Synthesis and structural characterization using synchrotron radiation of $[(C_6H_{13}N_2)_2(H_3O)(H_2O)][AgGe_4S_{10}]$ (dabco–AgGS–SB2): knitting sulfide metal clusters to form frameworks

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A novel framework comprised of $[Ge_4S_{10}]^{4-}$ adamantine clusters linked by Ag^+ is synthesized hydrothermally and its structure determined utilizing data collected on a 36 pl (36 × 10^{-12} l) single crystal using an X-ray synchrotron/imaging plate combination.

Novel framework structures capable of occluding organic guests are of interest for their potential as selective agents for molecular sieving, catalysis, ion exchange and ion conduction. By building upon experience with the hydrothermal synthesis of zeolites[1,2] the compositional and structural range of materials capable of forming open frameworks has increased greatly over the past decade. For example framework materials containing sulfide metal clusters are induced to form[3–5] using two procedures: self-condensation of the clusters in the presence of organic amines[6–9] and condensation from solution using transition-metal ions along with the organic amines.[10–12] There is evidence that both the organic amines and the transition metal act as structure directing agents.[3–6,10,11] Typically the metal sulfide reactants are sealed into bombs and these are heated under static conditions. However, condensation of pre-formed clusters from solution using transition elements[10] and transformations from one framework to another with ageing time[8] have recently been observed.

The efficacy of these tactics is best judged with feedback from crystal structure information. This allows synthetic conditions to be varied rationally and thereby direct the synthesis toward a particular structure type.[10,11] For example, depending upon conditions, germanium sulfide clusters can condense about Cu to form at least three structure types.[3,11,12] One of these frameworks[11] contains close to linear S–Cu^+–S linkages between $[Ge_4S_{10}]^{4-}$ clusters and its structure suggested similar chemistry[13] might be possible with Ag^+. In this publication, we report the synthesis and structural characterization using synchrotron/imaging plate-based diffractometry of a novel germanium sulfide condensed about silver, $[(C_6H_{13}N_2)_2(H_3O)(H_2O)][AgGe_4S_{10}]$, **1**.

Small equidimensional single crystals up to 40 μm on edge were formed in hydrothermal synthesis by heating a slurry of 0.2 g of amorphous GeS_2 (freshly precipitated by bubbling H_2S through acidified $GeCl_4$), 0.6 g of 1 mol dm^{-3} 1,4-diazabicyclo[2,2,2]octane (dabco) solution and 0.04 g of $Ag(MeCO_2)\cdot 4H_2O$. The slurry was sealed in a glass tube, which was placed into a hydrothermal bomb and heated at 130 °C for two days. The products were washed with water and ethanol solution in an ultrasonic cleaner. The yield was *ca.* 90% based on GeS_2. The powder X-ray diffraction pattern of the material obtained is unique,[3] indicative of a new structure type not previously reported and it was designated dabco–AgGS–SB2 in accordance with established nomenclature.[5] Electron-probe microanalysis, carried out using a Cameca Camebax instrument, indicated a composition of $Ag_{0.92}Ge_{4.00}S_{9.39}$ and the total mass percentage of these three detectable elements as 72.38%. These results are consistent with those expected from the crystal structure.[14]

The structure of **1** was determined† from data collected at beamline X3A1 of the National Synchrotron Light Source (NSLS). Conventional laboratory based diffractometry did not provide data suitable for structure determination. The material contains double chains, consisting of $[Ge_4S_{10}]^{4-}$ adamantine-like clusters as building units, connected by three-coordinate silver (Fig. 1). The chains are infinite along [100] (Fig. 1) and contain molecules of protonated dabco and water between them (Fig. 2). All the GeS_4 tetrahedra in dabco–AgGS–SB2 are slightly distorted with three longer Ge–S bonds at an average of

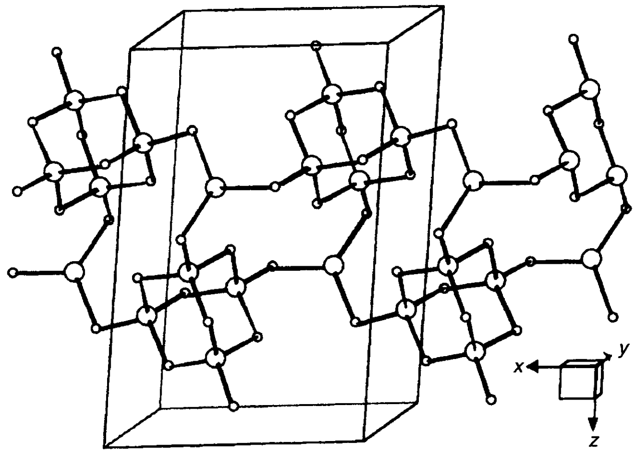

Fig. 1 A double chain consisting of $[G_4S_{10}]^{4-}$ anions joined by trigonally coordinated Ag^+ in the structure of **1**

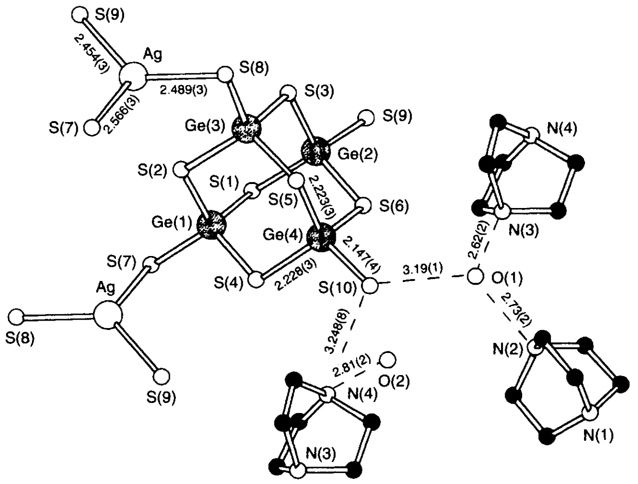

Fig. 2 Geometric details of the coordination about Ge, Ag and the relationship of the sulfide backbone to entrained organics in **1**. Although not located in the structure analysis, charge balance considerations and the short S–N and N–O distances suggest some of the molecules of dabco and water are protonated.

2.226 Å involving sulfur bound to two Ge (Fig. 2). Germanium–sulfur interatomic distances involving terminal sulfurs, or those bound to silver, are considerably shorter (Fig. 2): these distances average 2.142 Å and reflect the under bonding[14] of sulfur coordinated to Ag^+ or to only one Ge^{4+}. Similar structural systematics occur in other frameworks formed from the condensation of germanium sulfide adamantine units[3,6,10–12] The silver lies 0.35 Å below the mean plane defined by the three sulfurs to which it is coordinated with an average Ag–S interatomic distance of 2.502 Å (Fig. 2).

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Footnote

† *Crystal data* for $[(C_6H_{13}N_2)_2(H_3O)(H_2O)][AgGe_4S_{10}]$: triclinic, space group $P\bar{1}$, a = 9.855(2), b = 10.795(2), c = 16.051(2) Å, α = 115.50(1), β = 86.866(9), γ = 96.729(9)°, U = 1530.6(5) Å^3, Z = 2, $\mu[\lambda = 0.395(1)$ Å$] = 16.1$ cm^{-1}, imaging plate detector at beamline X3A1, NSLS, Fuji BAS2000 reader, 13477 allowed reflections integrated, 4104 uniques with $I > 1.0\sigma(I)$; direct methods,[15] Ag, Ge, C, N, S anisotropic; no absorption correction performed; refinement[17] on F^2, $R(F)$ = 0.058, $wR(F^2)$ = 0.120. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/118.

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