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Synthesis of New Channeled Structures in Supercritical Amines: Preparation and Structure of $RbAg_5S_3$ and $CsAg_7S_4$

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Performing reactions in superheated solvents[1] is a useful alternative to traditional fluxes[2] or molten polychalcogenides[3] as a route to new kinetically stabilized phases. Solvents which are in their supercritical state show enhanced ability to solvate normally intractable solids, as well as a tendency to lead to well-crystallized products.[4] In addition, many common solvents have critical temperatures between 150 and 500 °C, an intermediate thermal regime containing sufficient energy for rapid reactivity but not so much as to lead to densely packed, thermodynamically stabilized products. Since we have been actively investigating the coordination chemistry of polyatomic main group anions (Zintl ions) with transition metals,[5] we began exploring the reaction of polyatomic anions with metals in supercritical solvents. It is well-known that Zintl ions are stable in amine solvents,[6] and a number of amine solvents have critical temperatures in the desired intermediate range. They are known to lead to crystal formation at high temperatures,[7] so they seemed to be a suitable point to begin our investigations. We recently used a modification of the methods of Rabenau[8] to prepare new phases such as $K_2Ag_{12}Se_7$[9] and $M_2Ag_6S_4$ (M = Na, K)[10] in supercritical ethylenediamine. In this paper we report the extension of these techniques to the reaction of silver with heavy alkali metal sulfides, leading to two new structures, $RbAg_5S_3$ and $CsAg_7S_4$,[11] both of which have unique open channeled structures.

Experimental Procedure

Syntheses After the method of Rabenau,[8] Cs_2CO_3 (90 mg, 0.28 mmol), S_8 (54 mg, 0.21 mmol), and Ag powder (30 mg, 0.28 mmol) were placed in a 10 cm long, 6.5 mm o.d. quartz tube, along with 0.70 mL of ethylenediamine (en). The tube was sealed under vacuum and placed in a high-pressure autoclave. The autoclave was counterpressured to 2200 psi to prevent explosion of the ampule, placed in a tube furnace, and heated to 300 °C for 84 h. After cooling, the ampule was broken and the resulant dark red-black rods were washed with en and THF and dried under vacuum. The rubidium analog was prepared in a similar fashion using Rb_2CO_3 (129 mg, 0.56 mmol), S_8 (63 mg, 0.25 mmol), and Ag (30 mg, 0.28 mmol) and heating the reaction mixture to 340 °C for 60 h. The dark red-black needles and polyhedra were isolated in a fashion similar to that for the cesium complex. Unit cell determinations of a number of the rods and polyhedra confirm that they are all the same products in each case. Both products can be isolated in 40–50% yields based on silver. They are moderately air and water sensitive but can be handled under mineral oil conveniently.

Table 1. Crystal Data

formula	$CsAg_7S_4$	$RbAg_5S_3$
fw	1016.24	721.00
cryst syst	tetragonal	hexagonal
space group	$P4/n$ (No. 85)	$P\bar{6}$ (No. 174)
a, Å	11.093(3)	13.389(2)
c, Å	8.538(3)	8.040(1)
V, Å^3	1050.8(7)	1248.1(4)
Z	4	6
D_{calc}, g cm^{-3}	6.42	5.76
μ, mm^{-1}	16.91	18.02
R^a	0.0504	0.0306
$R_w{}^b$	0.0646	0.0404
T, °C	21	21

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

X-ray Crystallographic Analyses. The crystals were sealed in capillaries under dry N_2. Intensity data for both compounds were measured at 21 ± 1 °C using $\omega/2\theta$ scans on a Nicolet R3mV diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Lorentz and polarization corrections and empirical absorption corrections were applied. The structures were solved by direct methods and refined by using full-matrix least-squares techniques. The cesium compound crystallizes in the centrosymmetric space group $P4/n$. Two crystallographically unique cesium ions sit on the 4-fold axis, and one of the silver atoms sits on an inversion center; the remaining atoms occupy general positions within the cell. The rubidium compound crystallizes in the noncentrosymmetric space group $P\bar{6}$. None of the other space groups with this diffraction symmetry gave meaningful structural solutions. The asymmetric unit contains a pair of silver atoms and three sulfur atoms which lie on a crystallographic mirror plane at z = 0.0 and another pair of silver atoms and three sulfur atoms which lie on a crystallographic mirror plane at z = 0.5; approximately halfway between these mirror planes are three silver atoms occupying general positions and three rubidium ions, each lying on a different 3-fold axis. Translational symmetry of the silver and rubidium atoms along the c axis (corresponding to a repeat unit of $c/2$) is broken by the approximate $\bar{3}$ symmetry relating the two groups of three sulfur atoms, leading to systematic weaknesses in the data (l = odd). The rubidium compound is structurally similar to $NaCu_5S_3$, which crystallizes in a higher symmetry space group, $P6_322$.[12] The reduced symmetry of the present compound appears to be related to differences in the fit between the metal–sulfide framework and the rubidium ions, which prevent a symmetrical coordination of the alkali metal cations. Refinements were carried out for both crystal chiralities of the rubidium compound; the reported coordinates correspond to the model which led to significantly better agreement factors. Relevant crystallographic data are given in Table 1, atomic coordinates and isotropic displacements values are given in Table 2, and significant distances and angles are listed in Tables 3 and 4.

Results and Discussion

The reactions were performed in sealed quartz ampules at high pressures and temperatures using techniques first advanced by Rabenau.[8] It is well-known that alkali metal carbonates will induce disproportionation of sulfur to sulfate and sulfides at reasonably high temperatures, and these often serve as useful sources of alkali metal polysulfides.[13] Reaction of A_2CO_3 with elemental sulfur and silver in ethylenediamine at temperatures and pressures exceeding the critical point leads to formation of the title compounds. The initial stoichiometries are as follows, but since there are a number of other products formed both in the solid phase and in solution, we cannot write a meaningful balanced equation.

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$$4Rb_2CO_3 + 3S_8 + 4Ag \xrightarrow{300\ ^\circ C/3500\ psi} RbAg_5S_3 + \text{other products}$$

$$4Cs_2CO_3 + 3S_8 + 4Ag \xrightarrow{300\ ^\circ C/3500\ psi} CsAg_7S_4 + \text{other products}$$

Both structures are extended solids made up of silver sulfide networks which form large infinite channels containing the alkali metal cations. The cesium compound contains a series of silver(I) sulfide nets which are wrapped in tubes forming an infinite stack of eight-membered rings. Four of these stacks are connected to one another by bridging silver atoms to form columns containing wide channels where the cesium cations are located (see Figure 1). The infinite stacks of eight-membered rings contain three-coordinate silver atoms in slightly distorted trigonal environments, with Ag–S distances of 2.616(4) Å and one unusually long distance of 2.950(4) Å. The bridging Ag–S distances range from 2.413(3) to 2.605(4) Å, and the bridging silver atoms are linear two-coordinate. There are formal Ag(I)–Ag(I) contacts which range from 2.961(2) to 3.087(2) Å, but these are probably not indicative

Table 2. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³)

	x	*y*	*z*	*U*(eq)[a]
		$CsAg_7S_4$		
Cs(1)	1/4	1/4	6260(2)	18(1)
Cs(2)	1/4	1/4	1220(2)	19(1)
Ag(1)	2642(1)	−1126(1)	11242(1)	25(1)
Ag(2)	2871(1)	−1072(1)	6187(1)	27(1)
Ag(3)	233(1)	−431(1)	6591(2)	36(1)
Ag(4)	0	0	1	46(1)
S(1)	1918(3)	−112(3)	8676(4)	16(1)
S(2)	1932(3)	−42(3)	3778(4)	15(1)
		$RbAg_5S_3$		
Ag(1)	3375(3)	3758(5)	1/2	35(2)
Ag(2)	3291(3)	3721(5)	0	36(2)
Ag(3)	1492(2)	3337(2)	2469(7)	34(1)
Ag(4)	5176(2)	5174(2)	2489(7)	34(1)
Ag(5)	3333(2)	2033(2)	2477(6)	32(1)
Ag(6)	−371(4)	2999(4)	1/2	40(2)
Ag(7)	−336(4)	2961(5)	0	40(2)
Rb(1)	0	0	2505(15)	24(1)
Rb(2)	1/3	2/3	2513(12)	23(1)
Rb(3)	2/3	1/3	2518(15)	23(1)
S(1)	2226(9)	1381(9)	1/2	24(4)
S(2)	5518(10)	4421(9)	1/2	25(4)
S(3)	1942(8)	4455(9)	1/2	18(4)
S(4)	1136(10)	2232(10)	0	22(4)
S(5)	4444(9)	2489(9)	0	23(4)
S(6)	4728(9)	5855(8)	0	17(4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Bond Distances (Å) and Angles (deg) for $CsAg_7S_4$[a]

	Distances		
Cs(1)–S(1)	3.615(4)	Cs(1)–S(2)	3.583(4)
Cs(2)–S(2)	3.622(4)	Cs(2)–S(1a)	3.679(4)
Ag(1)–S(1)	2.591(4)	Ag(1)–S(1b)	2.643(4)
Ag(1)–S(2c)	2.599(4)	Ag(2)–S(1)	2.601(4)
Ag(2)–S(2)	2.574(4)	Ag(2)–S(2d)	2.504(3)
Ag(3)–S(1)	2.605(4)	Ag(3)–S(2e)	2.478(3)
Ag(4)–S(1)	2.413(3)		
	Angles		
S(1)–Ag(1)–S(1b)	117.3(1)	S(1)–Ag(1)–S(2c)	114.2(1)
S(1b)–Ag(1)–S(2c)	114.7(1)	S(1)–Ag(2)–S(2)	107.9(1)
S(1)–Ag(2)–S(2d)	121.5(1)	S(2)–Ag(2)–S(2d)	123.6(1)
S(1)–Ag(3)–S(2e)	138.9(1)	S(1)–Ag(4)–S(1f)	180.0(1)
Ag(1)–S(1)–Ag(2)	112.8(1)	Ag(1)–S(1)–Ag(3)	137.8(1)
Ag(1)–S(1)–Ag(4)	84.2(1)	Ag(1)–S(1)–Ag(1g)	70.8(1)
Ag(2)–S(1)–Ag(3)	71.2(1)	Ag(2)–S(1)–Ag(4)	139.7(1)
Ag(2)–S(1)–Ag(1g)	76.7(1)	Ag(3)–S(1)–Ag(4)	72.2(1)
Ag(3)–S(1)–Ag(1g)	69.6(1)	Ag(4)–S(1)–Ag(1g)	75.1(1)
Ag(2)–S(2)–Ag(1a)	109.7(1)	Ag(2)–S(2)–Ag(2h)	74.6(1)
Ag(2)–S(2)–Ag(3e)	126.0(1)	Ag(1a)–S(2)–Ag(2h)	72.4(1)
Ag(1a)–S(2)–Ag(3e)	106.6(1)	Ag(2n)–S(2)–Ag(3e)	80.1(1)

[a] Symmetry operators: (a) *x*, *y*, 1 − *z*; (b) 0.5 + *y*, −*x*, 2 − *z*; (c) *x*, *y*, 1 + *z*; (d) 0.5 + *y*, −*x*, 1 − *z*; (e) −*x*, −*y*, 1 − *z*; (f) −*x*, −*y*, 2 − *z*; (g) −*y*, −0.5 + *x*, 2 − *z*; (h) −*y*, −0.5 + *x*, 1 − *z*.

Table 4. Bond Distances (Å) and Angles (deg) for $RbAg_5S_3$

	Distances		
Ag(1)–S(1)	2.756(12)	Ag(1)–S(2)	2.543(14)
Ag(1)–S(3)	2.519(15)	Ag(2)–S(4)	2.559(11)
Ag(2)–S(5)	2.765(16)	Ag(2)–S(6)	2.524(9)
Ag(3)–S(3)	2.417(7)	Ag(3)–S(4)	2.377(8)
Ag(4)–S(2)	2.400(10)	Ag(4)–S(6)	2.397(9)
Ag(5)–S(1)	2.404(7)	Ag(5)–S(5)	2.375(8)
Ag(6)–S(3)	2.712(10)	Ag(6)–S(1a)	2.499(12)
Ag(6)–S(2b)	2.611(7)	Ag(7)–S(4)	2.600(17)
Ag(7)–S(5a)	2.498(12)	Ag(7)–S(6b)	2.711(12)
Rb(1)–S(1)	3.288(11)	Rb(1)–S(4)	3.280(11)
Rb(2)–S(3)	3.275(9)	Rb(2)–S(6)	3.284(12)
Rb(3)–S(2)	3.274(15)	Rb(3)–S(5)	3.297(12)
	Angles		
S(1)–Ag(1)–S(2)	106.5(5)	S(1)–Ag(1)–S(3)	109.8(4)
S(2)–Ag(1)–S(3)	143.7(4)	S(4)–Ag(2)–S(5)	106.5(4)
S(4)–Ag(2)–S(6)	143.7(5)	S(5)–Ag(2)–S(6)	109.8(4)
S(3)–Ag(3)–S(4)	177.1(5)	S(2)–Ag(4)–S(6)	176.9(4)
S(1)–Ag(5)–S(5)	173.6(5)	S(3)–Ag(6)–S(1a)	126.4(5)
S(3)–Ag(6)–S(2b)	100.3(4)	S(1a)–Ag(6)–S(2b)	133.3(5)
S(4)–Ag(7)–S(5a)	133.2(4)	S(4)–Ag(7)–S(6b)	100.2(3)
S(5a)–Ag(7)–S(6b)	126.6(4)	Ag(1)–S(1)–Ag(5)	72.2(2)
Ag(1)–S(1)–Ag(6c)	119.0(4)	Ag(5)–S(1)–Ag(5e)	115.1(4)
Ag(5)–S(1)–Ag(6c)	76.3(4)	Ag(1)–S(2)–Ag(4)	74.2(4)
Ag(1)–S(2)–Ag(6d)	118.8(6)	Ag(4)–S(2)–Ag(4e)	114.5(7)
Ag(4)–S(2)–Ag(6d)	73.8(3)	Ag(1)–S(3)–Ag(3)	76.8(3)
Ag(1)–S(3)–Ag(6)	122.8(4)	Ag(3)–S(3)–Ag(6)	73.3(2)
Ag(3)–S(3)–Ag(3e)	114.7(5)	Ag(2)–S(4)–Ag(3)	73.6(2)
Ag(2)–S(4)–Ag(7)	118.6(5)	Ag(3)–S(4)–Ag(7)	73.7(4)
Ag(3)–S(4)–Ag(3f)	113.2(5)	Ag(2)–S(5)–Ag(5)	71.9(4)
Ag(2)–S(5)–Ag(7c)	119.0(4)	Ag(5)–S(5)–Ag(5f)	113.9(5)
Ag(5)–S(5)–Ag(7c)	76.1(2)	Ag(2)–S(6)–Ag(4)	76.3(3)
Ag(2)–S(6)–Ag(7d)	122.6(5)	Ag(4)–S(6)–Ag(4f)	113.3(6)
Ag(4)–S(6)–Ag(7d)	73.1(3)		

[a] Symmetry operators: (a) −*y*, *x* − *y*, *z*; (b) −*x* + *y*, 1 − *x*, *z*; (c) −*x* + *y*, −*x*, *z*; (d) 1 − *y*, 1 + *x* − *y*, *z*; (e) *x*, *y*, 1 − *z*; (f) *x*, *y*, −*z*.

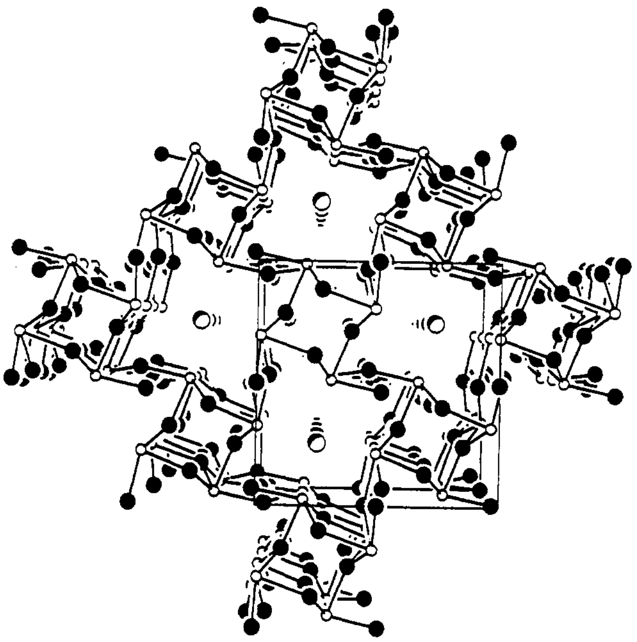

Figure 1. View of $CsAg_7S_4$ down the *c* axis showing the columns formed by the eight-membered rings stacking to form large open channels: S atoms, open spheres; Ag atoms, dark spheres; Cs atoms, shaded spheres.

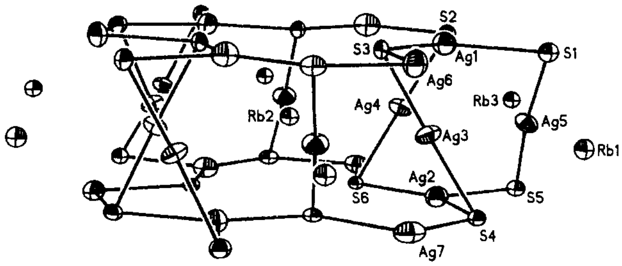

Figure 2. View of a fragment of RbAg$_5$S$_3$ showing the silver–sulfide layers joined by interlayer silver atoms, with lone Rb$^+$ ions in the same plane as the bridging silver atoms.

of bonds.[14] The eight-membered rings formed by the wrapped nets are similar to those observed previously in M$_2$Ag$_4$S$_3$ and MAg$_3$S$_2$.[15,16] However, instead of sharing edges to form infinite chains[15] or corners to form sheets,[16] the columns are bridged by independent Ag atoms to form large channels containing the Cs$^+$ ions. There are two different sulfur atoms. Those bound to the bridging silver atoms are five-coordinate, while the others are four-coordinate with a lone pair interacting with the cesium atoms in the channels. The cesium ions are eight-coordinate with Cs–S contacts of 3.583(4) and 3.679(4) Å.

The rubidium analog is considerably more unusual. It is a novel layered compound with sheets containing silver atoms coordinated in a distorted trigonal planar fashion (S–Ag–S angles range from 100.2(3) to 143.7(4)°) by sulfides to form a series of fused 12-membered rings (see Figure 2). Between the sheets are other silver atoms which are linearly coordinated (173.6(5)–177.1(5)°) by sulfides to link the sheets together (see Figure 3). The sheets are related by a $\bar{6}$ operation, forming infinite columns which are effectively lined with sulfides and contain the Rb(I) cations (average Rb–S distance is 3.283(9) Å). These cations lie between the silver sulfide planes and are in an irregular six-coordinate environment with respect to the sulfides. The planar Ag–S distances range from 2.50(1) to 2.76(2) Å, and the interplanar Ag–S distances range from 2.375(8) to 2.417(7) Å. As in the cesium compound, all of the silver atoms are formally 1+ (Ag(I)–Ag(I) distances range from 2.961(6) to 3.072(6) Å). It is known that d^{10}–d^{10} interactions can be somewhat complex, and there is a model proposed to account for closed-shell bonding.[14] However, it unclear whether the distances in the metal sulfide infrastructure are due to metal–metal interactions or are merely an artifact of the bridging sulfides.

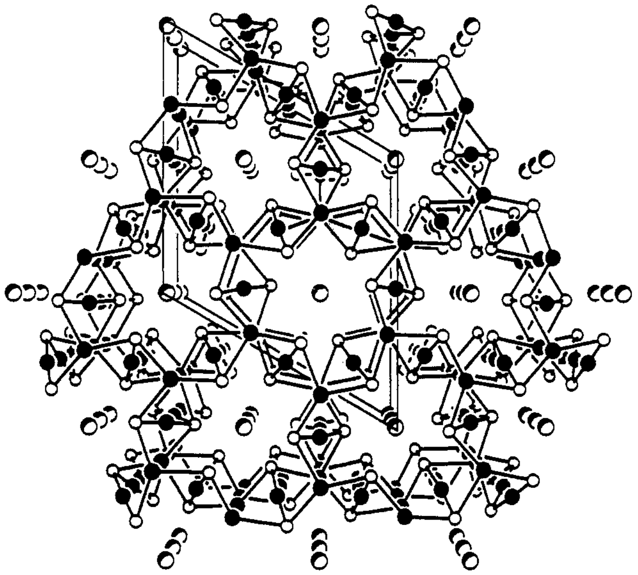

Figure 3. View of RbAg$_5$S$_3$ down the *c* axis showing columns containing Rb$^+$ ions: S atoms, open spheres; Ag atoms, dark spheres; Rb atoms, shaded spheres.

In both structures, there is a tightly held silver sulfide framework which creates infinite tunnels containing the alkali metal cations. Both compounds contain channels which are quite large (greater than 6 Å across and nearly 7 Å in the case of the rubidium), and the Ag–S framework appears to be self-supporting. We do not yet understand the reason for the substantial structural difference between the two phases. We also recently isolated a potassium analog of the rubidium phase which is essentially isostructural.[17] Since the effective ionic radius of eight-coordinate cations increases from 1.51 to 1.61 to 1.74 Å for potassium to cesium,[18] the role of the counterion in determining the structure is unclear. However, the ability of the metal sulfide superstructure to accommodate a variety of differently sized counterions raises the possibility of preparing microporous solids by this methodology.

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Supplementary Material Available: Tables of complete crystallographic data, all bond distances and angles, and anisotropic thermal parameters for both compounds and an ORTEP diagram of a fragment of the Cs compound (6 pages). Ordering information is given on any current masthead page.

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