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Incorporating Transition Metal Complexes into Tetrathioarsenates(V): Syntheses, Structures, and Properties of Two Unprecedented $[Mn(dien)_2]_n[Mn(dien)AsS_4]_{2n}\cdot 4nH_2O$ and $[Mn(en)_3]_2[Mn(en)_2AsS_4][As_3S_6]$

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Two transition-metal tetrathioarsenate complexes, $[Mn(dien)_2]_n[Mn(dien)AsS_4]_{2n}\cdot 4nH_2O$ (**1**) with one-dimensional water chain and $[Mn(en)_3]_2[Mn(en)_2AsS_4][As_3S_6]$ (**2**) with mixed-valence As^{3+}/As^{5+} character, have been synthesized and structurally characterized. The tetrathioarsenate(V) anion acts as a novel μ_2-η^1,η^2 ligand in **1** and as a chelating ligand in **2**. The two compounds exhibit intriguing semiconducting properties ($E_g = 2.18$ eV (**1**), 2.48 eV (**2**)) and strong photoluminescence with the emission maximum occurring around 440 nm.

The incorporation of transition-metals (tm's) into the main group chalcogenide (mgc) network has been extensively studied because of their exciting structural architectures[1] and potential applications in semiconductors,[2] storage materials,[3] magnetic materials,[4] etc. On the other hand, in contrast with crystalline oxide-based materials, the coordination chemistry of mgc incorporated with tm's is yet still in its early stages.[5] A great diversity of structures and interesting properties can be expected if a tm complex is introduced into the mgc network. Recently, the mild hydro(solvo)thermal techniques have been shown to be a promising synthetic technique for the preparation of tm chalcogenides, which are usually performed using amine solvents such as en (ethyleneamine) and dien (diethyleneamine), etc.[6] Due to the preference of formation of isolated $tm(amine)_m^{n+}$ complexes for tm ions in the presence of strongly chelating amines, there are only a few mgc compounds in which tm amine complexes are incorporated into the mgc anionic network. Substantial success has recently been achieved with thioantimonates[7,8] and selenoantimonate[9] compounds incorporated with tm complexes. However, to our knowledge, until now there is no report about a tm amine complex being incorporated into chalcogenoarsenates network despite several known tm chalcogenoarsenates(III,V) compounds.[10] We are interested in introducing tm amine complexes into the chalcogenoarsenate framework and understanding the role of template cations in constructing the inorganic framework structures of chalcogenoarsenates. In our recent work, the tm amine complex $[Mn(dien)_2]^{2+}$ and $[Mn(en)_3]^{2+}$ formed in situ has been successfully used in the syntheses of two unprecedented tetrathioarsenate compounds[11] $[Mn(dien)_2]_n[Mn(dien)AsS_4]_{2n}\cdot 4nH_2O$ (**1**) and $[Mn(en)_3]_2[Mn(en)_2AsS_4][As_3S_6]$ (**2**) containing the $[As^VS_4]^{3-}$ group with bridging μ_2-η^1,η^2 and terminal chelating coordination modes, which are the first

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(11) The two compounds were prepared under solvothermal condition in a 25 mL Teflon-lined steel autoclave under autogenous pressure. For **1**, a mixture of elemental manganese (55 mg, 1 mmol), arsenic (75 mg, 1 mmol), and sulphur (96 mg, 3 mmol) was heated with dien (1.5 mL, 13.5 mmol) and water (1.5 mL) at 140 °C for 6 days. For **2**, the same amounts of Mn, As, and S were applied, but 3 mL of en was used (170 °C for 5 days). The yellow crystals for both compounds were filtered, washed with dry diethyl ether, and stored under nitrogen atmosphere. Yield, 83% for **1** and 76% or **2** based on arsenic.

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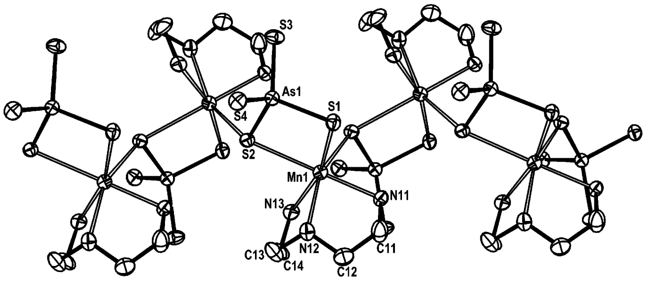

Figure 1. ORTEP view of $[Mn(dien)(AsS_4)]_n^{n-}$ zigzag anionic chain in **1** with ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

two examples of chalcogenoarsenates(V) incorporated with tm amine complexes.

X-ray crystallography reveals that compound **1** consists of the $[Mn(dien)_2]^{2+}$ template cation, an infinite anionic chain $[Mn(dien)AsS_4]_n^{n-}$, and four lattice water molecules.[12] As shown in Figure 1, the zigzag anionic chain, $[Mn(dien)(AsS_4)]_n^{n-}$, is composed of [Mn(dien)] fragments bridged by $[As^VS_4]$ group with a Mn···Mn distance of 4.717(1) Å. Each Mn atom is chelated by one tridentate dien ligand and coordinated by three S atoms from two $[As^VS_4]$ groups to form a distorted octahedron with a *cis*-configuration. The Mn octahedra corner-share to form a zigzag octahedral chain extending along the *b* direction, while the $[AsS_4]$ tetrahedra edge-share with Mn octahedra on both sides of the octahedral chain. The Mn1−N bond distances vary from 2.243(4) to 2.310(4) Å, and the Mn1−S bond distances range from 2.599(1) to 2.689(1) Å, which are comparable with those reported in the literature.[7b,13] The significantly distorted Mn octahedron is evident with the axial angles ranging from 153.8(1)° to 163.2(1)°. An interesting feature is that there exists hydrogen-bonding one-dimensional (1D) water chain in **1** with alternately O···O distances of 2.722(6) and 2.969(6) Å (Figure 2), which resembles the "arm-chair" motif proposed by Nagle.[14] The 1D water chain structures constitute a potentially important form of water that is poorly understood.[15] Many fundamental biological processes appear to depend on the unique properties of water chains.[16] However, the nature for requiring the structural constraints in stabilizing 1D water chains has not been fully illustrated.[17] The 1D water chains in **1** appear to be stabilized by strong H-bonds between neighboring water molecules along the chain as well as the H-bonds between water molecules and the infinite anionic chains. The anionic chains and the water chains are linked via O−H···S H-bonds to form layers in the (001) plane as shown in Figure 2, between which the discrete $[Mn(dien)_2]^{2+}$ template cations with the configuration of *s-fac* are located with interlayer separation of 10.441 Å (Figure S1). The FTIR spectrum of **1** exhibits a band centered around 3400 cm^{-1} attributable to the O−H stretching frequency pertaining to the 1D water chains.

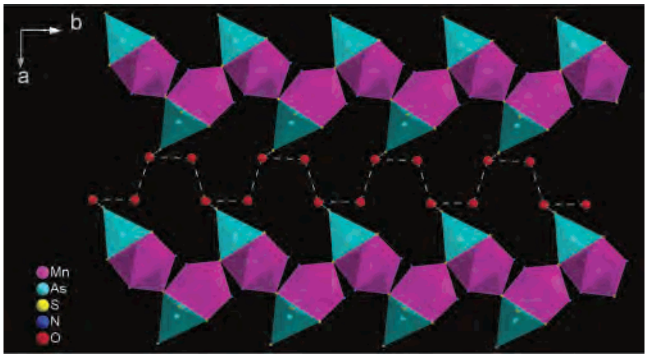

Figure 2. Layerlike structure of **1** constructed from H-bonding $[Mn(dien)AsS_4]_n^{n-}$ anionic chains and water chains viewed in the *ab* plane. The hydrogen bonds are represented as dashed lines (- - -). Carbon and hydrogen atoms are omitted for clarity.

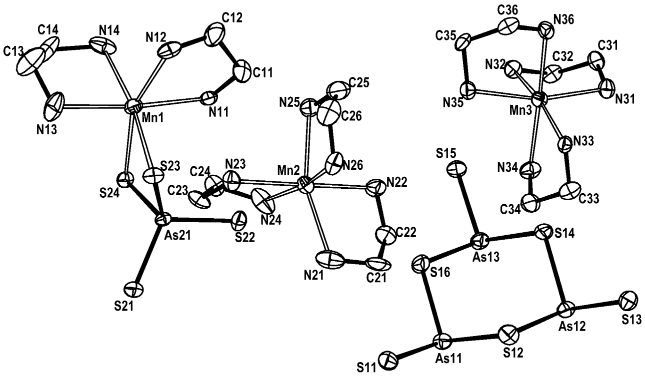

Figure 3. ORTEP view of **2** with ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Compound **2** comprises two crystallographically independent $[Mn(en)_3]^{2+}$ template cations, $[Mn(en)_2AsS_4]^-$ and $[As_3S_6]^{3-}$ anions (Figure 3).[18] The Mn1 atom in *cis*-$[Mn(en)_2AsS_4]^-$ anion is six-coordinated by two S atoms from a chelating $[As^VS_4]$ group and two chelating en ligands. The Mn1−N bond distances vary from 2.237(3) to 2.329(3) Å, and the Mn1−S bond distances are 2.632(1) and 2.633(1) Å, which are also comparable with those reported in the literature.[7b,13] The $[As_3S_6]^{3-}$ anion contains a chair-conformation six-membered ring in which the As atoms are in a pyramidal coordination environment. Although the $[As_3S_6]^{3-}$ anion has already been reported,[19] it is found for the first time to cocrystallize with the tm complex in **2**. It is

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(12) Crystal data for **1**: $[Mn(dien)_2]_n[Mn(dien)AsS_4]_{2n}\cdot 4nH_2O$, $C_{16}H_{60}Mn_3N_{12}O_4S_8As_2$, $M = 1055.90$, monoclinic, space group $P2_1/c$ (No. 14), $a = 13.4356(4)$ Å, $b = 7.2330(2)$ Å, $c = 22.4236(4)$ Å, $\beta = 111.363(2)°$, $V = 2029.39(9)$ Å^3, $Z = 2$, $\mu = 2.990$ mm^{-1}, $T = 293(2)$ K, 3547 unique reflections ($R_{int} = 0.0520$). R values for reflections with $I > 2\sigma(I)$: R1 = 0.0663 and wR2 = 0.1614, GOF = 1.013.

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(18) Crystal data for **2**: $[Mn(en)_3]_2[Mn(en)_2AsS_4][As_3S_6]$, $C_{16}H_{64}Mn_3N_{16}S_{10}As_4$, $M = 1265.93$, monoclinic, space group Cc (No. 9), $a = 24.3057(10)$ Å, $b = 16.2398(9)$ Å, $c = 15.8639(8)$ Å, $\beta = 129.082(1)°$, $V = 4860.7(4)$ Å^3, $Z = 4$, $\mu = 3.933$ mm^{-1}, $T = 293(2)$ K, 5012 unique reflections ($R_{int} = 0.0559$), R values for reflections with $I > 2\sigma$(I). R1 = 0.0663 and wR2 = 0.1550, GOF = 1.006.

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noteworthy that the feature of **2** is its mixed-valence As^{3+}/As^{5+} character.[10b,20] The discrete $[Mn(en)_3]^{2+}$ template cations are chelated by three en ligands with the configuration being $\Lambda(\delta\delta\delta)$ or $\Delta(\lambda\lambda\lambda)$.

The geometric features of the tetrahedral $[As^{V}S_4]^{3-}$ anions in **1** and **2** are similar to the discrete $[As^{V}S_4]^{3-}$ anion[21] except for the obviously lengthened As−S (binded to Mn atom) bond distances with about 0.04 Å due to the S atoms coordinating to Mn atoms, as in the case found in Cs_2AgAsS_4,[10d] and $A_8[Mn_2(AsS_4)_4]$ (A = K, Rb, Cs).[10c] However, in **1** it acts as a novel μ_2-η^1,η^2 coordination mode, while in **2** it acts as a seldom chelating terminal mode which is the same as the case found in the only known compounds $A_8[Mn_2(AsS_4)_4]$.[10c] Although a variety of compounds of chalcogenoarsenates(III)/chalcogenoantimonates(III) incorporated with tm complexes are known, those with chalcogenoarsenates(V)/chalcogenoantimonates(V) are limited, the known examples being chalcogenoantimonates(V) compounds $[Mn(C_6H_{18}N_4)(C_6H_{19}N_4)]SbS_4$,[8a] $[Mn(C_6H_{14}N_2)_3]_2[Mn(C_6H_{14}N_2)_2(SbS_4)_2]\cdot 6H_2O$,[8a] $Ni[N(CH_2CH_2NH_2)_3](SbS_4)$,[8d] and $[Mn(en)_3]_2[Mn_4(en)_9(SbSe_4)_4]\cdot 2H_2O$,[9] in which the coordination modes of the tetrachalcogenoantimonate(V) anion are different from that found in **1**.

Thermogravimetric analysis of **1** revealed two distinct steps with weight changes of about 7.55% and 39.68% before 331 °C (Figure S2), which correspond to the removal of the water molecules (calcd 6.81%) and dien ligands (calcd 39.08%). For **2**, it also shows a two step weight loss (21.87% and 21.02%) before 281 °C (Figure S3). The observed total weight losses are larger than the removal of the en ligands (calcd 37.98%), which is probably due to the emission of H_2S during the thermal decomposition.[22] In the following weight loss, compounds **1** and **2** began to decompose gradually, and the resulting black unknown residues can be found after decomposing completely.

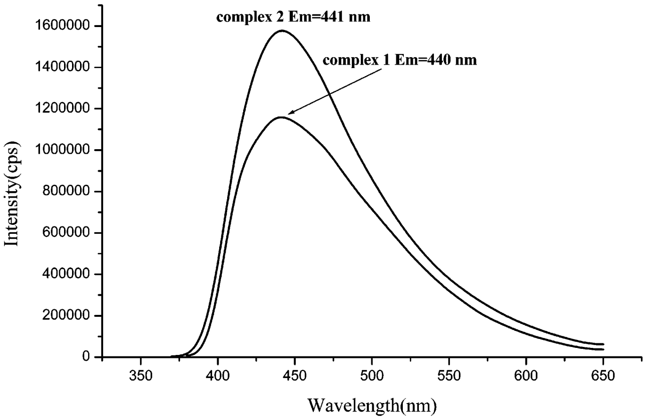

Figure 4. Solid-state photoluminescent spectra of **1** and **2** at room temperature.

The reflectance data suggest that the two compounds are semiconductors ($E_g = 2.18$ eV (**1**), 2.48 eV (**2**)) (Figure S4). Furthermore, the two compounds are strongly photoluminescent with the emission maximum occurring around 440 nm (Figure 4), which is similar to those found in the analogues of mgc.[3]

In summary, two interesting transition-metal tetrathioarsenate(V) complexes, $[Mn(dien)_2]_n[Mn(dien)AsS_4]_{2n}\cdot 4nH_2O$ (**1**) with one-dimensional water chain and $[Mn(en)_3]_2[Mn(en)_2AsS_4][As_3S_6]$ (**2**) with mixed-valence As^{3+}/As^{5+} character, have been synthesized and structurally characterized. The two compounds exhibit intriguing semiconducting properties and strong photoluminescence.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determination of **1** and **2**, TGA curves, IR spectra, optical absorption spectra, and solid emission spectra of **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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