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Hydrothermal Syntheses, Crystal Structures, and Magnetic Properties of Inorganic–Organic Hybrid Vanadium Selenites with Zero- to Three-Dimensional Structures: (1,10-Phenanthroline)$_2$V$_2$SeO$_7$, (2,2′-Bipyridine)VSeO$_4$, (4,4′-Bipyridine)V$_2$Se$_2$O$_8$, and (4,4′-Bipyridine)$_2$V$_4$Se$_3$O$_{15}$·H$_2$O

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A family of inorganic–organic hybrid vanadium selenites with zero-, one-, two-, and three-dimensional structures, (1,10-phen)$_2$V$_2$SeO$_7$, (2,2′-bipy)VSeO$_4$, (4,4′-bipy)V$_2$Se$_2$O$_8$, and (4,4′-bipy)$_2$V$_4$Se$_3$O$_{15}$·H$_2$O (where phen = phenanthroline and bipy = bipyridine), were hydrothermally synthesized and characterized by single-crystal X-ray diffraction. Different bidentate organodiamine ligands and reactant concentrations were used in the four reaction systems, which are responsible for the variety of structural dimensions of the compounds. (1,10-phen)$_2$V$_2$SeO$_7$ crystallizes in a monoclinic system with space group $P2_1/n$ and cell parameters $a = 8.6509(3)$ Å, $b = 7.8379(2)$ Å, $c = 34.0998(13)$ Å, $\beta = 91.503(2)°$, and $Z = 4$. (2,2′-bipy)VSeO$_4$ crystallizes in a monoclinic system with space group $C2/c$ and cell parameters $a = 17.0895(12)$ Å, $b = 14.7707(10)$ Å, $c = 11.7657(8)$ Å, $\beta = 131.354(3)°$, and $Z = 8$. (4,4′-bipy)V$_2$Se$_2$O$_8$ crystallizes in a triclinic system with space group $P\bar{1}$ and cell parameters $a = 7.1810(10)$ Å, $b = 10.8937(13)$ Å, $c = 11.1811(15)$ Å, $\alpha = 115.455(3)°$, $\beta = 107.582(3)°$, $\gamma = 91.957(4)°$, and $Z = 2$. (4,4′-bipy)$_2$V$_4$Se$_3$O$_{15}$·H$_2$O crystallizes in a monoclinic system with space group Pc and cell parameters $a = 7.9889(9)$ Å, $b = 7.8448$ Å, $c = 23.048(3)$ Å, $\beta = 99.389(4)°$, and $Z = 2$. (1,10-phen)$_2$V$_2$SeO$_7$ has an isolated structure, (2,2′-bipy)VSeO$_4$ has a chain structure, (4,4′-bipy)V$_2$Se$_2$O$_8$ has a layered structure, and (4,4′-bipy)$_2$V$_4$Se$_3$O$_{15}$·H$_2$O has a framework structure. The chains are constructed from VO$_4$N$_2$ octahedra and SeO$_3$ pyramids, laced by organic ligands (2,2′-bipy). The layers consist of vanadium selenite chains [(VO)$_2$(SeO$_3$)$_2$]$_\infty$, linked by 4,4′-bipy molecules. The framework is composed of vanadium selenite sheets [V$_4$Se$_3$O$_{16}$]$_\infty$, pillared by 4,4′-bipy molecules. All of the compounds are thermally stable to 300 °C, and the magnetic susceptibilities confirm the existence of tetravalent V atoms in the antiferromagnetic (4,4′-bipy)V$_2$Se$_2$O$_8$ complex and mixed tetravalent and pentavalent V atoms in the paramagnetic complex (4,4′-bipy)$_2$V$_4$Se$_3$O$_{15}$·H$_2$O.

Introduction

In the past few years, the design and synthesis of inorganic–organic hybrid materials have been of great interest for their novel crystallographic framework topologies and potential applications in the fields of catalysis and biochemistry.[1–5] The diversity of the compositions and structures of inorganic–organic hybrid materials were derived partially from the huge compositional and structural combinations from individual inorganic and organic components.[6–10] A number of inorganic–organic hybrid vana-

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dium phosphates with zero- (0-D), one- (1-D), two- (2-D), or three-dimensional (3-D) structures were prepared based on the particularly variable oxidation states and coordination geometries of the vanadium atom.[11] More recently, some novel inorganic−organic hybrid selenates were also reported, including $(CN_3H_6)_4[Zn_3(SeO_3)_5]$,[12] $[C_2N_2H_8]_{0.5}ZnSeO_3$,[13] $[C_4N_2H_{12}]_{0.5}[Fe_2F_3(SeO_3)_2]$,[13] $[CdCl_2(HSeO_3)_2](enH_2)$,[14] $[DABCO]_{0.5}[(V^{IV}O)(HSeO_3)(SeO_3)]\cdot H_2O$, $[enH_2][(V^{IV}O)_2(V^{V}O)O_2(SeO_3)_3]\cdot 1.25H_2O$,[15] $(H_3NCH_2CH_2NH_3)\cdot[(VO)(SeO_3)_2]$,[16] M(4,4′-bipy)$(H_2O)V_2Se_2O_{10}$ (M = Co, Ni),[17] and $[Cu(phen)]_2V_2Se_2O_{11}$.[18] Compared to the chemistry of vanadium phosphate, the obvious propensity for μ_3-coordination by selenium offered the opportunity for making new inorganic−organic hybrid materials containing an inorganic V/Se/O backbone decorated with organic ligands. As a sequel to our search for new inorganic−organic hybrid selenates, we are currently exploring the synthesis of inorganic−organic hybrid vanadium selenites in hydrothermal systems. We report here the synthesis and characterization of a family of inorganic−organic hybrid vanadium selenites, prepared by introducing appropriate organic components and changing the contents of ligands in synthetic systems. Four compounds, (1,10-phen)$_2V_2SeO_7$ (**1**), (2,2′-bipy)$VSeO_4$ (**2**), (4,4′-bipy)$V_2Se_2O_8$ (**3**), and (4,4′-bipy)$_2V_4Se_3O_{15}\cdot H_2O$ (**4**), where phen = phenanthroline and bipy = bipyridine, were synthesized, showing novel structures from zero to three dimensions. They were characterized by infrared spectroscopy (IR), differential thermal-thermogravimetric analysis (DT-TGA), elemental analysis, and magnetic susceptibilities.

Experimental Section

Materials and Methods. All reagents were of analytical grade and were used as received from commercial sources without further purification. The elemental analysis was performed on a Perkin-Elmer 2400 element analyzer, and the inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer Optima 3300 DV ICP spectrometer. IR spectra were collected on a Nicolet Impact 410 FTIR spectrometer using KBr pellets. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out in air on a Perkin-Elmer DTA 1700 differential thermal analyzer with a rate of 10 °C/min. Magnetic susceptibility data were collected over the temperature range of 2.4−300 K at a magnetic field of 5 kG on a Quantum Design MPMS-7 SQUID magnetometer.

Syntheses. Four compounds were hydrothermally crystallized from sealed 15 mL Teflon-lined stainless steel autoclave vessels at 160 °C under autogenous pressure. The synthetic details and IR data follow.

(1,10-phen)$_2$V$_2$SeO$_7$ (1). A reaction mixture of V_2O_5 (0.091 g, 0.5 mmol), SeO_2 (0.440 g, 4 mmol), 1,10-phen ($C_{12}H_8N_2$, 0.396 g, 2 mmol), $TMAOH\cdot 5H_2O$ (0.364 g, 2 mmol), and H_2O (5 mL, 278 mmol) in a molar ratio of 1:8:4:4:555 was heated in a sealed Teflon-lined steel autoclave at 160 °C for 120 h. The resulting yellow crystals were filtered, washed with distilled water, and dried in air at ambient temperature. Anal. Calcd (found) for **1** (wt %): V, 15.61 (15.68); Se, 12.09 (11.88); C, 44.09 (44.01); H, 2.45 (2.37); N, 8.57 (8.49). IR (KBr pellet, cm^{-1}): 1623(m), 1569(m), 1512(m), 1428(m), 1219(s), 1176(m), 1108(s), 857(s), 812(m), 667(m), 645(m), 521(s), 435(m).

(2,2′-bipy)VSeO$_4$ (2). A reaction mixture of V_2O_5 (0.091 g, 0.5 mmol), SeO_2 (0.550 g, 5 mmol), 2,2′-bipy ($C_{10}H_8N_2$, 0.194 g, 1 mmol), $TMAOH\cdot 5H_2O$ (0.182 g, 1 mmol), and H_2O (5 mL, 278 mmol) in a molar ratio of 1:10:2:2:555 was heated in a sealed Teflon-lined steel autoclave at 160 °C for 120 h. The resulting green block crystals were filtered, washed with distilled water, and dried in air at ambient temperature. Anal. Calcd (found) for **2** (wt %): V, 14.57 (14.68); Se, 22.57 (22.79); C, 34.29 (34.11); H, 2.29 (2.36); N, 8.00 (7.89). IR (KBr pellet, cm^{-1}): 1648(m), 1606(m), 1569(m), 1497(m), 1473(s), 1454(m), 1325(m), 1253(s), 1179(m), 1031(m), 933(s), 862(s), 804(m), 799(s), 678(m), 639(m), 511(s), 449(m).

(4,4′-bipy)V$_2$Se$_2$O$_8$ (3). A reaction mixture of V_2O_5 (0.091 g, 0.5 mmol), SeO_2 (0.550 g, 5 mmol), 4,4′-bipy ($C_{10}H_8N_2$, 0.194 g, 1 mmol), $TMAOH\cdot 5H_2O$ (0.182 g, 1 mmol), and H_2O (5 mL, 278 mmol) in a molar ratio of 1:10:2:2:555 was heated in a sealed Teflon-lined steel autoclave at 160 °C for 120 h. The resulting green block crystals were filtered, washed with distilled water, and dried in air at ambient temperature. Anal. Calcd (found) for **3** (wt %): V, 18.75 (18.68); Se, 29.05 (28.68); C, 22.13 (22.81); H, 1.47 (1.87); N, 5.21 (4.89). IR (KBr pellet, cm^{-1}): 1607(m), 1539(m), 1494(m), 1427(m), 1225(s), 1079(m), 1011(m), 854(s), 808(s), 685(m), 640(m), 516(s), 449(m).

(4,4′-bipy)$_2$V$_4$Se$_3$O$_{15}\cdot$H$_2$O (4). A mixture of V_2O_5 (0.091 g, 0.5 mmol), SeO_2 (0.550 g, 5 mmol), 4,4′-bipy ($C_{10}H_8N_2$, 0.970 g, 5 mmol), $TMAOH\cdot 5H_2O$ (0.182 g, 1 mmol), and H_2O (5 mL, 278 mmol) in a molar ratio of 1:10:10:2:555 was heated in a sealed Teflon-lined steel autoclave at 160 °C for 120 h. The resulting black block crystals were filtered, washed with distilled water, and dried in air at ambient temperature. Anal. Calcd (found) for **4** (wt %): V, 20.18 (19.68); Se, 23.44 (23.68); C, 23.74 (24.31); H, 1.78 (1.69); N, 5.54 (4.98). IR (KBr pellet, cm^{-1}): 1615(m), 1578(m), 1514(m), 1428(m), 1224(s), 1094(m), 1017(m), 954(s), 908(m), 854(m), 805(s), 698(m), 662(m), 521(s), 443(m).

Determination of Crystal Structures. Crystals of **1**−**4** suitable for single-crystal X-ray diffraction with sizes 0.11 × 0.11 × 0.10 mm^3, 0.27 × 0.13 × 0.13 mm^3, 0.40 × 0.40 × 0.35 mm^3, and 0.40 × 0.37 × 0.34 mm^3, respectively, were glued to thin glass fibers with epoxy resin and mounted on a Siemens SMART charge coupled device (CCD) diffractometer equipped with a normal-focus, 2.4 kW sealed-tube X-ray source (graphite-monochromatic Mo $K\alpha$ radiation, λ(Mo $K\alpha$) = 0.71073 Å). Intensity data were collected at a temperature of 20 ± 2 °C. Data processing was accomplished with the SAINT processing program. Direct methods were used to solve structures using the SHELXTL crystallographic software package.[19] Hydrogen atoms were located in the Fourier map for compounds **1**−**3** and were placed geometrically for compound **4**.

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Table 1. Crystal Data and Structure Refinement for Compounds **1**−**4**

	1	**2**	**3**	**4**
empirical formula	$C_{24}H_{16}N_4O_7SeV_2$	$C_{10}H_8N_2O_4SeV$	$C_{10}H_8N_2O_8Se_2V_2$	$C_{20}H_{18}N_4O_{16}Se_3V_4$
fw	653.25	350.08	543.98	1011.02
T (K)	293(2)	293(2)	293(2)	20(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
space group	$P2_1/n$	$C2/c$	$P\bar{1}$	Pc
a (Å)	8.6509(3)	17.0895(12)	7.1810(10)	7.9889(9)
b (Å)	7.8379(2)	14.7707(10)	10.8937(13)	7.8448(9)
c (Å)	34.0998(13)	11.7657(8)	11.1811(15)	23.048(3)
α (deg)			115.455(3)	
β (deg)	91.503(2)	131.354(3)	107.582(3)	90.389
γ (deg)			91.957(4)	
V (Å^3)	2311.34(13)	2229.4(3)	739.08(17)	989.90(7)
Z	4	8	2	2
ρ_{calc} (mg·m^{-3})	1.877	2.086	2.444	2.356
μ (mm^{-1})	2.440	4.162	6.235	5.188
R1 [$I > 2\theta(I)$][a]	0.0327	0.0243	0.0245	0.0223
wR2 [all data][b]	0.0697	0.0567	0.0675	0.0561

[a] $R1 = \sum|F_o| - |F_c|/\sum|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Crystal parameters and details of the data collection and refinement for structures of **1**−**4** are listed in Table 1. Atomic coordinates with isotropic temperature factors, selected bond lengths, and angles of compounds **1**−**4** are available in the Supporting Information.

Results and Discussion

In the synthesis of inorganic−organic hybrid materials, bidentate organodiamine 1,10-phen, 2,2′-bipy, and 4,4′-bipy ligands have been extensively used to achieve various open inorganic−organic frameworks.[20−24] On the basis of the study in the V/P/O system,[6,7] we began to study the V/Se/O system and isolated for the first time four novel inorganic−organic hybrid vanadium selenites, where the vanadium atoms are directly linked by the organodiamine in each compound. The compounds **1**, **2**, and **3** with 0-, 1-, and 2-D structures were obtained by using different ligands, such as 1,10-phen, 2,2′-bipy, and 4,4′-bipy, respectively, accounting for each ligand's different coordination ability and geometry. Interestingly, compounds **3** and **4** were templated by the same ligand, 4,4′-bipy, but different structures (2-D and 3-D) were formed by changing only the concentration of the ligand. It has been considered that the change of concentration of the same ligand affected the oxidation state of vanadium in hydrothermal systems and therefore led to its different coordination geometries and polymerization reactions. Although the hydrothermal reactions may be complicated and may include redox and coordination reactions, the systematic synthetic results offered a clue for understanding the mechanisms of such hydrothermal reactions and for creating novel materials with different structural dimensions.

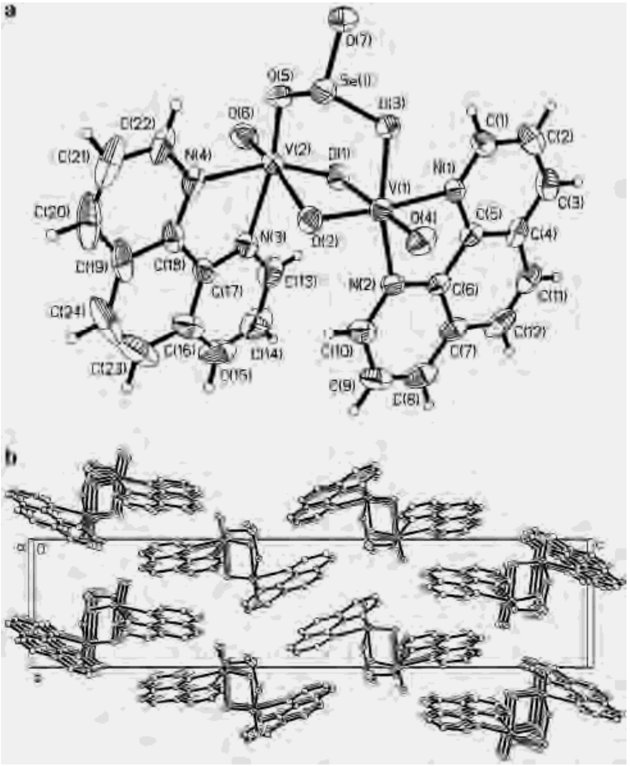

Figure 1. (a) ORTEP drawing of the asymmetric unit of **1** (50% thermal ellipsoids). (b) View of the packing structure of **1** along the *a* axis.

Figure 1a shows the asymmetry unit of compound **1**. There are two crystallographically distinct vanadium atoms, one selenite group, and two 1,10-phen ligands. Both V(1) and V(2) sites feature similar octahedra, coordinated by two cis nitrogen donors of 1,10-phen, one terminal apical oxygen atom (V(1)−O(4) = 1.616(3) Å, V(2)−O(6) = 1.605(3) Å), one oxygen from selenite, and two bridging oxygens connected to V(1) and V(2) (V(1)−O(1) = V(2) = 101.62(12)°, V(1) = O(2)−V(2) = 98.03(12)°). The pyramidal geometry around each selenium atom is completed by one terminal oxygen and two bridging oxygen atoms connected to V(1) and V(2) atoms. The [V_2SeO_7] units are in a close connection through 1,10-phen, via so-called $\pi\cdots\pi$ interactions of 1,10-

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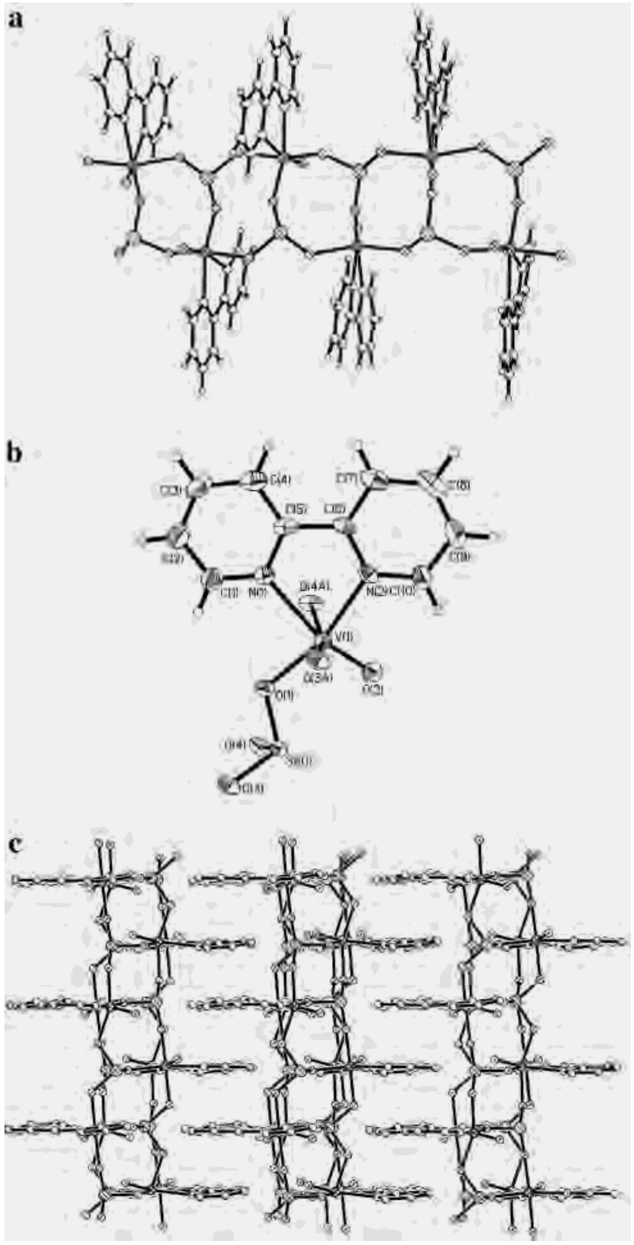

Figure 2. (a) View of the one-dimensional chains of **2**. (b) View of the coordination environments of the vanadium and selenium atoms. (c) View of the packing of adjacent chains in **2**.

phen as shown in Figure 1b. The close contact distance between adjacent rings in 1,10-phen is 3.49 Å.

The structure of **2**, shown in Figure 2a, consists of [$VSeO_4$] inorganic chains, laced by organic ligands (2,2′-bipy). The asymmetric unit contains one unique vanadium atom, one selenium atom, and one 2,2′-bipy molecule (Figure 2b). The vanadium atom is octahedrally coordinated by four oxygens and two nitrogen atoms: the nitrogen atoms come from the same 2,2′-bipy molecule with a N(1)−V(1)−N(2) bond angle of 72.34(10)°, one oxygen forms a vanadyl group (V(1)−O(2) = 1.601(3) Å), and three oxygens share corners with the neighboring SeO_3 pyramid. As a result, V and Se atoms, together with their associated oxygen and nitrogen atoms, form inorganic chains, which contain interconnected V_2Se_2 four-membered rings. These types of four-membered rings have also been reported previously and include such 2,2′-bipy ligand-based examples as [$VO(\mu_3\text{-}SO_4)(2,2'\text{-bipy})]_\infty$[25] and MoO_4\{FeCl(2,2′-bipy).[26] The building block units $V_2O_2(\mu\text{-}OH)_2(\mu\text{-}SO_4)$ \{$V_2O_2(\mu\text{-}OH)_2$\}-SO_4\} in the rear are significantly similar to the inorganic chains in **2** but with the replacement of μ_3-SO_4 (with a terminal oxo group (S═O bond)) by μ_3-SeO_3. Adjacent 2,2′-bipy ligands decorate the inorganic chains' interdigitation and provide weak $\pi\cdots\pi$ stacking interactions. Figure 2c shows the packing arrangement of the 1-D chains.

The structure of **3** consists of two-dimensional neutral sheets of 4,4′-bipy/VO/SeO. It may be viewed as bridges of 4,4′-bipy ligands, which are coordinated with V atoms in adjacent [$(VO)_2(SeO_3)_3$] chains to generate a 2-D layered structure. The bridged V⋯V distance along 4,4′-bipy is about 11.375 Å. Figure 3a shows the asymmetric unit of **3**. There are two chemically and crystallographically unique vanadium and selenium centers. The coordination geometry of the V(1) atom is between the square-pyramidal and trigonal-bipyramidal polyhedron;[27] the coordination consists of three bridging O atoms at distances in the range of 1.928(3)−2.002(8) Å, one apical vanadyl O(3) at a distance of 1.591(3) Å, and one nitrogen atom of a bipyridine ligand at a distance of 2.158(3) Å. The V(2) atom has a similar coordination environment as V(1) except that the terminal oxygen atoms sit in the opposite direction. Each selenium atom coordinates to three O atoms coming from three different vanadium polyhedra. A 4,4′-bipy molecule in the asymmetry unit is neutral coordinates to V(1), and extends away to V(2) with the two pyridine rings of the bipy molecule twisted at an angle of 31.7°. It may be viewed as bridges of 4,4′-bipy ligands, which are coordinated with V atoms in adjacent [$(VO)_2(SeO_3)_3$] chains to generate a 2-D layered structure (Figure 3b). The bridged V⋯V distance along 4,4′-bipy is about 11.375 Å. The V−N bonds in compound **3** connect each chain to produce the layer motif. The adjacent layers are in a close connection through weak van der Waals (VDW) interaction, and the stacking motif is shown in Figure 3c.

The structure of **4** has a 3-D framework, consisting of zigzag layers with the composition [$V_4Se_3O_{16}]_\infty$, linked by 4,4′-bipy coordinated with V atoms. The asymmetric unit contains four V atoms, three Se atoms, and two 4,4′-bipy ligands (Figure 4a). V(1) is bonded to three oxygen donors of selenite pyramids (V(1)−O(av) = 2.094 Å), one terminal oxygen (V(1)−O(4) = 1.589(4) Å), one bridging oxygen (V(1)−O(1) = 1.949(4) Å), and one nitrogen atom from 4,4′-bipy. The V(3) site has a similar octahedral environment as that of V(1) but with two oxygens from selenite pyramids and one oxygen from a water molecule (V(3)−O(10) = 2.314(4) Å). V(2) and V(4), in distorted bipyramids, are bonded to two O atoms of the SeO_3 group, one terminal O (V(2)−O(6) = 1.592(4) Å, V(4)−O(12) = 1.607(4) Å), one bridging O (V(2)−O(1) = 1.731(4) Å, V(4)−O(7) = 1.669-

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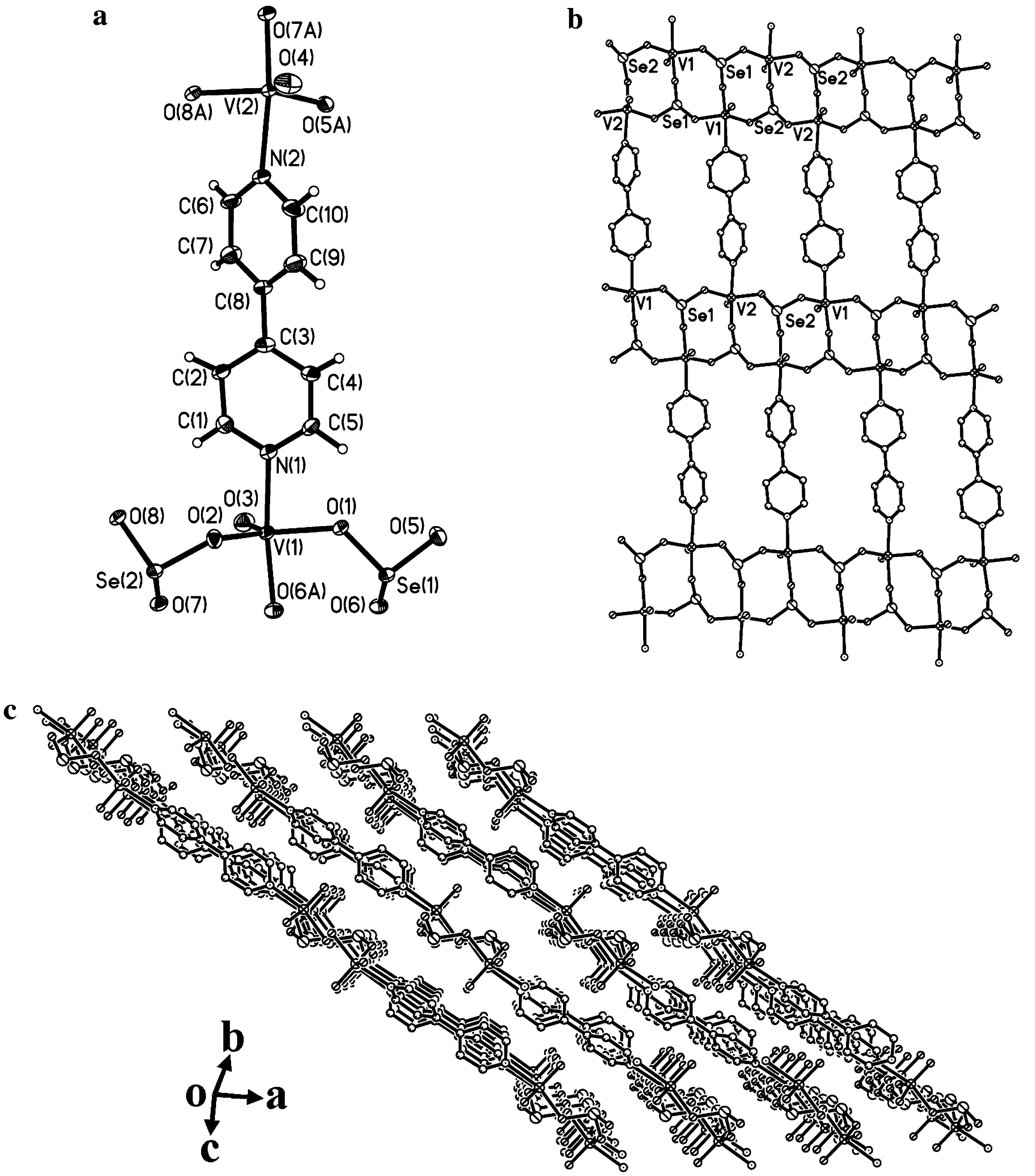

Figure 3. (a) ORTEP drawing of the asymmetric unit of **3** (50% thermal ellipsoids). (b) View of the layered 4,4′-bipy·$V_2Se_2O_8$ in **3**, showing the coordination environments of the vanadium and selenium atoms. (c) View of the packing of adjacent layers in **3**.

(4) Å), and one nitrogen of 4,4′-bipy. Each Se(1), Se(2), and Se(3) atom adopts the tridentate bridging mode to three adjacent vanadium polyhedra. Thus, two VO_5N, two VO_4N, and three SeO_3 units are linked up via corner-shared oxygen atoms with three-, four-, six-, and nine-membered rings; this array gives rise to the inorganic VO/SeO layers (Figure 4b). The 2-D vanadium selenite oxide layers are interconnected by 4,4′-bipy into a 3-D open framework. As shown in Figure 4c, the distance between the bridged V···V atoms along 4,4′-bipy is about 11.383 Å.

It is interesting to notice that the chain motif observed in compounds **2** and **3** is similar to that in our earlier reported compound $[VO(OH)(H_2O)(SeO_3)]_4·H_2O$.[16] Both consist of a strictly alternating vanadium and selenite polyhedral chain-linkage pattern with vertex-linked V and Se species segregated into four-membered rings. The main difference between the structure of $[VO(OH)(H_2O)(SeO_3)]_4·H_2O$ and the structures of **2** and **3** lies in the configuration of the V atoms. The sixth coordination site of V in $[VO(OH)(H_2O)(SeO_3)]_4·H_2O$ is satisfied by three oxygen donors of adjacent selenite pyramids, one terminal oxygen, one hydroxyl group, and one water molecule, whereas in compound **2**, the octahedrally coordinated vanadium atom is satisfied by one terminal apical oxygen, three bridging oxygens with the neighboring SeO_3, and two nitrogen atoms from 2,2′-bipy, and in compound **3**, the [1 + 4]-coordinate vanadium is bonded to three oxygen donors of adjacent selenite pyramids, a terminal oxo group, and a nitrogen donor of 4,4′-bipy.

To the best of our knowledge, our compounds described above are the first examples where organodiamine ligands were directly coordinated to vanadium atoms in the vanadium selenite system, although in some inorganic–organic hybrid

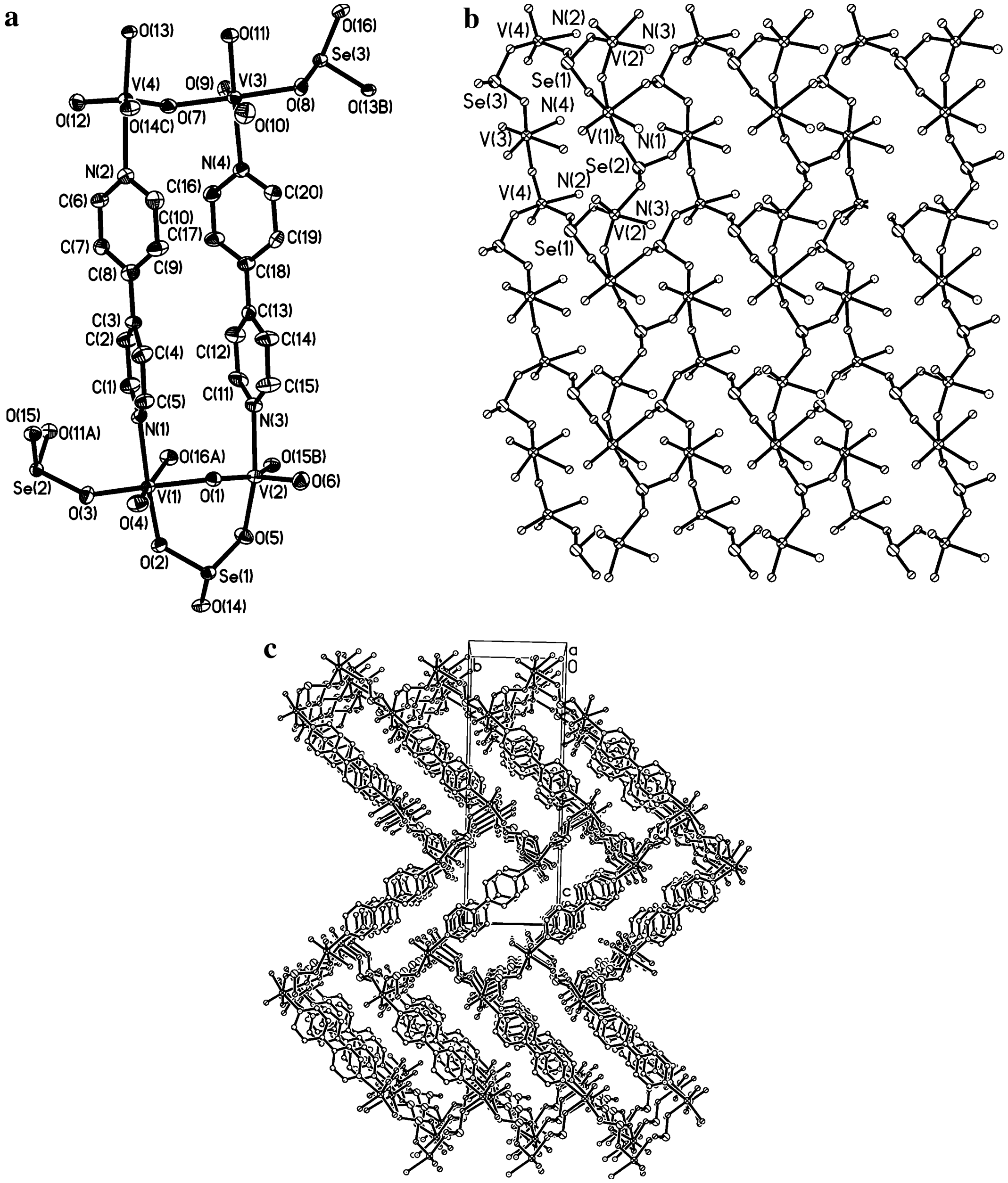

Figure 4. (a) ORTEP drawing of the asymmetric unit of **4** (50% thermal ellipsoids). (b) View along the *bc* plane of the $\{V_4Se_3O_{16}\}$ layer of **4**, showing the coordination environments of the vanadium and selenium atoms. (c) View of the crystal structure of **4** along the *a* axis.

phosphates, such as $(4,4'\text{-}H_2bpy)[V_2(HPO_4)_4(4,4'\text{-bpy})_2]$,[28] $NH_4[(V_2O_3)_2(4,4'\text{-bpy})_2(H_2PO_4)(PO_4)_2]\cdot 0.5H_2O$,[29] and $[(VO_2)_2(4,4'\text{-bpy})_{0.5}(4,4'\text{-Hbpy})(XO_4)]\cdot H_2O$ (X = P and As),[30] the connections of ligands to vanadium atoms were known.

The TGA curve of compound **1** showed a weight loss of 40.7% (calcd 55.10%) at 372 °C and another weight loss of 21.3% (calcd 17.03%) at 434 °C, contributed by the combustion of 1,10-phen and the sublimation of SeO_2, respectively. For compound **2**, from 320 to 480 °C, two successive weight losses of 35.8% (calcd 44.57%) at 320 °C and 36.6% (calcd 31.71%) at 480 °C are in agreement with the amounts expected from the release of 2,2′-bipy and the sublimation of SeO_2, respectively. Compound **3** is thermally stable below 390 °C. The two coterminous weight losses of 33.5% (calcd 28.67%) and 32.2% (calcd 40.88%) in the range of 390−480 °C were consistent with the combustion of 4,4′-bipy and the sublimation of SeO_2, respectively. In the TGA curve for compound **4**, the first weight loss of 3.6% (calcd 1.78%) from 300 to 315 °C was attributed to the removal of water and the second weight loss of 60.8% (calcd 64.90%) from 320 to 490 °C was attributed to the loss of 4,4′-bipy and SeO_2, consecutively. In agreement with the TGA curve of compound **4**, a weak endothermic peak was observed in the DTA peak at 310 °C, which correspond to the loss of H_2O. The exothermic peak and an endothermic peak at 380 and 420 °C were assigned to the loss of the 4,4′-bipy and SeO_2, respectively.

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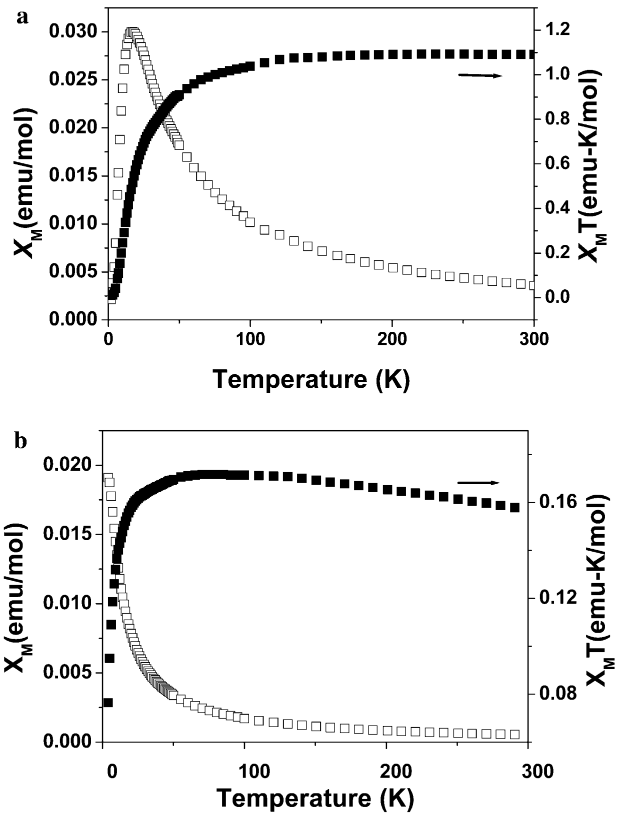

Figure 5. Thermal dependence of χ_M (open block) and $\chi_M T$ (solid block) for (a) compound **3** and (b) compound **4**.

Magnetic measurements of compounds **3** and **4** were performed on a powdered sample from 2.4 K to room temperature. Plots of χ_M and $\chi_M T$ vs T are shown in Figure 5. For compound **3** (Figure 5a), the molar magnetic susceptibility, χ_M, increased with decreasing temperature and reached a maximum at 17 K. Below this temperature, the susceptibility continuously decreased with cooling. The thermal variation of the molar susceptibility follows the Curie−Weiss law [$\chi_M = C_m/(T - \theta)$] above 50 K. The values of the Curie and Curie−Weiss constants are 0.346 emu·K^{-1}·mol^{-1} and −25.6 K. This result combined with the decrease in the $\chi_M T$ value below 17 K is indicative of antiferromagnetic interaction in this compound. At 300 K the magnetic moment (μ_{eff}) per vanadium, determined from the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$, is 1.62 μB which is slightly lower than that expected for an isolated tetravalent system with $\mu_{eff} =$ 1.73 μB. Magnetic susceptibility data for compound **4** show paramagnetic behavior between 4 and 290 K (Figure 5b). The higher temperature ($T > 50$ K) data were also modeled by a Curie−Weiss type law with $C_m = 0.351$ emu·K^{-1}·mol^{-1} and $\theta = 1.79$ K. The effective magnetic moment per V_2O_3 dimer ($\mu_{eff} = 2.828(\chi_M T)^{1/2} = 1.67$ μB) compares well with the spin-only moment (1.73 μB) calculated for a mixed-valence vanadium dimer (IV, V). Therefore, the valence of the vanadium atoms in **4** was confirmed by magnetic susceptibility.

Conclusions

We have successfully prepared four novel inorganic−organic hybrid vanadium selenites, (1,10-phen)$_2$V$_2$SeO$_7$, (2,2′-bipy)VSeO$_4$, (4,4′-bipy)V$_2$Se$_2$O$_8$, and (4,4′-bipy)$_2$V$_4$Se$_3$O$_{15}$·H$_2$O, by exploiting hydrothermal syntheses in the presence of the organic ligands, 1,10-phen, 2,2′-bipy, and 4,4′-bipy. The pseudopyramidal coordination for selenite, which is different from the coordination for phosphate, presents challenges in the synthesis of inorganic−organic hybrid open-framework selenites. The different ligands and the change of concentration of the same ligand, 4,4′-bipy, are expected to be the key factor for the variety in structures of the products. These inorganic−organic hybrid vanadium selenites show novel zero-, one-, two-, and three-dimensional structures. In their structures, inorganic chains of [(VO)$_2$(SeO$_3$)$_2$]$_\infty$ and inorganic layers of [V$_4$Se$_3$O$_{16}$]$_\infty$ were found, and their connections with corresponding organic ligands led to novel layered and framework structures. All of the compounds are thermally stable to 300 °C. Magnetic susceptibility confirmed the valences of the vanadium atoms to be +4 for compound **3** and +4/+5 mixed valence for compound **4**, respectively. Moreover, compound **3** showed antiferromagnetic behavior below 17 K and compound **4** showed paramagnetic behavior. Compared to the remarkable structural variety of the corresponding vanadium phosphates, there remains much room for development of novel inorganic−organic vanadium selenite compounds.

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Supporting Information Available: Crystallographic data (CIF), atomic coordinates with isotropic temperature factors, and selected bond lengths and angles for compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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