

catena-Poly[[*(2,2'*-bipyridyl)oxido- vanadium]-di- μ_2 -oxido-[(*2,2'*-bi- pyridyl)oxido-*vanadium*]- μ_3 -selenito- bis[(*2,2'*-bipyridyl)dioxidovanadium]- μ_3 -selenito]

Zhao-Xun Lian,* Ping Liu, Jia-Min Zhang, Tian-Xi Wang
and Tian-Jun Lou

School of Chemistry and Chemical Engineering, Henan Institute of Science and
Technology, Xinxiang 453003, People's Republic of China
Correspondence e-mail: zhxalian@hotmail.com

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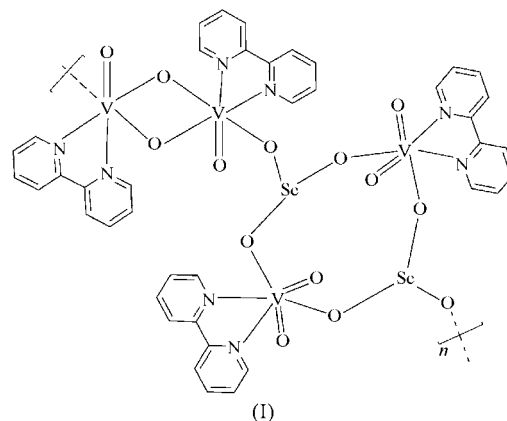
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In the title compound, $[\text{V}_4\text{O}_8(\text{SeO}_3)_2(\text{C}_{10}\text{H}_8\text{N}_2)_4]$, there are two distinct vanadium coordination environments. Alternating corner-shared VO_4N_2 octahedra and SeO_3 pyramids result in eight-membered centrosymmetric $\text{V}_2\text{Se}_2\text{O}_4$ rings. In addition, pairs of V centres form centrosymmetric $\text{V}_2\text{O}_6\text{N}_4$ clusters *via* edge-sharing. These two kinds of secondary building units are linked in an *ABABAB* fashion to give an infinite chain whose nature is unprecedented in Se–V–O systems.

Comment

A number of vanadates and vanadium phosphates have been explored extensively as a result of their catalytic properties in organic oxidations and their intercalation properties (Centi, 1993; Cheetham *et al.*, 1999; Chirayil *et al.*, 1997; Ouellette *et al.*, 2006; Sananes *et al.*, 1995; Shan *et al.*, 1999; Shi *et al.*, 2000). In contrast, the known chemistry of vanadium selenites is very limited (Harrison *et al.*, 1995; Halasyamini & O'Hare, 1997; Kim *et al.*, 2001; Kim, Kwon & Lee, 1996; Kim, Lee *et al.*, 1996; Kwon *et al.*, 1996; Lee & Kwon, 1996; Lee *et al.*, 1995; Vaughney *et al.*, 1994). Recently, many planned attempts have been made to modify structurally and to design hybrid vanadium selenites through the introduction of organic species as templates, charge-compensating cations or space-filling agents (Choudhury *et al.*, 2002; Dai, Chen *et al.*, 2003; Dai *et al.*, 2004, 2005; Dai, Shi, Li, Chen *et al.*, 2003; Dai, Shi, Li, Zhang *et al.*, 2003; De *et al.*, 2003; Harrison *et al.*, 2000; Pasha *et al.*, 2003; Shi *et al.*, 2002). This strategy appears to afford primitive control over the dimensionality of the solid through manipulation of the steric requirements and denticity of the ligand, and enjoys considerable success. In our previous work, we have successfully obtained a novel vanadyl selenite templated by an organic salt, *viz.* $[(\text{VO})(\text{H}_2\text{O})_2(\text{SeO}_3)]_2[(\text{H}_2\text{piperazine})\text{SO}_4]$

(Lian *et al.*, 2004). As an extension of our work, we report here the synthesis and crystal structure of the title compound, (I), which exhibits an infinite chain motif whose nature is unprecedented in Se–V–O–*L* systems, where *L* is an organic ligand.



In the asymmetric unit of (I), there are two crystallographically independent V atoms and one distinct Se atom (Fig. 1). Each V centre has a distorted octahedral coordination environment defined by four O atoms and two *cis*-positioned N-atom donors of the 2,2'-bipyridine (2,2'-bipy) ligand. Within the VO_4N_2 environment of atom V1, atoms O1 and O2 occur as terminal $\text{V}=\text{O}$. The remaining O atoms are from two centrosymmetrically related SeO_3 groups, thus forming two $\text{V}-\text{O}-\text{Se}$ linkages with one short and one long $\text{V}-\text{O}$ bond (Table 1). In the case of atom V2, two centrosymmetrically related V2 atoms are asymmetrically bridged *via* two symmetry-related μ_2 -O6 atoms to form a dimeric $\text{V}_2\text{O}_6\text{N}_4$ unit, similar to that in $(1,10\text{-phenanthroline})_2\text{V}_2\text{SeO}_7$ and $[\text{VO}_2(2,2'\text{-bipy})_2(\text{tp})]$ (tp is terephthalate) (Dai, Shi, Li, Zhang *et al.*, 2003; Yuan *et al.*, 2003). Atom O7 is coordinated to atom V2 as terminal $\text{V}=\text{O}$. One O-atom donor from an SeO_3 group is coordinated to atom V2 to make a $\text{V}-\text{O}-\text{Se}$ linkage.

The V–N bond lengths are in the range 2.142 (2)–2.289 (2) Å (Table 1), which are similar to those observed in similar compounds documented elsewhere (Dai, Shi, Li,

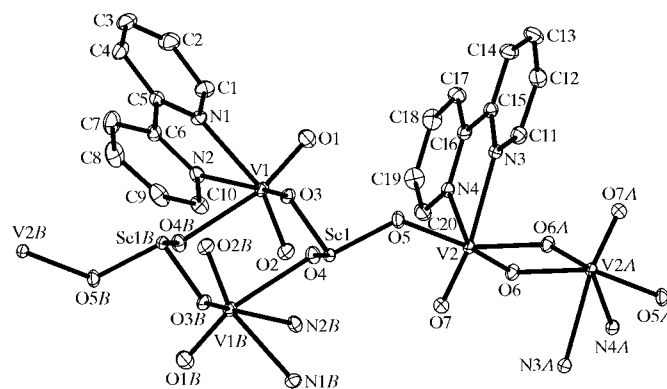


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (A) $-x, -y + 1, -z + 2$; (B) $-x + 1, -y + 1, -z + 1$.]

Zhang *et al.*, 2003; Yuan *et al.*, 2003). The V—O bond lengths vary from 1.6084 (2) to 2.3511 (2) Å and are grouped into four types. The shortest bond lengths are around 1.62 Å and correspond to terminal V=O. In the V—O—V linkages, the bridging O atoms are connected to two symmetry-related V atoms, with one short V—O bond corresponding with one long V—O bond. In the case of the V—O—Se linkages, similar patterns are observed, and longer V—O bonds correspond with shorter Se—O bonds. Given that the longest bridging V—O bond [V1—O4ⁱ; symmetry code: (i) 1 - x, 1 - y, 1 - z] is *trans* to a terminal V=O bond, it is hypothesized that the *trans* effect plays an appreciable role in governing the V—O bond lengths in compound (I).

The VO₄N₂ geometry for atom V1 is similar to those in (2,2'-bipyridine)VSeO₄ and [(VO)(H₂O)₂(SeO₃)₂][(H₂piperazine)SO₄] (Dai, Shi, Li, Zhang *et al.*, 2003; Lian *et al.*, 2004). In these two compounds, there is one V=O bond and three V—O bonds forming three V—O—Se linkages. The Se atom in (I) is tricoordinated by O atoms and exhibits pseudo-tetrahedral geometry, with the lone pair of electrons occupying the apical site. All of the O atoms around atom Se1 form

Se—O—V linkages, with an average Se—O bond length of 1.704 (3) Å and an average O—Se—O angle 100.6 (2)°. Bond-valence sum calculations (Brown & Altermatt, 1985; Brown & Shannon, 1973; Brese & O'Keeffe, 1991) give values of 4.7, 4.8 and 4.2 for atoms V1, V2 and Se1, respectively, showing that the V1 and V2 sites are in the +5 oxidation state and the Se site is in the +4 oxidation state. In [(VO)(H₂O)₂(SeO₃)₂][(H₂piperazine)SO₄], the V centres are in the +4 oxidation state.

The coordination patterns described above result in the structure of the title compound consisting of infinite chains constructed from SeO₃ pyramids, VO₄N₂ octahedra and V₂O₆N₄ clusters (Fig. 2). Two of the O atoms from the SeO₃ pyramids are corner-shared by two symmetrically equivalent V1O₄N₂ octahedra to form cyclic centrosymmetric eight-membered V₂Se₂O₄ rings. Such rings can often be connected into an infinite chain *via* edge-shared or corner-shared bridges. The former type is well documented elsewhere (Pasha *et al.*, 2003; Dai, Shi, Li, Zhang *et al.*, 2003; Dai, Shi, Li, Chen *et al.*, 2003; Dai *et al.*, 2005), while the latter is only exemplified by K(VO)(SeO₃)₂H (Kim, Lee *et al.*, 1996). These chains can be further developed into one-, two- and three-dimensional structures, similar to those in open-framework metal phosphates. In (I), the exocyclic nonterminal O atoms on each side of the V₂O₆N₄ clusters are bonded to Se atoms. This connection results in the secondary units of V₂Se₂O₁₀N₄ and V₂O₆N₄ being linked in an ABABAB fashion into infinite chains. Here, the V₄Se₂O₁₅N₈ unit can be viewed as the principal building block of the chain. To our knowledge, this type of chain has not been reported previously in Se—V—O systems.

In the case of the complex-linked vanadates, vanadium-oxygen polyhedra are assembled *via* corner-sharing or edge-sharing into building blocks. The metal complexes link these building blocks to result in zero-, one-, two- and three-dimensional frameworks (Debord *et al.*, 1996; Zhang *et al.*, 1997; Hagrman & Zubietta, 2001; Hui *et al.*, 2004), where metal complex fragments act either as a bridge between the vanadium-oxygen polyhedra or as a capping motif. In comparison with these compounds, the overall structure of (I) may be best depicted as 'isolated' VO₄N₂ octahedra and V₂O₆N₄ clusters bridged by SeO₃ in the μ₃ mode to form infinite chains.

In the packing arrangement of (I), the 2,2'-bipyridine ligands are arranged in a wave-like fashion. C20—H···π interactions with a C20···π distance of 3.59 Å occur within the infinite chains, while the chains are crosslinked by aromatic interactions between adjacent 2,2'-bipyridine rings with an interplanar spacing of 3.31 Å, and by C8—H···π interactions with a C8···π distance of 3.66 Å (Fig. 3).

Experimental

A mixture of V₂O₅ (0.036 g, 0.2 mmol), SeO₂ (0.060 g, 0.4 mmol), 2,2'-bipyridine (0.032 g, 0.2 mmol) and H₂O (5 ml) was stirred for about 30 min, and then sealed in a Teflon-lined stainless steel autoclave and heated to 393 K for 4 d. The container was cooled to ambient temperature spontaneously. An essentially quantitative yield

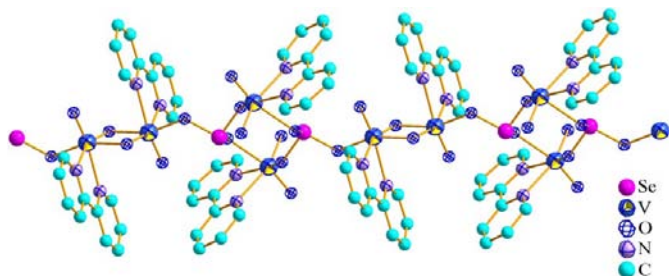


Figure 2
The chain structure of (I), viewed down [101].

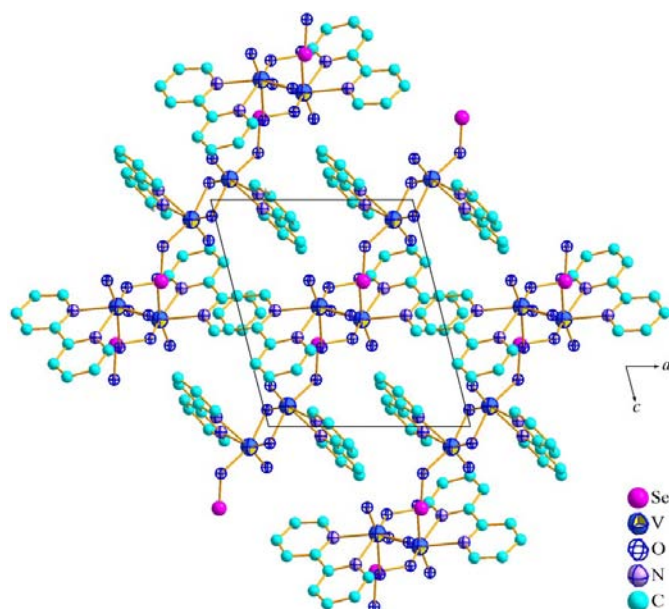


Figure 3
A view of the packing of the chains in (I) in the *ac* plane.

(about 75%, based on V) of red block-shaped single crystals of (I) was recovered by vacuum filtration and drying in air.

Crystal data

$[V_4O_8(SeO_3)_2(C_{10}H_8N_2)_4]$	$\gamma = 76.41 (3)^\circ$
$M_r = 605.21$	$V = 1027.0 (4) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 9.816 (2) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.026 (3) \text{ \AA}$	$\mu = 2.74 \text{ mm}^{-1}$
$c = 11.090 (2) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\alpha = 87.53 (3)^\circ$	$0.46 \times 0.43 \times 0.39 \text{ mm}$
$\beta = 75.49 (2)^\circ$	

Data collection

Rigaku R-AXIS RAPID diffractometer	3588 measured reflections
Absorption correction: multi-scan (TEXSAN; Molecular Structure Corporation, 2001)	3588 independent reflections
$T_{\min} = 0.302, T_{\max} = 0.361$	3458 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.040$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	308 parameters
$wR(F^2) = 0.087$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.89 \text{ e \AA}^{-3}$
3588 reflections	$\Delta\rho_{\text{min}} = -0.57 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$).

Se1—O4	1.6464 (16)	V1—O4 ⁱ	2.3511 (18)
Se1—O3	1.7210 (17)	V2—O7	1.6084 (18)
Se1—O5	1.7439 (17)	V2—O6	1.7337 (16)
V1—O1	1.6285 (19)	V2—O5	1.9093 (18)
V1—O2	1.6292 (17)	V2—O6 ⁱⁱ	1.9876 (18)
V1—O3	1.9466 (18)	V2—N4	2.210 (2)
V1—N2	2.142 (2)	V2—N3	2.289 (2)
V1—N1	2.274 (2)		
O4—Se1—O3	101.45 (8)	N1—V1—O4 ⁱ	76.03 (7)
O4—Se1—O5	103.77 (9)	O7—V2—O6	106.45 (9)
O3—Se1—O5	96.61 (8)	O7—V2—O5	97.50 (9)
O1—V1—O2	104.96 (10)	O6—V2—O5	103.55 (8)
O1—V1—O3	101.88 (8)	O7—V2—O6 ⁱⁱ	99.98 (9)
O2—V1—O3	101.74 (8)	O6—V2—O6 ⁱⁱ	81.99 (8)
O1—V1—N2	93.55 (9)	O5—V2—O6 ⁱⁱ	159.32 (7)
O2—V1—N2	94.56 (9)	O7—V2—N4	93.00 (9)
O3—V1—N2	153.69 (8)	O6—V2—N4	155.09 (8)
O1—V1—N1	90.74 (9)	O5—V2—N4	88.80 (8)
O2—V1—N1	160.71 (9)	O6 ⁱⁱ —V2—N4	79.37 (7)
O3—V1—N1	85.54 (8)	O7—V2—N3	164.14 (8)
O1—V1—O4 ⁱ	165.34 (8)	O6—V2—N3	89.38 (8)
O2—V1—O4 ⁱ	86.95 (8)	O5—V2—N3	79.25 (7)
O3—V1—O4 ⁱ	83.60 (7)	O6 ⁱⁱ —V2—N3	80.93 (7)
N2—V1—O4 ⁱ	76.74 (7)		

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y + 1, -z + 2$.

All H atoms were positioned geometrically, with C—H = 0.93 \AA , and refined using a riding model, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *RAPID-AUTO* (Rigaku, 2001); cell refinement: *RAPID-AUTO*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN3059). Services for accessing these data are described at the back of the journal.

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