

Syntheses and Crystal Structures of $\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$ and $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$ with a Discussion of $(\text{NH}_4)_x\text{S}_x$ Polyhedra

F. Pertlik

Institut für Mineralogie und Kristallographie, Universität Wien, A-1010 Wien, Austria

Summary. The atomic arrangements within the structures of $\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$ [$a = 9.557(2)$, $b = 7.414(2)$, $c = 16.29(1)$ Å; $\beta = 91.30(5)^\circ$; space group $P2_1/n$; $R(F) = 0.042$] and $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$ [$a = 64.49(6)$, $b = 6.471(2)$, $c = 12.806(4)$ Å; $\beta = 95.47(5)^\circ$; space group Cc ; $R(F) = 0.073$] were determined from single crystal X-ray data. In these two compounds the coordination spheres of the Ag atoms are quite different. In $\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$, the Ag atoms exhibit a $[2+2]$ - and a $[3+1]$ -coordination to S atoms up to 3.3 Å and with Ag atom neighbours at 2.93 Å and 3.05 Å respectively. In $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$, the Ag atoms are – with one exception – $[4]$ coordinated ($\text{Ag-S} < 3.3$ Å) and the distances to further Ag atom neighbours are greater than 3.1 Å. $\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$ represents an ordered cyclo-thioarsenate(III) with three-membered As_3S_6 rings, $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$ a neso-thioarsenate(V) with two split Ag atom positions. Both compounds were synthesized under moderate hydrothermal conditions.

Keywords. $\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$; $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$; Syntheses; Crystal Structure; Thioarsenates(III) and (V); Crystal Chemistry.

Synthesen und Kristallstrukturen von $\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$ und $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$ mit einer Diskussion über $(\text{NH}_4)_x\text{S}_x$ Polyeder

Zusammenfassung. Die Atomanordnungen in den Strukturen von $\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$ [$a = 9.557(2)$, $b = 7.414(2)$, $c = 16.29(1)$ Å; $\beta = 91.30(5)^\circ$; Raumgruppe $P2_1/n$; $R(F) = 0.042$] und $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$ [$a = 64.49(6)$, $b = 6.471(2)$, $c = 12.806(4)$ Å; $\beta = 95.47(5)^\circ$; Raumgruppe Cc ; $R(F) = 0.073$] wurden anhand von röntgenographischen Einkristalldaten bestimmt. In diesen beiden Verbindungen sind die Koordinationsverhältnisse um die Ag-Atome sehr unterschiedlich. In $\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$ besitzen die Ag-Atome bis 3.3 Å eine $[2+2]$ - und $[3+1]$ -Koordination durch S-Atome mit weiteren Ag-Atomen bei 2.93 Å und 3.05 Å. In $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$ sind die Ag-Atome mit einer Ausnahme $[4]$ -koordiniert ($\text{Ag-S} < 3.3$ Å), und die Abstände zu weiteren Ag-Atomen sind größer als 3.1 Å. $\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$ stellt ein geordnetes Cyclothioarsenat(III) mit dreigliedrigen As_3S_6 -Ring dar, $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$ ein Nesothioarsenat (V) mit zwei aufgespaltenen Ag-Positionen. Beide Verbindungen wurden unter mäßigen Hydrothermalbedingungen synthetisiert.

Introduction

Synthesis instructions for silver(I)thioarsenates(III and V), especially under hydrothermal conditions in alkaline solutions, have been given by *Peacock* [1] and *Beland*

[2]. Investigations in the system Ag–As–S and ammonia-water in the temperature range up to 500 K have been reported by *Auernhammer et al.* [3], *Pertlik* [4] and *Rosenstingl and Pertlik* [5]. Worth mentioning are also the investigations of phase relationships in the system Ag–As–S in a wide range of pressure and temperature by *Jaeger and Van Kloster* [6] and the experiments in the same system described by *Blachnik and Wickel* [7].

The first attempt of a crystal chemical characterization and classification of compounds in the system Ag–As–S under the name “sulphosalts” was made by *Nowacki* [8]. Comparable compilations of inorganic structures related to the title compounds under crystal chemical aspects are given by *Auernhammer et al.* [3]. The geometry of the coordination of monovalent Ag atoms against S atoms and the geometry of tetrathioarsenate(V) anions (e.g. mean values of As–S distances, mean square relative deviations from average bond lengths) have been investigated by *Pertlik* [4].

Results and discussion

Both structures of the title compounds represent three dimensional networks of metal and sulfur atoms. In cavities of these structures, NH_4 groups with irregular coordination and varying S atom neighbours are located (Figs. 1 and 2).

In $\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$, the two Ag atom positions show no disorder in location or occupation. In the second compound, $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$, two Ag atom positions are split with an occupation of one half each and a distance of 2.07(3) Å and 1.98(3) Å between the two positions, respectively. Further atom neighbours to these split up atom positions, especially S atoms, are at distances > 2.50 Å (cf. Table 3). It is worth mentioning that such a splitting up of Ag positions in sulphosalts is very common.

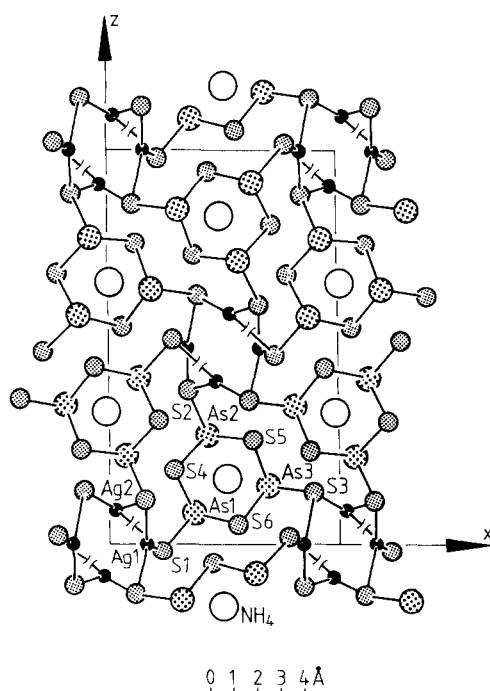


Fig. 1. Structure of $\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$ in a projection parallel to the two-fold axis with the As_3S_6 rings parallel to (010)

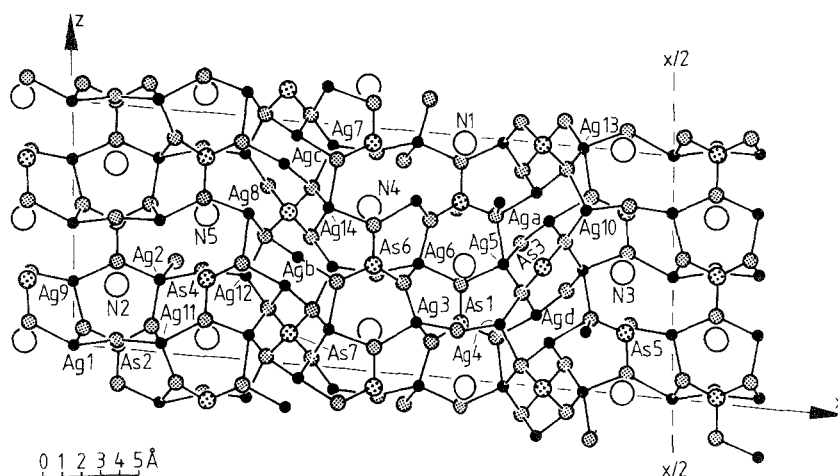


Fig. 2. Part of the structure of $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$ projected parallel to $[010]$ without signatures for the sulfur atoms

Engel and *Nowacki* [10] determined great differences in the main directions of the ellipsoids of thermal vibration for the Ag atoms in the crystal structure of monoclinic xanthoconite, Ag_3AsS_3 . These great differences were confirmed by structure refinements performed by *Rosenstingl* and *Pertlik* [11] on natural and synthetic xanthoconite. The authors of these articles did not decide on static or dynamic effects in connection with this disorder. The clear splitting up of two Ag atom positions in $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$ may be a static effect without ordering phenomena. This assumption is supported by the fact that in relation to the given lattice parameters (Table 1) no multiplication of any direction parameter and no diffuse patterns were observed, even on long exposed Weissenberg-type X-ray films.

Although in both title compounds the ordered Ag atoms are four-coordinated to S atoms within distances $< 3.2 \text{ \AA}$ and with no further S atom neighbours up to 3.5 \AA , a pronounced $[2+2]$ - and $[3+1]$ -coordination in $\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$ and a clear cut $[4]$ -coordination in $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$ were determined.

The sum of the three S–Ag(1)–S angles between the shorter Ag(1)–S distances in $\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$ are 359° ; one sulfur atom with Ag–S = 3.16 \AA completes this planar configuration to a $[4]$ -coordination. Ag(2) shows a tendency towards a linear S–Ag–S group with a corresponding angle of 153° . The two split up Ag atom positions in $(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$ are more or less one-sided $[4]$ - and $[5]$ -coordinated.

In the nomenclature for arsenates(III) or (V) and sulfarsenates(III) or (V) proposed by *Pertlik* [12, 13] and *Strunz* [14] in comparison with the nomenclature for silicates [15], the title compounds represent a cyclo-sulfarsenate(III) with a 3-membered $(\text{AsS}_2)_3$ ring and a neso-sulfarsenate(V). The geometry of the $(\text{AsS}_2)_3$ ring in $\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$ is similar in distances and conformation to the comparable rings in trechmannite [16] and smithite [17], two modifications of AgAsS_2 , but differs in symmetry which is 1 in the title compound, 2 in trechmannite and m in smithite. In all these three cases the As_3S_6 rings are of the “crown form” [16].

Geometric aspects of (NH₄)S_x polyhedra

Table 4 represents a compilation of compounds with (NH₄)S_x polyhedra. The (NH₄)S_x polyhedra of (NH₄)₂WO₂S₂ [18] with distances from the central N atom to oxygen atoms of 2.87, 2.88, 2x, and 2.91 Å and of the two thiocyanate compounds NH₄SCN [19] and NH₄Ag(SCN)₂ [20] have not been considered. In both structures distances from the N atom of the NH₄ tetrahedra to the N atom of the SCN group within the range of 2.96 to 3.61 Å and distances to the C atom of the SCN group of 3.59 to 3.94 Å have been determined.

The NH₄-S (*recte* N-S) distances determined in the structures mentioned in Table 4 are within the range of 3.2 Å to 4.0 Å, with mean values from 3.4 to 3.7 Å, and a clear correlation between the coordination number and the mean NH₄-S distance exists. In some cases, the NH₄ groups of the compounds compiled in Table 4 show a tendency towards a [4+x] coordination, especially in compounds with N atoms on point symmetry $\bar{4}$ or $\bar{4}2m$, in which four S atoms at a time show an equidistant (more or less tetrahedral) arrangement. This configuration enables the formation of hydrogen bridges between the N atom and the nearest four S atom neighbours. At the author's opinion, for potassium atoms and the homologous alkaline elements no greater differences in the form of such MeS_x polyhedra might

Table 1. Unit cell parameters, data for X-ray intensity measurements and structure refinements for NH₄Ag₂(AsS₂)₃ and (NH₄)₅Ag₁₆(AsS₄)₇. Equipment: Stoe four-circle diffractometer AED2; Mo X-ray tube; graphite monochromator

<i>a</i> (Å)	9.557(2)	64.49(6)
<i>b</i> (Å)	7.414(2)	6.471(2)
<i>c</i> (Å)	16.29(1)	12.806(4)
β (°)	91.30(5)	95.47(5)
<i>V</i> (Å ³)	1153.8	5319.9
<i>Z</i>	4	4
Space group	P2 ₁ /n	Cc
μ (MoK α) (cm ⁻¹)	136	118
Reflections for lattice parameters	20	20
2 θ -range for lattice parameters (°)	25.0 to 30.0	
Crystal dimensions (mm)	0.20 × 0.40 × 0.08	0.05 × 0.20 × 0.15
Colour	pale yellow	redish-yellow
Crystallographic forms	{011}, {101}, { $\bar{1}01$ }	{100}, {010}, {001}
2 θ_{max} for data collection (°)	60	50
2 θ ω Scan, min. scan width (°) + (α_1, α_2) dispersion	1.20	1.35
Background (each side) (°)	0.16	0.12
Reflections measured	6556	10217
Unique reflections	4665	6986
Internal <i>R</i> (I)	0.027	0.079
Reflections with $F_0 > 4\sigma(F_0)$	2708	4548
Absorption correction	ψ -scan data	
Transmission factors	0.02 to 0.11	0.13 to 0.20
$R/R_w = [\sigma(F_0)]^{-2}, F_0 > 4\sigma(F_0)$	0.042/0.036	0.073/0.069
$\Delta_{max} \cdot \sigma^{-1}$	< 10 ⁻³	
Variable parameters	110	336
Final difference Fourier map (eÅ ⁻³)	+1.7 to -2.3	

Table 2. Structural parameters with e.s.d.'s in parentheses. The anisotropic displacement factors are defined as

$$\exp\left(-2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} h_i h_j a_i^* a_j^* \right) [\text{pm}^2], \text{ the isotropic as } \exp(-8\pi^2 u^2 \sin^2 \theta / \lambda^2) [\text{nm}^2]$$

NH ₄ Ag ₂ (AsS ₂) ₃										
Atom	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂	
Ag(1)	0.1592(1)	0.0159(1)	0.0007(1)	376(4)	365(4)	424(5)	-8(2)	-5(2)	-11(2)	
Ag(2)	0.0304(1)	0.9378(1)	0.0869(1)	457(5)	496(5)	731(7)	46(3)	50(3)	75(2)	
As(1)	0.3701(1)	0.6173(1)	0.0790(1)	221(4)	280(4)	215(4)	-4(2)	-29(2)	6(2)	
As(2)	0.4274(1)	0.6282(1)	0.2776(1)	220(4)	259(4)	193(4)	0(2)	-14(2)	2(2)	
As(3)	0.6911(1)	0.6491(1)	0.1488(1)	185(4)	269(4)	229(4)	-7(2)	-17(2)	1(2)	
S(1)	0.2230(2)	0.6971(3)	0.9806(1)	256(10)	328(11)	216(10)	-2(6)	-44(4)	-4(4)	
S(2)	0.3442(2)	0.7488(3)	0.9802(1)	298(11)	329(11)	204(10)	-12(6)	8(4)	-13(5)	
S(3)	0.8900(2)	0.7936(3)	0.1335(1)	194(9)	325(11)	285(11)	4(6)	-25(4)	-14(4)	
S(4)	0.2821(2)	0.7746(3)	0.1862(1)	223(10)	371(11)	234(10)	0(6)	-20(4)	34(4)	
S(5)	0.6235(2)	0.7999(3)	0.2643(1)	227(10)	343(11)	206(10)	-15(5)	-13(4)	-13(4)	
S(6)	0.5602(2)	0.7952(3)	0.0510(1)	223(10)	409(12)	216(10)	26(6)	-25(4)	-8(5)	
N	0.0115(8)	0.3179(11)	0.6650(5)	355(43)	344(41)	349(45)	-7(23)	-48(18)	-11(17)	

(NH ₄) ₅ Ag ₁₆ (AsS ₄) ₇										
Atom	x	y	z	U _{11/iso}	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂	
Ag(1)	0.0 *	0.9630(17)	0.0 *	335(7)	518(6)	692(8)	258(4)	11(1)	5(1)	
Ag(2)	0.0718(2)	0.4675(16)	0.2948(12)	324(7)	402(6)	583(8)	12(4)	13(1)	2(1)	
Ag(3)	0.2850(2)	0.9867(18)	0.2097(11)	289(7)	703(6)	478(8)	-234(4)	0(1)	4(1)	
Ag(4)	0.3568(2)	0.9849(13)	0.2361(8)	440(7)	197(6)	290(8)	-50(4)	-1(1)	-3(1)	
Ag(5)	0.3590(2)	0.5119(17)	0.4792(13)	428(7)	475(6)	383(8)	-179(4)	-8(1)	12(1)	
Ag(6)	0.2871(2)	0.5299(14)	0.4544(9)	230(7)	395(6)	365(8)	-17(4)	-5(1)	0(1)	
Ag(7)	0.2153(2)	0.5071(12)	0.9081(12)	365(7)	264(6)	325(8)	24(4)	4(1)	-5(1)	
Ag(8)	0.1466(2)	0.0084(14)	0.6035(15)	580(7)	380(6)	784(8)	273(4)	24(1)	14(1)	
Ag(9)	0.9998(2)	0.4767(15)	0.2602(12)	324(7)	340(6)	442(8)	-23(4)	23(1)	-4(1)	
Ag(10)	0.4280(2)	0.9963(12)	0.7380(11)	557(7)	222(6)	303(8)	57(4)	11(1)	9(1)	
Ag(11)	0.0721(2)	0.9635(18)	0.0336(14)	422(7)	618(6)	692(8)	280(4)	12(1)	4(1)	
Ag(12)	0.1434(2)	0.5041(12)	0.3457(14)	489(7)	191(6)	473(8)	-20(4)	2(1)	7(1)	
Ag(13)	0.4252(2)	0.4945(16)	0.9913(13)	667(7)	298(6)	571(8)	-144(4)	-2(1)	7(1)	
Ag(14)	0.2125(2)	0.9995(16)	0.6539(14)	530(7)	446(6)	574(8)	-200(4)	14(1)	-11(1)	
As(1)	0.3232(2)	0.5029(13)	0.2271(11)	191(3)	97(3)	100(3)	15(2)	1(1)	1(1)	
As(2)	0.0362(2)	0.4834(14)	0.0190(13)	332(3)	269(3)	722(3)	-8(2)	4(1)	-2(1)	
As(3)	0.3932(3)	0.0287(11)	0.4879(13)	216(3)	67(3)	215(3)	-14(2)	8(1)	-2(1)	
As(4)	0.1107(2)	0.9838(14)	0.3165(13)	103(3)	86(3)	215(3)	-29(2)	1(1)	0(1)	
As(5)	0.4622(2)	0.4866(15)	0.2454(12)	86(3)	97(3)	179(3)	-10(2)	5(1)	1(1)	

(continued)

Table 2. (continued)

Atom	$(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$								
	x	y	z	U_{11}/iso	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
As(6)	0.2492(2)	0.0098(13)	0.4355(12)	178(3)	92(3)	77(3)	- 19(2)	1(1)	1(1)
As(7)	0.1794(3)	0.428(10)	0.1249(15)	139(3)	116(3)	156(3)	49(2)	- 2(1)	1(1)
S(1a)	0.3232(5)	0.5894(38)	0.3888(20)	0.24(5)					
S(1b)	0.3213(5)	0.1742(36)	0.2000(20)	0.30(6)					
S(1c)	0.2969(4)	0.3542(36)	0.6344(20)	0.32(6)					
S(1d)	0.3525(5)	0.3817(34)	0.6775(19)	0.20(5)					
S(2a)	0.0370(4)	0.4106(36)	0.3537(19)	0.23(5)					
S(2b)	0.0361(4)	0.1527(31)	0.0302(18)	0.18(5)					
S(2c)	0.0641(4)	0.3966(29)	0.6005(16)	0.15(4)					
S(2d)	0.0082(5)	0.3980(35)	0.5762(19)	0.29(5)					
S(3a)	0.4124(4)	0.1684(32)	0.8980(18)	0.28(5)					
S(3b)	0.3732(4)	0.1644(33)	0.0723(20)	0.32(5)					
S(3c)	0.3749(4)	0.2262(30)	0.3753(18)	0.24(4)					
S(3d)	0.4111(4)	0.2296(31)	0.5998(18)	0.25(5)					
S(4a)	0.1067(5)	0.3117(36)	0.3472(22)	0.32(6)					
S(4b)	0.1396(5)	0.8766(34)	0.3901(19)	0.22(5)					
S(4c)	0.0852(4)	0.1756(35)	0.8839(19)	0.26(5)					
S(4d)	0.1096(4)	0.9226(34)	0.1491(18)	0.21(5)					
S(5a)	0.4625(4)	0.4242(28)	0.0779(17)	0.17(4)					
S(5b)	0.4651(4)	0.1859(28)	0.7773(18)	0.22(4)					
S(5c)	0.4884(4)	0.3310(29)	0.3348(17)	0.18(4)					
S(5d)	0.4319(4)	0.3704(33)	0.2946(18)	0.28(5)					
S(6a)	0.2187(5)	0.8751(39)	0.8497(21)	0.34(6)					
S(6b)	0.2755(5)	0.1616(39)	0.3681(20)	0.29(6)					
S(6c)	0.2501(5)	0.0703(38)	0.5973(19)	0.30(6)					
S(6d)	0.2515(4)	0.3180(34)	0.9042(18)	0.20(5)					
S(7a)	0.1589(5)	0.3340(42)	0.5198(21)	0.36(6)					
S(7b)	0.1620(4)	0.2694(34)	0.2188(19)	0.22(5)					
S(7c)	0.1972(5)	0.2769(36)	0.0267(20)	0.26(5)					
S(7d)	0.1983(4)	0.6707(37)	0.2305(19)	0.28(6)					
N(1)	0.327(3)	0.832(33)	0.971(12)	0.61(10)					
N(2)	0.035(1)	0.925(9)	0.269(4)	0.35(10)					
N(3)	0.458(1)	0.076(9)	0.498(4)	0.21(10)					
N(4)	0.228(3)	0.560(34)	0.663(13)	0.22(10)					
N(5)	0.112(1)	0.579(7)	0.576(3)	0.10(10)					
Ag(a)**	0.3981(5)	0.5924(39)	0.6768(21)	0.86(7)					
Ag(b)**	0.1860(5)	0.0957(41)	0.4409(21)	0.89(8)					
Ag(c)**	0.1751(7)	0.0854(64)	0.8185(29)	1.54(13)					
Ag(d)**	0.5862(7)	0.6111(68)	0.2909(31)	1.72(14)					

* Fixes the origin

** occupation factor 0.5

Table 3. Selected bond distances [\AA] and bond angles [$^\circ$] with e.s.d.'s in parentheses. The intervals and quantities for the Ag–S and As–S distances ($< 3.3 \text{\AA}$), the Ag–Ag and the As–As distances ($< 3.5 \text{\AA}$) and the NH_4 –S (*recte* N–S) distances ($< 3.9 \text{\AA}$) are given

$\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$							
Ag(1)–S:	2.464(2)–	3.157(2);	4	S–As(3)–S	96.7(1) –104.1(1); 3		
S–Ag(1)–S:	71.2(1) –140.4(1);	6	NH ₄ –S:	3.42(1) –	3.81(1); 9		
Ag(2)–S	2.453(2)–	3.160(2);	4		Ag(1)–Ag(1') = 3.052(1)		
S–Ag(2)–S:	86.6(1) –152.5(1);	6			Ag(2)–Ag(2') = 2.931(1)		
As(1)–S:	2.189(2)–	2.299(2);	3		As(1)–As(3) = 3.271(1)		
S–As(1)–S:	99.5(1) –101.3(1);	3			–As(2) = 3.256(1)		
As(2)–S:	2.203(2)–	2.287(2);	3		As(2)–As(3) = 3.320(1)		
S–As(2)–S:	97.2(1) –	99.5(1);	3				
As(3)–S:	2.200(2)–	2.294(2);	3				
$(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$							
Ag(1)–S:	2.52(2)–	2.71(2);	4	Ag(d)–S:	2.50(2)–	3.26(2);	5
S–Ag(1)–S:	85.5(5) –145.2(5);	6	S–Ag(d)–S:	70.7(5) –140.6(9);	10		
Ag(2)–S:	2.49(2)–	2.66(2);	4	As(1)–S:	2.12(2)–	2.23(2);	4
S–Ag(2)–S:	89.4(5) –133.0(5);	6	S–As(1)–S:	104.6(7) –112.1(7);	6		
Ag(3)–S:	2.51(2)–	2.60(2);	4	As(2)–S:	2.16(2)–	2.23(2);	4
S–Ag(3)–S:	87.6(5) –143.8(5);	6	S–As(2)–S:	104.4(7) –113.9(7);	6		
Ag(4)–S:	2.51(2)–	2.69(2);	4	As(3)–S:	2.14(2)–	2.20(2);	4
S–Ag(4)–S:	94.5(5) –145.4(5);	6	S–As(3)–S:	107.1(7) –112.9(7);	6		
Ag(5)–S:	2.51(2)–	2.75(2);	4	As(4)–S:	2.16(2)–	2.19(2);	4
S–Ag(5)–S:	83.6(5) –135(5);	6	S–As(4)–S:	107.5(7) –112.5(7);	6		
Ag(6)–S:	2.54(2)–	2.71(2);	4	As(5)–S:	2.17(2)–	2.20(2);	4
S–Ag(6)–S:	90.8(5) –133.9(5);	6	S–As(5)–S:	107.7(7) –110.9(7);	6		
Ag(7)–S:	2.50(2)–	2.70(2);	4	As(6)–S:	2.14(2)–	2.24(2);	4
S–Ag(7)–S:	94.6(5) –142.6(5);	6	S–As(6)–S:	107.3(7) –110.6(7);	6		
Ag(8)–S:	2.48(2)–	2.82(2);	4	As(7)–S:	2.15(2)–	2.19(2);	4
S–Ag(8)–S:	82.5(5) –137.0(5);	6	S–As(7)–S:	106.7(7) –113.7(7);	6		
Ag(9)–S:	2.54(2)–	2.67(2);	4	NH ₄ (1)–S:	3.28(7)–3.70(7);	9	
S–Ag(9)–S:	90.4(5) –133.0(5);	6	NH ₄ (2)–S:	3.23(7)–3.55(7);	8		
Ag(10)–S:	2.47(2)–	2.65(2);	4	NH ₄ (3)–S:	3.33(7)–3.64(7);	9	
S–Ag(10)–S:	94.7(5) –141.3(5);	6	NH ₄ (4)–S:	3.39(7)–3.75(7);	9		
Ag(11)–S:	2.55(2)–	2.72(2);	4	NH ₄ (5)–S:	3.16(7)–3.83(7);	9	
S–Ag(11)–S:	84.8(5) –146.6(5);	6			Ag(4) –Ag(d) = 3.18(2)		
Ag(12)–S:	2.50(2)–	2.68(2);	4		Ag(5) –Ag(d) = 3.17(2)		
S–Ag(12)–S:	92.6(5) –141.8(5);	6			–Ag(a) = 3.41(2)		
Ag(13)–S:	2.53(2)–	2.76(2);	4		Ag(7) –Ag(b) = 3.26(2)		
S–Ag(13)–S:	84.2(5) –134.7(5);	6			Ag(8) –Ag(c) = 3.25(2)		
Ag(14)–S:	2.55(2)–	2.64(2);	4		–Ag(b) = 3.47(2)		
S–Ag(14)–S:	85.7(5) –132.6(5);	6			Ag(10)–Ag(a) = 3.36(2)		
Ag(a)–S:	2.53(2)–	3.26(2);	5		Ag(12)–Ag(c) = 3.43(2)		
S–Ag(a)–S:	71.0(6) –141.1(7);	10			Ag(13)–Ag(a) = 3.18(2)		
Ag(b)–S:	2.51(2)–	3.30(2);	4		Ag(14)–Ag(b) = 3.16(2)		
S–Ag(b)–S:	72.8(6) –139.5(8);	6			–Ag(c) = 3.39(2)		
Ag(c)–S:	2.54(2)–	3.14(2);	5				
S–Ag(c)–S:	75.3(7) –147.3(9);	10					

occur in comparison with the $(\text{NH}_4)\text{S}_x$ polyhedra. For monovalent Tl atoms, the coordination against S atoms is described somewhat one-sided [21]. This comment is given in the description of the structure of TlAs_5S_8 (bernardite) and explained as typical for the coordination chemistry of elements with stereochemical active lone pair electrons.

Experimental

Single crystals of the title compounds were synthesized from approximately equimolar mixtures of elementary silver and arsenic with different amounts of sulfur in concentrated ammonia at 200 °C (saturation vapour pressure, reaction time one week). The reaction vessels were teflon lined steel autoclaves. Depending on the amount of sulfur, crystallizations of thioarsenate compounds with trivalent or pentavalent arsenic could be achieved [5]. A pronounced excess of sulfur favoured the crystallization of the compound with pentavalent arsenic.

Preliminary investigations of the synthesized crystals were made with a Weissenberg type single crystal camera equipped with a Cu tube. Details about the experimental work on structure determination are summarized in Table 1. The atomic coordinates of the different Ag atom positions was found by the direct method strategy, those of the other atoms by subsequent Fourier and difference

Table 4. Compilation of $(\text{NH}_4)\text{-S}$ distances (Å) and point symmetry of the N atom in pure $(\text{NH}_4)\text{S}_x$ polyhedra

Formula	Coordination	Range (Å)	Mean (Å)	References	Point symmetry
NH_4SH	8	3.30–4.00	3.65	[22]	$\bar{4}2m$
$\text{NH}_4\text{Cu}_7\text{S}_4$	8	3.38	3.38	[23]	$\bar{4}$
$(\text{NH}_4)_2\text{WS}_4$	10	3.47–3.9	3.69	[24]	m
$(\text{NH}_4)_3\text{SbS}_4$	8	3.24–3.9	3.59	[25]	$\bar{4}2m$
$\text{CuNH}_4\text{MoS}_4$	12	3.48–3.8	3.66	[26]	$\bar{4}$
$(\text{NH}_4)_2\text{TeS}_3$	7	3.31–3.5	3.42	[27]	1
$(\text{NH}_4)_2\text{MoS}_4$	(N1)	10	3.50–3.95	[28]	m
	(N2)	9	3.23–3.56		m
$(\text{NH}_4)_3\text{AsS}_4$	(N1)	7	3.31–3.90	[29]	m
	(N2)	7	3.30–3.66		1
$(\text{NH}_4)_2\text{Sb}_4\text{S}_7$	(N1)	8	3.28–3.88	[30]	1
	(N2)	9	3.28–3.99		1
NH_4SbS_2	(N1)	7	3.22–3.66	[31]	1
	(N2)	7	3.32–3.50		1
$(\text{NH}_4)_2[\text{MoS}(\text{S}_2)_6]$	9	3.24–3.88	3.53	[32]	1
NH_4CuS_4	11	3.31–3.84	3.52	[33]	1
$(\text{NH}_4)_2\text{S}_5$	(N1)	10	3.32–3.68	[34]	1
	(N2)	11	3.25–3.86		1
$\text{NH}_4\text{Ag}_2\text{AsS}_4$	8	3.22–3.44	3.33	[3]	$\bar{4}2m$
$\text{NH}_4\text{Ag}_2(\text{AsS}_2)_3$	9	3.42–3.81	3.60	this work	1
$(\text{NH}_4)_5\text{Ag}_{16}(\text{AsS}_4)_7$	(N1)	9	3.28–3.70	this work	1
	(N2)	8	3.23–3.55		1
	(N3)	9	3.33–3.64		1
	(N4)	9	3.39–3.75		1
	(N5)	9	3.16–3.83		1

Fourier summations. During the final stage of refinement, anisotropic displacement factors were allowed to vary in parts. The structure parameters are given in Table 2, some relevant interatomic distances are compiled in Table 3. In both structure calculations neutral complex scattering functions [9] were used. The Lorentz and polarization effects were corrected in usual ways. ($|F_o| - |F_c|$) lists were deposited at the Institute for Mineralogy and Crystallography of the University of Vienna, Austria.

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