Synthesis and Crystal Structure Determination of (NH₄)Ag₂AsS₄, a Further Chalcopyrite-Type Compound

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Crystals of $(NH_4)Ag_2AsS_4$ were synthesized from an approximately equimolar mixture of Ag, As_2S_3, and S in ammonia solution under hydrothermal conditions. The crystals are tetragonal: $a = 6.780(1)$ Å, $c = 8.277(1)$ Å, space group $I\bar{4}2m$, $Z = 2$. The structure was determined from a Patterson map (277 single crystal X-ray data) and refined to final residual parameters of $R = 0.031$ and $R_W = 0.028$. In a first coordination sphere the atoms Ag and As as well as the NH_4 group are equidistant 4-coordinated to S atoms. The crystal structure represents a distorted chalcopyrite-type framework. The Ag–S bonds in the AgS_4 polyhedron of $(NH_4)Ag_2AsS_4$ exhibit a pronounced covalent character, deduced from the comparison of about twenty AgS_4 polyhedra mentioned in the literature. © 1993 Academic Press, Inc.

Introduction

The coordination chemistry of silver(I) atoms against sulfur atoms is characterized by the tendency to form (i) two "collinear bonds," considered as a *sp* hybridization of the Ag atom, and (ii) four more or less distorted "tetrahedral bonds," considered as a sp^3 hybridization. In a regular coordination tetrahedron the silver atom usually is shifted off the center toward two of the neighboring atoms rather than in an equidistant position to all four atoms. In addition, one-sided transitions between these two coordination types are very common. The physical properties of compounds with the silver atom in a one-sided coordination indicate an appreciable covalent portion of the "short" Ag–S bonds (e.g., color, electric conductivity).

Investigations of the system Ag–As–S in ammonia solution (different basicity of the solvent) yielded crystals of two new silver tetrathioarsenates, Ag_7AsS_6 and $(NH_4)Ag_2AsS_4$. For a crystal chemical characteriza-

tion their structures were determined from single crystal X-ray data. Ag_7AsS_6 has been known as the mineral billingsleyite (*1*), for its crystal structure cf. (*2*); $(NH_4)Ag_2AsS_4$ is presented in this paper.

To enable a comparison of sulfur polyhedra around Ag atoms with physical properties (in most cases only the color and reflectivity for the visible part of light are mentioned in the literature), "tetrahedral" AgS_4 coordination polyhedra are compiled (Ag–S distances, S–Ag–S angles, S–S distances, and distortion parameters). This compilation might be an attempt to get a hint regarding the nature of these $Ag^{[4]}$–S bonds.

Experimental

Crystals of $(NH_4)Ag_2AsS_4$ were synthesized in stainless steel autoclaves lined with Teflon. Approximately equimolar mixtures of elementary silver, arsenic(III) sulfide, and orthorhombic sulfur were heated in ammonia solution (25%, GR) to 220°C over 3 days. After cooling to room temperature,

crystals of $(NH_4)Ag_2AsS_4$ and Ag_7AsS_6 were formed; the liquid phase was not investigated.

The atomic coordinates of the title compound were determined from a Patterson summation applying crystal chemical considerations. Refinements were performed with full-matrix least-squares calculations using complex neutral atomic scattering functions (3). Since the parameters of the H atoms of the NH_4 group could not be determined, it is impossible to decide whether the H atoms form discrete hydrogen bonds to S atoms or the NH_4 group is statically or dynamically disordered.

Crystal data, details on data collection,

TABLE II
STRUCTURAL PARAMETERS

2 N on 2 b $(0, 0, \frac{1}{2})$, etc.	U_{11}	0.026(4)
	U_{33}	0.030(5)
4 Ag on 4 d $(0, \frac{1}{2}, \frac{3}{4})$, etc.	U_{11}	0.0295(3)
	U_{33}	0.0864(9)
2 As on 2 a $(0, 0, 0)$, etc.	U_{11}	0.0127(4)
	U_{33}	0.0175(7)
8 S on 8 i (x, x, z), etc.	x	0.8119(2)
	z	0.8543(2)
	U_{11}	0.0181(6)
	U_{33}	0.0283(10)
	U_{12}	$-0.0015(7)$
	U_{13}	$-0.0036(5)$

Note. The anisotropic displacement factors (ESDs in parentheses) are defined as $\exp - (2\pi^2 \Sigma_{i=1}^3 \Sigma_{j=1}^3 U_{ij} h_i h_j a_i^* a_j^*)$.

TABLE I
CRYSTAL DATA AND STRUCTURE DETERMINATION

Formula weight	436.96
Space group	$I\bar{4}2m$
a (Å)	6.780(1)
c (Å)	8.277(1)
Volume (Å³)	380.5
ρ_{calc} (g · cm⁻³)	3.814
Cell content	2
μ(Mo $K\alpha$) [cm⁻¹]	99.0
Range of hkl	$h, k, \pm l$
Total data	646
Total unique data	310
Internal consistency	0.053
Observed data ($I > 3 \sigma_I$)	277
Number of variables	14
Final R/R_w	0.031/0.028
Temperature (°C)	25(2)

Note. Stoe four-circle diffractometer AED2 was used with graphite monochromatized Mo $K\alpha$ radiation, λ = 0.7107 Å, 2 θ/ω scan mode, step width 0.03°, minimum number of 30 steps per reflection increased for α_1, α_2 dispersion; measuring time 0.5 to 1.5 sec per step, 2° < 2 θ < 60°. Empirical absorption correction (ψ-scan data), transmission factors from 0.81 to 0.99. Parameter for isotropic secondary extinction (4) is 15(3) × 10⁻⁴. Final least-squares refinement with shift/error < 10⁻³; final difference Fourier with ($\Delta\rho$) max. and ($\Delta\rho$) min, 0.47 and −0.44 e/Å³. Crystal shape and size: tetragonal disphenoid with edges of ~0.1 mm. Program system STRUCSY (5) on an Eclipse S 140 computer.

and results of structure refinement are summarized in Table I. The structure parameters are given in Table II, and selected interatomic distances and angles are compiled in Table III. A trial to refine the atomic coordinates with an atomic parameter set $(\bar{x}\ \bar{y}\ \bar{z})$ instead of $(x\ y\ z)$ increased R and R_w significantly, from 0.031 and 0.028 to 0.048 and 0.046, respectively. (A structure factor list was deposited at the Institut für Mineralogie und Kristallographie der Universität Wien, Vienna, Austria).

Discussion

Figure 1 compares the structures of $(NH_4)Ag_2AsS_4$ and chalcopyrite, $CuFeS_2$, in projections onto (100). The chalcopyrite type is a quite common structure type known from many compounds with different characters of the chemical bonds and different distortions of the individual polyhedra (6). The positions of the S atoms in $(NH_4)Ag_2AsS_4$ are comparable to the positions in $CuFeS_2$; only the arrangement of NH_4 groups and As atoms in layers parallel (001) alternating with Ag layers change the space group symmetry from $I\bar{4}2d$, (in $CuFeS_2$) to $I\bar{4}2m$. The deformation of the coordination polyhedra causes a decrease

TABLE III

BOND DISTANCES (Å) AND ANGLES (°)

N . . . S = 3.224(1) 4x	S . . . N . . . S = 98.0(1) 4x; 136.1(1) 2x
N . . . S = 3.443(1) 4x	
Ag–S = 2.616(1) 4x	S–Ag–S = 96.3(1) 4x; 141.5(1) 2x
As–S = 2.170(1) 4x	S–As–S = 108.0(1) 4x; 112.5(1) 2x
S–Ag = 2.616(1) 2x	Ag–S–Ag = 132.8(1)
S–As = 2.170(1)	Ag–S–As = 111.9(1) 2x
S–N = 3.224(1)	Ag–S–N = 85.0(1) 2x
	As–S–N = 124.3(1)

Note. The bond angles are given for the nearest neighbors in each polyhedron only.

of c/a from 1.966 in $CuFeS_2$ to 1.221 in $(NH_4)Ag_2AsS_4$.

The NH_4 group has four nearest S atom neighbors, with N . . . S = 3.224(1) Å. In accordance with point symmetry $\overline{4}2m$ of the N atom, these S atoms form a tetragonal disphenoid. The coordination figure is compressed parallel to the fourfold inversion axis: the S–S distances are 4.869(3) Å oblique to (001) and 5.981(3) Å in (001). Four additional S atoms with N . . . S = 3.443(1) Å complete the environment of the N atom. These S atoms form a tetragonal disphenoid elongated parallel to the four bar axis; S–S distances are 6.396(3) Å oblique to (001) and 3.607(3) Å in (001). The S–S distances between these two separately described coordination figures are at least 3.90 Å. As proposed by West (7), this environment of the NH_4 group by S atoms might be described as two "successive disphenoids."

Environments of NH_4 groups, comparable to the title compound, have been described for a few structures only; e.g., NH_4 groups in a [4 + 4] environment have been determined in $(NH_4)_3SbS_4$ (8, 9). Each four N . . . S distances are 3.23 Å and 3.94 Å,
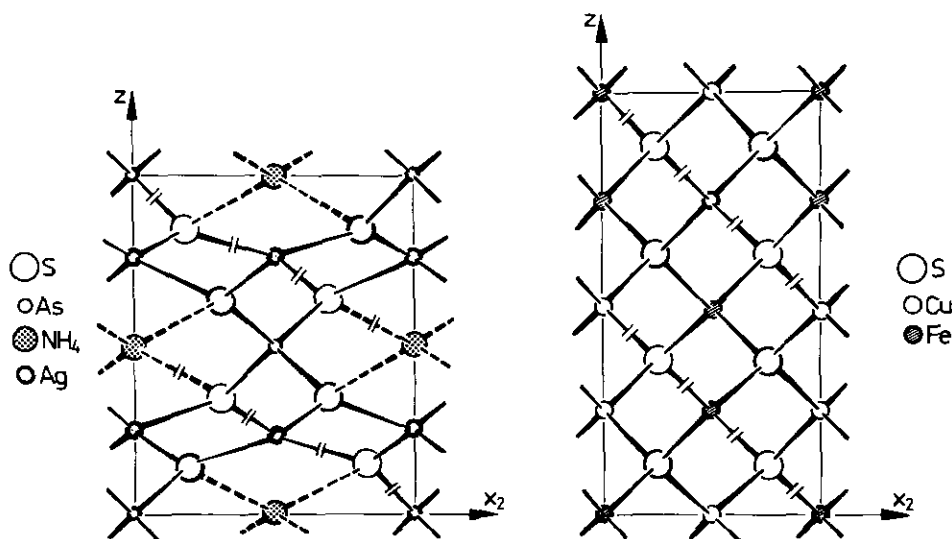

FIG. 1. The structures of $(NH_4)Ag_2AsS_4$ (left) and of $CuFeS_2$ (right) in projections onto (100).

TABLE IV

Geometry of AgS$_4$ Polyhedra

Chemical formula	Reference	Atom	Point symmetry	Distances and angles						⟨ ⟩	DP$_x$
PbTlAgAs$_2$S$_5$[a]	(12)		1	2.32	2.64	2.66	3.00			2.66	0.0658
				110.5	116.0	90.2	128.9	8.74	111.9	108.0	0.1104
				4.07	4.22	3.80	4.78	3.91	4.70	4.25	0.0776
AgCrS$_2$	(13)		3m	2.44	2.76	2.76	2.76			2.68	0.0448
				133.0	133.0	133.0	78.6	78.6	78.6	105.2	0.2585
				4.77	4.77	4.77	3.50	3.50	3.50	4.14	0.1535
AgAlS$_2$	(14)		3m	2.46	2.73	2.73	2.73			2.66	0.0389
				132.3	132.3	132.3	79.6	79.6	79.6	106.0	0.2486
				4.76	4.75	4.75	3.50	3.50	3.50	4.13	0.1513
Ag$_2$BaSnS$_2$	(15)		2	2.49	2.49	2.78	2.78			2.64	0.0549
				166.5	91.0	94.1	94.1	91.0	136.2	112.2	0.2331
				4.94	3.76	3.86	3.86	3.76	5.16	4.22	0.1303
Ag$_{10}$Si$_3$S$_{11}$	(16)	Ag(1)	1	2.56	2.57	2.59	2.65			2.59	0.0183
				102.4	136.1	102.2	100.6	104.9	107.3	108.9	0.0831
				4.00	4.78	4.05	3.97	4.13	4.22	4.19	0.0489
		Ag(2)	1	2.52	2.55	2.66	·2.80			2.63	0.0371
				129.9	125.5	98.0	99.7	100.3	93.0	107.7	0.1235
				4.59	4.59	4.01	3.97	4.10	3.95	4.20	0.0631
		Ag(7)	1	2.51	2.59	2.65	2.68			2.61	0.0220
				143.9	101.1	91.2	95.1	109.5	117.8	109.8	0.1281
				4.85	3.98	3.71	3.87	4.30	4.56	4.21	0.0851
Ag$_8$SiS$_6$	(17)	Ag(3)	1	2.56	2.62	2.69	2.76			2.66	0.0254
				137.4	102.6	106.3	101.6	106.1	94.7	108.1	0.0902
				4.82	4.09	4.25	4.11	4.30	4.00	4.26	0.0466
		Ag(4)	1	2.50	2.55	2.72	2.99			2.69	0.0613
				141.9	102.4	103.9	106.8	103.2	83.4	106.9	0.1088
				4.77	4.07	4.33	4.24	4.35	3.81	4.26	0.0520
		Ag(7)	1	2.56	2.61	2.65	2.70			2.63	0.0238
				100.9	107.2	111.7	117.0	103.5	115.6	109.3	0.0497
				3.99	4.20	4.35	4.49	4.17	4.53	4.29	0.0392
Ag$_8$GeS$_6$	(18)	Ag(2)	1	2.58	2.62	2.62	2.70			2.63	0.0133
				118.5	107.6	117.7	96.3	103.4	111.3	109.1	0.0614
				4.46	4.20	4.51	3.90	4.17	4.39	4.27	0.0425
		Ag(3)	1	2.55	2.58	2.75	2.94			2.71	0.0517
				141.6	101.1	105.4	106.1	105.1	81.4	106.6	0.1077
				4.85	4.10	4.38	4.26	4.39	3.72	4.28	0.0600
		Ag(6)	1	2.57	2.61	2.69	2.77			2.66	0.0263
				137.9	103.3	108.1	101.1	105.6	90.6	107.8	0.0945
				4.83	4.13	4.32	4.09	4.28	3.88	4.26	0.0520
Ag$_2$GeS$_3$	(19)		1	2.37	2.51	2.69	2.75			2.58	0.0504
				111.9	114.5	110.3	114.0	105.8	99.2	109.3	0.0413
				4.04	4.26	4.21	4.36	4.20	4.14	4.20	0.0179
Ag$_4$P$_2$S$_6$	(20)	Ag(1)	1	2.49	2.56	2.64	2.71			2.60	0.0288
				131.7	109.5	114.8	99.6	100.3	93.8	108.8	0.0954
				4.61	4.19	4.38	3.98	4.05	3.90	4.19	0.0497
		Ag(3)	1	2.50	2.61	2.63	2.70			2.61	0.0211
				114.8	113.4	127.5	122.0	82.9	92.2	108.8	0.1302
				4.30	4.28	4.66	4.58	3.51	3.84	4.20	0.0671
		Ag(4)	1	2.49	2.56	2.62	2.64			2.58	0.0203
				132.0	102.3	118.3	108.6	86.9	106.6	109.1	0.0979
				4.62	3.98	4.41	4.21	3.58	4.22	4.17	0.0624

TABLE IV—*Continued*

Chemical formula	Reference	Atom	Point symmetry	Distances and angles						⟨ ⟩	DP_x
$ZnAgPS_4$	(21)		1	2.54	2.55	2.58	2.65			2.58	0.0136
				114.9	110.8	104.2	110.0	119.9	104.4	110.7	0.0577
				4.29	4.21	4.09	4.20	4.31	4.13	4.21	0.0154
$TlAg_3S_2$	(22)		2	2.52	2.62	2.65	2.96			2.69	0.0405
				123.1	127.5	102.7	95.9	101.0	102.5	108.8	0.0964
				4.52	4.64	4.29	3.92	4.31	4.38	4.34	0.0392
$AgFe_2S_3{}^b$	(23)		m	2.48	2.52	2.63	2.63			2.57	0.0253
				138.6	105.6	105.6	99.4	99.4	104.3	108.8	0.0911
				4.67	4.07	4.07	3.93	3.93	4.16	4.14	0.0447
$(NH_4)Ag_2AsS_4$	(This work)		$\bar{4}$	2.62	2.62	2.62	2.62			2.62	0.0
				96.3	96.3	96.3	96.3	141.5	141.5	111.4	0.1804
				3.90	3.90	3.90	3.90	4.94	4.25	4.94	0.1090

Note. The following distances (Å), angles (°), and distortion parameters (DP_x) for the atoms in "AgS_4-tetrahedra" are given:

$$4\ \text{Ag–S (Å)};\ \langle \text{Ag–S}\rangle\ (\text{Å});\ DP_d = \left(\sum_{i=1}^{4} |d_i - d_m|\right)/4 \cdot d_m \quad \text{(first line)}$$

$$6\ \text{S–Ag–S (°)};\ \langle \text{S–Ag–S}\rangle\ (°);\ DP_{\measuredangle} = \left(\sum_{i=1}^{6} |\measuredangle_i - \measuredangle_m|\right)/6 \cdot \measuredangle_m \quad \text{(second line)}$$

$$6\ \text{S–S (Å)};\ \langle \text{S–S}\rangle\ (\text{Å});\ DP_e = \left(\sum_{i=1}^{6} |e_i - e_m|\right)/6 \cdot e_m \quad \text{(third line)}$$

The indices i and m indicate individual and mean values; average values in angle brackets.

  [a] Hatchite.

  [b] Sternbergite (mineral names).

the nearest and the distant S atom neighbors form distorted tetrahedra; the resulting polyhedron might be described as an irregular dodecahedron. Further comparable coordination polyhedra with high symmetry for the NH_4 groups occur in the compounds $(NH_4)SH$ (7) and $(NH_4)Cu_7S_4$ (10). The N . . . S distances in $(NH_4)SH$ are 3.30(4) Å (4x) and 4.02(4) Å (4x), the sulfur atoms are arranged in two tetrahedra around each nitrogen. In $(NH_4)Cu_7S_4$ the NH_4 group (site symmetry $\bar{4}$) is equidistant coordinated to eight S atoms; N . . . S is 3.38(10) Å. The polyhedron is a tetragonal prism, the shortest S–S distances are 3.83(6) Å and 3.93(6) Å. Although the structure determinations of these two compounds are less accurate, the N . . . S distances are of the same magnitude as the values in $(NH_4)Ag_2AsS_4$.

The AgS_4 coordination polyhedron in the title compound is a distorted tetragonal disphenoid with Ag–S = 2.62 Å (4x), distances to further Ag atom neighbors are longer than 3.5 Å. Monovalent Ag atoms coordinated to four S atoms occur in a lot of crystal structures. Table IV compiles compounds with Ag atoms surrounded by four sulfur atoms: Polyhedra with four Ag–S bond lengths below 3.00 Å and further S atom neighbors with Ag–S > 3.50 Å are taken into account; restrictions according to common corners or even edges between the AgS_4 polyhedra are not considered. The Ag–S distances vary from 2.3 Å to 3.0 Å, average values from 2.57 to 2.70 Å; the S–Ag–S angles vary in a wide range from about 80° to at least 170°. Nevertheless, these AgS_4 polyhedra are more or less distorted, the grand S–Ag–S angles are less

variable (105° to 112°), the grand S–S distances between the ligands vary from about 4.10 to 4.35 Å (individual values from 3.5 to 5.0 Å). The most common symmetry of the AgS_4 coordination polyhedra is 1, only in a few cases higher symmetries have been determined; the regular tetrahedron is unknown. The only example with a silver atom in a equidistant tetrahedral coordination has been determined for the compound $AgFeS_2$ (11). Obviously, the Ag–S bond lengths are too short, but the accuracy of refinement is very low; therefore this structure is not included in Table IV.

The compounds compiled in Table IV exhibit an interesting common feature: they are transparent for IR radiation (as far as investigated), in thin sections also for visible light; nevertheless, a metallic luster of these crystals is observed. Typical examples are hatchite, $PbTlAgAs_2S_5$, and argyrodite, Ag_8GeS_6. The compounds $Ag_{10}Si_3O_{11}$, Ag_2GeS_3, and the title compound are transparent for red or even orange red light.

From this behavior it is concluded that the silver–sulfur compounds under discussion have a considerable covalent portion to their chemical bonds, independent from other elements involved in the structure. Obviously the covalent nature of Ag–S bonds is widespread in silver compounds with more or less distorted "tetrahedral Ag–S bonds," consequently, a systematic spectroscopic investigation of these compounds seems to be worthwhile.

The AsS_4 group in $(NH_4)Ag_2AsS_4$ exhibits a distorted tetrahedral arrangement of four sulfur atoms around arsenium. The mean As–S value of 2.170 Å fits well to the mean values (2.156 to 2.815 Å) recalculated by Pertlik (24) for AsS_4 tetrahedra in 10 well determined crystal structures. As discussed in (24), the grand ⟨As–S⟩ in these compounds are obviously controlled by the variable character of the chemical bonds from the sulfur atoms to further cations.

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