INORGANIC COMPOUNDS

KAg$_2$AsS$_4$

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Abstract

The single-crystal characterization of potassium disilver tetrathioarsenate(V), KAg$_2$AsS$_4$, was undertaken. The structure type for this phase has been observed previously. This structure contains As^V and Ag^I atoms tetrahedrally coordinated to S atoms while K$^+$ cations are surrounded by eight S atoms in a compressed cubic geometry. The KAg$_2$AsS$_4$ framework is related to a distorted chalcopyrite structure type.

Comment

Some of the current work in our research program includes the structural characterization of new $A_wM_xPn_yS_z$ phases (A = Na–Cs; M = Cu, Ag; Pn = As, Sb) resulting from synthetic reactions in supercritical amines, such as ammonia and ethylenediamine. Most of the materials formed have valence-precise electron counts and thus have semiconducting behavior. In these systems, the alkali metal is an ionic cation separating Cu or Ag pnictide–sulfide anionic frameworks. One-dimensional anionic chains are found in Cs$_3$Ag$_2$Sb$_3$S$_8$ and Cs$_2$AgMS_4 (M = As, Sb) (Wood, Schimek & Kolis, 1996), two-dimensional anionic layers are formed in KCu$_2$AsS$_3$ (Jerome, Pennington & Kolis, 1994) and Rb$_2$AgSbS$_4$ (Schimek, Pennington, Wood & Kolis, 1996), and three-dimensional anionic frameworks are observed in K$_2$AgSbS$_4$ and RbAg$_2$SbS$_4$ (Schimek, Pennington, Wood & Kolis, 1996). Here we present the crystal structure of KAg$_2$AsS$_4$.

The structure type for KAg$_2$AsS$_4$ (Table 1) has been reported previously for the compounds BaAg$_2$GeS$_4$ (Teske, 1979), (NH$_4$)Ag$_2$AsS$_4$ (Auernhammer, Effenberger, Irran, Pertlik & Rosenstingl, 1993), and KAg$_2$SbS$_4$ (Schimek, Pennington, Wood & Kolis, 1996). The basic anionic framework is built from the condensation of vertex-shared arsenic and silver sulfide tetrahedra. As viewed parallel to the x or y axis, flattened eight-membered metal–sulfur rings are observed (Fig. 1). The K$^+$ cations reside at the origin and body center. The arsenic sulfide tetrahedra have nearly ideal geometry with d(As—S) = 2.166 (2) Å and corresponding angles of 108.35 (5)° × 4 and 111.7 (1)° × 2. In contrast,

the silver sulfide tetrahedra are quite distorted with the Ag atom disordered along the z axis. Ag1 was refined to 80% occupancy with the remaining 20% modeled by Ag1′ and its symmetry-related partner, 0.44 (1) Å on either side of Ag1. The primary Ag site has bond distances to S atoms of 2.6023 (7) Å and angles of 96.14 (2)° × 4 and 141.84 (7)° × 2, while the corresponding distances and angles about Ag1′ are 2.494 (2) × 2 and 2.777 (6) Å × 2 and 94.40 (9) × 4, 124.7 (4) and 161.0 (5)° (Table 2). This structural behavior, with rigid pnictide sulfide tetrahedra and very distorted silver sulfide building blocks, is observed in all the isostructural members mentioned above; however, no disordered Ag-atom positions are reported.
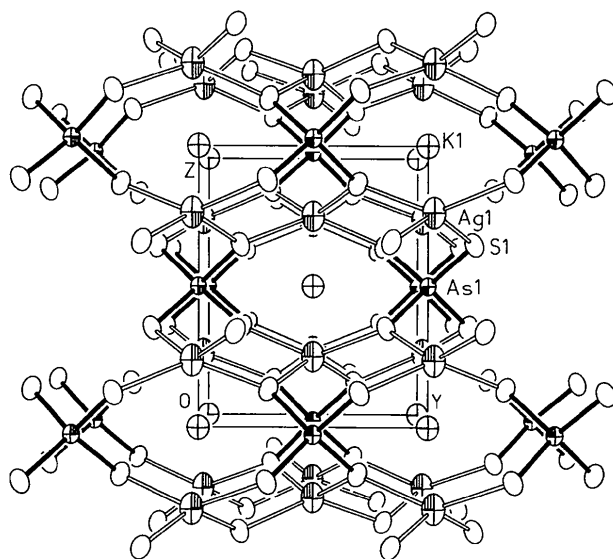

Fig. 1. View of the unit cell of KAg$_2$AsS$_4$ parallel to the x axis. Bonds to the As atoms are solid and bonds to the Ag atoms are open. S atoms are represented by boundary ellipsoids and the K$^+$ cation contacts and Ag1′ atoms have been omitted for clarity. Displacement ellipsoids are shown at the 70% probability level.

The reported structure type has previously been discussed with respect to chalcopyrite, CuFeS$_2$ (Auernhammer, Effenberger, Irran, Pertlik & Rosenstingl, 1993). The major difference between them is the ordered replacement of alkali metal cations and Ag and Pn atoms for Cu and Fe.

Experimental

The title compound was prepared as a mixture of microcrystalline powder and single crystals from supercritical ammonia. K$_2$CO$_3$, Ag, As$_2$S$_3$ and S$_8$ were loaded into a quartz tube

in an 8:8:8:5 mole ratio in an inert atmosphere drybox. The tube was subsequently evacuated and ammonia distilled onto the reagents to give a 40% fill by volume. The flame-sealed tube was loaded into a Parr autoclave and counterpressured with argon to 24 MPa before reacting at 433 K for four days. After cooling, the ammonia was decanted away from the orange crystals, the solvent frozen and the crystals isolated under Nujol. Further investigations revealed that this phase is indefinitely stable in air or water.

Crystal data

KAg_2AsS_4
$M_r = 458.02$
Tetragonal
$I\bar{4}2m$
$a = 6.7504\,(5)$ Å
$c = 8.265\,(1)$ Å
$V = 376.61\,(8)$ Å^3
$Z = 2$
$D_x = 4.038$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.2-18.6°$
$\mu = 11.096$ mm^{-1}
$T = 295$ K
Polyhedron
$0.32 \times 0.10 \times 0.08$ mm
Orange

Data collection

Rigaku AFC-7R diffractometer
$\omega-2\theta$ scans
Absorption correction: empirical via ψ scans (North, Phillips & Mathews, 1968)
$T_{min} = 0.330$, $T_{max} = 0.412$
732 measured reflections
120 independent reflections

117 reflections with $I > 2\sigma(I)$
$R_{int} = 0.0746$
$\theta_{max} = 24.91°$
$h = 0 \rightarrow 7$
$k = -7 \rightarrow 8$
$l = -9 \rightarrow 9$
3 standard reflections every 100 reflections intensity decay: 0.05%

Refinement

Refinement on F
$R = 0.024$
$wR = 0.022$
$S = 1.640$
117 reflections
19 parameters
$w = 1/[\sigma(F_{obs})]^2$
$(\Delta/\sigma)_{max} = 0.006$

$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.75$ e Å^{-3}
Extinction correction: Zachariasen type 2 Gaussian isotropic
Extinction coefficient: 37 (3) × 10^{-7}
Scattering factors from Cromer & Waber (1974)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

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

	x	y	z	U_{eq}
Ag1†	0	1/2	1/4	0.0373 (7)
Ag1'‡	0	1/2	0.303 (1)	0.043 (5)
As1	0	0	1/2	0.0160 (3)
K1	0	0	0	0.0315 (9)
S1	−0.1878 (2)	−x	0.3529 (2)	0.0233 (5)

† Site occupancy = 0.80. ‡ Site occupancy = 0.10.

Table 2. Selected geometric parameters (Å, °)

Ag1—S1	2.6023 (7)	As1—S1	2.166 (2)
Ag1'—S1	2.494 (2)	K1—S1^{iii}	3.218 (2)
Ag1'—S1^i	2.777 (6)	K1—S1	3.424 (2)

S1—Ag1—S1^i	96.14 (2)	S1—K1—S1^{vi}	63.16 (7)
S1—Ag1—S1^{iii}	141.84 (7)	Ag1—S1—Ag1^x	133.02 (7)
S1—Ag1'—S1^i	94.40 (9)	Ag1—S1—As1	111.85 (5)
S1^i—Ag1'—S1^{iii}	124.7 (4)	Ag1'—S1—Ag1$'^x$	134.03 (9)
S1—Ag1'—S1^{iii}	161.0 (5)	Ag1'—S1—As1	106.8 (2)
S1—As1—S1^v	108.35 (5)	Ag1—S1—K1^{x1}	84.97 (5)
S1—As1—S1^{vi}	111.7 (1)	Ag1—S1—K1	80.85 (4)
S1^{viii}—K1—S1^{iii}	98.20 (2)	Ag1'—S1—K1	89.1 (2)
S1—K1—S1^{vii}	71.23 (2)	Ag1'—S1—K1^{x1}	80.9 (1)
S1—K1—S1^{iii}	143.77 (6)	As1—S1—K1^{x1}	123.68 (7)
S1—K1—S1^{viii}	80.61 (2)	As1—S1—K1	92.55 (7)
S1^{viii}—K1—S1^{ix}	135.62 (6)	K1—S1—K1^{x1}	143.77 (6)
S1—K1—S1^{ix}	136.53 (4)		

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

The structure was solved by direct methods and refined by full-matrix least squares. All atomic displacement parameters were refined anisotropically. The maximum residual electron density was located 1.14 Å from As1 and the minimum residual electron density was located 0.19 Å from As1. Because $I\bar{4}2m$ is a non-centrosymmetric space group, the structure was also refined as the other enantiomorph. The final residuals obtained for the incorrect absolute structure were $R = 0.0279$ and $wR = 0.0240$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*.

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