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One-Dimensional Indium Sulfides with Transition Metal Complexes of Polyamines

Jian Zhou,† Guo-Qing Bian,*,† Yong Zhang,† Qin-Yu Zhu,† Chun-Yin Li,† and Jie Dai*,†,‡

Department of Chemistry and Key Laboratory of Organic Synthesis of Jiangsu Province, Suzhou University, Suzhou 215006, People's Republic of China, and State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

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Three new indium sulfides, $[Ni(dien)_2]_{0.5}[InS_2]$ (dien = diethylenetriamine) (**1**), $[Ni(dap)_3]_{0.5}[InS_2]$ (dap = 1,2-diaminopropane) (**2**), and $[Ni(tepa)]_2[In_4S_7(SH)_2]\cdot H_2O$ (tepa = tetraethylenepentamine) (**3**), have been prepared under solvothermal conditions and characterized by single-crystal X-ray diffraction. Compounds **1** and **2** consist of discrete 1-D $\{[InS_2]^-\}_\infty$ chains with complex cations as charge-compensating ions, while compound **3** consists of a novel 1-D anionic chain constructed from arachno-shaped In_4S_{11} clusters. The sulfide chain of **3** coordinates into the complex cations via the nonterminal S atoms of the polymeric anion, forming a covalently linked organic–inorganic hybrid compound.

Introduction

Mild hydro- or solvothermal techniques have been used increasingly for the preparation of new chalcogenometalates containing the main group elements, such as Group 13 (Ga, In), Group 14 (Ge, Sn), and Group15 (As, Sb).[1−3] In the case of indium sulfide, some compounds have been synthesized using organic amines as templating agents or structure-directing agents under solvothermal conditions.[4] The structures of these compounds are generally based on the InS_4 tetrahedra or their polytetrahedral clusters as structural building units. The polytetrahedral clusters mainly include the supertetrahedral clusters ($\mathbf{T}_n$) and the pentasupertetrahedral clusters ($\mathbf{P}_n$), as exemplified by $[In_4S_{10}]^{8-}$ ($\mathbf{T}_2$),[5] $[In_{10}S_{20}]^{10-}$ ($\mathbf{T}_3$),[4b] $[In_8S_{13}(S_3)_{1/2}(SH)]^{6-}$ ($\mathbf{P}_1$),[6] and $[Li_4In_{22}S_{44}]^{18-}$ ($\mathbf{P}_2$).[1a] These clusters can be assembled into 2−3-D open-frameworks by inorganic bridges, such as transition metal ions or the S^{2-} anion. The reported organic amines used for the solvothermal synthesis were usually nonchelating amines, which were protonated and fulfill the charge-balancing role, such as $Cd_4In_{16}S_{33}\cdot(H_2O)_{20}(C_{10}H_{28}N_4)_{2.5}$,[7] $(Cu_5In_{30}S_{54})(C_{13}H_{26}N_2H_2)_{6.5}$,[8] and UCR-8MInS-DBA (M = Fe, Co, Zn, Cd; DBA = di-*n*-butylamine).[9] However, there have been relatively few reports of the main group 13 (Ga, In) sulfide network in the presence of strongly chelating amines.[10] The introduction of the chelating amine into main group chalcogenometalates with transition metals usually leads to formation of $[M(amine)_m]^{n+}$ complex cations, which has been well documented for some chalcogenometalates.[11] The complex cations can act as a new kind of structure-directing agent with relatively rigid space, and the structure and the band gap of the materials are correlated to these cations.

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* To whom correspondence should be addressed. E-mail: daijie@suda.edu.cn (J.D.); biangq@suda.edu.cn (G.-Q.B.).

† Suzhou University.

‡ Nanjing University.

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Table 1. Crystal Data and Summary of X-ray Data Collection

	1	**2**	**3**
empirical formula	$C_8H_{26}In_2N_6NiS_4$	$C_{18}H_{60}In_4N_{12}Ni_2S_8$	$C_{16}H_{52}In_4N_{10}Ni_2OS_9$
fw	622.94	1277.96	1265.88
cryst color	light purple	light purple	light−purple
cryst dimensions (mm^3)	0.36 × 0.20 × 0.15	0.48 × 0.20 × 0.06	0.17 × 0.15 × 0.13
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$C2/c$	$Cmcm$	$P2_1/c$
a (Å)	8.9684(10)	9.525(2)	9.9738(11)
b (Å)	17.0237(18)	16.531(5)	20.749(2)
c (Å)	13.1317(15)	13.245(3)	19.403(2)
β (deg)	101.815(2)	90	103.651(3)
V (Å^3)	1962.4(4)	2085.4(9)	3902.0(7)
Z	4	2	4
T (K)	193(2)	193(2)	173(2)
calcd density (Mg m^{-3})	2.108	2.035	3.782
abs coeff (mm^{-1})	3.706	3.491	2.148
F(000)	1224	1264	2472
2θ(max) (deg)	50.68	50.70	50.70
reflns collected	9495	9946	37 713
unique reflns	1799	1061	7121
params	98	84	380
R1 [$I > 2\sigma(I)$]	0.0262	0.0403	0.0703
wR2 (all data)	0.0739	0.1142	0.1364
GOF on F^2	1.057	1.184	1.181

Some of them are chiral complexes, which can transfer the chirallity into the polymeric frameworks.[12] However, to our knowledge, until now there is no report about a $[M(amine)_m]^{n+}$ complex being incorporated into indium sulfide framework or even as counterions, although some indium tellurides have been reported.[11b] We now report three 1-D indium sulfides prepared under solvothermal conditions in the presence of strongly chelating amines, $[Ni(dien)_2]_{0.5}[InS_2]$ (**1**) (dien = diethylenetriamine), $[Ni(dap)_3]_{0.5}[InS_2]$ (**2**) (dap = 1,2-diaminopropane), and $[Ni(tepa)]_2[In_4S_7(SH)_2]\cdot H_2O$ (**3**) (tepa = tetraethylenepentamine). Compound **3** has a novel structure in which the complex cations are coordinated by the non-terminal S atoms of the polymeric anion.

Experimental Section

General Remarks. All analytical grade chemicals were obtained commercially and used without further purification. Elemental analysis was conducted with an EA 1110 elemental analyzer, and quantitative microprobe analyses were performed on a JSM-5600LV scanning electron microscope (SEM). FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr disks in the 4000−400 cm^{-1} range. UV−vis spectra were measured with a Shimadzu UV-3150 spectrometer at room temperature. The absorption (α/S) data were calculated from the reflectance using the Kubelka−Munk function, $\alpha/S = (1 - R)^2/2R$.[13] Thermal analysis was conducted on a SDT 2960 TGA-DCS microanalyzer. The samples were heated under a nitrogen stream of 100 mL/min with a heating rate of 5 °C /min. The XPS spectra were collected on an AEI (Kratos) ES 200 B X-ray photoelectron spectrometer with a base pressure of about $\sim 10^{-8}$ Torr.

Synthesis of Compounds. $[Ni(dien)_2]_{0.5}[InS_2]$ (1). Single crystals of the complex suitable for X-ray crystallographic analysis were obtained by solvothermal reaction. In_2S_3 (0.0651 g, 0.2 mmol), Ni (0.0117 g, 0.2 mmol), S_8 (0.0154 g, 0.06 mmol), and dien (2 mL) and H_2O (0.5 mL) were placed in a thick Pyrex tube (~20 cm long). The sealed tube was heated at 157 °C for 6 d to yield light-purple block-shaped crystals. The crystals were washed with ethanol and diethyl ether, dried, and stored under vacuum (31% yield based on In). Anal. Found: C, 15.59; H, 4.39; N, 13.46%. Calcd: C, 15.41; H, 4.17; N, 13.48%. IR (cm^{-1}): ν 3419 (vs), 3318 (s), 3280 (s), 3233 (s), 2925 (m), 2871 (m), 1636 (m), 1574 (vs), 1443 (m), 1389 (m), 1288 (s), 1250 (s), 1196 (s), 1134 (w), 1088 (vs), 1057 (s), 1011 (s), 964 (m), 887 (w), 787 (w), 571 (m), 517 (w).

$[Ni(dap)_3]_{0.5}[InS_2]$ (2). The purple crystals of **2** were prepared by a method similar to that used in the synthesis of the crystals of **1**, except that dien was replaced by dap (47% yield based on In). Anal. Found: C, 16.78; H, 4.88; N, 13.29%. Calcd: C, 16.90; H, 4.69; N, 13.15%. IR (cm^{-1}): ν 3429 (m), 3257 (m), 3280 (s), 3226 (s), 2963 (s), 2932 (s), 2871 (m), 1736 (vs), 1574 (m), 1458 (s), 1389 (w), 1335 (vw), 1250 (m), 1165 (s), 1018 (vs), 933 (w), 833 (vs), 740 (w), 656 (s), 501 (m), 447 (m).

$[Ni(tepa)]_2[In_4S_7(SH)_2]\cdot H_2O$ (3). The purple crystals of **3** were prepared by a method similar to that used in the synthesis of the crystals of **1**, except that dien was replaced by tepa (25% yield based on In). Anal. Found: C, 15.37; H, 4.28; N, 11.26%. Calcd: C, 15.16; H, 4.29; N, 11.05%. IR (cm^{-1}): ν 3394 (vs), 3309 (vs), 3243 (vs), 3190 (s), 2914 (m), 2874 (m), 1578 (vs), 1466 (vs), 1393 (m), 1295 (s), 1249 (s), 1196 (s), 1130 (w), 1064 (m), 1018 (w), 979 (vs), 795 (m), 669 (m), 604 (s), 571 (s).

Crystal Structure Determination. Data collections were performed on a Rigaku Mercury CCD diffractometer using a ω-scan method with graphite-monochromated Mo Kα radiation (λ = 0.071073 nm) at 193(2) or 173(2) K to a maximum 2θ value. The intensities were corrected for Lorentz and polarization effects. The structures were solved with direct methods using the SHELXS-97 program,[14] and the refinement was performed against F^2 using SHELXL-97.[15] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. Relevant crystal and collection data parameters and refinement results can be found in Table 1. Additional details of crystal data in CIF format

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1** and **2**[a]

	1	**2**
Ni−N	2.075(3) −2.169(3)	2.103(7) −2.156(7)
In−S	2.4677(9) −2.4728(9)	2.455(2) −2.4779(18)
In1−In1a	3.2668(5)	
In1−In1b		3.2796(10)
N−Ni−N(cis)	80.00(12) −103.72(12)	81.7(4) −94.1(4)
N−Ni−N(trans)	160.93(12) −174.636(9)	173.1(4) −173.8(3)
S−In−S	95.11(3) −118.44(3)	94.68(7) −116.91(3)

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

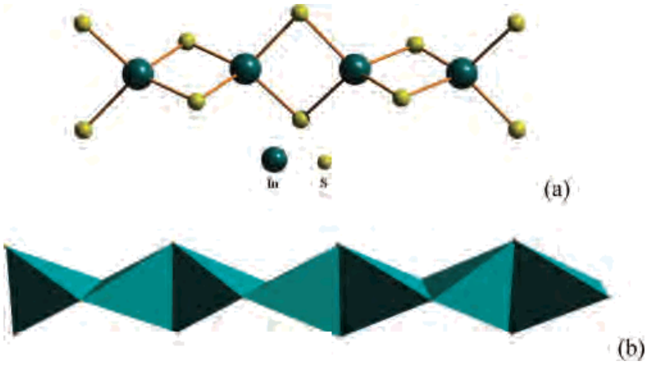

Figure 1. (a) 1-D chain of the polymeric $[InS_2]^-$ anion in **1** and **2**. (b) cpolyhedral view of the polymeric anion, showing the edge-sharing InS_4 tetrahedra.

can be found in the Supporting Information. Selected bond lengths and angles for compound **1**−**3** are listed in Tables 2 and 3.

Results and Discussion

Description of the Structures. Structures of $[Ni(dien)_2]_{0.5}$-$[InS_2]$ (1) and $[Ni(dap)_3]_{0.5}[InS_2]$ (2). Compound **1** crystallizes in the monoclinic space group *C*2/c, and compound **2** crystallizes in the orthorhombic space group *Cmcm*. Both compounds consist of discrete 1-D $\{[InS_2]^-\}_\infty$ chains (Figure 1) with charge-compensating $[Ni(dien)_2]^{2+}$ or $[Ni(dap)_3]^{2+}$ cations (Figure 2). The polymeric anion structures consist of InS_4 tetrahedra sharing opposite edges. The short metal−metal distances within the InS_4 units, along the $\{[InS_2]^-\}_\infty$ chain, are 3.2669(5) Å for **1** and 3.2807(11) Å for **2** and are consistent with those in other indium sulfides.[16] The In(III) atom is coordinated to four S atoms in the distance range of 2.4677(9)−2.4728(9) Å, forming a slightly distorted InS_4 tetrahedron with S−In−S angles ranging from 95.11(3) to 119.18(3)°.

The cations and anions in the crystal of **1** are arranged and stabilized by numerous weak N−H···S hydrogen bonds,[17] between N atoms of the coordinated dien ligands and S atoms of the polymeric anion, with distances varying from 3.497(3) to 3.630(3) Å. The complexes generate, by N−H···S hydrogen bonding, a 3-D H-bonding network structure with channels parallel to the *c*-axis (Figure 3), in which the $\{[InS_2]^-\}_\infty$ chains are developed and the line of the In atoms exhibits a slight S-wave shape. The organic−inorganic hybrid indium sulfides reported to date were prepared overwhelmingly in nonchelating amines,[7−9,18] while compounds **1** and **2** consist of metal complexes as counterions of 1-D $\{[InS_2]^-\}_\infty$ chains.

Structure of $[Ni(tepa)]_2[In_4S_7(SH)_2]\cdot H_2O$ (3). Compound **3** crystallizes in the monoclinic space group $P2_1/c$. An ORTEP view of the structure is shown in Figure 4. Bond valence sums are in agreement with the presence of a Ni(II) or Ni(III) ion in the $[Ni(tepa)]^{n+}$ complex anion. The XPS analysis of **3** showed a main signal of the Ni $2p_{3/2}$ peak at 854.4 eV with a satellite peak at 860.4 eV (Figure SI-1). These characters doubtlessly indicate to Ni(II).[19] The UV−vis spectrum of **3** is in agreement with those of **1** and **2** in d−d transition, which further confirms the assignment. The remaining two negative charges must be compensated by two additional hydrogen atoms that should be attached to the terminal S atoms, S(6) and S(9). The −SH group has also been reported in the other indium sulfides, such as $[(C_3H_7)_2NH_2]_3In_6S_{11}H$[16b] and $[In_8S_{13}(S_3)_{1/2}(SH)][In_4S_6\,(S_3)_{1/2}$-$(SH)](TMDPH_2)_5$.[6] Each Ni^{2+} ion in the $[Ni(tepa)]^{2+}$ units has a heavily distorted octahedral geometry composed of five N atoms from one tepa ligand and one S atom from the polymeric$\{[In_4S_9H_2]^{4-}\}_n$ anion. The Ni−S bond distances are 2.531(3) Å for Ni1−S3 and 2.660(3) Å for Ni2−S1. In the polymeric anion, four InS_4 tetrahedra (In1, In2A, In3A, and In4A, see Figures 4 and 5) are interconnected by corner sharing of vertex sulfur atoms to generate a substructure of arachno-shaped In_4S_{11} clusters. The clusters are further linked via the edge-sharing mode (S3−S4) to form an infinite chain $\{[In_4S_9]^{4-}\}_\infty$ parallel to the *c*-axis (Figure 5). The In−S bond lengths ranging from 2.404(3) to 2.506(3)Å are consistent with those reported materials.[16] The edge sharing of two InS_4 tetrahedra gives am In1−In2 contact of 3.3687(10) Å, which is longer than those in compounds **1** and **2**. The $[Ni(tepa)]^{2+}$ complex cations are regularly appended to the chain by the In−S−Ni bridges, just like grapes connected in grapevine of the anion. Viewed down the *c*-axis, the $[Ni(tepa)]^{2+}$ cations are arranged in four orientations (Figure 6), and no symmetric or helical axis was found. In addition, although the complex cations $[Ni(tepa)]^{2+}$ are chiral, the overall structure of the compound is achiral, because these chains are aligned in an antiparallel fashion, leading to the formation of inversion centers in the crystal.

The $[Ni(tepa)]^{2+}$ complex cations in **3** are linked into the indium sulfide framework. Solvothermal reactions involving transition metals in the presence of strongly chelating amines usually result in an isolated anionic framework with $[M(amine)_m]^{n+}$ complex cations as counterions, and there are only a few main group chalcogenometalates in which the transition metal amine complexes are incorporated into the

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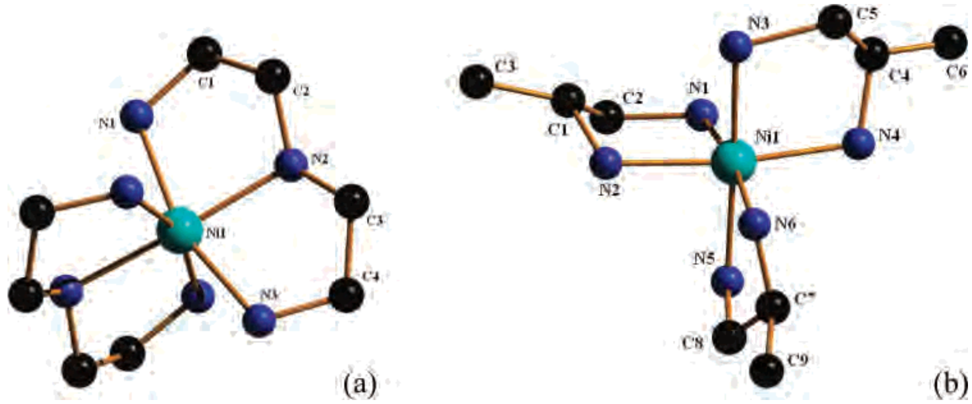

Figure 2. Structures of the transition metal complex cations in **1** (a) and **2** (b) with the labeling scheme. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **3**

Ni1−N	2.081(9)−2.132(9)	Ni2−N	2.074(10)−2.130(9)
Ni1−S3	2.531(3)	Ni2−S1	2.660(3)
In1−In2	3.3686(10)	In−S	2.405(3)−2.507(3)
N−Ni1−N(cis)	82.7(4)−98.3(4)	N−Ni2−N(cis)	80.7(4)−97.8(4)
N−Ni1−N(trans)	177.5(4)−177.6(3)	N−Ni2−N(trans)	161.6(4)−174.8(4)
N−Ni1−S(cis)	86.8(3)−95.4(2)	N−Ni2−S(cis)	87.7(2)−98.0(3)
N−Ni1−S(trans)	173.1(3)	N−Ni2−S(trans)	167.1(3)
S−In−S	94.30(8)−120.57(9)		

anionic structure.[12,20,21] To prevent the formation of a sulfide with discrete complex cations, tetra- or pentadentate chelating amines,[20a,12] or lanthanide ions[21] have been used to form a complex cation with an unsaturated coordination sphere, which was able to be further coordinated by the anion. Compound **3** in this work is the first example of the incorporation of a [M(amine)$_m$]$^{n+}$ complex into a polymeric indium sulfide anion, which is another example using this successful strategy.

The coordination of the non-terminal S atoms of polymeric anion coordinating to metal centers in compound **3** is unfamiliar. While the reported main group chalcogenidometalates with connected complex anions are generally bound to transition-metal ions by a terminal S atom.[12,20,22] The only exception that has been observed is Mn(en)$_2$Ga$_2$S$_4$,[10] in which [Mn(en)$_2$]$^{2+}$ complexes are joined by two bridging S atoms from two different {[GaS$_2$]$^-$} $_\infty$ chains.

The topology of this framework is significantly different from other 1-D main group chalcogenometalate chains containing MS$_4$ (M = Ga, Ge, Sn, Sb, and In) tetrahedra (this work **1** and **2**). For example, repeated edge-sharing of GaS$_4$ tetrahedra leads to the 1-D [GaS$_2$]$^-$chains observed in [M(en)$_3$]$_{0.5}$[GaS$_2$] (M = Mn, Co, Ni).[10] Repeated corner-sharing tetrahedral [SnS$_4$]$^{4-}$ anions result in the infinite 1-D [SnS$_3$]$^{2-}$ chains that have been found in structures of Na$_2$GeS$_3$, K$_2$SnS$_3$·2H$_2$O, Tl$_2$SnS$_3$, BaSnS$_3$, and SrSnS$_3$, summarized by W. S. Sheldrick.[11a] A 1-D polymeric [Sb$_4$S$_9$]$^{4-}$ anion with sinusoidal shape[23] is constructed from the Sb^{V}S$_4$ tetrahedra and Sb^{III}S$_3$ pyramids sharing corners. Therefore, compound **3** is a novel 1-D polymer of sulfide built by edge- and corner-sharing InS$_4$ tetrahedra combined with a [M(amine)$_m$]$^{n+}$ complex.

Synthesis and Characterization. These new 1-D indium sulfides were conveniently isolated from an In$_2$S$_3$/Ni/S/amine/H$_2$O synthetic system under mild solvothermal conditions. Single crystals of the compounds suitable for X-ray crystallographic analysis were successfully obtained in the amine−

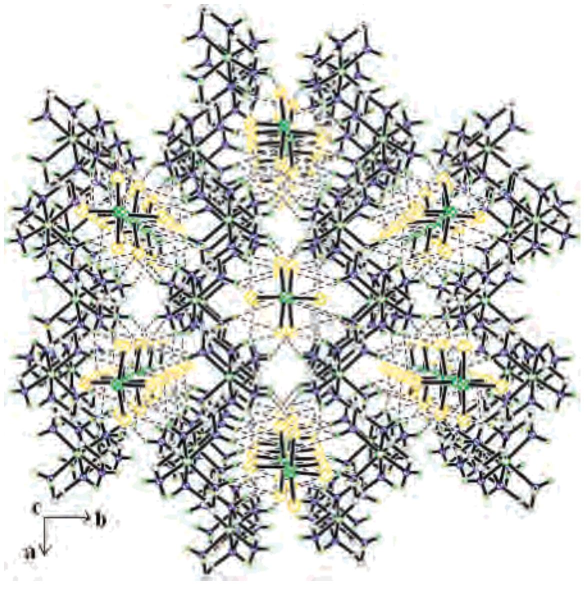

Figure 3. 3-D H−bonding network structure with channels along [001] in **1**. Hydrogen atoms of C−H are omitted for clarity.

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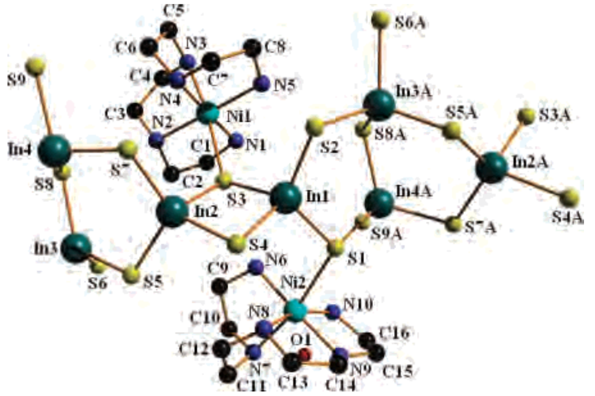

Figure 4. Structure of **3** with labeling scheme. Symmetry code: A x, $3/2 - y$, $1/2 + z$. Hydrogen atoms are omitted for clarity.

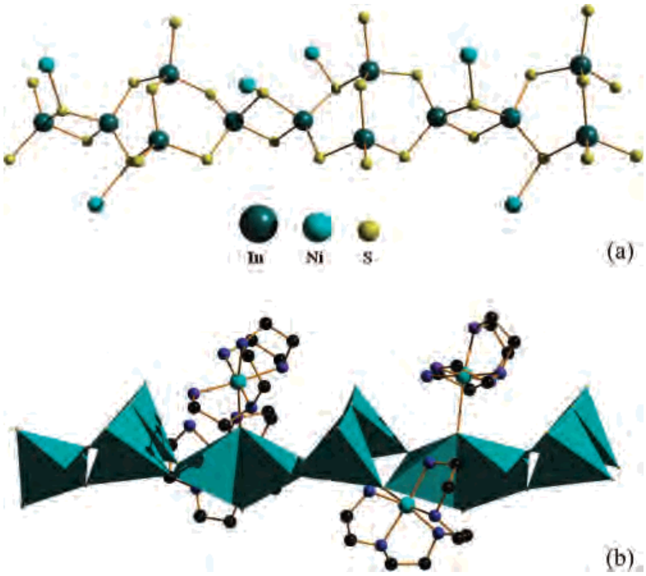

Figure 5. (a) 1-D chains of the polymeric anion in **3**. Complex cations are omitted for clarity. (b) Polyhedral view of polymeric anion in **3**. Hydrogen atoms are omitted for clarity.

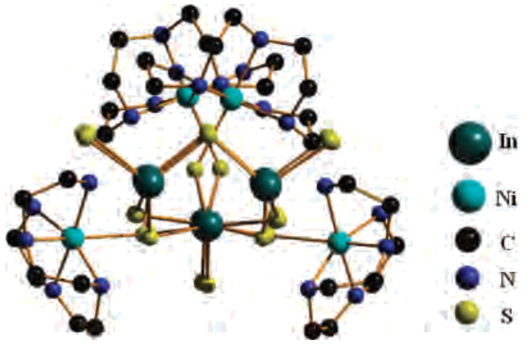

Figure 6. View down the *c*-axis of **3** showing the complex cations appended in the four orientations.

aqueous mixed solvent, which is very promising for the crystal growth of the indium sulfide reported here. However, in the pure amine solvents the growth of crystals failed, so the water plays a very important role in the crystallization. In general, the amines, especially the polyamines, have higher boiling temperature, which is disadvantageous for the solvothermal synthesis of indium sulfides. The mix of water into the amines enables us to carry out the reaction at a proper temperature and pressure.

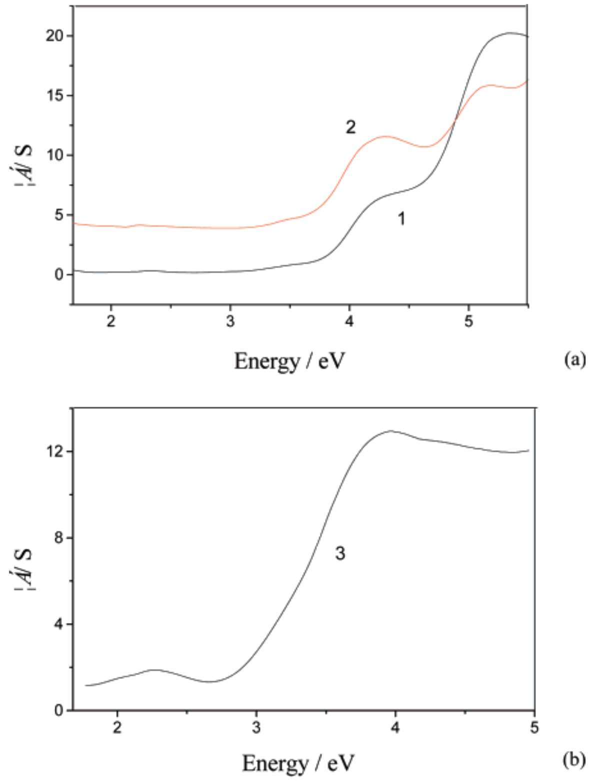

Figure 7. Solid-state optical absorption spectra of compounds **1** and **2** (a) and **3** (b).

The solubility of the compounds is very low, so that they are insoluble in ordinary solvents including DMF. Solid-state UV−vis absorption spectra of the indium sulfides are depicted in Figure 7, which were calculated from the data of diffuse reflectance. The strong absorptions at 4.29 (289 nm) and 4.61 eV (269 nm) for **1** and 4.28 (290 nm) and 4.72 eV (263 nm) for **2** are assigned to the electronic excitations located at the polymeric anions. While in **3**, the strong absorption at about 4.0 eV (310 nm) shows a red shift compared to the corresponding values for compounds **1** and **2**. This phenomenon might result from the different structures of the anions. The excitation band gap (E_{onset}) for **3** is estimated to be about 3.28 eV (378 nm) and was obtained by extrapolation of the linear portion of the absorption edge. The result was close to the value of $[In_8S_{13}(S_3)_{1/2}(SH)][In_4S_6(S_3)_{1/2}(SH)](TMDPH_2)_5$ (3.1 eV),[6] which exhibits properties of semiconductor. A very weak d−d transition appears at about 2.2 eV for all these compounds.

XRD spectra of compounds **1** and **3** are shown in Figure SI-2. The results of the thermal behavior of compounds **1** and **3** are shown in Figure SI-3. Compound **1** loses dien ligands in one step with a mass loss of 33.61% (calcd 31.06%), accompanied by one endothermic signal on the DSC curve with peak temperature ($T_{\mathrm{p}} = 342.72$ °C). The tepa ligand of **3** decomposes with a mass loss of 29.62% (calcd 30.02%), accompanied by an endothermic peak at 337.19 °C (T_{p}) in the DSC curve. The mass loss of 1.83% at low temperature is attributed to the loss of the cocrystallized H_2O molecule (calcd 1.42%).

Conclusion

Three interesting indium sulfides constitute the first example of 1-D chains with metal complexes as counterions. The structure of compound **3** is a novel indium sulfide with several characters. The first is that the indium sulfide anion have been coordinated into the $[\mathrm{Ni(tepa)}]^{2+}$ complex cations, forming a covalent linked organic−inorganic hybrid compound. The second is that it is unfamiliar for the non-terminal S atoms of sulfide anion, which coordinates to the metal center of the complex cation. The third is the arachno-shaped $\mathrm{In_4S_{11}}$ cluster, which appears as building block here, appears to be unique because the most of 1-D structures of the main group chalcogenometalates are based on simple $[\mathrm{MS_4}]^{n-}$ or $[\mathrm{MS_3}]^{n-}$ units.

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Supporting Information Available: Crystallographic data of **1**−**3** in CIF format, XPS spectra, XRD spectra, and TG-DSC curves. This material is available free of charge via the Internet at http://pubs.acs.org.

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