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Synthesis and Characterization of One-Dimensional and Molecular M(tren)InAsS_4 (M = Mn, Co, and Zn) Compounds with a Noncondensed AsS_3^{3-} Unit

Zhenqing Wang,[†,‡] Hongjie Zhang,[*,†] and Cheng Wang[*,†]

[†]*State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, People's Republic of China, and* [‡]*Graduate School of the Chinese Academy of Sciences, Beijing, 100049, People's Republic of China*

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Four transition-metal–amine complexes incorporating indium thioarsenates with the general formula M(tren)InAsS_4 (M = Mn, Co, and Zn) and a noncondensed AsS_3^{3-} unit have been prepared and characterized. Single-crystal X-ray diffraction analyses show that compound **1** (M=Mn) crystallizes in the triclinic crystal system (space group: $P\bar{1}$) and consists of a one-dimensional (1D) inorganic $^{1}{}_{\infty}\{[InAsS_4]^{2-}\}$ chain and $[Mn(tren)]^{2+}$ groups bonded to the opposite sides of an eight-membered $In_2As_2S_4$ ring along the backbone of the infinite inorganic chains. Compounds **2** (M=Mn), **3** (M=Zn), and **4** (M=Co) are isomorphous molecular compounds. They all crystallize in the monoclinic crystal system (space group: $P2_1/c$). The Mn^{2+} cation of $[Mn(tren)]^{2+}$ in **1** has a distorted octahedral environment, while the transition-metal cations of $[M(tren)]^{2+}$ in the other three compounds locate in trigonal-bipyramidal environments. This difference results in different bonding modes of $[M(tren)]^{2+}$ to indium thioarsenates between compound **1** and the other three compounds.

Introduction

Chalcoarsenates consisted of anionic pyramidal AsE_3^{3-} or tetrahedral AsE_4^{3-} (E = S or Se) subunits in their lattices, and main, transition, or rare-earth metals are promising solid materials with properties varying from semiconductivity[1−4] to magnetism[5,6] to thermoelectricity[7] that might find applications in solar cell devices,[8] Peltier devices,[7] and so on.[9,10] Their synthesis could be achieved by mid-temperature (< 600 °C) approaches such as the molten flux[11] and solvothermal[12] (the solvents could be water, alcohols, or supercritical amines) methods. The ready condensation of mononuclear AsS_3^{3-} via corner bridging leads to the formation of polynuclear linear $As_xS_{2x+1}^{(x+2)-}$ ($x = 2-4$)[1,13,14] or cyclic $As_xS_{2x}^{x-}$ (x = 3 or 4)[3,15,16] anions, as depicted in Figure 1. Only a few anions have been synthesized based on the edge-sharing or As–As bond formation (Figure 1) condensation of AsS_3^{3-} units.[17] Usually, these condensations are highly dependent on the reaction parameters such as the reaction temperature, reaction time, initial pH value, or sizes and categories of the countercations.[18] Similar to deprotonated carboxylic acids as coordinative ligands in which either two O atoms or only one O atom might be involved to coordinate with metal atoms, the nucleophilic condensed anions can be connected with metal cations by two or one S atoms (Figure 2a,b).[13,14,19,20] More interestingly, an As atom with a 4s lone pair of electrons can also participate in coordination (Figure 2c).[21] Recently, it was pointed out that the stereochemically active lone pair of

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*To whom correspondence should be addressed. E-mail: hongjie@ciac.jl.cn (H.Z.), cwang@ciac.jl.cn (C.W.).

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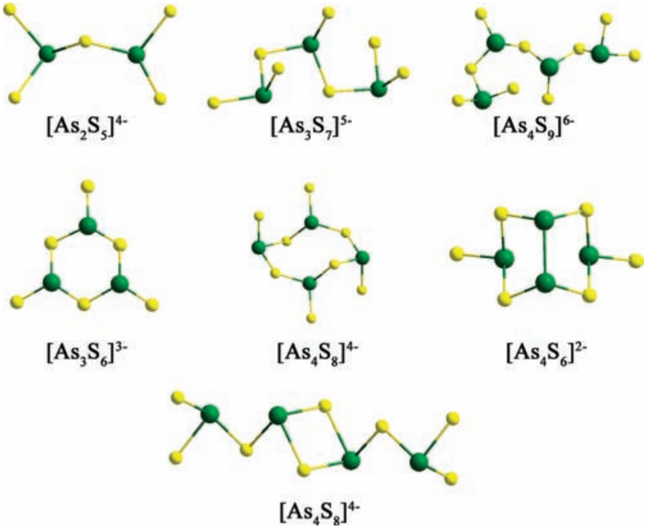

Figure 1. Several kinds of polythioarsenate anions. Color code: yellow, S^{2-}; green, As^{3+}.

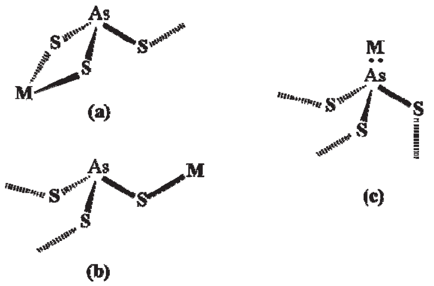

Figure 2. Three typical bonding motifs for poly(As−S−M).

electrons on As^{3+} could act as an enhancement factor for nonlinear optical properties.[22] In addition to finite structures, the condensed anions could also form infinite structures through further condensations. Chains with the formula $^1_\infty[As_2S_4]^{2-}$ could result when further corner sharing of mononuclear AsS_3^{3-} or polynuclear linear $As_xS_{2x+1}^{(x+2)-}$ anions occurs. For cyclic $As_xS_{2x}^{x-}$ anions subjected to further condensation, however, only a $^1_\infty[As_6S_{10}]^{2-}$ chain with $x = 3$ was reported in the literature. The neighboring $^1_\infty[As_6S_{10}]^{2-}$ chains could be joined together through edge or terminal bridging S atoms.[23,24] In the latter case, surprisingly, half of the $As_3S_6^{3-}$ units were opened to facilitate the linkage of the constituent single chains of the polymeric anion. Furthermore, the cyclic $As_3S_6^{3-}$ anion and mononuclear AsS_3^{3-} or bipyramidal $As_2S_5^{4-}$ anion could be also linked through the bridging S atoms in alternative manners.[24] These infinite structures are likely to be stabilized or templated by large counterions such as alkali metal, R_4N^+ ($R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_7), Ph_4P^+, and so on. However, similar condensations are unlikely to occur for tetrahedral AsE_4^{3-} with 5+ valent As because the local charge of bridging chalcogens may violate the well-known Pauling's electrostatic valence rule.[25] This has been exemplified by the formation of $(NH_4)Ag_2AsS_4$,[26] Cs_2AgAsS_4,[27] $[Mn_2(AsS_4)_4]^{8-}$ and $[Cd_2(AsS_4)_2(AsS_5)_2]^{8-}$,[5] $(NH_3CH_2CH_2NH_3)AgAsS_4$,[28] $[Mn(dien)_2]_n[Mn(dien)AsS_4]_{2n}\cdot 4nH_2O$ and $[Mn(en)_3]_2[Mn(en)_2AsS_4][As_3S_6]$,[3] $[Mn_3(2,2'\text{-bipy})_3(As^VS_4)_2]_n\cdot nH_2O$,[6] $K_3Ln(AsS_4)_2$ (Ln = Nd, Sm, Gd),[29] and $[Ln(dien)_2(\mu_3\text{-}AsSe_4)]$ (Ln = Nd, Sm).[4]

Despite its strong condensation tendency, the isolated pyramidal AsS_3^{3-} could still be stabilized and efforts toward this would yield new derivatives of chalcoarsenates. The first example of a molecular metal complex with an isolated AsS_3^{3-} was $(MeCp)_3Ti_2OAsS_3$ (MeCp = η^5-$CH_3C_5H_4$) reported by Rauchfuss et al. in 1984.[19] Other isolated pyramidal AsE_3^{3-} (E = S, Se) anions were reported to be connected with metal cations such as Cu,[21] Ag,[30] Sn,[31] Bi,[32] and Eu,[33] in which they may coexist with their condensed polymeric anions[30,32] or the 4s lone pair of electrons on As^{3+} is also involved in coordination.[21]

In this work, we reported the solvothermal synthesis of one-dimensional (1D) $[Mn(tren)]InAsS_4$ (**1**) and molecular $[M(tren)]_4(In_2As_2S_8)_2$ [M = Mn (**2**), Zn (**3**), Co (**4**)]. Compound **1** consists of an infinite anionic chain side-terminated by a manganese complex, while compounds **2**−**4** are isomorphous molecular metal complexes. In both cases, the pyramidal AsS_3^{3-} anion is stabilized by incorporating In^{3+} in chalcoarsenate. Prior to this work, Chou and Kanatzidis reported the synthesis of a $(Ph_4P)_2[InAs_3S_7]$ chain structure, which consists of In^{3+} and polymeric $[As_3S_7]^{5-}$ anions and remains the only known poly(thioarsenate) for the In−As−S system.[14]

In situ formed transition-metal−amine complexes can act as structure-directing agents for the growth of main-group anionic frameworks.[34,35] Generally speaking, they play three different roles as templates. First, they could be used as countercations for charge balancing.[36,37] In this case, their roles are similar to those of alkaline-metal ions or protonated amines in synthesizing zeolites, microporous metal oxides,[38] and chalcogenides.[39−41] They can be connected with terminal chalcogens of oligomeric,[42] 1D,[43] or two-dimensional (2D)[44]

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metal chalcogenides to impede their further propagation. In addition, they could be also incorporated into the frameworks.[45] Although the transition-metal−amine complexes have been widely and successfully utilized in the synthesis of chalcostannates[42,43,46,47] and chalcoantimonates[48−52] since their introduction in 1997,[53] only a few efforts have been put forward to the synthesis of chalcoarsenates using such complexes as structure-directing agents.[54,55]

Experimental Section

Synthesis of Compounds. All reagents were purchased commercially and used without further purification. To prepare compound **1**, 99 mg of $MnCl_2\cdot 4H_2O$ (0.5 mol), 123 mg of orpiment As_2S_3 (0.5 mmol), 190 mg of $In(NO_3)_3\cdot 4.5H_2O$ (0.5 mmol), 80 mg of sulfur (2.5 mmol), and 2.0 mL (12.8 mmol) of tris(2-aminoethyl)amine (tren) were mixed in a 15 mL Teflon-lined stainless steel autoclave and stirred for 15 min. Then the autoclave was heated at 160 °C for 6 days without being disturbed. After cooling to room temperature, the products were washed with ethanol and water. Yellow crystals were obtained with about 70% yield (based on Mn). Semiquantitative energy-dispersive X-ray spectroscopy (EDXS) analysis (Bruker Quantax 200 attached to a Hitachi S-4800 field emission scanning electron microscope) reveals the presence of all four heavy constituent elements and gives a 1.00:1.18:1.40:4.28 ratio for In/As/Mn/S. CHN anal. (Vario EL). Calcd: C, 10.57; H, 2.66; N, 8.22. Found: C, 10.59; H, 2.52; N, 8.29. IR (Bruker Vertex 70 FTIR between 4000 and 400 cm^{-1}, cm^{-1}): 2954 (w), 1466 (m) ($-CH_2-$); 1575 (s), 1228 (m), 1178 (w), 1163 (m), 1107 (m), 1066 (m), 1044 (w), 1031 (m) (RNH_2 and $N(CH_2)_2$).

The same synthetic protocol was applied for the synthesis of compounds **2**−**4**. For preparing compound **2**, 107 mg of realgar As_4S_4 (0.25 mmol) and 122.5 mg $Mn(CH_3COO)_2$ (0.5 mmol) were used to replace the orpiment and $MnCl_2$ in the synthesis of compound **1**. For the other two compounds, 148 mg of $Zn(NO_3)_2\cdot 6H_2O$ (0.5 mmol) for **3** or 119 mg $CoCl_2\cdot 6H_2O$ (0.5 mmol) for **4**, instead of $MnCl_2\cdot 4H_2O$, was added to the mixtures for compound **1**. Semiquantitative EDXS confirmed the presence of all constituent heavy elements in these three compounds. CHN anal. Calcd for **2**: C, 13.88; H, 3.49; N, 10.79. Found: C, 13.90; H, 3.40; N, 10.90. Calcd for **3**: C, 13.61; H, 3.43; N, 10.58. Found: C, 13.72; H, 3.08; N, 10.68. Calcd for **4**: C, 13.71; H, 3.50; N, 10.46. Found: C, 13.58; H, 3.35; N, 10.55. IR for **3** (cm^{-1}): 2922 (w), 2848 (m), 1470 (m), 1453 (m) ($-CH_2-$); 1583 (m), 1569 (m), 1180 (m), 1124 (w), 1112 (m), 1079 (m), 1066 (m), 1057 (m) (RNH_2 and $N(CH_2)_2$).

Physical Measurements. Diffuse-reflectance measurements were collected using a Hitachi U-4100 spectrophotometer. $BaSO_4$ powder was used as the reference (100% reflectance). The absorption data were calculated from the reflectance using the Kubelka−Munk function.[56] Thermal analysis was conducted on a Pyris Diamond thermal analyzer. The sample of **1** (2.381 mg) or **3** (2.693 mg) was heated under a nitrogen stream with a heating rate of 5 °C/min in the range of 40−800 °C. Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 Focus diffractometer with Cu Kα radiation and a Lynx Eye detector at a scanning rate of 15°/min in the 2θ range of 10−50°.

Single-Crystal Structure Determination. A Bruker Apex II CCD diffractometer equipped with graphite-monochromatized Mo Kα radiation was used to collect X-ray intensity data at 293 K. The structures were solved with direct methods using *SHELXS-97*, and structure refinements were performed against F^2 using *SHELXL-97*.[57] All non-H atoms were refined anisotropically. The H atoms were positioned by geometry and refined using a riding model. Relevant crystallographic data and refinement details for the four compounds are summarized in Table 1. The ranges of selected bond lengths and angles are given in Table 2.

Results and Discussion

Crystal Structures. The most important feature of our solvothermal synthesis to the title compounds is the stabilization of the isolated AsS_3^{3-} unit in their structures. Compound **1** crystallizes in the triclinic space group $P\bar{1}$ and consists of a 1D inorganic ${}^1_\infty\{[InAsS_4]^{2-}\}$ chain and metal complexes $[Mn(tren)]^{2+}$ as charge-compensating cations. In the 1D chain of **1**, the In and As are coordinated with four and three S atoms to form a slightly distorted tetrahedral InS_4 and a pyramidal AsS_3, respectively. Each tetrahedral InS_4 unit is connected with two pyramidal AsS_3 units and shares one edge with another symmetry-related InS_4 moiety, forming a four-membered In_2S_2 ring. Each pyramidal AsS_3 is connected with two tetrahedral InS_4 and one $[Mn(tren)]^{2+}$ complex. Two InS_4 tetrahedra and two AsS_3 pyramidal polyhedra are interconnected to generate an eight-membered $In_2As_2S_4$ cluster, which is condensed to the final infinite anionic ${}^1_\infty\{[InAsS_4]^{2-}\}$ chain along [100]. The In−In distances of an In_2S_2 ring and an eight-membered $In_2As_2S_4$ cluster are 3.239(2) and 5.654(3) Å, respectively (Table 1 in the Supporting Information, SI). The inorganic anionic chain can be also viewed as a string of fused eight-membered $In_2As_2S_4$ rings and four-membered In_2S_2 rings in an alternating fashion. A four-membered $AsMnS_2$ heteroring is also formed between a pyramidal AsS_3 and a metal complex $[Mn(tren)]^{2+}$ by sharing two S atoms. Two $[Mn(tren)]^{2+}$ complexes are bonded to the opposite sides of the eight-membered $In_2As_2S_4$ ring along the backbone of the infinite inorganic chains. Note that S2 is the only site with tricoordination that bridges As, Mn, and In. The corner-sharing mode between AsS_3 and InS_4 units differs from that of $(Ph_4P)_2[InAs_3S_7]$, where $[As_3S_7]^{5-}$ units share an edge with a distorted trigonal-bipyramidal InS_5 unit.[14] Interestingly, the backbone of this infinite anionic chain can find its ancestors in thioantimonates,

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Table 1. Crystal Data and Structure Refinement for Compounds **1**−**4**

	1	**2**
formula	[Mn(tren)]InAsS$_4$	[Mn(tren)]$_4$(In$_2$As$_2$S$_8$)$_2$
fw	519.16	2076.82
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	8.663(5)	19.3432(6)
b (Å)	9.480(5)	8.9228(3)
c (Å)	10.515(5)	23.2771(6)
α (deg)	106.666(5)	90
β (deg)	100.234(5)	126.911(2)
γ (deg)	100.228(5)	90
V (Å^3)	789.8(7)	3212.29(17)
Z	2	2
T (K)	293(2)	153(2)
D_c (g/cm^3)	2.183	2.147
total reflns/total unique reflns/no. of param	4071/2731/162	24 369/6359/307
GOF	1.064	1.145
R1, wR2 [$I > 2\sigma(I)$]	0.0226, 0.0568	0.0200, 0.0519
R1, wR2 (all data)	0.0232, 0.0571	0.0259, 0.0630

	3	**4**
formula	[Zn(tren)]$_4$(In$_2$As$_2$S$_8$)$_2$	[Co(tren)]$_4$(In$_2$As$_2$S$_8$)$_2$
fw	2118.38	2092.78
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a (Å)	19.491(2)	19.3875(10)
b (Å)	8.7074(10)	8.6827(5)
c (Å)	23.5084(18)	23.4082(9)
α (deg)	90	90
β (deg)	126.750(6)	126.873(3)
γ (deg)	90	90
V (Å^3)	3196.8(5)	3152.2(3)
Z	2	2
T (K)	293(2)	153(2)
D_c (g/cm^3)	2.201	2.205
total reflns/total unique reflns/no. of param	16 067/5633/307	16 789/6220/307
GOF	0.959	1.026
R1, wR2 [$I > 2\sigma(I)$]	0.0415, 0.0755	0.0231, 0.0551
R1, wR2 (all data)	0.0700, 0.0820	0.0290, 0.0573

Table 2. Ranges of Bond Distances (Å) and Angles (deg) in Compounds **1** and **2**

	1	**2**
Mn−N	2.218(3)−2.327(3)	2.172(3)−2.349(2)
Mn−S	2.494(2)−2.884(2)	2.432(1)−2.455(1)
As−S	2.220(1)−2.275(1)	2.213(1)−2.275(1)
In−S[a]	2.455(1)−2.485(1)	2.432(1)−2.606(1)[a]
N−Mn−N	76.11(11)−146.41(12)	77.06(10)−118.61(11)
N−Mn−S	81.11(8)−176.49(8)	96.15(7)−175.46(7)
S−As−S	97.12(4)−101.21(4)	95.64(3)−105.83(3)
S−In−S[a]	97.69(5)−115.00(4)	91.24(3)−135.65(3)[a]
H···A	2.47−2.85	2.48−2.75
D···A	3.323(4)−3.667(4)	3.321(4)−3.606(3)

[a] Weak In−S bond distances and their derived S−In−S bond angles are not included.

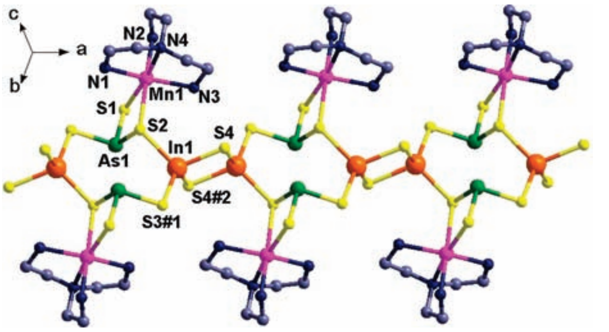

Figure 3. 1D chain structure of compound **1**. Color code: orange, In^{3+}; green, As^{3+}; pink, Mn^{2+}; yellow, S^{2-}; dark blue, N; blue gray, C. All H atoms were omitted for clarity. Symmetry transformations used to generate equivalent atoms: #1, $-x+1, -y, -z+2$; #2, $-x, -y, -z+2$.

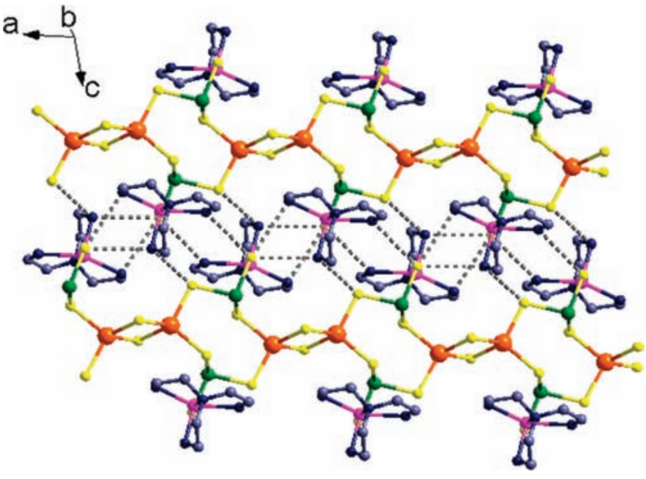

Figure 4. Interconnection of the chains into layers via the N−H···S hydrogen bonds in compound **1** (dashed lines). The color code is the same as that used in Figure 3. H atoms are omitted for clarity.

e.g., ${}^1_\infty\{[Sb_2S_4]^{2-}\}$[48] or ${}^1_\infty\{[FeSbS_4]^{2-}\}$,[58] in which the trigonal SbS$_3$ pyramid is replaced by a AsS$_3$ unit while the SbS$_4$ or FeS$_4$ unit is replaced by an InS$_4$ tetrahedron.

Each Mn^{2+} cation in [Mn(tren)]$^{2+}$ has a distorted octahedral environment and is coordinated with four N atoms from one tren ligand and two S atoms from the 1D chain. All bond lengths and angles, as summarized in Table 2, are in their normal ranges except the bond length of Mn1−S2. A 2.884(2) Å length for this Mn−S bond is a little longer than those in other cases such as ${}^1_\infty[\{Mn(tren)\}(As_4S_7)]$,[16] [Mn(tren)]Sb$_2S_4$,[48] and [Mn(tren)]Sb$_4S_7$[49] and results in a distortion of its octahedral environment. Such distortion could be further manifested by the three trans angles ranging from 146.41(12) to 176.49(8)° and four N−Mn−N cis angles falling in the range of 81.11(8)−98.46(11)°. Valence sums for In, Mn, and As are 3.093, 1.909, and 3.170, respectively.

Each chain interacts with neighboring chains via weak interchain N−H···S hydrogen bonds and forms a layered arrangement parallel to the (010) plane (Figure 4). The N···S and H···S distances and the N−H···S angles (Table 2 in the SI) are in accordance with the values reported in the literature.[48,50] This layer structure is further packed into a three-dimensional superlattice through van der Waals forces instead of hydrogen bondings.

Single-crystal XRD analyses revealed that compounds **2**−**4** are isomorphous. They all crystallize in the monoclinic space group $P2_1/c$, and the structure of **2** is illustrated here as an example. The inorganic anion consists of an InS$_4$ tetrahedron and an AsS$_3$ pyramid as the primary building units (Figure 5). There are two crystallographically distinct In and As atoms in the asymmetric

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(58) Kiebach, R.; Bensch, W.; Hoffmann, R. D.; Pottgen, R. *Z. Anorg. Allg. Chem.* **2003**, *629*, 532–538.

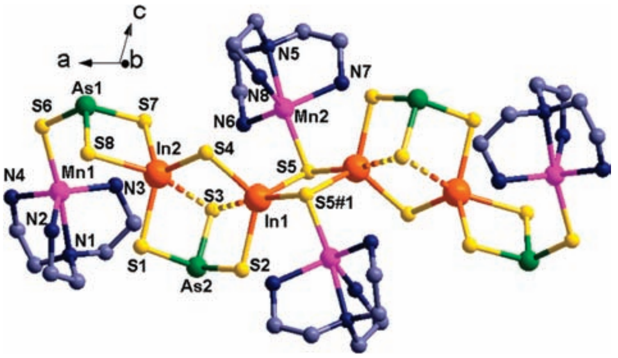

Figure 5. Molecular structure of compound **2**. The color code is the same as that used in Figure 3. The relatively strong interactions between In2−S3 [2.796(1) Å] and In1−S3 [2.998(1) Å] are indicated as dashed lines. Symmetry transformations used to generate equivalent atoms: #1, −x − 1, −*y*, −z − 1.

unit. The observed bond lengths of In−S and bond angles of S−In−S (Tables 1 and 2 in the SI) deviate severely from the values in **1** and those reported in the literature for the typical tetrahedral InS_4.[37,59] In addition, there are two further In−S interactions at longer distances of 2.998(1) Å for In1−S3 and 2.796(1) Å for In2−S3, which are significantly larger than the normal In−S bond length but less than the sum of the van der Waals radii of In and S. These observations suggest a strong distortion of the tetrahedral coordination of In. Taking the weak In−S bond into considerations, one As atom (As2), two crystallographically distinct In atoms, and four S atoms (S1−S4) form a pseudosemicube structure (In_2AsS_4), which is common in thiostannates[46] and thioantimonates[49] but not in thioarsenates. Besides coordinated with S atoms in the pseudosemicube, the two In atoms share edges with either a $As1S_3$ pyramid (In2) or another symmetry-related InS_4 unit (In1). The edge sharing of two symmetry-related InS_4 tetrahedra results in the formation of a In_2S_2 ring, which is similar to the case in compound **1**.

Both of the two crystallographically distinct As atoms are tricoordinated with S atoms in the normal bond ranges and S−As−S bond angles (Table 2 and 1 in the SI). One AsS_3 unit is located in the pseudosemicube, while the other one is linked to one of the InS_4 units in the pseudosemicube via edge sharing and connected with a $[Mn(tren)]^{2+}$ complex via corner sharing. The two asymmetric units consisting of a pseudosemicube In_2AsS_4 and a $As1S_3$ unit are linked by the In_2S_2 ring to form the inorganic $In_4As_4S_{16}{}^{8-}$ anion of compound **2**.

The Mn atom in $[Mn(tren)]^{2+}$ locates in a trigonal-bipyramidal environment and is coordinated by four N atoms from one tren ligand, one μ_2-S (S6), or one μ_3-S (S5). Therefore, two connection modes could be observed for the four complexes in isomorphous **2**−**4**, which are bonded to the terminal S sites of two AsS_3 units or two bridging S atoms in the In_2S_2 ring. Both of the coordination environments of the three transition-metal cations and the connection modes of the complex differ from those in **1**. The Mn−N and M−S bond lengths are in their normal range (Table 2). The axial trans N−Mn−S angles are 175.46(7)° for Mn1 and 173.02(7)° for Mn2 and suggest their moderate distortions from trigonal-bipyramidal modes, which could be further evidenced by the deviations of the axial N−Mn−N angles (Table 1 in the SI) from 90° for an ideal geometry. Similar to **1**, weak N−H···S hydrogen bonds (Table 2 in the SI) existing between adjacent compounds help to make 2D layers (Figure 6), but only the van der Waals force is responsible for their further stackings.

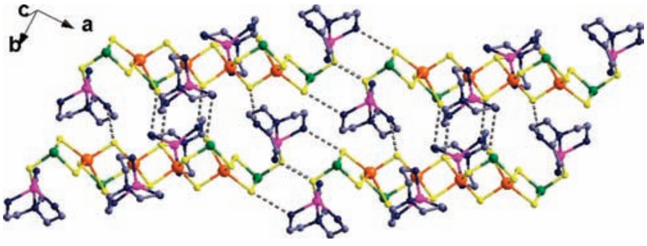

Figure 6. Interconnection of compound **2** into layers via N−H···S hydrogen bonds (dashed lines). The color code is the same as that used in Figure 3. H atoms are omitted for clarity.

Chemical Synthesis. In our solvothermal process, some first-row transition-metal (metal = Cr, Mn, Fe, Co, Ni, Cu, or Zn) salts and two arsenic sulfides (orpiment and realgar) were chosen to investigate their effects on the formation of the title compounds. Besides ligands for the transition metals, the amine tren could also induce the disproportionation of S, a well-known process that can produce a S^{2-} anion.[34,35] When the orpiment (As_2S_3) was chosen as the As source, it would dissolve into the tren alkaline solution to afford pyramidal $AsS_3{}^{3-}$ anions together with oxo and oxothio anions. The overall reaction would be written as eq 1.

$$Mn^{2+} + In^{3+} + AsS_3{}^{3-} + S^{2-} + tren \rightarrow Mn(tren)InAsS_4 \qquad (1)$$

When the realgar (As_4S_4) was used, it might undergo alternation to pararealgar (γ-AsS) under our solvothermal conditions. Such an alternation needs to be confirmed in the future, although it has been verified by light-induced processes.[60] An oxidation−reduction process is proposed here to convert the pararealgar into an $AsS_3{}^{3-}$ anion, as shown in eq 2. Then eq 1 could be fulfilled to yield the title compounds.

$$2AsS + S + 3S^{2-} \rightarrow 2AsS_3{}^{3-} \qquad (2)$$

Among the transition-metal salts investigated, no crystal or crystals with poor quality could be yielded for the Fe, Ni, or Cu systems. For the Cr case, we obtained crystals with a formula of $[Cr(tren)AsS_3]$ (Figure SI-1 in the SI). Here, In was not incorporated in its molecular compound, and its structure resembles that of $[Cr(tren)SbS_3]$.[50] The occurrence of such a structure could be due to the high 3+ valence of Cr because the negative charge of the $AsS_3{}^{3-}$ anion can be easily compensated for by a $Cr(tren)^{3+}$ complex. Different As sources do have effects on the formation of the four title compounds. When the Zn^{2+} cation was used as a metallic source, compound **3**

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(60) Douglass, D. L.; Shing, C. C.; Wang, G. *Am. Mineral.* **1992**, *77*, 1266–1274.

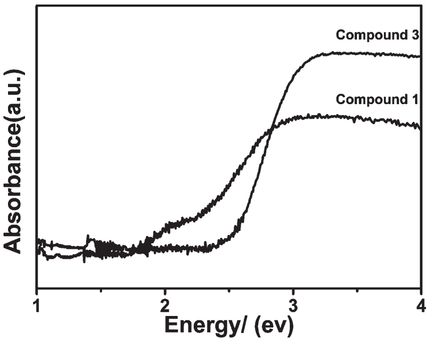

Figure 7. Optical absorption spectra of compounds **1** and **3**.

was the only product that could be obtained by using either orpiment or realgar under similar conditions. For the case of Co^{2+}, crystals of compound **4** suitable for single-crystal XRD can only be collected in an orpiment system, while poor crystals were produced in the realgar reaction system. The most distinct variation occurs for the synthetic system of Mn^{2+}, as exemplified by the infinite structure of compound **1** from orpiment and the molecular compound **2** from realgar. Several factors might be involved for the observed difference among these three metal cation systems. First, orpiment is less thermodynamically stable than realgar and could be easily converted into an AsS_3^{3-} anion under this solvothermal process. This might favor the expedited assemblings of constituents along the infinite 1D structure of compound **1**. The configurations of the metal complexes should be another key factor in determining the structures of the title compounds. For isomorphous compounds **2**−**4**, the three transition metals are all pentacoordinated by four N atoms and one S atom, while the Mn atom in compound **1** takes an octahedral coordination environment.

Optical Properties and Thermogravimetric Analyses. The optical properties of **1** and **3** were studied by solid-state diffuse-reflectance UV/vis/NIR spectroscopy at room temperature (Figure 7). The purities of these two hand-picked products were confirmed by powder XRD, given in Figures SI-2 and SI-3 in the SI, compared with their simulated XRD data. We failed to obtain the same optical properties for **2** and **4** because of the coexistence of impurities even for hand-picked products. Both **1** and **3** are wide-gap semiconductors with energy gaps of 2.09 and 2.53 eV, respectively, as calculated from reflectance data by using the Kubelka−Munk function.[56]

The thermal stabilities of **1** and **3** were investigated with a thermogravimetry−differential thermal analysis (TG−DTA) method under a N_2 atmosphere (Figure SI-4 in the SI). Compounds **1** and **3** could be stable up to 263 and 250 °C, respectively. The weight losses between their stable temperature points and 305 °C are 22.65% for **1** and 27.58% for **3**, with their corresponding endothermic peaks around 296 °C given in the DTA results. In the case of **3**, the total weight loss percentage before 305 °C is close to the calculated amount (27.60%) of the organic tren ligand in the compound. However, there was more than 5.5% tren remaining in **1** when the temperature reached the same point. These observations suggest that compound **1** shows a better thermal stability than compound **3**. The progressive weight loss between 305 and 800 °C could be attributed to the evolution of H_2S and the continuous sublimation and decomposition of arsenic sulfides at elevated temperature, together with the further decomposition of tren in compound **1**.

Conclusion

In summary, four organic−inorganic hybrid solids consisting of transition-metal−amine complexes and indium thioarsenate anions are reported here. The most interesting feature is that the pyramidal AsS_3^{3-} anion remains isolated in the inorganic anions despite its strong condensation tendency. The transition metals in the complexes are either octahedral or bipyramidal coordinated and might serve as structure-directing agents for the formation of the 1D chain or the three molecular compounds. Compounds **1** and **3** are wide-gap semiconductors with energy gaps of 2.09 and 2.53 eV, respectively.

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Supporting Information Available: CIFs, detailed bond lengths and angles for compounds **1**−**4**, structure and synthesis of compound **5**, and XRD patterns and TG−DTA curves for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.