

Hydrothermal Syntheses and Characterizations of Thioarsenates [Fe(phen)₃][As₃S₆]·dien·7H₂O and [Mn₂(phen)₄(As₂S₅)]·phen·2H₂O: A New Coordination Mode of the As₂S₅⁴⁻ Anion

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Novel hydrogen-bonded supramolecular thioarsenates [Fe(phen)₃][As₃S₆]·dien·7H₂O (**1**) and [Mn₂(phen)₄(As₂S₅)]·phen·2H₂O (**2**) (dien = diethylenetriamine, phen = 1,10-phenanthroline) were hydrothermally synthesized and characterized. The structure of **1** consists of [As₃S₆]³⁻–H₂O anionic layers and [Fe(phen)₃]³⁺–dien cationic layers assembled via O–H···S and O–H···N hydrogen-bonding interactions. The layers stack alternately and are parallel to each other to give a 3D network structure with channels accommodating unique branched water chains, which are anchored on the anionic and cationic layers via hydrogen bonds. In **2**, the [As₂S₅]⁴⁻ anion acts as a tetradentate bridging ligand via four terminal S atoms to link two [Mn(phen)₂]²⁺ cations, forming the neutral complex [Mn₂(phen)₄(As₂S₅)]. This is a new coordination mode for the [As₂S₅]⁴⁻ ion. [Mn₂(phen)₄(As₂S₅)], phen, and H₂O form a 3D network structure via O–H···S, O–H···O, and π – π stacking interactions.

Introduction

Much interest has been focused on the synthesis and characterization of main group chalcogenometalates because of their potential application as semiconductors;¹ photoconductors;² optical, ion exchange, and magnetic materials;^{3–5} and chemical sensors.⁶ Since the cobalt thioantimonate [Co(en)₃]CoSb₄S₈ was prepared in superheated ethylenediamine in 1996,⁷ a number of main group chalcogenometalates containing transition metals (TM) have been synthesized using hydrothermal and solvothermal methods.⁸ Mild

solvothermal synthesis is usually conducted in the presence of amines as structure-directing agents, such as ethylenediamine (en) and diethylenetriamine (dien). These amines act as chelating ligands to coordinate with TMⁿ⁺, forming complex cations, which act as space fillers or charge-compensating ions in the chalcogenometalates. The self-assembly directed by transition metal complexes is a powerful approach for the construction of chalcogenometalates. However, the coordinate sites of TMⁿ⁺ ions are prone to be saturated by three bidentate en ligands or two tridentate dien ligands due to the formation of octahedral complexes [TM(en)₃]ⁿ⁺ and [TM(dien)₂]ⁿ⁺, so the incorporation of TM into the main group chalcogenometalate network is difficult to achieve in the presence of en and dien. The limited examples of chalcogenometalates integrated with TM complexes are [Cr(en)₂(GeSe₄)]⁻, [Cr(en)₂(SnSe₄)]⁻,⁹ [Mn₂(en)₂(Sb₂S₅)],¹⁰ [Mn₂(dien)(Sb₂S₅)],¹¹ [Cr(en)₂(SbS₃)],¹² [Mn(en)₃]₂–[Mn₄(en)₉(SbSe₄)₄],¹³ [Mn(en)₃][Mn₂(en)₄(SbSe₄)₂(H₂O)],¹⁴ [Mn(dien)₂][Mn(dien)AsS₄]₂·4H₂O, and [Mn(en)₃]₂[Mn(en)₂AsS₄][As₃S₆].¹⁵ The strategy of incorporating TM into

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a chalcogenometalate network is best achieved by choosing the tetradentate amine tris(2-aminoethyl)amine (tren) as the structure-directing agent. The tetradentate ligand leaves one or two coordination sites free at the TM ion, enabling bond formation to the chalcogenometalate network,¹⁶ and a series of chalcogenometalates containing the $[\text{TM}(\text{tren})]^{n+}$ complexes have been synthesized.¹⁷ The incorporation of TM with the main group chalcogenometalate anionic network enriches the structural diversity and properties of the chalcogenometalate compounds.

On the other hand, the solvothermal synthesis of chalcogenometalates with TM complexes containing a rigid amine ligand which can exhibit different structure-directing effects compared to flexible amine ligands remains almost unexplored. The only reported examples of a chalcogenometalate incorporated TM complex with a rigid ligand are the thioarsenates $[\text{Mn}_3(2,2'\text{-bipy})_3(\text{AsS}_4)_2]\cdot\text{H}_2\text{O}$ and $[\text{Mn}_2(2,2'\text{-bipy})\text{As}_2\text{S}_5]$.¹⁸ In the present work, we use the rigid bidentate ligand 1,10-phenanthroline (phen) in the preparation of chalcogenometalate under hydrothermal conditions and obtain two novel transition metal thioarsenates, $[\text{Fe}(\text{phen})_3][\text{As}_3\text{S}_6]\cdot\text{dien}\cdot 7\text{H}_2\text{O}$ (**1**) and $[\text{Mn}_2(\text{phen})_4(\text{As}_2\text{S}_5)]\cdot\text{phen}\cdot 2\text{H}_2\text{O}$ (**2**), in which an infinite 1D water chain and a new coordination mode of the $\text{As}_2\text{S}_5^{4-}$ anion are observed, respectively.

Experimental Section

Materials and Methods. All chemicals are analytical grade and were obtained commercially and used without further purification. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer using dry KBr pellets. Elemental analysis was carried out on a MOD 1106 elemental analyzer. Thermal thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses were conducted on an SDT 2960 microanalyzer, and the samples were heated at a rate of 5°C min^{-1} under a 100 mL min^{-1} nitrogen stream.

Synthesis of $[\text{Fe}(\text{phen})_3][\text{As}_3\text{S}_6]\cdot\text{dien}\cdot 7\text{H}_2\text{O}$ (1**).** $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ (270 mg, 1 mmol), As_2O_3 (396 mg, 2 mmol), S (192 mg, 6 mmol), and phen (546 mg, 3 mmol) were mixed in 6 mL of water. Diethylenetriamine (310 mg, 3 mmol) was added dropwise to the above solution and stirred for 5 min. The mixture was loaded into a Teflon-lined stainless steel autoclave with an inner volume of 15 mL, and then the sealed autoclave was heated under autogenous pressure at 140°C for 5 days. Upon cooling to ambient temperature, crystals of **1** were filtered off and washed with ethanol and ether (45% yield based on As_2O_3). The compound is stable in air and water. Anal. calcd for

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

	1	2
empirical formula	$\text{C}_{40}\text{H}_{51}\text{N}_9\text{O}_7\text{FeAs}_3\text{S}_6$	$\text{C}_{60}\text{H}_{44}\text{N}_{10}\text{O}_2\text{Mn}_2\text{As}_2\text{S}_5$
fw	1242.87	1357.07
color of cryst	red	dark-red
cryst dimensions, mm^3	$0.25 \times 0.22 \times 0.10$	$0.37 \times 0.30 \times 0.30$
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$
<i>a</i> , Å	11.947(2)	12.959(2)
<i>b</i> , Å	13.444(3)	20.696(3)
<i>c</i> , Å	16.825(3)	21.970(4)
α , deg	104.361(3)	90
β , deg	106.783(4)	99.173(6)
γ , deg	93.384(4)	90
<i>V</i> , Å ³	2481.5(8)	5817.1(16)
<i>Z</i>	2	4
<i>T</i> , K	193(2)	193(2)
calcd density, mg m^{-3}	1.663	1.550
abs coeff, mm^{-1}	2.598	1.796
<i>F</i> (000)	1262	2744
2θ (max), deg	49.00	49.00
total reflns collected	23 172	53 274
unique reflns	8241 ($R_{\text{int}} = 0.0810$)	9661 ($R_{\text{int}} = 0.0817$)
no. of params	608	740
$R1 [I > 2\sigma(I)]$	0.0768	0.0765
wR2 (all data)	0.1939	0.1669
GOF on F^2	1.144	1.131

$\text{C}_{40}\text{H}_{51}\text{N}_9\text{O}_7\text{FeAs}_3\text{S}_6$: C, 38.66; H, 4.43; N, 10.14. Found: C, 37.52; H, 4.37; N, 9.97. IR data (KBr, cm^{-1}): 3508 (m), 3492 (m), 3386 (m), 3210 (vs), 3079 (w), 3054 (w), 3046 (w), 2928 (vs), 2919 (vs), 2863 (s), 1628 (m), 1592 (s), 1578 (s), 1520 (vs), 1428 (m), 1208 (m), 1150 (m), 1106 (s), 1073 (s), 1011 (s), 972 (s), 903 (s), 857 (s), 812 (m), 756 (m), 741 (m), 722 (m), 667 (m), 594 (w), 586 (w).

Synthesis of $[\text{Mn}_2(\text{phen})_4(\text{As}_2\text{S}_5)]\cdot\text{phen}\cdot 2\text{H}_2\text{O}$ (**2**).

Dark-red block crystals of **2** (51% yield based on As_2O_3) were prepared with a procedure similar to the synthesis of **1**, except that $\text{MnCl}_2\cdot 4\text{H}_2\text{O}$ was used instead of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$. The compound is stable in air and water. Anal. calcd for $\text{C}_{60}\text{H}_{44}\text{N}_{10}\text{O}_2\text{Mn}_2\text{As}_2\text{S}_5$: C, 53.10; H, 3.50; N, 10.33. Found: C, 52.86; H, 3.45; N, 10.24. IR data (KBr, cm^{-1}): 3511 (m), 3499 (m), 3462 (m), 3058 (w), 3034 (w), 1626 (m), 1591 (s), 1578 (w), 1516 (m), 1427 (m), 1148 (m), 1102 (s), 857 (s), 812 (m), 757 (m), 727 (m), 665 (m).

X-Ray Crystal Structure Determinations. Data were collected on a Rigaku Mercury CCD diffractometer using ω -scan methods with graphite monochromated Mo K α radiation ($\lambda = 0.071073\text{ nm}$) at 193 K. The X-ray data of single crystals were collected to a maximum 2θ value of 49.00° . An absorption correction was applied for both compounds. The structures were solved with direct methods using the program SHELXS-97.^{19a} The structure refinement was done against F^2 using SHELXL-97.^{19b} All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters applying a riding model. Technical details of data acquisition and selected refinement results are summarized in Table 1.

Results and Discussion

Synthesis and Infrared Spectra. Compounds **1** and **2** were prepared through the reactions of $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$ ($\text{MnCl}_2\cdot 4\text{H}_2\text{O}$), As_2O_3 , S, phen, and dien in water at 140°C for 5 days. In our previous works, we demonstrated that chalcogenidoarsenates can be conveniently prepared using As_2O_3 and S (or Se) as starting materials in amine solution under solvothermal

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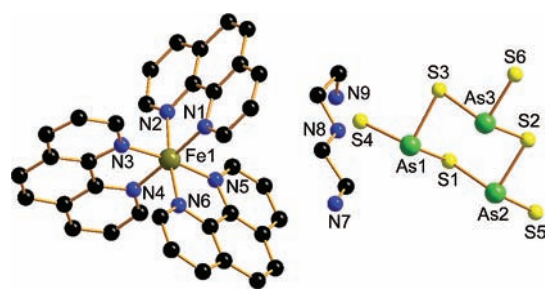


Figure 1. Crystal structure of **1** with the labeling scheme. Hydrogen atoms and H₂O molecules are omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1** and **2**

	1 (M = Fe)	2 (M = Mn)
As–S _t	2.155(3)–2.165(3)	2.203(2)–2.221(2)
As–S _b	2.258(3)–2.304(3)	2.294(2), 2.300(2)
M–S		2.497(2)–2.542(2)
M–N	1.961(7)–1.974(7)	2.252(7)–2.365(7)
S–As–S	98.87(10)–101.37(11)	99.14(9)–104.64(9)
As–S–As	93.56(10)–98.10(11)	96.50(9)
As–S–Mn		86.77(8)–87.97(8)
S–M–S		83.48(8), 85.47(8)
S–M–N		91.51(17)–173.3(2)
N–M–N	82.9(3)–177.0(3)	71.6(2)–151.3(2)

conditions,²⁰ although the traditional starting materials are binary arsenic chalcogenides or ternary alkali chalcogenidoarsenate salts.²¹ In the present work, the title compounds were prepared in water solution, but amine dien is needed. Besides being a crystal solvent, the amine dien may play an important role in the conversion of S₈ to the S²⁻ ion needed to form thioarsenates during the hydrothermal reactions. The chalcogens can undergo a disproportionation process to produce chalcogenide ions in the presence of a basic amine solution under solvothermal conditions, and this method has been widely used in the preparation of chalcogenidometalates.^{8a,8b}

In the IR spectra of **1** and **2**, the relatively weak absorption bands in the frequency range 3058–3038 cm⁻¹ are due to the C–H vibrations of the aromatic ring hydrogen atoms. The C–H modes involving the aliphatic hydrogen atoms of dien in **1** are at 2928 and 2919 cm⁻¹. The absorption bands in the range 1628–1427 cm⁻¹ correspond to ring vibrations of the phen ligand. The broad absorption bands in the range 3511–3492 cm⁻¹ are assigned to the O–H modes of H₂O. The broad band indicates the presence of hydrogen bonds, which has been confirmed by crystal structure determination.

Crystal Structures. The structure of the ionic complex **1** consists of a mononuclear [Fe(phen)₃]³⁺ cation, a trinuclear [As₃S₆]³⁻ anion, and solvent molecules of dien and water. The iron(III) ion is coordinated by six phen nitrogen atoms, forming a slightly distorted octahedral

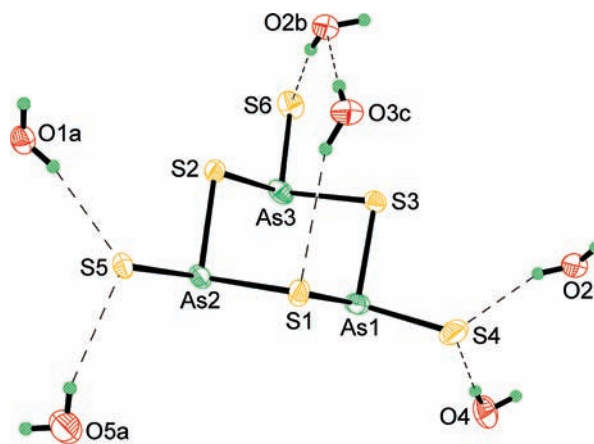


Figure 2. A view of O–H...S hydrogen-bonding interactions with the labeling scheme (50% thermal ellipsoids) between the [As₃S₆]³⁻ anion and H₂O molecules in **1**.

geometry (Figure 1), with the cis N–Fe–N and trans N–Fe–N bond angles varying from 82.9(3) to 96.4(3)^o and 173.3(3) to 177.0(3)^o, respectively (Table 2). The Fe–N bond lengths varying in the narrow range 1.961(7)–1.974(7) Å are in agreement with those found in iron(III) phen complexes.²² The cyclic [As₃S₆]³⁻ anion is formed by three vertex-linked AsS₃ trigonal pyramids (Figure 1), generating a six-membered ring, As₃S₃, with a chair conformation. The bridging As–S_b bond (2.258(3)–2.304(3) Å) in the As₃S₃ ring is significantly longer than the terminal As–S_t bonds (2.155(3)–2.165(3) Å). The only previously known cyclic trimeric [As₃S₆]³⁻ anions were observed in thioarsenates [Mn(en)₃]₂–[Mn(en)₂As₄][As₃S₆]¹⁵ and [enH₂]₃[As₃S₆]₂·6en,²³ which were prepared in en as the solvent. Compound **1** is the first example of an [As₃S₆]³⁻ anion with a rigid chelating ligand complex cation as the counterion.

There are seven crystal water molecules in the crystallographic asymmetric unit of **1**. All water molecules are not involved in any metal–ligand interactions. Five water molecules (O(1)–O(5)) have contacts with the S atoms of the [As₃S₆]³⁻ anion via O–H...S hydrogen bonds (Figure 2) with O...S distances between 3.238(10) and 3.634(8) Å. The [As₃S₆]³⁻ anions are interlinked by water molecules through the O–H...S bonds, generating an [As₃S₆]³⁻–H₂O anionic layer within the (101) plane (Figure 3), while [Fe(phen)₃]³⁺ cations and dien molecules propagate along the anion layers to form the [Fe(phen)₃]³⁺–dien cationic layer. Two terminal N atoms (N7 and N9) of dien in the cationic layer are connected with two adjacent anionic layers (Figure S1 in the Supporting Information) via hydrogen bonds O(6)–H...N(7) (O(6)...N(7) = 2.818(16) Å) and N(9)–H...O(3) (N(9)...O(3) = 2.830(14) Å). In addition, the atom N(8) of dien has a contact with [As₃S₆]³⁻ via the N(8)–H...S(6)#4 bond (N(8)...S(6) = 3.712(13) Å). The anionic and cationic layers stack alternately and are parallel to each other to give a 3D network structure with spacious and straight channels parallel to the *b* axis, in which the hydrogen-bonded H₂O molecules are

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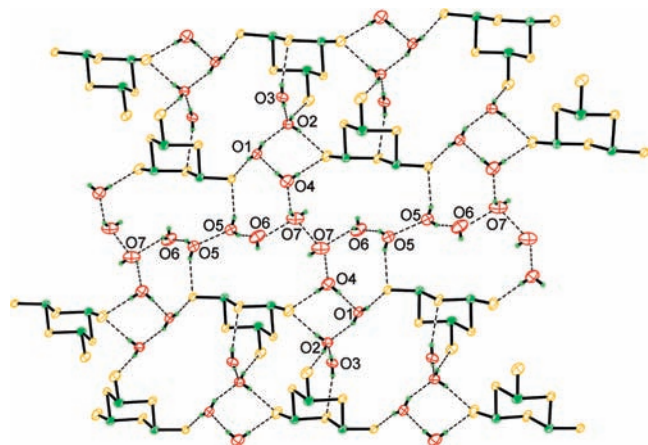


Figure 3. The layer of $[\text{As}_3\text{S}_6]^{3-}$ anions and H_2O molecules assembled via $\text{O}-\text{H}\cdots\text{S}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonding interactions (50% thermal ellipsoids).

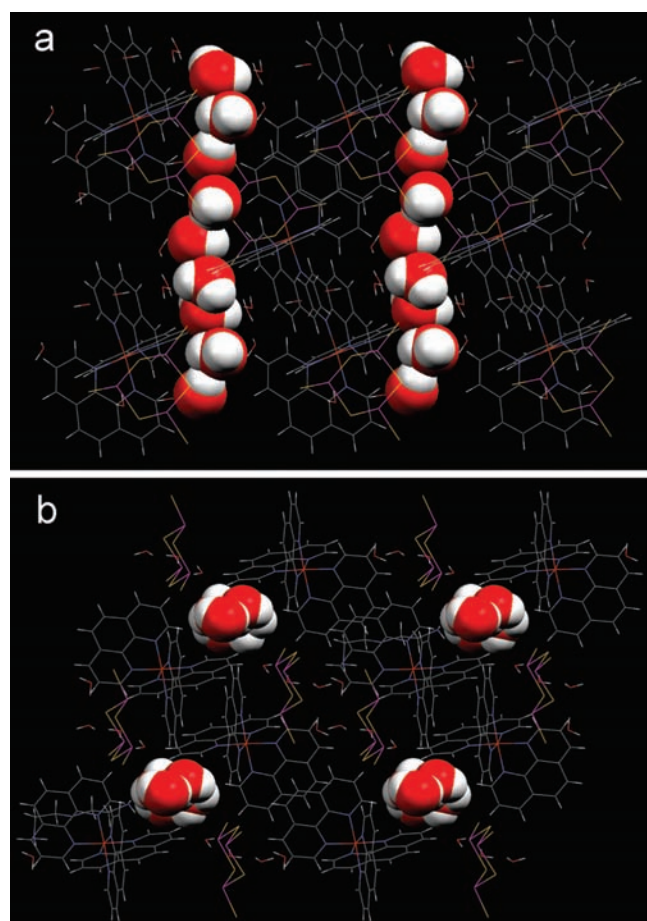


Figure 4. Depiction of the water chains in **1**: (a) viewed down the crystallographic c axis and (b) viewed down the crystallographic b axis. The dien molecules are omitted for clarity.

sandwiched (Figure 4 and Figure S1, Supporting Information). The overall structure is stabilized by the $\text{O}-\text{H}\cdots\text{S}$, $\text{O}-\text{H}\cdots\text{N}$, $\text{N}-\text{H}\cdots\text{O}$, and $\text{N}-\text{H}\cdots\text{S}$ interactions.

A notable feature of the structure of **1** is the presence of a one-dimensional water chain with branches. The complete water chain structure is built up from three crystallographically independent water molecules, O(5), O(6), and O(7), which are arranged in the sequence

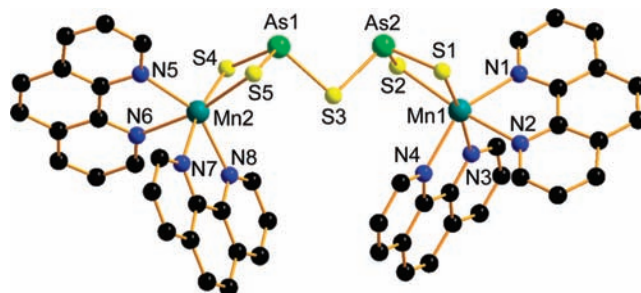


Figure 5. Crystal structure of **2** with the labeling scheme. Hydrogen atoms are omitted for clarity.

$\text{O}(5)-\text{O}(6)-\text{O}(7)-\text{O}(7)-\text{O}(6)-\text{O}(5)$ (Figure 3). The chain is branched at O(7) by water molecules O(1), O(2), O(3), and O(4) (Figure 3). The $\text{O}\cdots\text{O}$ separations vary from 2.752(10) to 2.878(13) Å, which are within the range of the other reported water chains.²⁴ The water chain and its branches are anchored on the anionic layers by water molecules O(1), O(2), O(3), O(4), and O(5) via $\text{O}-\text{H}\cdots\text{S}$ hydrogen bonds and on the cationic layers by water molecules O(3) and O(6) via $\text{O}-\text{H}\cdots\text{N}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds. In recent years, several water clusters have been structurally characterized. However, these water clusters are traditionally stabilized by $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ interactions between water molecules and O or N atoms in the organic or inorganic host.^{24,25} The water clusters hosted in the chalcogenometalate compounds and stabilized by $\text{O}-\text{H}\cdots\text{S}$ interactions are relatively rare in chalcogenometalates. In the thioarsenate **1**, the water chain is formed and stabilized by hydrogen-bonding interactions $\text{O}-\text{H}\cdots\text{S}$ and $\text{N}-\text{H}\cdots\text{S}$, as well as $\text{O}-\text{H}\cdots\text{N}$ and $\text{O}-\text{H}\cdots\text{O}$. This water chain is first observed in the chalcogenometalates.

The structure of **2** consists of a neutral complex $[\text{Mn}_2(\text{phen})_4(\text{As}_2\text{S}_5)]$, phen, and water molecules. The complex $[\text{Mn}_2(\text{phen})_4(\text{As}_2\text{S}_5)]$ is composed of two $[\text{Mn}(\text{phen})_2]^{2+}$ cations bridged by the $[\text{As}_2\text{S}_5]^{4-}$ anion (Figure 5). Each Mn(II) center is bonded to four nitrogen atoms of two phen and two sulfur atoms of the $[\text{As}_2\text{S}_5]^{4-}$ anion, forming a distorted octahedral geometry. The cis $\text{N}-\text{Mn}-\text{N}$ and $\text{S}-\text{Mn}-\text{N}$ bond angles vary from 71.6(2)° to 103.76(19)° for Mn(1) and 72.3(3)° to 105.84(18)° for Mn(2), while the trans $\text{N}-\text{Mn}-\text{N}$ and $\text{S}-\text{Mn}-\text{N}$ bond angles are between 149.8(2)° and 173.3(2)° for Mn(1) and 151.3(2)° and 167.75(18)° for Mn(2) (Table 2). The $\text{Mn}-\text{N}$ (2.252(7)–2.365(7) Å)

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and Mn–S (2.497(2)–2.542(2) Å) bond lengths are in agreement with those reported in the literature.^{18,26} The $[\text{As}_2\text{S}_5]^{4-}$ anion is constructed from two AsS_3 trigonal pyramids sharing a common corner. It acts as a μ_4 - As_2S_5 bridging ligand to link two $[\text{Mn}(\text{phen})_2]^{2+}$ cations forming the neutral complex $[\text{Mn}_2(\text{phen})_4(\text{As}_2\text{S}_5)]$ (Figure 5). The rigid bidentate ligand phen exhibits a different structure-directing effect compared to the flexible ligand en on the formation of manganese thioarsenates. The solvothermal reaction of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, As_2O_3 , and S in the presence of en produces $[\text{Mn}(\text{en})_3]_2\text{As}_2\text{S}_5$.^{20a} Because the coordinate sites of the Mn(II) ion are saturated by three en's, the $[\text{As}_2\text{S}_5]^{4-}$ anion cannot coordinate with the Mn(II) ion and exists as a discrete ion in the ionic compound $[\text{Mn}(\text{en})_3]_2\text{As}_2\text{S}_5$. In the As_2S_5 unit of $[\text{Mn}_2(\text{phen})_4(\text{As}_2\text{S}_5)]$, the terminal As– S_t bonds (av. As– S_t : 2.215(2) Å) are shorter than the bridging As– S_b bonds (av. As– S_b : 2.298(2) Å) (Table 2). But, the As– S_t bonds are slightly longer than the As– S_t bonds of the anion $[\text{As}_3\text{S}_6]^{3-}$ (av. As– S_t : 2.160(3) Å) in **1**, due to the coordination of terminal S atoms of the As_2S_5 unit with Mn(II) ion. Also, because of the coordination of As_2S_5 , two AsS_3 trigonal pyramids of **2** are more distorted than those of the discrete $[\text{As}_2\text{S}_5]^{4-}$ anion. The S–As–S angles in **2** are in the wide range of 99.13(10)–104.65(10)° (Table 2), while the S–As–S angles of the isolated $[\text{As}_2\text{S}_5]^{4-}$ anion in $[\text{Mn}(\text{en})_3]_2\text{As}_2\text{S}_5$ are in the narrow range of 101.20(6)–103.70(7)°.^{20a}

The As_2S_5 units have been known as structural fragments in polymeric multinary thioarsenates for a long time,²⁷ while the free $[\text{As}_2\text{S}_5]^{4-}$ anion is observed in $[\text{Mn}(\text{en})_3]_2\text{As}_2\text{S}_5$.^{20a} The only example of an $[\text{As}_2\text{S}_5]^{4-}$ anion acting as a ligand to a transition metal complex before is the compound $[\text{Mn}_2(2,2'\text{-bipy})(\text{As}_2\text{S}_5)]$.¹⁸ In $[\text{Mn}_2(2,2'\text{-bipy})(\text{As}_2\text{S}_5)]$, $[\text{As}_2\text{S}_5]^{4-}$ acts as a pentadentate μ_5 - As_2S_5 ligand with all S atoms coordinating with the Mn(II) center, leading to a layered structure. Because phen is more sterically hindered than the 2,2'-bipy ligand, only terminal S atoms of the $[\text{As}_2\text{S}_5]^{4-}$ anion are involved in bonding to the $[\text{Mn}(\text{phen})_2]^{2+}$ cation, and $[\text{As}_2\text{S}_5]^{4-}$ acts as a tetradentate μ_4 - As_2S_5 ligand in **2**. This is a new coordination mode for the $[\text{As}_2\text{S}_5]^{4-}$ anion. The bridging angle As–S–As (96.50(9)°) of $[\text{As}_2\text{S}_5]^{4-}$ in $[\text{Mn}_2(\text{phen})_4(\text{As}_2\text{S}_5)]$ is smaller than that of the free $[\text{As}_2\text{S}_5]^{4-}$ anion in $[\text{Mn}(\text{en})_3]_2\text{As}_2\text{S}_5$ (As–S–As: 97.29(6)°),^{20a} indicating the steric hindrance between ligands phen(2) and phen(4) in $[\text{Mn}_2(\text{phen})_4(\text{As}_2\text{S}_5)]$ (Figure 5).

In the structure of compound **2**, the water molecules have contacts to S atoms with $\text{O} \cdots \text{S}$ distances between 3.182(9) Å and 3.468(10) Å, indicating $\text{O} \cdots \text{H} \cdots \text{S}$ hydrogen-bonding interactions (Figure S2 in the Supporting Information). The aromatic plane of one phen molecule (that containing N3 and N4) is parallel

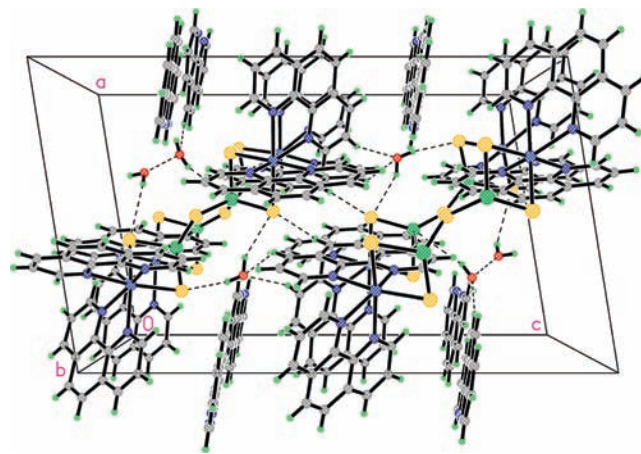


Figure 6. Crystal packing of **2**, viewed down the crystallographic *b* axis.

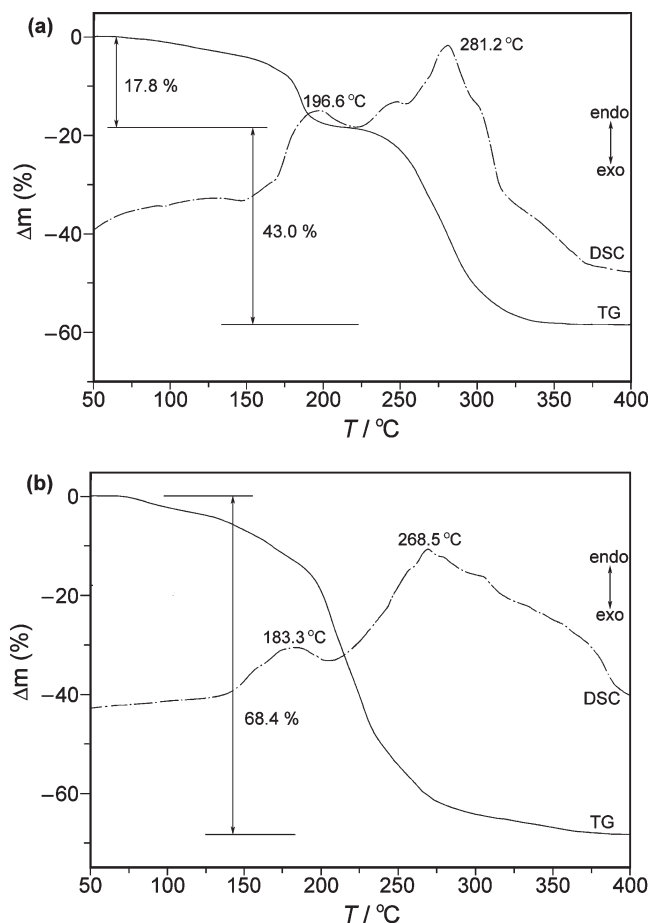


Figure 7. TG-DSC curves of compounds **1** (a) and **2** (b).

to that of a neighbor complex molecule (that containing N7 and N8). The interplane distance between the centroids of two rings of the phen (C16–C24 and N3–C24) molecule and that of two rings of the phen (C40–C48 and N7–C47) molecule belonging to a neighbor $[\text{Mn}_2(\text{phen})_4(\text{As}_2\text{S}_5)]$ motif are 3.52 and 3.58 Å, indicating weak intermolecular π – π stacking interactions (Figure S3 in the Supporting Information). The interplane distances are in the range of phen complexes reported in the literature.²⁸ In **2**, $[\text{Mn}_2(\text{phen})_4(\text{As}_2\text{S}_5)]$, phen, and H_2O form a 3D network structure via hydrogen bonds and π – π stacking interactions (Figure 6).

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Thermogravimetric Analyses. The thermal stabilities of compounds **1** and **2** are investigated under a nitrogen atmosphere, and TG–DSC curves are shown in Figure 7. Compound **1** decomposes in two distinct steps at $T_{\text{onset}} = 148.7$ °C with mass losses of 17.8% and 43.0%. The mass losses are in good accordance with the removal of dien and water molecules in the first step (theoretical values: 18.4% for dien and $7\text{H}_2\text{O}$) and three phen ligands (theoretical values: 43.5%) in the second step, which are accompanied by strong endothermic signals in the DSC curve with the peak temperatures 196.6 and 281.2 °C, respectively (Figure 7a). Compound **2** decomposes in multiple steps at $T_{\text{onset}} = 143.6$ °C, with a total mass loss of 68.4% (Figure 7b), which is attributed to the loss of two water molecules and five phen molecules (theoretical values: 69.2%). Two distinct endothermic signals in the DSC curve with the peak temperatures 183.3 and 268.5 °C are observed during the decomposition.

Conclusion

In summary, the novel thioarsenate-hosting unique water chains, **1**, were hydrothermally synthesized in the presence of rigid phen ligands. Unlike the water clusters and chains,

which are usually stabilized by $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{N}$ interactions, the water chains in **1** are mainly stabilized by $\text{O}-\text{H}\cdots\text{S}$ interactions between water molecules and S atoms in the inorganic host. The structural determination of the water chains in thioarsenate **1** is helpful for a detailed understanding of the possible structures and stabilities of water clusters in diverse surroundings and provides novel structural aspects of water clusters. In **2**, a new tetradentate coordination mode $\mu_4\text{-As}_2\text{S}_5$ is observed for the $[\text{As}_2\text{S}_5]^{4-}$ ion, indicating different structure directing in the formation of manganese thioarsenate between rigid phen and flexible amine (such as en) ligands. Compounds **1** and **2** are the first examples of chalcogenometalates combined with the rigid phen ligand complexes of transition metals.

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Supporting Information Available: Additional tables and figures (PDF) and crystal data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.