

INORGANIC COMPOUNDS

Acta Cryst. (1997). **C53**, 163–165

Ba₆V₄O₅S₁₁

J. BRIAN LITTEER, JAMES C. FETTINGER AND BRYAN W. EICHHORN

Department of Chemistry, University of Maryland, College Park, MD 20742, USA. E-mail: b.eichhorn@umail.umd.edu

(Received 21 June 1996; accepted 20 September 1996)

Abstract

Hexabarium tetravanadium pentaoxide undecasulfide, Ba₆V₄O₅S₁₁, contains isolated VS₄³⁻, VOS₃³⁻, and VO₂S₂³⁻ tetrahedra separated by Ba²⁺ ions. The V—S and V—O bond distances are in the range 2.102 (5)–2.175 (3) Å and 1.682 (9)–1.722 (7) Å, respectively. The shortest V—S distances are associated with the VS₄³⁻ tetrahedra whereas the longest V—S distances are found in the VO₂S₂³⁻ tetrahedra.

Comment

We have been examining the synthesis and structure of early transition metal sulfide and oxysulfide compounds in an attempt to understand the trends and systematics of magnetic and transport properties, and crystal chemistry (Eichhorn, 1994; Tranchitella, Fettinger & Eichhorn, 1996). The few known vanadium sulfides include the sylvanite Cu₃VS₄ (Pauling & Hultgren, 1933; Lundquest & Westgren, 1936; Van den Beÿg & DeVries, 1964), LaCrS₃ misfit layer (Murugesan, Ramesh, Gopalakrishnan & Rao, 1981; Gotoh, Onoda, Goto & Oosawa, 1989; Gotoh, Goto, Kawaguchi, Oosawa & Onoda, 1990; Onoda & Kato, 1990), and BaNiO₃-type structures (Gardner, Vlasse & Wold, 1969). The latter two structure types contain edge- and face-sharing octahedra, respectively, whereas the former contains isolated VS₄³⁻ tetrahedra. Vanadium oxysulfides are of interest as cathode materials in solid-state batteries (Ouvrard, Tchangbedji, Deniard & Prouzet, 1995) but little structural information is available for these compounds.

The reaction of BaS, V, V₂O₅, and S (in the molar ratio 20:8:1:20) at 1198 K gives single crystals of the title compound and a black powder. The black powder does not contain the title phase. The crystal structure revealed isolated VS₄³⁻, VOS₃³⁻, and VO₂S₂³⁻ tetrahedra separated by Ba²⁺ ions. The relative ratios of the three types of tetrahedra are given by the formula Ba₆(VS₄)(VOS₃)(VO₂S₂)₂. The V—S distances range from 2.102 (5) to 2.175 (3) Å with the shortest contacts being found in the VS₄³⁻ tetrahedra. The lengthening of the V—S contacts as the

number of O atoms in the tetrahedral coordination sphere increases is thought to be related to the π-bonding abilities of oxygen as compared to sulfur, as has been noted elsewhere (Gardner, Fettinger & Eichhorn, 1994; Krebs, Buss & Ferwanah, 1972; Müller & Diemann, 1969). The four crystallographically distinct Ba²⁺ ions are nine or ten coordinate with the following coordination environments: Ba(1)OS₉, Ba(2)O₃S₆, Ba(3)O₂S₇, Ba(4)O₄S₅. The Ba—S contacts are in the range 3.091 (3)–3.699 (3) Å, whereas the Ba—O contacts are in the range 2.777 (6)–2.983 (7) Å. No obvious systematic trends are apparent in these bond distances.

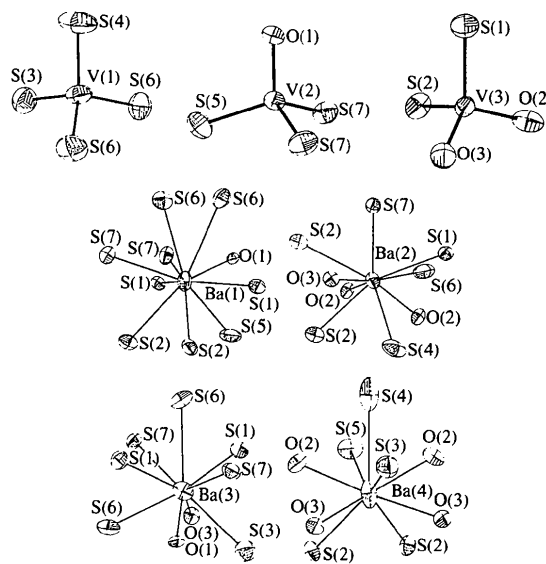


Fig. 1. An approximate (010) view of the Ba₆V₄O₅S₁₁ unit cell.

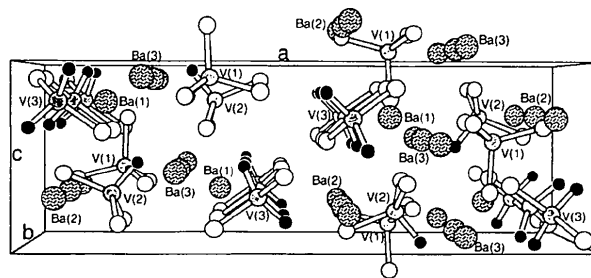


Fig. 2. ORTEPII (Johnson, 1976) drawings of the V(1)S₄³⁻, V(2)OS₃³⁻, and V(3)O₂S₂³⁻ tetrahedra and the Ba(1)OS₉, Ba(2)O₃S₆, Ba(3)O₂S₇, and Ba(4)O₄S₅ polyhedra. Displacement ellipsoids are plotted at the 50% probability level.

Experimental

The title compound was prepared by reaction of BaS, V, V₂O₅, and S (molar ratios 20:8:1:20) for four days at 1198 K, cooling at 1° min⁻¹ to room temperature in an evacuated silica

ampoule. The black single crystals represented approximately 10% of the product mixture.

Crystal data

Ba₆V₄O₅S₁₁

$M_r = 1460.46$

Orthorhombic

Pnma

$a = 23.2581(13) \text{ \AA}$

$b = 13.8504(6) \text{ \AA}$

$c = 7.5293(5) \text{ \AA}$

$V = 2425.4(2) \text{ \AA}^3$

$Z = 4$

$D_x = 4.000 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 17.9\text{--}24.6^\circ$

$\mu = 11.992 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Block

$0.275 \times 0.175 \times 0.100 \text{ mm}$

Block

Data collection

Enraf CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

ψ scans (SHELXL93);

Sheldrick, 1993)

$T_{\min} = 0.163$, $T_{\max} = 0.319$

2218 measured reflections

2218 independent reflections

1934 reflections with

$F_o > 4\sigma(F_o)$

$\theta_{\max} = 24.97^\circ$

$h = 0 \rightarrow 27$

$k = -16 \rightarrow 0$

$l = 0 \rightarrow 8$

4 standard reflections

every 60 reflections

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.039$

$wR(F^2) = 0.102$

$S = 1.061$

2218 reflections

131 parameters

$w = 1/[\sigma^2(F_o^2) + (0.057P)^2$

$+ 40.081P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.001$

$\Delta\rho_{\max} = 3.55 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -1.84 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93

Extinction coefficient:

0.00047 (7)

Scattering factors from

International Tables for

Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Ba1	0.34787(4)	1/4	0.71179(11)	0.0160(2)
Ba2	0.07413(2)	0.01561(4)	0.70811(8)	0.0166(2)
Ba3	0.22405(2)	0.08120(4)	1.08003(8)	0.0176(2)
Ba4	0.54348(4)	1/4	0.31916(14)	0.0244(3)
V1	0.16640(10)	1/4	0.5816(4)	0.0171(5)
V2	0.33816(10)	1/4	1.2010(3)	0.0106(5)
V3	0.41933(7)	-0.00525(11)	0.7059(2)	0.0101(4)
S1	0.34559(10)	0.0390(2)	0.8638(3)	0.0154(5)
S2	0.46186(10)	0.1173(2)	0.5884(3)	0.0173(5)
S3	0.1714(2)	1/4	1.3028(5)	0.0235(8)
S4	0.0773(2)	1/4	0.6528(7)	0.0312(10)
S5	0.4232(2)	1/4	1.0926(5)	0.0244(9)
S6	0.20828(12)	0.1232(2)	0.6798(4)	0.0228(6)
S7	0.32318(11)	0.1214(2)	0.3589(3)	0.0155(5)
O1	0.2900(4)	1/4	1.0345(12)	0.009(2)
O2	0.0337(3)	0.0656(5)	0.3435(9)	0.0158(14)
O3	0.1039(3)	0.0825(5)	1.0471(9)	0.0143(14)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Ba1—O1	2.778(9)	Ba3—S7 ^{vi}	3.168(3)
Ba1—S1 ⁱ	3.139(2)	Ba3—S1	3.314(2)
Ba1—S1	3.139(2)	Ba3—S6 ⁱⁱⁱ	3.325(3)
Ba1—S7	3.250(3)	Ba3—S7 ⁱⁱⁱ	3.443(2)

Ba1—S7 ⁱ	3.250(3)	Ba4—O2 ^{vii}	2.841(7)
Ba1—S2	3.357(3)	Ba4—O2 ^{viii}	2.841(7)
Ba1—S2 ⁱ	3.357(3)	Ba4—S3 ^{ix}	3.113(4)
Ba1—S5	3.360(4)	Ba4—S5 ^t	3.276(4)
Ba1—S6	3.699(3)	Ba4—S2 ⁱ	3.330(3)
Ba1—S6 ⁱ	3.699(3)	Ba4—S2	3.330(3)
Ba2—O2 ⁱⁱ	2.777(6)	Ba4—S4 ^{vii}	3.639(5)
Ba2—O3	2.801(6)	V1—S3 ^t	2.102(5)
Ba2—O2	2.983(7)	V1—S6 ⁱ	2.140(3)
Ba2—S7 ⁱⁱⁱ	3.255(3)	V1—S6	2.140(3)
Ba2—S4	3.2739(9)	V1—S4	2.140(5)
Ba2—S1 ^{iv}	3.283(3)	V2—O1	1.682(9)
Ba2—S2 ^v	3.339(3)	V2—S5	2.140(4)
Ba2—S6	3.464(3)	V2—S7 ^{xi}	2.169(3)
Ba2—S2 ⁱⁱⁱ	3.506(3)	V2—S7 ^{vii}	2.169(3)
Ba3—O3	2.807(6)	V3—O3 ^{ix}	1.693(7)
Ba3—O1	2.817(5)	V3—O2 ⁱⁱⁱ	1.722(7)
Ba3—S6	3.091(3)	V3—S2	2.155(3)
Ba3—S3	3.127(3)	V3—S1	2.175(3)
Ba3—S1 ⁱⁱⁱ	3.156(3)		
S3 ^t —V1—S6 ⁱ	108.66(12)	S5—V2—S7 ^{vii}	110.95(11)
S3 ^t —V1—S6	108.66(12)	S7 ^{xi} —V2—S7 ^{vii}	110.4(2)
S6 ⁱ —V1—S6	110.3(2)	O3 ^{ix} —V3—O2 ⁱⁱⁱ	108.7(3)
S3 ^t —V1—S4	107.6(2)	O3 ^{ix} —V3—S2	110.7(2)
S6—V1—S4	110.75(13)	O2 ⁱⁱⁱ —V3—S2	109.8(2)
O1—V2—S5	109.4(3)	O3 ^{ix} —V3—S1	108.3(2)
O1—V2—S7 ^{xi}	107.5(2)	O2 ⁱⁱⁱ —V3—S1	107.9(2)
S5—V2—S7 ^{xi}	110.95(11)	S2—V3—S1	111.36(11)
O1—V2—S7 ^{vii}	107.5(2)		

Symmetry codes: (i) $x, \frac{1}{2} - y, z$; (ii) $-x, -y, 1 - z$; (iii) $\frac{1}{2} - x, -y, \frac{1}{2} + z$; (iv) $\frac{1}{2} - x, -y, z - \frac{1}{2}$; (v) $x - \frac{1}{2}, y, \frac{3}{2} - z$; (vi) $x, y, 1 + z$; (vii) $\frac{1}{2} + x, y, \frac{1}{2} - z$; (viii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (ix) $\frac{1}{2} + x, y, \frac{3}{2} - z$; (x) $x, y, z - 1$; (xi) $x, \frac{1}{2} - y, 1 + z$.

All crystallographic calculations were performed on a PC with a 486 DX2/66 processor and 20 Mb of extended memory. Intensities were corrected for Lorentz and polarization factors. Systematic absences indicated the centrosymmetric space group *Pnma* (No. 62) or the non-centrosymmetric space group *Pn2₁a* (No. 33), intensity statistics clearly favored the centrosymmetric case. The SHELXTL (Sheldrick, 1994) program package was implemented to confirm the orthorhombic centrosymmetric space group *Pnma*, to apply the absorption correction, and set up the initial files. The structure was determined by direct methods with the successful location of the fourteen heavy atoms (4 Ba, 3 V, and 7 S). The remaining three O atoms were found from a subsequent difference Fourier map. Initial refinement of the model, on F_o^2 and $\sigma(F_o^2)$, proceeded smoothly with all atoms isotropic. All atoms were refined anisotropically during the final series of cycles. A final difference Fourier map revealed rather large peaks, $|\Delta\rho| < 3.55 \text{ e \AA}^{-3}$ within 1.0 \AA of the heavy atoms.

Data collection: CAD-4 EXPRESS (Enraf-Nonius, 1994). Cell refinement: CAD-4 EXPRESS. Data reduction: CAD-4 EXPRESS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXTL (Sheldrick, 1994).

We acknowledge the National Science Foundation, Division of Materials Research for financial support of this work.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1155). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Eichhorn, B. W. (1994). *Progress in Inorganic Chemistry*, Vol. 42, edited by K. D. Karlin, pp. 139–237. New York: John Wiley & Sons.
- Enraf–Nonius (1994). *CAD-4 EXPRESS*. Enraf–Nonius, Delft, The Netherlands.
- Gardner, D. R., Fettinger, J. C. & Eichhorn, B. W. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 1859–1860.
- Gardner, R. A., Vlasse, M. & Wold, A. (1969). *Acta Cryst.* **B25**, 781–787.
- Gotoh, Y., Goto, M., Kawaguchi, K., Oosawa, Y. & Onoda, M. (1990). *Mater. Res. Bull.* **25**, 307–314.
- Gotoh, Y., Onoda, M., Goto, M. & Oosawa, Y. (1989). *Chem. Lett.* pp. 1281–1282.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Krebs, B., Buss, B. & Ferwanah, A. (1972). *Z. Anorg. Allg. Chem.* **387**, 142–153.
- Lundquest, D. & Westgren, A. (1936). *Sven. Kem. Tidskr.* **4**, 241.
- Müller, A. & Diemann, E. (1969). *Chem. Ber.* **102**, 2044–2049.
- Murugesan, T., Ramesh, S., Gopalakrishnan, J. & Rao, C. N. R. (1981). *J. Solid State Chem.* **38**, 165–172.
- Onoda, M. & Kato, K. (1990). *Acta Cryst.* **B46**, 487–492.
- Ouvrard, G., Tchahbedji, G., Deniard, P. & Prouzet, E. (1995). *J. Power Sources*, **54**, 246–249.
- Pauling, L. & Hultgren, R. (1933). *Z. Kristallogr.* **84**, 204–206.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1994). *SHELXTL*. Version 5. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Tranchitella, L. J., Fettinger, J. C. & Eichhorn, B. W. (1996). *Chem. Mater.* In the press.
- Van den Berg, J. M. & DeVries, R. (1964). *Proc. K. Ned. Akad. Wet.* **B67**, 178–179.

Acta Cryst. (1997). **C53**, 165–167

K₂WSe₄

DANIEL RÖHNERT, CHRISTIAN NÄTHER AND WOLFGANG BENSCH

Institut für Anorganische Chemie der Universität Frankfurt, Marie-Curie-Strasse 11, 60439 Frankfurt/Main, Germany. E-mail: bensch@chemie.uni-frankfurt.de

(Received 24 July 1996; accepted 5 November 1996)

Abstract

The crystal structure of dipotassium tungsten tetraselenide is based on isolated, slightly distorted WSe₄ tetrahedra joined *via* K⁺ ions. The compound is isotopic with the previously reported Rb and Cs analogues and crystallizes in the β-K₂SO₄ structure type.

Comment

Ternary alkali metal tungsten chalcogenides A₂WQ₄ (A = Rb, Cs, NH₄⁺; Q = S, Se) have been prepared

using classical solution chemistry (Müller & Sievert, 1974; Müller, Diemann & Heidborn, 1970). The crystal structures of these compounds were reported about 20 years ago. It is interesting to note that these preparation methods did not lead to the successful synthesis of the potassium selenide. During our research on the preparation of new tungsten chalcogenides using the so-called 'reactive flux' method (Sunshine, Kang & Ibers, 1987; Kanatzidis & Sutorik, 1995), the previously unknown ternary tungsten selenide K₂WSe₄ was obtained. It is most likely that conventional preparation methods, either in aqueous solution or at high temperatures, are destined to favour the thermodynamically more stable binary compounds (Kanatzidis, 1990).

The structure of K₂WSe₄ consists of slightly distorted WSe₄²⁻ tetrahedra located on crystallographic mirror planes, with W—Se bond lengths ranging from 2.3050 (7) to 2.3266 (9) Å and Se—W—Se angles between 107.16 (4) and 111.79 (4)°. These data are within the range reported for other ternary tungsten tetraselenides (Müller, Krebs & Beyer, 1968). The K⁺ ions are coordinated by eight and nine Se centres with K—Se distances between 3.263 (2) and 3.722 (3) Å (Fig. 1). The coordination sphere of K1 (CN = 9) is of

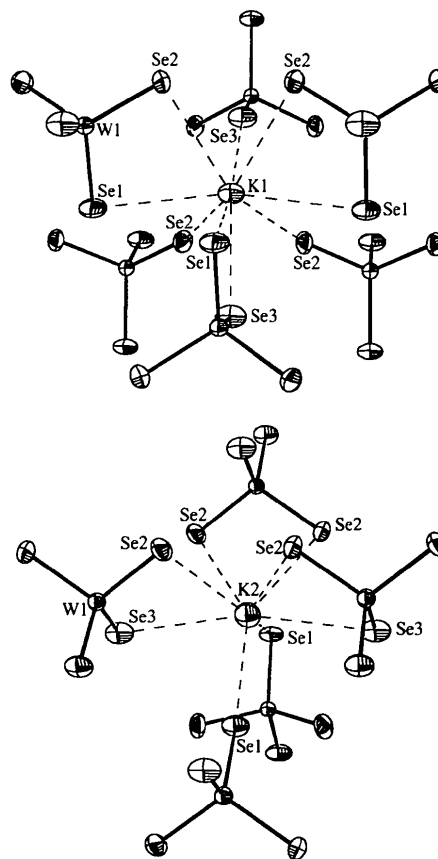


Fig. 1. The coordination spheres of K1 and K2 in K₂WSe₄. Displacement ellipsoids are plotted at the 50% probability level.