

## Organically Templated Vanadyl Selenites with Layered Structures

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Two layered vanadyl selenites with the compositions,  $[\text{DABCOH}_2]_{0.5}[(\text{V}^{\text{IV}}\text{O})(\text{HSeO}_3)(\text{SeO}_3)] \cdot \text{H}_2\text{O}$ , **I**, and  $[\text{enH}_2][(\text{V}^{\text{IV}}\text{O})_2(\text{V}^{\text{V}}\text{O})\text{O}_2(\text{SeO}_3)_3] \cdot 1.25\text{H}_2\text{O}$ , **II**, have been prepared by the reaction of  $\text{NaVO}_3$  with  $\text{SeO}_2$  or  $\text{H}_2\text{SeO}_4$  under hydrothermal conditions in the presence of organic amines. Crystal data: **I**, orthorhombic, space group *Pbcn* (No. 60),  $a = 6.3152(3)$  Å,  $b = 18.1918(8)$  Å,  $c = 17.7172(8)$  Å,  $V = 2035.4(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $R_1(\text{all data}) = 0.0368$ ; **II**, triclinic, space group  $\bar{P}1$  (No. 2),  $a = 6.3406(2)$  Å,  $b = 10.2085(3)$  Å,  $c = 13.2551(10)$  Å,  $\alpha = 101.238(2)^\circ$ ,  $\beta = 96.503(2)^\circ$ ,  $\gamma = 104.332(2)^\circ$ ,  $V = 803.47(4)$  Å<sup>3</sup>,  $Z = 2$ ,  $R_1(\text{all data}) = 0.0814$ . While **I** contains the ladder motif, commonly found in open-framework metal phosphates, **II** is formed by a secondary building unit composed of a  $\text{V}_4\text{O}_{18}$  cluster along with  $\text{SeO}_3$  and  $\text{VO}_5$  groups. The study demonstrates that the selenite unit can be fruitfully exploited to design interesting open-framework structures.

## Introduction

Although a majority of the inorganic open-framework structures reported in the literature are silicates,<sup>1</sup> phosphates,<sup>2</sup> or carboxylates,<sup>3</sup> there have been recent efforts to synthesize open-framework structures using other anionic units. We have been trying to design inorganic open architectures making use of sulfate, selenite, selenate, and such oxy-anions. Thus, interesting open-framework cadmium and iron sulfates have been prepared in this laboratory.<sup>4</sup> In the case of selenites, the first organically templated zinc selenite with a layered structure,  $(\text{CN}_3\text{H}_6)_4[\text{Zn}_3(\text{SeO}_3)_5]$ , was reported by Harrison et al.<sup>5</sup> Choudhury et al.<sup>6</sup> have reported the first three-dimensional organically templated iron(III) selenite,

$(\text{C}_4\text{N}_2\text{H}_{12})_{0.5}[\text{Fe}_2\text{F}_3(\text{SeO}_3)_2]$ , and an organically pillared zinc selenite,  $[\text{C}_2\text{N}_2\text{H}_8]_{0.5}(\text{ZnSeO}_3)$ . Our interest in the selenite-based frameworks was concerned with the possible role of the lone pair of electrons as an invisible structure-directing agent. The stereochemically active lone pair of electrons in Se(IV) generally leads to a pyramidal coordination for the selenite species. It was hoped that this may cause the selenites to crystallize in a noncentrosymmetric structure possessing interesting physical properties such as nonlinear optical second harmonic generation (SHG).<sup>7</sup> Open framework structures having a lone pair of electrons on the metal ion have been synthesized recently in the case of Sn(II)<sup>8</sup> and Sb(III)<sup>9</sup> phosphates. In this article, we report the synthesis and characterization of two new layered vanadyl selenites  $[\text{DABCOH}_2]_{0.5}[(\text{V}^{\text{IV}}\text{O})(\text{HSeO}_3)(\text{SeO}_3)] \cdot \text{H}_2\text{O}$ , **I**, and  $[\text{enH}_2][(\text{V}^{\text{IV}}\text{O})_2(\text{V}^{\text{V}}\text{O})\text{O}_2(\text{SeO}_3)_3] \cdot 1.25\text{H}_2\text{O}$ , **II**, synthesized by the reaction of  $\text{NaVO}_3$  with  $\text{H}_2\text{SeO}_4$  or  $\text{SeO}_2$  in the presence of organic amines under hydrothermal conditions. A few dense vanadium selenite structures have been reported in the literature,<sup>10</sup> among which the 2D-layered structures related to hexagonal tungsten oxide are noteworthy.<sup>10a–c</sup> The first

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coordination-complex-linked vanadium selenite,  $[\text{Cu}(\text{Phen})_2\text{V}_2\text{Se}_2\text{O}_{11}]^{11a}$  and an organo-templated molecular vanado selenite have been reported recently.<sup>11b</sup> Compounds **I** and **II**, however, are the first examples of organically templated vanadyl selenites with an extended structure, belonging to the new family of open-framework selenites.

## Experimental Section

**Synthesis and Initial Characterization.** Compounds **I** and **II** were synthesized by the hydrothermal method in the presence of organic amines. Synthesis of open-framework transition metal selenites using primary amines as templates is difficult because of the low reduction potential of the  $\text{Se}^{\text{IV}}/\text{Se}^0$  couple and the reducing atmosphere created by the amine under hydrothermal conditions. Attempts to employ the fluoride route to stabilize the higher oxidation state of the metal were not successful. The primary amines were better reducing agents ( $\text{Se}^{4+}$  to  $\text{Se}$ ) than the secondary amines which in turn are better reducing agents than the tertiary amines. A judicious choice of the amine and the synthetic conditions has enabled us to synthesize **I** and **II**. We have used a tertiary amine to decrease the possibility of reduction in the case of **I**. For compound **II**, we controlled the reaction kinetically by terminating it after a short period of time.

In a typical synthesis of **I**, 0.1462 g of  $\text{NaVO}_3$  was dispersed in 5.4 mL of deionized water. To this were added 1.28 mL of selenic acid (40 wt %), 0.08 mL of morpholine, and 0.1121 g of DABCO (1,4-diazabicyclooctane) one after the another with continuous stirring. The resulting mixture with the final molar ratio  $1.2\text{NaVO}_3/5\text{H}_2\text{SeO}_4/\text{C}_4\text{H}_9\text{NO}/\text{DABCO}/300\text{H}_2\text{O}$  was homogenized for ~30 min, transferred in to a PTFE-lined stainless steel autoclave, and heated at 150 °C for 3 days. Plenty of pale green rodlike crystals were obtained by this means. The pure phase of **I** in the powdered form could also be obtained without using morpholine, by starting with a mixture of the composition  $\text{NaVO}_3/4\text{H}_2\text{SeO}_4/\text{DABCO}/300\text{H}_2\text{O}$  at 150 °C for 3 days. For the synthesis of **II**, hydrothermal reactions were carried out at 150 °C for 20 h (or 180 °C for 4 h) starting with the following composition,  $\text{NaVO}_3$  (0.1219 g, 1 mmol)/ $6\text{SeO}_2$  (0.6657 g, 6 mmol)/en (0.06 mL, 1 mmol)/ $278\text{H}_2\text{O}$  (5 mL, 278 mmol) (en = ethylenediamine). The product contained a large number of dark green platelike crystals. Heating at 180 °C beyond 4 h yielded a different phase along with selenium metal. The products were dried at ambient conditions and used for further study. The yields of **I** and **II** were 56% and 49%, respectively, based on vanadium. Initial characterization of both **I** and **II** was carried out by powder X-ray diffraction (PXRD), energy dispersion analysis of X-rays (EDAX), and IR spectroscopy. The PXRDs of compounds **I** and **II** immediately revealed that these are new phases. EDAX indicated that the ratios of V and Se are 1:2 and 1:1 in **I** and **II**, respectively, and also precluded the presence of Na in the sample. The compounds gave satisfactory elemental analysis. The experi-

**Table 1.** Crystal Data and Structure Refinement Parameters for **I** and **II**

structural param	<b>I</b>	<b>II</b>
empirical formula	$\text{C}_3\text{H}_{10}\text{NO}_8\text{Se}_2\text{V}$	$\text{C}_2\text{H}_{10}\text{N}_2\text{O}_{15.25}\text{Se}_3\text{V}_3$
cryst syst	orthorhombic	triclinic
space group	<i>Pbcn</i> (No. 60)	<i>P1</i> (No. 2)
<i>a</i> (Å)	6.3152(3)	6.3406 (2)
<i>b</i> (Å)	18.1918(8)	10.2085 (3)
<i>c</i> (Å)	17.7172(8)	13.2551 (10)
$\alpha$	90°	101.238 (2)°
$\beta$	90°	96.503 (2)°
$\gamma$	90°	104.332(2)°
<i>V</i> (Å <sup>3</sup> )	2035.4(2)	803.47 (4)
<i>Z</i>	8	2
formula mass	396.98	695.82
$\rho_{\text{obsd}}$ (g cm <sup>-3</sup> )	0.000	0.000
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	2.591	2.876
$\mu$ (cm <sup>-1</sup> )	81.52	85.86
<i>T</i> (K)	293(2)	293(2)
$\lambda$ (Å)	0.71073	0.71073
<i>R</i> <sub>int</sub>	0.0470	0.0500
<i>R</i> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0274, w <i>R</i> 2 = 0.0583	<i>R</i> 1 = 0.0532, w <i>R</i> 2 = 0.1171
<i>R</i> (all data)	<i>R</i> 1 = 0.0368, <sup>a</sup> w <i>R</i> 2 = 0.0619 <sup>b</sup>	<i>R</i> 1 = 0.0814, <sup>a</sup> w <i>R</i> 2 = 0.1288 <sup>b</sup>

<sup>a</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $wR2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ ,  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$  where  $P = [F_o^2 + 2F_c^2] / 3$ ;  $a = 0.0226$  and  $b = 5.9637$  for **I**,  $a = 0.0484$  and  $b = 0.0$  for **II**.

mental and calculated (in wt %) values for C, H, and N follow. Anal. Found for **I**: C, 8.75; N, 3.29; H, 2.26. Calcd: C, 9.06; N, 3.52; H, 2.52. Anal. Found for **II**: C, 3.37; N, 3.50; H, 1.65. Calcd: C, 3.45; N, 4.02; H, 1.43.

**Single-Crystal Structure Determination.** A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued to a thin glass fiber with cyanoacrylate (super glue) adhesive. Single-crystal structure determination by X-ray diffraction was performed on a Siemens smart-CCD diffractometer equipped with a normal focus, 2.4 kw sealed tube X-ray source (Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å) operating at 50 kV and 40 mA. A hemisphere of intensity data was collected at room temperature in 1321 frames with  $\omega$  scans (width of 0.30° and exposure time of 20 s per frame) in the  $2\theta$  range 3–46.5°. The structure was solved by direct methods using SHELXS-86<sup>12</sup> and difference Fourier synthesis. An empirical absorption correction based on symmetry equivalent reflections was applied for both the compounds using the SADABS program.<sup>13</sup> All the hydrogen positions were initially located in the difference Fourier maps, and for the final refinement, the hydrogen atoms were placed geometrically and held in the riding mode. However, hydrogen positions for the extra framework water (O10) for **I** have not been included in the final refinement because of disorder in that site [O(10) with SOF = 0.3 and O(10A) with SOF = 0.7]. On the other hand, hydrogen positions for the extra framework water molecules (O<sub>100</sub>, O<sub>200</sub>) for **II** were also not included in the final refinement as they were unstable during the refinement cycles in spite of soft constraints for the distances and angles. The last cycle of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares structure refinement against  $|F^2|$  was carried out using SHELXTL-PLUS<sup>14</sup> package of programs. Details

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**Table 2.** Selected Bond Distances and Angles for [DABCOH<sub>2</sub>]<sub>0.5</sub>[(V<sup>IV</sup>O)(HS<sub>2</sub>O<sub>3</sub>)(SeO<sub>3</sub>)<sub>2</sub>]<sub>2</sub>·H<sub>2</sub>O, **I**

moiety	distance (Å)	moiety	angle (deg)	moiety	angle (deg)
Se(1)–O(1)	1.657(3)	O(1)–Se(1)–O(2)	101.1(2)	O(2)–V(1)–O(6) <sup>#2a</sup>	161.71(14)
Se(1)–O(2)	1.706(3)	O(1)–Se(1)–O(3)	100.2(2)	O(5)–V(1)–O(6) <sup>#2</sup>	89.86(14)
Se(1)–O(3)	1.765(4)	O(2)–Se(1)–O(3)	96.3(2)	O(7)–V(1)–O(1) <sup>#3</sup>	174.8(2)
Se(2)–O(4)	1.681(3)	O(4)–Se(2)–O(5)	99.8(2)	O(4) <sup>#1</sup> –V(1)–O(1) <sup>#3</sup>	82.8(2)
Se(2)–O(5)	1.689(3)	O(4)–Se(2)–O(6)	102.8(2)	O(2)–V(1)–O(1) <sup>#3</sup>	83.30(13)
Se(2)–O(6)	1.727(3)	O(5)–Se(2)–O(6)	101.9(2)	O(5)–V(1)–O(1) <sup>#3</sup>	80.93(14)
V(1)–O(7)	1.608(4)	O(7)–V(1)–O(4) <sup>#1</sup>	100.5(2)	O(6) <sup>#2</sup> –V(1)–O(1) <sup>#3</sup>	78.48(13)
V(1)–O(4) <sup>#1</sup>	1.990(4)	O(7)–V(1)–O(2)	100.8(2)	Se(1)–O(1)–V(1) <sup>#3</sup>	114.2(2)
V(1)–O(2)	2.022(3)	O(4) <sup>#1</sup> –V(1)–O(2)	85.92(14)	Se(1)–O(2)–V(1)	122.3(2)
V(1)–O(5)	2.032(3)	O(7)–V(1)–O(5)	96.2(2)	Se(1)–O(3)–H(8)	109.47(13)
V(1)–O(6) <sup>#2</sup>	2.034(3)	O(4) <sup>#1</sup> –V(1)–O(5)	162.5(2)	Se(2)–O(4)–V(1) <sup>#4</sup>	139.0(2)
V(1)–O(1) <sup>#3</sup>	2.277(3)	O(2)–V(1)–O(5)	85.72(14)	Se(2)–O(5)–V(1)	120.6(2)
		O(7)–V(1)–O(6) <sup>#2</sup>	97.3(2)	Se(2)–O(6)–V(1) <sup>#5</sup>	116.8(2)
		O(4) <sup>#1</sup> –V(1)–O(6) <sup>#2</sup>	93.3(2)		
		Organic Moiety			
N(1)–C(2)	1.486(7)	C(2)–N(1)–C(3)	110.0(5)		
N(1)–C(3)	1.490(7)	C(2)–N(1)–C(1)	109.7(4)		
N(1)–C(1)	1.491(7)	C(3)–N(1)–C(1)	110.2(5)		
C(1)–C(2) <sup>#6</sup>	1.531(8)	N(1)–C(1)–C(2) <sup>#6</sup>	108.2(5)		
C(3)–C(3) <sup>#6</sup>	1.496(11)	N(1)–C(2)–C(1) <sup>#6</sup>	108.9(4)		
		N(1)–C(3)–C(3) <sup>#6</sup>	109.2(3)		

<sup>a</sup> Symmetry operations used to generate equivalent atoms: #1  $x + 1, y, z$ ; #2  $x + 1/2, -y + 3/2, -z + 1$ ; #3  $-x, -y + 1, -z + 1$ ; #4  $x - 1, y, z$ ; #5  $x - 1/2, -y + 3/2, -z + 1$ ; #6  $-x - 1, y, -z + 1/2$ .

**Table 3.** Selected Bond Distances and Angles for Compound **II**, [enH<sub>2</sub>][(V<sup>IV</sup>O)(V<sup>VO</sup>O)<sub>2</sub>(SeO<sub>3</sub>)<sub>3</sub>]<sub>2</sub>·1.25H<sub>2</sub>O

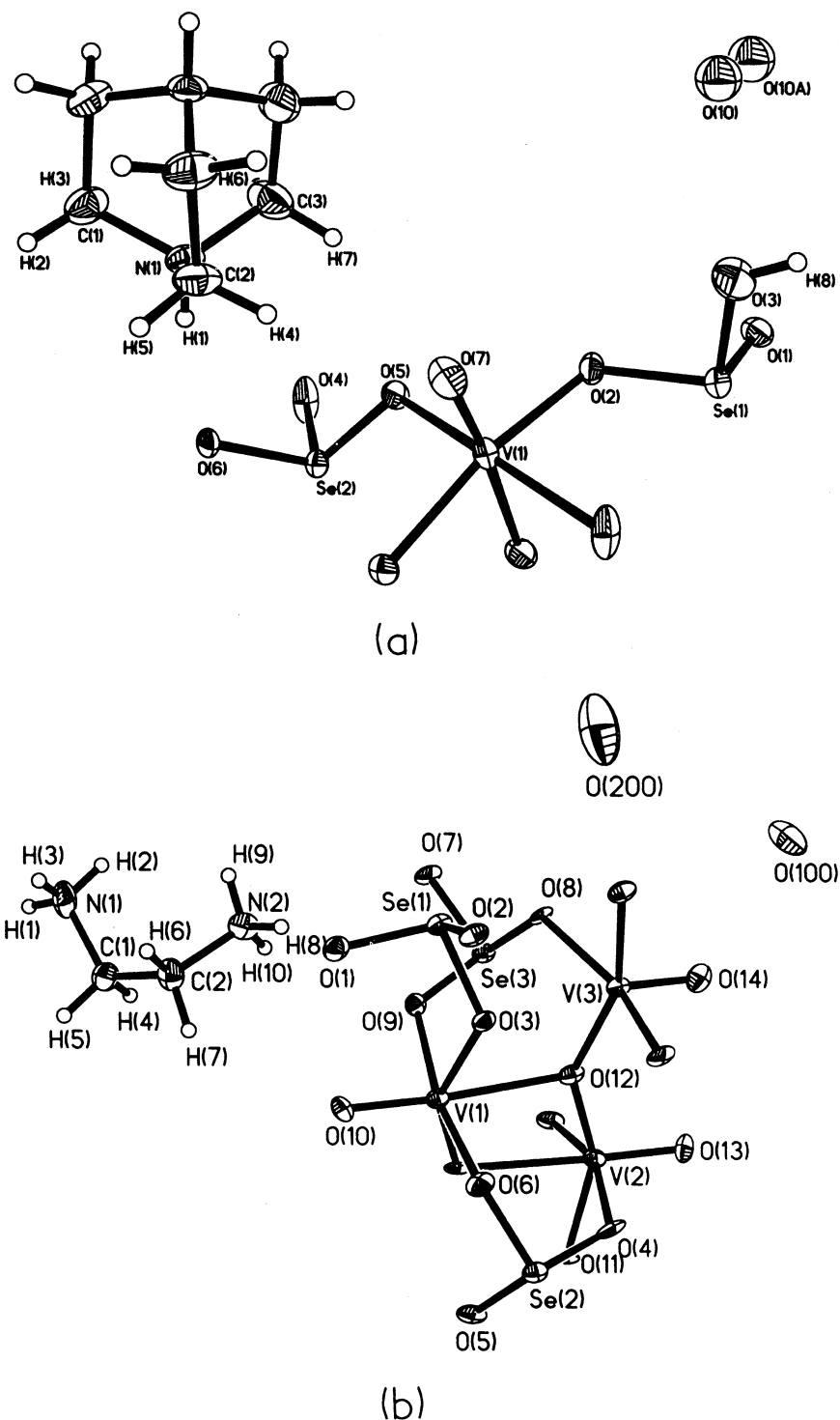
moiety	distance (Å)	moiety	angle (deg)	moiety	angle (deg)
Se(1)–O(1)	1.673(7)	O(1)–Se(1)–O(2)	101.0(4)	O(11)–V(2)–O(4)	80.4(3)
Se(1)–O(2)	1.730(7)	O(1)–Se(1)–O(3)	101.8(4)	O(5) <sup>#1</sup> –V(2)–O(4) <sup>a</sup>	159.2(3)
Se(1)–O(3)	1.756(7)	O(2)–Se(1)–O(3)	94.5(3)	O(13)–V(2)–O(11) <sup>#1</sup>	177.8(3)
Se(2)–O(4)	1.700(8)	O(4)–Se(2)–O(5)	105.2(4)	O(12)–V(2)–O(11) <sup>#1</sup>	74.1(3)
Se(2)–O(5)	1.704(7)	O(4)–Se(2)–O(6)	101.2(4)	O(11)–V(2)–O(11) <sup>#1</sup>	76.6(3)
Se(2)–O(6)	1.717(7)	O(5)–Se(2)–O(6)	103.7(4)	O(5) <sup>#1</sup> –V(2)–O(11) <sup>#1</sup>	80.9(3)
Se(3)–O(7)	1.684(7)	O(7)–Se(3)–O(8)	99.7(3)	O(4)–V(2)–O(11) <sup>#1</sup>	84.1(3)
Se(3)–O(8)	1.693(7)	O(7)–Se(3)–O(9)	97.5(4)	O(14)–V(3)–O(12)	99.7(4)
Se(3)–O(9)	1.707(7)	O(8)–Se(3)–O(9)	101.3(4)	O(14)–V(3)–O(7) <sup>#2</sup>	100.4(4)
V(1)–O(10)	1.596(7)	O(10)–V(1)–O(11) <sup>#1</sup>	105.7(4)	O(12)–V(3)–O(7) <sup>#2</sup>	95.3(3)
V(1)–O(11) <sup>#1</sup>	1.746(7)	O(10)–V(1)–O(9)	92.5(4)	O(14)–V(3)–O(2) <sup>#3</sup>	104.1(4)
V(1)–O(9)	1.977(7)	O(11) <sup>#1</sup> –V(1)–O(9)	99.3(3)	O(12)–V(3)–O(2) <sup>#3</sup>	155.9(3)
V(1)–O(3)	1.988(7)	O(10)–V(1)–O(3)	106.2(4)	O(7) <sup>#2</sup> –V(3)–O(2) <sup>#3</sup>	84.2(3)
V(1)–O(6)	1.991(8)	O(11) <sup>#1</sup> –V(1)–O(3)	147.1(3)	O(14)–V(3)–O(8)	102.9(4)
V(1)–O(12)	2.376(8)	O(9)–V(1)–O(3)	87.1(3)	O(12)–V(3)–O(8)	87.1(3)
V(2)–O(13)	1.599(7)	O(10)–V(1)–O(6)	95.8(4)	O(7) <sup>#2</sup> –V(3)–O(8)	155.8(3)
V(2)–O(12)	1.775(7)	O(11) <sup>#1</sup> –V(1)–O(6)	87.5(3)	O(2) <sup>#3</sup> –V(3)–O(8)	83.9(3)
V(2)–O(11)	1.953(7)	O(9)–V(1)–O(6)	167.6(3)	Se(1)–O(2)–V(3) <sup>#3</sup>	122.4(4)
V(2)–O(5) <sup>#1</sup>	1.978(8)	O(3)–V(1)–O(6)	81.6(3)	Se(1)–O(3)–V(1)	128.3(4)
V(2)–O(4)	1.993(8)	O(10)–V(1)–O(12)	174.6(3)	Se(2)–O(4)–V(2)	126.6(4)
V(2)–O(11) <sup>#1</sup>	2.376(8)	O(11) <sup>#1</sup> –V(1)–O(12)	74.6(3)	Se(2)–O(5)–V(2) <sup>#1</sup>	130.4(4)
V(3)–O(14)	1.601(8)	O(9)–V(1)–O(12)	82.2(3)	Se(2)–O(6)–V(1)	124.9(4)
V(3)–O(12)	1.916(7)	O(3)–V(1)–O(12)	74.5(3)	Se(3)–O(7)–V(3) <sup>#4</sup>	138.7(5)
V(3)–O(7) <sup>#2</sup>	1.980(7)	O(6)–V(1)–O(12)	89.7(3)	Se(3)–O(8)–V(3)	121.2(4)
V(3)–O(2) <sup>#3</sup>	1.996(7)	O(13)–V(2)–O(12)	103.8(4)	Se(3)–O(9)–V(1)	125.8(4)
V(3)–O(8)	2.001(7)	O(13)–V(2)–O(11)	105.6(4)	V(1) <sup>#1</sup> –O(11)–V(2)	145.8(5)
		O(12)–V(2)–O(11)	150.1(4)	V(1) <sup>#1</sup> –O(11)–V(2) <sup>#1</sup>	105.1(3)
		O(13)–V(2)–O(5) <sup>#1</sup>	98.9(4)	V(2)–O(11)–V(2) <sup>#1</sup>	103.4(3)
		O(12)–V(2)–O(5) <sup>#1</sup>	98.6(3)	V(2)–O(12)–V(3)	143.5(4)
		O(11)–V(2)–O(5) <sup>#1</sup>	82.2(3)	V(2)–O(12)–V(1)	104.1(3)
		O(13)–V(2)–O(4)	96.7(4)	V(3)–O(12)–V(1)	109.6(3)
		O(12)–V(2)–O(4)	91.0(3)		

<sup>a</sup> Symmetry transformations used to generate equivalent atoms: #1  $-x + 1, -y + 1, -z + 1$ ; #2  $x + 1, y, z$ ; #3  $-x + 1, -y + 1, -z + 1$ ; #4  $x - 1, y, z$ .

of the structure determination and final refinements are listed in Table 1. The selected bond distances and bond angles for **I** and **II** are given in Tables 2 and 3, respectively. The powder X-ray diffraction patterns for both the compounds are in good agreement with the simulated patterns generated from the single-crystal XRD data.

(14) Sheldrick, G. M. *SHELXS-93 Program for Crystal Structure Solution and Refinement*; University of Gottingen: Gottingen, Germany, 1993.

Infrared spectra of pure samples of both **I** and **II** were recorded with KBr pellets in the frequency range 400–4000 cm<sup>-1</sup>. The spectra showed characteristic absorption bands. Besides the bands due to amine and water in the range 2462–3520 cm<sup>-1</sup>, the IR spectrum of **I** showed peaks at 950 cm<sup>-1</sup> due to the stretching mode of the selenite, at 844 and 806 cm<sup>-1</sup> due to symmetric stretching of VO<sub>6</sub>, and at 655 and 736 cm<sup>-1</sup> due to asymmetric stretching of VO<sub>6</sub>. Peaks at 479 and 528 cm<sup>-1</sup> could be assigned for bending



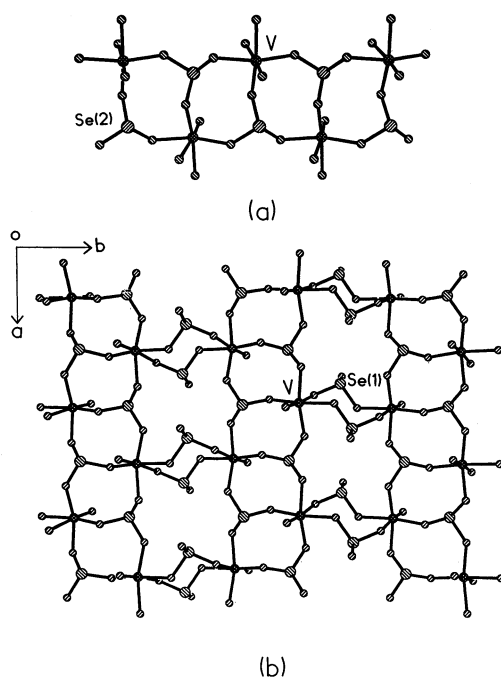
**Figure 1.** ORTEP plots of (a) **I**,  $[\text{DABCOH}_2]_{0.5}[(\text{V}^{\text{IV}}\text{O})(\text{HSeO}_3)(\text{SeO}_3)] \cdot \text{H}_2\text{O}$ , and (b) **II**,  $[\text{enH}_2][(\text{V}^{\text{IV}}\text{O})_2(\text{V}^{\text{VO}}\text{O})_2(\text{SeO}_3)_3] \cdot 1.25\text{H}_2\text{O}$ . Thermal ellipsoids are given at 50% probability.

modes of the selenite. For **II**, the IR spectra bands will be assigned as follows:  $2554\text{--}3631\text{ cm}^{-1}$  due to amine and water,  $1622\text{ cm}^{-1}$  due to bending mode of OH group,  $972\text{ cm}^{-1}$  due to the selenite,  $619\text{--}818\text{ cm}^{-1}$  due to vanadium polyhedra, and in the range  $418\text{--}525\text{ cm}^{-1}$  due to bending mode of the selenite.

## Results and Discussion

$[\text{DABCOH}_2]_{0.5}[(\text{V}^{\text{IV}}\text{O})(\text{HSeO}_3)(\text{SeO}_3)] \cdot \text{H}_2\text{O}$ , **I**. The asymmetric unit of **I** consists of 16 non-hydrogen atoms, which

include one vanadium and two crystallographically distinct Se atoms as shown in Figure 1a. The vanadium atom is octahedrally coordinated by six oxygens, of which one occurs as terminal  $\text{V}=\text{O}$ , two make  $\text{V}-\text{O}-\text{Se}(1)$  linkages, and the remaining three form  $\text{V}-\text{O}-\text{Se}(2)$  linkages. The short  $\text{V}=\text{O}$  distance of  $1.608\text{ \AA}$  and the average  $\text{V}-\text{O}$  distance of  $1.99\text{ \AA}$  are in the known ranges for these distances.<sup>9</sup> The two Se atoms are tricoordinated by oxygen atoms. The three oxygens, around  $\text{Se}(2)$ , are connected to the neighboring  $\text{VO}_6$



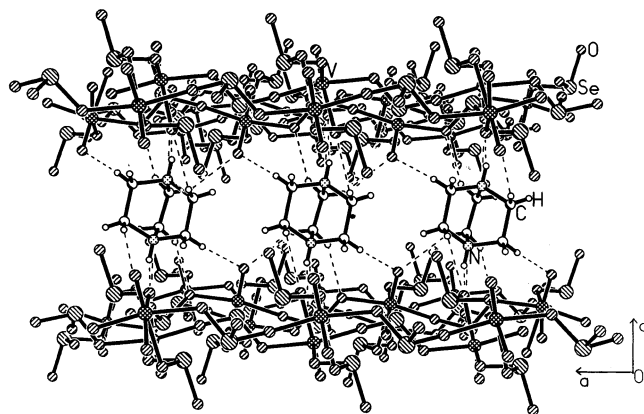
**Figure 2.** (a) Ladder unit in **I**, along the *a*-axis. (b) Extension of the ladders in **I** along the *b*-axis to form a layer in the *ab*-plane.

**Table 4.** Important Hydrogen Bonding Interactions in **I** and **II**

D—H···A	H···A	D···A	D—H···A
<b>I</b>			
N(1)—H(1)···O(6)	1.843(5)	2.732(5)	164.7(5)
O(3)—H(8)···O(10A)	2.072(8)	2.637(8)	125.7(6)
C(1)—H(2)···O(1)	2.568(6)	3.222(6)	124.8(5)
C(1)—H(3)···O(7)	2.579(7)	3.320(7)	133.3(6)
C(2)—H(4)···O(7)	2.381(7)	3.343(7)	170.8(6)
C(2)—H(5)···O(1)	2.583(7)	3.270(7)	127.9(5)
C(2)—H(5)···O(10A)	2.524(15)	3.376(15)	146.7(6)
C(3)—H(6)···O(7)	2.516(7)	3.252(8)	132.6(5)
C(3)—H(7)···O(5)	2.384(6)	3.191(7)	140.3(6)
<b>II</b>			
N(1)—H(1)···O(13)	2.203(13)	2.987(13)	146.8(12)
N(1)—H(2)···O(1)	1.954(13)	2.770(13)	151.9(12)
N(1)—H(3)···O(14)	2.552(14)	2.958(14)	108.5(11)
N(1)—H(3)···O(100)	1.999(14)	2.766(14)	143.5(12)
N(2)—H(8)···O(10)	1.876(13)	2.733(13)	161.1(12)
N(2)—H(9)···O(2)	2.045(12)	2.8689(12)	153.5(11)
N(2)—H(10)···O(6)	2.033(12)	2.875(12)	157.5(11)
C(1)—H(4)···O(6)	2.576(16)	3.349(16)	136.7(13)
C(1)—H(5)···O(5)	2.502(16)	3.450(16)	165.9(13)

octahedra with an average bond angle of 125.4°. The stereochemically active lone pair of electrons on selenium occupies the tetrahedral site. In the case of Se(1), however, only two of the oxygens form such linkages while the third is protonated. The presence of a longer Se(1)—O(3) bond distance of 1.765 Å, the nature of the electron density near this oxygen in the difference Fourier map, as well as bond valence sum calculations support the presence of a terminal OH group. The average Se—O bond distance is 1.709 Å in the case of Se(1) and 1.699 Å in the case of Se(2). The important bond lengths and bond angles of **I** are given in Table 2.

The framework layer of **I** is built up of VO<sub>6</sub>, SeO<sub>3</sub>, and HSeO<sub>3</sub> units. All three oxygen atoms of Se(2)O<sub>3</sub> are shared by three neighboring vanadium—oxygen octahedra in such

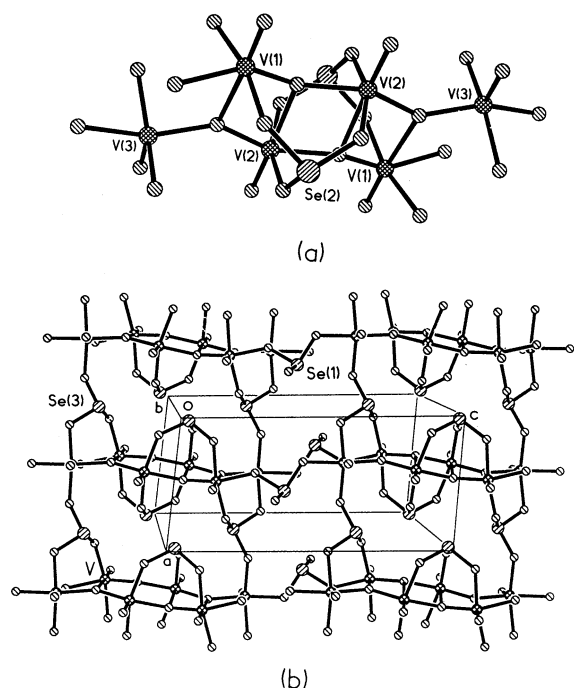


**Figure 3.** Alternate stacking of the inorganic and the organic layers in **I**. Dotted lines represent hydrogen bonding interactions.

a manner as to form a ladder consisting of edge-shared four-membered rings, each ring with two Se and two V atoms as shown in Figure 2a. These ladders are connected to one another by HSe(1)O<sub>3</sub> groups along the *b*-axis to form a layer in the *ab*-plane as shown in Figure 2b. This connectivity leads to the formation of an eight-membered bifurcated aperture with the dimensions 6.33 Å × 5.772 Å (the longest atom—atom distance, not including the van der Waals radii). The layers thus formed interact strongly with the organic layers composed of diprotonated DABCO and water molecules through hydrogen bonding. The important hydrogen bonding interactions in **I** and **II** are given in Table 4. The alternating organic and inorganic layers are stacked in an ABAB (and so forth) fashion as shown in Figure 3. Bond valence sum calculations<sup>15</sup> showed that both the V and Se atoms are in the +4 oxidation state, giving a framework a charge of −1, [(VO)(HSeO<sub>3</sub>)(SeO<sub>3</sub>)]<sup>−</sup>. The protonated amine compensates for the negative charge.

[enH<sub>2</sub>][[(V<sup>IV</sup>O)<sub>2</sub>(V<sup>V</sup>O)O<sub>2</sub>(SeO<sub>3</sub>)<sub>3</sub>]·1.25H<sub>2</sub>O, **II**. The asymmetric unit of **II** consists of 26 non-hydrogen atoms out of which 20 belong to the inorganic framework and 6 are extra framework atoms, as shown in Figure 1b. The inorganic framework contains three crystallographically distinct vanadium and three distinct selenium atoms. While V(1) and V(2) are octahedrally coordinated by six oxygen atoms, V(3) is five-coordinated. Each vanadium forms one terminal V=O with a shorter bond length. V(1) makes four V—O—V linkages through two tricoordinated oxygen atoms and three V—O—Se linkages with three distinct Se atoms. V(2) forms six V—O—V linkages through three tricoordinated O atoms and two V(2)—O—Se(2) linkages. V(3) forms two V—O—V linkages through one tricoordinated oxygen, two V(3)—O—Se(3) and one V(3)—O—Se(1) linkages. In the VO<sub>6</sub> octahedra, the long V—O bond distances are in the range 1.746–2.376 Å. In the case of the five-coordinated vanadium, the V—O distance is in the range 1.916–2.001 Å. Of the three distinct tricoordinated Se atoms, Se(2) and Se(3) form Se—O—V linkages whereas Se(1) forms two Se—O—V linkages, having a terminal oxygen. The terminal Se(1)—O(1) bond is comparatively short. No electron density was observed in the Fourier map for this oxygen, indicating that

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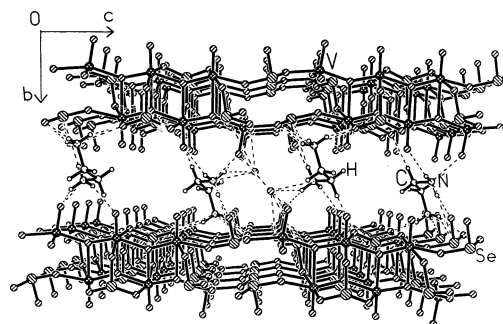


**Figure 4.** (a) Vanadium–oxygen metal cluster (SBU) in **II**. (b) Layer structure formed by the joining of the SBUs along the *a*-axis and the *c*-axis in **II**.

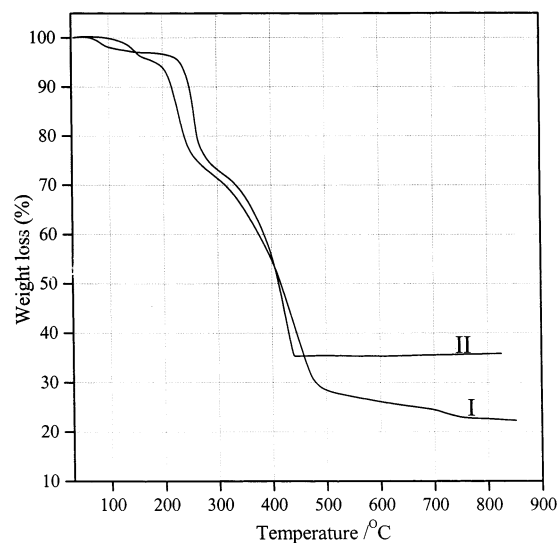
oxygen atom is not protonated. Bond lengths and angles of **II** are given in Table 3.

The framework in **II**,  $[(V^{IV}O)_2(V^VO)O_2(SeO_3)_3]^{-2}$ , is made up of  $VO_6$ ,  $VO_5$ , and  $SeO_3$  units. The four  $VO_6$  units belonging to the two distinct vanadiums share edges to form a  $V_4O_{18}$  cluster. The apical oxygens of the octahedra in the cluster are capped by Se(2) from either side. The two  $VO_5$  square pyramids are joined to this cluster from the two ends by sharing two tricoordinated corner oxygen atoms. The entire unit composed of two  $SeO_3$  groups, two  $VO_5$  groups, and one  $V_4O_{18}$  cluster can be considered as the secondary building unit (SBU). We show this SBU in Figure 4a. The SBUs run along the *c*-axis, connected by two  $Se(1)O_3$  groups to form a ribbon in this direction. This connectivity results in a six-membered ring with four vanadium and two Se atoms. The ribbons are joined together by  $Se(3)O_3$  groups along the *a*-axis to form a layer in the *ac*-plane as shown in Figure 4b. This creates an eight-membered aperture with six vanadium and two selenium atoms. The negative charge of the inorganic layer is compensated by the organic layer, comprising diprotonated ethylenediamine, which interacts through hydrogen bonding (Figure 5). Water molecules trapped between the inorganic layers interact with the amine through hydrogen bonding.

Thermogravimetric analysis (TGA) of **I** and **II** was carried out in  $O_2$  atmosphere from 30–900 °C at a heating rate of 5 °C/min, and the results are presented in Figure 6. TGA of **I** showed a weight loss of 4.5% at 152 °C corresponding to the loss of water (4.8% calcd). The second step at ~230 °C involves the loss of the amine (obsd, 21.3%; calcd, 23.3%). The decomposition of  $SeO_2$  starts at a higher temperature, which completes at around 440 °C with 55.4% weight loss. PXRD of a calcined sample indicated that  $V_3O_5$  (JCPDS 09-



**Figure 5.** Hydrogen bonding interactions between the protonated amine and the inorganic framework in **II**.



**Figure 6.** TGA curves of **I** and **II**.

0148) was left after heating to 900 °C. TGA of **II** also showed three steps with the weight losses of 3%, 22%, and 38% at 80, 257, and 422 °C corresponding to the loss of water, amine, and selenium dioxide, respectively. After heating to 900 °C,  $VO_2$  (JCPDS 44-0252) remained.

Compounds **I** and **II** have many interesting features besides being the first examples of organically templated vanadium selenites with an extended structure. Among the so far reported vanadium selenites,  $(NH_4)(VO_2)_3(SeO_3)_2$ ,<sup>10a</sup>  $AV_3Se_2O_{12}$  ( $A = K, Rb, Cs, NH_4$ ),<sup>10b</sup> and  $K(VO_2)_3(SeO_3)_2$ <sup>10c</sup> adopt the hexagonal tungsten bronze type layer structure in which  $VO_6$  octahedra share vertices resulting in six- and three-membered rings. The selenium caps three-membered rings through apical oxygens of three corner-shared vanadium octahedra.  $NH_4$  or  $A$  sits in six-membered rings. In  $KV_2SeO_7$ ,<sup>10e</sup> the  $VO_4$  tetrahedra, the  $VO_6$  octahedra, and the  $SeO_3$  pyramidal units share corners to form a double layer of  $[V_2SeO_7]^-$  which is stabilized by interlayer  $K^+$  ions. In the case of  $AVSeO_5$  ( $A = Rb, Cs$ ),<sup>10b</sup> alternating  $VO_5$  and  $SeO_3$  structural motifs form spires in all three directions. In  $K(VO)(SeO_3)_2H$ <sup>10f</sup> also, the selenite group acts as a bridge between two  $VO_5$  square pyramids to form a one-dimensional chain. Thus, the selenite group acts as either a capping motif as in 2D  $V-O-V-$  networks or as a bridge between two vanadium–oxygen polyhedra or  $V-O-V-O-$  infinite linkages. In the present study, the selenite group acts as the

bridge between the vanadium–oxygen polyhedra in **I** and plays both roles by capping and connecting  $V_4O_{18}$  clusters in **II**.

The ladder motif observed in **I** is similar to that commonly found in open-framework metal phosphates.<sup>16</sup> The ladder is considered to be a building unit in the phosphates, whose progressive building up process, from the one-dimensional structure to two- and three-dimensional complex structures has been demonstrated.<sup>17</sup> The structure of **I** is unique among the metal selenites and is comparable to that of the indium phosphate,  $[C_5H_5NH][In(HPO_4)_2]$ .<sup>18</sup> In the phosphate, ladders are made up of  $InO_6$  octahedra and  $HPO_4$  tetrahedra joined by  $H_2PO_4$  groups just as the  $HSeO_3$  groups in **I**. The main difference between the indium phosphate and **I** lies in the fact that in the former the sixth coordination site of In is satisfied by connection through oxygen to a pendant  $H_2PO_4$  group. In **I**, there is a terminal  $V=O$  group.

The metal–oxygen cluster in **II** is interesting. A similar cluster is known in piypite,  $K_4[Cu_4O_2](SO_4) \cdot MCl$  ( $M = Na$  or  $K$ ),<sup>19</sup> a sulfate ore. In piypite, a metal–oxygen cluster is formed by six copper and six oxygen atoms where copper is four-coordinated. Bond valence sum calculations on **II** indicate that V(1) and V(2) are in the +5 oxidation state and V(3) is in the +4 state.  $KV_2SeO_7$ , reported by Kwon et al.,<sup>10b</sup> also contains mixed-valent vanadium. In this compound,  $V^{4+}$  assumes octahedral geometry while  $V^{5+}$  assumes square pyramidal geometry. In **II**,  $V^{5+}$  is octahedral, and  $V^{4+}$  is square-pyramidal. Square pyramids with  $V^{4+}$  are known in phosphates (22% out of the 117 structures reviewed by Boudin et al.).<sup>20</sup>

Although the presence of a polar moiety is necessary, it is not a sufficient condition for a compound to crystallize in a noncentrosymmetric structure, because an antiparallel alignment can destroy it. In the present study, both the selenites are centric because of this reason. Interestingly, all the organically templated/pillared selenites reported to date<sup>5,6,21</sup> adopt centrosymmetric structures. It is also possible that the protonated amine also affects the structure of the compound and compensates for the effect of the selenium lone pair.

We have carried out magnetic measurements on both **I** and **II**. Both the selenites are paramagnetic obeying the Curie law. The magnetic moments of vanadium in **I** and **II** are 1.65 and 1.58  $\mu_B$ , indicating that **II** is mixed valent.

## Conclusions

The first two organically templated open-framework vanadium selenites with an infinite structure have been synthesized by the hydrothermal method. These selenites with layer structures exhibit interesting structural features, the presence of the ladder motif being one of them. The present study suggests the possibility of building up other novel open-framework structures making use of selenite as one of the building units.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for the structure determination of **I** and **II**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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