Ca—OW	2.441 (9)	I—H^{x}	3.10 (4)
Ca—O^{v,III}	2.454 (3)	I—H^{x,ix}	3.10 (4)
Ca—O^{v}	2.454 (3)	I—H	3.10 (4)
Ca—O^{ix}	2.454 (3)	I—H^{x,III}	3.10 (4)
O—H	0.92 (2)		

Symmetry codes: (i) $-x, -y, -z$; (ii) $-x+y, -x, z$; (iii) $-y, x-y, z$; (iv) $x-y, x, -z$; (v) $y, -x+y, -z$; (vi) $1-y, x-y, z$; (vii) $1-x+y, 1-x, z$; (viii) $1+x-y, x, -z$; (ix) $1-x, 1-y, -z$; (x) $\frac{2}{3}-x, \frac{4}{3}-y, \frac{1}{3}-z$; (xi) $\frac{2}{3}+x-y, \frac{1}{3}+x, \frac{1}{3}-z$; (xii) $y-\frac{1}{3}, \frac{1}{3}-x+y, \frac{1}{3}-z$; (xiii) $1-y, 1+x-y, z$; (xiv) $-x+y, 1-x, z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O—H···I	0.92 (2)	3.10 (4)	3.911 (3)	148 (5)
OW—HW···I	0.95 (2)	2.78 (8)	3.620 (3)	148 (11)

The structure was refined in the $R\bar{3}$ space group. Attempts to refine the model in the non-centrosymmetric $R3$ space group did not lead to a better fit. The H atoms of the hydroxy group and water molecule were located from a difference Fourier map and allowed to refine subject to an O—H *DFIX* restraint of 0.95 Å, with a fixed individual isotropic displacement parameter $U_{iso} = 1.2U_{eq}(O)$. The O atom (OW) of the water molecule was located on a special site, 6(c), whereas its H atoms occupy the general site, 18(f), with an occupancy factor of $\frac{2}{3}$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *DREAM* (Blessing, 1987). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ATOMS* (Dowty, 1995).

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KCu$_2$VSe$_4$

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Abstract

The reaction of Cu and V in a K$_2$Se$_5$ melt yields black crystals of potassium dicopper vanadium tetraselenide, KCu$_2$VSe$_4$. The structure is comprised of [Cu$_2$VSe$_4$]$^-$ layers within the (010) plane separated by K$^+$ cations. The layers consist of a network of edge- and corner-sharing [VSe$_4$] and [CuSe$_4$] tetrahedra parallel to (010).

Comment

The structure determination of the title compound was undertaken as part of a project on the systematic investigation of the A/Cu/V/Q system (A = K, Rb, Cs; Q = S, Se). Recently, a number of one- and two-dimensional compounds were synthesized and characterized within this system, *e.g.* K$_2$CuVS$_4$ (Dürichen & Bensch, 1996), K$_2$CuVSe$_4$ (Rumpf, Tillinski *et al.*, 1997) and KCu$_2$VS$_4$ (Bensch *et al.*, 1996).

KCu$_2$VSe$_4$ is isostructural with KCu$_2$VS$_4$, NaCu$_2$NbS$_4$ (Rumpf, Näther *et al.*, 1997) and KCu$_2$NbS$_4$ (Lu & Ibers, 1991). The structure is built up by chains of corner-sharing [VSe$_4$] and [CuSe$_4$] tetrahedra. These [CuVSe$_4$]$_n^{2n-}$ chains are linked into layers by [CuSe$_4$] tetrahedra which share edges between [VSe$_4$] tetrahedra on neighbouring chains. The [Cu$_2$VSe$_4$]$^-$ layers are within the (010) plane and are separated by K$^+$ cations.

The shortest interlayer Se···Se distance is 3.783 (2) Å. There are three crystallographically distinct metal atoms, *i.e.* Cu1, Cu2 and V. All have a distorted tetrahedral coordination of four Se atoms. The average M—Se distances are 2.399 (2) Å for M = Cu and 2.324 (2) Å for M = V, and lie within the normal range. The Se—Cu—Se angles about the two independent Cu atoms indicate stronger distorted tetrahedral environments [105.09 (4)–112.22 (3)° for Cu1 and 104.32 (4)–119.17 (4)° for Cu2] than for the VSe$_4$ tetrahedron, with Se—V—Se angles deviating less from ideal values [108.09 (3)–110.36 (5)°]. Because the [MSe$_4$] tetrahedra are connected *via* common edges, the large differences in the Cu—Se and V—Se bond lengths must lead to severe distortions which primarily affect the [CuSe$_4$] tetrahedra. The V···Cu distances are 2.777 (1), 2.788 (1) and 2.775 (1) Å [average 2.779 (2) Å], which are far too long for bonding interactions. As expected, the distances are

slightly longer than those observed in KCu$_2$VS$_4$ (average 2.70 Å). Each K$^+$ cation is coordinated by nine Se atoms and the resulting polyhedra may be described as distorted tricapped trigonal prisms. The K$\cdots$Se distances range from 3.361 (2) to 3.822 (1) Å, with an average of 3.599 (2) Å, which is just the sum of the ionic radii.
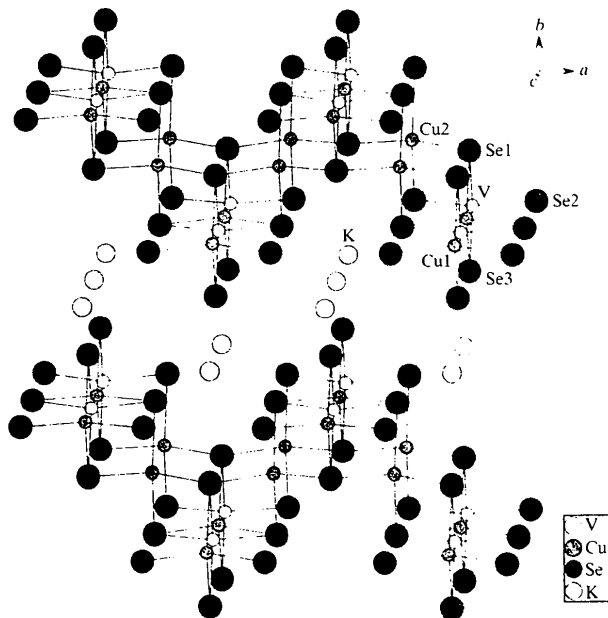

Fig. 1. The crystal structure of KCu$_2$VSe$_4$ viewed along the c axis.

Experimental

KCu$_2$VSe$_4$ was prepared by the reaction of K$_2$Se$_5$, Cu and V in the ratio 6:2:1. K$_2$Se$_5$ was prepared from stoichiometric amounts of K and Se 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^{-3} mbar (1 bar = 10^5 Pa). The ampoule was heated at 673 K for 6 d and then cooled to 293 K at a rate of 3 K h^{-1}. The resulting melt was washed with dimethylformamide and diethyl ether. Finally, the residue was dried in a vacuum.

Crystal data

KCu$_2$VSe$_4$
M_r = 532.96
Orthorhombic
$Ama2$
a = 7.5803 (8) Å
b = 18.4838 (12) Å
c = 5.5653 (5) Å
V = 779.77 (12) Å^3
Z = 4
D_x = 4.540 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 11 reflections
θ = 10–24°
μ = 25.674 mm^{-1}
T = 293 (2) K
Polyhedral
0.05 × 0.03 × 0.02 mm
Black

Data collection

Stoe AEDII four-circle diffractometer
ω/θ scans
Absorption correction: empirical (*XEMP* in *SHELXTL/PC*; Siemens, 1990)
T_{min} = 0.407, T_{max} = 0.598
2108 measured reflections
670 independent reflections (plus 411 Friedel-related reflections)

925 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 30.01°
h = 0 → 10
k = −26 → 26
l = −7 → 4
4 standard reflections frequency: 120 min intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.047
S = 1.036
1081 reflections
46 parameters
w = 1/[$\sigma^2(F_o^2)$ + (0.0240P)^2]
where P = (F_o^2 + 2F_c^2)/3
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.594 e Å^{-3}
$\Delta\rho_{min}$ = −0.672 e Å^{-3}

Extinction correction: *SHELXL*93
Extinction coefficient: 0.0056 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.03 (2)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
V	1/4	0.39050 (5)	0.2500 (2)	0.0129 (2)
Cu1	1/4	0.39107 (5)	0.7510 (2)	0.0200 (2)
Cu2	1/2	1/2	0.22943 (15)	0.0204 (2)
Se1	1/4	0.49517 (2)	0.49423 (10)	0.01578 (12)
Se2	0.50193 (4)	0.38821 (2)	0.01146 (8)	0.02095 (10)
Se3	1/4	0.28918 (3)	0.4836 (2)	0.0329 (2)
K1	1/4	0.68415 (8)	0.4905 (4)	0.0422 (3)

Table 2. *Selected geometric parameters (Å, °)*

V—Se3	2.2797 (13)	Cu2—Se2	2.3961 (6)
V—Se2	2.3262 (8)	Cu2—Se1	2.4023 (7)
V—Se1	2.3644 (11)	K1—Se1	3.493 (2)
V—Cu2	2.7750 (7)	K1—Se3^{iii}	3.361 (2)
V—Cu1^i	2.7773 (12)	K1—Se3^{iv}	3.425 (2)
V—Cu1	2.7881 (12)	K1—Se2^v	3.526 (2)
Cu1—Se1	2.3966 (10)	K1—Se2^{vi}	3.706 (2)
Cu1—Se2^{ii}	2.3982 (7)	K1—Se3^{vii}	3.8222 (4)
Cu1—Se3	2.4003 (10)		
Se3—V—Se2	108.09 (3)	Se2^{ii}—Cu1—Se3	110.94 (3)
Se2^{viii}—V—Se2	110.36 (5)	V^{iii}—Cu1—V	179.57 (7)
Se3—V—Se1	110.14 (5)	Se2—Cu2—Se2^{vii}	119.17 (4)
Se2—V—Se1	110.06 (3)	Se2—Cu2—Se1^{vii}	109.744 (14)
Se1—Cu1—Se2^{ii}	112.22 (3)	Se2—Cu2—Se1	106.459 (14)
Se2^{ii}—Cu1—Se2^{ix}	105.56 (4)	Se1^{vii}—Cu2—Se1	104.32 (4)
Se1—Cu1—Se3	105.09 (4)	V—Cu2—V^{vii}	175.27 (5)

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

Data collection: *DIF*4 (Stoe & Cie, 1991a). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1991b). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93.

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Ammonium trivanadate(V), $NH_4V_3O_8$

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Abstract

The structure of the title compound is made up of vanadium oxide layers, with NH_4^+ cations intercalated between the layers. Each pair of VO_5 square pyramids is bridged by an edge to form a double V_2O_8 group. The V_2O_8 groups are connected by sharing corners to produce a twisted zigzag chain. Each VO_6 octahedron is connected to two V_2O_8 groups by two edges and to another two V_2O_8 groups by two corners. Hence, the twisted zigzag chains are held together through VO_6 octahedra by sharing corners and edges to form a layer

structure. There are $N—H \cdots O$ hydrogen bonds between the vanadium oxide layer and the NH_4^+ cations.

Comment

$NH_4V_3O_8$ was first prepared by Norblad (1875) and is one stable solid phase in the $NH_3–V_2O_5–H_2O$ system at 303 K (Kelmers, 1961a). Based on X-ray powder diffraction, Kelmers revealed that $NH_4V_3O_8$ was probably isostructural with KV_3O_8, RbV_3O_8 and CsV_3O_8 (Kelmers, 1961b). The crystal structures of KV_3O_8 and CsV_3O_8 were described by Block and Evens (Block, 1960; Evens & Block, 1966). However, powder diffraction techniques were inadequate for revealing the detailed structure or for confirming the possibility of hydrogen bonding in the title compound. We report herein the hydrogen bonding in the crystal structure of the title compound and two new synthetic routes for its preparation.

As illustrated in Fig. 1, the structure of $NH_4V_3O_8$ consists of layers fused by VO_5 square pyramids and VO_6 octahedra, with ammonium cations occupying the interlayer positions. The VO_5 square pyramids are connected in pairs by sharing an edge to form a V_2O_8 group. In the V_2O_8 group, the two apices of the two square pyramids point away from each other (Fig. 2). The V_2O_8 groups are joined through corners (O4) into a twisted zigzag chain along the b axis. One VO_6 octahedron and two V_2O_8 groups are linked by sharing
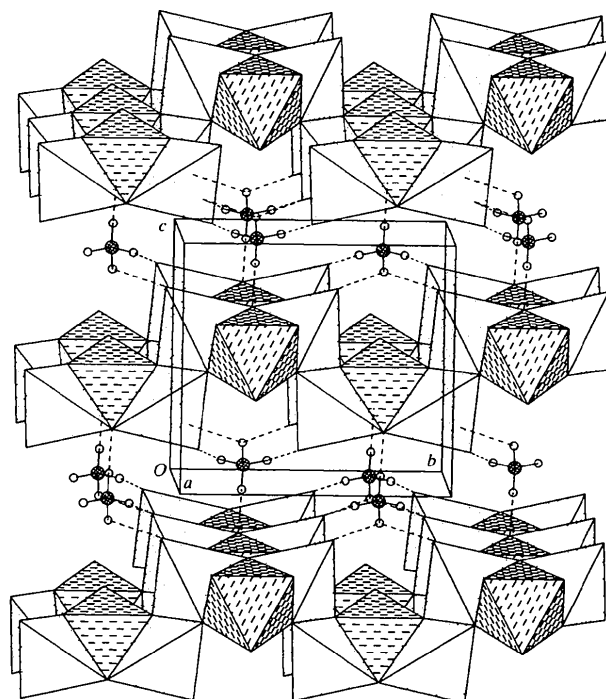
Fig. 1. The structure of $NH_4V_3O_8$ viewed along the a axis, showing the buckled layers and the interlayer hydrogen bonds (dashed lines). The N and H atoms are represented by large cross-hatched circles and small open circles, respectively.