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Accepted Version

Vaqueiro, P. ORCID: <https://orcid.org/0000-0001-7545-6262> and Romero, L. (2008) Gallium-sulphide supertetrahedral clusters as building blocks of covalent organic-inorganic networks. *Journal of the American Chemical Society*, 130. pp. 9630-9631. ISSN 0002-7863 doi: 10.1021/ja801619e Available at <https://centaur.reading.ac.uk/34232/>

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Published version at: <http://pubs.acs.org/doi/abs/10.1021/ja801619e>

To link to this article DOI: <http://dx.doi.org/10.1021/ja801619e>

Publisher: American Chemical Society

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Gallium-sulphide supertetrahedral clusters as building blocks of covalent organic-inorganic networks

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In recent years a significant progress has been made in the synthesis of inorganic open-frameworks built from supertetrahedral clusters, which can be described as tetrahedrally-shaped fragments of the ZnS structure.¹ However, only a small number of three-dimensional topologies, such as CrB₄² or C₃N₄,³ have been found, with the single- and double-diamond lattice being by far the most common.⁴ This paucity of topological types has been attributed to the lack of flexibility of the metal-sulphur-metal angle,⁵ which limits the ways in which tetrahedral clusters can be joined together. In order to obtain new three-dimensional structural types, it is necessary to devise alternative ways of linking the clusters. A route that offers enormous potential is the incorporation of organic moieties as linkers between clusters, as this would result in the generation of novel organic-inorganic architectures. A small number of reports on metal-thiolate cluster superlattices⁶ demonstrate the feasibility of this approach which, to the best of our knowledge, has never been applied to metal-chalcogenide tetrahedral clusters.

Following our recent report of an unprecedented supertetrahedral cluster, [Ga₁₀S₁₆(NC₇H₉)₄]²⁻,⁷ in which the gallium atoms at the corners of the cluster exhibit a tetrahedral environment through additional coordination to organic amines, we describe here our initial results on the synthesis and characterisation of novel covalent organic-inorganic architectures containing organically-functionalised supertetrahedra. These unique materials, in which bidentate ligands act as linkers between gallium-sulphide supertetrahedral clusters, can be described as a new type of metal-organic frameworks.⁸ Such hybrid materials may possess unique optical and photochemical properties due to the interaction at the microscopic level between the organic and the inorganic components.⁹

By using 1,2-di(4-pyridyl)ethylene (DPE) as a linker between gallium-sulphide supertetrahedral clusters, we have succeeded in the synthesis¹⁰ of one- and two-dimensional covalent organic-inorganic networks. The building units of these materials are supertetrahedral clusters in which the sulphur atoms at the vertexes have been replaced by a combination of mono- and bidentate pyridine derivatives. These clusters are closely related to the series of supertetrahedral T_n clusters,¹¹ where n refers to the number of individual tetrahedra along the edge of the cluster, with the materials reported here containing T3-type clusters. In these clusters, all gallium atoms exhibit tetrahedral coordination, whereas the sulphur atoms located on the faces of the supertetrahedron are trigonally coordinated and the remaining sulphur atoms are bicoordinated. In the structures reported here, the Ga-N distances take average values of 2.03-2.06 Å respectively, which are significantly shorter than the Ga-S distances (*ca.* 2.27 Å), and similar to that found for the isolated [Ga₁₀S₁₆(NC₇H₉)₄]²⁻ cluster (2.045(5) Å).⁷

The structure¹² of [C₆H₈N]₂[Ga₁₀S₁₆(NC₆H₇)₂(N₂C₁₂H₁₂)] (1) contains one-dimensional zigzag chains of alternating T3-type

clusters and dipyridyl ligands (Figure 1a). The two remaining vertexes of the supertetrahedral clusters are terminated by monodentate 4-methylpyridine molecules. Under the reducing solvothermal conditions in which this reaction has taken place, hydrogenation of DPE has resulted in the formation of 1,2-di(4-pyridyl)ethane, which is capable of adopting the conformation shown in Figure 1b. The zigzag hybrid chains are packed in layers parallel to the (010) plane (Figure 1c), with the 4-methylpyridine ligands oriented towards the outer part of the layers. Given that the [Ga₁₀S₁₆(NC₆H₇)₂(N₂C₁₂H₁₂)]²⁻ chains are anionic, and that the determined crystal structure contains *ca.* 39% of void space, protonated amine cations are assumed to be located within the crystal structure cavities. Elemental analysis¹⁰ is consistent with the incorporation of two 4-methylpyridinium cations per formula unit. Using pyridine as a solvent, an isostructural material, with stoichiometry [C₅H₆N]₂[Ga₁₀S₁₆(NC₅H₅)₂(N₂C₁₂H₁₂)], can be prepared.¹³

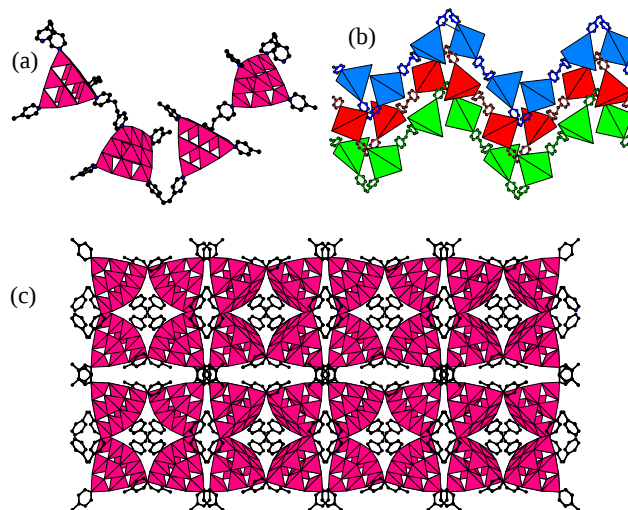


Figure 1. (a) A one-dimensional [Ga₁₀S₁₆(NC₆H₇)₂(N₂C₁₂H₁₂)]²⁻ chain. (b) Schematic representation of a layer of (1) parallel to (010) showing the arrangement of the zigzag chains. (c) View of (1) along [001].

The structure¹² of [C₇H₁₀N]₂[Ga₁₀S₁₆(NC₇H₉)(N₂C₁₂H₁₀)_{3/2}] (2) contains T3-type supertetrahedral clusters in which three of the terminal S²⁻ anions have been replaced by DPE, while the remaining vertex is terminated by a 3,5-dimethylpyridine molecule. The bidentate DPE molecules act as linkers between the supertetrahedral clusters, resulting in the formation of covalent organic-inorganic layers with a honeycomb-type topology (Figure 2a). These corrugated layers, which have a pore diameter of *ca.* 30 Å, are stacked parallel to the (135) plane. The staggered arrangement of the layers within the crystal structure resembles

that of grey arsenic (Figure 2b), and leads to the partial filling of the pores in a given layer by supertetrahedra from neighbouring layers. However, the crystal structure of (2) still contains *ca.* 38% of solvent accessible void space, and a two-dimensional network of channels of approximately 3–4 Å diameter, running parallel to the *b*- and *a*-axes, is apparent in space-filling representations of this structure. Given the anionic nature of the hybrid layers, these channels are likely to be filled with protonated amine cations. Elemental analysis results are reasonably consistent with the presence of two protonated 3,5-dimethylpyridinium cations per formula unit.¹⁰ The topology of (2) can be considered to be related to that of the wholly inorganic compound $[\text{Ba}_3(\text{H}_2\text{O})_{16}][\text{Mn}_6(\text{H}_2\text{O})_3(\mu_6\text{-Se})(\text{GeSe}_4)_4]$,¹⁴ which consists of $[\text{Mn}_6\text{Ge}_4\text{Se}_{17}]^{6-}$ building units linked into honeycomb-like layers.

Thermogravimetric analysis indicates that, under a N_2 atmosphere, (1) and (2) are stable up to *ca.* 270 and 370°C, respectively. Both phases are insoluble in common solvents, such as water, DMF or THF. The optical behaviour of these covalent organic-inorganic phases is comparable to that previously reported for wholly inorganic gallium-sulphide frameworks.^{2(b), 4(e)} From the optical absorption spectra band gaps of 3.3 and 3.7 eV were estimated for (1) and (2) respectively.

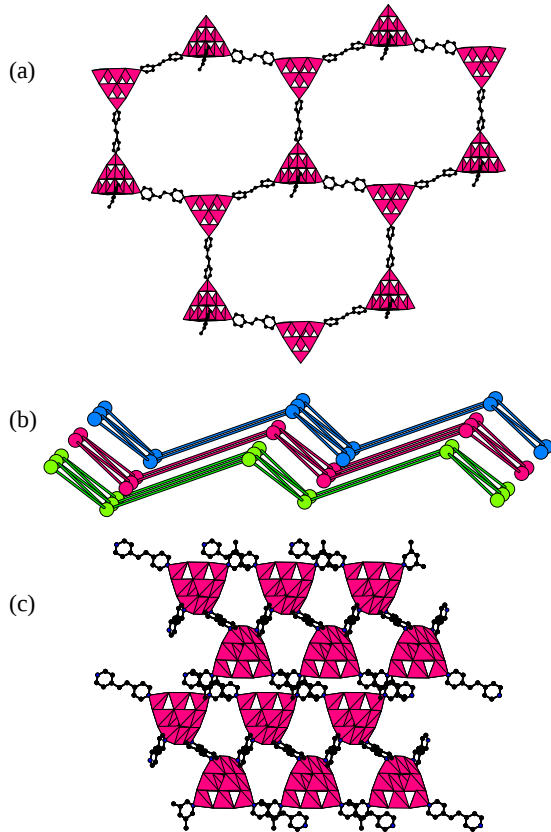


Figure 2. (a) View of a two-dimensional $[\text{Ga}_{10}\text{S}_{16}(\text{NC}_6\text{H}_7)(\text{N}_2\text{C}_{12}\text{H}_{10})_{3/2}]^{2-}$ layer parallel to the (135) plane. (b) Framework topology of (2); each node represents a supertetrahedral cluster. (c) View of (2) along [100].

In conclusion, we have established that dipyriddy ligands can be used as linkers between supertetrahedral clusters to generate novel organic-inorganic networks. We anticipate that the materials reported here are the first representatives of a large family of hybrid supertetrahedra-based materials. Our synthetic efforts to date indicate that, in the gallium-sulphide system, organically-functionalised supertetrahedra are a prevalent building block, found under a variety of solvothermal conditions. While we have

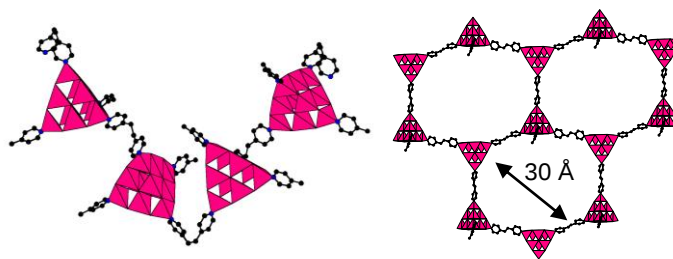
demonstrated the feasibility of the synthesis of supertetrahedra-based networks using ditopic ligands, we envisage that multitopic linkers will enable the design covalent organic-inorganic architectures with a wide range of connectivities, in which both the composition and the structure of the clusters and the organic ligands can be tuned to optimise desirable properties.

Acknowledgment. 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.

Supporting Information Available: Space filling views of the structure of (2). Crystallographic data in CIF format, observed and simulated powder X-ray diffraction data, UV-Vis diffuse reflectance, FT-IR and TGA data. This material is available free of charge via the Internet at <http://pubs.ac.org>.

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- (10) Compound (1) was prepared by mixing gallium metal (Alfa Aesar 99.99%, 139 mg), sulphur (Alfa Aesar 99.5%, 144 mg), DPE (Fluka $\geq$ 98%, 182 mg) and 4-methylpyridine (Aldrich 98%, 3 mL) in a 23 mL Teflon-lined stainless steel autoclave. The vessel was sealed and heated at 170°C for 5 days and then allowed to cool to room temperature at 1°C min⁻¹. For the synthesis of (2) 3,5-dimethylpyridine (Aldrich, 98+%) was used as a solvent, and crystals were produced by heating a mixture with an approximate molar composition Ga:S:DPE:3,5-dimethylpyridine 2:4.5:1:26 at 200°C for 20 days. Elemental analysis: (1) found: C=23.92%, H=2.91%; N=5.36%; calc.: C=24.44%, H=2.39%, N=4.75%; (2) found: C=25.70%, H=2.87%, N=5.86%; calc.: C=25.92%, H=2.45%, N=4.65%.
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- (12) Crystal structures: (a) $[\text{Ga}_{10}\text{S}_{16}(\text{NC}_6\text{H}_7)_2(\text{N}_2\text{C}_{12}\text{H}_{10})]^{2-}$ (1), *M*=1580.75, orthorhombic, space group *Pcca*, *a* = 37.4329(14) Å, *b* = 19.7762(8) Å, *c* = 18.5622(7) Å, *V* = 13741.2(9) Å³, *Z* = 8. Crystal dimensions: 0.28 x 0.24 x 0.1 mm³. 156171 reflections measured, 20783 unique (*R*_{meas} = 0.0513, 6921 observed with *I* > 2σ(*I*)) which were used in all calculations. Final values of *R*(*F*) and *wR*(*F*) were 0.0424 and 0.0448 respectively. (b) $[\text{Ga}_{10}\text{S}_{16}(\text{NC}_6\text{H}_7)(\text{N}_2\text{C}_{12}\text{H}_{10})_{3/2}]^{2-}$ (2), *M*=1590.75, triclinic, space group *P-1*, *a* = 12.4678(12) Å, *b* = 13.6806(13) Å, *c* = 20.385(2) Å, α=81.599(6)°, β=88.542(5)°, γ=82.967(5)° *V* = 3413.8(6) Å³, *Z* = 2. Crystal dimensions: 0.7 x 0.36 x 0.16 mm³. 89986 reflections measured, 20798 unique (*R*_{meas} = 0.0336, 11508 observed with *I* > 2σ(*I*)) which were used in all calculations. Final values of *R*(*F*) and *wR*(*F*) were 0.0636 and 0.0788 respectively. Data collections using a Bruker X2 APEX 2 diffractometer (Mo *K*_α λ=0.71073 Å), at 100 K. The structures were solved by direct methods using the program SIR92 and model refined using CRYSTALS. The C and N atoms of the amine molecules were modeled isotropically. In (2) some of the dipyriddy ligands were found to be disordered over two crystallographically inequivalent positions, and therefore their site occupancies refined. The data were treated with SQUEEZE, to correct the effect of the disordered organic cations.
- (13) Lattice parameters at 100K: *a* = 37.055(3) Å, *b* = 19.3093(13) Å, *c* = 18.5411(12) Å, space group *Pcca*.
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The synthesis and characterisation of novel covalent organic-inorganic architectures containing organically-functionalised supertetrahedra is described. The structures of these unique materials consist of one-dimensional zigzag chains or of honeycomb-type layers, in which gallium-sulfide supertetrahedral clusters and dipyrrolyl ligands alternate.
