

Crystal Structure and Properties of V_2Se_9

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The crystal structure of V_2Se_9 has been determined by three-dimensional single crystal X-ray methods. The structure is monoclinic, space group $C2/c$. The unit cell has the dimensions $a=10.5899(8)$ Å, $b=12.4127(14)$ Å, $c=8.1198(8)$ Å, $\beta=94.910(10)^\circ$, and contains 4 formula units. V_2Se_9 can be described as a pseudo-one-dimensional compound, characterized by infinite $(V_2Se_9)_x$ -chains parallel to $[101]$. The shortest distances between atoms in different chains are too long to be considered binding.

During the last years, several chalcogen-rich compounds of the IV and V group transition metals have been investigated. The majority of these crystallize in layer structures, e.g. the $ZrSe_3$ -type structure,¹ or the closely related $TaSe_3$,² $NbSe_3$,³ and $HfTe_5$ -type structures. The compounds Nb_2Se_5 ⁵ and VS_4 ,⁶ however, are examples of chain structures. We here report on a new compound, V_2Se_9 , which has structural features also found in Nb_2Se_9 .

Till now no vanadium selenide with higher content of selenium than VSe_2 ⁷ has been reported.

EXPERIMENTAL

Preparation. V_2Se_9 has been prepared by direct reaction between the elements at temperatures in the range 280–400 °C. The pure compound was obtained by heating accurately weighed quantities of the components ("Selenium Granules", 99.999 % from Koch-Light Laboratories LTD., and "Vanadium Powder" 99.5 % from A.D. Mackay Inc.) in sealed, evacuated silica tubes at 350 °C for 7 d. The product was finely crushed, reannealed for 21 d at 350 °C, and cooled over a period of 3 d. The resulting product was a dark

gray, extremely fine grained powder. After extended annealing periods (~2 months), needle shaped single crystals (too small for X-ray work) had grown on the ampoule walls.

Single crystals suitable for structure determination were prepared from V_2Se_9 -powder by chemical transport reaction. The V_2Se_9 -powder was enclosed in silica tubes ~150 mm long, internal diameter 20 mm. 5 mg iodine per cm^3 capsule volume was used as a transport agent. A temperature gradient of 0.15 °C/mm was applied, and single crystals formed in the cold part of the ampoule at 300 °C. The crystals were small (max 1.5 mm long), needle-shaped, and gray with metallic lustre. They easily split into extremely thin needles on handling, and were also pliable.

Characterization. Single crystals were examined in a scanning electron microscope with energy dispersive X-ray analyzer. No trace of iodine was detected. Microprobe analysis of single crystals gave the composition $VSe_{4.62}$ (17.8 ± 0.9 % V). The composition V_2Se_9 was established by the structure determination.

The crystal symmetry and cell dimensions were obtained from single crystal Weissenberg data. The possible space groups were Cc or $C2/c$. X-ray powder diffraction data from a Guinier-Hägg focusing camera with strictly monochromatic $CuK\alpha_1$ -radiation ($\lambda=1.54059$ Å) and with KCl ($a=6.2931$ Å) as an internal standard, were applied in a least squares refinement of the cell dimensions. The powder diffraction data are listed in Table 1.

Magnetic measurements (Faraday method, maximum field 10 kØ) showed the compound to be weakly diamagnetic in the temperature range -196–+340 °C.

Tentative measurements of conductivity on a powdered sample compressed in a silica tube, showed a slight increase with temperature in the range 25–225 °C, suggesting that the compound is a semiconductor.

DTA measurements were performed with a Mettler thermoanalyzer in closed silica crucibles. V_2Se_9 is thermally stable up to 410 °C, at which temperature it decomposes, giving VSe_2 and Se.

Our investigations, including variation of composition and reaction temperature, have given no evidence neither for compounds with composition between VSe_2 and V_2Se_9 , nor for any compound with higher selenium content than V_2Se_9 .

Intensity data collection. The needle-formed crystal used in the photographic single crystal measurements, having dimensions of 0.19×0.05×0.04 mm, was mounted in a general orientation on a SYNTEX P1 autodiffractometer. Intensity data were registered at room temperature by the θ - 2θ scan technique, the scan speed (in 2θ) being 1.5 °min⁻¹, the scan range from 1.0° below the α_1 - to 1.2° above the α_2 -value, a background to scanning time ratio of 0.7, and using graphite-monochromatized MoK α radiation ($\lambda=71069$ Å).

At first intensity data up to 55° (in 2θ) were recorded. Three standard reflections measured at 60 reflection intervals showed no significant fluctuations and indicated long term stability better than 0.5 %. Then data up to 80° (in 2θ) were recorded using a prescan to discriminate weak reflections. A slight misalignment of the

crystal was indicated by different decreases in intensity for the monitoring reflections.

The standard reflections were used for scaling the data, the largest correction being about 4 % in intensity for part of the high angle data. The estimated standard deviations were calculated from counting statistics including a 2 % term due to long term fluctuations. Intensities greater than 3σ were considered observed, the unobserved data were only used in the structure determination by direct methods. The data were corrected for absorption using a program based on the gaussian grid method, the transmission factor varying from 0.141 to 0.309. The X-ray cross sections were taken from Ref. 8.

The unit cell dimensions determined by least squares refinement of the 2θ -values for 30 reflections from diffractometer measurements were not significantly different from those obtained by Guinier technique.

CRYSTAL DATA

Monoclinic, space group $C2/c$. Needle axis along $[1\ 0\ 1]$. V_2Se_9 , $M=496.68$, $Z=4$, $F(000)=1408$. $a=10.5899(8)$ Å, $b=12.4127(14)$ Å, $c=8.1198(8)$ Å. $\beta=94.910(10)^\circ$, $V=1063.43(16)$ Å³ (from Guinier data). $T=20$ °C,

Table 1. Powder diffraction data for V_2Se_9 (s=strong, m=medium, w=weak, vw=very weak).

<i>hkl</i>	$2\theta_o$	$2\theta_c$	I_o	I_c/I_c max	<i>hkl</i>	$2\theta_o$	$2\theta_c$	I_o	I_c/I_c max
110	10.960	10.996	m	.28	312		35.945	m	.06
020	14.211	14.257	s	1.00	331	35.949	35.951		.44
11 $\bar{1}$	14.970	15.010	s	.74	023	36.287	36.291	m	.60
021	17.981	17.999	vw	.08	420	36.996	36.998	m	.42
002	21.924	21.955	m	.21	150	37.195	37.172	w	.09
220	22.083	22.095	vw	.08	15 $\bar{1}$	38.644	38.642	m	.28
22 $\bar{1}$	24.060	24.051	vw	.06	33 $\bar{2}$	39.050	39.059	m	.23
221	25.314	25.357	w	.07	13 $\bar{3}$	40.162	40.182	vw	.09
131	25.897	25.905	w	.14	31 $\bar{3}$	41.006	41.008	m	.25
310	26.293	26.316	m	.53	133	41.439	41.434	w	.15
31 $\bar{1}$	27.682	27.702	m	.23	332	41.558	41.586	vw	.08
040	28.727	28.744	m	.25	51 $\bar{1}$	43.983	43.979		.17
202	28.901	28.917	w	.08	152	43.983	43.983	m	.23
311	29.397	29.413	s	.64	313	44.618	44.620	vw	.06
22 $\bar{2}$	30.263	30.281	m	.27	440	45.077	45.070	vw	.06
132	32.561	32.567	s	.81	114	45.489	45.486	m	.20
31 $\bar{2}$	33.043	33.058	m	.31	351	46.684	46.660		.13
330	33.411	33.409	m	.29	20 $\bar{4}$	46.684	46.664	m	.03
24 $\bar{1}$	34.853	34.837	w	.09	024	47.231	47.225	w	.07
113	35.763	35.773		.08	26 $\bar{1}$	48.186	48.183	vw	.08
241		35.781	m	.30	42 $\bar{3}$	48.396	48.391	m	.20

$d_x=5.074$, g/cm³, $\mu(\text{MoK}\alpha)=321.6$ cm⁻¹. Magnetic susceptibility: diamagnetic, $\chi=-1.2 \cdot 10^{-5}$ e.m.u/g. V₂Se₉ decomposes thermally at 410 °C.

STRUCTURE DETERMINATION AND REFINEMENT

The crystal structure was determined by direct methods (MULTAN¹⁰). The space group was assumed to be C2/c. From the peaks of the fourier map, the content within an asymmetric unit was established to be VSe_{4.5}, one selenium atom located at a twofold axis and the other atoms in general positions.

Full matrix least-squares refinement of $M=\Sigma [(|F_o|-|F_c|)/\sigma(F_o)]^2$ using anisotropic temperature factors for all atoms yielded an *R*-value of 0.042 ($R_w=0.042$, "goodness of fit" $S=1.92$) for the 1805 observed reflections after an isotropic extinction correction term of 0.3×10^{-5} had been introduced. The choice of the space group C2/c is thereby confirmed. The agreement indices for a refinement including only the 1009 reflections having $\sin \theta/\lambda$ less than 0.65 were $R=0.033$, $R_w=0.038$ and $S=2.19$. The differences between the positional parameters of the two refinements were all less than 0.5 e.s.d.'s whereas differences up to 3 e.s.d.'s, were observed for the thermal parameters. The parameters of the refinement including all data, which resulted in slightly smaller e.s.d.'s are listed in Table 2. Inspection of the weight analysis indicated that errors caused by inaccuracy in absorption and/or extinction correction of the data might be present.

Inclusion of anomalous dispersion effects in a final refinement gave no significant improvement. The only significant changes were the slightly increased thermal parameters of V.

A difference fourier synthesis based upon the atomic parameters of Table 2 and the 1009 low angle reflections showed no interpretable features; the difference electron density fluctuating between -1.4 and 1.0 eÅ⁻³ and containing no local maxima or minima at atomic positions. Form factors for neutral atoms taken from Ref. 8 were applied in all calculations using programs⁹ for a ND100/500 computer. A list of observed and calculated structure factors is available from one of the authors (S.F.) upon request.

RESULTS AND DISCUSSION

The atomic arrangement of V₂Se₉ is shown in Fig. 1. The shortest interatomic distances are listed in Table 3, and some of the bond angles are listed in Table 4. The structure resembles closely the triclinic structure of Nb₂Se₉,⁵ and the presentation will thereby be given in similar terms.

The characteristic feature of the structure is the separate chains extending in the [101] direction, corresponding to a translational period of 12.78 Å and with V₄Se₁₈ units along the repetition period, see Fig. 1. The bonding between different chains is weak. Only Se-Se distances of 3.43 Å (Se1-Se2) or more are found, while the value for a normal Se-Se single bond is about 2.34 Å, and the distance corresponding to the van der Waals radius is 4.0 Å. This fact reflects the strongly anisotropic properties of the crystals (e.g. the flexibility and the splitting into thin needles parallel to the V₄Se₁₈ chains). The compound may thus be looked upon as a quasi one-dimensional substance.

The vanadium atoms appear in pairs along the chain. The distance between one vanadium atom and its nearest centrosymmetric equivalent V' is

Table 2. Atomic coordinates $\times 10^5$ and temperature parameters $\times 10^4$ (Å⁻²). The temperature factor is given by $\exp(-2\pi^2(U_{11}a^2h^2 + \dots + 2U_{23}bckl))$; W=Wyckoff position.

Atom	W	x	y	z	U11	U22	U33	U12	U13	U23
Se1	4(e)	0	41439(8)	25000	172(5)	129(4)	214(4)	00	-43(3)	00
Se2	8(f)	-06048(7)	34921(6)	54030(8)	184(3)	234(4)	160(3)	43(3)	27(2)	-40(3)
Se3	8(f)	-10171(7)	18925(6)	39086(8)	154(3)	191(3)	151(3)	-21(3)	19(2)	16(2)
Se4	8(f)	23812(7)	08396(6)	44424(9)	203(4)	137(3)	215(3)	20(3)	-21(2)	-27(3)
Se5	8(f)	16440(7)	15743(6)	67689(8)	172(3)	232(3)	163(3)	-12(3)	15(2)	46(3)
V	8(f)	12909(11)	26691(8)	41393(12)	106(4)	113(4)	106(4)	17(4)	10(3)	04(4)

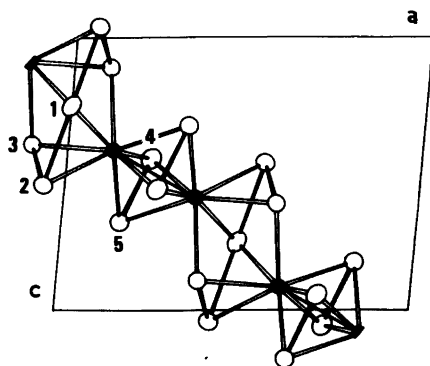


Fig. 1. An ORTEP view of a V_4Se_{18} chain fragment, V and Se filled and open circles, respectively. (Thermal ellipsoids are drawn at 75% probability level). The selenium atoms in the asymmetric unit are numbered according to Table 2. Se–Se and the partial V–V bonds are drawn as filled and Se–V as open bonds. The *b*-axis is towards the viewer, *a* and *c* are indicated on the figure.

2.84 Å. The metallic radius for V is 1.34 Å (coordination number 12) and a bonding interaction must thus be taken into account. The shortest distance between two vanadium atoms related to each other by twofold symmetry is 3.65 Å.

Four selenium atoms form two distinct pairs with short interatomic distances, Se2–Se3=2.35 Å and Se4–Se5=2.29 Å, corresponding to the shortest distances found in other compounds. Se1 is situated (at a twofold axis) 2.62 Å from Se2 (and Se2''). Even if this exceeds the length of a single bond, it is short enough to suggest a bonding interaction. Accordingly, the Se atoms

Table 3. Interatomic distances.

Distance	(Å)	Distance	(Å)
V–V'	2.842(2)	Se3–V	2.619(1)
Se1–Se2	2.623(1)	Se3–V''	2.649(1)
Se2–Se3	2.348(1)	Se4–V	2.550(1)
Se4–Se5	2.294(1)	Se4–V'	2.540(1)
Se1–V	2.585(1)	Se5–V	2.532(1)
Se2–V	2.545(1)	Se5–V'	2.546(1)

appear as Se_5 units possessing twofold symmetry, and Se_2 units. The bond angles of the Se_5 unit are Se2–Se1–Se2'' of 144.0° and Se1–Se2–Se3 of 81.1°.

In addition to the bond between the vanadium atoms within one pair, each vanadium atom is coordinated to eight selenium atoms forming a distorted rectangular antiprism. Two Se_2 units, Se4–Se5 and its centrosymmetrically equivalent form corners of a rectangle (Se4–Se5'=3.54 Å). These four V–Se bonds fall within a narrow range (2.532–2.540 Å) and the V–V bonds is normal to the rectangle. The symmetrical arrangement is also reflected in the bond angle values of Table 4.

The Se_5 unit is coordinated on both sides to vanadium by four bonds. These bond distances vary somewhat more, from 2.55 to 2.65 Å. The arrangement is far less symmetrical, which can be seen from the values of the Se–Se–V angles as well as from the bonding of the different Se atoms.

Se1 forms four pyramidally oriented bonds, two fractional bonds to Se2 atoms, and two bonds of normal length to vanadium atoms. Se2 forms one single and one fractional bond, to Se3 and

Table 4. Bond angles.

Angle	(°)	Angle	(°)
Se2–Se1–Se2''	144.1(1)	V–Se4–V'	67.9(1)
Se1–Se2–Se3	81.1(1)	Se5–Se4–V	62.8(1)
V–Se1–V''	89.8(1)	Se5–Se4–V'	63.3(1)
Se2–Se1–V	58.5(1)	V–Se5–V'	68.1(1)
Se2–Se1–V''	94.9(1)	Se4–Se5–V	63.6(1)
Se1–Se2–V	60.0(1)	Se4–Se5–V'	63.1(1)
Se3–Se2–V	64.6(1)	Se2–V–Se3	54.1(1)
V–Se3–V''	87.7(1)	Se4–V–Se5	53.7(1)
Se2–Se3–V	61.4(1)	Se4–V'–Se5	53.6(1)
Se2–Se3–V''	100.1(1)		

Se1 respectively, and one bond to vanadium. Finally, Se3 forms one Se–Se single bond and two Se–V bonds, similar to the bonding of Se4 and Se5.

The root-mean-square amplitudes along the principal axes of the thermal ellipsoids are similar for all selenium atoms indicating that the relative thermal vibrations are reasonably well described. The thermal motion of the vanadium atom is close to isotropic.

As mentioned earlier, all calculations are based on scattering from neutral atoms. The difference in scattering factors between V and V^{5+} is significant for low angle reflections. No definite conclusions about the covalency or ionicity can be drawn from our data. However, a model based on V^{5+} is rather improbable.

The structure of V_2Se_9 closely resembles the triclinic structure of Nb_2Se_9 reported by Meerschaut *et al.*⁵ In Nb_2Se_9 separate chains of (Nb_2Se_9) with alternating short and long Me–Me distances are also found. Pairs of chalcogen atoms appear, the shortest Se–Se distances being 2.28–2.36 Å, corresponding to 2.29–2.35 Å in V_2Se_9 . However, the twofold crystallographic symmetry is absent. The crystal packing of V_2Se_9 and Nb_2Se_9 differs mainly in the stacking of the chains. Meerschaut *et al.* compare Nb_2Se_9 with $NbSe_2Cl_2$, pointing out the common feature of two close Nb-atoms linked by two pairs of selenium atoms. We will here also draw attention to the similarity with VS_4 ,⁶ where the same configuration occurs. VS_4 also crystallizes in a typical chain structure with alternating short and long V–V distances, where the metal atoms are linked together on both sides by two pairs of sulfur atoms, giving a rectangular antiprismatic coordination.

It is possible to look upon the V_2Se_9 -structure as the result of forcing one more chalcogen atom (Se1) into the VS_4 -type structure. This leads to a more irregular coordination polyhedron, and is also reflected in the fact that the distance between vanadium pairs is increased from 3.22 Å in VS_4 to 3.65 Å in V_2Se_9 , whereas the shortest V–V distance remains the same in the two compounds. The same effect can also be recognized in the chain structure of V_2PS_{10} ,¹¹ where a short V–V distance of 2.852 Å occurs between metals linked by two chalcogen pairs. The longer V–V distance in the chain is increased to 3.627 Å as one S_2 and a PS_4 -tetrahedron are inserted.

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