{5+}, and W^{6+}) and cations with nonbonded electron pairs (Se^{4+}, Te^{4+}, and Bi^{3+}). For the former, the distortion is understood to be a consequence of the second-order Jahn−Teller effect,[2−4] in which the empty dπ orbitals of the metal mix with the filled pπ orbitals of the ligands. The amplitude of the distortion is determined by the extent of this mixing as well as the size and charge of the metal cation.[5] With the latter group, it is the nonbonded electron pair that places the cation in asymmetric coordination. The occurrence of this nonbonded electron pair is thought to be due to the hybridization of the s and p orbitals.[6] From a synthetic and crystal chemical perspective, it is suggested that, by synthesizing compounds with cations from the aforementioned two groups, one can increase the probability of new noncentrosymmetric materials.

The d^0 transition metal−selenium(IV)−oxide family has been relatively unexplored with few reported compounds, namely Se_2TiO_6,[7] $(NH_4)(VO_2)_3(SeO_3)_2$,[8] $CsVSeO_5$,[9] $(NH_4)_2(MoO_3)_3SeO_3$,[10] $Cs_2(MoO_3)_3(SeO_3)$,[10] and $M_2(WO_3)_3SeO_3$ (M = NH_4, Rb, or Cs).[11] Typically, in mixed-metal selenites the Se^{4+} is found either as the monoselenite $[SeO_{3/2}]^+$ cation[7] (in which each oxygen is bonded to a selenium and another metal) or as the diselenite $[Se_2O_{5/2}]^{3+}$ cation[12] (where one oxygen bridges the seleniums and the remaining link to another metal). The monoselenite group may also be involved in extensive hydrogen bonding, as with $MH_3(SeO_3)$ (M = Li^+, K^+, Rb^+, or Cs^+),[13−16] where the SeO_3 groups are linked through O−H···O hydrogen bonds. Crystals of mixed-metal selenites can be grown either by hydrothermal means, in acid or base, by using H_2SeO_3 or SeO_2,[17−23] or from the melt, by using SeO_2 and another metal oxide, in sealed quartz tubes.[12,24,25]

This paper reports the synthesis, crystal structure, and properties of a new Se^{4+}/V^{5+} oxide, $(VO)_2(SeO_3)_3$.

Experimental Section

Synthesis. *Caution*! Use appropriate safety measures to avoid toxic SeO_2 dust contamination. SeO_2 (0.22 g, 2×10^{-3} mol) and V_2O_5 (0.091 g, 5×10^{-4} mol) were combined in a fused-silica tube that was evacuated and sealed. The tube was held at 400 °C for 3 days, cooled at a rate of 6 °C/h to 250 °C, and subsequently removed from the furnace and air-cooled to room temperature. The product, orange crystals of $(VO)_2(SeO_3)_3$, was manually extracted from the tube. Powder diffraction data on ground samples of $(VO)_2(SeO_3)_3$ gave good agreement with the calculated pattern. Anal. Calcd (found) for $(VO)_2(SeO_3)_3$: Se, 46.02 (43.1); V, 19.8 (17.2).

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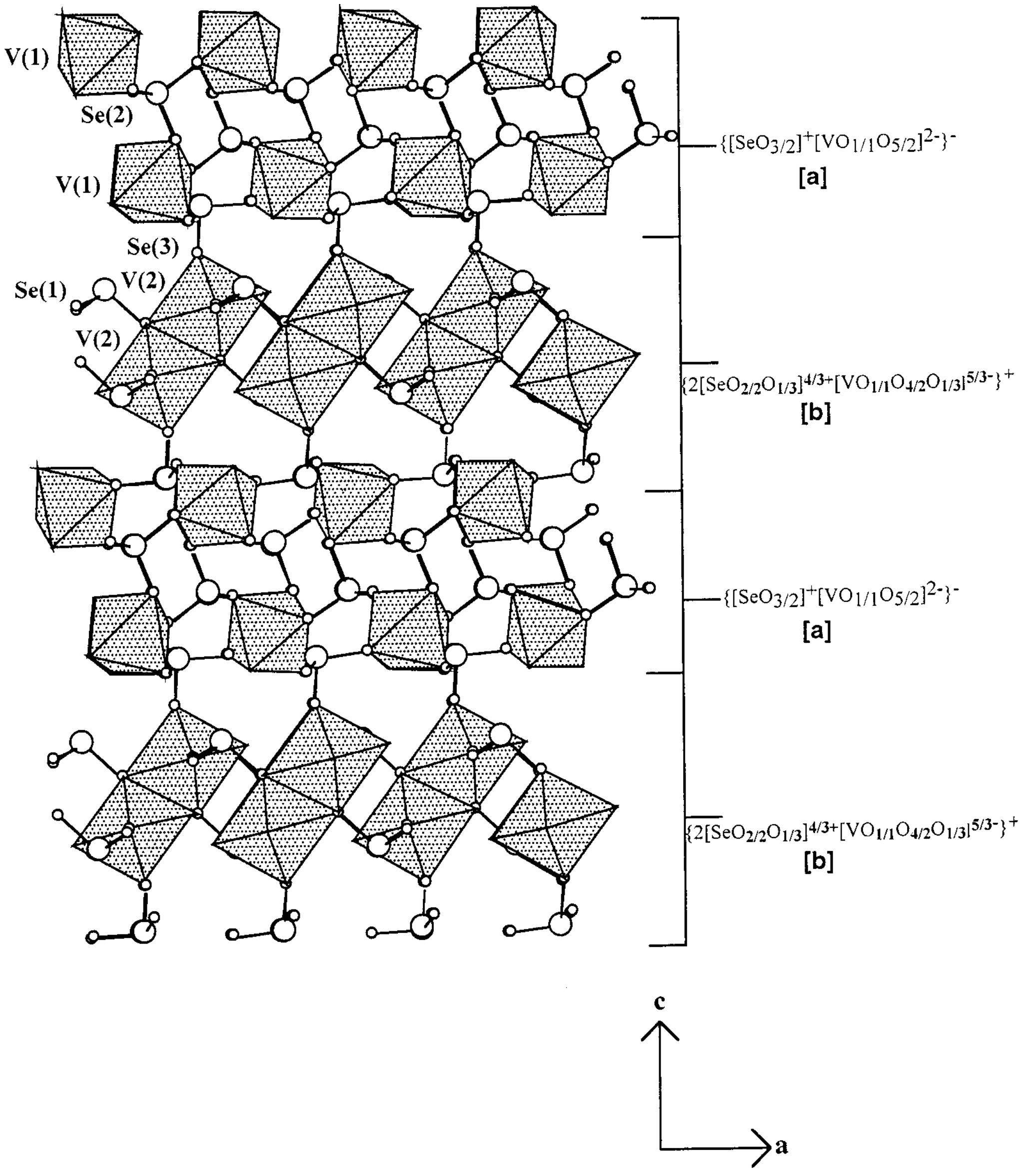

Figure 1. Polyhedral and ball-and-stick diagram of $(VO)_2(SeO_3)_3$. The V^{5+} octahedra are dotted, Se^{4+} cations are large clear circles, and the oxygen atoms are small clear circles. Note the V^{5+} octahedra are either isolated (layer a) or edge-shared (layer b).

Crystal Structure Determination. The structure of $(VO)_2(SeO_3)_3$ was determined by standard crystallographic methods: A faceted orange rod (dimensions ca. 0.1 × 0.1 × 0.05 mm) was mounted on a thin glass fiber with Paratone, and low-temperature [200.0(5) K] intensity data were collected on an image-plate Enraf-Nonius DIP 2000 diffractometer using graphite-monochromated Mo Kα radiation. Ninety frames at steps of 2° yielded 8034 reflections ($\theta_{max} = 26°$) of which 1920 were unique and 1148 were observed with $I > 5\sigma(I)$. A DIFABS[26] absorption correction was made as well as corrections for Lorentz and polarization effects.[27]

The crystal structure of $(VO)_2(SeO_3)_3$ was solved in space group $P2_1/a$ (No. 14) with initial heavy-atom positions, selenium and vanadium, located by direct methods by using SIR92.[28] A Chebyshev weighting scheme[29] was applied during the refinement. The oxygens were located by subsequent cycles of refinements and Fourier difference maps. The final full-matrix least-squares refinement was against F and included anisotropic thermal parameters for Se and V and isotropic parameters for oxygen. The final refinement was based on 1148 reflections and 90 variable parameters and converged with $R(F) = 0.0456$ and $R_w(F) = 0.0534$. The maximum and minimum peaks on the final difference map corresponded to −1.24 and 1.34 e/Å^3, respectively. All crystallographic calculations were performed using the Oxford CRYSTALS system[30] running on a Silicon Graphics Indigo R4000 computer. Crystallographic data for $(VO)_2(SeO_3)_3$ are given in Table 1.

Table 1. Crystallographic Data for $(VO)_2(SeO_3)_3$

fw = 514.75	$Z = 4$
space group $P2_1/a$ (No. 14)	$T = 200.0(5)$ K
$a = 9.151(1)$ Å	$\lambda = 0.710\ 71$ Å
$b = 6.353(1)$ Å	$\rho = 3.95$ g/cm^3
$c = 14.922(1)$ Å	$\mu = 146.3$ cm^{-1}
$\beta = 93.538(5)°$	$R(F)^a = 0.0456$
$V = 865.86(3)$ Å^3	$R_w(F)^b = 0.0534$

$^a\ R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $^b\ R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$.

Results

Crystal Structure of $(VO)_2(SeO_3)_3$. $(VO)_2(SeO_3)_3$ is a new ternary Se^{4+}/V^{5+} oxide containing SeO_3 and VO_6 units, which

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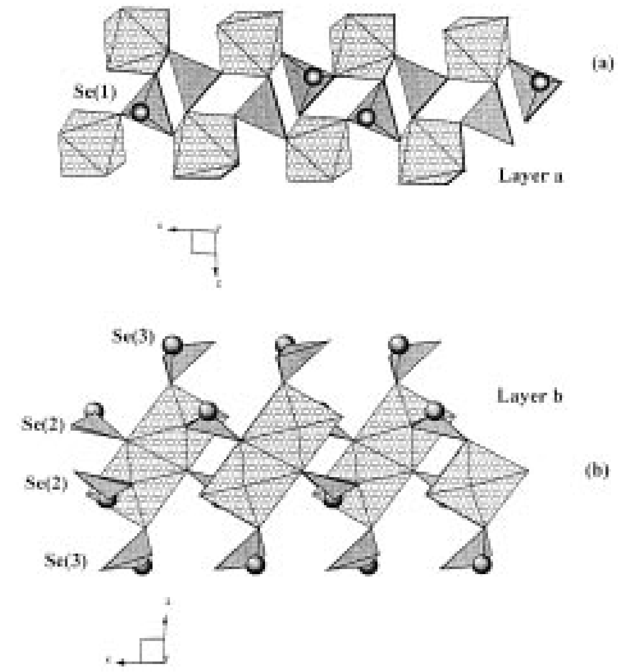

Figure 2. Polyhedral representation of layers a and b. The nonbonded electron pair on Se^{4+} is represented as a gray sphere.

are connected through V−O−Se and V−O−V bonds. The asymmetric unit contains three unique selenium and two unique vanadium atoms. Each selenium is in a distorted trigonal pyramidal coordination, bonded to three oxygen atoms. The Se−O distances range from 1.667(9) to 1.722(9) Å, with O−Se−O angles ranging from 93.1(4) to 102.7(4)°. The distances and angles are in good agreement with those of previously reported selenites.[10,23] Bond valence calculations[31] for Se(1), Se(2), and Se(3) result in values of 3.97, 4.02, and 3.99, respectively, which are in very good agreement with the expected value of 4.00. Each oxygen around the selenium is bonded to a vanadium cation. Thus, in connectivity terms, each SeO_3 unit may be formulated as a $[SeO_{3/2}]^+$ cation. Se(1) connects the V(2) polyhedra through O(1), O(2), and O(3), whereas Se(2) links the V(1) octahedra together via O(5), O(6), and O(7). The third selenium, Se(3), connects to V(2) through O(10) and to V(1) through O(8) and O(9).

The two unique vanadiums are in distorted octahedral coordination environments. V(1) is connected to O(5), O(6), O(7), O(8), O(9), and O(11), all of which, except for O(11), are bonded to a selenium. O(11) is a terminal oxygen with a "short" V−O distance of 1.58(1) Å. V(2) is also octahedrally coordinated to O(1), O(2), O(3), O(4), and O(10) and has a "long" sixth bond (2.65(1) Å) to a symmetry-equivalent O(1). All of these oxygens, with the exception of O(4), are linked to a selenium. O(4) is a terminal oxygen with a "short" V−O distance of 1.57(1) Å. However although V(1) and V(2) are octahedrally coordinated, for V(2) the octahedra are isolated linked only through an $[SeO_{3/2}]^+$ bridge, whereas for V(1) the octahedra are edge-linked with V(1)···V(1) = 3.71 Å, compared with 3.02 Å in vanadium metal.[32] Bond valence calculations for V(1) and V(2) resulted in values of 5.09 and 4.99, respectively, consistent with the expected value of 5.00.

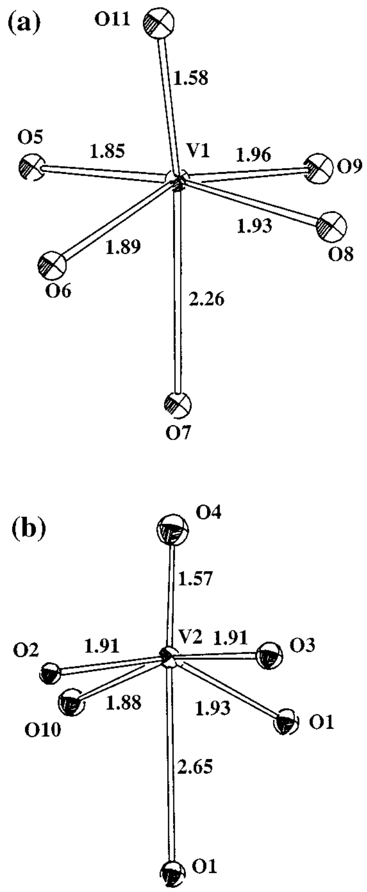

Figure 3. ORTEP diagrams (50% probability) of the vanadium octahedra. The vanadium atoms are anisotropic, whereas the oxygens are isotropic. Note the difference in axial bond distances for both V(1) and V(2).

Discussion

A polyhedral representation of $(VO)_2(SeO_3)_3$ is shown in Figure 1. The structure may be rationalized in terms of two connecting layers, a and b. Layer a can be described as consisting of two chains of $[V(1)O_{1/1}O_{5/2}]^{2-}$ octahedra that are connected in both an inter- and intrachain manner by $[Se(2)O_{3/2}]^+$ cations. The $[SeO_{3/2}]^+$ cations, which may be schematically formulated as SeO_3E, where E is the nonbonded electron pair, are in staggered pairs between the V(1) octahedra. The $Se(2)O_3E$ groups have the nonbonded electron pair pointing along the [010] direction, in an alternating [up−down−down−up−up−down−down−up] fashion (see Figure 2a). This alternation has the effect of minimizing the electrostatic interactions between the electron pairs. Combining the $[Se(2)O_{3/2}]^+$ cations with the $[V(1)O_{1/1}O_{5/2}]^{2-}$ anion forms an anionic sheet that can be formulated as $\{[SeO_{3/2}]^+[VO_{1/1}O_{5/2}]^{2-}\}^-$.

The second layer, termed b, contains pairs of $[V(2)O_{1/1}O_{4/2}O_{1/3}]^{5/3-}$ octahedra which are linked by $[Se(1)O_{2/2}O_{1/3}]^{4/3+}$ and $[Se(3)O_{3/2}]^+$ cations. The $[Se(3)O_{3/2}]^+$ cation also links the $[V(1)O_{1/1}O_{5/2}]^{2-}$ and $[V(2)O_{1/1}O_{4/2}O_{1/3}]^{5/3-}$ octahedra. In layer b, the nonbonded electron pairs of adjacent Se(1) again point in alternate directions, approximately parallel to the [001] direction. The third selenite, Se(3), which links V(1) to V(2) has its nonbonded electron pair pointing approximately parallel to the $[10\bar{1}]$ direction (Figure 2b). Thus, in all three SeO_3E groups, the nonbonded electron pairs are directed away from each other. In terms of connectivity, combining the Se(1), Se(3), and V(2) polyhedra results in a cationic sheet that may be formulated as $\{2[SeO_{2/2}O_{1/3}]^{4/3+}[VO_{1/1}O_{4/2}O_{1/3}]^{5/3-}\}^+$. Thus $(VO)_2(SeO_3)_3$ may be rationalized as having an a−b−a−b−a−b pattern, which can be structurally described as $\{[SeO_{3/2}]^+[VO_{1/1}O_{5/2}]^{2-}\}^-$−$\{2[SeO_{2/2}O_{1/3}]^{4/3+}[VO_{1/1}O_{4/2}O_{1/3}]^{5/3-}\}^+$−$\{[SeO_{3/2}]^+[VO_{1/1}O_{5/2}]^{2-}\}^-$−$\{2[SeO_{2/2}O_{1/3}]^{4/3+}[VO_{1/1}O_{4/2}O_{1/3}]^{5/3-}\}^+$ (see Figure 1). The layers are also connected along

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Table 2. Comparison of V−O Bond Lengths (Å) in $(VO)_2(SeO_3)_3$ to Those in $(NH_4)(VO_2)_3(SeO_3)_2$ and V_2O_5

$(VO)_2(SeO_3)_3$		$(NH_4)(VO_2)_3(SeO_3)_2$[8]	V_2O_5[37]
$V(1)^{5+}$	$V(2)^{5+}$	V^{5+}	V^{5+}
1.575	1.567	1.637	1.585
1.884	1.884	1.650	1.780
1.890	1.913	1.927	1.878
1.931	1.915	1.975	1.878
1.961	1.927	2.181	2.021
2.265	2.651	2.198	2.785
Maximum Difference (Å) between V−O Bonds			
0.68	**1.08**	0.56	**1.12**

the [010] direction through $[SeO_{3/2}]^+$ cations, thus affording three-dimensionality to the structure.

Another interesting feature of $(VO)_2(SeO_3)_3$ is the vanadium coordination. Both V(1) and V(2) are in highly distorted octahedral coordination environments (Figure 3a). For d^0 transition metal oxides, off-center distortions are understood to be a consequence of second-order Jahn−Teller effects.[2,3] In addition, for ferroelectric oxides such as $LiNbO_3$[33] and $BaTiO_3$,[34] it is thought that the constructive addition of the intraoctahedral distortions is responsible for their technologically important physical properties.[35,36] In $(VO)_2(SeO_3)_3$, both V(1) and V(2) exhibit substantial off-center axial displacements toward the octahedral vertex, unlike the vanadium displacement in $(NH_4)(VO_2)_2(SeO_3)$,[8] which is toward an octahedral edge. When compared to that of other selenium(IV) vanadium(V) oxides, the magnitude of the intraoctahedral distortions in $(VO)_2(SeO_3)_3$ is among the largest. Table 2 compares the V−O distances of $(VO)_2(SeO_3)_3$ and $(NH_4)(VO_2)_2(SeO_3)$[8] as well as V_2O_5.[37] ($CsVSeO_5$[9] contains five-coordinate vanadium.) In $(VO)_2(SeO_3)_3$, the observed distortion, in V(2), is comparable to that in V_2O_5, with the differences between the "short" axial and "long" trans bonds being 1.08(2) and 1.12(2) Å, respectively. Although $(VO)_2(SeO_3)_3$ contains cations that are substantially distorted from the center of their coordination polyhedra, the distortions are aligned in an antiparallel manner, thus producing macroscopic centricity.

Both vanadium octahedra contain "short" V−O bonds, V(1)−O(11) and V(2)−O(4), that are found with a nonbridging oxygen. Bond valence sums[31] for these two bonds are 1.85 and 1.89, respectively, consistent with V═O characteristics. These terminal V−O bonds are staggered in the structure. For the V(1) octahedra, the terminal bond points in the $[\bar{1}01]$ direction whereas, for the edge-shared octahedra of V(2), the terminal bonds point along the [100] direction. In addition, the occurrence of edge-shared vanadium(V) octahedra in a selenite is unique to $(VO)_2(SeO_3)_3$; in fact, the pairs of edge-shared octahedra in layer b (see Figure 2b) form a $[V_2O_{6.66}]^{3.33-}$ anionic group, with a V···V distance of 3.71 Å, compared to 3.02 Å in vanadium metal.[32]

Conclusion

We have synthesized a new Se^{4+}/V^{5+} oxide, $(VO)_2(SeO_3)_3$, which contains isolated as well as edge-shared VO_6 octahedra that are bridged through SeO_3^{2-} groups. The vanadium cations are in highly distorted octahedral coordination, whereas the seleniums are found in distorted trigonal pyramidal geometry. Although all of the selenium and vanadium cations are found in local noncentrosymmetric coordination, the cationic distortions are aligned in an antiparallel manner. We have extended the $Se^{4+}-d^0$ transition metal−oxide family to include $Se^{4+}-Nb^{5+}$ and have grown single crystals of $Se_4Nb_2O_{13}$, a new *noncentrosymmetric* material. We will report its structure and properties shortly.[38] Although we have been successful in synthesizing a new acentric material within the $Se^{4+}-Nb^{5+}$ system, it remains an ongoing challenge to synthesize rationally new second-order NLO materials.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, is available on the Internet only. Access information is given on any current masthead page.

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