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Solvothermal synthesis and characterisation of new one-dimensional indium and gallium sulphides: $[C_{10}N_4H_{26}]_{0.5}[InS_2]$ and $[C_{10}N_4H_{26}]_{0.5}[GaS_2]$

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Abstract

Two new main group metal sulphides, $[C_{10}N_4H_{26}]_{0.5}[InS_2]$ (**1**) and $[C_{10}N_4H_{26}]_{0.5}[GaS_2]$ (**2**) have been prepared solvothermally in the presence of 1,4-bis(3-aminopropyl)piperazine and their crystal structures determined by single-crystal X-ray diffraction. Both compounds are isostructural and crystallise in the monoclinic space group $P2_1/n$ $(Z = 4)$, with $a = 6.5628(5)$, $b = 11.2008(9)$, $c = 12.6611(9)$ Å and $\beta = 94.410(4)^\circ$ ($wR = 0.035$) for compound (**1**) and $a = 6.1094(5)$, $b = 11.2469(9)$, $c = 12.7064(10)$ Å and $\beta = 94.313(4)^\circ$ ($wR = 0.021$) for compound (**2**). The structure of $[C_{10}N_4H_{26}]_{0.5}[MS_2]$ ($M =$ In,Ga) consists of one-dimensional $[MS_2]^-$ chains which run parallel to the crystallographic a axis and are separated by diprotonated amine molecules. These materials represent the first example of solvothermally prepared one-dimensional gallium and indium sulphides.

Keywords: Solvothermal synthesis; Crystal structure; Indium sulphides; Gallium sulphides

1. Introduction

There have been extensive research efforts to develop new microporous materials during the last few decades, because of their technological importance for applications such as catalysis or molecular sieves [1]. Although research has focused primarily on oxygen-based frameworks, there has been an increasing interest in the preparation of microporous sulphide-based materials [2], since the extension to sulphides by Bedard et al. [3,4] of the synthetic methodologies used for zeolites. Microporous sulphides have enormous technological potential as multifunctional materials, capable of combining the ion-exchanging and catalytic features of zeolites with the semiconducting behaviour of metal chalcogenides. Potential areas of application for semiconducting microporous materials range from molecule discriminating sensors [5] to fast-ion conductors [6] for electrochemical devices.

Solvothermal synthesis has been applied increasingly to the synthesis of open-framework sulphides containing elements of Group 13 (In) [7], Group 14 (Ge, Sn) [8,9] and Group 15 (As, Sb) [8,9]. The structures of these materials are based on a variety of building units such as $In_{10}S_{20}^{10-}$ supertetrahedra [7], adamantane-like $Ge_4S_{10}^{4-}$ units [8] and $Sb_3S_6^{3-}$ semicubes [10], which differ markedly from those found in oxide materials. The supertetrahedral clusters, which constitute the building units of the majority of the reported structures for indium sulphides, contain corner-sharing InS_4 tetrahedra, and can be described as tetrahedrally shaped fragments of the cubic ZnS-type lattice. These supertetrahedral clusters are generally denoted as T_p, where the index p indicates the number of individual InS_4 tetrahedron along each edge. Isolated T2 supertetrahedral clusters, $[In_4S_{10}]^{8-}$, have been obtained from aqueous solutions [11], while linkage of supertetrahedral units by their vertices results in the formation of two- or three-dimensional structures. For example, a non-interpenetrating three-dimensional indium sulphide containing T3 units, $[In_{10}S_{20}]^{10-}$ which delimit intersecting

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channels of 15 Å diameter, has been reported [12], while three-dimensional materials containing larger heterometallic T4 clusters, $[M_4In_{16}S_{33}]^{10-}$ (M = Mn, Co, Zn, Cd) [13], and T5 clusters, $[Cu_5In_{30}S_{54}]^{13-}$, have also been prepared [14]. Structures containing building units not related to supertetrahedral clusters are very scarce, and appear to be limited to those of $[(C_3H_7)_2NH_2]_3[In_6S_{11}H]$ [15] and $[C_{13}H_{28}N_2]_{6.5}[In_{33}S_{56}]$ [16]. The layered structure of $[(C_3H_7)_2NH_2]_3[In_6S_{11}H]$ can be described as containing In_6S_{11} chains linked by edge-sharing InS_4 tetrahedra [15], while the three-dimensional framework of $[C_{13}H_{28}N_2]_{6.5}[In_{33}S_{56}]$ is constructed from the cross-linking of helical chains of corner-sharing InS_4 tetrahedra [16]. It is worth noting that no solvothermally prepared one-dimensional indium sulphides have been reported to date. In contrast to the indium sulphides, little is known about the related gallium sulphides. Zheng et al. [17,18] reported recently the first solvothermal syntheses of a small number of three-dimensional gallium frameworks containing T2 $[Ga_{4-x}M_xS_{10}]^{8-x}$ (M = Ge, Sn), T3 $[Ga_{10}S_{20}]^{10-}$ and T4 $[Zn_4Ga_{16}S_{33}]^{10-}$ clusters. These results suggest that their structural chemistry may be similar to that of the indium sulphides. Gallium sulphides with building units not related to the supertetrahedral clusters have not been reported.

In the present contribution, the solvothermal synthesis and crystal structure of two novel one-dimensional indium and gallium sulphides, $[C_{10}N_4H_{26}]_{0.5}[InS_2]$ and $[C_{10}N_4H_{26}]_{0.5}[GaS_2]$, is described. Both materials contain isolated one-dimensional $[MS_2]^-$ chains (M = Ga, In), formed by edge-linked MS_4 tetrahedra, and represent the first example of solvothermally prepared one-dimensional gallium and indium sulphides.

2. Synthesis and characterisation

For the synthesis of $[C_{10}N_4H_{26}]_{0.5}[InS_2]$ (**1**), a mixture of In (0.2298g; 2 mmol) and S (0.1600 g; 5 mmol) was loaded into a 23 mL Teflon-lined stainless-steel autoclave. Then 4.6 mL of 1,4-bis(3-aminopropyl)piperazine (BAPP) was added to form a mixture with an approximate molar composition In:S:BAPP of 1:2.5:11. After stirring the mixture, the container was closed, heated at 145 °C for 5 days, and then cooled to room temperature at a cooling rate of 1 °C min^{-1}. $[C_{10}N_4H_{26}]_{0.5}[GaS_2]$ (**2**) was prepared from a mixture of Ga_2S_3:S:BAPP, with an approximate molar composition 1:1:15, heated in a 23 ml autoclave at 160 °C for 10 days. The products were filtered, washed with ethanol and deionised water and dried in air at room temperature. Under these conditions, the product of the reaction containing In consists of a mixture of clear needles and white powder, while the product of the reaction containing gallium contains a small number of transparent cubes and a white powder. Powder X-ray diffraction data on a ground portion of the bulk samples were collected with nickel-filtered Cu$K\alpha$ radiation (λ = 1.5418 Å), using a Philips PA2000 powder diffractometer. The diffraction pattern of the product of the reaction containing indium indicates the presence of a single phase that can be indexed on the basis of the monoclinic unit cell determined for (**1**) from the single-crystal diffraction study (Fig. 1(a)). The product of the reaction containing gallium is a mixture of Ga_2S_3 and an unidentified phase (Fig. 1(b)). Peaks arising from (**2**), which is a minority phase cannot be identified in the powder diffraction pattern. Synthetic studies, directed at attempts to produce a single-phase material of (**2**) and single crystals of the majority phase are underway. Compounds (**1**) and (**2**) were found to be stable in air for a period of several months.

The clear crystals of (**1**) were separated from the bulk product by handpicking. A compositional analysis of (**2**) was not attempted owing to the small amount of crystals available. Combustion analysis for the crystals of (**1**) gave C 22.57, H 4.86 and N 10.56% which compare favourably with the values calculated from the crystallographically determined formula $[C_{10}N_4H_{26}]_{0.5}[InS_2]$ (C 21.44, H 4.68 and N 10.00%). Thermogravimetric analysis was performed using a DuPont Instruments 951 thermal analyser. Approximately 10 mg of finely ground crystals of (**1**) were heated under a flow of dry nitrogen over the temperature range 25–350 °C at a heating rate of 2 °C min^{-1}. Decomposition takes place in a single sharp step, the onset of which is at 240 °C. The total weight loss of 39.4% is slightly larger than that expected for the total removal of the amine (calculated 36%), which may indicate the concomitant loss of a fraction of the sulphur (ca. 15%). Powder X-ray diffraction of the decomposition product indicates that thermal decomposition produces an amorphous material.

3. Crystal structure determination

Crystals of (**1**) (dimensions 0.02 × 0.02 × 0.14 mm) and of (**2**) (dimensions 0.06 × 0.08 × 0.08 mm) were mounted on glass fibres and X-ray intensity data collected at 100 K using a Bruker X8 APEX 2 diffractometer [19] with graphite monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). Full crystallographic details are given in Table 1. The structure was solved by direct methods using the program SIR92 [20] that located In, Ga and all S atoms. Subsequent Fourier calculations and least-squares refinements on F were carried out in the CRYSTALS program suite [21]. The C and N atoms of the amine were located in difference Fourier maps. All non-hydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were placed geometrically after each cycle of refinement, but not refined. A three-term Chebyshev polynomial was applied as a weighting scheme [22]. After locating all the non-hydrogen atoms, R-factors for (**1**) remained high (over 15%). Careful examination of the data suggested that the crystal could be twinned, and the program ROTAX [23] was used to identify a possible twin law. The twin law was

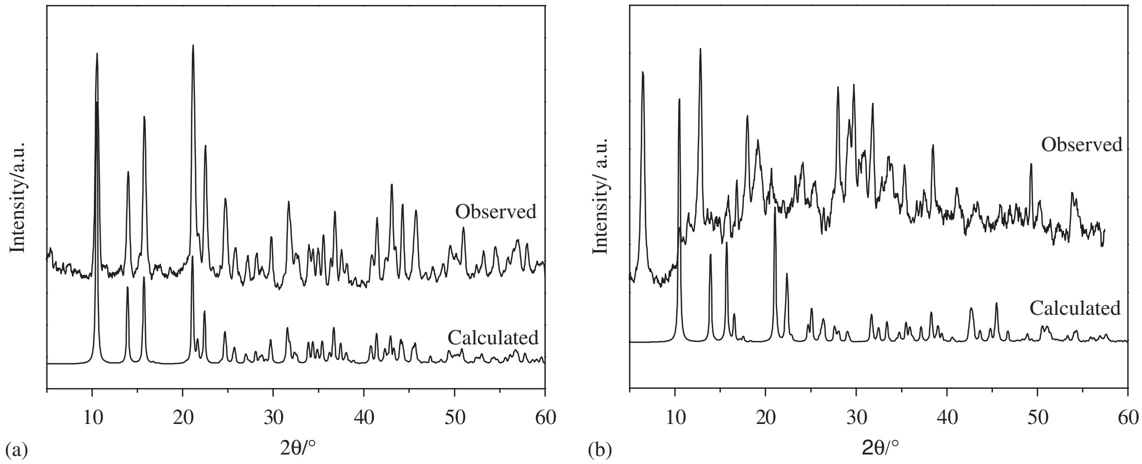

Fig. 1. Observed powder X-ray diffraction patterns for the bulk product of (a) reaction producing $[C_{10}N_4H_{26}]_{0.5}[InS_2]$ (**1**) and (b) reaction producing $[C_{10}N_4H_{26}]_{0.5}[GaS_2]$ (**2**). Calculated powder diffraction patterns for (**1**) and (**2**), respectively, have been included for comparison purposes.

Table 1
Crystallographic data for $[C_{10}N_4H_{26}]_{0.5}[InS_2]$ and $[C_{10}N_4H_{26}]_{0.5}[GaS_2]$

Formula	$[C_{10}N_4H_{26}]_{0.5}[InS_2]$ (**1**)	$[C_{10}N_4H_{26}]_{0.5}[GaS_2]$ (**2**)
M_r	280.12	235.02
Crystal habit	Colourless needle	Colourless block
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
T (K)	100	100
a (Å)	6.5628(5)	6.1094(5)
b (Å)	11.2008(8)	11.2469(9)
c (Å)	12.6611(9)	12.7064(10)
β (deg.)	94.410(4)	94.313(4)
V (Å)	927.94(12)	870.61(12)
Z	4	4
μ (cm^{-1})	2.931	3.569
Measured data	23956	25269
Unique data	2715	2546
Observed data ($I>3\sigma(I)$)	1173	1577
R_{merg}	0.040	0.030
R	0.034	0.019
wR	0.035	0.021

identified as the matrix:

$$\begin{pmatrix} 1 & 0 & 0.003 \\ 0 & -1 & 0 \\ -0.286 & 0 & -1 \end{pmatrix},$$

which corresponds to two-fold axis rotation about the [−701] reciprocal lattice direction. Twin fractions refined to 0.577(4) and 0.423(4) respectively, giving a final residual R of 0.034 and wR of 0.035.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre, with the CCDC Nos. 283556 and 283557. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 44 1223 336 033, e-mail: deposit@ccdc.cam.ac.uk).

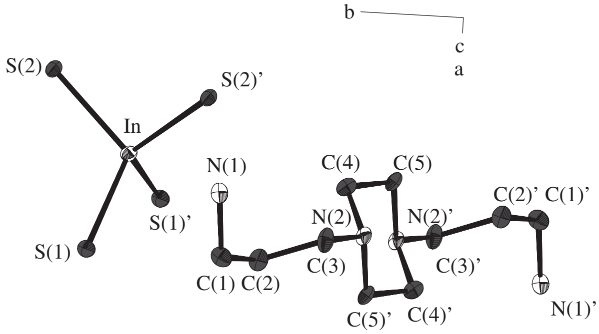

Fig. 2. Local coordination of the non-hydrogen atoms in $[C_{10}N_4H_{26}]_{0.5}$ $[InS_2]$ (**1**) showing the atom labelling scheme and ellipsoids at 50% probability.

4. Results

The local coordination and atom-labelling scheme is depicted in Fig. 2 and selected bond lengths and angles are given in Table 2. The structures of (**1**) and (**2**) consist of MS_4 tetrahedra (M = Ga, In), linked together by sharing opposite edges to form one-dimensional $[MS_2]^-$ chains as shown in Fig. 3. The indium atom in (**1**) is coordinated to four sulphur atoms at distances in the range 2.4547(15)–2.4774(15) Å, while the gallium-sulphur distances in (**2**) lie in the range 2.2913(6)–2.3043(6) Å (Table 2). These values are consistent with those reported for tetrahedrally coordinated indium and gallium discrete sulphide clusters [11]. The edge sharing of the MS_4 units results in short metal–metal distances along the $[MS_2]^-$ chain, of ca. 3.28 Å for (**1**) and ca. 3.06 Å for (**2**). Although these distances are comparable with the average metal–metal distances in indium and gallium metals (3.34 and 2.70 Å, respectively) [24], bond valence sums [25] are

Table 2
Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) for non-hydrogen atoms in $[C_{10}N_4H_{26}]_{0.5}[InS_2]$ (**1**) and $[C_{10}N_4H_{26}]_{0.5}[GaS_2]$ (**2**)

	$[C_{10}N_4H_{26}]_{0.5}[MS_2]$	
	$M = \text{In}$	$M = \text{Ga}$
M		
x	0.24974(6)	0.24974(4)
y	0.49707(4)	0.49802(2)
z	0.50056(4)	0.49926(2)
U_{iso}	0.0129	0.0108
S(1)		
x	0.0187(2)	0.02081(8)
y	0.43137(13)	0.43850(5)
z	0.63260(12)	0.62401(4)
U_{iso}	0.0146	0.0145
S(2)		
x	0.4976(2)	0.49788(8)
y	0.34787(12)	0.35845(5)
z	0.44366(12)	0.44932(4)
U_{iso}	0.0143	0.0143
N(1)		
x	0.1976(7)	0.1801(3)
y	0.8153(4)	0.81313(16)
z	0.2972(4)	0.29485(14)
U_{iso}	0.0156	0.0171
N(2)		
x	0.4357(7)	0.4394(3)
y	0.5314(4)	0.53010(15)
z	0.1017(4)	0.10296(14)
U_{iso}	0.0142	0.0152
C(1)		
x	0.4262(9)	0.4239(4)
y	0.8046(6)	0.8025(2)
z	0.2932(5)	0.29073(17)
U_{iso}	0.0191	0.0179
C(2)		
x	0.4854(10)	0.4888(4)
y	0.7327(5)	0.7308(2)
z	0.1972(5)	0.19578(16)
U_{iso}	0.0189	0.0169
C(3)		
x	0.4026(10)	0.4057(4)
y	0.6043(5)	0.6030(2)
z	0.1959(5)	0.19695(17)
U_{iso}	0.0202	0.0190
C(4)		
x	0.3213(9)	0.3040(3)
y	0.5705(6)	0.5669(2)
z	0.0049(5)	0.00815(17)
U_{iso}	0.0202	0.0178
C(5)		
x	0.6551(9)	0.6708(4)
y	0.5202(5)	0.52357(19)
z	0.0840(5)	0.07917(17)
U_{iso}	0.0198	0.0178

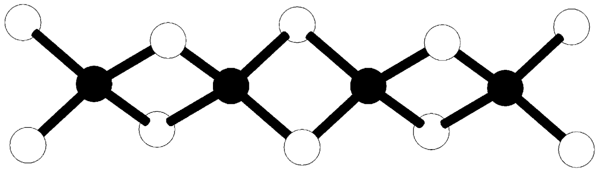

Fig. 3. View of a fragment of one isolated $[InS_2]^-$ chain. Key: indium, large solid circles; sulphur, large open circles.

Table 3
Selected bond distances (Å), bond valences (v.u.) and angles (deg.) for $[C_{10}N_4H_{26}]_{0.5}[InS_2]$ (**1**) and $[C_{10}N_4H_{26}]_{0.5}[GaS_2]$ (**2**)

	$[C_{10}N_4H_{26}]_{0.5}[MS_2]$			
	$M = \text{In}$		$M = \text{Ga}$	
		v^a		v^a
Bond				
M–S(1)	2.4547(15)	0.77	2.2913(6)	0.72
M–S(1)^b	2.4763(15)	0.73	2.3034(6)	0.70
M–S(2)	2.4774(15)	0.73	2.3043(6)	0.70
M–S(2)^c	2.4666(14)	0.75	2.2931(6)	0.72
Sum		2.98		2.84
M–*M*	3.278(1)		3.0533(5)	
	3.287(1)		3.0568(5)	
Angle				
S(1)–*M*–S(1)^b	96.68(5)		96.71(2)	
S(1)–*M*–S(2)^c	116.93(5)		116.16(2)	
S(2)–*M*–S(1)	116.72(5)		116.10(2)	
S(2)–*M*–S(1)^b	117.97(5)		118.50(2)	
S(2)–*M*–S(2)^c	96.68(4)		96.65(2)	
S(2)^c–*M*–S(1)^b	113.23(5)		114.10(2)	

[a] Bond valences and their sums calculated using parameters from Ref. [25].

[b] Symmetry transformations used to generate equivalent atoms: $-x$, $1-y$, $1-z$.

[c] Symmetry transformations used to generate equivalent atoms: $1-x$, $1-y$, $1-z$.

consistent with the formal oxidation states of In(III) and Ga(III) and indicate that electrons are localised. Charge balancing requires diprotonation of the amine. The MS_4 tetrahedra are slightly distorted as evidenced by S–*M*–S angles varying between 96.68(4) and 117.97(5)° for (**1**) and between 96.65(2) and 118.50(2) for (**2**). Similar distortions have been reported for edge-shared MS_4 units in ternary sulphides containing isolated $[M_2S_6]^{6-}$ ions, such as $Na_6Ga_2S_6$ [26] or $A_6In_2S_6$ ($A = \text{Na, Rb}$) [27,28], and in $[(C_3H_7)_2NH_2]_3[In_6S_{11}H]$ [15] (Table 3).

The one-dimensional $[MS_2]^-$ chains of (**1**) and (**2**) are similar to those found in SiS_2 [29], in $KFeS_2$-type compounds [30] and in $[NH_4][CuMoS_4]$ [31], which is an ordered variant in which Cu and Mo atoms alternate along the chain. A gallium selenide containing six gallium atom fragments, $[Ga_6Se_{14}]^{10-}$ [32], of this type of one-dimensional chains has also been reported and recently a solvothermally prepared gallium selenide, $[C_4H_{11}N_2][GaSe_2]$, which

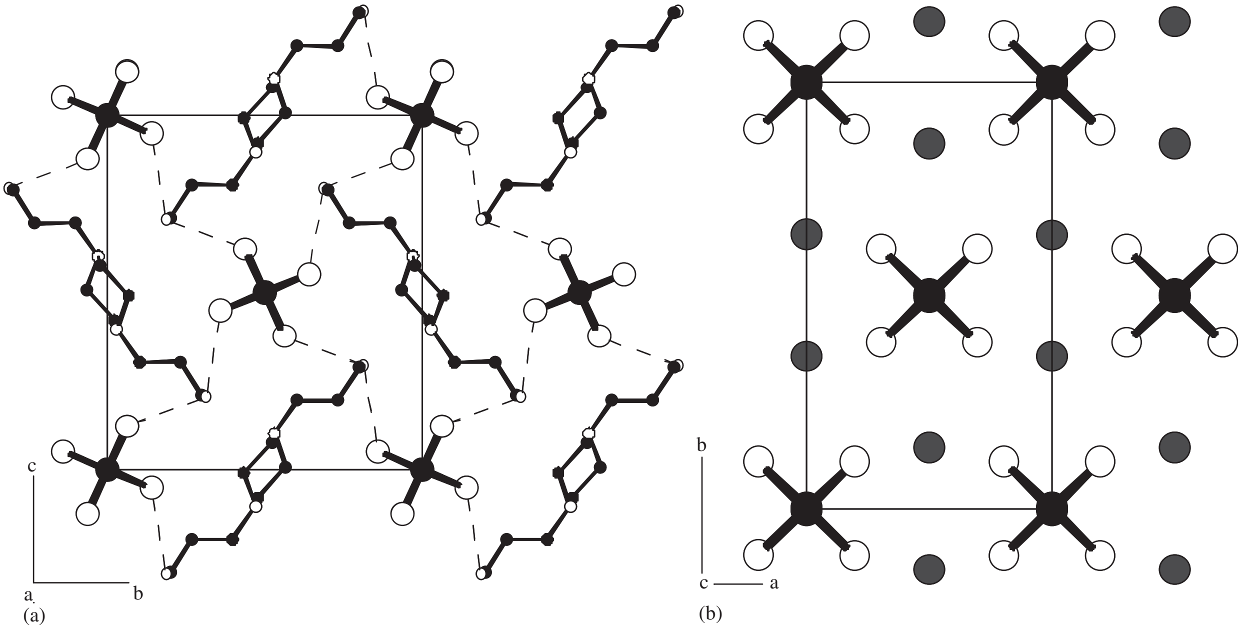

Fig. 4. Comparison of the structure of (a) $[C_{10}N_4H_{26}]_{0.5}[InS_2]$ (**1**) viewed along [100] and (b) $KFeS_2$[30] viewed along [001]. The short sulphur–nitrogen distances in (a) are indicated by dashed lines. Hydrogen atoms have been omitted for clarity. Key: indium/iron, large solid circles; sulphur, large open circles; potassium, large shaded circles; carbon, small solid circles and nitrogen, small open circles.

contains $[GaSe_2]^-$ chains separated by monoprotonated piperazine cations has been described [33]. However, the packing of the chains in the title compound differs significantly from that found in compounds such as $KFeS_2$ or SiS_2. In $[C_{10}N_4H_{26}]_{0.5}[MS_2]$, the infinite $[MS_2]^-$ chains run parallel to the *a*-axis and are separated from each other by BAPP cations (Fig. 4a). The two-fold screw axis along $\frac{1}{4}$, y, $\frac{1}{4}$ generates two $[MS_2]^-$ chains per unit cell. The two chains, related approximately by a lattice translation of (0, $\frac{1}{2}$, $\frac{1}{2}$), are rotated by ca. 45° with respect to each other. This contrasts with the packing of the chains in previously reported compounds, in which all the $[MS_2]^-$ chains are parallel and exhibit an identical orientation; a representative example is $KFeS_2$, for which the crystal packing is shown in Fig. 4b. The differences in packing might be related to the presence, in the title compound, of a hydrogen-bond network. In $[C_{10}N_4H_{26}]_{0.5}[MS_2]$, the organic cations lie approximately parallel to the (100) plane, in two alternating orientations. Each terminal N atom in the BAPP cations has two sulphur neighbours, in two different chains, within hydrogen-bonding distance (ca. 3.25 Å) and, as shown in Fig. 4a, each BAPP cation appears to exhibit hydrogen-bonding interactions with the four nearest $[MS_2]^-$ chains.

While materials containing one-dimensional chains of $[MS_2]^-$ have been reported previously, $[C_{10}N_4H_{26}]_{0.5}[MS_2]$ ($M = $ Ga,In) represents the first example of a sulphide containing isolated $[MS_2]^-$ chains separated by organic cations. The successful synthesis of isostructural gallium and indium sulphides appears to corroborate previous suggestions [18] of a large degree of similarity between the structural chemistry of solvothermally prepared indium and gallium sulphides. Given that the vast majority of the structures reported to date for solvothermally prepared indium sulphides and all of those reported for gallium sulphides, are based on supertetrahedral clusters [34], the possibility of forming $[MS_2]^-$ chains in solvothermal reactions suggests that greater structural diversity than previously thought might be possible within these systems. Cross-linking of these $[MS_2]^-$ chains with other building units might give access to novel two- or three-dimensional structures, and further work, particularly within the Ga–S system, might result in the identification of other structural building units.

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