Solvothermal Syntheses and Crystal Structures of Two Thioarsenate Metal Complexes $[Co(dien)_2]_3[As_3S_6]_2$ and $[Mn(teta)]_2As_2S_5$

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Two thioarsenates $[Co(dien)_2]_3[As_3S_6]_2$ (**1**, dien = diethylenetriamine) and $[Mn(teta)]_2As_2S_5$ (**2**, teta = triethylenetetramine) have been solvothermally synthesized and structurally characterized. **1** consists of isolated cyclic $[As_3S_6]^{3-}$ anions in a chair-conformation and two different isomeric $[Co(dien)_2]^{2+}$ cations, while **2** consists of neutral $[Mn(teta)]_2As_2S_5$ moieties built up from saddle-like As_2S_5 anions as a tetradentate ligand connecting two $[Mn(teta)]^{2+}$ groups *via* terminal S atoms. The optical absorption spectrum of **1** is described.

Key words: Solvothermal Synthesis, Crystal Structure, Thioarsenates, Metal Complexes

Introduction

Chalcoarsenate materials have generated a lot of interest due to the rich structural diversity based on the condensation of pyramidal $AsQ_3{}^{3-}$ or tetrahedral $AsQ_4{}^{3-}$ (Q = S, Se) units and potential applications in semiconductors, magnetism, thermoelectricity and nonlinear optics [1]. These compounds are generally prepared by flux methods at mid-temperature [2] and mild solvothermal methods in the presence of a structure-directing agent (such as an organic amine) [3]. The fundamental building unit $[As^{III}S_3]^{3-}$ favors polymerization through corner- or edge-sharing and As–As bonds into a variety of $As_xS_y{}^{n-}$ anions. These anions can also be considered as the secondary building units to take part in the construction of novel thioarsenates. For instance, the larger cage cluster ion $[Pt(As_3S_5)_2]^{2-}$ [4] is constructed by one Pt^{4+} ion and two cyclic $As_3S_5{}^{3-}$ anions, the macroanion 1-D $[Ni_2As_4S_8]_n{}^{2-}$ [5] is built up from square-planar Ni^{2+} ions and $[As_4S_8]^{4-}$ units formed by a central core of edge-sharing $[AsS_3]^{3-}$ units capped by two corner-sharing pyramidal $[AsS_3]^{3-}$ units, and the framework 2-D $[HgAs_3S_6]_n{}^{-}$ [6] is composed of distorted tetrahedral by coordinated Hg^{2+} atoms and linear $[As_3S_6]^{3-}$ anions formed from corner-sharing $AsS_3{}^{3-}$ units. Among these thioarsenates, the counterions are either organic cations (such as protonated amines, R_4N^+ and Ph_4P^+ ions) or metal cations [4 – 7]. However, thioarsenates combined with complex cations as counterions are still a less explored area, the limited examples including $[M(en)_3]_2As_2S_5$ (M = Mn, Ni) [8], $[Mn(en)_3]_2[Mn(en)_2AsS_4][As_3S_6]$ [9], $[Mn(dien)_2]$-$[Mn(dien)AsS_4]_2 \cdot 4H_2O$ [9], $[Mn_2(phen)As_2S_5]$ [10], $[Mn_3(phen)_3(AsS_4)_2]\cdot H_2O$ [10], $[Mn_3(2,2'\text{-bipy})_3$-$(AsS_4)_2]\cdot H_2O$ [11], and $[Mn_2(2,2'\text{-bipy})As_2S_5]$ [11]. To understand the role of complex cations in determining the inorganic framework structures of thioarsenates, we started to explore the system $As_2O_3/MCl_2/S$/amine (M = transition metal, amine = chelating organic amine) with the goal to synthesize new thioarsenates containing complex cations. Herein, we report on the solvothermal syntheses of two new thioarsenates $[Co(dien)_2]_3[As_3S_6]_2$ (**1**) and $[Mn(teta)]_2As_2S_5$ (**2**).

Results and Discussion

X-Ray crystallography reveals that **1** consists of $[Co(dien)_2]^{2+}$ cations and discrete heterocyclic $[As_3S_6]^{3-}$ anions (Fig. 1). The Co^{2+} ions are in a distorted octahedral environment chelated by two dien ligands with one unique $[Co(dien)_2]^{2+}$ cation in the *u-fac* conformation (Co2) and the other in the *s-fac* conformation. The Co–N distances range from 2.158(6) to 2.204(4) Å. The coordination octahedron of *u-fac* is more distorted than that of the *s-fac* unit. The $[As_3S_6]^{3-}$ anion displays a chair-conformation and contains a six-membered $[As_3S_3]$ ring constructed by three vertex-linked AsS_3 trigonal pyramids. Although the anion of the heavier homolog Sb is observed in $[Ni(dien)_2]_3(Sb_3S_6)_2$ [12], its $[Sb_3S_6]^{3-}$ anion exhibits

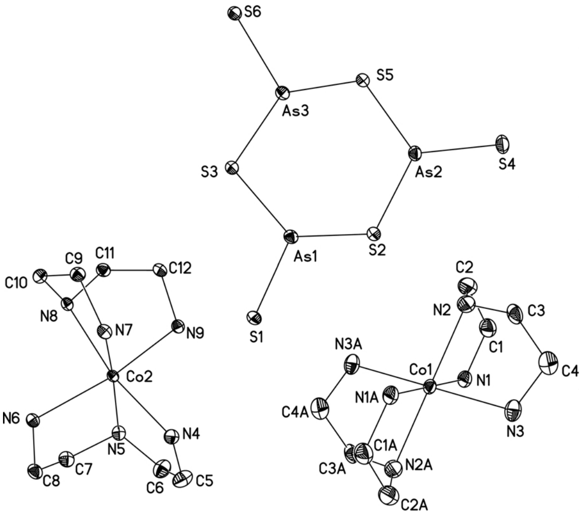

Fig. 1. Molecular structure of **1** in the crystal with crystallographic labeling scheme used (H atoms are omitted for clarity).

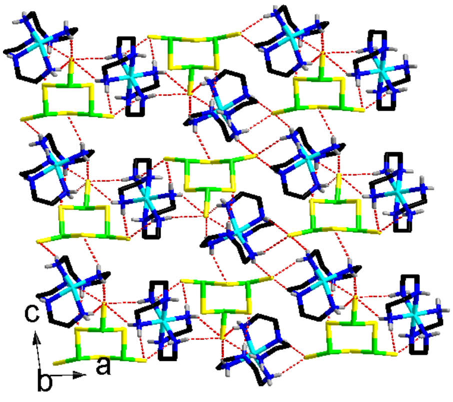

Fig. 2. The 3-D supramolecular framework of **1** constructed by N–H$\cdots$S hydrogen bonds (H atoms bonded to C atoms are omitted for clarity).

a boat-like conformation. The As–S bond lengths vary from 2.1334(17) to 2.3104(15) Å, and the S–As–S bond angles range from 93.37(5) to 105.42(6)°, comparable with those in other thioarsenates [8].

In **1**, three terminal S atoms of the $[As_3S_6]^{3-}$ anion are oriented toward the same side of the $[As_3S_3]$ ring. The anions are arranged in a tripod-like manner along the *b* axis with opposite orientations in neighboring tripods (Fig. 2). The $[As_3S_6]^{3-}$ anions are separated from each other by $[Co(dien)_2]^{2+}$ cations. Short H$\cdots$S distances between 2.61 and 2.81 Å with corresponding N–H$\cdots$S angles ranging from 145 to 162° indicate weak hydrogen bonding between cations and anions, resulting in a 3-D H-bonding network structure with 1-D channels running parallel to the *b* axis.

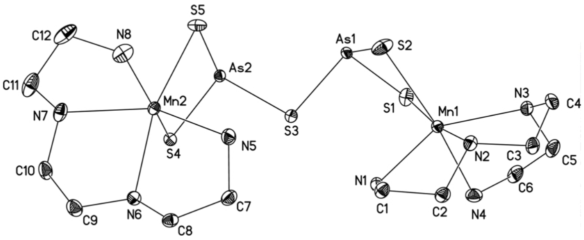

Fig. 3. Molecular structure of **2** in the crystal with crystallographic labeling scheme used (H atoms are omitted for clarity).

Compound **2** crystallizes in the monoclinic crystal system with space group $P2_1/c$ and consists of neutral $[Mn(teta)]_2As_2S_5$ molecules (Fig. 3). Each Mn^{2+} center is chelated by one teta ligand and coordinated by two S atoms from one $[As_2S_5]^{4-}$ anion to form a distorted octahedron. The Mn–N bond lengths vary from 2.271(5) to 2.315(6) Å, while the Mn–S bonds range from 2.526(2) to 2.583(2) Å. These data are in agreement with those reported in the literature [9 – 11, 13]. The dinuclear $[As_2S_5]^{4-}$ anion is formed from two corner-sharing AsS_3 trigonal pyramids. Two AsS_3 pyramids are in *cis*-conformation, so the $[As_2S_5]^{4-}$ anion has a saddle-like shape. The terminal As–S_t bonds are shorter than the bridging As–S_b bonds (Table 2). The S2–As1–S3 and S5–As2–S3 angles are 105.4(3) and 104.76(19)°, respectively, slightly larger than those in the discrete $[As_2S_5]^{4-}$ anions [8], but the other S–As–S angles in the range of 95.2(2) – 99.6(2)° are slightly smaller than those in discrete $[As_2S_5]^{4-}$ anions [8]. This might be due to the coordination of terminal S atoms to the Mn^{2+} ion. Two $[Mn(teta)]^{2+}$ groups are connected by bridging $[\mu_4\text{-}As_2S_5]^{4-}$ anions to form neutral $[Mn(teta)]_2As_2S_5$ moieties. The binding mode of the $[\mu_4\text{-}As_2S_5]^{4-}$ anion is similar to that of analogous $[Sb_2S_5]$ groups in $[Mn(tren)]_2[Sb_2S_5]$ [13a] and $[La(dien)_2(\mu_4\text{-}Sb_2S_5)(\mu_3\text{-}SO_4)]_n$ [14].

Significant hydrogen bonding interactions are observed in **2** (Fig. 4). All the S atoms of a $[As_2S_5]^{4-}$ unit are involved in weak N–H$\cdots$S H-bonds with eight neighboring molecules with N$\cdots$S distances between 3.41 and 3.55 Å, and N–H$\cdots$S angles between 135 and 155°. The intermolecular H-bonding contacts connect the $[Mn(teta)]_2As_2S_5$ moieties into a 3-D H-bonding network structure.

The optical absorption spectrum of **1** was measured out at r. t. (Fig. 5). The absorption data were

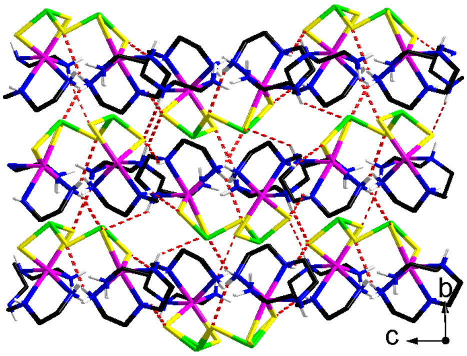

Fig. 4. The 3-D supramolecular framework of **2** constructed by N–H···S hydrogen bonds (H atoms bonded to C atoms are omitted for clarity).

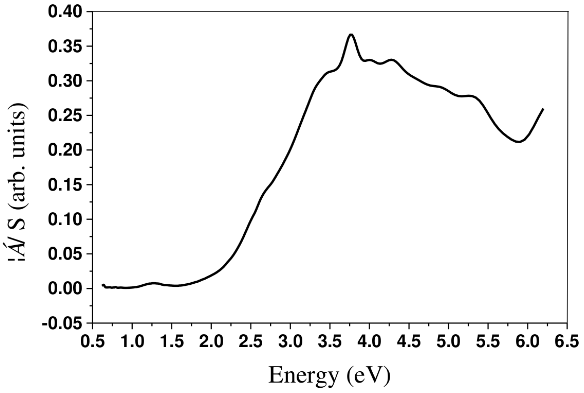

Fig. 5. Solid-state optical absorption spectrum of **1**.

calculated using the Kubelka-Munk function $\alpha/S = (1 - \mathrm{R})^2/2R$ [15], where R is the reflectance at a given energy, α the absorption and S the scattering coefficient. The optical band gap obtained by extrapolation of the linear portion of the absorption edge is estimated to 2.07 eV, which can be assigned to the electronic excitation of the $[As_3S_6]^{3-}$ anion and is in agreement with the color of the crystals. This band gap is close to that of the thioarsenates $[Mn_2(phen)(As_2S_5)]_n$ (2.01 eV) [10] and $[Mn_3(phen)_3(AsS_4)_2]_n \cdot nH_2O$ (1.97 eV) [10], suggesting that **1** is a semiconductor. The weak absorption at 1.28 eV presumably arises from *d-d* electronic transitions as previously reported for related Co^{2+} complexes [16].

Experimental Section

Table 1. Crystal structure data for **1** and **2**.

	1	**2**
Formula	$C_{24}H_{78}As_6Co_3N_{18}S_{12}$	$C_{12}H_{36}As_2Mn_2N_8S_5$
Fw	1630.19	712.56
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a, Å	18.935(2)	14.314(4)
b, Å	8.6053(10)	11.864(3)
c, Å	18.536(2)	16.181(5)
β, deg	96.190(2)	95.755(4)
V, Å^3	3002.7(6)	2734.0(13)
Z	2	4
T, K	293(2)	293(2)
Calcd. density, g cm^{-3}	1.80	1.73
Abs. coeff., mm^{-1}	4.6	3.7
$F(000)$, e	1638	1440
$2\theta_{\max}$, deg	50.20	50.20
Total reflns. collected	15965	14245
Unique reflns. / R_{int}	5345 / 0.029	4829 / 0.051
No. of ref. param.	286	281
$R1$ $[I \geq 2\sigma(I)]$	0.0392	0.0528
$wR2$ (all data)	0.1117	0.1593
GOF on F^2	1.032	1.051
$\Delta\rho$fin (max / min), e Å^{-3}	1.88 / −1.71	1.35 / −0.54

General: All purchased starting materials were analytically pure and used without additional purification. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer from dry KBr pellets. Elemental analysis was carried out on an EA-1110 elemental analyzer. The UV/Vis spectra were recorded at r. t. using a computer-controlled PE Lambda 900 UV/Vis spectrometer equipped with an integrating sphere in the wavelength range of 250 – 1800 nm.

*Synthesis of $[Co(dien)_2]_3[As_3S_6]_2$ (**1**)*

A mixture of As_2O_3 (0.05 mmol), S (0.60 mmol), $CoCl_2$ (0.10 mmol), and dien (2.0 mL) was transferred into a thick-walled Pyrex tube. The sealed tube was heated at 170 °C for 8 d to yield yellow block-shaped crystals (43 % yield based on As_2O_3). – Anal. for **1**: calcd. C 17.68, H 4.82, N 15.47; found C 17.59, H 4.78, N 15.53. – IR (cm^{-1}): ν = 3243(m), 3173(m), 2922(m), 2869(m), 1576(w), 1505(w), 1464(m), 1306(s), 1166(m), 1067(m), 743(s), 856(m), 762(m), 645(m), 552(w), 505(w), 487(w), 428(vs).

*Synthesis of $[Mn(teta)]_2As_2S_5$ (**2**)*

A mixture of As_2O_3 (0.10 mmol), S (0.80 mmol), $MnCl_2$ (0.10 mmol), and teta (1.5 mL) was transferred into a thick-walled Pyrex tube. The sealed tube was heated at 160 °C for 12 d to yield yellow block-shaped crystals (57 % yield based on As_2O_3). – Anal. for **2**: calcd. C 20.23, H 5.09, N 15.73; found C 20.26, H 5.13, N 15.68. – IR (cm^{-1}): ν = 3290(s), 3197(s), 2904(m), 2858(m), 1582(m), 1447(m), 1312(m), 1166(w), 1119(w), 1089(w), 1008(m), 926(vs), 879(s), 827(m), 786(w), 587(m), 493(m), 411(s).

Table 2. Selected bond lengths (Å), and angles (deg) for **1** and **2**[a].

1				**2**			
As1–S1	2.1584(16)	As2–S4	2.1334(17)	As1–S1	2.253(8)	As1–S2	2.181(4)
As1–S2	2.2868(16)	As2–S5	2.2957(16)	As1–S3	2.253(7)	As2–S3	2.300(6)
As1–S3	2.3001(15)	As2–S2	2.3078(17)	As2–S4	2.200(5)	As2–S5	2.222(5)
As3–S6	2.1542(16)	As3–S3	2.3104(15)	Mn1–N1	2.271(5)	Mn2–N5	2.274(6)
As3–S5	2.2875(15)	Co2–N7	2.160(4)	Mn1–N2	2.280(5)	Mn2–N7	2.308(6)
Co1–N2	2.158(6)	Co2–N4	2.162(5)	Mn1–N3	2.331(6)	Mn2–N6	2.309(5)
Co1–N3	2.172(6)	Co2–N6	2.166(4)	Mn1–N4	2.367(6)	Mn2–N8	2.315(6)
Co1–N1	2.196(6)	Co2–N9	2.179(4)	Mn1–S1	2.526(2)	Mn2–S4	2.572(2)
Co2–N5	2.204(5)	Co2–N8	2.191(4)	Mn1–S2	2.561(3)	Mn2–S5	2.583(2)
S1–As1–S2	98.43(6)	S4–As2–S5	101.49(7)	S2–As1–S3	105.4(3)	S4–As2–S5	99.6(2)
S1–As1–S3	101.86(6)	S4–As2–S2	103.68(7)	S2–As1–S1	96.8(3)	S4–As2–S3	95.2(2)
S2–As1–S3	101.16(6)	S5–As2–S2	96.55(6)	S3–As1–S1	95.89(14)	S5–As2–S3	104.76(19)
S6–As3–S5	100.00(6)	S5–As3–S3	100.86(5)	N1–Mn1–N2	76.40(19)	N5–Mn2–N7	142.0(2)
S6–As3–S3	105.42(6)	N7–Co2–N4	91.64(18)	N1–Mn1–N3	143.7(2)	N5–Mn2–N6	75.7(2)
N2–Co1–N2$^{\#1}$	180.0(3)	N7–Co2–N6	94.25(17)	N2–Mn1–N3	76.3(2)	N7–Mn2–N6	75.9(2)
N2–Co1–N3	80.7(3)	N4–Co2–N6	101.86(18)	N1–Mn1–N4	88.1(2)	N5–Mn2–N8	89.5(2)
N2$^{\#1}$–Co1–N3	99.3(3)	N7–Co2–N9	97.44(18)	N2–Mn1–N4	100.3(2)	N7–Mn2–N8	74.8(3)
N2–Co1–N3$^{\#1}$	99.3(3)	N4–Co2–N9	92.62(19)	N3–Mn1–N4	73.9(2)	N6–Mn2–N8	106.2(2)
N2$^{\#1}$–Co1–N3$^{\#1}$	80.7(3)	N6–Co2–N9	161.10(17)	N1–Mn1–S1	108.42(15)	N5–Mn2–S4	106.07(18)
N3–Co1–N3$^{\#1}$	180.0(3)	N7–Co2–N8	79.89(17)	N2–Mn1–S1	171.34(15)	N7–Mn2–S4	97.04(16)
N2–Co1–N1	80.0(2)	N4–Co2–N8	167.57(17)	N3–Mn1–S1	101.97(17)	N6–Mn2–S4	86.86(15)
N2$^{\#1}$–Co1–N1	100.0(2)	N6–Co2–N8	87.92(17)	N4–Mn1–S1	87.21(19)	N8–Mn2–S4	161.88(17)
N3–Co1–N1	92.2(2)	N9–Co2–N8	79.61(17)	N1–Mn1–S2	90.93(17)	N5–Mn2–S5	96.31(16)
N3$^{\#1}$–Co1–N1	87.8(2)	N7–Co2–N5	167.24(18)	N2–Mn1–S2	91.51(15)	N7–Mn2–S5	116.82(17)
N2–Co1–N1$^{\#1}$	100.0(2)	N4–Co2–N5	79.30(18)	N3–Mn1–S2	113.14(18)	N6–Mn2–S5	163.89(17)
N2$^{\#1}$–Co1–N1$^{\#1}$	80.0(2)	N6–Co2–N5	79.04(17)	N4–Mn1–S2	167.57(19)	N8–Mn2–S5	87.42(19)
N3–Co1–N1$^{\#1}$	87.8(2)	N9–Co2–N5	91.98(18)	S1–Mn1–S2	81.34(8)	S4–Mn2–S5	81.88(7)
N3$^{\#1}$–Co1–N1$^{\#1}$	92.2(2)	N8–Co2–N5	110.42(17)				
N1–Co1–N1$^{\#1}$	180.0(4)						

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x$, $-y$, $-z$.

X-Ray structure determination

The data collection was performed on a Rigaku Mercury CCD diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 293(2) K with a maximum 2θ value of 50.20°. The intensities were corrected for Lorentz and polarization effects. The structure was solved with Direct Methods using the program SHELXS-97 [17], and the refinement was performed against F^2 using SHELXL-97 [18]. All non-hydrogen atoms were refined anisotropically. The H atoms of C/N atoms were refined using the riding model. The As1 and As2 atoms in **1** are disordered over two sites (0.76/0.24). In **2**, a high ratio of maximum/minimum residual density suggests slight disorder of atom S2, but this could not be resolved. Relevant crystal and collection data and refinement results can be found in Table 1. Selected bond lengths and angles for **1** and **2** are listed in Table 2.

CCDC 801599 (**1**) and 801600 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

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