



Syntheses, structures and characterizations of three novel vanadium selenites with organically bonded copper/nickel complex



Cheng Qian^{a,b}, Fang Kong^b, Jiang-Gao Mao^{a,b,*}

^a College of Chemistry, Fuzhou University, Fuzhou, Fujian 350002, PR China

^b State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, PR China

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ABSTRACT

A series of vanadium selenites covalently bonded with metal-organic complex, namely, Ni(2,2-bipy)₂V₂O₄(SeO₃)₂ (**1**), Cu(2,2-bipy)V₂O₄(SeO₃)₂ · 0.5H₂O (**2**) and Cu₂(2,2-bipy)₂V₅O₁₂(SeO₃)₂ (**3**) (2,2-bipy = 2,2-bipyridine) have been hydrothermally synthesized and structurally characterized. They exhibit three different structural dimensions, from 0D cluster, 1D chain to 2D layer. Compound **1** features a 0D {Ni(2,2-bipy)₂V₂O₄(SeO₃)₂}₂ dimeric cluster composed of two {Ni(2,2-bipy)₂}²⁺ moieties connected by the {V₄O₈(SeO₃)₄}⁴⁻ cluster. Compound **2** shows a 1D {Cu(2,2-bipy)V₂O₄(SeO₃)₂}_n chain in which the {Cu₂(2,2-bipy)₂}⁴⁺ moieties are bridged by the {V₄O₈(SeO₃)₄}⁴⁻ clusters. Compound **3** displays a 2D structure consisted of mixed valence vanadium selenites layers {V^{IV}V₄Se₂O₁₈}_n⁴⁻ and {Cu(2,2-bipy)}²⁺ complex moieties. The adjacent layers are further interconnected via π-π interactions between the 2,2-bipy ligands exhibiting an interesting 3D supramolecular architecture. Both compound **1** and **2** contain a new {V₄O₈(SeO₃)₄}⁴⁻ cluster and compound **3** exhibits the first 2D vanadate polyhedral layer in vanadium selenites/tellurites with organic moieties.

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1. Introduction

Inorganic-organic hybrid materials have received enormous attention over the past few years due to their potential applications in magnetism, molecular adsorption, optical properties, electro-conductivity and catalysis [1–10]. Many of these materials are synthesized in the presence of organic amines as structure-directing agents and charge compensator cations [11–17]. A remarkable variety of such organically templated or linked metal selenites or tellurites have been reported because the stereochemically active lone pair electrons of Se(IV) or Te(IV) have a dramatic effect on the structures of their metal compounds formed [18–39]. In the case of vanadium selenites or tellurites, a series of intriguing frameworks ranging from 0D clusters to 3D frameworks have been reported, such as (2,2-bipy)V₂SeO₇ (0D), (2,2-bipy)₄V₄O₈(SeO₃)₂ (1D), [H₂en][(VO₂)(TeO₃)₂] · H₂O, (2D), (en = ethylenediamine), (4,4-bipy)₂V₄O₆(SeO₃)₃ · H₂O (3D), (4,4-bipy = 4,4-bipyridine), (C₂N₂H₁₀)VO(SeO₃)₂ (3D) and (R), (S)-C₅H₁₄N₂(VO(SeO₃)(HSeO₃))₂ · 2H₂O (3D) [29–34].

However, vanadate selenites or tellurites decorated with {M_xL_y} (M = transition metal ions, L = organic ligands) are still rare. To the best

of our knowledge, only seven kinds of structures were reported [33–39]. Most of such compounds exhibit a 2D layered framework except M(4,4-bipy)(H₂O)V₂O₄(SeO₃)₂ (M = Co, Ni), which displays a 3D skeleton composed of {VO₂(SeO₃)₂}⁻ 1D chains and {M(4,4-bipy)(H₂O)}²⁺ (M = Co, Ni) fragments. The 2D structures of M(phen)V₂TeO₈ (M = Cu, Ni), Cu(TATP)V₂TeO₈ and Zn₂(bipy)₂V₄TeO₁₄ are composed of 1D vanadium selenite (or tellurite) chains bridged by {M_xL_y} moieties while Cu(phen)(H₂O)₂V₃O₅(SeO₃)₃ · H₂O, [Cu(phen)]₂V₂Se₂O₁₁ and Cu(DPPZ)V₂Te₂O₁₀ consist of 2D vanadium selenite (or tellurite) layers decorated by {M_xL_y} moieties.

Herein, we present three new vanadium selenites with organically linked copper/nickel complex, namely, Ni(2,2-bipy)₂V₂O₄(SeO₃)₂ (**1**), Cu(2,2-bipy)V₂O₄(SeO₃)₂ · 0.5H₂O (**2**) and Cu₂(2,2-bipy)₂V₅O₁₂(SeO₃)₂ (**3**) by hydrothermally syntheses. They display three different structural dimensions, from 0D cluster, to 1D chain and 2D layer. The three compounds are characterized by single crystal X-ray diffraction studies. Optical, thermal and magnetic properties are also reported.

2. Experimental section

2.1. Reagents and physical measurements

SeO₂ (99+%, AR), V₂O₅ (99.5+%, AR), Ni(Ac)₂ · 4H₂O (99+%, AR), 2,2-bipy (99+%, AR), CuCl₂ · 2H₂O (99+%, AR) and Cu(Ac)₂ · H₂O (99.9+%, AR) are used as received. All of the

* Corresponding author at: State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, PR China.

E-mail address: mjg@fjirsm.ac.cn (J.-G. Mao).

chemicals are supplied by the Shanghai Reagent Factory. Microprobe elemental analyses for the V, Cu, Ni and Se elements were carried out on a field-emission scanning electron microscope (FESEM, JSM6700 F) equipped with an energy dispersive X-ray spectroscope (EDS, Oxford INCA). Elemental analyses on H, N and C were taken on a German Elementary Vario EL III instrument. X-Ray powder diffraction (XRD) patterns were collected on a XPERT-MPD θ - 2θ diffractometer using graphite monochromated Cu-K α radiation in the angular range from 5 to 50° (2θ) with a step size of 0.02. Infrared spectra were collected on a Magna 750 FT-IR spectrometer as KBr pellets in the spectral range of 4000–400 cm^{-1} with a resolution of 2 cm^{-1} at room temperature. Optical diffuse-reflectance spectra were recorded with the aid of PE Lambda 900 UV-vis spectrophotometer equipped with an integrating sphere attachment and BaSO₄ as the reference at room temperature. The absorption spectra were calculated from the reflection spectra using the Kubelka-Munk formula: $\alpha/S = (1 - R)^2 / 2R$ [40], in which α is the absorption coefficient, S is the scattering coefficient, and R is the reflectance. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with a NETZCH STA449 C unit at a heating rate of 10 °C min^{-1} under an air atmosphere. Magnetic property measurements were performed on the PPMS-9T magnetometer.

2.2. Syntheses of compounds 1–3

Synthesis of Ni(2,2-bipy)₂V₂O₄(SeO₃)₂ 1: Compound **1** was synthesized by hydrothermal reactions of Ni(Ac)₂·4H₂O (125 mg, 0.5 mmol), 2,2-bipy (76 mg, 0.5 mmol), SeO₂ (220 mg, 2 mmol), V₂O₅ (45 mg, 0.25 mmol) and 10 mL distilled water and the resultant mixture was sealed into an autoclave equipped with a Teflon liner (23 mL) and heated at 120 °C for 5 days. After gradually cooling to room temperature, the brown block-shaped crystals were collected in 51.5% yield based on V₂O₅ and its purity was confirmed by XRD studies (Fig. S1a). Results of EDS on the single crystals of **1** gave average molar ratios of Ni: V: Se of 1.0: 1.9: 2.0, respectively, and elemental analyses gave molar ratios of H: N: C of 7.99: 2.01: 9.98, respectively, which are very close to that determined from single-crystal X-ray structural studies. IR data (KBr, cm^{-1}): 3112 (w), 3072 (w), 1604 (m), 1440 (s), 1311 (w), 1176 (w), 977 (s), 889 (m), 840 (m), 780 (s), 740 (s), 586 (w), 526 (m).

Synthesis of Cu(2,2-bipy)V₂O₄(SeO₃)₂·0.5H₂O 2: The compound **2** was obtained by the reactions of Cu(Ac)₂·H₂O (100 mg, 0.5 mmol), 2,2-bipy (75 mg, 0.5 mmol), SeO₂ (220 mg, 2 mmol), V₂O₅ (45 mg, 0.25 mmol), and 10 mL distilled water and the resultant mixture was sealed into an autoclave equipped with a Teflon liner (23 mL) and heated at 120 °C for 5 days. After

gradually cooling to room temperature, the green rod-like crystals were collected in 64.3% yield based on V₂O₅ and its purity was confirmed by XRD studies (Fig. S1b). EDS gave average molar ratios of Cu: V: Se of 1.0: 1.9: 2.1, and results of elemental analyses gave molar ratios of H: N: C of 7.98: 1.99: 9.97, which are comparable to that determined from single-crystal X-ray structural studies. IR data (KBr, cm^{-1}): 3445 (m), 3115 (w), 1599 (m), 1443 (s), 1309 (w), 1170 (w), 970 (s), 885 (m), 835 (m), 775 (s), 740 (s), 579 (w), 512 (m), 490 (m).

Synthesis of Cu₂(2,2-bipy)₂V₅O₁₂(SeO₃)₂ 3: The compound **3** was obtained with the reactions of CuCl₂·2H₂O (85 mg, 0.5 mmol), 2,2-bipy (75 mg, 0.5 mmol), SeO₂ (220 mg, 2 mmol), V₂O₅ (45 mg, 0.25 mmol), and 10 mL distilled water and the resultant mixture was sealed into an autoclave equipped with a Teflon liner (23 mL) and heated at 160 °C for 5 days. After gradually cooling to room temperature, the dark green block-shaped crystals were collected in 57.7% yield based on V₂O₅ and its purity was confirmed by XRD studies (Fig. S1c). Results of EDS on the single crystals of **3** gave average molar ratios of Cu: V: Se of 2.0: 5.3: 2.2, respectively, and results of elemental analyses gave mass ratios of H: N: C of 7.99: 1.99: 9.98, which are very close to that determined from single-crystal X-ray structural studies. IR data (KBr, cm^{-1}): 3116 (w), 1605 (m), 1443 (m), 1320 (w), 1153 (w), 997 (s), 824 (m), 734 (s), 534 (m), 472 (m), 417 (m).

2.3. Single-crystal structure determination

Data collections for the three compounds were performed on SuperNova (Cu) X-ray Source, Cu-K α radiation (1 $\frac{1}{4}$ 0.71073 Å) at 293(2) K. All data sets were corrected for Lorentz and polarization factors as well as for absorption by the multi-scan method [41a]. All structures were solved by direct methods and refined by a full-matrix least-squares fitting on F^2 by SHELX-97 [41b]. All hydrogen atoms are located at geometrically calculated positions and refined with isotropic thermal parameters. The lattice water molecule (O(1 W)) in compound **2** was disordered with O(1 W)...O(1 W) (symmetry code: -x, -y, -z) separation of 1.068(18) Å and its occupancy is also reduced to 50%. All structures were also checked for possible missing symmetry with the program PLATON [41c]. Crystallographic data and structural refinements for the three compounds are summarized in Table 1 and important bond distances are listed in Table 2. More information about the crystallographic studies as well as atomic displacement parameters are given in Table S1. The CCDC reference numbers are 1,447,384, 1,447,385 and 1,447,386 for **1**, **2** and **3**, respectively. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +441223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1
Crystal data and structure determination for compounds.

| Formula | Ni(2,2-bipy) ₂ V ₂ O ₄ (SeO ₃) ₂ | Cu(2,2-bipy)V ₂ O ₄ (SeO ₃) ₂ ·0.5H ₂ O | Cu ₂ (2,2-bipy) ₂ V ₅ O ₁₂ (SeO ₃) ₂ |
|--|--|---|---|
| Formula Weight | 790.88 | 648.54 | 1140.07 |
| Space group | <i>P</i> 21/ <i>n</i> | <i>P</i> -1 | <i>P</i> -1 |
| <i>a</i> (Å) | 7.6436(4) | 9.0239(4) | 9.8790(5) |
| <i>b</i> (Å) | 25.0112(10) | 10.6596(5) | 10.4128(6) |
| <i>c</i> (Å) | 13.0248(6) | 11.0608(6) | 16.2641(8) |
| α (deg) | 90 | 62.134(5) | 76.463(4) |
| β (deg) | 95.708(4) | 69.284(5) | 73.915(4) |
| γ (deg) | 90 | 89.034(4) | 84.660(4) |
| <i>V</i> (Å ³) | 2477.7(2) | 865.47(7) | 1562.19(14) |
| <i>Z</i> | 4 | 2 | 2 |
| μ (Mo K α) (mm ⁻¹) | 4.493 | 6.540 | 16.952 |
| GOF on F^2 | 1.072 | 1.105 | 1.007 |
| R1, wR2 [$I > 2\sigma(I)$] ^a | R1 = 0.0281, wR2 = 0.0611 | R1 = 0.0239, wR2 = 0.0532 | R1 = 0.0365, wR2 = 0.0872 |
| R1, wR2 (all data) ^a | R1 = 0.0347, wR2 = 0.0640 | R1 = 0.0297, wR2 = 0.0559 | R1 = 0.0536, wR2 = 0.0781 |

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

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