

## Synthesis of New Low-Dimensional Quaternary Compounds, $\text{KCu}_2\text{AsS}_3$ and $\text{KCu}_4\text{AsS}_4$ , in Supercritical Amine Solvent. Alkali Metal Derivatives of Sulfosalts

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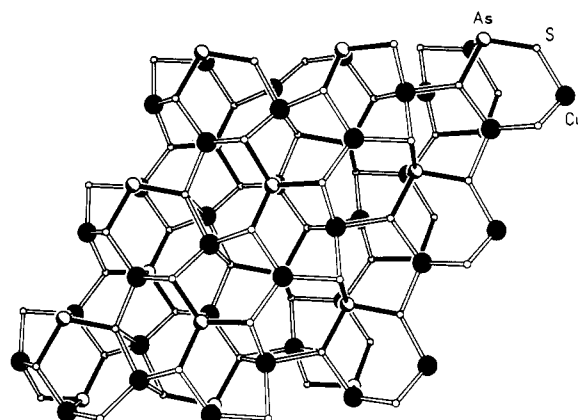
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One of the goals of modern solid-state chemistry is to prepare new compounds at relatively low temperatures.<sup>1</sup> Our approach to this problem has been to use supercritical solvents as reaction media. The supercritical phase has a number of unique properties which make it especially suitable for the purpose of preparing new solids.<sup>2</sup> It generally has a very low viscosity, which often leads to very good crystal growth. In addition, the critical temperature of many polar solvents is often in the desired intermediate thermal region (200–500 °C). Nonaqueous solvents are excellent media for the preparation of a wide variety of new phases.<sup>3,4</sup> We have been extending ideas by using supercritical amines as reaction media for the preparation of a number of ternary alkali metal–transition metal sulfides and selenides.<sup>5–7</sup> To further develop this technique, we were attracted to the use of mixed group 15/16 anions as the source of reactant and mineralizer. This system is interesting because the trivalent nature of the group 15 elements and the increased connectivity should lead to a great increase in structural variety.<sup>8</sup> In this paper we report the initial realization of these expectations with the preparation of two new quaternary phases,  $\text{KCu}_2\text{AsS}_3$  and  $\text{KCu}_4\text{AsS}_4$ , via the reaction of the ternary compound  $\text{KAsS}_2$  with copper powder in supercritical ethylenediamine.

The title compounds were prepared by combining  $\text{KAsS}_2$ , copper powder, and elemental sulfur in various ratios in supercritical ethylenediamine for several days. The resultant reaction mixtures usually contained a mixture of black, red-orange, and pale orange crystals. The black crystals were predominantly rodlike and proved to be a mixture of  $\text{Cu}_2\text{S}$ , As, and  $\text{KCu}_3\text{S}_2$ <sup>9</sup> by X-ray powder diffraction. In most reaction mixtures the product was predominantly a mixture of red-orange prisms and pale orange plates of the two title compounds,  $\text{KCu}_2\text{AsS}_3$  and  $\text{KCu}_4\text{AsS}_4$ , respectively.<sup>10</sup> These two crystal types could easily be separated manually from the black mixture and each other under a protective layer of mineral oil. Both of the title compounds are reasonably air and water stable and were characterized by single-crystal X-ray diffraction, powder diffraction, far-IR, and semiquantitative EDAXS.

The red-orange material proved to have the empirical formula  $\text{KCu}_2\text{AsS}_3$ , and the X-ray study showed it to contain a unique layered structure.<sup>11</sup> Each layer is a complex structure consisting of formal Cu(I) ions linked in a complicated manner by a series of trigonal  $\text{AsS}_3^{3-}$  groups (Figure 1). Thus Cu(3) and Cu(4) are approximately tetrahedrally coordinated by four sulfur atoms while Cu(1) and Cu(2) are approximately tetrahedrally coordinated by three sulfur atoms and the lone pair from the arsenic atom of an  $\text{AsS}_3^{3-}$  group. The two copper atoms that are bound

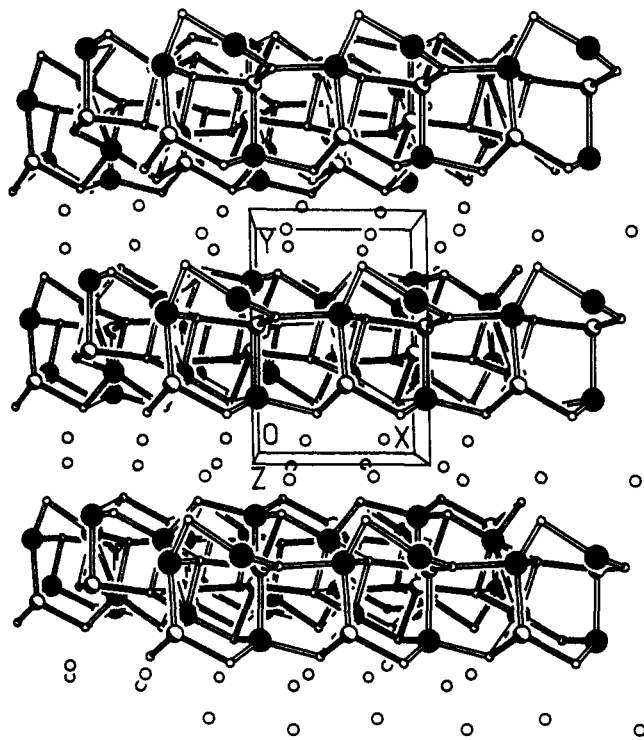


**Figure 1.** View of  $\text{KCu}_2\text{AsS}_3$  down the  $b$  axis showing the copper arsenic sulfide connectivity in a layer: copper atoms, large filled spheres; arsenic atoms, shaded spheres; sulfur atoms, small open spheres. Note that the As–S connectivity is highlighted by filled lines.

only by sulfur atoms (Cu(3) and Cu(4)) are also brought into close proximity to symmetry-equivalent copper atoms by two sulfides S(5) and S(3), which act as bridging ligands. The Cu–Cu distances are 2.803(2) and 3.011(3) Å, and these distances are probably a result of the bridging ligand rather than any  $d^{10}$ – $d^{10}$  Cu(I) interaction.

- (1) Stein, A.; Keller, S. W.; Mallouk, T. E. *Science* **1993**, *259*, 1558.
- (2) Laudise, R. A. *Chem. Eng. News* **1987**, *65* (Sept 28), 30.
- (3) Rabenau, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1026.
- (4) Jacobs, H.; Schmidt, D. *Curr. Top. Mater. Sci.* **1982**, *8*, 381.
- (5) Wood, P. T.; Pennington, W. T.; Kolis, J. W. *J. Chem. Soc., Chem. Commun.* **1993**, 235.
- (6) Wood, P. T.; Pennington, W. T.; Kolis, J. W. *Inorg. Chem.*, in press.
- (7) Wood, P. T.; Pennington, W. T.; Kolis, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 9233.
- (8) (a) Schäfer, H. *Annu. Rev. Mater. Sci.* **1985**, *15*, 1. (b) Schäfer, H.; Eismann, B. *Rev. Inorg. Chem.* **1981**, *3*, 29.
- (9) Burschka, C.; Bronger, W. *Z. Naturforsch.* **1977**, *32b*, 11.

- (10) Visual inspection reveals that both compounds are usually present regardless of conditions. The preparations given represent those providing maximized yield of each product. Semiquantitative EDAXS on individual single crystals indicates approximately correct elemental ratios for each compound. The starting material “ $\text{KAsS}_2$ ” was prepared by stirring stoichiometric amounts of the elements in liquid ammonia at  $-78$  °C for 6 h. Synthesis of  $\text{KCu}_2\text{AsS}_3$ : A mixture of  $\text{KAsS}_2$  (70 mg, 0.39 mmol), Cu powder (25 mg, 0.39 mmol), and S (6 mg, 0.19 mmol) was combined in a 7 mm o.d. quartz tube which was then filled to 40% capacity with freshly distilled en. The tube was frozen, sealed under vacuum, and placed in a high-pressure autoclave. The interior of the autoclave was counterpressured to 2500 psi with an inert gas to prevent the quartz tube from bursting, and the entire apparatus was heated to 300 °C in a tube furnace for 6 days. The reaction tube contained a mixture of black and red-orange crystals, as well some gray powder. The tube was opened, the en was decanted off, and the solids were washed with water. This did not affect the orange and black crystals but cleanly removed the gray solid. The red-orange crystals were separated manually under a layer of mineral oil, and the yield of title compound was 35% based on copper. IR (Nujol mull): 625 (m), 414 (m), 339 (w), 260 (w), 212 (m), 197 (m), 110  $\text{cm}^{-1}$  (m). Synthesis of  $\text{KCu}_4\text{AsS}_4$ : A mixture of  $\text{KAsS}_2$  (50 mg, 0.28 mmol), Cu powder (18 mg, 0.28 mmol), and elemental sulfur (13 mg, 0.41 mmol) was combined in a 1.4-mL quartz tube with 0.6 mL of en, and the resultant mixture was treated as described above. It was heated at 350 °C for 3 days. After workup and washing with water, orange crystals of  $\text{KCu}_4\text{AsS}_4$  could be isolated in approximately 12% yield by manual separation from the black crystals and red crystals of  $\text{KCu}_2\text{AsS}_3$ . IR (Nujol mull): 629 (m), 332 (w), 259 (m), 186 (m), 111  $\text{cm}^{-1}$  (m).
- (11) Crystallographic details for  $\text{KCu}_2\text{AsS}_3$  (Syntex P21 diffractometer, graphite-monochromated Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å,  $T = 21$  °C): triclinic  $P\bar{1}$ ,  $a = 6.270(1)$  Å,  $b = 8.942(2)$  Å,  $c = 10.281(1)$  Å,  $\alpha = 90.72(1)^\circ$ ,  $\beta = 91.47(1)^\circ$ ,  $\gamma = 91.06(1)^\circ$ ,  $V = 576.1$  Å<sup>3</sup>,  $Z = 4$ ,  $D_{\text{calc}} = 3.89$  g/cm<sup>3</sup>,  $\mu = 14.74$  mm<sup>-1</sup>, empirical absorption correction (transmission factors 0.75–1.00), 2036 total reflections, 2029 unique reflections ( $R_{\text{int}} = 0.028$ ), 1686 observed reflections ( $I > 3\sigma(I)$ ),  $R = 0.0388$ ,  $R_w = 0.0516$ . Crystallographic details for  $\text{KCu}_4\text{AsS}_4$  (Nicolet P3 diffractometer, graphite-monochromated Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å,  $T = 21$  °C): monoclinic  $P2_1$ ,  $a = 6.636(2)$  Å,  $b = 6.396(1)$  Å,  $c = 9.579(2)$  Å,  $\beta = 103.48(2)^\circ$ ,  $V = 395.4$  Å<sup>3</sup>,  $Z = 2$ ,  $D_{\text{calc}} = 4.17$  g/cm<sup>3</sup>,  $\mu = 16.24$  mm<sup>-1</sup>, empirical absorption correction (transmission factors 0.55–1.00), 842 total reflections, 769 unique reflections ( $R_{\text{int}} = 0.022$ ), 725 observed reflections ( $I > 3\sigma(I)$ ),  $R = 0.0343$ ,  $R_w = 0.0428$  ( $R = 0.0381$ ,  $R_w = 0.0477$  for incorrect enantiomer).

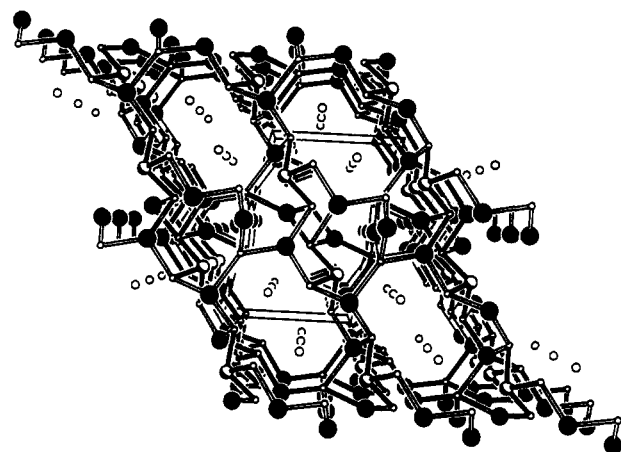


**Figure 2.** View of  $\text{KCu}_2\text{AsS}_3$  down the  $c$  axis showing the corrugated copper arsenic sulfide layers with  $\text{K}^+$  ions between the layers (atom types same as above).

Each arsenic is bound to three sulfur atoms and one copper, also in a tetrahedral environment. The As–S distances are all quite similar and range from 2.257(2) to 2.295(2) Å and average 2.269 Å. This distance is typical for As(III)–S distances in metal arsenic sulfides (between 2.25 and 2.28 Å)<sup>12</sup> but is considerably longer than the typical As(V)–S distances (2.16(2) Å in  $\text{K}_3\text{AsS}_4$ , for example).<sup>13</sup> Four of the sulfur atoms (S(1), S(2), S(4), S(6)) are each bound to two copper atoms and an arsenic atom and are pyramidal, with a lone pair occupying the apical position. The other two sulfur atoms (S(3), S(5)) are each tetrahedral and are bound to three copper atoms and an arsenic. These are the two sulfur atoms responsible for bridging to the copper atoms linking the  $\text{CuAsS}_3$  layers together.

The overall effect of such extensive interactions is the formation of two parallel hexagonal nets linked together by As–Cu and Cu–S–Cu bonds (Figure 2). The layers are crenelated, ensuring that the lone pairs of the sulfur atoms (S(1), S(2), S(4), S(6)) point out of the layers toward the potassium ions located between the layers. The slabs stack along the  $b$  axis and are separated by approximately 6.2–6.3 Å. Solids formed by metal centers linked by pyramidal group 15 sulfide anions ( $\text{ES}_3^{3-}$ ) are called sulfosalts and are very well-known in mineralogy.<sup>14</sup> To our knowledge, however, this is the first example of an alkali metal derivative of a sulfosalt. A compound with the parent formula  $\text{Cu}_3\text{AsS}_3$  has been described, although it actually has the formula  $\text{Cu}_{12}\text{As}_4\text{S}_{13}$  and is a member of the tetrahedrite family.<sup>15</sup> However, the structure is an unusual one based on chalcopyrite with several tetrahedral sulfur atoms removed to octahedral holes. The tetrahedrite family is an extensive and complex class of mineral compounds containing many interstitial derivatives,<sup>16</sup> and there is some doubt that the ideal formulations  $\text{M}_{12}\text{E}_4\text{S}_{13}$  are

- (12) (a) Sommer, H.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1977**, *430*, 199. (b) Berry, L. G. *Am. Miner.* **1965**, *50*, 301.  
 (13) Palazzi, M.; Jaulmes, S.; Laruelle, P. *Acta Crystallogr.* **1974**, *B30*, 2378.  
 (14) (a) Hellner, E. *J. Geol.* **1958**, *66*, 503. (b) Takeuchi, Y.; Sadanaga, R. *Z. Kristallogr.* **1969**, *130*, 346.  
 (15) (a) Pauling, L.; Neumann, E. W. *Z. Kristallogr.* **1934**, *88*, 54. (b) Wuensch, B. J.; Takeuchi, Y.; Nowacki, W. *Z. Kristallogr.* **1966**, *123*, 1.  
 (16) Wuensch, B. J. In *Sulfide Mineralogy*; Ribbe, P. H., Ed.; Mineralogical Society of America: Washington DC, 1974.



**Figure 3.** View of  $\text{KCu}_4\text{AsS}_4$  showing the rows of alternating  $\text{AsS}_3$  tetrahedra linked by copper sulfide chains to create large tunnels occupied by two rows of  $\text{K}^+$  ions: atom types same as above. Again note the  $\text{AsS}_3^{3-}$  groups highlighted by filled bonds.

even stable.<sup>17</sup> The added electrons provided by the alkali metal appear to reduce the sulfosalt framework, leading to formation of the two-dimensional solid, with intercalated  $\text{K}^+$  ions.

The pale orange crystals of formula  $\text{KCu}_4\text{AsS}_4$  have an extremely complex structure with copper ions ligated by  $\text{AsS}_3^{3-}$  groups as well as  $\text{S}^{2-}$  ions. The  $\text{AsS}_3^{3-}$  groups are bound to copper atoms through the sulfur atoms, creating a layered structure with the pyramids of the  $\text{AsS}_3^{3-}$  groups alternating up and down (Figure 3). Unlike those in  $\text{KCu}_2\text{AsS}_3$ , the lone pairs of the arsenic are not involved in bonding to any copper atoms. The slabs are linked by infinite zigzag chains of  $\text{CuS}_2$  in a complex fashion. These connections linking the slabs create infinite oval-shaped channels in which the  $\text{K}^+$  cations reside. Each channel contains two rows of cations which appear on alternate sides of the oval as the channels translate along the  $b$  axis.

Each copper atom is in a very irregular coordination environment. The Cu ions within the slabs are ligated by  $\text{AsS}_3^{3-}$ , and each is coordinated by three or four sulfur atoms, while the Cu atoms in the  $\text{CuS}_2$  chains are two-coordinate and nearly linear (S–Cu–S angle 166.4(1)°). If each arsenic trisulfide group is assigned as a trianion ( $\text{AsS}_3^{3-}$ ), then the presence of the sulfide group and the  $\text{K}^+$  ion suggests that each copper is formally Cu(I). However, unlike  $\text{KCu}_2\text{AsS}_3$ , this compound contains extensive Cu–Cu interactions. The distances range from 2.6060(2) to 3.007(2) Å, and there are a number of such contacts involving each Cu. These Cu–Cu distances are quite short, but the light orange color and lack of metallic luster of the crystals suggest there is not substantial d<sup>10</sup>–d<sup>10</sup> bonding.<sup>18</sup> The  $\text{K}^+$  ions are in a very irregular coordination environment with contacts to five sulfur atoms ranging from 3.148(4) to 3.363(5) Å.

The appearance of two such novel solids from the same reaction mixture suggests that groups like  $\text{QE}_3^{3-}$  and  $\text{QE}_4^{3-}$  (Q = group 15 element, E = chalcogen) are excellent building blocks for new low-dimensional solids, leading to new synthetic derivatives of sulfosalts. In addition, the presence of a sulfide ion as well as a sulfosalt anion in the framework is very rare and suggests that an even greater number of new low-dimensional solids could be prepared by this methodology.

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**Supplementary Material Available:** Tables of complete crystallographic data, positional and anisotropic thermal parameters, and complete distances and angles for both compounds (9 pages). Ordering information is given on any current masthead page.

- (17) Tatsuka, K.; Morimoto, N. *Am. Mineral.* **1973**, *58*, 425.  
 (18) (a) Jansen, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1098. (b) Cui, C. X.; Kertesz, M. *Inorg. Chem.* **1990**, *29*, 2568.