Collection des données

Diffractomètre CAD-4
Balayage $\omega/2\theta$
Correction d'absorption: empirique par ψ scans (North *et al.*, 1968)
$T_{min} = 0{,}274$, $T_{max} = 0{,}549$
1153 réflexions mesurées
1063 réflexions indépendantes
973 réflexions avec $I > 2\sigma(I)$
$R_{int} = 0{,}013$
$\theta_{max} = 25{,}96°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 8$
1 réflexion de référence
fréquence: 120 min
variation d'intensité: 0,3%

Affinement

Affinement à partir des F^2
$R[F^2 > 2\sigma(F^2)] = 0{,}034$
$wR(F^2) = 0{,}081$
$S = 1{,}264$
1063 réflexions
113 paramètres
$w = 1/[\sigma^2(F_o^2) + (0{,}0108P)^2 + 45{,}5442P]$
où $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1{,}123$ e Å^{-3}
$\Delta\rho_{min} = -1{,}183$ e Å^{-3}
Correction d'extinction: *SHELXL*93 (Sheldrick, 1993)
Coefficient d'extinction: 0,0058 (2)
Facteurs de diffusion des *International Tables for Crystallography* (Tome C)

Tableau 1. *Coordonnées atomiques et facteurs d'agitation thermique isotrope équivalents (Å^2)*

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

	x	y	z	$U_{éq}$
Ni1	0	0	0	0,0086 (4)
Ni2	0	0,3764 (1)	0	0,0090 (3)
Ni3	0,32852 (9)	0,69184 (7)	0,1763 (1)	0,0078 (3)
As1	0,09083 (7)	0,19103 (5)	0,2751 (1)	0,0061 (2)
As2	0,3055 (1)	0	−0,9735 (2)	0,0079 (3)
K1†	0,6145 (4)	0,1113 (3)	0,5179 (6)	0,0184 (8)
K2†	0,8051 (7)	1/2	0,5350 (10)	0,038 (2)
K3†	0,4375 (12)	1/2	0,4797 (14)	0,070 (4)
O1	0,5104 (5)	0,7836 (4)	0,7738 (8)	0,012 (1)
O2	0,4836 (5)	0,6038 (4)	0,1995 (8)	0,009 (1)
O3	0,8005 (5)	0,2044 (4)	0,8636 (8)	0,009 (1)
O4	0,8377 (5)	0,1732 (4)	0,4818 (8)	0,014 (1)
O5	0,8108 (5)	0,4056 (4)	0,8788 (8)	0,011 (1)
O6	0,8079 (8)	0	0,8506 (13)	0,012 (2)
O7	0,5474 (8)	0	0,8147 (12)	0,014 (2)

† Facteur d'occupation = 0.50.

Tableau 2. *Paramètres géométriques (Å, °)*

Ni1—O2^{i}	2,052 (5)	Ni3—O5^{xii}	2,046 (6)
Ni1—O2^{ii}	2,052 (5)	Ni3—O4^{xiii}	2,052 (5)
Ni1—O2^{iii}	2,052 (5)	Ni3—O3^{xi}	2,059 (5)
Ni1—O2^{iv}	2,052 (5)	Ni3—O2	2,100 (5)
Ni1—O6^{v}	2,100 (8)	Ni3—O1^{ix}	2,169 (6)
Ni1—O6^{vi}	2,100 (8)	As1—O4^{ix}	1,651 (5)
Ni2—O1^{vii}	2,054 (6)	As1—O3^{ix}	1,698 (5)
Ni2—O1^{viii}	2,054 (6)	As1—O2^{i}	1,715 (5)
Ni2—O5^{ix}	2,078 (5)	As1—O1^{viii}	1,719 (6)
Ni2—O5^{vi}	2,078 (5)	As2—O6^{xiv}	1,656 (8)
Ni2—O7^{x}	2,311 (6)	As2—O5^{xv}	1,698 (6)
Ni2—O7^{xi}	2,311 (6)	As2—O5^{xvi}	1,698 (6)
Ni3—O3^{xii}	2,035 (5)	As2—O7^{xiv}	1,702 (8)

Codes de symétrie: (i) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (iv) $\frac{1}{2} - x, y - \frac{1}{2}, -z$; (v) $1 - x, -y, 1 - z$; (vi) $x - 1, y, z - 1$; (vii) $x - \frac{1}{2}, y - \frac{1}{2}, z - 1$; (viii) $\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$; (ix) $1 - x, y, 1 - z$; (x) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (xi) $x - \frac{1}{2}, \frac{1}{2} + y, z - 1$; (xii) $1 - x, 1 - y, 1 - z$; (xiii) $x - \frac{1}{2}, \frac{1}{2} + y, z$; (xiv) $1 - x, -y, -z$; (xv) $x - \frac{1}{2}, y - \frac{1}{2}, z - 2$; (xvi) $x - \frac{1}{2}, \frac{1}{2} - y, z - 2$.

La largeur de balayage est $(1{,}00 + 0{,}5\mathrm{tg}\theta)$. Les intensités ont été corrigées des facteurs de Lorentz–polarisation. La structure a été résolue par la méthode de l'atome lourd (*SHELXS*86; Sheldrick, 1990) puis affinée par la méthode des moindres carrés (*SHELXL*93; Sheldrick, 1993).

Collection des données: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994; Duisenberg, 1992; Macíček & Yordanov, 1992). Affinement des paramètres de la maille: *CAD*-4 *EXPRESS*. Réduction des données: *MolEN* (Fair, 1990). Graphisme moléculaire: *ATOMS* (Dowty, 1993). Logiciel utilisé pour préparer le matériel pour publication: *SHELXL*93.

Des documents complémentaires concernant cette structure peuvent être obtenus à partir des archives électroniques de l'UICr (Référence: GS1015). Les processus d'accès à ces archives sont donné au dos de la couverture.

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KCu_4Se_3

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Abstract

The reaction of K_2Se_5 and Cu yields single cryst of potassium tetracopper triselenide, KCu_4Se_3, whi is isotypic with the sulfides ACu_4S_3 (A = K, R Cs, Tl) and the selenide $CsCu_4Se_3$. The structu consists of double layers of copper cations, tetrahedrally coordinated by selenium and separated by potassium cations.

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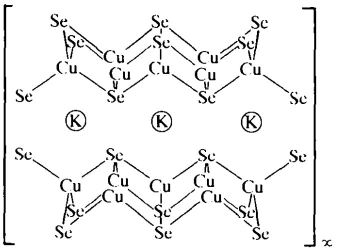
Comment

A relatively large number of ternary copper chalcogenides are known, which can be differentiated into those compounds which only exhibit one valency and those in which mixed valency must be proposed. Our interest is predominantly focused on the mixed-valence compounds, because most of them exhibit interesting physical properties. We have therefore studied the preparation of such compounds using the so-called molten-flux synthesis method. During a systematic investigation of the K–Cu–Se system, we obtained the title ternary mixed-valence copper compound, potassium tetracopper triselenide, KCu_4Se_3, (I), in the form of single black crystals. In earlier investigations using Weissenberg and Debye–Scherrer photographs, only the space group and the lattice parameters were reported, but no structural details were elucidated (Klepp *et al.*, 1980).



(I)

The title compound adopts a layered structure and is isostructural with $CsCu_4Se_3$ (Hartig *et al.*, 1994), KCu_4S_3 (Rüdorff *et al.*, 1952; Brown *et al.*, 1980), $RbCu_4S_3$ (Rüdorff *et al.*, 1952), $CsCu_4S_3$ (Burschka, 1980) and $TlCu_4S_3$ (Klepp *et al.*, 1980). The empirical formulae of these compounds indicate a mixed-valence state, but the crystallographic results from (I) showed that all the copper cations are equivalent. However, these compounds are known to exhibit electrical conductivity characteristic of a metal (Rüdorff *et al.*, 1952; Brown *et al.*, 1980). KCu_4Se_3 crystallizes in the tetragonal space group *P*4/*mmm*. Its crystal structure is based on distorted $CuSe_4$ tetrahedra, which are connected *via* common edges to form double layers parallel to the (001) plane. These double layers are built up of two single layers of edge-sharing $CuSe_4$ tetrahedra, which are connected *via* a common Se^{2-} anion in the middle of the double layer. Each Se^{2-} anion at the surface of this double layer belongs to four tetrahedra, whereas each Se^{2-} anion in the middle of the layers shares eight tetrahedra. The double layers are separated by the potassium cations. Each K^+ cation is surrounded by eight Se^{2-} anions within a cube. The K—Se distances are 3.4371 (4) Å.

The Cu—Cu distance of 2.8417 (2) Å within the single layers is slightly shorter than that of 2.895 (1) Å in the selenide, $CsCu_4Se_3$ (Hartig *et al.*, 1994). As expected, in the sulfides KCu_4S_3 (Cu—Cu 2.7570 Å; Brown *et al.*, 1980), $RbCu_4S_3$ (Cu—Cu 2.78 Å; Rüdorff *et al.*, 1952) and $CsCu_4S_3$ (Cu—Cu 2.810 Å; Burschka, 1980), shorter distances are found. The shortest distance between Cu cations in adjacent layers in (I) is significantly longer than the interlayer distance, at 3.139 (2) Å. The Cu—Se distances of 2.5497 (5) for Cu—Se1 and 2.4248 (6) Å for Cu—Se2 agree well with those in other copper selenides such as Cu_3Se_2 (Cu—Se 2.48–2.54 Å; Heyding & MacLaren Murray, 1976), α-CuSe [Cu—Se 2.386 (4)–2.445 (4) Å; Effenberger & Pertlik, 1981], KCuSe (Cu—Se 2.41 Å; Savelsberg & Schäfer, 1978), NaCuSe (Cu—Se 2.55 Å; Savelsberg & Schäfer, 1978) and $CsCu_4Se_3$ [Cu—Se 2.557 (1) and 2.422 (1) Å; Hartig *et al.*, 1994]. The Cu-centered tetrahedra are only slightly distorted, with Se1—Cu—Se2 angles of 110.152 (8)°, Se1—Cu—Se1 angles of 104.02 (3)° and Se2—Cu—Se2 angles of 111.93 (4)°. With respect to the mixed valency, the formation of valence band holes must be postulated, as copper is always in an oxidation state of one in a chalcogene environment. Further investigations are under way to elucidate the physical properties of KCu_4Se_3.

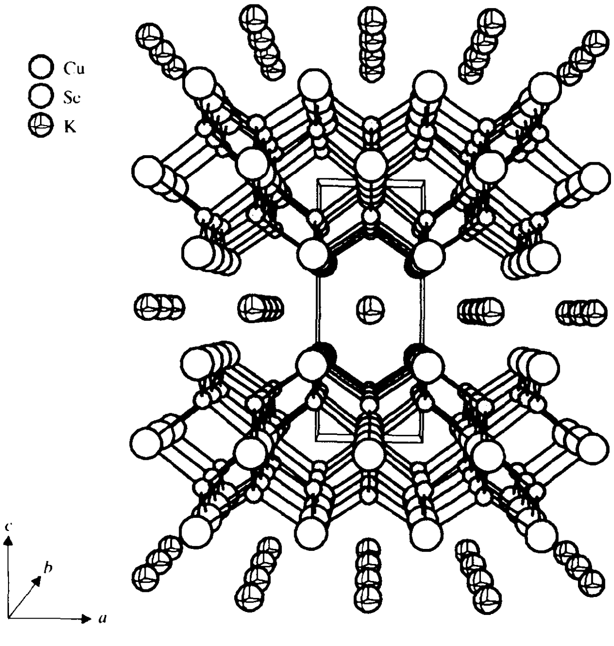


Fig. 1. The crystal structure of KCu_4Se_3 viewed down (010).

Experimental

The title compound was prepared by the reaction of K_2Se_5 and Cu in the ratio 1:4; the K_2Se_5 was prepared from stoichiometric amounts of K and Se in liquid ammonia under an argon atmosphere. The starting materials were thoroughly mixed in a dry box and sealed into a Pyrex glass ampoule, which was evacuated to 10^{-5} Pa. The ampoule was heated at 723 K for 3 d, cooled to 523 K at 3 K h^{-1} and then to 323 K within 3 h. The resulting melt was washed with dimethylformamide and the residue was dried *in vacuo*.

Crystal data

KCu_4Se_3
$M_r = 530.14$
Tetragonal
$P4/mmm$
$a = 4.0188\ (3)$ Å
$c = 9.7200\ (10)$ Å
$V = 156.99\ (2)$ Å^3
$Z = 1$
$D_x = 5.608$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 82 reflections
$\theta = 11.0–22.5°$
$\mu = 31.277$ mm^{-1}
$T = 293\ (2)$ K
Plate
$0.07 \times 0.06 \times 0.02$ mm
Black

Data collection

Stoe AED-II four-circle diffractometer
ω/θ scans
Absorption correction: analytical (*XP* in *SHELXTL/PC*; Siemens, 1990)
$T_{\min} = 0.223$, $T_{\max} = 0.535$
1026 measured reflections
174 independent reflections

160 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.058$
$\theta_{\max} = 29.93°$
$h = 0 \rightarrow 5$
$k = -5 \rightarrow 5$
$l = -13 \rightarrow 13$
4 standard reflections
frequency: 120 min
intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.062$
$S = 1.170$
174 reflections
13 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0368P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.839$ e Å^{-3}
$\Delta\rho_{\min} = -1.002$ e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.07 (1)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	$U_{\rm eq}$
Cu	0	1/2	0.16146 (8)	0.0238 (3)
Se1	1/2	1/2	0	0.0139 (3)
Se2	0	0	0.30109 (7)	0.0143 (3)
K	1/2	1/2	1/2	0.0210 (5)

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

Cu—Se2	2.4248 (6)	Cu—Cu$^{\rm i}$	2.8417 (2)
Cu—Se1	2.5497 (5)	Se2—K	3.4371 (4)
Se2$^{\rm ii}$—Cu—Se2	111.93 (4)	Se1$^{\rm iii}$—Cu—Se1	104.02 (3)
Se2—Cu—Se1$^{\rm iii}$	110.152 (8)		

Symmetry codes: (i) $-y, x, z$; (ii) $x, 1 + y, z$; (iii) $x - 1, y, z$.

Data collection: *DIF4* (Stoe & Cie, 1992*a*). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1992*b*). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *XP* in *SHELXTL/PC* (Siemens, 1990). Software used to prepare material for publication: *CIFTAB* in *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1247). Services for accessing these data are described at the back of the journal.

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A new vanadium(IV) monophosphate, $Sr(VO)_2(PO_4)_2$, isotypic with $Ca(VO)_2(PO_4)_2$

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Abstract

A new vanadium(IV) phosphate, namely, strontium bis[oxovanadium(IV)] bis(phosphate), $Sr(VO)_2(PO_4)_2$, has been synthesized. It crystallizes in the *Fdd*2 space group with $a = 11.992\ (3)$, $b = 15.932\ (2)$ and $c = 7.222\ (2)$ Å. This new phase is isostructural with $Ca(VO)_2(PO_4)_2$ and $Cd(VO)_2(PO_4)_2$ (orthorhombic form). The three-dimensional framework consists of infinite $[VO_3]_\infty$