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Methanothermal Synthesis of Two Dimeric Vanadium Polyselenides, $[V_2O_2Se_{10}]^{4-}$ and $[V_2O_2Se_8]^{4-}$

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Introduction

Recently, we have shown that the solvothermal method[1-4] has been used successfully to synthesize a series of novel transition metal and main group metal polychalcogenide compounds, $K_{12}Mo_{12}Se_{56}$,[5] $K_8Mo_9Se_{40}\cdot4H_2O$,[6] $K_2Mo_3Se_{18}$,[6] K_2PdSe_{10},[7] $(Pr_4N)_2In_2Se_{10}$,[8] and $[(Ph_3P)_2N]_2In_2Se_{10}$.[8] Unlike hydrothermal techniques, which use hard bases as mineralizers and yield monochalcogenide compounds,[9,10] our approach uses the polychalcogenides themselves as mineralizers giving rise to polychalcogenide compounds. The Mo/Se system has produced cluster compounds in which the trimeric $[Mo_3Se_7]^{4+}$ core exists as a building block, and the Mo is in the 4+ oxidation state.[5,6] Given the known chemical similarity between Mo and V, we extended this technique to the vanadium system to see if the analogous, hitherto unknown, $[V_3Se_7]^+$ (containing formally V^{3+}) could be produced. Although this cluster core was not found, we were able to synthesize and crystallize two new vanadium polyselenide compounds, $K_4V_2O_2Se_{10}\cdot2MeOH$ (**I**), $K_4V_2O_2Se_8\cdot0.65MeOH$ (**II**). In contrast to the Mo and In systems, we found that due to the stronger affinity of V ions for oxygen, water is not a suitable solvent for the V/Se system, causing product hydrolysis. A weaker Lewis base, methanol, was used to avoid the formation of oxovanadates.

Experimental Section

Chemicals in this work were used as obtained from commercial sources. All manipulations were carried out in a glovebox under nitrogen atmosphere. K_2Se_4 was prepared by dissolving the stoichiometric amount of the elements in liquid ammonia. Quantitative microprobe analysis of the compounds was performed with a JEOL JSM-35C scanning electron microscope (SEM) equipped with a Tracor Northern Energy Dispersive Spectroscopy (EDS) detector. Data were acquired using an accelerating voltage of 20 kV and a 1-min accumulation time. The standardless quantitative (SQ) analysis program used multiple least-squares analysis and a ZAF matrix correction procedure to calculate elemental concentrations. FT-IR spectra of the two compounds were recorded as solids in a CsI matrix. The spectra were recorded in 4-cm^{-1} resolution using a Nicolet 740 FT-IR spectrometer equipped with a TGS/PE detector and silicon beam splitter.

Synthesis. $K_4V_2O_2Se_{10}\cdot2MeOH$ (I). A 0.025-g (0.5-mmol) sample of V metal, 0.197 g (0.5 mmol) of K_2Se_4 and 0.3 mL (7.37 mmol) of MeOH were mixed in a heavy-wall (2 mm thickness) Pyrex tube of ~5 mL total capacity. The tube was placed in an oven at 135 °C for 4 days at the end of which it afforded black needlelike crystals of $K_4V_2O_2Se_{10}\cdot2MeOH$. Quantitative microprobe analysis on the single crystals gave a composition of $K_{1.7}V_{1.0}Se_{4.9}$. (The Se ratio is always underestimated due to the artifact of the program, a correction factor (×2.0) was applied in V/Se systems.)

Table I. Crystallographic Data for $K_4V_2O_2Se_{10}\cdot2MeOH$ (**I**) and $K_4V_2O_2Se_8\cdot0.65MeOH$ (**II**)

	(I)	(II)
chem formula	$K_4V_2Se_{10}O_4C_2H_8$	$K_4V_2Se_8O_2$
a, Å	14.229(3)	7.577(3)
b, Å	24.136(9)	17.672(6)
c, Å	6.907(4)	13.810(5)
β, deg	90.0	105.74(3)
V, Å^3	2372(2)	1780(2)
Z	4	4
fw	1143.96	932.35
space group	$Pnc2$ (No. 30)	$P2_1/n$ (No. 14)
T, °C	–90	23
λ, Å	0.710 69	0.710 69
ρ_{calc}, g/cm^3	3.209	3.479
μ, cm^{-1}	166.70	181.46
R^a	0.054	0.049
$R_w{}^b$	0.062	0.052

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

Table II. Positional Parameters and Equivalent Isotropic Displacement Values (Å^2)[a] for $K_4V_2O_2Se_{10}\cdot2MeOH$ with Estimated Standard Deviations in Parentheses

atom	x	y	z	B(eq)
Se(1)	–0.1176(3)	0.0354(2)	0.8745	1.5(2)
Se(2)	0.1909(2)	0.0766(2)	0.798(1)	1.6(2)
Se(3)	0.2240(3)	0.1760(2)	0.781(1)	2.2(2)
Se(4)	0.1079(3)	0.2091(2)	0.992(1)	2.0(2)
Se(5)	–0.0173(2)	0.1504(2)	0.888(1)	1.7(2)
Se(6)	0.6240(3)	0.0240(2)	0.361(1)	1.7(2)
Se(7)	0.3262(2)	0.0944(2)	0.302(1)	1.8(2)
Se(8)	0.3234(3)	0.1947(2)	0.289(1)	2.0(2)
Se(9)	0.4486(3)	0.2143(2)	0.498(1)	2.2(2)
Se(10)	0.5566(2)	0.1475(2)	0.379(1)	1.6(2)
V(1)	0.0431(4)	0.0545(3)	0.967(1)	1.2(3)
V(2)	0.4704(4)	0.0588(3)	0.459(1)	1.1(3)
K(1)	0.0891(6)	0.1455(4)	0.418(2)	2.6(5)
K(2)	0.1384(5)	–0.0303(4)	0.378(2)	2.1(4)
K(3)	0.4492(6)	0.1472(4)	–0.071(2)	2.0(4)
K(4)	0.6414(5)	0.0200(3)	0.867(2)	1.7(4)
O(1)	0.053(2)	0.056(1)	1.204(4)	1.5(5)
O(2)	0.465(1)	0.061(1)	0.688(4)	1.2(5)
O(3)	0.641(1)	0.133(1)	0.831(4)	1.3(5)
O(4)	–0.107(2)	0.139(1)	0.330(5)	3.1(6)
C(1)	0.698(3)	0.181(2)	0.87(1)	5(1)
C(2)	–0.153(3)	0.189(2)	0.393(9)	4(1)

[a] $B(eq) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

$K_4V_2O_2Se_8\cdot0.65MeOH$ (II). A 0.125 g (2.5-mmol) sample of V metal, 0.985 g (2.5 mmol) of K_2Se_4, and 1.5 mL (36.9 mmol) of MeOH were mixed in a Parr bomb of 22 mL total capacity at 135 °C for 24 days, giving black plate-like crystals of $K_4V_2O_2Se_8\cdot0.65MeOH$. Quantitative microprobe analysis on the single crystals gave a composition of $K_{1.5}V_{1.0}Se_{3.0}$.

These compounds were characterized by infrared and UV–visible spectroscopy and single-crystal X-ray diffraction analyses. At room temperature **I** and **II** are insoluble in methanol, sparingly soluble in CH_3CN, and soluble in DMF. In water the compounds dissolve with concomitant hydrolysis. IR (CsI): ν(V═O) 936 cm^{-1} for both **I** and **II**; ν(V—Se), ν(Se–Se) 365, 201 cm^{-1} for **I**; 363, 351, 183 cm^{-1} for **II**. UV-vis spectra of both **I** and **II** in DMSO and DMF lack strongly characteristic features. In DMSO and DMF, both **I** and **II** gave a wide shoulder from 800 to 520 nm and a wide shoulder from 520 to 350 nm. Preliminary experiments to obtain ^{77}Se NMR spectra of the complexes did not succeed probably due to the quadrupolar nature of the ^{51}V nuclei, $I = {}^7/_2$, natural abundance 99.76%, and even possible decomposition in these solvents.

X-ray Crystallography and Structure Solution. Diffraction data for **I** and **II** were collected at –90 and +23 °C to a $2\theta_{max}$(Mo) of 50° using a Rigaku AFC6S diffractometer equipped with graphite-monochromated

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Table III. Positional Parameters and Equivalent Isotropic Displacement Values (Å^2)^a for $K_4V_2O_2Se_8 \cdot 0.65MeOH$ with Estimated Standard Deviations in Parentheses

atom	*x*	*y*	*z*	*B*(eq)
Se(1)	−0.0742(4)	0.6655(2)	0.2893(2)	2.0(1)
Se(2)	−0.0849(4)	0.5658(2)	0.4039(2)	2.8(1)
Se(3)	−0.2327(5)	0.6276(2)	0.5096(2)	3.3(2)
Se(4)	−0.0856(4)	0.7533(2)	0.5189(2)	2.4(1)
Se(5)	0.0900(4)	0.8943(2)	0.4735(2)	1.8(1)
Se(6)	0.1016(4)	0.8081(2)	0.2263(2)	2.0(1)
Se(7)	0.2152(4)	0.9971(2)	0.1853(2)	2.3(1)
Se(8)	0.1268(4)	1.0487(2)	0.3225(2)	2.6(1)
V(1)	0.1020(6)	0.7668(3)	0.3983(3)	1.3(2)
V(2)	0.2226(6)	0.9132(3)	0.3343(3)	1.6(2)
K(1)	0.297(1)	1.0175(4)	0.6639(4)	2.9(3)
K(2)	0.5352(8)	0.8366(4)	0.5652(4)	2.4(3)
K(3)	0.1605(9)	0.0933(4)	0.9628(4)	2.8(3)
K(4)	0.989(1)	0.2296(5)	0.1958(5)	4.4(4)
O(1)	0.307(2)	0.731(1)	0.449(1)	1.9(8)
O(2)	0.442(2)	0.901(1)	0.382(1)	2.8(9)
O(3)	−0.174(4)	0.360(2)	0.291(2)	2.7(6)

^{a} $B(\mathrm{eq}) = {}^4/_3[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

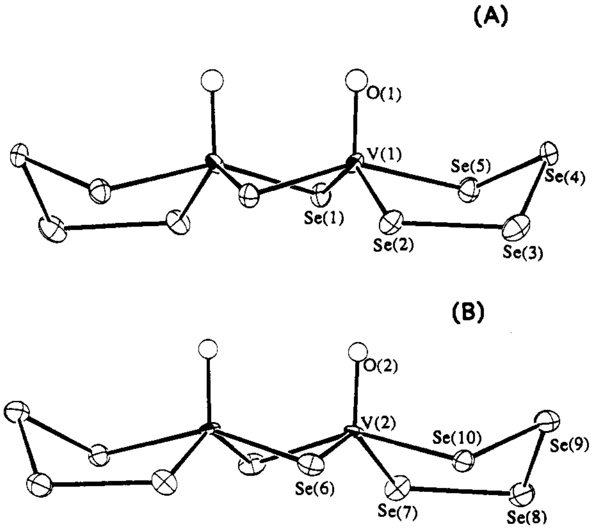

Figure 1. Ortep representation and labeling scheme of $[V_2O_2Se_{10}]^{4-}$.

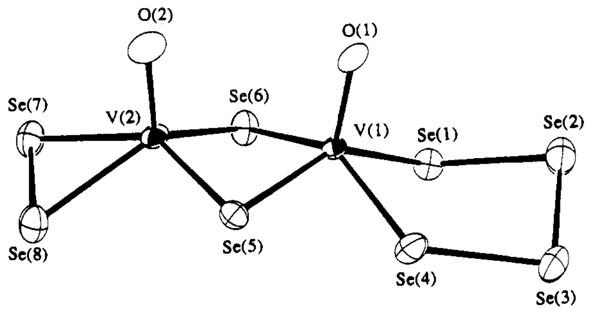

Figure 2. Ortep representation and labeling scheme of $[V_2O_2Se_8]^{4-}$.

Mo Kα radiation. Three standard reflections were monitored for every 200 reflections for both I and II. The number of observed reflections ($I > 3\sigma(I)$) were 1231 for I and 1185 for II. No significant decay was observed. Reflections were corrected for Lorentz-polarization effects, and an empirical ψ-scan absorption correction was applied to all data. The structure was solved by direct methods (SHELXS-86). In I, all non-hydrogen atoms except oxygen and carbon were refined anisotropically. The positions of all hydrogen atoms were calculated and included in the structure factor calculation but were not refined. In II, the cocrystallized solvent MeOH was found to be disordered, with the occupancy of O atoms being refined to be ~0.65. The position of C and H atoms could not be located. The structural models were refined with full-matrix least-squares techniques using the TEXSAN package of crystallographic software.

Table IV. Selected Bond Distances (Å) and Angles (deg) for $K_4V_2O_2Se_{10} \cdot 2MeOH$ with Standard Deviations in Parentheses

V(1)–O(1)	1.64(3)	V(2)–O(2)	1.59(3)
V(1)–Se(1)	2.418(7)	V(2)–Se(6)	2.439(7)
V(1)–Se(1)	2.497(7)	V(2)–Se(6)	2.502(8)
V(1)–Se(2)	2.465(7)	V(2)–Se(7)	2.474(7)
V(1)–Se(5)	2.529(8)	V(2)–Se(10)	2.528(8)
V(1)–V(1)	2.90(1)	V(2)–V(2)	2.96(1)
Se(2)–Se(3)	2.447(6)	Se(7)–Se(8)	2.424(6)
Se(3)–Se(4)	2.342(7)	Se(8)–Se(9)	2.342(6)
Se(4)–Se(5)	2.385(6)	Se(9)–Se(10)	2.376(6)
O(3)–C(1)	1.46(5)	K(2)–O(4)	2.67(3)
O(4)–C(2)	1.44(5)	K(3)–Se(3)	3.434(9)
K(1)–Se(2)	3.43(1)	K(3)–Se(7)	3.37(1)
K(1)–Se(3)	3.24(1)	K(3)–Se(8)	3.27(1)
K(1)–Se(4)	3.56(1)	K(3)–Se(9)	3.38(1)
K(1)–Se(4)	3.33(1)	K(3)–Se(9)	3.38(1)
K(1)–Se(5)	3.59(1)	K(3)–Se(10)	3.47(1)
K(1)–Se(7)	3.68(1)	K(3)–O(2)	2.68(3)
K(1)–Se(8)	3.65(1)	K(3)–O(3)	2.83(2)
K(1)–O(1)	2.67(3)	K(4)–Se(1)	3.44(9)
K(1)–O(4)	2.86(3)	K(4)–Se(2)	3.36(9)
K(2)–Se(1)	3.44(1)	K(4)–Se(6)	3.51(1)
K(2)–Se(1)	3.49(1)	K(4)–Se(6)	3.42(1)
K(2)–Se(6)	3.386(9)	K(4)–O(2)	2.97(2)
K(2)–O(1)	2.70(3)	K(4)–O(2)	2.76(3)
K(2)–O(1)	3.04(3)	K(4)–O(3)	2.73(2)
Se(1)–V(1)–Se(1)	99.7(3)	Se(6)–V(2)–Se(6)	97.5(3)
Se(1)–V(1)–Se(2)	136.4(4)	Se(6)–V(2)–Se(7)	137.8(3)
Se(1)–V(1)–Se(2)	72.8(2)	Se(6)–V(2)–Se(7)	73.3(2)
Se(1)–V(1)–Se(5)	78.3(2)	Se(6)–V(2)–Se(10)	78.2(2)
Se(1)–V(1)–Se(5)	152.3(4)	Se(6)–V(2)–Se(10)	151.3(3)
Se(1)–V(1)–O(1)	110.3(9)	Se(6)–V(2)–O(2)	109.4(9)
Se(5)–V(1)–O(1)	66.4(4)	Se(10)–V(2)–O(2)	66.2(4)
Se(2)–V(1)–Se(5)	89.4(3)	Se(7)–V(2)–Se(10)	90.7(3)
Se(2)–V(1)–O(1)	113.3(9)	Se(7)–V(2)–O(2)	112.8(9)
Se(5)–V(1)–O(1)	103(1)	Se(10)–V(2)–O(2)	103(1)
V(1)–Se(2)–Se(3)	113.5(2)	V(2)–Se(7)–Se(8)	112.2(2)
Se(2)–Se(3)–Se(4)	99.7(2)	Se(7)–Se(8)–Se(9)	99.5(2)
Se(3)–Se(4)–Se(5)	98.0(2)	Se(8)–Se(9)–Se(10)	98.1(2)
Se(4)–Se(5)–V(1)	103.0(2)	Se(9)–Se(10)–V(2)	100.6(2)

The crystallographic data and detailed information of structure solution and refinement for I and II are listed in Table I. Atomic coordinates and equivalent isotropic thermal parameters are given in Tables II and III, respectively.

Results and Discussion

Compound I contains two crystallographically independent but structurally similar anionic molecules, $[V_2O_2Se_{10}]^{4-}$ (**Ia** and **Ib**), while II contains a single $[V_2O_2Se_8]^{4-}$ molecule. Both complexes contain the same central $[V_2O_2Se_2]$ core. This core consists of a bent V_2Se_2 rhombus and two cis-terminal oxygen atoms. The latter are presumed to come from methanol. The V atoms in these $[V_2O_2Se_2]$ cores are chelated by two Se_4^{2-} ligands in I and one Se_4^{2-} ligand and one Se_2^{2-} ligand in II. The structures of $[V_2O_2Se_{10}]^{4-}$ and $[V_2O_2Se_8]^{4-}$ are shown in Figures 1 and 2. There is a C_2 rotation axis passing through the center of $[V_2O_2Se_{10}]^{4-}$. All the V–O bonds in the acentric space group of I are pointed in the same direction. $[V_2O_2Se_{10}]^{4-}$ is isostructural with $[Mo_2O_2S_{10}]^{2-}$ and $[W_2O_2S_{10}]^{2-}$, while $[V_2O_2Se_8]^{4-}$ is isostructural with $[Mo_2O_2S_8]^{2-}$ all of which belong to the family of $[M_2X_2Q_2(Q_x)(Q_y)]^{2-}$ [11-19] complexes (M = Mo, W; X = O, S; Q = S, Se). The V atoms in I and II have the formal oxidation

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Table V. Selected Bond Distances (Å) and Angles (deg) for $K_4V_2O_2Se_8 \cdot 0.65MeOH$ with Standard Deviations in Parentheses

V(1)–O(1)	1.65(2)	V(2)–Se(6)	2.402(5)
V(1)–Se(1)	2.482(5)	V(2)–Se(7)	2.525(5)
V(1)–Se(4)	2.477(5)	V(2)–Se(8)	2.496(6)
V(1)–Se(5)	2.494(5)	Se(1)–Se(2)	2.385(4)
V(1)–Se(6)	2.485(5)	Se(2)–Se(3)	2.338(5)
V(2)–O(2)	1.63(2)	Se(3)–Se(4)	2.473(5)
V(2)–Se(5)	2.421(5)	Se(7)–Se(8)	2.358(4)
V(1)–V(2)	2.958(7)		
O(1)–V(1)–Se(1)	108.7(6)	V(1)–Se(5)–V(2)	74.0(2)
O(1)–V(1)–Se(4)	105.7(6)	V(1)–Se(6)–V(2)	74.5(2)
O(1)–V(1)–Se(5)	107.8(6)	O(2)–V(2)–Se(5)	104.9(6)
O(1)–V(1)–Se(6)	106.2(6)	O(2)–V(2)–Se(6)	109.0(7)
Se(1)–V(1)–Se(4)	91.5(2)	O(2)–V(2)–Se(7)	101.8(7)
Se(1)–V(1)–Se(6)	76.8(1)	O(2)–V(2)–Se(8)	113.6(8)
Se(4)–V(1)–Se(5)	73.4(2)	Se(5)–V(2)–Se(6)	102.5(2)
Se(5)–V(1)–Se(6)	98.1(2)	Se(5)–V(2)–Se(8)	90.4(2)
V(1)–Se(1)–Se(2)	103.9(1)	Se(6)–V(2)–Se(7)	91.6(2)
V(1)–Se(4)–Se(3)	112.6(2)	Se(7)–V(2)–Se(8)	56.0(1)
Se(1)–Se(2)–Se(3)	100.2(2)	V(2)–Se(7)–Se(8)	61.4(1)
Se(2)–Se(3)–Se(4)	89.3(2)	V(2)–Se(8)–Se(7)	62.6(1)

state of +4 and thus the same d^1 electronic configuration as their Mo^{5+} and W^{5+} analogs. Although the $[M_2O_2Q_2]^{2+}$ (M = Mo, W; Q = S, Se) core has a high formation tendency, its isoelectronic analog $[V_2O_2Se_2]$ is reported here for the first time. The only other known vanadium polyselenide anion is $[V_2Se_{13}]^{2-}$,[20] which was synthesized by reducing VO_3^- with bis(dimethyloctylsilyl) selenide in toluene/acetonitrile solution at room temperature. The structure of $[V_2Se_{13}]^{2-}$ is unique, compared to the Mo/W polychalcogenide anions. The lack of previous examples of vanadium analogs of $[M_2X_2Q_2(Q_x)(Q_y)]^{2-}$ may be attributed to the difficulty in crystallizing the tetraanions using the typical large organic cations, since in this case four cations instead of two are needed to balance the charge in the crystal lattice. The crystallization problem could be overcome if significantly smaller cations were used (e.g. alkali metal ions), since such crystallizations from DMF or CH_3CN, the typical solvents for classical synthesis, seldom succeed. However, the difficulty can be overcome by the solvothermal method which has been proven useful in promoting crystallization in alkali metal polyselenide salts.[5–7]

Selected bond distances and angles for **I** and **II** are given in Tables IV and V, respectively. The average V–Se distances in $[V_2O_2Se_{10}]^{4-}$ and $[V_2O_2Se_8]^{4-}$ are 2.48(4) and 2.47(4) Å, respectively. The Se–V–Se angle formed by the diselenide ligand is much smaller than that formed by tetraselenide ligand, 56.0(1) and 91.5(2)°, respectively. The V–V distances of 2.90(1) Å in **Ia**, 2.96(1) Å in **Ib**, and 2.958(7) Å in **II** in the $[V_2O_2Se_2]$ unit are longer than the V–V bonds in the $[V_2(Se_2)_2]^{4+}$ units of $[V_2Se_{13}]^{2-}$ (2.779(5) Å) and V_2Se_9[21] (2.842(2) Å) as well as in the $[V_2(Se_2)_2(Se)]^{2+}$ unit of $V_2(C_6H_7)_2Se_5$[22] (2.779(4) Å). The average $V{=}O_t$ distances in $[V_2O_2Se_{10}]^{4-}$ is 1.62(4) Å, while in $[V_2O_2Se_8]^{4-}$ is 1.64(2) Å. The Se–Se distance in the Se_4^{2-} ligands lie within the normal range, but both complexes exhibit Se–Se bond alternation. In both **I** and **II** the average central Se–Se distance is shorter, 2.341 (2) Å. The average terminal Se–Se distance in the Se_4^{2-} ligands is 2.42(4) Å. This is opposite to the bond alternation observed in the structure of free $[Se_4]^{2-}$ and consistent with the corresponding lengths observed in the Se_4^{2-} ligand of $[W_2Se_{10}]^{2-}$.[19,23] This phenomenon is probably due to the M(dπ)–Se(dπ) interaction which has been proposed in the Mo/S system.[17] The Se–Se distance in the Se_2^{2-} ligand is 2.358(4) Å. In retrospect the formation of a $[V_3Se_7]^+$ cluster, isoelectronic and isostructural to $[Mo_3Se_7]^{4+}$, would be unlikely under the relatively oxidizing conditions employed here considering the difficulty in reducing V^{4+} to V^{3+}.

In conclusion, solvothermal methods readily promote synthesis and crystallization of new compounds, in many cases achievable only with difficulty by classical solution techniques. This has given access to new V/Se chemistry and promises to do the same for other unexplored systems as well. The two complexes reported here represent potential new starting materials for further exploration of V/Se chemistry.

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Supplementary Material Available: Tables giving crystal data and details of the structure determination and anisotropic thermal parameters of all atoms except hydrogens (3 pages). Ordering information is given on any current masthead page.

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