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Synthesis of a Novel Open-Framework Sulfide, $\mathrm{CuGe_2S_5{\cdot}(C_2H_5)_4N}$, and Its Structure Solution Using Synchrotron Imaging Plate Data

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Open-framework sulfides are potentially useful materials for separation, ion exchange, catalytic, and optical applications.[1−3] These low-density kinetically stabilized phases often possess large pore volumes and typically crystallize either as powders or as small crystals, unsuitable for conventional X-ray diffractometry. The consequent lack of structural information has hampered an understanding of the chemistry of these systems. For example, hydrothermal treatment of slurries containing organic amines, transition metals, and germanium sulfide results in a new family of frameworks (MeGS).[1,4] Different structure types are produced when the amine or/and the transition metal are changed. Meaningful discussion of the roles of these modifiers requires accurate single-crystal structure determinations.

Recent innovations in synchrotron imaging plate technology, instigated in the protein crystallography community,[5] can also be applied to inorganic compounds. Here, we report the synthesis of a new copper germanium sulfide. Its structure was determined from synchrotron imaging plate data, which were collected at low temperature using a closed-cycle helium refrigerator. This data set was expected to aid in better defining the relationship between the organic template and the sulfide framework. This compound, $\mathrm{CuGe_2S_5{\cdot}(C_2H_5)_4N}$, has a diamond-like framework and results from the polymerization of $\mathrm{Ge_4S_{10}}^{4-}$ tetrahedral clusters bridged by 2-coordinated Cu(I) cations. The tetraethylammonium (TEA) template cations reside within the openings of this framework.

In a typical preparation, freshly precipitated amorphous $\mathrm{GeS_2}$ (0.2 g), $\mathrm{TEAHCO_3}$ solution (0.58 g, prepared by bubbling $\mathrm{CO_2}$ into 40% TEAOH solution until pH = 9.7), $\mathrm{Cu(CH_3COO)_2{\cdot}H_2O}$ (0.03 g), and water (0.2 g) were slurried together. The mixture was heated at 150 °C under autogenous hydrothermal conditions in a Pyrex-lined bomb for 1 day. Colorless tetragonal needle-shaped crystals were recovered by washing with water and ethanol and dried in air. The yield was 55% based on copper. The powder X-ray diffraction pattern suggested a unique structure type, which we designated TEA-CuGS-SB1 consistent with the nomenclature adopted in patent literature.[1] A small portion of $\mathrm{GeO_2}$ was found in the product, the strongest peak for this phase in the X-ray powder diffraction pattern being less than 5% of the strongest peak for TEA-CuGS-SB1. In some batches, several shapeless crystals less than 40 μm in dimension were characterized to be orthorhombic α-$\mathrm{S_8}$ by the microprobe analysis and single-crystal diffraction.

Electron probe microanalysis indicated the presence of Cu, Ge, and S in a 1:2:5 molar ratio. Chemical analysis for the elements S, C, N, and H gave weight percentages of 32.56, 20.17, 2.70, and 3.72, respectively; these values are consistent with those expected from the following crystal structure determination (32.12, 19.25, 2.80, and 4.01 wt %). The IR spectrum between 4000 and 625 cm^{-1} contains only the characteristic features attributable to the TEA$^+$ ion.[6] This spectrum was recorded from 4000 to 400 cm^{-1} on a Perkin-Elmer 1600 Series FTIR spectrophotometer using KBr pellets. Another absorption peak, at 430 cm^{-1}, could not be unambiguously assigned because of the distribution of both Ge−S and Cu−S vibration modes around 400 cm^{-1}.[7,8] Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer thermal analysis system. A 1.8 mg sample was heated in air at the rate of 2.0 °C/min from room temperature to 400 °C. Two distinct steps of weight loss were observed: a 13.3% loss from 250 to 290 °C and a further 16.7% decrease in weight between 290 to 360 °C.

A crystal, about 0.02 × 0.02 × 0.1 mm, was mounted on a fiber of 0.02 mm diameter and analyzed at the X3A beamline of the National Synchrotron Light Source (NSLS) using an imaging plate (IP) as a detector. A sideways scattering triangular Si(111) single-crystal monochromator was used (λ = 0.643 Å).[9] The experiment was performed in a closed-cycle helium refrigerator (DISPLEX CT-211) mounted on a HUBER 511.1 four-circle diffractometer. The temperature of the cold "finger", 16 mm away from the sample, was 16 K.[10] The crystal's temperature was estimated to be 50 ± 3 K using independent measurements of the phase transition in $\mathrm{NiTa_2Se_7}$ at 52.5 K.[11]

Each image was processed first to obtain the refined crystal-to-plate distance and the IP tilt angles.[12] Five of the 46 images were discarded due to unreasonable offsets. The final integration of the peak intensities was performed with the program HIPPO.[13] Only fully recorded reflections were used, those close to the oscillation axis and oscillation boundaries being discarded. A total of 9504 reflections with $I > 1.0\sigma(I)$ were integrated using the "seed-skewness" method.[13] They were merged using the program SORTAV.[14]

The structure[15] consists of four-connected $\mathrm{Ge_4S_{10}}^{4-}$ tetrahedral clusters, whose centers are located at the nodes of a diamond-

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(6) (a) Peak positions in cm^{-1}: 2950.6 (m), 1448.2 (s), 1393.9 (m), 1366.8 (w), 1300.2 (m), 1180.6 (s), 1122.1 (w), 1078.5 (m), 1033.7 (m), 1002.8 (s), and 790.2 (s); s, strong; m, medium; w, weak. (b) *The Aldrich Library of Infrared Spectra*; IIIrd ed.; Pouchert, C. J., Ed.; Aldrich Chemical Company Inc.: Milwaukee, 1981.

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(10) An antiscatter device was employed to eliminate the parasitic scattering arising from the interaction of the direct synchrotron beam with the Be-vacuum shroud.[26] An IP cassette with a HR-V-type imaging plate, 201 × 252 mm in size, was mounted on the detector arm replacing the scintillation counter. This made a variable crystal-to-plate distance and an adjustable 2θ offset angle possible. In this experiment, the distance and the angle were set to 136 mm and 0°, respectively. The crystal made two oscillations during the 3 min exposures with a 2° overlap between the consecutive scans of 10° each. A total of 23 imaging plates for one data set, covering 186° of rotation, were processed with a BAS-2000 FUJI scanner. In order to overcome the scanner's intrinsic limitation in dynamic range and to adequately measure the weak and strong reflections, two images were taken at every oscillation range and read with different sensitivities. Additionally, to obtain an accurate orientation matrix and cell parameters at low temperature, a set of 27 reflections with 2θ angles in the range 11−30° was measured with a scintillation counter.

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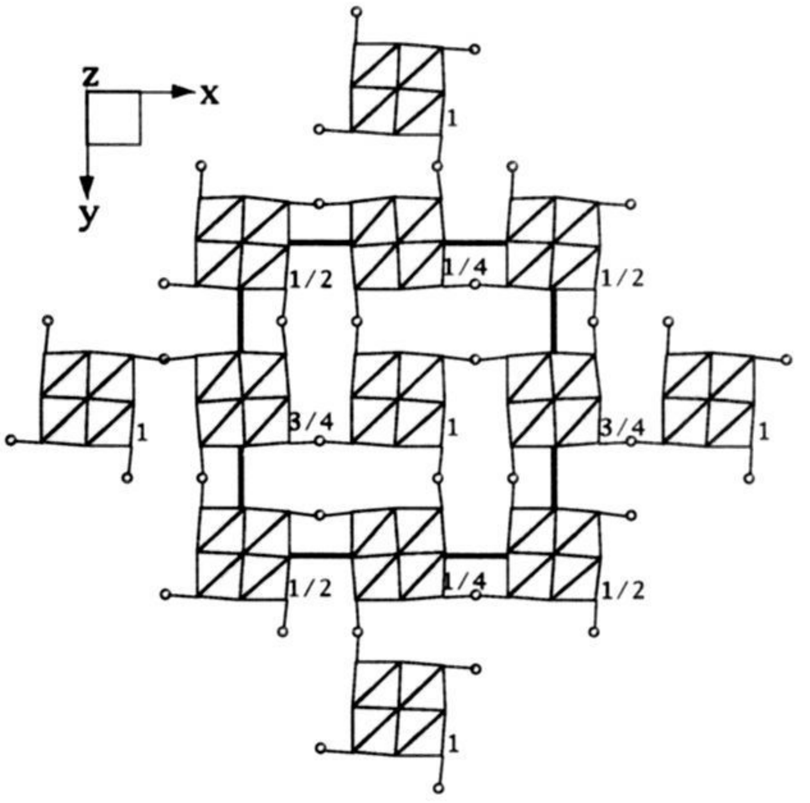

Figure 1. Unit cell content of TEA-CuGS-SB1 in projection on the (001) plane as outlined by the dark solid lines. $Ge_4S_{10}^{4-}$ polyhedra are drawn with the *z* coordinate of their centers displayed. Cu(I) atoms are represented by open circles.

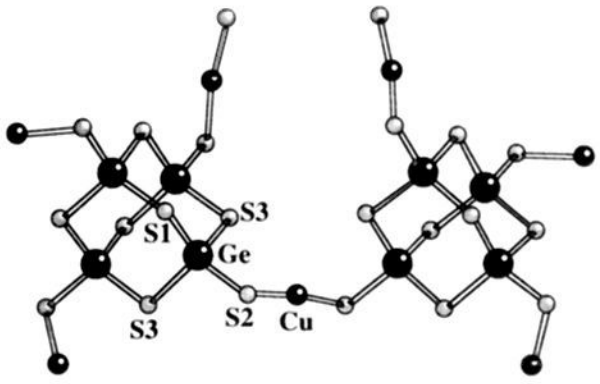

Figure 2. The two crystallographically equivalent $Ge_4S_{10}^{4-}$ clusters connected by 2-coordinated Cu(I).

like framework (Figure 1).[16] The tetrahedra are bridged linearly via reduced Cu(I) as shown in Figure 2. The assignment of the Cu(I) was made on the basis of the geometry of the S−Cu−S linkage (172.0°)[17] and the bond strength,[18] 1.073; the latter may be slightly overestimated since the data was collected at low temperature. This indicates that Cu(II) added to the starting material was reduced during hydrothermal treatment.

The $Ge_4S_{10}^{4-}$ species has been found as a secondary building unit in compounds produced from solid state reaction, hydrothermal synthesis, and solution diffusion.[7,19] In recent years, the latter two methods have been adapted to explore microporous materials based on this adamantine-like cluster (Figure 2). Starting from isolated $Ge_4S_{10}^{4-}$ monomers, there are two ways to build frameworks. One is through self-condensation, as in the structure of $Cs_4Ge_4S_{10}$ where two $Ge_4S_{10}^{4-}$ units share a corner.[20] Recently, a new compound synthesized in the presence of dipropylamine has been found to consist of zigzag chains of $Ge_4S_{10}^{4-}$ [21] akin to the ionosilicates.[22] In these systems, alkali metals or alkaline earth metals as well as organic molecules behave as counterions to the negatively charged clusters or chains.

These monomers can also be induced to condense through the introduction of transition metals. Two other open-framework germanium sulfides have been reported utilizing this strategy.[4,23] Like TEA-CuGS-SB1, they are also built from four-connected $Ge_4S_{10}^{4-}$ anions linked by transition metals. However, in TMA-CoMnGS-2,[4] each metal atom (Co or Mn) connects three $Ge_4S_{10}^{4-}$ clusters. In the compound obtained by using manganese only to join the tetrahedra,[23] the metal atom is four connected with S−Mn−S angles of 102.53° or 124.47°. Interestingly, their structures are different although the organic templates added as structure-directing agents were the same. In TEA-CuGS-SB1, the S−Cu(I)−S angle (172.0°) is almost linear. Considering the diversity of transition metal−sulfur bonding,[17] introduction of different metals can lead to different ways of bridging the $Ge_4S_{10}^{4-}$ tetrahedra to produce a variety of structures. The structure-directing role for the transition metals in the sulfides differs from that of alkali− and alkaline earth−metal templates used in the synthesis of zeolite molecular sieves. The latter are not incorporated into the framework.[24]

With the aid of the synchrotron imaging plate system, the structure determinations of other compounds in the MeGS system are in progress. Prediction of these structures and design of new materials in this series are possible based on the rigidity of the $Ge_4S_{10}^{4-}$ cluster, geometric limitation on the Me−S−Me angle, and the coordination of the transition metal. Also critical are the shape, size, and charge of particular organic molecules, which can be fitted into framework openings.[24,25] In the copper germanium sulfide system, for example, two other structure types, analogous to TMA-CoMnGS-2[4] and $MnGe_4S_{10}{\cdot}2\text{-}(CH_3)_4N$,[23] are possible using 4-coordinated Cu. Each of them can be further fine-tuned by introducing different metals and organic templates.

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Supporting Information Available: Complete crystallographic data for $CuGe_2S_5{\cdot}(C_2H_5)_4N$ and tables of fractional coordinates, isotropic and anisotropic thermal parameters, and complete geometric parameters (3 pages); structure factor amplitudes (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(15) The starting structure model was obtained in space group $I\bar{4}2d$ with 1198 unique reflections using the direct methods routines in SHELXS-86.[27] The subsequent refinement was carried out by using a package of programs written and maintained by J. C. Calabrese.[28] Besides framework atoms (Ge, Cu, and S), one unique TEA was identified in the structure. The relatively large displacement parameter for one C atom indicated some degree of static disorder, and this atom was split over two equally occupied sites. The final refinement converged with discrepancy indices $R = 4.20$ and $R_w = 3.08$. The maximum residual peak density in the Fourier difference map, 1.259 Å away from the split C atoms, is 1.09 e Å^{-3}. Crystallographic data of $(C_2H_5)_4N{\cdot}CuGe_2S_5$: a = 17.448(4) Å, c = 11.012(4) Å, V = 3352(3) Å^3, $Z = 8$, D_{calcd} = 1.978 g cm^{-3}. Ge−S bonds range from 2.165(2) to 2.232(2) Å with an average bond length of 2.213(2) Å. S−Ge−S angles vary from 106.2(1)° to 111.77(7)° while Ge−S−Ge angles deviate slightly from 105.2(1)° to 105.4(1)°.

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