Synthesis of $M_2Ag_6S_4$ (M = Na, K) in Supercritical Ethylenediamine Solvent: a Novel Solid containing Unusual Closed-shell Bonding

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A novel solid $M_2Ag_6S_4$ (M = Na, K) has been synthesized in supercritical ethylenediamine, and has an unusual framework structure with an extended array of face-sharing silver octahedra

The preparation of solid state compounds in superheated solvents is an old but somewhat undeveloped technique.[1] Solvents begin to take on especially intriguing properties when the temperature and pressure conditions exceed their critical values and the solvent enters the supercritical state. Methodology has recently been developed whereby a wide variety of solvents can be employed above their boiling points as media for the synthesis of well crystallized solids.[2] Water is the most common superheated solvent, and is used extensively for the industrial crystallization of normally intractable solids such as quartz,[1] microporous solids,[3] and even metal chalcogenides.[4] Other solvents such as methanol and ammonia have also been useful for the preparation of main-group polymers[5] and close-packed compounds.[6]

We are particularly interested in developing chemistry in supercritical amines. One attractive feature of supercritical amine solvents is that their critical temperature is usually between 150 and 400 °C. The thermal region is cool enough to inhibit the formation of dense thermodynamically stable phases. Thus we anticipate that chemistry under these conditions could lead to isolation of kinetically stabilized solids. In attempting to prepare solids containing new transition metal–main group element combinations, we have been investigating the reaction of alkali-metal salts of main-group clusters (Zintl phases) with various transition metals and their salts.[7]

In this communication we report a novel alkali metal silver sulfide phase, $M_2Ag_6S_4$ (M = Na, K) with an unusual framework, prepared from the reaction of M_2S, elemental sulfur and silver powder in supercritical ethylenediamine (en).† It appears to be crucial that the solvent be in the supercritical state as reactions at subcritical temperatures led only to powdery amorphous products. The potassium reaction also contains black rods which are a hexagonal phase that we have thus far been unable to characterize structurally.

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† The new solids were prepared by a variation of the method of Rabenau.[2] Thus $Na_2Ag_6S_4$ was prepared by combining 22 mg (0.289 mmol) Na_2S, 44 mg (1.375 mmol) S and 30 mg (0.28 mmol) Ag powder in 0.7 ml of en in a ¼ inch quartz tube (1.4 ml vol) and sealed under vacuum. Since this amount of en exceeds the critical density ($\rho_c = 0.29$ g ml^{-1}), heating the tube to a value near its critical temperature (320 °C) will generate a supercritical fluid within the ampule. The tube was placed in a high-pressure autoclave which was counterpressured to 2400 psi (1 psi $\approx 6.89 \times 10^3$ Pa) with argon, placed in a tube furnace and heated to 300 °C for six days. The products were isolated and washed with several aliquots of dry en and tetrahydrofuran under argon, and isolated as well formed dark red–black octahedra which are air and water stable over several hours. The yield can be as high as 80% based on silver. The potassium compound is prepared in the same fashion.

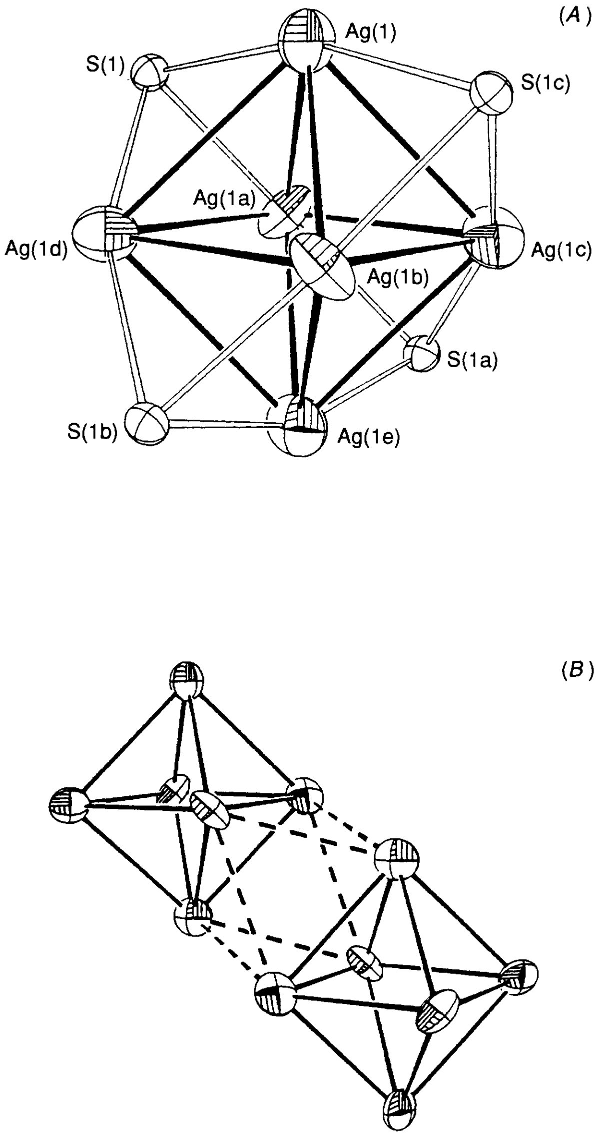

Fig. 1 (A) ORTEP view (50% probability) of the basic octahedral building block of $M_2Ag_6S_4$. Symmetry operators: (a) z, x, y; (b) $z, 1/4 - x, 1/4 - y$; (c) y, z, x; (d) $1/4 - y, z, 1/4 - x$; (e) $1/4 - x, 1/4 - y, z$. (B) View showing how the octahedra face share to generate a trigonal antiprism.

The $M_2Ag_6S_4$ compounds have been characterized by crystallography and are isostructural.‡ The framework is built up of octahedra of silver atoms situated about crystallographic $\bar{4}3m$ sites with four opposite faces capped by sulfur atoms (Fig. 1). The Ag atoms lie on $2mm$ sites and the S atoms on $3m$ sites. For the potassium salt, the Ag–Ag distance within the octahedra is 3.085(1) Å with an Ag–S distance of 2.477(1) Å. The octahedra are linked together on all the uncapped faces by longer Ag–Ag distances of 3.331(1) Å, forming uncapped prolate octahedra or trigonal antiprisms [Fig. 1, (*B*)]. This face sharing generates an infinite three-dimensional lattice with orthogonal channels lined by sulfur atoms. Since each cluster is linked to another *via* opposite faces of the octahedra, a line connecting the centre of all octahedra forms the diamond lattice (heavy line in Fig. 2). The pseudo-octahedral holes ($\bar{3}$ sites) are occupied by the alkali metal ions, which, in the case of potassium, form six bonds to the face capping sulfur atoms of 2.910(2) Å [with S–K–S angles of 82.6(1)°]. Although the silver–sulfur lattice appears to create an open architecture, the relatively short sulfur–alkali-metal contacts imply a fairly closely packed structure. Several phases with the same empirical formula MAg_3S_2, have been prepared using high-temperature methods, where M is Tl,[8] Rb and Cs,[9] but none have the structure described here. (Attempts to prepare the analogous potassium compound by these workers resulted in formation of $K_2Ag_4S_3$ containing chains of linked eight-membered rings.[10])

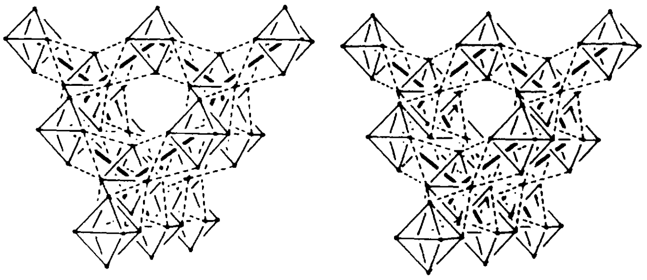

Fig. 2 Extended stereoview showing the channels generated by the packing of the octahedral building blocks of $M_2Ag_6S_4$, with heavy line emphasizing the centres of the octahedra forming the diamond lattice

It is known that d^{10}–d^{10} interactions are often quite complex.[11] In these new compounds there does appear to be substantial Ag–Ag interactions despite the fact that they are all formally Ag^I. The formation of the face-capped octahedra could be readily understood as being stabilized by the μ^3 sulfides, but the framework is formed *via* unbridged Ag–Ag interactions. The unbridged interoctahedral distance is somewhat long (3.33 *vs.* 2.883 Å in Ag metal). However, there can be no doubt that there is some Ag–Ag interaction holding the clusters together, as it would seem unlikely that such a dense, well-ordered structure would be formed on the basis of the alkali cation–sulfur interactions. There are also a number of close packed silver octahedra known containing less valence electrons.[12]

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‡ *Crystal data* for $K_2Ag_6S_4$ at 294 K: a = 12.318(1) Å, V = 1869.1(6) Å^3, Z = 8, D_c = 6.07 g cm^{-3}, space group $Fd\bar{3}m$ (no. 227). Of the 615 reflections collected (Mo-Kα, 3.5 < 2θ < 55°), 130 were unique (R_{int} = 0.060) and the 112 having $F > 6\sigma(F)$ were used in the refinement. All atoms were refined anisotropically. Final residuals are $R(F)$ = 0.032 and $R_w(F)$ = 0.043. The sodium analogue is isostructural. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

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