

RbCu<sub>2</sub>VS<sub>4</sub>

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Received 7 June 2000

Accepted 4 December 2000

The reaction of Cu and V in a Rb<sub>2</sub>S<sub>5</sub> melt yields black crystals of rubidium dicopper vanadium tetrasulfide, RbCu<sub>2</sub>VS<sub>4</sub>. The structure is comprised of [Cu<sub>2</sub>VS<sub>4</sub>]<sup>−</sup> layers within the (010) plane which are separated by Rb<sup>+</sup> cations. The layers consist of a network of edge- and corner-sharing [VS<sub>4</sub>] and [CuS<sub>4</sub>] tetrahedra parallel to (010). The optical band gap was determined as 1.45 eV.

## Comment

In recent years, we systematically investigated the quaternary system *A/Cu/V/Q* (with *A* = K, Rb, Cs; *Q* = S, Se), and prepared and characterized some new compounds with one- and two-dimensional structures, e.g. K<sub>2</sub>CuVS<sub>4</sub> (Dürichen & Bensch, 1996), K<sub>2</sub>CuVSe<sub>4</sub> (Rumpf, Tillinski *et al.*, 1997), KCu<sub>2</sub>VS<sub>4</sub> (Bensch *et al.*, 1996) and KCu<sub>2</sub>VSe<sub>4</sub> (Tillinski *et al.*, 1999).

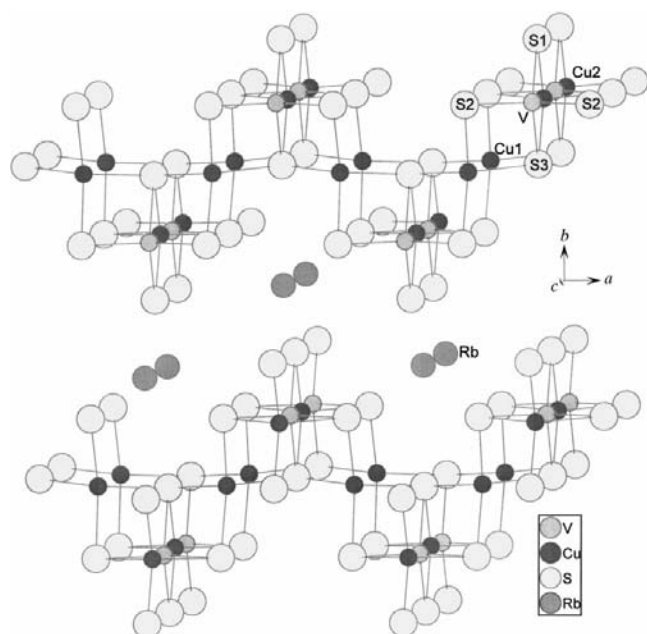
The title compound, RbCu<sub>2</sub>VS<sub>4</sub>, is isostructural with KCu<sub>2</sub>VS<sub>4</sub>, KCu<sub>2</sub>VSe<sub>4</sub>, NaCu<sub>2</sub>NbS<sub>4</sub> (Rumpf, Näther *et al.*,

1997) and KCu<sub>2</sub>NbS<sub>4</sub> (Lu & Ibers, 1991). The main feature of the layered structure is the existence of two-dimensional anionic [Cu<sub>2</sub>VS<sub>4</sub>]<sup>−</sup> sheets within the (010) plane which are separated by Rb<sup>+</sup> cations. These layers are comprised of [CuVS<sub>4</sub>]<sub>*n*</sub><sup>2*n*−</sup> chains of corner-sharing [VS<sub>4</sub>] and [CuS<sub>4</sub>] tetrahedra that are linked into the final sheets by [CuS<sub>4</sub>] tetrahedra sharing edges between [VS<sub>4</sub>] tetrahedra of neighbouring chains.

Three crystallographically unique metal atoms (Cu1, Cu2 and V) are found, each coordinated by four S atoms in a distorted tetrahedral environment. The average *M*–S distances are 2.30 (1) Å for *M* = Cu and 2.19 (1) Å for *M* = V, and lie within the normal range. The S–V–S angles are in the range 109.05 (12)–109.9 (3)°, indicating only very weak distortion of the [VS<sub>4</sub>] tetrahedra. In contrast, the S–Cu–S angles about the two independent Cu atoms indicate strong deviation from ideal tetrahedral geometry [103.03 (11)–120.4 (2)° for Cu1 and 102.0 (2)–114.67 (12)° for Cu2]. Due to the large differences of the Cu–S and V–S bond lengths, the connection of the [MS<sub>4</sub>] tetrahedra *via* common edges must introduce strong distortion mainly affecting the [CuS<sub>4</sub>] tetrahedra. The V–Cu distances are 2.703 (4), 2.709 (2) and 2.711 (4) Å, indicating no metal-to-metal interactions. Each Rb<sup>+</sup> cation is coordinated by nine S atoms. The resulting polyhedra may be described as distorted tricapped trigonal prisms. The Rb–S distances range from 3.356 (9) to 3.713 (2) Å, with an average value of 3.55 (1) Å, in good agreement with the sum of the ionic radii. A UV–vis diffuse reflection spectrum was recorded in order to determine the optical band gap of RbCu<sub>2</sub>VS<sub>4</sub>; a value of 1.45 eV was found, which corresponds well with the black colour of the compound.

## Experimental

RbCu<sub>2</sub>VS<sub>4</sub> was prepared by the reaction of Rb<sub>2</sub>S<sub>5</sub>, Cu and V in the ratio 6:2:1. Rb<sub>2</sub>S<sub>5</sub> was prepared from stoichiometric amounts of the elements in liquid ammonia under an argon atmosphere. The starting materials were mixed thoroughly in a dry box and sealed into a Pyrex-glass ampoule, which was evacuated at 1.0 × 10<sup>−3</sup> mbar (1 mbar = 100 Pa). The ampoule was heated at 673 K for 6 d and cooled to



**Figure 1**  
The crystal structure of RbCu<sub>2</sub>VS<sub>4</sub> viewed along the *c* axis.

**Table 1**

Selected geometric parameters (Å, °).

V–S1	2.153 (7)	Cu2–S3	2.300 (4)
V–S2	2.186 (4)	Cu2–S2 <sup>ii</sup>	2.302 (3)
V–S3	2.232 (5)	Rb–S1 <sup>iii</sup>	3.356 (9)
V–Cu2 <sup>i</sup>	2.703 (4)	Rb–S3 <sup>iv</sup>	3.453 (4)
V–Cu1	2.709 (2)	Rb–S1 <sup>v</sup>	3.458 (10)
V–Cu2	2.711 (4)	Rb–S2 <sup>vi</sup>	3.486 (4)
Cu1–S2	2.290 (3)	Rb–S2 <sup>vii</sup>	3.645 (4)
Cu1–S3	2.307 (3)	Rb–S1 <sup>vi</sup>	3.713 (2)
Cu2–S1	2.288 (6)		
S1–V–S2 <sup>viii</sup>	109.88 (14)	S3 <sup>ix</sup> –Cu1–S3	106.7 (2)
S2 <sup>viii</sup> –V–S2	109.9 (3)	V–Cu1–V <sup>ix</sup>	175.0 (2)
S1–V–S3	109.1 (2)	S1–Cu2–S3	102.3 (2)
S2 <sup>viii</sup> –V–S3	109.05 (12)	S1–Cu2–S2 <sup>ii</sup>	111.79 (13)
S2–Cu1–S2 <sup>ix</sup>	120.4 (2)	S3–Cu2–S2 <sup>ii</sup>	114.67 (12)
S2–Cu1–S3 <sup>ix</sup>	111.61 (10)	S2 <sup>ii</sup> –Cu2–S2 <sup>vii</sup>	102.0 (2)
S2 <sup>ix</sup> –Cu1–S3 <sup>ix</sup>	103.03 (11)	V <sup>ii</sup> –Cu2–V	177.58 (14)

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

293 K at a rate of 3 K h<sup>-1</sup>. The resulting melt was washed with dimethylformamide and diethyl ether. Finally, the residue was dried in a vacuum.

## Crystal data

RbCu<sub>2</sub>VS<sub>4</sub>  
*M<sub>r</sub>* = 391.73  
 Orthorhombic, *Ama*2  
*a* = 7.382 (3) Å  
*b* = 18.187 (11) Å  
*c* = 5.413 (2) Å  
*V* = 726.7 (6) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 3.580 Mg m<sup>-3</sup>

## Data collection

Stoe AED-II four-circle diffractometer  
 $\omega$ - $\theta$  scans  
 Absorption correction: empirical (*XEMP* in *SHELXTL/PC*; Siemens, 1990)  
*T<sub>min</sub>* = 0.290, *T<sub>max</sub>* = 0.345  
 1230 measured reflections  
 628 independent reflections

## Refinement

Refinement on *F*<sup>2</sup>  
*R* [*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.033  
*wR*(*F*<sup>2</sup>) = 0.078  
*S* = 1.039  
 628 reflections  
 46 parameters

Mo *K* $\alpha$  radiation  
 Cell parameters from 10 reflections  
 $\theta$  = 13–24°  
 $\mu$  = 14.74 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Block, black  
 0.08 × 0.08 × 0.07 mm

483 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.055  
 $\theta_{\max}$  = 24.97°  
*h* = 0 → 8  
*k* = -21 → 21  
*l* = -6 → 4  
 4 standard reflections  
 frequency: every 120 min  
 intensity decay: negligible

$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.95 \text{ e } \text{Å}^{-3}$   
 $\Delta\rho_{\min} = -0.66 \text{ e } \text{Å}^{-3}$   
 Absolute structure: Flack (1983)  
 Flack parameter = -0.01 (3)

Data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *CIFTAB* in *SHELXL97*.

This work is supported by the state of Schleswig-Holstein.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1402). Services for accessing these data are described at the back of the journal.

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