Inorganic Chemistry

Communication

Zero-Dimensional Units of Ligand-Bridged Gallium-Sulfide Supertetrahedra

Paz Vaqueiro* and M. Lucia Romero

Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, U.K.

The synthesis and characterization of the first anions containing two gallium-sulfide supertetrahedra linked via an organic moiety are described.

Hybrid materials, built up from covalently bonded organic and inorganic moieties, have developed into an important new class of solid-state materials.[1] Stable inorganic clusters with well-defined connectivity can be linked via organic molecules to form porous metal−organic frameworks (MOFs), also known as coordination polymers.[2] MOFs offer new perspectives for the design of multifunctional materials in which applications associated with their porous character are combined with applications arising from their physical properties (magnetic, conducting, or optical).[1,3] While extensive efforts have been devoted to the preparation of new oxygen-based MOFs, little is known about the equivalent chalcogen-based materials, which are, however, expected to be promising candidates for the integration of porosity with electronic or optical properties. Following the work of Dance on isolated metal thiolate clusters,[4] Feng has developed a range of coordination polymers in which such clusters and bifunctional covalent linkers alternate.[5] The functionalization of $[W_6S_8]$ clusters with thiophene derivatives to produce polymerizable building blocks has been reported.[6] A small number of coordination polymers and oligomers containing octahedral $[Re_6Q_8]$ (Q = S, Se) clusters bridged by multi-

dentate ligands, have also been described.[7] We present here unique examples of two-cluster units based on gallium-sulfide supertetrahedral clusters, which can be considered as building blocks for gallium-sulfide coordination polymers.

Since the pioneering work of Bedard and co-workers,[8] solvothermal synthesis has been widely used for the preparation of main-group metal chalcogenides.[9] While in the vast majority of solvothermally prepared chalcogenides containing a main-group element the template molecules are incorporated into the structure through weak hydrogen bonding,[9,10] we have found that in the gallium-sulfide system covalent bonding between the metal and amine molecules is possible.[11] We have exploited the ability of gallium to form covalent bonds with amines under solvothermal conditions to prepare novel organically-functionalized supertetrahedra,[12] in which the terminal S^{2-} anions have been replaced by covalently bonded pyridine derivatives. It has been previously reported that substituted pyridines are excellent ligands for metal−organic gallium halides and sulfides.[13] Through incorporation of ditopic ligands into the reaction mixtures, we have recently demonstrated that the organically-functionalized gallium-sulfide clusters can be used for the preparation of one- and two-dimensional covalent organic−inorganic networks.[14] We have now prepared the first two-cluster hybrid anions containing organically-functionalized supertetrahedra, which are described here.

By using 1,2-di-4-pyridylethylene (DPE) and 4,4′-bipyridine (bipy) as covalent linkers, the two-cluster anions

---

* To whom correspondence should be addressed. E-mail: chepv@hw.ac.uk.

(1) (a) Cheetham, A. K.; Rao, C. N. R.; Feller, R. K. *Chem. Commun.* **2006**, 4780. (b) Maspoch, D.; Ruiz-Molina, D.; Veciana, J. *Chem. Soc. Rev.* **2007**, *36*, 770. (c) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191.

(2) (a) Janiak, C. *Dalton Trans.* **2003**, 2781. (b) Robson, R. *Dalton Trans.* **2008**, 5113.

(3) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334.

(4) (a) Choy, A.; Craig, D.; Dance, I.; Scudder, M. *J. Chem. Soc., Chem. Commun.* **1982**, 1246. (b) Lee, G. S. H.; Craig, D. C.; Ma, I.; Scudder, M. L.; Bailey, T. D.; Dance, I. G. *J. Am. Chem. Soc.* **1988**, *110*, 4863. (c) Lee, G. S. H.; Fisher, K. J.; Craig, D. C.; Scudder, M. L.; Dance, I. G. *J. Am. Chem. Soc.* **1990**, *112*, 6435.

(5) (a) Xie, J.; Bu, X.; Zheng, N.; Feng, P. *Chem. Commun.* **2005**, 4916. (b) Zheng, N.; Bu, X.; Lu, H.; Chen, L.; Feng, P. *J. Am. Chem. Soc.* **2005**, *127*, 14990.

(6) Perruchas, S. S.; Flores, S.; Jousselme, B.; Lobkovsky, E.; Abruña, H.; DiSalvo, F. J. *Inorg. Chem,* **2007**, *46*, 8976.

(7) Selby, H. D.; Roland, B. K.; Zheng, Z. *Acc. Chem. Res.* **2003**, *36*, 933.

(8) Bedard, R. L.; Wilson, S. T.; Vail, L. D.; Bennett, J. M.; Flanigen, E. M. In *Zeolites: Facts, Figures, Future*; Jacobs, P., van Santen, R. A., Eds.; Elsevier: Amsterdam, The Netherlands, 1989.

(9) (a) Li, J.; Chen, Z.; Wang, R. J.; Proserpio, D. M. *Coord. Chem. Rev.* **1999**, *190−192*, 707. (b) Sheldrick, W. S.; Wachhold, M. *Coord. Chem. Rev.* **1998**, *176*, 211.

(10) (a) Puls, A.; Shaefer, M.; Näther, C.; Bensch, W.; Powell, A. V.; Boissière, S.; Chippindale, A. M. *J. Solid State Chem.* **2005**, *178*, 1171. (b) Vaqueiro, P. *Inorg. Chem.* **2008**, *47*, 20.

(11) Vaqueiro, P. *Inorg. Chem.* **2006**, *45*, 4150.

(12) Vaqueiro, P.; Romero, M. L. *Chem. Commun.* **2007**, 3282.

(13) (a) Nogai, S. D.; Schmidbaur, H. *Dalton Trans.* **2003**, 2488. (b) Schmidbaur, H.; Nogai, S. D. *Z. Anorg. Allg. Chem.* **2004**, *630*, 2218.

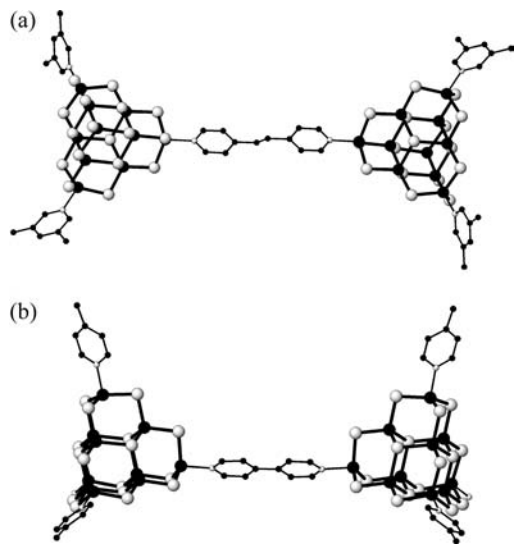(14) Vaqueiro, P.; Romero, M. L. *J. Am. Chem. Soc.* **2008**, *130*, 9630.

Figure 1. Two-cluster anions of supertetrahedral gallium-sulfide units found in (a) compound **1** and (b) compound **2**. Key: gallium, large black circles; sulfur, large open circles; carbon, small black circles; nitrogen, small open circles. Hydrogen atoms have been omitted.

shown in Figure 1 can be obtained.[15] In both cases, each of the amine groups of the organic linker is covalently bonded to a T3-type supertetrahedral cluster. In the crystal structure[16] of $(C_7H_{10}N)_6[Ga_{20}S_{34}H_2(NC_7H_9)_4(N_2C_{12}H_{10})]$ (**1**), two of the remaining three vertexes of each supertetrahedral cluster are terminated by 3,5-dimethylpyridine molecules, while in the fourth vertex, a SH^- anion is found. The average Ga−N distance has been found to be 2.042(3) Å, significantly shorter

(15) Compound **1** was prepared by mixing of gallium metal (Alfa Aesar; 99.99%, 139.4 mg), sulfur (Alfa Aesar; 99.5%, 144 mg), DPE (Fluka ≥ 98%, 182 mg), FeCl$_2$·4H$_2$O (Aldrich; 99%, 59.6 mg), and 3,5-dimethylpyridine (Aldrich; 98+%, 3 mL) in a 23 mL Teflon-lined stainless steel autoclave. This corresponds to a molar ratio of Ga:S: DPE:FeCl$_2$:3,5-dimethylpyridine = 2:4.5:1:0.3:26. After the vessel was sealed, the reaction mixture was heated at 200 °C for 10 days and then allowed to cool to room temperature at 1 °C min^{-1}. The product consisted of a mixture of white crystals of **1** (yield 50%) and a dark-gray polycrystalline powder. For the synthesis of **2**, bipy (Aldrich; 98%) was used as the organic linker. Crystals of **2** were produced by heating of a mixture with an approximate molar composition of Ga: S:bipy:3,5-dimethylpyridine = 2:4.5:1:22 at 200 °C for 20 days. The reaction product contained orange needles of **2** (yield 90%), together with a small amount of unreacted gallium. Elem anal. Calcd for **1**: C, 26.3; H, 2.9; N, 4.5. Found: C, 25.9; H, 2.8; N, 4.6. Calcd for **2**: C, 25.05; H, 2.5; N, 5.4. Found: C, 27.1; H, 2.9; N, 5.7.
(16) Crystal structures: (a) $(C_7H_{10}N)_6[Ga_{20}S_{34}H_2(NC_7H_9)_4(N_2C_{12}H_{10})]$ (**1**), $M = 3746.48$, triclinic, space group $P\bar{1}$, $a = 12.0720(6)$ Å, $b = 12.2402(7)$ Å, $c = 22.7189(12)$ Å, $\alpha = 89.774(3)°$, $\beta = 80.018(3)°$, $\gamma = 76.112(3)°$, $V = 3207.1(3)$ Å^3, $Z = 1$, 85 265 reflections measured, 19 455 unique [$R_{merg} = 0.0269$; 11 777 observed with $I > 3\sigma(I)$, which were used in all calculations]. Final values of $R(F)$ and $wR(F)$ [with $I > 3\sigma(I)$] were 0.0242 and 0.0270, respectively. (b) $(C_7H_{10}N)_6[Ga_{10}S_{16}(NC_7H_9)(N_2C_{10}H_8)_3][Ga_{20}S_{32}(NH_3)_2(NC_6H_7)_4-(N_2C_{10}H_8)]$ (**2**), $M = 5201.90$, monoclinic, space group $P2_1/m$, $a = 14.8534(6)$ Å, $b = 34.1528(15)$ Å, $c = 21.0321(9)$ Å, $\beta = 91.630(3)°$, $V = 10665.0(8)$ Å^3, $Z = 2$, 32 644 reflections measured, 32 644 unique [$R_{merg} = 0.0421$; 10 626 observed with $I > 3\sigma(I)$, which were used in all calculations]. Final values of $R(F)$ and $wR(F)$ [with $I > 3\sigma(I)$] were 0.0431 and 0.0478, respectively. Data collections using a Bruker X2 APEX 2 diffractometer (Mo K$_\alpha$; $\lambda = 0.71073$ Å), at 100 K. The structures were solved by direct methods using the program *SIR92* and models refined using *CRYSTALS*. Carbon and nitrogen atoms were located in the difference Fourier maps. Hydrogen atoms on the organic moieties were placed geometrically. Data for **2** were treated with *SQUEEZE* to correct the effect of the disordered organic cations. Those that could be located in the difference Fourier maps were modeled isotropically because their large thermal parameters suggest a certain degree of disorder.
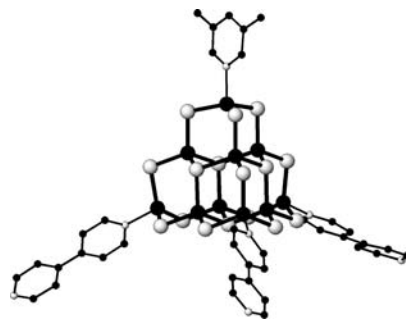
Figure 2. $[Ga_{10}S_{16}(NC_7H_9)(N_2C_{10}H_8)_3]^{2-}$ anion found in **2**. The key is as for Figure 1.
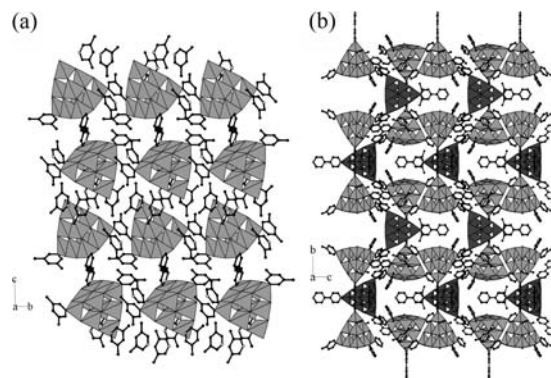

Figure 3. Polyhedral representation of the structure of the (a) compound **1** along [100] and (b) **2** along [100]. Dark gray is used for supertetrahedral one-cluster anions, while pale gray is used for two-cluster anions.

than the Ga−SH$^-$ distance [2.2681(7) Å]. The latter is comparable to the remaining Ga−S distances within the supertetrahedral cluster, which lie within the range 2.2105(7)− 2.3512(7) Å. In the crystal structure[16] of $(C_7H_{10}N)_6-[Ga_{10}S_{16}(NC_7H_9)(N_2C_{10}H_8)_3][Ga_{20}S_{32}(NH_3)_2(NC_6H_7)_4(N_2C_{10}H_8)]$ (**2**), two-cluster (Figure 1b) and one-cluster anions (Figure 2) coexist. In the supertetrahedral clusters found in the two-cluster anions, two of the terminal S^{2-} anions have been replaced by monodentate amines, one vertex is terminated by NH$_3$, and the remaining vertex is linked to a second supertetrahedral cluster via a bipy molecule. The one-cluster supertetrahedral anion is terminated by one 3,5-dimethylpyridine and three bipy molecules (Figure 2).

In both materials, charge balancing is achieved through the incorporation of protonated 3,5-dimethylpyridinium cations. Elemental analysis[15] results are consistent with the proposed formulas, which take into account the crystallographically determined structures together with charge-balancing requirements. The crystal structure of **1** can be described as consisting of sheets of two-cluster anions parallel to the *ab* plane, as shown in Figure 3a, with the organic cations residing between the anions. The crystal packing of cations and anions in **1** is likely to arise as a consequence of a number of N−H···S contacts, together with π−π interactions between phenyl groups. Each nitrogen atom in a protonated organic cation has a neighboring sulfur atom in a supertetrahedral cluster at distances in the range 3.186(4)−3.391(3) Å, implying hydrogen-bonding interactions. Slipped parallel stacking of organic cations occurs along the [−110] direction, with an approximate inter-ring distance of 3.5 Å, which is comparable to the sum of the

van der Waals radii of two carbon atoms (3.4 Å). Parallel stacking of pairs of phenyl rings in neighboring supertetrahedral clusters, as well as of pairs of organic cations and phenyl groups from the dimeric anions, is also apparent.

By contrast, no short N−H···S contacts between the cations and the organically-functionalized supertetrahedral clusters can be identified in **2**. Furthermore, approximately 33% of the organic cations are disordered, suggesting that hydrogen-bonding interactions are weak. In the crystal structure of **2** (Figure 3b), two- and one-cluster anions are arranged in an alternating fashion, in layers parallel to the *ab* plane, with the cations located between the anions. Parallel stacking of pairs of phenyl rings from organic cations and organically-functionalized clusters and of phenyl rings from neighboring clusters is apparent. Some of the inter-ring distances are comparable to the sum of the van der Waals radii of two carbon atoms (3.4 Å), suggesting the presence of $\pi-\pi$ interactions.

Thermogravimetric analysis (TGA) indicates that, under a N_2 atmosphere, these materials are stable up to approximately 220 °C. The powder X-ray diffraction pattern collected on a bulk ground sample of **2** is in good agreement with the pattern calculated using the crystallographically determined structure (Supporting Information). The observed diffraction pattern of the product of the reaction containing **1** is consistent with the presence of **1** together with a second unidentified phase, which is a dark-gray polycrystalline powder. A number of unsuccessful reactions were attempted to grow crystals of this unidentified phase, in order to establish its structure. Similar problems in the solvothermal synthesis of chalcogenides have been encountered by other authors.[17] Fourier transform infrared (FTIR) data (Supporting Information) for hand-picked crystals of compounds **1** and **2** are consistent with the presence of aromatic and amine functional groups. A peak at ca. 3450 cm^{-1} can be assigned to N−H stretching vibrations, while those over the range 3150−3000 cm^{-1} can be attributed to aromatic and alkane C−H stretching vibrations. In addition, over the region 1600−1000 cm^{-1}, there are a number of peaks characteristic of aromatic compounds. In the case of compound **1**, a peak at ca. 2500 cm^{-1}, characteristic of S−H stretching vibrations, is found. This confirms the presence of SH$^-$ anions, given that hydrogen atoms could not be located in the Fourier maps.

The optical absorption spectra of both materials,[18] which were determined using a diffuse reflectance technique, are shown in Figure 4. From the absorption edges,[19] we have estimated that the band gaps are 3.4 and 2.6 eV for **1** and **2**, respectively. The latter is consistent with the orange color of the crystals of **2**. While the band gap of compound
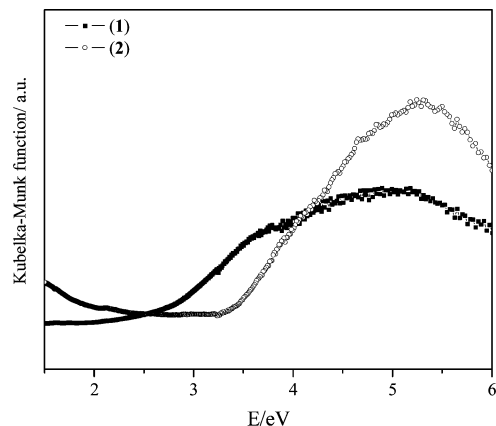

Figure 4. Optical absorption spectra of **1** and **2**.

1 is similar to that previously reported for $[C_7H_{10}N]_2[Ga_{10}S_{16}(NC_7H_9)_4]$,[12] there is a red shift in the absorption edge of compound **2**. It has been recently reported that the formation of ion-pair charge-transfer salts by metal-thiolate clusters result in a marked shift of the absorption edge.[20] The diffuse reflectance spectra of the latter compounds show a characteristic charge-transfer absorption band, which is, however, not evident in the data for **2**. Further studies would be required to elucidate the origin of the red shift in **2**.

The results presented here shed light on some of the species found in solution under solvothermal conditions and also indicate that oligomers and monomers of organically-functionalized clusters can coexist in solution. Other species likely to be present are those arising from the nucleophilic attack of sulfur by amines[21] as well as from the decomposition reactions that amines undergo under solvothermal conditions. Relatively minor modifications in the reaction conditions used for the preparation of **1** resulted in the linkage of such building blocks into a two-dimensional hybrid material.[14] Given the complexity of these multicomponent heterogeneous reactions, we are far from being able to predict the nature of the products. The successful synthesis of other gallium-sulfide hybrid materials may provide the information needed for a more rational synthetic approach. These initial results, however, demonstrate the potential of the gallium-sulfide system to generate a family of hybrid supertetrahedra-based materials.

Supporting Information Available: Crystallographic data in CIF format and observed and simulated powder X-ray diffraction, FTIR, and TGA data. This material is available free of charge via the Internet at http://pubs.acs.org.

IC8020723

(17) Cahill, C.; Parise, J. B. *J. Chem. Soc., Dalton Trans.* **2000**, 1475.
(18) Diffuse reflectance measurements were collected using a Perkin Elmer Lambda 35 UV−visible spectrometer. Data were collected on ground hand-picked crystals of **1** and **2**. BaSO$_4$ powder was used as a reference, and the absorption data were calculated from the reflectance data using the Kubelka−Munk function.
(19) (a) Tandon, S. P.; Gupta, J. P. *Phys. Status Solidi* **1970**, *38*, 363. (b) Wedlandt, W. W.; Hecht, H. G. *Reflectance Spectroscopy*; Interscience Publishers: New York, 1966.
(20) Zhang, Q.; Wu, T.; Bu, X.; Tran, T.; Feng, P. *Chem. Mater.* **2008**, *20*, 4170.
(21) Davies, R. E.; Nakshbendi, H. F. *J. Am. Chem. Soc.* **1961**, *84*, 2085.