Inorg. Chem. **2006**, *45*, 4150–4156

Inorganic Chemistry
Article

From One-Dimensional Chains to Three-Dimensional Networks: Solvothermal Synthesis of Thiogallates in Ethylenediamine

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Received November 28, 2005

Five new thiogallates have been prepared solvothermally in the presence of ethylenediamine and characterized by single-crystal X-ray diffraction, thermogravimetry, and elemental analysis. $[enH_2][Ga_4S_7(en)_2]$ (**1**), which crystallizes in the monoclinic space group $P2_1/c$ with lattice parameters $a = 12.8698(12)$ Å, $b = 10.4812(9)$ Å, $c = 16.5473(14)$ Å and $\beta = 102.457(4)°$ ($Z = 4$), exhibits a layered structure in which both covalently and hydrogen-bonded template molecules coexist. The structures of $[M(en)_3]_{0.5}[GaS_2]$ (M = Mn (**2**) (orthorhombic, *Cmcm*, $a = 9.5555(6)$ Å, $b = 15.0696(10)$ Å, $c = 12.2893(7)$ Å, $Z = 8$) M = Co (**3**) (orthorhombic, *Cmcm*, $a = 9.4660(7)$ Å, $b = 15.0990(11)$ Å, $c = 12.2540(8)$ Å, $Z = 8$), M = Ni (**4**) (orthorhombic, *Cmcm*, $a = 9.4510(10)$ Å, $b = 15.1416(15)$ Å, $c = 12.2387(11)$ Å, $Z = 8$)) and $Mn(en)_2Ga_2S_4$ (**5**) (monoclinic, *C*2/*c*, $a = 14.3002(11)$ Å, $b = 7.9509(5)$ Å, $c = 12.1184(6)$ Å, $\beta = 100.191(4)°$, $Z = 4$) are closely related and contain one-dimensional $[GaS_2]^-$ chains, which are separated by $[M(en)_3]^{2+}$ counterions in **2**, **3**, and **4**, and linked into a three-dimensional structure by $[Mn(en)_2]^{2+}$ units in **5**.

Introduction

Following the report by Bedard[1] that template-directed synthesis can be applied to effect the crystallization of tin and germanium sulfides, there has been considerable interest in the solvothermal synthesis of chalcogenides. The majority of materials produced to date contain the main-group elements of Group 13 (In),[2,3] Group 14 (Ge, Sn),[4,5] and Group 15 (As, Sb).[4,5] The structures of these materials are based on a variety of building units such as $[In_{10}S_{20}]^{10-}$ supertetrahedra,[2] adamantane-like supertetrahedral $[Ge_4S_{10}]^{4-}$ units,[4] and $[Sb_3S_6]^{3-}$ semicubes.[6] Of those building units, supertetrahedral clusters such as $[In_{10}S_{20}]^{10-}$ or $[Ge_4S_{10}]^{4-}$ are particularly interesting because by replacing regular tetrahedra with supertetrahedral clusters in structures such as diamond, crystalline microporous solids with large pores, representing more than 80% of their crystal volume, can be generated.[7,8] These supertetrahedral clusters, which can be described as tetrahedrally shaped fragments of the cubic ZnS-type lattice, are generally denoted as T*n*, where the index *n* indicates the number of individual tetrahedron along each edge. The nature of the cations involved in these clusters is as follows. T2 clusters, such as $[Ge_4S_{10}]^{4-}$ or $[In_3GeS_{10}]^{7-}$,[9] contain tetravalent ions or a mixture of tetra- and trivalent ions; T3 clusters, such as $In_{10}S_{20}{}^{10-}$,[2] contain trivalent ions; T4 clusters, such as $[M_4In_{16}S_{33}]^{10-}$ (M = Mn, Co, Zn, Cd),[10] contain a mixture of tri- and divalent ions; while T5 clusters, such as $[Cu_5In_{30}S_{54}]^{13-}$,[11] contain tri- and monovalent ions. The progressive introduction of lower valences with increasing the size of the cluster limits the expansion of the negative charge in the cluster, which would render the solid unstable.[7] Other types of tetrahedral clusters, such as the pentasupertetrahedral clusters,[12] have been recently reported.[13]

While a number of indium sulfide structures based on supertetrahedral clusters have been reported,[3] little is known about the related thiogallates. Isolated T2 $[Ga_4S_{10}]^{8-}$ anions have been described,[14] and Zheng et al. have reported the

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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,[9,15] while the present author described recently a solvothermally prepared gallium sulfide $[C_{10}N_4H_{26}]_{0.5}[GaS_2]$ containing one-dimensional $[GaS_2]^-$ chains.[16] Three-dimensional frameworks of supertetrahedral T3 and T4 gallium selenide clusters have also been described recently,[17] and Dong et al. reported a layered gallium selenide, $[enH]_2[Ga_4Se_7(en)_2]$,[18] which does not contain supertetrahedral clusters.

In this work, the crystal structures of five thiogallates prepared under solvothermal conditions in the presence of ethylenediamine (en) are described. $[enH_2][Ga_4S_7(en)_2]$ (**1**) is the first example of a solvothermally prepared thiogallate in which covalently and hydrogen-bonded template molecules coexist. The structures of $[M(en)_3]_{0.5}[GaS_2]$ (M = Mn (**2**), Co (**3**), Ni (**4**)) and $Mn(en)_2Ga_2S_4$ (**5**) are closely related and contain one-dimensional $[GaS_2]^-$ chains, which are isolated in $[M(en)_3]_{0.5}[GaS_2]$ but linked into a three-dimensional structure by $[Mn(en)_2]^{2+}$ units in **5**.

Experimental Section

Synthesis of $[enH_2][Ga_4S_7(en)_2]$ (1). A mixture of Ga_2S_3 (0.400 g; 1.7 mmol) and S (0.054 g; 1.7 mmol) was loaded into a 23 mL Teflon-lined stainless steel autoclave. Ethylenediamine (3.4 mL) was added to form a mixture with an approximate molar composition Ga_2S_3/S/en = 1:1:30. After stirring the mixture, the container was closed, heated at 160 °C for 10 days, and then cooled to room temperature at a cooling rate of 1 °C min^{-1}. The reaction mixture was filtered, washed with ethanol and deionized water, and dried in air at room temperature. Under these conditions, the product consists of a mixture of an unidentified white powder and transparent plates of **1**. Subsequent synthetic studies were directed at attempts to produce a single-phase material. A single-phase sample containing only clear plates of **1** was subsequently prepared by heating a mixture with a molar composition Ga/S/en of 2:4:30 at a temperature of 170 °C for a 5 day period. For the remaining syntheses, yield of the main phase is always greater than 80%.

Synthesis of $[Mn(en)_3]_{0.5}[GaS_2]$ (2). A mixture of Ga_2S_3 (0.267 g; 1.15 mmol), S (0.037 g; 1.15 mmol), $MnCl_2{\cdot}4H_2O$ (0.113 g; 0.6 mmol), and en (2.3 mL), which corresponds to a molar composition of $Ga_2S_3/S/MnCl_2{\cdot}4H_2O$/en = 1:1:0.5:30, was loaded into a 23 mL Teflon-lined stainless steel autoclave. The container was closed and heated at a temperature of 170 °C for 12 days. The remainder of the procedure is identical to the one described above. The product consists of a large number of crystals of **2** and some crystals of **1**.

Synthesis of $[Co(en)_3]_{0.5}[GaS_2]$ (3). A mixture of Ga_2S_3 (0.540 g; 2.3 mmol), S (0.110 g; 3.4 mmol), $CoCl_2{\cdot}6H_2O$ (0.271 g; 1.1 mmol), and en (4.6 mL), which corresponds to a molar composition of $Ga_2S_3/S/CoCl_2{\cdot}6H_2O$/en = 1:1.5:0.5:30, was loaded into a 23 mL Teflon-lined stainless steel autoclave. The sealed container was heated at 160 °C for 20 days. The product contains mainly orange plates of **3** but also some clear plates of **1**.

Synthesis of $[Ni(en)_3]_{0.5}[GaS_2]$ (4). A mixture of Ga (0.160 g; 2.3 mmol), S (0.184 g; 5.7 mmol), NiS (0.104 g; 1.15 mmol), and en (4.6 mL), which corresponds to a molar composition of Ga/S/NiS/en = 1:2.5:0.5:30, was loaded into a 23 mL Teflon-lined stainless steel autoclave. $[Ni(en)_3]_{0.5}[GaS_2]$ was prepared by heating this reaction mixture at a temperature of 180 °C for 6 days. The product of the reaction contains mainly violet plates of **4** together with a small amount of clear plates of **1**.

Synthesis of $Mn(en)_2Ga_2S_4$ (5). A mixture of Ga_2S_3 (0.267 g; 1.1 mmol), S (0.055 g; 1.7 mmol), $MnCl_2{\cdot}4H_2O$ (0.113 g; 0.6 mmol), and en (1.2 mL), which corresponds to a molar composition of $Ga_2S_3/S/MnCl_2{\cdot}4H_2O$/en = 1:1.5:0.5:15, was loaded into a 23 mL Teflon-lined stainless steel autoclave. The container was closed and heated at a temperature of 170 °C for 13 days. The product consists of a large amount of clear hexagonal blocks of **5** and some crystals of **1**.

CHN Analysis. Combustion analysis was carried out on hand-picked crystals. **1**, found: C = 10.64%, H = 3.37%, N = 12.18%; calcd: C = 10.51%, H = 3.79%, N = 12.25%; **2**, found: C = 14.10%, H = 4.68%, N = 16.39%; calcd: C = 14.33%, H = 4.81%, N = 16.71%; **3**, found: C = 14.14%, H = 4.72%, N = 15.83%; calcd: C = 14.22%, H = 4.77%, N = 16.58%; **4**, found: C = 13.48%, H = 4.63%, N = 15.73%; calcd: C = 14.22%, H = 4.77%, N = 16.59%; **5**, found: C = 10.81%, H = 3.57%, N = 12.42%; calcd: C = 10.85%, H = 3.64%, N = 12.65%.

Thermogravimetric Analysis. Thermogravimetric analysis was performed using a DuPont Instruments 951 thermal analyzer. Approximately 10 mg of finely ground crystals were heated under a flow of dry nitrogen over the temperature range 30−600 °C at a heating rate of 2 °C min^{-1}. All the products are stable up to 210−280 °C, with the exception of **2**, which starts to decompose at 140 °C. In all cases, the weight loss is a multistage process, with the overall weight change corresponding approximately to the complete removal of the amine. The found weight losses, together with those calculated for the removal of the amine, are as follows. **1**, found: 25.0%; calcd: 26.5%; **2**, found: 36.0%; calcd: 35.9%; **3**, found: 37.1%; calcd: 35.6%; **4**, found: 39.5%; calcd: 35.6%; **5**, found: 26.7%; calcd: 27.1%. Powder X-ray diffraction indicates that the products of thermal decomposition are amorphous materials.

Crystal Structure Determination. Crystals were mounted on glass fibers and X-ray intensity data collected using a Bruker X8 APEX 2 diffractometer[19] with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$Å). After initial data collections at 293 K, it was found that the structures of **2**, **3**, and **4** contain disordered amine molecules, and therefore, the final data collection for these three materials was carried out at 100 K. Full crystallographic details are given in Table 1. The structures were solved by direct methods using the program SIR92[20] which located Ga, transition metals, 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. For **1** and **5**, all non-hydrogen atoms were refined anisotropically, while for **2**, **3**, and **4**, the N and C atoms, which were found to be disordered, were refined isotropically. The amine H atoms were placed geometrically after each cycle of refinement, but not refined. A Chebyshev polynomial was applied as a weighting scheme.[22]

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Table 1. Crystallographic Data for $[enH_2][Ga_4S_7(en)_2]$, $[M(en)_3]_{0.5}[GaS_2]$ (M = Mn, Co, Ni), and $Mn(en)_2Ga_2S_4$

formula	$[enH_2][Ga_4S_7(en)_2]$ (**1**)	$[Mn(en)_3]_{0.5}[GaS_2]$ (**2**)	$[Co(en)_3]_{0.5}[GaS_2]$ (**3**)	$[Ni(en)_3]_{0.5}[GaS_2]$ (**4**)	$Mn(en)_2Ga_2S_4$ (**5**)
M_r	685.66	251.46	253.47	253.36	442.83
crystal habit	colorless plate	colorless plate	orange plate	violet plate	colorless block
dimensions/mm^3	0.06× 0.01 × 0.02	0.07× 0.02 × 0.01	0.07× 0.01 × 0.01	0.05× 0.03 × 0.01	0.10× 0.10 × 0.06
cryst syst	monoclinic	orthorhombic	orthorhombic	orthorhombic	monoclinic
space group	$P2_1/c$	*Cmcm*	*Cmcm*	*Cmcm*	$C2/c$
T/K	293	100	100	100	293
a/Å	12.8698(12)	9.5555(6)	9.4660(7)	9.4510(10)	14.3002(11)
b/Å	10.4812(9)	15.0696(10)	15.0990(11)	15.1416(15)	7.9509(5)
c/Å	16.5473(14)	12.2893(7)	12.2540(8)	12.2387(11)	12.1184(6)
β/°	102.457(4)	-	-	-	100.191(4)
V/Å^3	2179.4(3)	1769.63(19)	1751.4(2)	1751.4(3)	1356.12(15)
Z	4	8	8	8	4
wavelength/Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ/cm^{-1}	5.587	4.193	4.463	4.591	5.452
measured data	34 328	16 286	12 578	10 577	8780
unique data	3984	1439	1413	1552	1964
observed data ($I > 3\sigma(I)$)	2201	861	690	763	1490
R_{merg}	0.039	0.036	0.049	0.042	0.028
$R(F_o)^a$	0.020	0.021	0.020	0.024	0.024
$R_w(F_o)^b$	0.022	0.025	0.021	0.023	0.027

^{a} $R(F_o) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. ^{b} $R_w(F_o) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

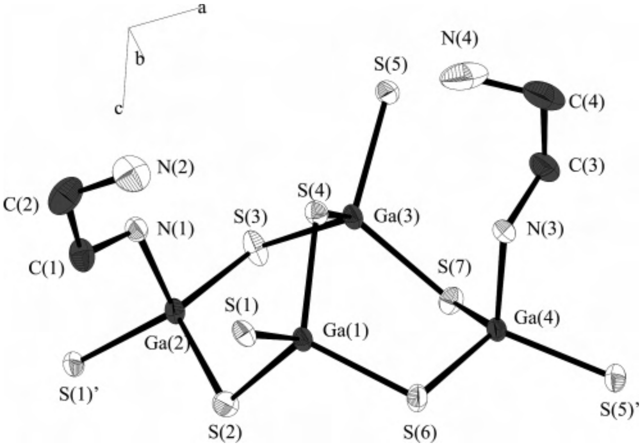

Figure 1. Local coordination of the non-hydrogen atoms in the layers of $[enH_2][Ga_4S_7(en)_2]$ (**1**) showing the atom labeling scheme and ellipsoids at 50% probability.

Results and Discussion

Structure of $[enH_2][Ga_4S_7(en)_2]$ (1). The structure of **1** consists of anionic layers of stoichiometry $[Ga_4S_7(en)_2]^{2-}$, between which protonated template molecules reside. Figure 1 shows the local coordination of the framework atoms, while selected bond lengths and angles are presented in Table 2. The gallium atoms Ga(1) and Ga(3) exhibit a distorted tetrahedral coordination, with an average Ga−S distance of 2.29 Å, comparable to values in the literature for thiogallates in tetrahedral coordination.[14] The atoms Ga(2) and Ga(4) are trigonal-pyramidally coordinated by sulfur. In addition, these two gallium atoms have a neighboring nitrogen from an ethylenediamine molecule at a distance of ca. 2.01 Å, resulting in overall tetrahedral coordination. In the structure of **1**, two GaS_4 and two GaS_3N tetrahedra are linked by their corners, forming a building unit with stoichiometry $[Ga_4S_7(en)_2]^{2-}$ (Figure 1), which can also be described as being constructed from two fused six-membered Ga_3S_3 rings in boat conformation. It is worth noting that, while the majority of the previously reported structures of solvothermally prepared thiogallates are based on supertetrahedral clusters,[9,15] this is not the case in **1**. The $[Ga_4S_7(en)_2]^{2-}$ building units are connected by their four terminal sulfurs to four other building units, forming a layer (Figure 2), which contains pores. When the van der Waals' radii[23] of Ga and S are taken into account, the effective aperture of these pores is ca. 4 × 1 Å^2. In this layer, the $[Ga_4S_7(en)_2]^{2-}$ units exhibit two alternating orientations in which the apex of the tetrahedra (and therefore the covalently bonded en molecules) point in opposite directions. Similar layers to those present in the structure of **1** have been found in the gallium selenide $[enH]_2[Ga_4Se_7(en)_2]$.[18] There are, however, differences between **1** and $[enH]_2[Ga_4Se_7(en)_2]$ in the orientation and amount of ethylenediamine molecules situated between the layers. The structure of **1** (Figure 3) contains 3 mol of en per formula

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[enH_2][Ga_4S_7(en)_2]$ (**1**)

Ga(1)−S(1)	2.3027(14)	Ga(3)−S(3)	2.2665(15)
Ga(1)−S(6)^a	2.2708(13)	Ga(3)−S(4)	2.2801(13)
Ga(1)−S(2)^b	2.2796(14)	Ga(3)−S(5)	2.3054(14)
Ga(1)−S(4)^b	2.2841(13)	Ga(3)−S(7)^c	2.2968(14)
Ga(2)−S(1)	2.2430(14)	Ga(4)−S(5)	2.2484(13)
Ga(2)−S(2)	2.2643(14)	Ga(4)−S(6)	2.2446(13)
Ga(2)−S(3)	2.2372(14)	Ga(4)−S(7)	2.2594(14)
Ga(2)−N(1)	2.015(3)	Ga(4)−N(3)	2.005(3)
S(4)^b−Ga(1)−S(2)^b	114.31(5)	S(7)^c−Ga(3)−S(3)	107.77(5)
S(4)^b−Ga1−S(6)^a	111.74(5)	S(7)^c−Ga(3)−S(4)	113.00(5)
S(2)^b−Ga(1)−S(6)^a	111.67(5)	S(3)−Ga(3)−S(4)	112.76(5)
S(4)^b−Ga(1)−S(1)	101.40(5)	S(7)^c−Ga(3)−S(5)	112.25(5)
S(2)^b−Ga(1)−S(1)	109.07(5)	S(3)−Ga(3)−S(5)	108.58(5)
S(6)^a−Ga(1)−S(1)	107.95(5)	S(4)−Ga(3)−S(5)	102.42(5)
S(1)−Ga(2)−S(2)	105.58(5)	S(5)−Ga(4)−S(6)	113.58(5)
S(1)−Ga(2)−S(3)	115.68(5)	S(5)−Ga(4)−S(7)	111.31(5)
S(2)−Ga(2)−S(3)	116.75(5)	S(6)−Ga(4)−S(7)	114.98(5)
S(1)−Ga(2)−N(1)	108.14(12)	S(5)−Ga(4)−N(3)	106.93(12)
S(2)−Ga(2)−N(1)	106.92(12)	S(6)−Ga(4)−N(3)	102.09(12)
S(3)−Ga(2)−N(1)	103.20(12)	S(7)−Ga(4)−N(3)	106.98(13)

^{a} Symmetry transformations used to generate equivalent atoms: $-1 + x, y, z$. ^{b} $1 - x, 1/2 + y, 3/2 - z$. ^{c} $2 - x, -1/2 + y, 3/2 - z$.

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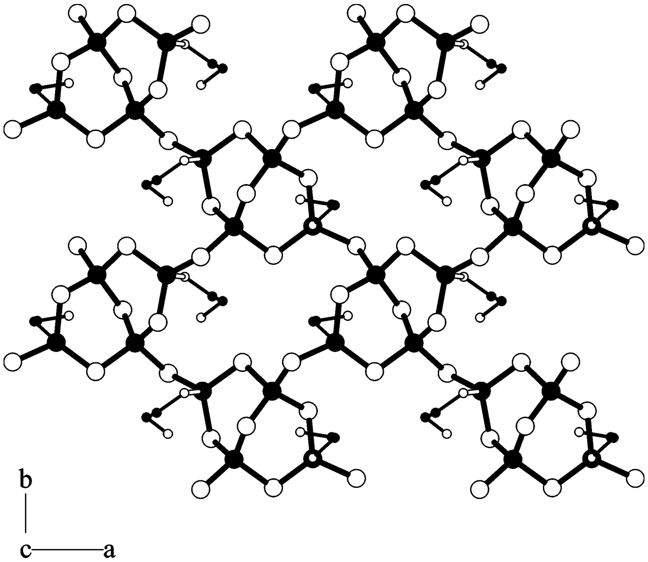

Figure 2. View along the [001] direction showing a $[Ga_4S_7(en)_2]^{2-}$ layer formed by linking $[Ga_4S_7(en)_2]^{2-}$ building units through their terminal sulfurs. Key: gallium, large black circles; sulfur, large open circles; carbon, small black circles; nitrogen, small open circles. Gallium−nitrogen bonds are shown in white. Hydrogen atoms have been omitted for clarity.

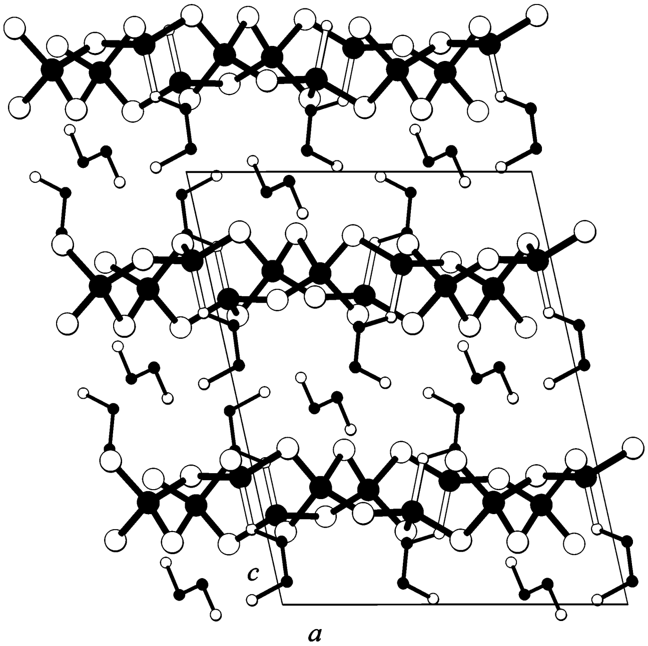

Figure 3. View along the [010] direction showing the location of the ethylenediamine molecules in **1** with the unit cell outlined. Gallium−nitrogen bonds are shown in white. Key as for Figure 2. Hydrogen atoms have been omitted for clarity.

unit, while $[enH]_2[Ga_4Se_7(en)_2]$ contains four. In both structures, 2 mol of en per formula unit are covalently bonded to the gallium atoms, while the remaining en resides as discrete molecules between the layers. In **1**, the nitrogen atoms of these isolated en molecules have a number of sulfur neighbors at distances in the range 3.25−3.8 Å, as well as other nitrogen atoms at distances of 2.8−2.95 Å, implying hydrogen-bonding interactions. Similar hydrogen-bonding interactions have been proposed for $[enH]_2[Ga_4Se_7(en)_2]$. Given the anionic nature of the thiogallate layers in **1**, charge balancing requires protonation of some of the amine molecules. The structural study is unable to establish directly the degree of protonation of the template molecules, but it is very unlikely that those acting as ligands would be protonated. Therefore, charge-balancing considerations require diprotonation of the isolated en molecules located between the layers. The IR spectrum of **1** is consistent with the presence of both protonated and unprotonated primary amine funcional groups.

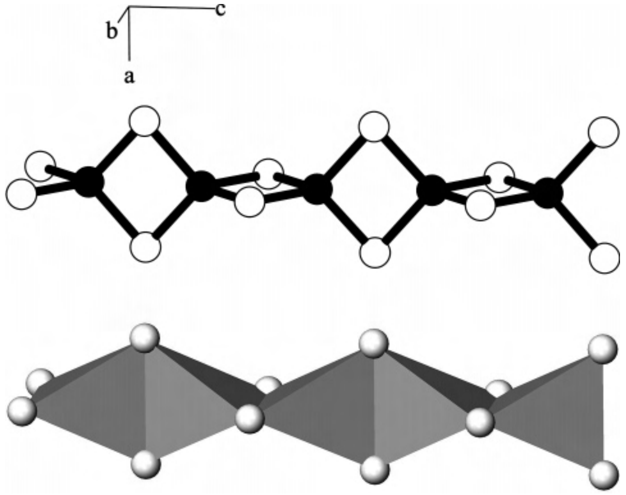

Figure 4. Two representations of the one-dimensional $[GaS_2]^-$ chain in **2**, **3**, and **4**, showing the edge-sharing GaS_4 tetrahedra. Key: gallium, large black circles; sulfur, large open circles.

Generally, the organic template molecules used in the solvothermal synthesis of metal chalcogenides enter the structure through weak hydrogen bonding. In extended chalcogenide structures, covalent bonding of the template molecules has only been found in a small number of hybrid chalcogenides such as CdQ·0.5en (Q = S, Se, Te)[24] and ZnTe·0.5L (L = aliphatic diamine)[25,26] or in rare examples of sulfides containing transition metals octahedrally coordinated both by sulfur and amines, such as $Mn_2Sb_2S_5$·L (L = amine).[27,28] **1** is the first example of a thiogallate in which the amine plays a dual role as a ligand and a structure directing agent.

Structure of $[M(en)_3]_{0.5}[GaS_2]$ (M = Mn (2), Co (3), Ni (4)). The structure of $[M(en)_3]_{0.5}[GaS_2]$ (M = Mn, Co, Ni) contains GaS_4 tetrahedra linked together by sharing opposite edges to form one-dimensional $[GaS_2]^-$ chains, as shown in Figure 4. Selected bond lengths and angles for $[M(en)_3]_{0.5}[GaS_2]$ are presented in Table 3. The average Ga−S distance is ca. 2.29 Å, comparable to the literature values for tetrahedrally coordinated thiogallates.[14] The GaS_4 tetrahedra are distorted, as evidenced by S−M−S angles which extend over the range 95.1−118.7°. Similar distortions have been reported for edge-shared MS_4 units in ternary sulfides containing isolated $[M_2S_6]^{6-}$ ions, such as $Na_6Ga_2S_6$,[29] or in

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Table 3. Selected Bond Lengths (Å), Bond Valences (v.u.) and Angles (deg) for $[Mn(en)_3]_{0.5}[GaS_2]$ (M = Mn, Co, Ni)

$[M(en)_3]_{0.5}[GaS_2]$

	M = Mn (**2**)		M = Co (**3**)		M = Ni (**4**)	
bonds		ν^a		ν^a		ν^a
Ga(1)−S(1)	2.2782(11)	0.75	2.2688(15)	0.77	2.2683(17)	0.77
Ga(1)−S(2)	2.3030(10)	0.70	2.3017(14)	0.70	2.3049(15)	0.70
Ga(1)−S(3)	2.2985(6)	0.71	2.2946(8)	0.71	2.2960(8)	0.71
Ga(1)−S(3)^b	2.2985(6)	0.71	2.2946(8)	0.71	2.2960(8)	0.71
	sum	2.87	sum	2.89	sum	2.89
M(1)−N(1)	2.274(3)	0.34	2.169(4)	0.41	2.127(4)	0.36
M(1)−N(1)^c	2.274(3)	0.34	2.169(4)	0.41	2.127(4)	0.36
M(1)−N(2)	2.287(4)	0.33	2.180(4)	0.40	2.135(4)	0.35
M(1)−N(2)^c	2.287(4)	0.33	2.180(4)	0.40	2.135(4)	0.35
M(1)−N(3)	2.276(4)	0.16	2.172(4)	0.20	2.129(5)	0.18
M(1)−N(3)^c	2.276(4)	0.16	2.172(4)	0.20	2.129(5)	0.18
M(1)−N(3)^d	2.276(4)	0.16	2.172(4)	0.20	2.129(5)	0.18
M(1)−N(3)^e	2.276(4)	0.16	2.172(4)	0.20	2.129(5)	0.18
	sum	1.98	sum	2.42	sum	2.14

$[M(en)_3]_{0.5}[GaS_2]$

angles	M = Mn (**2**)	M = Co (**3**)	M = Ni (**4**)
S(1)−Ga(1)−S(2)	95.05(3)	95.12(4)	95.26(4)
S(1)−Ga(1)−S(3)	114.62(2)	114.75(3)	114.72(3)
S(2)−Ga(1)−S(3)	118.70(2)	118.46(3)	118.28(3)
S(3)^b−Ga(1)−S(1)	114.62(2)	114.75(3)	114.72(3)
S(3)^b−Ga(1)−S(2)	118.70(2)	118.46(3)	118.28(3)
S(3)^b−Ga(1)−S(3)	96.58(3)	96.71(4)	96.96(4)

[a] Bond valences and their sums calculated using parameters from ref 31. [b] Symmetry transformations used to generate equivalent atoms: −*x*, −*y*, 1 − *z*. [c] −*x*, *y*, 1/2 − *z*. [d] *x*, *y*, 1/2 − *z*. [e] −*x*, *y*, *z*.

$[C_{10}N_4H_{26}]_{0.5}[MS_2]$ (M = Ga, In),[16] which contains one-dimensional $[MS_2]^-$ chains. The edge sharing of the GaS_4 units results in short metal−metal distances along the $[GaS_2]^-$ chain, of ca. 3.0 Å, which are comparable to those found in gallium metal.[30] The one-dimensional $[GaS_2]^-$ chains in the structure of $[M(en)_3]_{0.5}[GaS_2]$ run parallel to the crystallographic *c* axis and are separated by $[M(en)_3]^{2+}$ complexes. Bond valence sums[31] are consistent with the formal oxidation states of Ga(III) and divalent transition-metal cations. The en ligands of the $[M(en)_3]^{2+}$ complexes are disordered, with these complexes adopting either Λ or Δ conformations. The M−N bonds are within the expected range for M^{2+} cations octahedrally coordinated by nitrogen atoms.[32−34] Due to the preference for the formation of transition-metal complexes in the presence of strongly chelating amines, introduction of transition-metal ions into solvothermal reactions often results in the formation of an anionic main-group-element framework together with a charge-balancing cationic transition-metal complex, as exemplified by $[Mn(en)_3][Sb_2S_4]$ (M = Co, Ni),[32] $[M(en)_3][Sb_4S_7]$ (M = Fe, Ni),[32] and $[M(en)_3]_2[Ge_2S_6]$ (M = Mn, Ni),[33] as well as in the materials reported here, $[M(en)_3]_{0.5}[GaS_2]$ (M = Mn, Co, Ni).

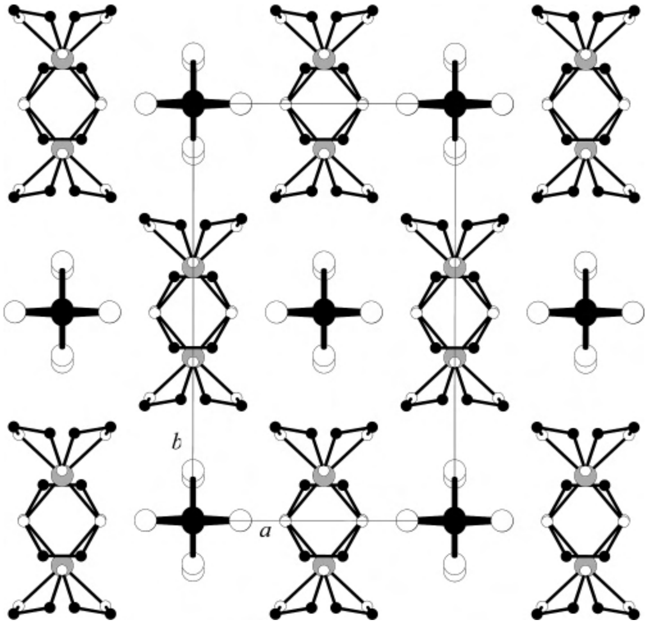

Figure 5. View along the [001] direction of $[Co(en)_3]_{0.5}[GaS_2]$ (**3**) with the unit cell outlined. Key: gallium, large black circles; sulfur, large open circles; cobalt, large shaded circles carbon, small black circles; nitrogen, small open circles. Hydrogen atoms have been omitted for clarity.

When compared with oxides, sulfides exhibit a greater tendency for the formation of low dimensional structures, and therefore, sulfides containing one-dimensional chains have been previously observed. For example, two types of one-dimensional chains with stoichiometry $[SbS_2]^-$, involving vertex-linked[32] or edge-linked[35] SbS_3^{3-} trigonal pyramids, have been reported. Repeated vertex-linking of tetrahedral MS_4^{4-} anions (M = Ge, Sn) results in the formation of one-dimensional $[MS_3]^{2-}$ chains, such as those observed in Na_2GeS_3[36] or Tl_2SnS_3.[37] One-dimensional chains involving

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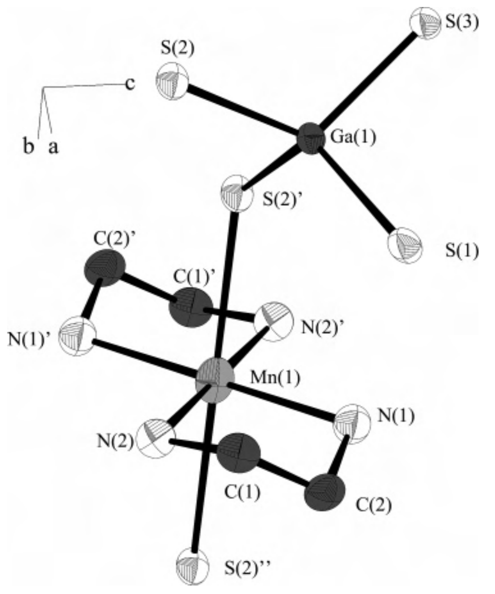

Figure 6. Local coordination of the non-hydrogen atoms in $Mn(en)_2Ga_2S_4$ (**5**) showing the atom labeling scheme and ellipsoids at 50% probability.

Table 4. Selected Bond Lengths (Å), Bond Valences (v.u.) and Angles (deg) for $Mn(en)_2Ga_2S_4$ (**5**)

		ν^c
Ga(1)−S(1)	2.2811(7)	0.74
Ga(1)−S(2)	2.2982(6)	0.71
Ga(1)−S(3)	2.2792(6)	0.74
Ga(1)−S(2)^a	2.3007(6)	0.70
	sum	2.89
Mn(1)−S(2)	2.7430(6)	0.23
Mn(1)−S(2)^b	2.7430(6)	0.23
Mn(1)−N(1)	2.247(2)	0.36
Mn(1)−N(2)	2.244(2)	0.36
Mn(1)−N(1)^b	2.247(2)	0.36
Mn(1)−N(2)^b	2.244(2)	0.36
	sum	1.90
S(1)−Ga(1)−S(2)	118.694(18)	
S(1)−Ga(1)−S(3)	97.97(2)	
S(2)−Ga(1)−S(3)	113.770(18)	
S(2)^a−Ga(1)−S(1)	117.082(17)	
S(2)^a−Ga(1)−S(2)	96.173(19)	
S(2)^a−Ga(1)−S(3)	114.322(17)	
S(2)−Mn(1)−N(1)	89.13(5)	
S(2)−Mn(1)−N(2)	83.78(5)	
S(2)^b−Mn(1)−N(1)	90.87(5)	
S(2)^b−Mn(1)−N(2)	96.22(5)	
N(1)−Mn(1)−N(2)	79.04(7)	
N(1)^b−Mn(1)−S(2)^b	89.13(5)	
N(1)^b−Mn(1)−S(2)	90.87(5)	
N(1)^b−Mn(1)−N(2)	100.96(7)	
N(2)^b−Mn(1)−N(1)	100.96(7)	
N(2)^b−Mn1−N(1)^b	79.04(7)	
N(2)^b−Mn(1)−S(2)	96.22(5)	
N(2)^b−Mn(1)−S(2)^b	83.78(5)	

^{a} Symmetry transformations used to generate equivalent atoms: $1 - x$, $-y$, $2 - z$. ^{b} $3/2 - x$, $-1/2 - y$, $2 - z$. ^{c} Bond valences and their sums calculated using parameters from ref 31.

edge-linked tetrahedra, similar to those present in $[M(en)_3]_{0.5}[GaS_2]$, have been found in SiS_2,[38] in $KFeS_2$-type compounds[39] and very recently in $[C_{10}N_4H_{26}]_{0.5}[MS_2]$ (M = Ga, In).[16] A gallium selenide containing six-gallium-atom fragments, $[Ga_6Se_{14}]^{10-}$,[40] of edge-linked tetrahedra chains has also been reported and a solvothermally prepared gallium selenide, $[C_4H_{11}N_2][GaSe_2]$, which contains $[GaSe_2]^-$ chains separated by monoprotonated piperazine cations has been described.[17] While $[C_{10}N_4H_{26}]_{0.5}[GaS_2]$ and $[C_4H_{11}N_2][GaSe_2]$ are examples of a gallium chalcogenides containing one-dimensional $[GaQ_2]^-$ (Q = S, Se) chains separated by organic cations, the compounds reported here constitute the first example containing this type of one-dimensional chain with metal complexes as counterions.

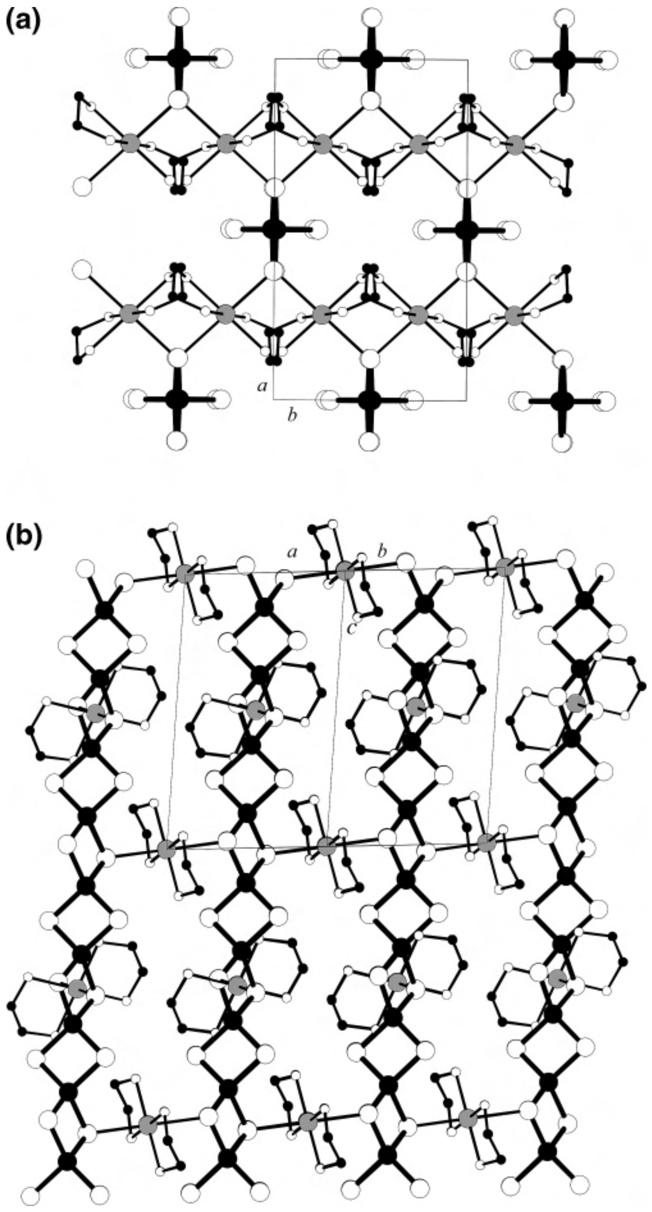

Figure 7. View of **5** (a) along the [001] direction and (b) along the [110] direction. The unit cell is outlined. Key: gallium, large black circles; sulfur, large open circles; manganese, large shaded circles; carbon, small black circles; nitrogen, small open circles. Hydrogen atoms have been omitted for clarity.

Structure of $Mn(en)_2Ga_2S_4$ (5). The structure of $Mn(en)_2Ga_2S_4$ is closely related to that of $[M(en)_3]_{0.5}[GaS_2]$

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and contains one-dimensional $[GaS_2]^-$ chains linked into a three-dimensional structure by $[Mn(en)_2]^{2+}$ complexes. It is worth noting that the reaction conditions employed for the synthesis of **2** and **5** are almost identical but differ in the amount of en added to the reaction mixture. Although the synthesis of the analogous $M(en)_2Ga_2S_4$ with M = Co, Ni was attempted, reactions always resulted in the formation of $[M(en)_3]_{0.5}[GaS_2]$, containing isolated chains.

Figure 6 shows the local coordination of the non-hydrogen atoms for **5**, while selected bond lengths and angles are presented in Table 4. In the $[GaS_2]^-$ chains of **5**, the Ga−S distances lie in the range 2.2792(6)−2.3007(6) Å. As in the case of $[M(en)_3]_{0.5}[GaS_2]$, the edge-sharing of the GaS_4 tetrahedra results in short metal−metal distances (ca. 3.0 Å) and in distortions of the GaS_4 units. Bond valence sums[31] are consistent with the presence of Ga(III) and divalent $[Mn(en)_2]^{2+}$ complexes and indicate that electrons are localized. The Mn^{2+} ion is coordinated by two S(2) atoms of two different $[GaS_2]^-$ chains, at a Mn−S distance of 2.7430(6) Å, and by four N atoms of two en ligands, yielding distorted octahedral coordination. The Mn−S distances are slightly longer than those observed in MnS[41] (2.61 Å) or in compounds containing Mn^{2+} octahedrally coordinated by sulfur and amine molecules, such as $[Mn(en)_3]_2[Mn(en)_2AsS_4][As_3S_6]$.[42] Mn−S distances comparable to those reported here have been found in $[Mn(C_6H_{18}N_4)]_4[Mn_2Sb_4S_{12}]$[43] and have been considered to indicate a weakened Mn−S interaction. However, bond valence sums (Table 4) are consistent with the presence of significant bonding interactions between the Mn and S atoms. The relatively large Mn−S bonds might be a consequence of steric interactions between the en ligands and the $[GaS_2]^-$ chains. The Mn−N distances of 2.244(2)−2.247(2) Å are similar to those observed for Mn^{2+} cations octahedrally coordinated by sulfur and nitrogen atoms.[42]

As illustrated by Figure 7, each unit cell of **5** contains two $[GaS_2]^-$ chains, which run parallel to the crystallographic *c* axis and are related by a lattice translation of (1/2, 1/2, 0). These chains are joined by $[Mn(en)_2]^{2+}$ complexes, with the two S(2) atoms from two different $[GaS_2]^-$ chains in a trans arrangement. These complexes connect the $[GaS_2]^-$ chains in directions approximately parallel to [110] and $[1\bar{1}0]$ in an alternating fashion, forming a three-dimensional network. Although Figure 7b suggests that this structure contains narrow rectangular channels along [110] (and $[1\bar{1}0]$), when the van der Waals' radii of Ga and S are taken into account, there are no free apertures.

Due to the preference for the formation of transition-metal complexes in the presence of strongly chelating amines, solvothermal reactions involving a transition metal generally result in the formation of an anionic main-group-sulfide framework together with a charge-balancing cationic transition-metal complex, and there have been comparatively few reports in which transition metals have been partially or fully incorporated into a main-group anionic network. Most reports on partial incorporation concern antimony sulfides, such as $[Mn(C_6H_{18}N_4)]_4[Mn_2Sb_4S_{12}]$[43] or $Mn_2Sb_2S_5 \cdot L$ (L = amine),[27,28] although recently, two thioarsenates, $[Mn(en)_3]_2[Mn(en)_2AsS_4][As_3S_6]$ and $[Mn(dien)_2]_n[Mn(dien)AsS_4]_{2n} \cdot 4nH_2O$,[42] have also been described. Nonchelating amines have been used as templating agents in the solvothermal synthesis of transition-metal indium sulfides,[10] and therefore, the transition-metal cations have been fully incorporated into the main-group framework. The structure reported here is the first example of incorporation of a transition-metal complex into a thiogallate network, and also the first example of a three-dimensional thiogallate formed by linkage of one-dimensional chains. One-dimensional chains linked by units containing transition metals resulting in structures with higher dimensionality have also been observed in other main-group sulfides. For example, $[Co(en)_3][CoSb_4S_8]$ contains $[SbS_2]^-$ chains linked by tetrahedrally coordinated Co(II) atoms, resulting in the formation of $[CoSb_4S_8]^{2-}$ layers.[44] Initial work on the Ga−S system suggests that the one-dimensional $[GaS_2]^-$ chains are a common building unit, and cross linking of these chains with other building units, such as $[Mn(en)_2]^{2+}$ in **5**, might give access to a range of new two- or three-dimensional structures.

Acknowledgment. The author thanks the UK EPSRC for an Advanced Research Fellowship.

Supporting Information Available: CIFs; tables of atomic coordinates; TGA curves for **1**−**5**; and IR spectrum of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC052043S

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