

# First coordination complex-linked vanadium selenite, [Cu(phen)]<sub>2</sub>V<sub>2</sub>Se<sub>2</sub>O<sub>11</sub>: hydrothermal synthesis and crystal structure

Zhan Shi, Dong Zhang, Shouhua Feng,\* Guanghua Li, Zhimin Dai, Wensheng Fu, Xiaobo Chen and Jia Hua

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130023, P.R. China. E-mail: shfeng@mail.jlu.edu.cn

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A novel bimetallic selenite, [Cu(phen)]<sub>2</sub>V<sub>2</sub>Se<sub>2</sub>O<sub>11</sub>, which is the first example of a coordination complex-linked vanadium selenite, has been hydrothermally prepared and characterized by X-ray crystallography.

The design and synthesis of inorganic–organic hybrid materials have received extensive attention over the past few years due to their ability to encompass interesting functions such as catalysis, biology, electrical conductivity, magnetism and photochemistry.<sup>1</sup> A number of coordination complex-linked molybdates, vanadates, molybdenum phosphates and vanadium phosphates with one- (1D), two- (2D), and three-dimensional (3D) frameworks in the systems of M<sub>x</sub>L<sub>y</sub>/Mo/O,<sup>2</sup> M<sub>x</sub>L<sub>y</sub>/V/O,<sup>3</sup> M<sub>x</sub>L<sub>y</sub>/Mo/P/O,<sup>4</sup> M<sub>x</sub>L<sub>y</sub>/V/P/O,<sup>5</sup> (M = transition metal, L = organic ligand, x : y = 1 : 1, 1 : 2 or 1 : 3) have been reported, but little study has been done on the systems of coordination complex-linked vanadium selenites. Some of the simple vanadium selenites, such as (VO)<sub>2</sub>(SeO<sub>3</sub>)<sub>3</sub>,<sup>6a</sup> NH<sub>4</sub>(VO<sub>2</sub>)<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub>,<sup>6b</sup> CsVSeO<sub>5</sub>,<sup>6c</sup> Cd(VO<sub>2</sub>)<sub>4</sub>(SeO<sub>3</sub>)<sub>3</sub>·H<sub>2</sub>O<sup>6d</sup> and Cu(VO)(SeO<sub>3</sub>)<sub>2</sub>,<sup>6e</sup> have already been synthesized. However, recently, three organically templated selenites, (CN<sub>3</sub>H<sub>6</sub>)<sub>4</sub>[Zn<sub>3</sub>(SeO<sub>3</sub>)<sub>5</sub>],<sup>6f</sup> [C<sub>4</sub>N<sub>2</sub>H<sub>12</sub>]<sub>0.5</sub>[Fe<sub>2</sub>F<sub>3</sub>(SeO<sub>3</sub>)<sub>2</sub>]<sup>6g</sup> and [C<sub>2</sub>N<sub>2</sub>H<sub>8</sub>]<sub>0.5</sub>ZnSeO<sub>3</sub><sup>6g</sup> have been prepared. In addition, two four-nuclear complexes, [(n-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>N]<sub>3</sub>[SeV<sub>3</sub>O<sub>11</sub>]·0.5H<sub>2</sub>O and [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P]<sub>2</sub>N<sub>2</sub>[Se<sub>2</sub>V<sub>2</sub>O<sub>10</sub>], were reported by Yagasaki and co-workers.<sup>6h</sup> We are broadening our research fields in order to include not only traditional phosphates but also selenite systems in that the latter presents the structural variety of the coordination. Here, we report the hydrothermal synthesis and X-ray crystal structure of a novel framework coordination complex-linked bimetallic selenite, [Cu(phen)]<sub>2</sub>V<sub>2</sub>Se<sub>2</sub>O<sub>11</sub> (**1**) (phen = 1,10-phenanthroline).

In a typical synthesis procedure for **1**, a mixture of NaVO<sub>3</sub>·2H<sub>2</sub>O (0.158 g), SeO<sub>2</sub> (0.555 g), Cu(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.291 g), phen·H<sub>2</sub>O (0.198 g), NaHCO<sub>3</sub> (0.336 g) and H<sub>2</sub>O (10 mL) in a molar ratio of 1 : 5 : 1 : 1 : 4 : 556 was heated in a sealed Teflon-lined steel autoclave at 160 °C for 120 h. Dark green crystals were obtained which were washed with deionized water, filtered off and dried in air (60% yield based on vanadium). The use of V<sub>2</sub>O<sub>5</sub> as an alternative vanadium source could also lead to the same product. The elemental analysis, ICP and IR spectra<sup>†</sup> in combination with X-ray single-crystal analysis<sup>‡</sup> confirmed the formula of **1**, [Cu(phen)]<sub>2</sub>V<sub>2</sub>Se<sub>2</sub>O<sub>11</sub>. The TGA–DTA showed that **1** has a relatively high thermal stability in air (320 °C) and the phen groups are combusted in the range 330–400 °C with weight losses of 38.51% (calculated value, 39.12%). SeO<sub>2</sub> was sublimated on heating in the temperature range 400–540 °C with weight losses of 24.90% (calculated value, 24.04%).

In the asymmetric unit of **1**, there is a crystallographically unique site for copper, vanadium and selenium, as shown in Fig. 1. The Cu center exhibits {CuN<sub>2</sub>O<sub>3</sub>} square-pyramidal coordination geometry through bonding to two *cis* nitrogen donors of phen, two oxygen donors of selenite in the basal plane and an oxygen of vanadate in the apical position. The V site shows VO<sub>4</sub> tetrahedral geometry. Each V atom bonds to a terminal oxygen (V=O), connects to a bridging oxygen from the {CuN<sub>2</sub>O<sub>3</sub>} square-pyramid, and shares two corners with an

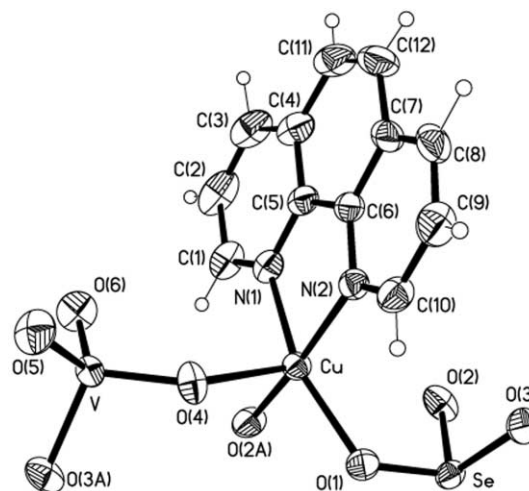


Fig. 1 View of the coordination environments of the copper, vanadium and selenium atoms, showing the atom-labeling scheme and 50% thermal ellipsoids. Selected bond lengths (Å): Se–O(1) 1.684(3), Se–O(2) 1.673(3), Se–O(3) 1.733(3), Cu–O(1) 2.013(2), Cu–O(2) 1.952(3), Cu–O(4) 2.184(2), Cu–N(1) 2.036(3), Cu–N(2) 2.007(3), V–O(3<sup>ii</sup>) 1.865(3), V–O(4) 1.643(3), V–O(5) 1.7859(5), V–O(6) 1.609(3). Symmetry code: (i)  $-x + 1/2, y, -z + 3/2$ ; (ii)  $x + 1/2, -y, z + 1/2$ .

SeO<sub>3</sub> pyramid and a VO<sub>4</sub> tetrahedron. Typically, in mixed-metal selenites, Se<sup>4+</sup> ions are found as either the monoselenite cation [SeO<sub>3/2</sub>]<sup>+</sup>, in which each oxygen is bonded to a selenium atom and another metal, or the diselenite cation [Se<sub>2</sub>O<sub>5/2</sub>]<sup>3+</sup>, where one oxygen bridges the Se atoms and the remainder link to another metal.<sup>6a</sup> In our case, the selenite group, bridging two Cu atoms and one V atom, is a monoselenite cation [SeO<sub>3/2</sub>]<sup>+</sup>. The bond valence sum calculations, giving the oxidation states of the corresponding ions, indicate the occurrence of Cu<sup>2+</sup>, V<sup>5+</sup> and Se<sup>4+</sup>.<sup>7</sup>

The structure of **1** consists of neutral sheets of copper–vanadium selenite in the *ac*-plane, constructed from [V<sub>2</sub>Se<sub>2</sub>O<sub>11</sub>]<sup>2-</sup> units and [Cu(phen)]<sup>2+</sup> fragments attached covalently *via* oxygen atoms, as shown in Fig. 2. The anionic [V<sub>2</sub>Se<sub>2</sub>O<sub>11</sub>]<sup>2-</sup> unit is composed of two V tetrahedra that share a vertex and each V tetrahedron shares a vertex with a Se pyramid, thus forming short zigzag chains (Se–O–V–O–V–O–Se) and infinite double chains (Cu–O–V–O–Se) on 8-membered ring (8-MR) and 4.6-MR, respectively. To our knowledge, this array has not been reported for any vanadium selenites so far, in which [SeV<sub>3</sub>O<sub>11</sub>]<sup>3-</sup> tetramers and [Se<sub>2</sub>V<sub>2</sub>O<sub>10</sub>]<sup>2-</sup> rings normally exist.<sup>6h</sup> The coordination complex, [Cu(phen)]<sup>2+</sup> links the anionic vanadium selenite [V<sub>2</sub>Se<sub>2</sub>O<sub>10</sub>]<sup>2-</sup> units, forming a 4.6.8-MR network. The compositions of these three rings are represented as {Cu<sub>2</sub>Se<sub>2</sub>O<sub>4</sub>} (4-MR), {Cu<sub>2</sub>V<sub>2</sub>Se<sub>2</sub>O<sub>6</sub>} (6-MR) and {Cu<sub>2</sub>V<sub>4</sub>Se<sub>2</sub>O<sub>8</sub>} (8-MR). The distance between the two Cu atoms in the 4-, 6- and 8-MR are 3.63, 6.75 and 6.79 Å, and between the two Se atoms 3.58, 4.74 and 9.86 Å, respectively. It is interesting to compare **1** with the structure of a 2D aluminophosphate, Al<sub>3</sub>P<sub>4</sub>O<sub>16</sub>·3C<sub>3</sub>H<sub>7</sub>NH<sub>3</sub>, where a 4.6.8-network was also observed,

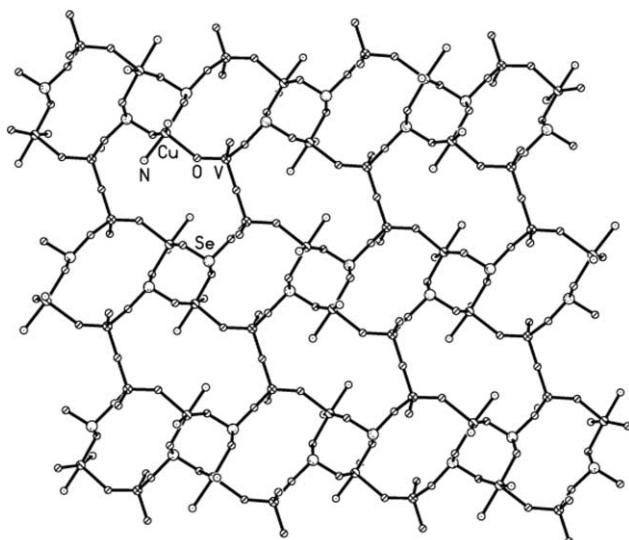


Fig. 2 View of the bimetallic selenite layer along the *b*-axis.

but the 6-MR in the aluminophosphate was capped, *e.g.*, the P atom was located in the center of the 6-MR.<sup>8</sup> However, the topological structure of **1** is novel and no analogue has been found in any 2D aluminophosphate.

The layers of copper–vanadium selenite are stacked in an AAAA sequence along the *b*-axis, as shown in Fig. 3. The

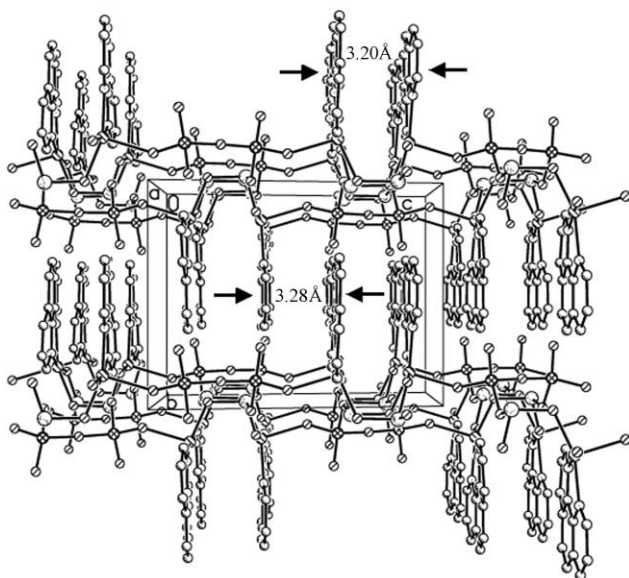


Fig. 3 View of the intercalation of the bimetallic selenite layers with the unit cell outlined.

adjacent layers are closely connected through very strong  $\pi$ – $\pi$  interactions of the phen which alternate side-to-side on the layers. There are two kinds of  $\pi$ – $\pi$  interactions, namely, within the same layer and between the adjacent layers. The close contact distance between adjacent phen rings is 3.20 and 3.28 Å, respectively. Therefore, the 2D layers of **1** are further extended into a 3D supramolecular array *via* the zipper-like intercalation of the lateral aromatic groups.

In summary, the hydrothermal isolation of a novel coordination complex-linked bimetallic selenite,  $[\text{Cu}(\text{phen})]_2\text{V}_2\text{Se}_2\text{O}_{11}$ , has provided the possibility for preparing selenium-containing inorganic–organic hybrid materials in a wide range of systems. We are currently carrying out the substitution of copper for other metals and phen for other organic ligands in similar hydrothermal systems and are studying the rational synthesis of new inorganic–organic materials.

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## Notes and references

† Anal. Calc. for **1**  $\text{C}_{24}\text{H}_{16}\text{N}_4\text{Cu}_2\text{V}_2\text{Se}_2\text{O}_{11}$ : C, 31.22; H, 1.75; N, 6.07; Cu, 13.76; V, 11.03; Se, 17.10%. Found: C, 31.09; H, 1.84; N, 6.19; Cu, 13.62; V, 11.11; Se, 17.02%. IR (KBr,  $\text{cm}^{-1}$ ): 3080w, 3044w, 2008w, 1624w, 1582m, 1514s, 1425s, 1343m, 1319m, 1226m, 1149m, 1109m, 1046m, 952s, 920s, 862s, 783s, 666s, 571s, 459s.

‡ Crystal data for **1**  $\text{C}_{24}\text{H}_{16}\text{N}_4\text{Cu}_2\text{V}_2\text{Se}_2\text{O}_{11}$ :  $M = 923.29$ , monoclinic, space group  $P2_1/n$  (no. 13),  $a = 11.1059(3)$ ,  $b = 9.8725(3)$ ,  $c = 13.0827(3)$  Å,  $\beta = 101.191(2)^\circ$ ,  $V = 1407.15(7)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 2.179$  g cm<sup>-3</sup>,  $\mu = 4.790$  mm<sup>-1</sup>. Data collection  $2.06 \leq \theta \leq 23.24^\circ$  for **1** were performed on a Siemens SMART CCD diffractometer using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda(\text{Mo-K}\alpha) = 0.71073$  Å). The data were collected at 293 K. Data processing was accomplished with the SAINT processing program.<sup>9</sup> The structures were solved with direct methods using the SHELXTL crystallographic software package and refined with full-matrix least-squares,<sup>10</sup> giving a final  $R_1$  value of 0.0293 for 236 parameters and 2016 unique reflections with  $I \geq 2\sigma(I)$  [ $R(\text{int}) = 0.0347$ ] and  $wR_2$  of 0.0775 for all 6659 reflections. CCDC reference number 177805. See <http://www.rsc.org/suppdata/dt/b2/b201955h/> for crystallographic data in CIF or other electronic format.

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