Synthesis and Structural Characterization of a New Series of Vanadoselenites, $[Se_xV_{4-x}O_{12-x}]^{(4-x)-}$ ($x = 1, 2$)

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Two new vanadoselenites, $[SeV_3O_{11}]^{3-}$ and $[Se_2V_2O_{10}]^{2-}$, were synthesized by reacting SeO_2 with VO_3^-. Single-crystal X-ray structural analyses of $[(n\text{-}C_4H_9)_4N]_3[SeV_3O_{11}]\cdot0.5H_2O$ [orthorhombic, space group $P2_12_12$, $a = 22.328(5)$ Å, $b = 44.099(9)$ Å, $c = 12.287(3)$ Å, $Z = 8$] and $[\{(C_6H_5)_3P\}_2N]_2[Se_2V_2O_{10}]$ [monoclinic, space group $P2_1/n$, $a = 12.2931(3)$ Å, $b = 13.5101(3)$ Å, $c = 20.9793(5)$ Å, $\beta = 106.307(1)°$, $Z = 2$] revealed that both anions are composed of $Se_xV_{4-x}O_4$ rings. The ^{51}V, ^{77}Se, and ^{17}O NMR spectra established that both $[SeV_3O_{11}]^{3-}$ and $[Se_2V_2O_{10}]^{2-}$ anions maintain this ring structure in solution.

Introduction

The chemistry of polyvanadates has developed dramatically recently. Scores of new species have been reported during the past decade.[2−4] Many of these newer polyvanadates are of mixed valence. The examples of fully oxidized polyvanadate, on the other hand, are still relatively limited. This is especially true for heteropolyvanadates. Structurally characterized heteropolyvanadates in which all vanadium atoms are in the V oxidation state remain a rarity. Only a handful of such examples have been reported to date.[5−13] This apparent lack of information and interest does not necessarily mean that the chemistry of fully oxidized polyvanadates itself is limited and uninteresting. Recent results from our and other laboratories suggest just the opposite.[14−20]

As a part of our ongoing research effort to synthesize fully oxidized polyoxometalates and elucidate their behavior in solution, we have recently isolated two new vanadoselenites, $[SeV_3O_{11}]^{3-}$ and $[Se_2V_2O_{10}]^{2-}$. Here we report the syntheses and crystal structure analyses of these new polyvanadates together with their characterization in solution. A vanadoselenite that has an Se_2V_2 stoichiometry was reported about a century ago,[21] but that with a SeV_3 composition has never been reported before.

Experimental Section

Reagents, Solvents, and General Procedures. The following were purchased from commercial sources and used without further purification: acetone, V_2O_5, SeO_2, and P_2O_5 (Kishida), 10% aqueous solution of $[(n\text{-}C_4H_9)_4N]OH$ (Tokyo Kasei), $[\{(C_6H_5)_3P\}_2N]Cl$ (Aldrich), $[(C_6H_5)_4P]Br$ (Wako), D_2O (ISOTEC), and 10% ^{17}O enriched water (Cambridge Isotope Laboratories). Deuterated dimethyl sulfoxide (DMSO-d_6, ISOTEC) was dried over 4 Å molecular sieves. Acetonitrile (Kishida) was routinely dried over 3 Å molecular sieves except that used for ^{17}O enrichment, ^{17}O NMR measurements, and preparation of single crystals of $[(n\text{-}C_4H_9)_4N]_3[SeV_3O_{11}]\cdot0.5H_2O$ for the structure analysis. Acetonitrile used for these experiments was distilled from P_2O_5 under N_2 and stored over 3 Å molecular sieves. Diethyl ether and toluene (Kishida) were distilled from sodium benzophenone ketyl under N_2 and stored over 4 Å molecular sieves.

Analytical Procedures. Elemental analyses were performed by Toray Research Center, Shiga, Japan. Infrared spectra were recorded from mineral oil (Nujol) mulls between KBr plates on a Hitachi I-3000 spectrometer. Absorptions are described as follows: very strong (vs), strong (s), medium (m), weak (w), and shoulder (sh). NMR spectra were recorded on a Varian Unity-Plus spectrometer. ^{51}V NMR spectra were recorded at 78.855 MHz and referenced externally against $VOCl_3$. ^{77}Se NMR spectra were recorded at 57.269 MHz and referenced externally against SeO_2 saturated in D_2O.[22] ^{17}O NMR spectra were recorded at 40.685 MHz and referenced externally to D_2O.

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Preparation of $[(n\text{-}C_4H_9)_4N]VO_3$. A slightly modified literature procedure was employed to prepare this compound.[23] To a 10% aqueous solution of $[(n\text{-}C_4H_9)_4N]OH$ (56 mL, 22 mmol) was added 2.0 g of V_2O_5 (11 mmol), and the mixture was stirred overnight. The resulting colorless solution was evaporated to dryness under reduced pressure. The solid thus obtained was further dried under vacuum for 8 h before it was dissolved in 40 mL of acetone. The white powder that formed on adding 150 mL of diethyl ether to this solution was collected by filtration and dried under vacuum for 8 h to yield 4.4 g of the product (13 mmol, 59%). ^{51}V NMR (78.755 MHz, CH_3CN): δ −570, −576. IR (Nujol, 400−1000 cm^{-1}): 576 (m), 656 (w), 672 (w), 736 (sh), 770 (s), 924 (s).

Preparation of $[(n\text{-}C_4H_9)_4N]_3[SeV_3O_{11}]\cdot 0.5H_2O$. To a solution of $[(n\text{-}C_4H_9)_4N]VO_3$ (2.0 g, 5.9 mmol) in 5 mL of acetonitrile was added SeO_2 (0.22 g, 2.0 mmol) with stirring to give a pale yellow solution. The solution was stirred for 2 h before it was evaporated to dryness under reduced pressure. The resulting solid was washed with 10 mL of diethyl ether and dried under vacuum to yield 2.0 g of crude product. Crystallization was accomplished by dissolving 0.30 g of the crude product in 3.0 mL of acetonitrile and adding diethyl ether to the point of saturation (ca. 9 mL) with stirring. Colorless rectangular crystals appeared after allowing the solution to stand at 10 °C for 1 day (0.070 g, 0.061 mmol, 23%). An ^{17}O-enriched sample was prepared by dissolving the crystalline material (0.10 g, 0.087 mmol) in 2 mL of CH_3CN, adding 7.5 μL (0.41 mmol) of ^{17}O-enriched water, stirring the solution for 3 h, adding 60 mL of diethyl ether, collecting the precipitate then formed by filtration, and drying it under vacuum for 5 h (0.070 g, 0.061 mmol, 70%). Anal. Calcd for $C_{48}H_{109}N_3SeV_3O_{11.5}$: C, 50.39; H, 9.60; N, 3.67; Se, 6.90; V, 13.4. Found: C, 50.18; H, 9.56; N, 3.78; Se, 6.90; V, 13.3. IR (Nujol, 400−1000 cm^{-1}): 494 (w), 564 (w), 636 (w), 754 (vs), 826 (s), 894 (s), 920 (vs), 930 (vs). ^{51}V NMR (78.755 MHz, CH_3CN): δ −556 (2V), −566 (1V). ^{77}Se NMR (57.269 MHz, DMSO-d_6): δ 71.9. ^{17}O NMR (40.685 MHz, CH_3CN): δ 271 (3O), 477 (2O), 1004 (2O), 1032 (4O).

Preparation of $[(C_6H_5)_4P]_2[Se_2V_2O_{10}]$. To a solution of $[(n\text{-}C_4H_9)_4N]VO_3$ (0.50 g, 1.5 mmol) in 5 mL of acetonitrile was added SeO_2 (0.16 g, 1.5 mmol) with stirring to give a dark red solution. The solution was stirred for 2 h before it was added dropwise to a solution of $[(C_6H_5)_4P]Br$ (0.61 g, 1.5 mmol) in 3 mL of acetonitrile. Pale yellow precipitate that formed on adding 40 mL of diethyl ether to the mixture was collected by filtration and dried under vacuum for 8 h to yield 0.65 g of the product (0.59 mmol, 79% based on V). Crystallization was accomplished by dissolving 0.20 g of the crude product in 10 mL of acetonitrile, adding 10 mL of diethyl ether gently to make a second layer, and allowing the mixture to stand at 10 °C. Colorless crystals appeared in 1 day, which weighed 0.060 g after drying under vacuum (0.055 mmol, 30%). Anal. Calcd for $C_{48}H_{40}P_2Se_2V_2O_{10}$: C, 52.48; H, 3.67; P, 5.65; Se, 14.37; V, 9.27. Found: C, 52.34; H, 3.78; P, 5.60; Se, 14.60; V, 9.20. IR (Nujol, 400−1000 cm^{-1}): 460 (w), 528 (s), 612 (s), 688 (s), 722 (vs), 760 (s), 924 (s), 954 (s), 996 (w). ^{51}V NMR (78.755 MHz, CH_3CN): δ −547.

Preparation of $[\{(C_6H_5)_3P\}_2N]_2[Se_2V_2O_{10}]$. To a solution of $[(n\text{-}C_4H_9)_4N]VO_3$ (0.50 g, 1.5 mmol) in 5 mL of acetonitrile was added SeO_2 (0.16 g, 1.5 mmol) with stirring to give a dark red solution. The solution was stirred for 2 h before it was added dropwise to a solution of $[\{(C_6H_5)_3P\}_2N]Cl$ (0.84 g, 1.5 mmol) in 10 mL of acetonitrile. Pale yellow microcrystals that formed on adding 80 mL of diethyl ether to the mixture were collected by filtration and dried under vacuum for 8 h to yield 0.88 g of the product (0.59 mmol, 79% based on V). An ^{17}O-enriched sample was prepared by dissolving the crystalline material (0.10 g, 0.067 mmol) in 10 mL of CH_3CN, adding 5.2 μL (0.29 mmol) of ^{17}O-enriched water, stirring the solution for 2 h, adding 80 mL of diethyl ether, collecting the precipitate then formed by filtration, and drying it under vacuum for 5 h (0.076 g, 0.051 mmol, 76%). Anal. Calcd for $C_{72}H_{60}P_4N_2Se_2V_2O_{10}$: C, 57.77; H, 4.04; N, 1.87; P, 8.28. Found: C, 57.44; H, 3.97; N, 1.90; P, 8.32. IR (Nujol, 400−1000 cm^{-1}): 442 (w), 500 (w), 532 (s), 552 (s), 686 (s), 722 (vs), 756 (s), 770 (s), 802 (w), 926 (m), 954 (s), 996 (w). ^{51}V NMR (78.755 MHz, CH_3CN): δ −547. ^{77}Se NMR (57.269 MHz, DMSO-d_6): δ 66.7. ^{17}O NMR (40.685 MHz, CH_3CN): δ 290 (3O), 1100 (2O).

Table 1. Crystallographic Data for $[\{(C_6H_5)_3P\}_2N]_2[Se_2V_2O_{10}]$ and $[(n\text{-}C_4H_9)_4N]_3[SeV_3O_{11}]\cdot 0.5H_2O$

	$[\{(C_6H_5)_3P\}_2N]_2$-$[Se_2V_2O_{10}]$	$[(n\text{-}C_4H_9)_4N]_3$-$[SeV_3O_{11}]\cdot 0.5H_2O$
empirical formula	$C_{72}H_{60}N_2O_{10}P_4Se_2V_2$	$C_{48}H_{109}N_3O_{11.5}SeV_3$
fw	1496.97	1144.16
space group	$P2_1/n$ (No. 14)	$P2_12_12$ (No. 18)
a/Å	12.2931(3)	22.328(5)
b/Å	13.5101(3)	44.099(9)
c/Å	20.9793(5)	12.287(3)
β/deg	106.3070(10)	90
V/Å^3	3344.09(14)	12098(4)
Z	2	8
λ/Å	0.71073	0.71073
T/K	253 (2)	93 (2)
ρ_{calcd}/Mg m^{-3}	1.49	1.26
μ/mm^{-1}	1.52	1.11
R $[F_o^2 > 2\sigma(F_c^2)]^a$	0.0367	0.1210
R_w (all reflns)^b	0.0903^c	0.3239^d

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$. [c] $a = 0.0487$, $b = 0.4918$. [d] $a = 0.1899$, $b = 46.6033$.

Table 2. Bond Distances (Å) for $[SeV_3O_{11}]^{3-}$

Se(1)−O(1)	1.62(2)	Se(2)−O(12)	1.64(4)
Se(1)−O(8)	1.74(2)	Se(2)−O(19)	1.71(3)
Se(1)−O(11)	1.73(2)	Se(2)−O(22)	1.71(2)
V(1)−O(2)	1.65(2)	V(4)−O(13)	1.63(3)
V(1)−O(3)	1.63(2)	V(4)−O(14)	1.62(3)
V(1)−O(8)	1.89(2)	V(4)−O(19)	1.87(2)
V(1)−O(9)	1.79(2)	V(4)−O(20)	1.78(2)
V(2)−O(4)	1.65(2)	V(5)−O(15)	1.61(2)
V(2)−O(5)	1.65(3)	V(5)−O(16)	1.63(2)
V(2)−O(9)	1.81(2)	V(5)−O(20)	1.81(2)
V(2)−O(10)	1.81(2)	V(5)−O(21)	1.78(2)
V(3)−O(6)	1.64(3)	V(6)−O(17)	1.59(3)
V(3)−O(7)	1.62(2)	V(6)−O(18)	1.66(3)
V(3)−O(10)	1.78(2)	V(6)−O(21)	1.82(2)
V(3)−O(11)	1.89(2)	V(6)−O(22)	1.88(3)

Crystal Structure Determination. Rectangular crystals of $[(n\text{-}C_4H_9)_4N]_3[SeV_3O_{11}]\cdot 0.5H_2O$ used for structural analysis were prepared under a dry N_2 atmosphere by dissolving 0.10 g of the crude product in 0.25 mL of acetonitrile, adding toluene to the point of saturation (ca. 1.7 mL) with stirring, heating the mixture to make a clear solution, and then allowing it to stand at ambient temperature for 1 day. Block-shaped crystals of $[\{(C_6H_5)_3P\}_2N]_2[Se_2V_2O_{10}]$ used for the diffraction study were prepared by dissolving 0.014 g of the microcrystalline material in 0.5 mL of acetonitrile with heating and allowing the solution to stand at ambient temperature for 1 h. Diffraction data were collected on a Siemens Smart CCD diffractometer using Mo Kα radiation. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELX-97 program suite.[24] Atoms in the $[SeV_3O_{11}]^{3-}$ anions were refined anisotropically for $[(n\text{-}C_4H_9)_4N]_3[SeV_3O_{11}]\cdot 0.5H_2O$, and all non-hydrogen atoms were refined anisotropically for $[\{(C_6H_5)_3P\}_2N]_2[Se_2V_2O_{10}]$. Crystallographic parameters are summarized in Table 1. Selected bond distances for the $[SeV_3O_{11}]^{3-}$ and $[Se_2V_2O_{10}]^{2-}$ anions are listed in Tables 2 and 3.

Results

A dark red compound is obtained when $[(n\text{-}C_4H_9)_4N]VO_3$ is reacted with an equal amount of SeO_2 in acetonitrile at an ambient temperature. This very hygroscopic compound gives a single peak in the ^{51}V NMR spectrum at −547 ppm. Although

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Table 3. Bond Distances[a] (Å) for $[Se_2V_2O_{10}]^{2-}$

V−O(2)	1.612(3)	Se−O(1)	1.610(3)
V−O(3)	1.597(3)	Se−O(4)	1.736(3)
V−O(4)	1.847(3)	Se−O(5)^i	1.724(3)
V−O(5)	1.875(3)		

[a] Symmetry code: (i) −*x*, −*y*, −*z*.

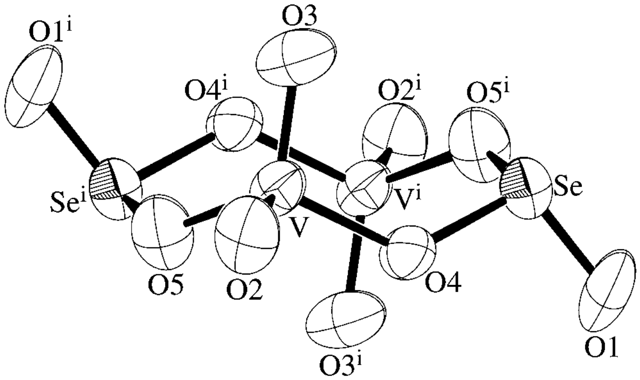

Figure 1. Perspective drawing of the $[Se_2V_2O_{10}]^{2-}$ anion. Displacement ellipsoids are scaled to enclose 50% probability levels. Atoms labeled with superscripted i are related to those without superscripts by the crystallographic inversion center at (0, 0, 0).

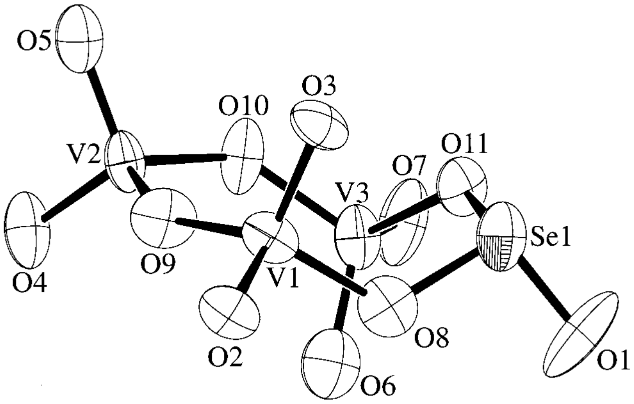

Figure 2. Perspective drawing of the $[SeV_3O_{11}]^{3-}$ anion. Displacement ellipsoids are scaled to enclose 50% probability levels.

this compound is too hygroscopic to be isolated in a form suitable for further characterization, it yields crystalline $[(C_6H_5)_4P]^+$ and $[\{(C_6H_5)_3P\}_2N]^+$ salts when reacted with $[(C_6H_5)_4P]Br$ and $[\{(C_6H_5)_3P\}_2N]Cl$. These salts also give a single peak at −547 ppm in their ^{51}V NMR spectra and analyze as $A_2[Se_2V_2O_{10}]$ (A = $[(C_6H_5)_4P]^+$ or $[\{(C_6H_5)_3P\}_2N]^+$). X-ray structural analysis of the $[\{(C_6H_5)_3P\}_2N]^+$ salt revealed that it is composed of the cations and discrete $[Se_2V_2O_{10}]^{2-}$ anions having the structure shown in Figure 1. The bond distances in the $[Se_2V_2O_{10}]^{2-}$ anion are listed in Table 3.

When $[(n\text{-}C_4H_9)_4N]VO_3$ is reacted with SeO_2 in a 3:1 molar ratio, on the other hand, a colorless compound is obtained. This compound gives two ^{51}V NMR peaks at −556 and −566 ppm in a 2:1 intensity ratio and analyzes as $[(n\text{-}C_4H_9)_4N]_3[SeV_3O_{11}]\cdot 0.5H_2O$ after crystallization from acetonitrile/diethyl ether. X-ray structural analysis revealed that an asymmetric unit of $[(n\text{-}C_4H_9)_4N]_3[SeV_3O_{11}]\cdot 0.5H_2O$ contains six $[(n\text{-}C_4H_9)_4N]^+$ cations, one water molecule, and two discrete $[SeV_3O_{11}]^{3-}$ anions having the structure shown in Figure 2. [Only one of the two crystallographically independent anions is shown. The structure of the other anion is depicted in Figure S1 (Supporting Information). There are no significant structural differences between these two anions.] The water molecule of crystallization is hydrogen-bonded to one of the anions [O23···O1, 2.71(8) Å; O23···O6, 2.86(8) Å]. The bond distances in the $[SeV_3O_{11}]^{3-}$ anion are listed in Table 2.

All ^{51}V, ^{77}Se, and ^{17}O NMR data for the $[SeV_3O_{11}]^{3-}$ and $[Se_2V_2O_{10}]^{2-}$ anions are consistent with the structures shown in Figures 1 and 2 and strongly suggest that these solid state structures are maintained in solution.

Discussion

The chemical equations for the formation of the $[SeV_3O_{11}]^{3-}$ and $[Se_2V_2O_{10}]^{2-}$ anions suggest that those reactions would not produce any byproducts and would proceed cleanly.

$$2VO_3^- + 2SeO_2 \rightarrow [Se_2V_2O_{10}]^{2-}$$

$$3VO_3^- + SeO_2 \rightarrow [SeV_3O_{11}]^{3-}$$

Indeed, those vanadoselenites form almost quantitatively. When $[(n\text{-}C_4H_9)_4N]VO_3$ and SeO_2 are mixed in a 1:1 molar ratio, the peak for $[Se_2V_2O_{10}]^{2-}$ is the only peak observed in the ^{51}V NMR spectrum of the reaction mixture. When [V]:[Se] = 3, only the $[SeV_3O_{11}]^{3-}$ peak is observed. Moreover, an equimolar mixture of VO_3^- and $[SeV_3O_{11}]^{3-}$ is obtained when [V]:[Se] = 4:1. Basically no peak other than those of VO_3^-, $[Se_2V_2O_{10}]^{2-}$, and $[SeV_3O_{11}]^{3-}$ is observed in the range [V]:[Se] ≥ 1. Something different occurs, however, if the relative amount of Se is increased beyond [V]:[Se] = 1. At [V]:[Se] = 1:3 the dark red mixture gives a single broad ^{51}V NMR peak at −528 ppm ($\Delta\nu_{1/2}$ = 2200 Hz). The compound in this mixture has so far evaded our effort for further characterization.

Both $[SeV_3O_{11}]^{3-}$ and $[Se_2V_2O_{10}]^{2-}$ anions are composed of tetrahedral VO_4 and trigonal pyramidal SeO_3 units that share vertices to form ring structures (Figures 1 and 2). In $[Se_2V_2O_{10}]^{2-}$ V tetrahedra and Se trigonal pyramids connect alternately in a centrosymmetric manner to complete a $Se_2V_2O_4$ ring. The conformation of this ring can be loosely classified as twisted-chair (TC), although it lacks a 2-fold rotation symmetry and a mirror plane necessary for an ideal TC.[25−27] The anion is located on a crystallographic inversion center and thus has a rigorous $\bar{1}$ symmetry. One of the SeO_3 trigonal pyramids in this ring is substituted with a VO_4 tetrahedron in the $[SeV_3O_{11}]^{3-}$ structure. This substitution results in a loss of the center of symmetry, and $[SeV_3O_{11}]^{3-}$ has a chiral structure. Both of the two crystallographically independent anions in $[(n\text{-}C_4H_9)_4N]_3[SeV_3O_{11}]\cdot 0.5H_2O$ are of the same enantiomorph. The other enantiomorph can easily be obtained with a slight conformational change of the eight-membered SeV_3O_4 ring. The irregular structure of the SeV_3O_4 ring in $[SeV_3O_{11}]^{3-}$ can be attributed to the cooperative conformational change associated with the accommodation of a larger VO_4 unit in place of the SeO_3 unit.

Tetrahedral VO_4 units are rare for polyvanadate structures,[15,16,20,23,28,29] and the current anions are the first examples of a heteropolyvanadate that is exclusively made up of such units to our knowledge. The $Se_2V_2O_4$ ring found in the $[Se_2V_2O_{10}]^{2-}$ structure has been observed for $VOSeO_3\cdot H_2O$[30] and $(VO)_2(SeO_3)_3$[31] as a building unit of infinite structures.

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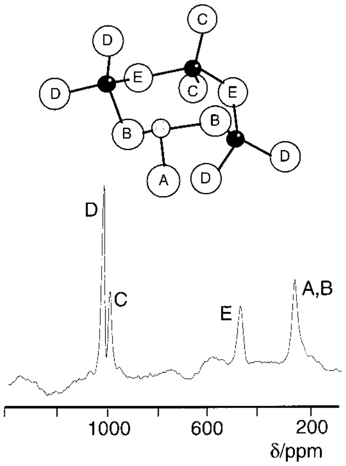

Figure 3. Schematic drawing of the $[SeV_3O_{11}]^{3-}$ anion (top) and its ^{17}O NMR spectrum in acetonitrile (bottom).

However, the V atoms are in the IV oxidation state in these compounds. The compound $CsVSeO_5$ has the same composition as the salts of $[Se_2V_2O_{10}]^{2-}$,[32] but this hydrothermally synthesized compound has an infinite layer structure that has little resemblance to that of $[Se_2V_2O_{10}]^{2-}$. The compound that is most closely related to $[Se_2V_2O_{10}]^{2-}$ from the structural point of view is $S_2V_2O_{10}(OH_2)_6$,[33] although here the V atoms are in the IV oxidation state and octahedral and the ring structure is completed by tetrahedral SO_4 units instead of trigonal pyramidal SeO_3 units. Still $S_2V_2O_{10}(OH_2)_6$ is molecular and has a discrete structure. It also has a $\bar{1}$ symmetry, and its $S_2V_2O_4$ ring has a conformation very similar to that of the $Se_2V_2O_4$ ring in $[Se_2V_2O_{10}]^{2-}$.

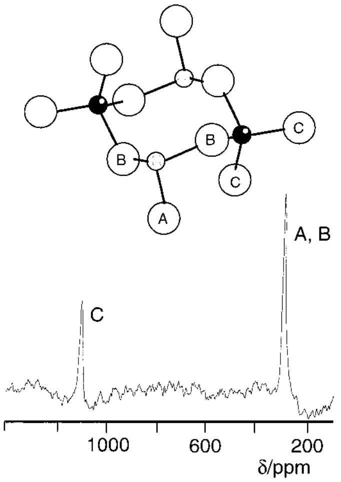

Figure 4. Schematic drawing of the $[Se_2V_2O_{10}]^{2-}$ anion (top) and its ^{17}O NMR spectrum in acetonitrile (bottom).

Both $[SeV_3O_{11}]^{3-}$ and $[Se_2V_2O_{10}]^{2-}$ anions give NMR spectra consistent with the ring structure mentioned above. The anion $[SeV_3O_{11}]^{3-}$ gives two ^{51}V NMR peaks in a 2:1 intensity ratio that are assignable to the two V atoms that sandwich the SeO_3 unit (−556 ppm) and the unique V atom that is sandwiched between two VO_4 units (−566 ppm). This anion gives a single ^{77}Se NMR peak at 71.9 ppm. Its ^{17}O NMR is given in Figure 3 together with the assignments. The assignments have been made according to the peak intensities and the known correlation between ^{17}O NMR chemical shifts and metal−oxygen bond lengths.[34] The oxygens A and B give a single peak. The chemical shift difference of the oxygens bound to Se seems to be small. This is in agreement with the general observation that the heavier main group elements yield only a limited range of ^{17}O chemical shifts.[35−37] The anion $[Se_2V_2O_{10}]^{2-}$ gives a single peak in both ^{51}V (−547 ppm) and ^{77}Se (66.7 ppm) NMR spectra. Its ^{17}O NMR spectrum is shown in Figure 4. Here again the oxygens bound to Se give an unresolved single peak.

The isolation of two anions with the general formula $[Se_xV_{4-x}O_{12-x}]^{(4-x)-}$ ($x = 1, 2$) implies the existence of yet another compound, $[Se_3VO_9]^-$. However, our search for such an anion is so far unsuccessful.

Supporting Information Available: X-ray crystallographic files in CIF format for the structures of $[(n\text{-}C_4H_9)_4N]_3[SeV_3O_{11}]\cdot 0.5H_2O$ and $[\{(C_6H_5)_3P\}_2N]_2[Se_2V_2O_{10}]$, structure of the $[SeV_3O_{11}]^{3-}$ anion that is crystallographically independent of that shown in Figure 2 (Figure 1S), and packing diagrams for $[(n\text{-}C_4H_9)_4N]_3[SeV_3O_{11}]\cdot 0.5H_2O$ and $[\{(C_6H_5)_3P\}_2N]_2[Se_2V_2O_{10}]$ (Figures 2S and 3S). This material is available free of charge via the Internet at http://pubs.acs.org.

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