$[Ga_{10}S_{16}(NC_7H_9)_4]^{2-}$: a hybrid supertetrahedral nanocluster†

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Received (in Cambridge, UK) 29th March 2007, Accepted 15th May 2007
First published as an Advance Article on the web 7th June 2007
DOI: 10.1039/b704724j

The synthesis and characterisation of a hybrid supertetrahedral nanocluster, $[Ga_{10}S_{16}(NC_7H_9)_4]^{2-}$, in which the terminal S^{2-} anions have been replaced by covalently bonded amine molecules, is described.

Nanoclusters and colloids of semiconducting materials are interesting because their transport and optical behaviours vary as a function of crystallite size.[1] In the size regime of 10 to a few hundred Å, quantum effects lead to severe perturbations in the electronic properties, but difficulties with the exact interpretation of the measured effects arise when the materials investigated contain a distribution of particle sizes, as is generally the case for colloids. For this reason, there is growing interest in the synthesis and characterisation of nanoclusters with well-defined sizes and structures.[2] For example, a number of metal thiolate clusters, containing Zn,[3] Cd,[4] Hg[5] and Si,[6] have been reported. Large metalloid gallium clusters, such as $[Ga_{23}\{N(SiMe_3)_2\}_{11}]$, have also been described.[7] The relationship between molecular nanoclusters and nanoparticles,[8] as well as their potential applications in areas such as optical devices and transistors, have been reviewed.[9] In addition to their potential applications in nanotechnology, chalcogenide nanoclusters are being increasingly exploited as building blocks for the design of open-framework structures.[10] Open-framework chalcogenides have tremendous technological potential as multifunctional materials, capable of combining the ion-exchanging and catalytic features of zeolites with the semiconducting behaviour of metal chalcogenides. Perceived areas of application for these novel microporous semiconductors range from molecule discriminating sensors[11] to selective ion-exchange[12] and size- or shape-selective photocatalysis.[13] We believe that the hybrid isolated cluster described here could be used to design novel organic–inorganic microporous materials.

In the present contribution, we report the synthesis and crystal structure of isolated clusters of gallium sulfide $[Ga_{10}S_{16}(NC_7H_9)_4]^{2-}$, which are related to the series of supertetrahedral T*n* clusters,[14] where *n* refers to the number of individual tetrahedra along the edge of the cluster. A T1 cluster is simply a tetrahedron such as GaS_4^{5-}, T2 clusters are adamantane cages such as $Ga_4S_{10}^{8-}$ and T3 clusters have the composition $Ga_{10}S_{20}^{10-}$. While isolated T2 anions $Ga_4S_{10}^{8-}$ have been reported,[15] the next member of the series, $Ga_{10}S_{20}^{10-}$, has only been found in extended frameworks,[16] owing to the large negative charge that the isolated cluster would exhibit. In this work, we have succeeded in preparing an isolated T3-type gallium sulfide cluster, by replacing the four S^{2-} anions at the vertexes of the cluster by covalently bonded amines (Fig. 1). The $[Ga_{10}S_{16}(NC_7H_9)_4]^{2-}$ cluster could be considered as a member of a new family of supertetrahedral clusters, in which the gallium atoms at the corners of the cluster exhibit a tetrahedral environment through additional coordination to organic ligands.

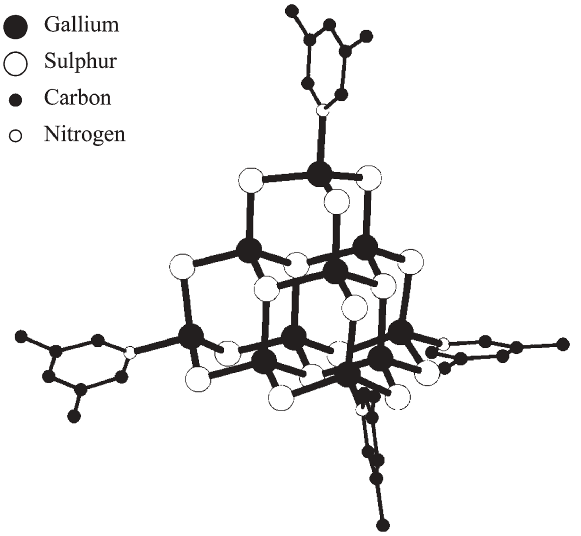

Fig. 1 The gallium sulfide cluster $[Ga_{10}S_{16}(NC_7H_9)_4]^{2-}$. Hydrogen atoms have been omitted for clarity.

To prepare $[C_7H_{10}N]_2[Ga_{10}S_{16}(NC_7H_9)_4]$,‡ gallium metal (Alfa Aesar 99.99%, 139.4 mg, 2.0 mmol), sulfur (Alfa Aesar 99.5%, 128.0 mg, 4.0 mmol) and 3,5-dimethylpyridine (Aldrich, 98+%, 2.5 mL, 22 mmol) were mixed in a 23 ml Teflon-lined stainless steel autoclave. The vessel was sealed and heated at 170 °C for 13 days and then allowed to cool to room temperature at 1 °C min^{-1}. The reaction product, which consists of colourless crystals and a small amount of gallium metal, was filtered off and washed with methanol, deionised water and acetone. Droplets of gallium metal were manually removed from the product. Elemental analysis results§ are in agreement with the crystallographically determined formula of $[C_7H_{10}N]_2[Ga_{10}S_{16}(NC_7H_9)_4]$. Powder X-ray diffraction data (see ESI†) collected on a ground portion of the bulk sample are in good agreement with the powder diffraction pattern calculated using the crystal structure determined by single-crystal X-ray diffraction. In subsequent reactions, we established that the title compound can be formed at 170 °C, using prolonged heating times, and Ga : S molar ratios over the range 0.63 to 0.44. At temperatures above 180 °C, reaction products consist of gallium metal and an amorphous powder. In an effort to produce larger clusters, reactions in which divalent transition metal salts were added were also carried out, but no crystals were produced.

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† Electronic supplementary information (ESI) available: Powder diffraction data and thermogravimetric analysis data. See DOI: 10.1039/b704724j

The crystal structure of $[C_7H_{10}N]_2[Ga_{10}S_{16}(NC_7H_9)_4]$‡ contains discrete tetrahedral anionic units of $[Ga_{10}S_{16}(NC_7H_9)_4]^{2-}$. Interestingly, these anions appear to exhibit D_2 symmetry. Disordered monoprotonated 3,5-dimethylpyridine cations reside between the anions in the crystal (Fig. 2). While all gallium atoms are tetrahedrally coordinated, the sulfur atoms located on the faces of the supertetrahedron are trigonally coordinated, and the remaining sulfur atoms are bicoordinated. The Ga–S distances lie within the range 2.2271(15)–2.3225(14) Å, with the larger distances corresponding to trigonally coordinated sulfur, and are similar to those found in the literature for tetrahedrally coordinated gallium sulfides.[16,17] The Ga–N distance, 2.045(5) Å, is significantly shorter than Ga–S distances, and similar to those found in other gallium compounds.[17] Although a small number of hybrid chalcogenides containing covalently bonded amines, such as CdQ·0.5en (Q = S, Se, Te),[18] have been recently described, in most of the solvothermally prepared main-group metal chalcogenides (containing As, Sb, Sn, In and Ge)[10,19] the organic template molecules are incorporated into the structure through weak hydrogen bonding. By contrast, our recent work on the Ga–S system has resulted in the identification of a number of gallium sulfides containing covalently bonded molecules, such as $[enH_2][Ga_4S_7(en)_2]$[17] and the title compound. This suggests that the relative stabilities of the Ga–S and Ga–N bonds under solvothermal conditions are finely balanced, and would seem to indicate that Ga^{3+} cations have a greater hard acid character than other main-group cations, such as In^{3+}, for which incorporation of amine molecules into the framework through covalent bonding has not been reported.

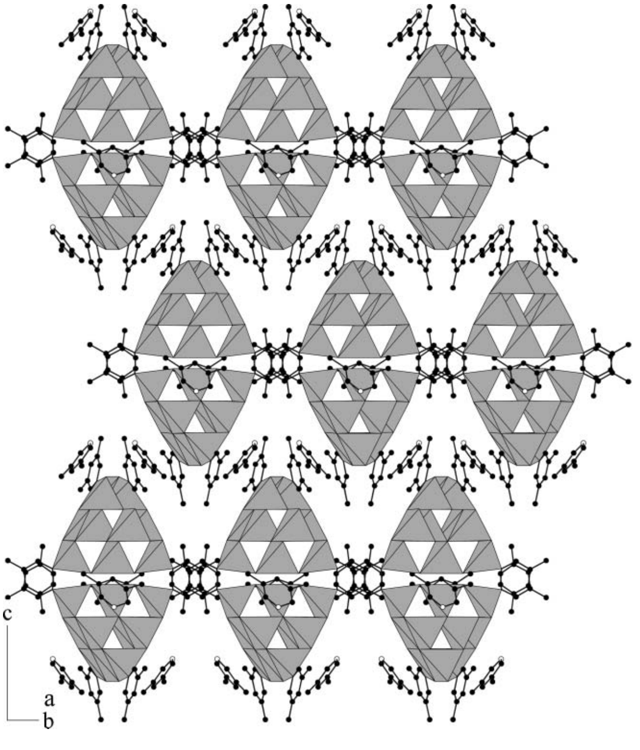

Fig. 2 Polyhedral representation of the crystal structure of $[C_7H_{10}N]_2[Ga_{10}S_{16}(NC_7H_9)_4]$ along [1−10]. Only one of the sites over which the protonated 3,5-dimethylpyridine cations are disordered is shown.

Thermogravimetric analysis (ESI†) indicates that the material $[C_7H_{10}N]_2[Ga_{10}S_{16}(NC_7H_9)_4]$ is stable up to 300 °C. Decomposition occurs in a single step, with the overall weight change (observed 33.0%; calculated 34.8%) corresponding approximately to the complete removal of the amine. The optical absorption spectrum of $[C_7H_{10}N]_2[Ga_{10}S_{16}(NC_7H_9)_4]$, measured using a diffuse reflectance technique,¶ is shown in Fig. 3. The band gap, which can be estimated from the absorption edge, was found to have a value of 3.3(1) eV. This indicates that this material exhibits semiconducting behaviour. When compared with extended frameworks containing T3 clusters, such as $[C_4NH_{12}][Ga_{10}S_{18}]$ (E = 4.0(1) eV),[17] there is a red shift of the absorption edge.

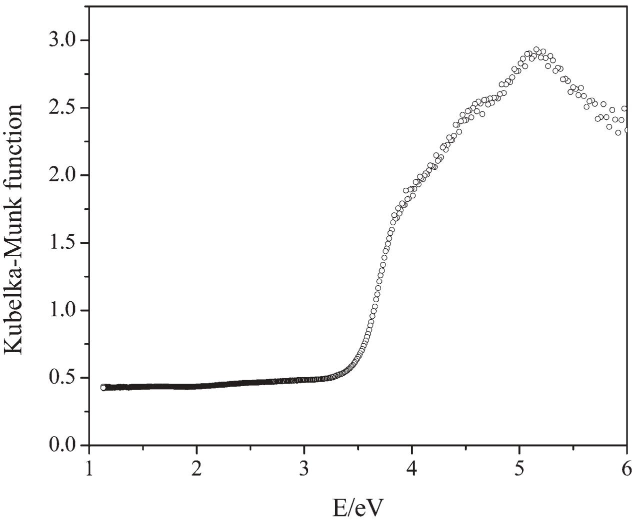

Fig. 3 Optical absorption spectrum of $[C_7H_{10}N]_2[Ga_{10}S_{16}(NC_7H_9)_4]$.

The formation of the hybrid cluster $[Ga_{10}S_{16}(NC_7H_9)_4]^{2-}$ demonstrates that, under appropriate solvothermal conditions, covalent bonding of organic ligands to gallium sulfide clusters occurs. By judicious choice of bidentate or multidentate organic ligands, the design of covalent organic–inorganic architectures containing organically-functionalised supertetrahedra will become possible. While in purely inorganic frameworks the lack of flexibility of the Ga–S–Ga angle places a significant constraint on the number of topologies that can be obtained, linkage of supertetrahedral clusters *via* organic moieties will result in a greater flexibility and therefore in a larger number of potential structures. We envisage that, by using these organically-functionalised supertetrahedral clusters, the preparation of a family of hybrid gallium sulfides, in which both the composition and the structure of the clusters and the organic ligands can be tuned to optimise desirable properties, will become possible. Such inorganic–organic hybrid materials may possess unique optical and photochemical properties due to the interaction at the microscopic level between the organic and the inorganic components. Our current synthetic efforts are directed at exploring the synthesis of such hybrid materials.

The authors thank the UK EPSRC for grants in support of a project studentship (M. L. R.) and an Advanced Research Fellowship for P. V.

Notes and references

‡ *Crystal structure determination*: $[C_7H_{10}N]_2[Ga_{10}S_{16}(NC_7H_9)_4]$, M = 1850.21, orthorhombic, space group *Fddd*, a = 15.4885(10), b = 26.9605(17), c = 35.320(2) Å, V = 14748.9(16) Å^3, Z = 8. Data collection using a Bruker X2 APEX 2 diffractometer (Mo-Kα, λ = 0.71073 Å), on a crystal of dimensions 0.4 × 0.4 × 0.5 mm, at 100 K. 64594 reflections measured, 6974 unique (R_{int} = 0.027, 2490 observed with ($I > 3\sigma(I)$) which were used in all calculations. Final values of $R(F)$ and $wR(F)$ were 0.0451 and 0.0535, respectively. The structure was solved by direct methods using the program SIR92 and model refined using CRYSTALS. The C and N atoms of the protonated 3,5-dimethylpyridine cations, which were found to be disordered, were modelled isotropically. CCDC 642160. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704724j

§ Elemental analysis: found: C, 26.50; H, 3.59; N, 4.40; calc.: C, 27.19; H, 3.04; N, 4.53%.

¶ Diffuse reflectance measurements were collected using a Perkin Elmer Lambda 35 UV-Vis Spectrometer. $BaSO_4$ powder was used as a reference (100% reflectance). Absorption data were calculated from the reflectance data using the Kubelka–Munk function.

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