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Article

Hydrothermal Syntheses and Crystal Structures of Complex-Linked Three-Dimensional Coordination Vanadium Selenites: $M(4,4'\text{-bipy})(H_2O)V_2Se_2O_{10}$ (M = Co, Ni)

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Two inorganic–organic hybrid compounds with the formula $M(4,4'\text{-bipy})(H_2O)V_2Se_2O_{10}$ (M = Co, Ni) were hydrothermally synthesized and characterized by single-crystal X-ray diffraction. Compounds $Co(4,4'\text{-bipy})(H_2O)V_2Se_2O_{10}$ (**1**) and $Ni(4,4'\text{-bipy})(H_2O)V_2Se_2O_{10}$ (**2**), which are structural analogues, crystallize in the triclinic space group $P\bar{1}$ with crystal data $a = 7.9665(3)$ Å, $b = 8.1974(3)$ Å, $c = 13.8096(4)$ Å, $\alpha = 85.704(2)°$, $\beta = 73.5180(10)°$, $\gamma = 75.645(2)°$, $V = 837.76(5)$ Å^3, and $Z = 2$ and $a = 7.9489(19)$ Å, $b = 8.128(2)$ Å, $c = 13.709$ Å, $\alpha = 85.838(6)°$, $\beta = 73.736(8)°$, $\gamma = 75.594(9)°$, $V = 823.5(4)$ Å^3, and $Z = 2$, respectively. $[M(4,4'\text{-bipy})(H_2O)V_2Se_2O_{10}]$ (M = Co, Ni) have a three-dimensional structure and consist of two subunits, $[(VO_2)(SeO_3)]^-$ infinite chains and $[M(4,4'\text{-bipy})(H_2O)]^{2+}$ fragments. The $[(VO_2)(SeO_3)]^-$ chains are composed of $[V_2Se_4O_{14}]^{4-}$ clusters linked by VO_4N triangular bipyramids. The 4,4′-bipy molecule as a bifunctional organic ligand is directly linked to Co or Ni and V atoms, affording the three-dimensionality. The compounds were characterized by infrared spectroscopy and differential thermal and thermogravimetric analyses.

Introduction

Recently, the diversity in the structures of inorganic−organic hybrid materials has been greatly developed for their potential applications in catalysis, biology, and material science.[1] Novel compounds with one (1D), two (2D), and three (3D) dimensional structures were prepared by using organic templates and metal coordination complexes as structural directors or bridging ligands of frameworks.[2] Contemporary interest in the chemistry of vanadium phosphates characterized over the past 10 years derives from their notable structural variety, whereas the chemistry of vanadium selenites was less known, even though some simple vanadium selenites such as $AVSeO_5$ (A = Rb, Cs), $AV_3Se_2O_{12}$ (A = K, Rb, Cs, NH_4), $K(VO)(SeO_3)_2H$, $V_2Se_2O_9$, and $Cd(VO_2)_4(SeO_3)_3 \cdot H_2O$ have been synthesized.[3] More recently, three organically templated selenites, $(CN_3H_6)_4[Zn_3(SeO_3)_5]$, $[C_4N_2H_{12}]_{0.5}[Fe_2F_3(SeO_3)_2]$, and $[C_2N_2H_8]_{0.5}ZnSeO_3$, were prepared.[4] A layered vanadium selenite templated by organic amine, $(H_3NCH_2CH_2NH_3)\cdot[(VO)(SeO_3)_2]$,[5] has been obtained by our group.

In the cases of coordination-complex-linked compounds, a large number of coordination-complex-linked molybdates

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(1) (a) Férey, G. *Chem. Mater*. **2001**, *13*, 3084−3098. (b) Cheetham, A. K.; Férey, G.; Loiseau, T. *Angew. Chem., Int. Ed*. **1999**, *38*, 3268−3292. (c) Chui, S. S.-Y.; Lo, S. M.-F.; Charmant, J. P. H.; Orpen, A. G.; Williams, I. D. *Science* **1999**, *283*, 1148−1150. (d) Zaworotko, M. J. *Angew. Chem., Int. Ed.* **1998**, *37*, 1211−1213. (e) Janiak, C. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 1431−1434.

(2) (a) Lii, K. H.; Huang, Y. F. *Inorg. Chem*. **1999**, *38*, 1348−1350. (b) Zhang, Y.; Debord, J. R. D.; O'Connor, C. J.; Haushalter, R. C.; Clearfield, A.; Zubieta, J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 989−991. (c) Zapf, P. J.; Warren, C J.; Haushalter, R. C.; Zubieta. J. *Chem. Commun*. **1997**, 1543−1544. (d) DeBord, J. R. D.; Haushalter, R. C.; L. M.; Meyer, Rose, D. J.; Zapf, P. J.; Zubieta, J. *Inorg. Chim. Acta* **1997**, *256*, 165−168. (e) Zapf, P. J.; Hammond, R. P.; Haushalter, R. C.; Zubieta, J. *Chem. Mater*. **1998**, *10*, 1366−1373. (f) Hagrman, D.; Zapf, P. J.; Zubieta, J. *Chem. Commun*. **1998**, 1283−1284. (g) Shi, Z.; Zhang, L.; Zhu, G.; Hua, J.; Ding, H.; Feng, S. *Chem. Mater*. **1999**, *11*, 3565−3570. (h) Hagrman, D.; Zubieta, C.; Rose, D. J.; Zubieta, J.; Haushalter, R. C. *Angew. Chem.* **1997**, *109*, 9904−907; *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 873−876.

(3) (a) Kim, Y. H.; Kwon, Y.-U.; Lee, K.-S. *Bull. Korean Chem. Soc*. **1996**, *17*, 1123−1127. (b) Kwon, Y.-U.; Lee, K.-S.; Kim, Y. H. *Inorg. Chem*. **1996**, 35, 1161−1167. (c) Kim, Y. H.; Lee, K.-S.; Kwon, Y.-U.; Han, O. H. *Inorg. Chem*. **1996**, *35*, 7394−7398. (d) Lee, K.-S.; Kwon, Y.-U. *J. Korean Chem. Soc*. **1996**, *40*, 379−383. (e). Kim, Y.-T.; Kim, Y.-H.; Park, K.; Kwon, Y.-U. *J. Solid State Chem*. **2001**, *161*, 23−30.

(4) (a) Harrison, W. T. A.; Phillips, M. L. F.; Stanchfield, Je.; Nenoff, T. M. *Angew. Chem., Int. Ed*. **2000**, *39*, 3808−3810. (b) Choudhury, A.; Kumar D, U.; Rao, C. N. R. *Angew. Chem., Int. Ed*. **2002**, *41*, 166−169.

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Table 1. Crystal Data and Structure Refinement for **1** and **2**

	1	**2**
empirical formula	$C_{10}H_{10}N_2CoO_{11}Se_2V_2$	$C_{10}H_{10}N_2NiO_{11}Se_2V_2$
fw	652.93	652.71
T (K)	293(2)	293(2)
λ (Å)	0.7103	0.7103
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.9665(3)	7.9489(19)
b (Å)	8.1974(3)	8.128(2)
c (Å)	13.8096(4)	13.709(4)
α (deg)	85.704(2)	85.838(6)
β (deg)	73.5180(10)	73.736(8)
γ (deg)	75.645(2)	75.594(9)
V (Å^3)	837.76(5)	823.5(4)
Z	2	2
ρ_{calcd} (Mg m^{-3})	2.588	2.632
μ (mm^{-1})	6.481	6.729
no. of reflns collected/unique	4118/2396 [*R*(int) = 0.0238]	4024/2349 [*R*(int) = 0.0308]
limiting indices	$-7 \leq h \leq \mp 8$, $-9 \leq k \leq \mp 7$, $-15 \leq l \leq \mp 15$	$-7 \leq h \leq \mp 8$, $-8 \leq k \leq \mp 9$, $-12 \leq l \leq \mp 15$
R1[a] [$I > 2\theta(I)$]	0.0258	0.0289
wR2[b] [$I > 2\theta(I)$]	0.0626	0.0685

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

(M_xL_y/Mo/O),[6] vanadates (M_xL_y/V/O),[7] molybdenum phosphates (M_xL_y/Mo/P/O),[8] and vanadium phosphates (M_xL_y/V/P/O)[9] have been synthesized (M = transition metal, L = organic). The transition-metal coordination complexes may function as templates to direct the structures of 1-, 2-, and 3D open frameworks. Recently, we have focused our studies on the structural variety of coordination-complex-linked vanadium selenite systems, which are expected to be different from the vanadium phosphate systems. A layered compound, $[Cu(phen)]_2V_2Se_2O_{11}$,[10] was reported by our group, but no 3D open-framework structure with the coordination-complex-linked vanadium selenite has been isolated to date. As a part of our ongoing study, we have been carrying out the syntheses in 4,4′-bipy−V−Se−Co(Ni)−H_2O hydrothermal systems. Here, we report the syntheses of two 3D coordination-complex-linked vanadium selenites, $[Co(4,4'\text{-bipy})(H_2O)(V_2Se_2O_{10})]$ (**1**) and $[Ni(4,4'\text{-bipy})(H_2O)(V_2Se_2O_{10})]$ (**2**).

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) for **1**

	x	y	z	*U*(eq)
Co(1)	2186(1)	−4892(1)	1485(1)	16(1)
V(1)	4714(1)	−2031 (1)	278(1)	11(1)
V(2)	−432(1)	−1527(1)	2831(1)	15(1)
Se(1)	1350(1)	1250(1)	1306(1)	17(1)
Se(2)	−3448(1)	−165(1)	1560(1)	18(1)
O(1)	3171(4)	−2742(4)	1176(2)	18(1)
O(2)	103(4)	−3588(4)	2635(2)	21(1)
O(3)	653(5)	−3807(5)	421(3)	40(1)
O(4)	5941(4)	−3771(4)	−328(2)	19(1)
O(5)	3688(4)	534(4)	870(2)	15(1)
O(6)	1029(5)	3128(4)	1783(3)	33(1)
O(7)	970(4)	148(4)	2416(2)	19(1)
O(8)	−1290(4)	−798(4)	1639(2)	22(1)
O(9)	−3072(4)	1222(4)	585(2)	19(1)
O(10)	−3481(4)	−1943(4)	1001(2)	20(1)
O(11)	−2308(4)	−1062(4)	3705(2)	25(1)
N(1)	3886(5)	−5777(5)	2459(3)	24(1)
N(2)	8889(5)	−8034(5)	6062(3)	22(1)
C(1)	5526(8)	−5516(8)	2294(4)	41(2)
C(2)	6566(8)	−5963(8)	2953(5)	42(2)
C(3)	5925(7)	−6761(6)	3846(3)	23(1)
C(4)	4281(9)	−7142(12)	3989(5)	70(3)
C(5)	3320(9)	−6610(11)	3288(5)	66(2)
C(6)	9550(10)	−7417(13)	5175(5)	87(3)
C(7)	8648(10)	−7005(14)	4441(5)	93(4)
C(8)	6956(6)	−7219(6)	4613(4)	23(1)
C(9)	6272(8)	−7877(10)	5535(5)	55(2)
C(10)	7266(9)	−8271(10)	6228(5)	55(2)

Experimental Section

Compounds **1** and **2** were synthesized by hydrothermally treating a reaction mixture of vanadium pentoxide, selenium dioxide, cobaltous nitrate (or nickel nitrate), and 4,4′-bipyridine. A typical procedure of synthesis was as follows: For compound **1**, a mixture of V_2O_5 (0.091 g), SeO_2 (0.22 g), $Co(NO_3)_2{\cdot}6H_2O$ (0.296 g), 4,4′-bipy (0.194 g), and H_2O (2 mL) in a molar ratio of 1:2:1:1:110 was heated in a sealed Teflon-lined steel autoclave at 160 °C for 120 h. The synthesis of compound **2** was similar to the above description for compound **1**. The products were collected by filtration, washed with distilled water, and dried in air at ambient temperature. The resulting dark red columnar crystals of **1** and the dark brown columnar crystals of **2** were obtained in the reaction of **1** and **2** with a little unidentified yellow powder produced. The pH value of the reaction systems was ~2.0. The elemental analysis and inductively coupled plasma (ICP) and IR spectra in combination with X-ray single-crystal analysis confirmed the formulas of **1**, $[Co(4,4'\text{-bipy})(H_2O)(V_2Se_2O_{10})]$, and **2**, $[Ni(4,4'\text{-bipy})(H_2O)(V_2Se_2O_{10})]$. The elemental analysis was performed on a Perkin-Elmer 2400 element analyzer, and inductively coupled plasma (ICP) analysis was performed on a Perkin-Elmer optima 3300 DV ICP spectrometer. Anal. Calcd (Found) for **1**: V, 15.62 (15.68); Se, 24.20 (24.68); Co, 9.08 (9.15); C, 18.38 (18.31); H, 1.53 (1.38); N, 4.29 (4.38). Anal. Calcd (Found) for **2**: V, 15.62 (15.53); Se, 24.21 (24.10); Ni, 9.08 (9.03); C, 18.37 (18.31); H, 1.50 (1.41); N, 4.29 (4.21). The 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. The IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer.

Crystallography. Crystals of **1** and **2** suitable for single-crystal X-ray diffraction with sizes 0.30 mm × 0.24 mm × 0.16 mm and 0.36 mm × 0.26 mm × 0.20 mm were glued to a thin glass fiber with epoxy resin and mounted onto a Siemens SMART CCD diffractometer equipped with a normal-focus, 2.4 kW sealed-tube

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(5) Dai, Z. M.; Shi, Z.; Li, G. H.; Chen, X. B.; Lu, X. Y.; Xu, Y. H.; Feng, S. H. *J. Solid State Chem.*, submitted for publication.

(6) (a) Zapf, P. J.; Warren, C. J.; Haushalter, R. C.; Zubieta, J. *Chem. Commun.* **1997**, 1543−1544. (b) Hagrman, D.; Zapf, P. J.; Zubieta, J. *Chem. Commun.* **1998**, 1283−1284. (c) Zheng, L.-M.; Wang, Y.; Wang, X.;. Korp, J. D.; Jacobson, A. J. *Inorg. Chem.* **2001**, *40*, 1380−1385.

(7) (a) Shi, Z.; Zhang, L.; Zhu, G.; Hua, J.; Ding, H.; Feng, S. *Chem. Mater.* **1999**, *11*, 3565−3570. (b) LaDuca, R. L., Jr.; Finn, R.; Zubieta, J. *Chem. Commun.* **1999**, 1669−1670. (c) Zheng, L.-M.; Whitfield, T.; Wang, X.; Jacobson, A. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 4528−4531. (d) Zhang, X.-M.; Tong, M.-L.; Chen, X.-M. *Chem. Commun.* **2000**, 1817−1818. (e) LaDuca, R. L.; Jr.; Rarig, R. S.; Zubieta, J. *Inorg. Chem.* **2001**, *40*, 607−612. (f) Hagrman, P. J.; Zubieta, J. *Inorg. Chem.* **2001**, *40*, 2800−2809. (g) Tao, J.; Zhang, X.-M.; Tong, M.-L.; Chen, X.-M. *J. Chem. Soc., Dalton Trans.* **2001**, 770−771.

(8) Lu, J.; Xu, Y.; Goh, N. K.; Chia, L. S. *Chem. Commun.* **1998**, 2733−2734.

(9) (a) Shi, Z.; Feng, S.; Gao, S.; Zhang, L.; Yang, G.; Hua, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2325−2327. (b) Shi, Z.; Feng, S.; Zhang, L.; Yang, G.; Hua, J. *Chem. Mater.* **2000**, *12*, 2930−2935. (c) Finn, R. C.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **2000**, 1821−1823. (d) Zhang, X.-M.; Tong, M.-L.; Feng, S.; Chen, X.-M. *J. Chem. Soc., Dalton Trans.* **2001**, 2069−2070.

(10) Shi, Z.; Zhang, D.; Feng, S.; Li, G. H.; Dai, Z. M.; Fu, W. S.; Chen, X. B.; Hua, J. *J. Chem. Soc., Dalton Trans.* **2002**, *9*, 1873−1874.

Table 3. Bond Lengths (Å) and Angles (deg) for **1**[a]

Co(1)−O(6)#1	2.019(3)	V(1)−O(4)	1.647(3)
Co(1)−O(4)#2	2.020(3)	V(1)−O(1)	1.665(3)
Co(1)−O(1)	2.070(3)	V(1)−O(9)#3	1.977(3)
Co(1)−O(2)	2.073(3)	V(1)−O(10)#4	1.987(3)
Co(1)−N(1)	2.137(4)	V(1)−O(5)	2.187(3)
Co(1)−O(3)	2.174(4)	V(1)−O(5)#5	2.231(3)
V(2)−O(11)	1.612(3)	Se(1)−O(6)	1.653(3)
V(2)−O(2)	1.661(3)	Se(1)−O(7)	1.710(3)
V(2)−O(7)	1.934(3)	Se(1)−O(5)	1.747(3)
V(2)−O(8)	1.955(3)	Se(2)−O(8)	1.701(3)
V(2)−N(2)#6	2.177(4)	Se(2)−O(9)	1.704(3)
		Se(2)−O(10)	1.709(3)
O(6)#1−Co(1)−O(4)#2	87.94(13)	O(1)−Co(1)−N(1)	90.04(14)
O(6)#1−Co(1)−O(1)	175.37(14)	O(2)−Co(1)−N(1)	93.00(14)
O(4)#2−Co(1)−O(1)	94.83(12)	O(6)#1−Co(1)−O(3)	92.45(16)
O(6)#1−Co(1)−O(2)	88.58(13)	O(4)#2−Co(1)−O(3)	87.94(14)
O(4)#2−Co(1)−O(2)	175.21(12)	O(1)−Co(1)−O(3)	83.95(14)
O(1)−Co(1)−O(2)	88.43(12)	O(2)−Co(1)−O(3)	88.92(14)
O(6)#1−Co(1)−N(1)	93.65(16)	N(1)−Co(1)−O(3)	173.65(16)
O(4)#2−Co(1)−N(1)	90.50(14)		
O(4)−V(1)−O(1)	102.06(16)	O(9)#3−V(1)−O(5)	83.39(12)
O(4)−V(1)−O(9)#3	99.52(14)	O(10)#4−V(1)−O(5)	79.51(12)
O(1)−V(1)−O(9)#3	93.49(14)	O(4)−V(1)−O(5)#5	89.75(13)
O(4)−V(1)−O(10)#4	93.49(14)	O(1)−V(1)−O(5)#5	167.10(14)
O(1)−V(1)−O(10)#4	101.86(14)	O(9)#3−V(1)−O(5)#5	79.30(11)
O(9)#3−V(1)−O(10)#4	157.36(13)	O(10)#4−V(1)−O(5)#5	82.33(12)
O(4)−V(1)−O(5)	165.15(13)	O(5)−V(1)−O(5)#5	76.42(12)
O(1)−V(1)−O(5)	92.24(13)		
O(11)−V(2)−O(2)	108.31(17)	O(7)−V(2)−O(8)	85.01(13)
O(11)−V(2)−O(7)	118.95(16)	O(11)−V(2)−N(2)#6	91.60(15)
O(2)−V(2)−O(7)	131.37(15)	O(2)−V(2)−N(2)#6	88.92(15)
O(11)−V(2)−O(8)	100.06(15)	O(7)−V(2)−N(2)#6	79.38(14)
O(2)−V(2)−O(8)	98.05(15)	O(8)−V(2)−N(2)#6	163.71(14)
O(6)−Se(1)−O(7)	98.07(17)	O(8)−Se(2)−O(9)	97.18(15)
O(6)−Se(1)−O(5)	104.75(15)	O(8)−Se(2)−O(10)	96.94(15)
O(7)−Se(1)−O(5)	99.50(14)	O(9)−Se(2)−O(10)	104.26(15)
V(1)−O(1)−Co(1)	138.08(18)	Se(1)−O(6)−Co(1)#7	137.9(2)
V(2)−O(2)−Co(1)	126.33(17)	Se(1)−O(7)−V(2)	128.99(17)
V(1)−O(4)−Co(1)#2	154.64(19)	Se(2)−O(8)−V(2)	128.69(18)
Se(1)−O(5)−V(1)	116.74(14)	Se(2)−O(9)−V(1)#3	123.85(16)
Se(1)−O(5)−V(1)#5	119.93(15)	Se(2)−O(10)−V(1)#8	123.40(17)
V(1)−O(5)−V(1)#5	103.58(12)		

[a] Symmetry transformations used to generate equivalent atoms: #1, $x, y - 1, z$; #2, $-x + 1, -y - 1, -z$; #3, $-x, -y, -z$; #4, $x + 1, y, z$; #5, $-x + 1, -y, -z$; #6, $-x + 1, -y - 1, -z + 1$; #7, $x, y + 1, z$; #8, $x - 1, y, z$.

X-ray source (graphite-monochromated Mo Kα radiation, λ(Mo Kα) = 0.71073 Å) operating at 50 kV and 40 mA. 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.[11] The structure was solved in the space group $P\bar{1}$ for compounds **1** and **2** by direct methods and refined on F^2 by full-matrix least-squares using SHELXT97. Crystal parameters and details of the data collection and refinement for the structures of **1** and **2** are listed in Table 1. Atomic coordinates of compound **1** are listed in Table 2. Selected bond lengths and angles of compound **1** are listed in Table 3.

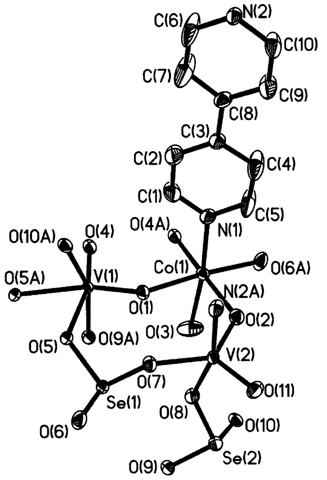

Figure 1. ORTER drawing of the asymmetric unit of **1** (50% thermal ellipsoids).

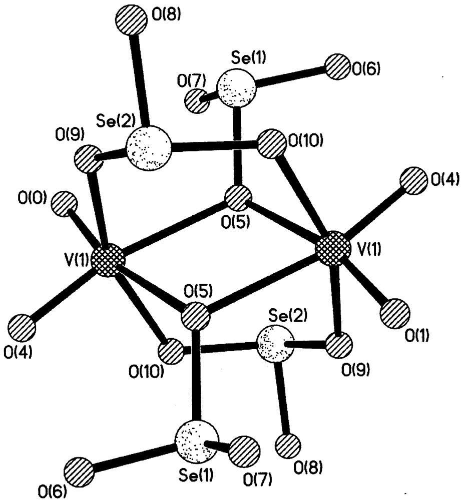

Figure 2. Structure of the cluster anions $[V_2Se_4O_{14}]^{4-}$ of **1**.

Results and Discussion

Single-crystal X-ray diffraction analysis reveals that compounds **1** and **2** have 3D frameworks and consist of infinite layers of M/V/Se/O, linked by the coordination of 4,4′-bipy with M and V atoms. In the asymmetric unit of **1**, there are two crystallographically independent vanadium and selenium atoms, and a unique site for cobalt (Figure 1). The octahedral coordination about V(1) atom is surrounded by two oxygen atoms corner-shared with two CoO_5N octahedra, two oxygen atoms coming from two $Se(2)O_3$ units, and two μ_3-oxo groups which are edge bridged to the next octahedron of $V(1)O_6$ and also shared by two $Se(1)O_3$ units. The V(2) center exhibits $[VO_4N]$ triangular-bipyramid coordination. Each V(2) atom bonds to a terminal oxygen (V═O = 1.614(4) Å), connects to a nitrogen atom of 4,4′-bipy, shares two corners with $Se(1)O_3$ and $Se(2)O_3$ pyramids, respectively, and connects to an oxygen in $[CoO_5N]$ octahedra. Both Se(1) and Se(2) atoms are monoselenite cations $[SeO_{3/2}]^+$. Se(1) connects V(1), V(2), and Co(1) polyhedra through O(5), O(7), and O(6), whereas Se(2) connects to V(2) through O(8) and to V(1) through O(9) and O(10). The Co coordination geometry is an octahedral configuration, which is defined by two oxygen donors of $V(1)O_6$, one oxygen donor of VO_4N, one oxygen donor of $Se(1)O_3$, one oxygen donor of water, and one nitrogen donor of 4,4′-bipy. The bond valence sum calculations, giving oxidation states of corresponding ions, indicate the occurrence of Co^{2+}, V^{5+}, and Se^{4+}.

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(11) Software packages SMART and SAINT, Siemens Analytical X-ray Instrument Inc., Madison, WI, 1996. SHELXTL, Version 5.1, Siemens Industrial Automation, Inc., 1997.

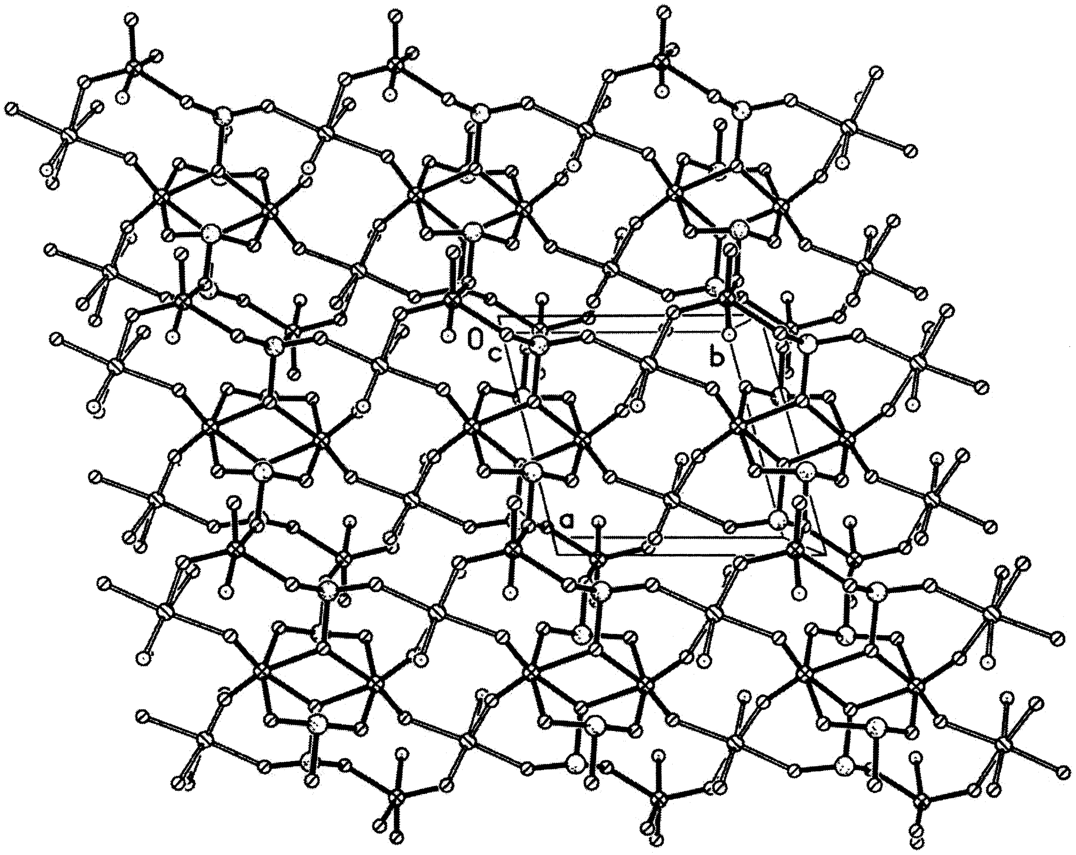

Figure 3. View of the Co/V/Se/O layer in the *ab*-plane of **1**.

An unusual feature of the structure is the presence of clusters $[V_2Se_4O_{14}]^{4-}$ (Figure 2), which are connected by two $V(1)O_6$ octahedra edged-linked together with two $Se(1)O_3$ and two $Se(2)O_3$ pyramids. $Se(1)O_3$ connects two V(1) atoms through the bridging oxygen atoms O(5), while Se(2) connects two V(1) atoms through O(9) and O(10). The edge-sharing interaction between $V(1)O_6$ polyhedral triangular bipyramids also appears in the structure of a vanadium selenite, $(VO)_2(SeO_3)_3$.[12] The clusters are connected through $V(2)O_4N$ polyhedra, thus forming the infinite chains $[(VO_2)(SeO_3)]^-$, where V(2) atoms adopt the distorted unusual triangular-bipyramidal geometry with an angle of 160° between the axial oxygen and nitrogen. An inorganic layer motif, Co/V/Se/O, in the *ab*-plane is shown in Figure 3. The pyridine rings of 4,4′-bipy linking V(2) and Co atoms are twisted by 6.6°. Thus, the structure of **1** may be rationalized in terms of Co/V/Se/O layers connected by 4,4′-bipy, which afford the complex three-dimensional structure (Figure 4). Although $M(4,4'\text{-bipy})(H_2O)V_2Se_2O_{10}$ is similar to $[M(4,4'\text{-bipy})_2(VO)_2(HPO_4)_4]$ (M = Co, Ni)[13] in that the 4,4′-bipy has the same coordination mode which is directly linked to M (Co or Ni) and V atoms in the P−V−O chains, the structures of $[M(4,4'\text{-bipy})_2(VO)_2(HPO_4)_4]$ are constructed from $[(VO_2)(HPO_4)]_\infty$ helical chains and $[M(4,4'\text{-bipy})_2]^{2+}$ fragments. When 1,10′-phen is used instead of 4,4′-bipy, the layered coordination-complex-linked vanadium selenite $[Cu(phen)]_2V_2Se_2O_{11}$ is synthesized,[10] which consists

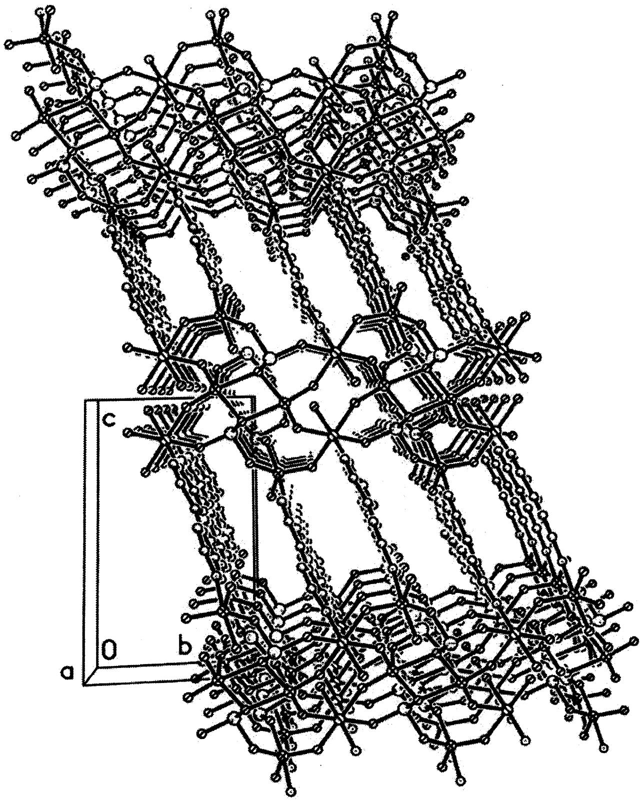

Figure 4. View of the crystal structure of **1** along the *c*-axis.

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[12] Halasyamani, P. Shiv.; O'Hare, D. *Inorg. Chem.* **1997**, *36*, 6409−6412.

[13] Shi, Z.; Feng, S.; Gao, S.; Zhang, L.; Yang, G.; Hua, J. *Angew. Chem., Int. Ed.* **2000**, *39*, 2325−2327.

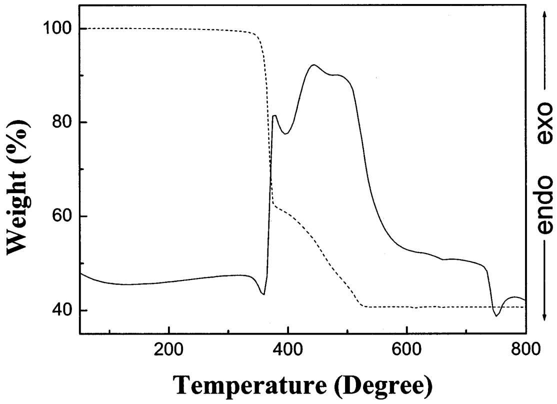

Figure 5. Thermogravimetric analysis (—) and differential thermal analysis (---) curves for compound **1**.

of neutral sheets of copper−vanadium selenite in the *ac*-plane, constructed from $[V_2Se_2O_{11}]^{2-}$ units and $[Cu(phen)]^{2+}$ fragments.

In the TGA curves for **1** and **2** (shown in Figure 5), two weight losses of 2.76% and 23.93% in the range of 320−390 °C are consistent with the loss of H_2O and 4,4′-bipy, respectively. Compounds **1** and **2** are thermally stable below 300 °C. Finally, SeO_2 was sublimated on heating in the temperature range 400−520 °C with a weight loss of 34.04%. In agreement with the TGA curve, a weak endothermic peak and a weak exothermic peak were observed in the DTA curve at ca. 320 and 360 °C, which correspond to the loss of H_2O and 4,4′-bipy. The following endothermic peak at ca. 400 °C is assigned to the decomposition of SeO_2. At higher temperature, the endothermic peak at ca. 750 °C may be due to a phase transformation.

The title compounds are also characterized by the FTIR spectrum. In the IR spectrum of the compounds, the strong bands at 942.4, 869.7, 773.3, and 618.0 cm^{-1} are due to the terminal V═O stretch or a V−O−V stretch, while the SeO_3 anion is also expected to have adsorptions in the same region. Adsorption bands from 1608.3 to 1413.6 cm^{-1} are due to the pyridine ring breathing bands of 4,4′-bipy.

Conclusions

We have synthesized two novel 3D coordination-complex-linked vanadium selenites which have M/V/Se/O inorganic layers bridged through 4,4′-bipy ligands. This structure contains unusual clusters, $[V_2Se_4O_{14}]^{4-}$, and these clusters are combined with Co or Ni ions, giving infinite inorganic layers, with which the 4,4′-bipy molecule is linked to form a 3D framework of $M(4,4'\text{-bipy})(H_2O)V_2Se_2O_{10}$ (M = Co, Ni). Further study on extensive synthesis in related systems and property measurement is in progress.

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Supporting Information Available: Two X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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