Hydrothermal Synthesis and Crystal Structure Determination of Heptasilver(I)–Disulfur–Tetrathioarsenate(V), Ag₇S₂(AsS₄), with a Survey on Thioarsenate Anions

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The compound $Ag_7S_2(AsS_4)$ has been synthesized by hydrothermal techniques and characterized by single-crystal X-ray diffraction data. Crystals suitable for structure determination were grown from a mixture of elementary silver, sulfur, and arsenic(III) sulfide in ammonia water. The compound is cubic, $P2_13-T^4$, with $a = 10.475(1)$ Å. The structure was solved by Patterson and Fourier methods and refined to $R = 0.044$, $R_w = 0.028$. The three crystallographically independent Ag atoms are surrounded by two, three, and four S atoms (Ag–S < 3.3 Å) and three or four Ag atom neighbors (Ag–Ag < 3.3 Å). These Ag polyhedra and the AsS₄ tetrahedra form a three-dimensional framework. © 1994 Academic Press, Inc.

INTRODUCTION

The complex and frequently irregular coordination of monovalent silver to chalcogen atoms was investigated on the basis of single-crystal X-ray work on synthetic and natural compounds (1–4) at the present institute. The syntheses of crystals of the silver sulfosalts Ag_3AsS_4, Ag_3AsS_3 (in two modifications), $AgAsS_2$, and Ag_7S_2 (AsS_4), under hydrothermal conditions and with ammonia water or aqueous solutions of alkaline hydroxids as solvents, are described in (5–7).

The phase relations of the ternary system Ag–As–S were established by DTA and X-ray investigations (8), and several stable compounds, including Ag_7AsS_6, were described by these authors. For Ag_7AsS_6 a phase transformation at 260(2)°C from space group $P2_13$ to $F43m$ with lattice constants of 10.469(2) Å, 30°C, and 10.550(5) Å, 300°C, is mentioned. This transformation is combined with fewer changes in the atomic arrangement and a small enlargement of the cell volume.

The mineral billingsleyite with composition Ag_7AsS_6, orthorhombic, space group $C222_1$ ($a = 14.82$, $b = 14.82$, $c = 10.48$ Å), was described by Frondell and Honea (9) from oxidation of silver ores from the North Lily mine, East Tintic District, Utah. Bayliss (10) showed that the diffraction pattern (powder data) for this mineral (cf. 9)

can also be explained with a cubic lattice, $a = 10.481(4)$ Å, space group $P2_13$, and that these patterns are more or less identical to the patterns for synthetic Ag_7AsS_6 (8).

In the opinion of the author, the value for the lattice constant, the same space group and chemical formula for the mineral billingsleyite, for Ag_7AsS_6 (synthesized in the dry system Ag–As–S), and for $Ag_7S_2(AsS_4)$ (this work) confirms the identity of these three compounds. X-ray powder patterns of the title compound were sent to JCPDS (International Centre for Diffraction Data) and accepted for the Mineral Powder Diffraction File.

SYNTHESES AND CRYSTAL STRUCTURE DETERMINATION

Crystals of $Ag_7S_2(AsS_4)$ were prepared by heating 1 g of a mixture of elementary silver and arsenic(III)sulfide (5:1 wt%) with an excess, 4 g, of orthorhombic sulfur (powder) in concentrated ammonia water in a Teflon-coated steel vessel. The vessel was filled to 80% capacity and heated to 220°C for about 2 months. Crystals of the title compound are opaque, silver white, with a tetrahedron {111} crystallographic form and edge lengths from 0.05 to 0.1 mm. If the sulfur content is reduced to about 1 g, these experiments yield crystals of $NH_4Ag_2(AsS_4)$, tetragonal, with the predominent form being tetragonal disphenoid (11).

The "quality" of the crystal used for X-ray structure investigation was checked by oscillation and Weissenberg film methods. Crystal data, details on data collection, and results of structure refinement are summarized in Table 1. The reflection array (h00 with $h = 2n$) together with the morphology of the crystals indicates the possible space group $P2_13-T^4$, which was confirmed by the structure solution and refinement within the limit of accuracy. The atomic coordinates of the three crystallographically different Ag atom positions were found by a Patterson summation and those of the other atoms by subsequent Fourier and difference Fourier summations. During the final stage of refinement, anisotropic displacement factors

TABLE 1

Crystal Data, Intensity Measurements, and Refinement Parameters for Ag$_7$S$_2$(AsS$_4$)

Space group	$P2_13-T^4$	Total data ($h, k, \pm l$)	1966
a (Å)	10.475(1)	Total unique data	657
Formula weight	1022.4	Internal consistency	0.078
Volume (Å^3)	1149.5	Observed data ($I > 3\sigma_l$)	497
ρ_{calc} (g · cm^{-3})	6.81	Empirical absorption correction min/max	0.73/0.80
Cell content	4	Number of variables	44
$F(000)$	1832	Extinction parameter	$1.3(1) \times 10^{-5}$
μ(MoKα) (cm^{-1})	145.6	Final least-squares shift/error	$<10^{-3}$
Temperature (°C)	25(2)	Final difference Fourier with ($\Delta\rho$)max/($\Delta\rho$)min	1.8/−1.4
2 Θ/ω scan mode with step width (°)	0.03	Final R/R_w	0.044/0.028
Steps/reflection + (α_1, α_2 splitting)	30	Crystal shape and size (mm)	Tetrahedron; edges, 0.1
Time/step (s)	0.5–1.5		
Range of data, 2 Θ max (°)	60		

Note. Stoe four-circle diffractometer AED2 was used with graphite monochromatized MoKα radiation, λ = 0.7107 Å. The program system was STRUCSY (13) on an Eclipse S 140 computer.

were allowed to vary. Complex neutral atomic scattering functions from the "International Tables for X-Ray Crystallography" (12) were employed. The structure parameters are given in Table 2, and some relevant interatomic distances are compiled in Table 3. An ($|F_o| - |F_c|$) list was deposited at the Institute for Mineralogy and Crystallography of the University of Vienna, Austria. A short note about the structure of Ag$_7$S$_2$(AsS$_4$) was published by Pertlik (14).

Since Ag$_7$S$_2$(AsS$_4$) crystallizes in the acentric space group $P2_13$, anomalous dispersion effects were used to determine the absolute orientation of the structure. A refinement with the $x\,y\,z$ coordinate set resulted in R = 0.044, and a refinement with $\bar{x}\,\bar{y}\,\bar{z}$ resulted in R = 0.064. This might be an indication that the given configuration is correct for the crystal examined in this work.

RESULTS AND DISCUSSION

The coordination spheres of the three silver atoms (Ag–Ag and Ag–S <3.3 Å) and the four sulfur atoms

(S–Ag and S–As <3.3 Å) at different crystallographic positions are drawn in Fig. 1, and a projection of the crystal structure is shown in Fig. 2. The silver atoms are coordinated to silver as well as to sulfur atoms. The Ag–Ag distances, from 2.97 to 3.11 Å, are comparable with the Ag–Ag distances in the element of 2.889 Å (15). The Ag–S distances in the silver polyhedra vary from 2.41 to 3.11 Å. They are within the range of Ag–S distances recalculated by Frueh (16) on the basis of the crystal structure determinations of about 10 compounds with individual Ag–S bonds from 2.24 to 3.13 Å. A compilation of Ag–S distances in AgS$_4$ polyhedra (mean Ag–S distances of 2.57 to 2.71 Å) as well as statistics about the geometry of these polyhedra by Auernhammer *et al.* (11) is also worth mentioning.

For each atom in the title compound, monoclinic Ag$_2$S (cf. 16), and elementary silver (15), Table 4 gives the coordination number according to Hoppe (18) and O'Keeffe (19) and the volume of the atom's single space-filling polyhedron. The transition from a covalent bond character in the Ag polyhedra to a metallic character is

TABLE 2

Atomic Parameters and Anisotropic Displacement Factors ($U_{ij} \times 10^4$; ESD's in Parentheses)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag(1)	0.3960(1)	$= x$	$= x$	474(6)	$= U_{11}$	$= U_{11}$	−136(6)	$= U_{12}$	$= U_{12}$
Ag(2)	0.2315(1)	0.0233(1)	0.2590(1)	600(6)	285(6)	583(8)	27(7)	−312(8)	−50(7)
Ag(3)	0.3466(1)	0.8246(1)	0.9849(1)	495(8)	329(7)	546(9)	1(7)	15(7)	48(6)
As	0.9973(1)	$= x$	$= x$	141(4)	$= U_{11}$	$= U_{11}$	0(5)	$= U_{12}$	$= U_{12}$
S(1)	0.5298(3)	$= x$	$= x$	240(12)	$= U_{11}$	$= U_{11}$	−3(15)	$= U_{12}$	$= U_{12}$
S(2)	0.8764(3)	$= x$	$= x$	246(14)	$= U_{11}$	$= U_{11}$	−31(15)	$= U_{12}$	$= U_{12}$
S(3)	0.2632(3)	$= x$	$= x$	219(11)	$= U_{11}$	$= U_{11}$	−33(13)	$= U_{12}$	$= U_{12}$
S(4)	0.1221(3)	0.8734(3)	0.1075(3)	205(18)	176(17)	224(17)	19(13)	−23(15)	17(15)

Note. ATF = exp($-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij}h_ih_ja_i^* a_j^*$).

TABLE 3
Selected Bond Distances (Å) and Angles (°) in Ag$_7$S$_2$(AsS$_4$)

Ag(1)polyhedron

Ag(1)	Ag(3)	Ag(3')	Ag(3″)	S(1)	S(3)
Ag(3)	**3.063(1)**	4.236(3)	4.236(3)	2.514(4)	4.906(3)
Ag(3')	87.5(1)	**3.063(1)**	4.236(3)	2.514(4)	4.906(3)
Ag(3″)	87.5(1)	87.5(1)	**3.063(1)**	2.514(4)	4.906(3)
S(1)	53.0(1)	53.0(1)	53.0(1)	**2.426(3)**	4.836(4)
S(3)	127.0(1)	127.0(1)	127.0(1)	180.0(−)	**2.410(3)**

Ag(2)polyhedron

Ag(2)	Ag(3)	Ag(3')	S(1)	S(3)	S(4)	S(4')
Ag(3)	**3.110(2)**	4.757(3)	5.996(4)	2.750(3)	4.853(4)	3.683(4)
Ag(3')	103.0(1)	**2.968(1)**	2.514(4)	2.750(3)	5.075(4)	4.166(4)
S(1)	149.2(1)	48.8(1)	**3.109(3)**	4.484(4)	4.050(5)	4.050(5)
S(3)	57.2(1)	59.3(1)	104.7(1)	**2.536(3)**	4.639(4)	4.412(5)
S(4)	119.1(1)	135.6(1)	91.6(1)	133.7(1)	**2.509(3)**	3.973(7)
S(4')	80.2(1)	97.3(1)	90.5(1)	119.6(1)	102.9(1)	**2.569(3)**

Ag(3)polyhedron

Ag(3)	Ag(1)	Ag(2)	Ag(2')	S(1)	S(2)	S(3)	S(4)
Ag(1)	**3.063(1)**	5.110(2)	4.432(2)	2.426(4)	3.724(4)	5.506(3)	5.053(4)
Ag(2)	115.8(1)	**2.968(1)**	3.307(3)	3.109(4)	5.435(4)	2.536(3)	4.104(4)
Ag(2')	91.8(1)	65.9(1)	**3.110(2)**	3.926(4)	4.414(4)	2.536(3)	5.589(4)
S(1)	50.4(1)	68.5(1)	87.9(1)	**2.514(3)**	4.653(5)	4.484(4)	4.248(5)
S(2)	82.2(1)	157.2(1)	101.4(1)	132.1(1)	**2.577(3)**	4.218(5)	3.738(5)
S(3)	142.5(1)	52.5(1)	50.8(1)	116.7(1)	104.7(1)	**2.750(3)**	4.061(4)
S(4)	121.4(1)	92.1(1)	146.3(1)	108.2(1)	89.6(1)	95.7(1)	**2.728(3)**

As–tetrahedron

As	S(2)	S(4)	S(4')	S(4″)
S(2)	**2.193(3)**	3.533(5)	3.533(5)	3.533(5)
S(4)	108.2(1)	**2.174(3)**	3.581(6)	3.581(6)
S(4')	108.2(1)	110.9(1)	**2.174(3)**	3.581(6)
S(4″)	108.2(1)	110.9(1)	110.9(1)	**2.174(3)**

responsible for the lower coordination numbers and the greater volumes of the space-filling polyhedra calculated for the title compound compared with Ag$_2$S and Ag, respectively.

The AsS$_4$ group shows the typical tetrahedral arrangement of the four sulfur atoms around arsenium. A compilation of individual As–S and mean ⟨As–S⟩ bond lengths as AsS$_4$ tetrahedra determined for different inorganic crystal structures is given in Table 5. The first seven compounds are translucent for visible light, and the last three are opaque. Obviously, there are two groups: The mean ⟨As–S⟩ distances in the compounds with elements of the first two periods (or related elements) are significantly shorter than the distances in Cu$_3$AsS$_4$, Ag$_3$AsS$_4$, and the title compound. An explanation might be the pronounced

covalent character of the Cu–S and Ag–S bonds compared to the M–S bonds (M = alkaline, alkaline earth, or related elements). The covalent character of the As–S bond decreases with an increase of the As–S bond lengths. Comparable relations were determined in scheelite-type compounds for the mean MoO$_4$ and WO$_4$ distances (32).

The differences in the values of the mean square relative deviations from average bond lengths in the AsS$_4$ tetrahedra (Table 5) from ∼1 × 10^{-5} to 25 × 10^{-5} are in the same range as the values for PO$_4$ and AsO$_4$ tetrahedra from ∼10 × 10^{-5} to 20 × 10^{-5} (4, 30). AsX_4 tetrahedra (X = O, S) therefore seem to be more or less rigid groups in crystal structures, in some cases even comparable with SO$_4$ and SiO$_4$ tetrahedra.

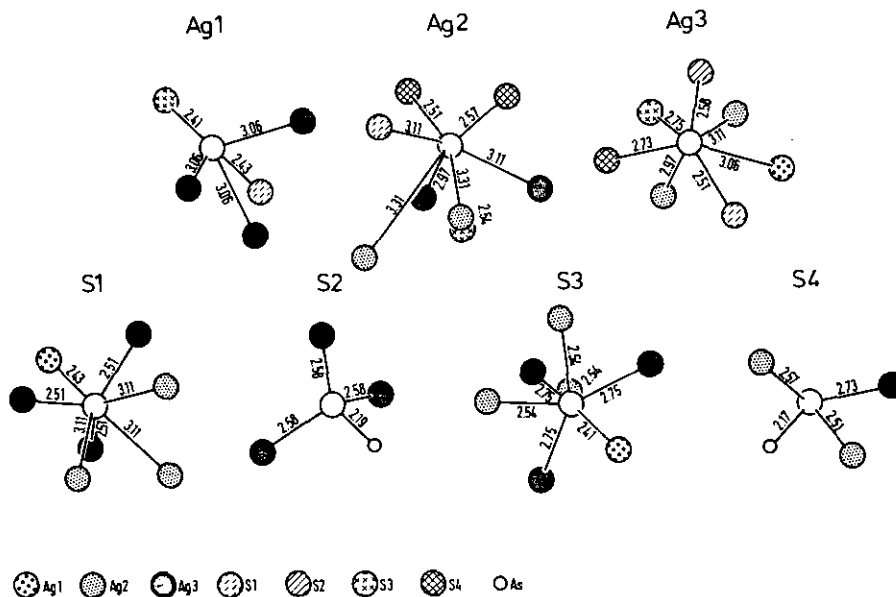FIG. 1. The coordination of the Ag and S atoms in directions parallel to [001]; interatomic distances are in Å.

FIG. 2. Projection of the crystal structure of Ag₇S₂(AsS₄) onto (100).

TABLE 4

Data for Coordination and Space-Filling Polyhedra (Based on the Radii $r_{Ag}:r_{As}:r_S = 1:1:1$)

Atom	(a)	(b)	(c)	(d)
Compound Ag₇S₂(AsS₄)				
Ag(1)	5.81	5.20	23.33	17
Ag(2)	5.31	5.23	21.17	13
Ag(3)	5.76	5.62	20.70	12
As	4.87	4.39	16.26	10
S(1)	6.42	6.10	19.38	10
S(2)	5.09	4.48	20.97	13
S(3)	4.96	5.20	17.08	10
S(4)	5.11	4.40	21.63	16
Compound Ag₂S				
Ag(1)	7.48	6.59	20.43	16
Ag(2)	7.50	6.72	18.97	12
S	6.95	6.59	17.30	12
Element Ag				
Ag	12	12	17.05	12

Note. These calculations are performed with the program "Kristallchemie" (17). Coordination numbers are from (a) Hoppe (18) and (b) O'Keeffe (19). (c) Volume of the single polyhedron in Å³. (d) Number of faces of the space-filling polyhedra with an area >5% of the greatest face.
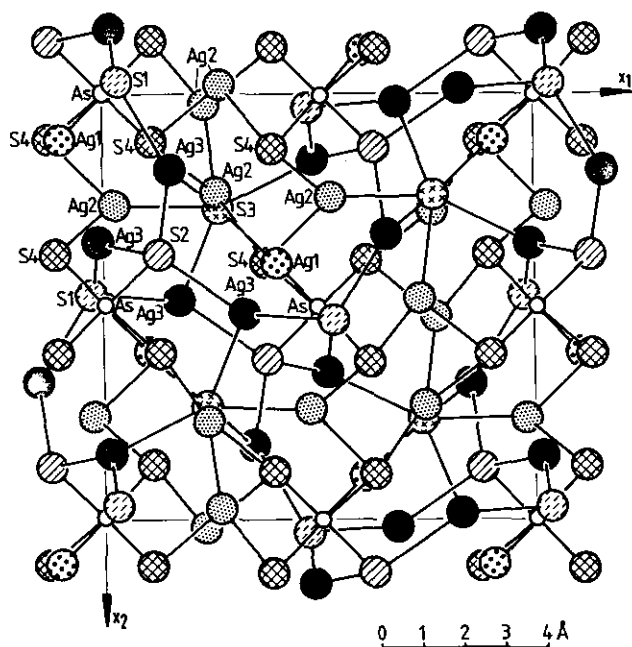
TABLE 5
As–S Distances (Å) in Tetrathioarsenate(V) Tetrahedra

Na₃AsS₄·8H₂O (20)	2.176(2)	2.140(3)	2.140(3) R	2.168(3)	⟨2.156⟩ ‖5.7‖
Na₃AsS₄·8D₂O (21)	2.713(1)	2.145(1)	2.160(1) R/N	2.168(1)	⟨2.162⟩ ‖2.4‖
K₃AsS₄ (22)	2.16(1)	2.11(2)	2.18(1) R	2.20(2)	⟨2.163⟩ ‖23.9‖
Tl₃AsS₄ (23)	2.183(5)	2.153(5)	2.166(4) × 2 N		⟨2.167⟩ ‖2.4‖
(NH₄)₃AsS₄ (24)	2.159(1)	2.188(1)	2.167(1) × 2 R		⟨2.165⟩ ‖3.1‖
NH₄Ag₂(AsS₄) (11)	2.170(1) × 4		R		⟨2.170⟩ ‖⊢⊣‖
Ba₃(AsS₄)₂·7H₂O (25)	2.163(3) 2.164(3)	2.163(3) 2.166(3)	2.167(3) 2.166(3) R	2.178(3) 2.169(3) ‖0.8‖	⟨2.168⟩ ⟨2.166⟩ ‖0.7‖
Cu₃AsS₄ (26)	2.182(2)	2.162(2)	2.192(2) × 2 R		⟨2.182⟩ ‖3.2‖
Ag₃AsS₄ (5)	2.162(4)	2.176(4)	2.186(3) × 2 R		⟨2.178⟩ ‖2.0‖
Ag₇S₂(AsS₄) (this article)	2.193(3)	2.174(3) × 3	R		⟨2.179⟩ ‖1.4‖

Note. R, X ray work; N, neutron work; ⟨ ⟩, mean values of As–S distances; ‖ ‖, mean square relative deviation from average bond length = $10^5 \times (1/4) \sum_{i=1}^{4} [(As-S_i) - \langle As-S \rangle /\langle As-S \rangle]^2$ (27). The structure parameters of the first structure determinations of (NH₄)₃AsS₄ (28) and Cu₃AsS₄ (29) are within limits of error to the refined structures. A reinvestigation of the structure of Ba₃(AsS₄)₂·7H₂O at 125 K with a distinctly greater accuracy to clarify hydrogen bonding (31) confirms the first investigations (25) results.

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