

Silver Orthoselenoarsenite

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Abstract. Ag_3AsSe_3 , rhombohedral, $R3c$, $a_{\text{hex}} = 11.298$ (3), $c_{\text{hex}} = 8.757$ (3) Å, $c/a = 0.7750$, $Z = 6$, $D_x = 6.54$ g cm $^{-3}$. The structure is isomorphous with Ag_3AsS_3 (proustite) and Ag_3SbS_3 (pyrargyrite). Bond lengths and angles are as follows; As–Se: 2.411, Se–Ag: 2.527, Se–Ag: 2.548 Å, Se–As–Se: 98.1, As–Se–Ag: 107.5, As–Se–Ag: 97.4, Se–Ag–Se: 158.8, Ag–Se–Ag: 79.9°.

Introduction. The synthesis of Ag_3AsSe_3 was first reported by Wernick & Benson (1957), but no crystal data of this material were given. In our laboratory, one of us (TK) succeeded in synthesizing this material. The mixture of pure Ag, As and Se was sealed in an evacuated silica tube, melted at 1000°C for four days and then quenched. The glass phase of Ag_3AsSe_3 was formed in this process. The powdered glass of Ag_3AsSe_3 was sealed again in an evacuated silica tube, annealed at 345°C for two weeks and then quenched. One of us (Koide, 1972) showed that this material was stable from 385°C (m.p.) down to 200°C.

The lattice constants obtained by applying a least-squares method to the four-circle diffractometer data were closely consistent with the results based on powder diffractometer data calibrated with superimposed silicon powder.

The crystal used for intensity measurements was hexagonal prismatic in shape, 0.15 mm in height and 0.12 mm in width. Systematic absences are $hkl: -h + k + l = 3n + 1$ and $h0l: l = 2n \pm 1$, giving possible space groups $R3c$ and $R\bar{3}c$.

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Intensities were collected on a Rigaku automated four-circle diffractometer up to $2\theta = 55^\circ$ by the ω - 2θ scan technique with Mo $K\alpha$ radiation monochromated with graphite. The scan width was determined according to the formula $1.1 + 0.5 \tan \theta$. 266 independent reflections were measured, of which 33 were unobserved. Lorentz and polarization corrections were performed. For the absorption correction the crystal was assumed to be of a cylindrical shape. The linear absorption coefficient, μ , is 321.8 cm $^{-1}$ for Mo $K\alpha$ radiation.

Lattice constants, the space group and the powder diffraction pattern indicated that the structure was isomorphous with proustite (Ag_3AsS_3 , $a_{\text{hex}} = 10.82$, $c_{\text{hex}} = 8.69$ Å, $R3c$, Engel & Nowacki, 1966) and pyrargyrite (Ag_3SbS_3 , $a_{\text{hex}} = 11.04$, $c_{\text{hex}} = 8.72$ Å, $R3c$, Engel & Nowacki, 1966).

A full-matrix least-squares refinement with anisotropic temperature factors was carried out with the ORFLS program written by Busing, Martin & Levy (1962). The space group $R3c$ was chosen for this refinement because the crystal was isomorphous with proustite.

Neutral-atom form factors were taken from *International Tables for X-ray Crystallography* (1968). The atomic coordinates of proustite were employed for the initial parameters. The conventional R value was reduced to 0.069 (excluding unobserved reflections) and 0.096 for all the reflections. The final fractional coordinates and anisotropic temperature factors are given in Table 1.‡

‡ A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33743 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final atomic parameters ($\times 10^4$) and estimated standard deviationsThe temperature factor is of the form $\exp [-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + 2hkB_{12} + 2hlB_{13} + 2klB_{23})]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ag	2498 (9)	3066 (8)	2281 (14)	302 (17)	186 (12)	277 (15)	132 (12)	77 (14)	164 (12)
As	0	0	0	40 (6)	40 (6)	30 (8)	20 (3)	0	0
Se	2144 (4)	946 (4)	3653 (9)	38 (4)	58 (5)	98 (6)	19 (4)	15 (5)	4 (6)

Discussion. The present crystal is isomorphous with proustite and pyrargyrite. Bond lengths and angles are given in Table 2 and Table 3 respectively with those of proustite given by Engel & Nowacki (1966).

Fig. 1 shows a projection of the structure parallel to the c axis. Each As atom is surrounded by three Se atoms, making an AsSe_3 pyramid. Ag and Se atoms make $-\text{Se}-\text{Ag}-\text{Se}-\text{Ag}-$ infinite spiral chains parallel to the c axis. There is little difference in the Ag-As distance between Ag_3AsSe_3 and proustite (3.26 and 3.25 Å), while the differences in the Ag-X-Ag and X-Ag-X angles are quite large (79.9:83.2 and 158.8:162.7°) in comparison with the differences in the other bond angles. These data are illustrated in Fig. 2, which is somewhat exaggerated. The Ag-As distance appears to become short in Ag_3AsSe_3 in this projection; however, this distance is actually constant and the apparent shortening is due to the c axis being somewhat extended in Ag_3AsSe_3 . The X-Ag-X and Ag-X-Ag angles become smaller by substitution of Se for S in proustite.

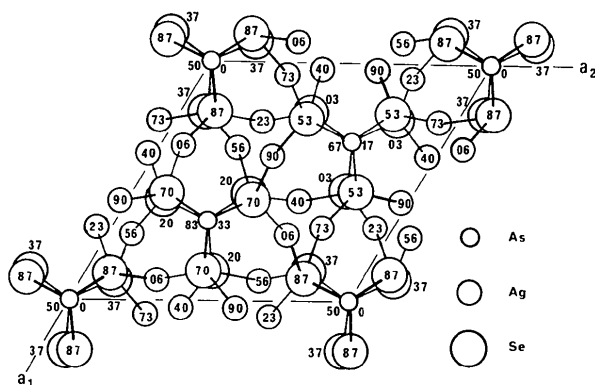


Fig. 1. The structure viewed down the c axis.

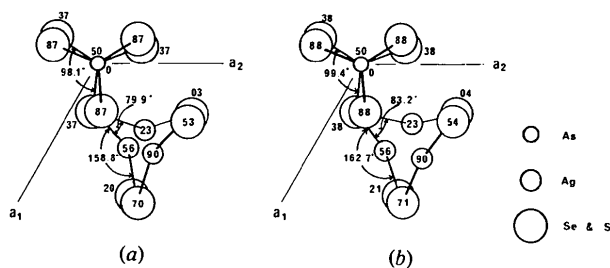


Fig. 2. The schematic description near the 3_2 screw axis of (a) Ag_3AsSe_3 (present study) and (b) Ag_3AsS_3 (Engel & Nowacki, 1966).

The axial lengths of the thermal vibration ellipsoids and the direction cosines of the axes referred to orthogonal axes ($1 \parallel a_{\text{hex}}^*$, $2 \parallel b_{\text{hex}}$, $3 \parallel c_{\text{hex}}$) are given in Table 4. The anomalous nature of the thermal vibration is similar to that of proustite, in which the anisotropy of the Ag atom is distinctive. The thermal vibration of the Ag atom is rather small along the direction of the

Table 4. Axial lengths of the thermal vibration ellipsoids and the direction cosines of the axes referred to orthogonal axes $1 \parallel a_{\text{hex}}^*$, $2 \parallel b_{\text{hex}}$ and $3 \parallel c_{\text{hex}}$ in Ag_3AsSe_3

B_{iso} : Isotropic temperature factors calculated from anisotropic thermal parameters. Length: Thermal displacement parameters.

	B_{iso} (Å ²)	Axes	B (Å ²)	Length (Å)	$\cos\alpha_1$	$\cos\alpha_2$	$\cos\alpha_3$
Ag	8.74	1	11.22	0.377	0.911	-0.353	-0.213
		2	2.22	0.168	0.146	0.759	-0.634
		3	12.77	0.402	0.386	0.547	0.743
As	1.35	1	1.57	0.140	1.0	0.0	0.0
		2	1.57	0.140	0.0	1.0	0.0
		3	0.92	0.108	0.0	0.0	1.0
Se	2.54	1	1.46	0.136	0.994	-0.030	-0.101
		2	2.37	0.173	0.038	0.996	0.080
		3	3.78	0.219	0.098	-0.083	0.992

Table 2. Atomic distances (Å)

	$X = \text{S and Se.}$				
	As-X	Ag-X	Ag-X	X-X	Ag-Ag
Ag_3AsSe_3 (Present study)	2.411 (5)	2.527 (12)	2.548 (11)	3.641 (5)	3.260 (10)
Ag_3AsS_3 (Engel & Nowacki, 1966)	2.254	2.443	2.448	3.43	3.25

Table 3. Bond angles (°)

	$X = \text{S and Se.}$				
	X-As-X	As-X-Ag	As-X-Ag	X-Ag-X	Ag-X-Ag
Ag_3AsSe_3 (Present study)	98.1 (2)	107.5 (3)	97.4 (4)	158.8 (4)	79.9 (4)
Ag_3AsS_3 (Engel & Nowacki, 1966)	99.4	108.0	99.9	162.7	83.2

Se—Ag—Se bond, whereas it is very large along the other direction, resulting in a very oblate ellipsoid.

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Hexaamminechromium(III) Aquapentachloromanganate(II)

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Abstract. [Cr(NH₃)₆][MnCl₅(H₂O)], monoclinic, $P2_1/c$, $a = 17.203$ (3), $b = 11.417$ (2), $c = 14.912$ (3) Å, $\beta = 92.64$ (2)°, $Z = 8$, $D_o = 1.82$, $D_c = 1.836$ g cm⁻³. The compound was prepared in an attempt to produce the [MnCl₅]³⁻ anion. The structure consists of [Cr(NH₃)₆]³⁺ and [MnCl₅(H₂O)]³⁻ ions.

$\mu = 25.65$ cm⁻¹; transmission factors range from 0.293 to 0.454. Of 6722 measured reflexions, 608 with $I < 0$

Table 1. *Atomic coordinates* ($\times 10^5$) *of the non-hydrogen atoms*

	<i>x</i>	<i>y</i>	<i>z</i>
Cr(1)	12700 (2)	68670 (3)	13256 (3)
N(11)	10809 (18)	80124 (23)	23729 (17)
N(12)	15138 (15)	54983 (21)	22141 (17)
N(13)	1153 (14)	63542 (22)	12808 (18)
N(14)	10042 (14)	82141 (19)	4310 (16)
N(15)	24379 (14)	73134 (22)	13646 (18)
N(16)	14469 (15)	58151 (20)	2261 (16)
Cr(2)	38352 (2)	19151 (3)	36501 (3)
N(21)	46507 (14)	32359 (20)	37638 (16)
N(22)	30036 (14)	31031 (19)	40356 (17)
N(23)	35792 (15)	23811 (22)	23274 (16)
N(24)	47113 (14)	7995 (21)	32747 (17)
N(25)	40535 (14)	14181 (21)	49765 (16)
N(26)	30010 (15)	5854 (20)	35440 (18)
Mn(1)	12140 (2)	18679 (4)	11650 (3)
Cl(11)	14430 (5)	24101 (7)	28065 (5)
Cl(12)	968 (4)	4505 (6)	14489 (5)
Cl(13)	2005 (4)	35136 (6)	9702 (5)
Cl(14)	22344 (4)	33060 (6)	6735 (5)
Cl(15)	22453 (4)	2767 (6)	13101 (6)
O(1)	9720 (14)	14166 (20)	-3028 (15)
Mn(2)	37461 (2)	68568 (4)	38622 (3)
Cl(21)	39722 (5)	82823 (6)	26500 (5)
Cl(22)	51698 (4)	61712 (6)	40280 (5)
Cl(23)	39804 (5)	85037 (6)	50301 (5)
Cl(24)	23151 (4)	72119 (8)	39545 (5)
Cl(25)	34801 (4)	52709 (6)	26679 (5)
O(2)	35913 (13)	55244 (19)	49594 (15)

Introduction. Initial cell parameters were obtained from precession photographs (Mo $K\alpha$ radiation), which also indicated the space group $P2_1/c$ ($h0l$ reflexions absent for odd l , $0k0$ absent for odd k). The asymmetric unit contains two cations and two anions.

A yellow crystal with faces parallel to the unit-cell faces was mounted, in a Lindemann-glass tube, on a Hilger & Watts Y290 four-circle diffractometer, with c slightly misaligned from the ϕ axis. Unit-cell parameters and the orientation matrix were refined by least squares from 12 reflexions ($2\theta > 40^\circ$, Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å, Zr filter). Intensities were collected for all unique reflexions with $2\theta \leq 55^\circ$ (θ - 2θ scan, 2 s count at each of 50 steps of 0.02° in θ , background counts of 25 s at each end of the scan range; calibrated attenuators were inserted into the beam for intense reflexions). Three standard reflexions monitored periodically showed no significant intensity variation. The crystal was measured with a travelling microscope for absorption corrections (Gaussian integration method;

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