Articles

Synthesis and Characterization of $(Ph_4P)_2[Ni_2As_4S_8]$, $(Me_4N)_2[Mo_2O_2As_2S_7]$, and $(Et_4N)_2[Mo_2O_2As_2Se_7]$. New One-Dimensional Polymeric Compounds Containing Thio- and Selenoarsenate Ligands

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The compounds $(Ph_4P)_2[Ni_2As_4S_8]$ (**I**), $(Me_4N)_2[Mo_2O_2As_2S_7]$ (**II**), and $(Et_4N)_2[Mo_2O_2As_2Se_7]$ (**III**) were synthesized by the hydrothermal reactions of $NiCl_2/K_3AsS_3/Ph_4PBr$, $MoO_3/K_3AsS_3/Me_4NCl$, and $MoO_3/K_3AsSe_3/Et_4NBr$ in a 1:3:4, 1:2:4, and 1:4:6 molar ratio, respectively. The $(Ph_4P)_2[Ni_2As_4S_8]$ (**I**) crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with $a = 10.613(3)$ Å, $b = 13.230(2)$ Å, $c = 9.617(2)$ Å, $\alpha = 93.53(2)°$, $\beta = 96.69(2)°$, $\gamma = 71.59(2)°$, $V = 1272(1)$ Å^3, and $Z = 2$. The one-dimensional $[Ni_2As_4S_8]_n^{2n-}$ consists of alternating square planar Ni^{2+} ions and $[As_4S_8]^{4-}$ ligands. The $(Me_4N)_2[Mo_2O_2As_2S_7]$ (**II**) crystallizes in the orthorhombic space group *Pbca* (No. 61) with $a = 18.176(4)$ Å, $b = 17.010(2)$ Å, $c = 16.556(7)$ Å, $V = 5118(4)$ Å^3, and $Z = 4$. The $[Mo_2O_2As_2S_7]_n^{2n-}$ macroanion possesses a one-dimensional chain-like structure consisting of $[Mo_2O_2S_2]^{2+}$ cores linked by $[As_2S_5]^{4-}$ ligands. The $(Et_4N)_2[Mo_2O_2As_2Se_7]$ (**III**) crystallizes in the orthorhombic space group *Cmca* No. 64) with $a = 15.480(2)$ Å, $b = 18.506(2)$ Å, $c = 22.793(2)$ Å, $V = 6350(1)$ Å^3, and $Z = 4$. The $[Mo_2O_2As_2Se_7]_n^{2n-}$ is isostructural to the anion in **II**. The solid state optical spectra of these compounds are reported.

Introduction

Recently, the hydro(solvo)thermal technique was demonstrated to be a useful synthetic tool toward the synthesis of novel transition and main group metal polychalcogenides that are often inaccessible by traditional solution methods.[1−3] In previous communications, this methodology was applied to the $R_4E^+/M^{n+}/[AsQ_3]^{3-}$ (E = P, R = Ph; E = N, R = alkyl, M = metal; Q = S, Se) system to synthesize a number of unusual compounds such as $[InAs_3S_7]^{2-}$,[4] $[BiAs_6S_{12}]^{3-}$,[4] $[HgAs_3S_6]^{-}$,[5a] $[Hg_2As_4S_9]^{2-}$,[5a] $(Me_4N)[HgAsSe_3]$,[5b] $(Et_4N)[HgAsSe_3]$,[5b] $(Ph_4P)_2[Hg_2As_4Se_{11}]$,[5b] $[Pt(As_3S_5)_2]^{2-}$, $[Pt_3(AsS_4)_3]^{3-}$,[6] β-Ag_3AsSe_3,[7] $(Me_3NH)[Ag_3As_2Se_5]$,[7] $K_5Ag_2As_3Se_9$,[7] and $KAg_3As_2S_5$.[7] The most characteristic feature of these compounds is the presence of $[As_xQ_y]^{n-}$ ligands formed by condensation reactions of a fundamental building unit $[AsQ_3]^{3-}$. The hydrothermal behavior of the $R_4E^+/M^{n+}/[AsQ_3]^{3-}$ (E = P, R = Ph; E = N, R = Me, Et; Q = S, Se; M = Ni, Mo) systems was explored in order to further probe the tendency of the $[AsQ_3]^{3-}$ (Q = S, Se) unit for condensation. There are several examples of early transition metal complexes which contain discrete thioarsenate ligands. One of the early complexes which demonstrated that the thioarsenate anion, $[AsS_3]^{3-}$, could be used as a ligand toward transition metals was $Cp'_3Ti_2O(AsS_3)$ ($Cp' = \eta^5$-$CH_3C_5H_4$).[8] Another interesting species was the discrete complex $[Mo_2O_2As_4S_{14}]^{2-}$, which contains the multidentate $[As_4S_{12}]^{4-}$ ligand.[8] Of course, the very large number of sulfosalt minerals,[9] which contain various $[As_xS_y]^{n-}$ ligands in amazingly elaborate binding modes, suggests that these anions would be excellent building blocks for other solid state and coordination compounds. Here we report the successful synthesis of three polymeric compounds using transition metals. These three low-dimensional compounds, $(Ph_4P)_2[Ni_2As_4S_8]$ (**I**), $(Me_4N)_2[Mo_2O_2As_2S_7]$ (**II**), and $(Et_4N)_2[Mo_2O_2As_2Se_7]$ (**III**), feature higher order thio- and selenoarsenate ligands derived from the condensation of the $[AsQ_3]^{3-}$ (Q = S, Se) anions.

Experimental Section

Reagents. Chemicals in this work, other than solvents, were used as obtained: $NiCl_2$, 98% purity; MoO_3, 99% purity; tetraphenylphosphonium bromide (Ph_4PBr), 98% purity; tetramethylammonium chloride. (Me_4NCl), 99% purity; tetraethylammonium bromide (Et_4NBr), Aldrich Chemical Co. Inc., Milwaukee, WI.

Syntheses. All syntheses were carried out under dry nitrogen atmosphere in a Vacuum Atmosphere Dri-Lab glovebox except where specifically mentioned. All compounds have satisfactory elemental analyses.

K_3AsS_3. This material was synthesized by using stoichiometric amounts of alkali metal, arsenic sulfide, and sulfur in liquid ammonia.

[†] Camille and Dreyfus Teacher Scholar, 1993−1995.

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Table 1. Summary of Crystallographic Data and Structural Analysis for $(Ph_4P)_2[Ni_2As_4S_8]$ (**I**), $(Me_4N)_2[Mo_2O_2As_2S_7]$ (**II**), and $(Et_4N)_2[Mo_2O_2As_2Se_7]$ (**III**)[a]

	I	**II**	**III**
formula	$C_{48}H_{40}P_2Ni_2As_4S_8$	$C_8H_{24}N_2Mo_2O_2As_2S_7$	$C_{16}H_{40}N_2Mo_2O_2As_2Se_7$
fw	1351.1	745.72	1146.63
a, Å	10.612(4)	18.176(4)	15.480(2)
b, Å	13.230(2)	17.010(2)	18.506(2)
c, Å	9.617(2)	16.556(7)	22.793(2)
α, deg	93.53(1)	90.00	90.00
β, deg	96.69(2)	90.00	90.00
γ, deg	71.59(2)	90.00	90.00
Z	2	4	4
V, Å^3	1272(1)	5118(4)	6350(1)
space group	$P\bar{1}$ (No. 2)	*Pbca* (No. 61)	*Cmca* (No. 64)
color, habit	dark brown, plate	orange yellow, plate	dark orange, polyhedra
D_{calc}, g/cm^3	1.69	1.94	2.33
μ, cm^{-1}	73.76	40.75	105.01
$2\theta_{max}$, deg	45.0	45.0	50.0
final $R^b/R_w{}^c$, %	3.7/4.3	4.9/6.4	5.4/5.8

[a] Radiation, Mo Kα. [b] $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$. [c] $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$; $w = (1/\sigma(F_o{}^2))$.

The reaction gives a yellow-brown powder upon evaporation of ammonia. K_3AsSe_3 was synthesized under similar conditions giving rise to a orange-brown powder.

$(Ph_4P)_2[Ni_2As_4S_8]$ (I). A mixture of 0.025 g (0.2 mmol) of $NiCl_2$, 0.172 g (0.6 mmol) of K_3AsS_3, and 0.419 g (1 mmol) of Ph_4PBr was sealed in a thick-wall Pyrex tube (~4 mL) under vacuum with 0.3 mL of water. The reaction was carried out at 110 °C for 1 week. The product was isolated by washing away excess starting material and KCl with H_2O, methanol, and ether to give 0.105 g (76% yield) of dark brown plate-like crystals.

$(Me_4N)_2[Mo_2O_2As_2S_7]$ (II). The reaction of 0.024 g (0.2 mmol) of MoO_3, 0.057 g (0.4 mmol) of K_3AsS_3, and 0.13 g (0.12 mmol) of Me_4NCl was prepared as above. The mixture was heated to 110 °C for 1 week. Large yellow chunky crystals were isolated in H_2O and washed with methanol and ether (yield = 88% based on Mo).

$(Et_4N)_2[Mo_2O_2As_2Se_7]$ (III). The reaction of 0.014 g (0.1 mmol) of MoO_3, 0.172 g (0.4 mmol) of K_3AsSe_3, and 0.127 g (0.6 mmol) of Et_4NBr was prepared as above. The mixture was heated at 110 °C for 3 days. Red-brown crystals were isolated by filtration with methanol and washed with water, methanol, and ether (yield = 54% based on Mo).

Physical Measurements. Optical diffuse reflectance measurements were made at room temperature with a Shimadzu UV-3101PC double beam, double-monochromator spectrophotometer.

X-ray Crystallography. The single-crystal X-ray diffraction data of all three compounds were collected with a Rigaku AFC6 diffractometer equipped with a graphite-crystal monochromator at 23 °C. The data were collected with the $\theta/2\theta$ scan technique. None of the crystals showed any significant intensity decay as judged by three check reflections measured every 150 reflections throughout the data collection. The space groups were determined from systematic absences and intensity statistics. The structures were solved by directed methods of SHELXS-86[10a] and refined by full-matrix least-squares techniques of TEXSAN[10b] software package of crystallographic programs. An empirical absorption correction based on ψ-scans was applied to each data set, followed by a DIFABS[11] correction to the isotropically refined structures. All non-hydrogen atoms except carbon and nitrogen were refined anisotropically. During the structure refinement it was observed that one of the cations in (**II**) and (**III**) respectively was slightly disordered in one of the carbon atoms (C5 for compound (**II**) and C6 for compound (**III**)). The occupancy of the C5, C5′ and C6, C6′ was refined to be about 50:50. All calculations were performed on a VAXstation 310076 computer. Complete data collection parameters and details of the structure solution and refinement are given in Table 1. The fractional atomic coordinates, average temperature factors, and their estimated standard deviations are given in Tables 2−4.

Table 2. Selected Atomic Coordinates and Estimated Standard Deviations for $(Ph_4P)_2[Ni_2As_4S_8]$

atom	*X*	*Y*	*Z*	$B_{eq}{}^a$, Å^2
Ni	0.50000	0.50000	0.00000	3.4(1)
As1	0.7376(1)	0.31671(7)	0.1454(1)	4.44(6)
As2	0.8697(1)	0.46009(7)	−0.0314(1)	4.00(6)
S1	1.0617(3)	0.4380(2)	−0.1377(2)	5.1(2)
S2	0.9398(2)	0.2983(2)	0.0646(2)	4.2(1)
S3	0.5966(2)	0.3278(2)	−0.0452(3)	5.0(1)
S4	0.6608(2)	0.4927(2)	0.1695(2)	4.6(1)
P1	1.1891(2)	0.1744(2)	0.4976(2)	3.4(1)
C1	1.1655(9)	0.0844(6)	0.3592(8)	3.5(1)
C2	1.041(1)	0.0827(6)	0.3073(8)	4.0(5)
C3	1.026(1)	0.0070(8)	0.207(1)	5.2(7)
C4	1.137(1)	−0.0688(8)	0.159(1)	6.1(8)
C5	1.261(1)	−0.0669(7)	0.209(1)	6.0(1)
C6	1.277(1)	0.0106(7)	0.308(1)	5.0(1)
C7	1.2995(8)	0.2410(6)	0.449(1)	4.1(5)
C8	1.291(1)	0.2701(7)	0.310(1)	5.2(6)
C9	1.378(1)	0.3228(8)	0.276(1)	6.0(7)
C10	1.466(1)	0.3455(8)	0.377(2)	6.7(8)
C11	1.475(1)	0.3176(9)	0.513(1)	6.9(8)
C12	1.392(1)	0.2646(6)	0.547(1)	5.6(7)
C13	1.0314(8)	0.2672(6)	0.5286(8)	3.1(5)
C14	0.9817(9)	0.3635(6)	0.4621(8)	3.6(5)
C15	0.858(1)	0.4329(6)	0.486(1)	4.5(6)
C16	0.7849(9)	0.4058(7)	0.579(1)	4.7(6)
C17	0.833(1)	0.3100(8)	0.6469(9)	4.7(6)
C18	0.9561(9)	0.2419(6)	0.6209(9)	4.2(5)
C19	1.2574(9)	0.0998(6)	0.6525(9)	4.2(5)
C20	1.258(1)	0.1549(7)	0.783(1)	5.8(6)
C21	1.310(1)	0.091(1)	0.905(1)	7.4(8)
C22	1.362(1)	−0.010(1)	0.897(1)	7.5(9)
C23	1.360(1)	−0.0638(8)	0.744(1)	6.6(7)
C24	1.308(1)	−0.0106(7)	0.651(1)	4.9(6)

[a] $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Results and Discussion

Syntheses. $(Ph_4P)_2[NiAs_4S_8]$ (**I**) was prepared by heating $NiCl_2$ with K_3AsS_3 and Ph_4PBr in H_2O at 110 °C. It is well-known in metal polychalcogenide chemistry that different cations can stabilize different structure types.[12] Since, conceptually, chalcoarsenate anions are similar to polychalcogenide ligands, we explored several different tetraalkyl ammonium cations. It was observed that upon addition of water the reaction

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Table 3. Selected Atomic Coordinates and Estimated Standard Deviations for $(Me_4N)_2[Mo_2O_2As_2S_7]$

atom	X	Y	Z	$B_{eq}{}^a$, Å^2
Mo1	0.6397(1)	0.7862(1)	0.1285(1)	1.85(7)
Mo2	0.6021(1)	0.9237(1)	0.2174(1)	1.83(7)
As1	0.6469(1)	0.6090(1)	0.0516(1)	2.5(1)
As2	0.5127(1)	1.0394(1)	0.3516(1)	2.6(1)
S1	0.4868(3)	0.9961(3)	0.2268(3)	3.0(3)
S2	0.5847(3)	0.9331(3)	0.3632(3)	2.4(2)
S3	0.6654(3)	0.8132(3)	0.2640(3)	2.4(2)
S4	0.5425(3)	0.8728(3)	0.1040(3)	2.3(2)
S5	0.5672(3)	0.7071(3)	0.0345(3)	2.7(3)
S6	0.6650(3)	0.6543(3)	0.1768(3)	2.6(3)
S7	0.5830(3)	0.4969(3)	0.0728(3)	2.6(3)
O1	0.7135(7)	0.8096(7)	0.0719(7)	2.5(6)
O2	0.6652(7)	0.9920(7)	0.1887(8)	2.6(7)
N1	0.299(1)	0.045(1)	0.094(1)	2.5(8)
N2	0.594(1)	0.235(1)	0.165(1)	4(1)
C1	0.354(1)	0.112(1)	0.107(1)	3(1)
C2	0.292(1)	−0.003(1)	0.169(1)	4(1)
C3	0.229(1)	0.074(2)	0.070(2)	8(2)
C4	0.330(2)	−0.007(2)	0.028(2)	6(2)
C5	0.511(3)	0.219(3)	0.164(3)	5(1)
C5′	0.515(2)	0.231(2)	0.196(2)	1.5(9)
C6	0.611(2)	0.311(3)	0.134(3)	3(1)
C6′	0.620(3)	0.317(3)	0.196(4)	6(1)
C7	0.612(2)	0.188(3)	0.101(3)	12(1)
C8	0.633(3)	0.207(2)	0.235(3)	13(1)

^{a} $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table 4. Selected Atomic Coordinates and Estimated Standard Deviations for $(Et_4N)_2[Mo_2O_2As_2Se_7]$

atom	X	Y	Z	$B_{eq}{}^a$, Å^2
Mo1	$^1/_2$	0.2081(2)	0.3907(2)	2.7(2)
Mo2	$^1/_2$	0.0806(2)	0.3158(2)	2.6(1)
As1	$^1/_2$	−0.0358(2)	0.1936(2)	3.6(3)
As2	$^1/_2$	0.3805(3)	0.4489(2)	3.8(3)
Se1	0.3760(2)	0.1607(2)	0.3348(1)	3.3(2)
Se2	0.3943(2)	0.3147(2)	0.3959(2)	3.8(2)
Se3	0.3936(3)	0.0411(2)	0.2354(2)	4.2(2)
Se4	$^1/_2$	0.4995(2)	0.4072(2)	3.8(3)
O1	$^1/_2$	0.014(1)	0.364(1)	3(2)
O2	$^1/_2$	0.171(1)	0.456(1)	4(2)
N1	0.213(3)	$^1/_2$	$^1/_2$	3.9(9)
N2	$^1/_2$	0.229(2)	0.654(2)	4(1)
C1	0.151(3)	0.438(2)	0.502(2)	8(1)
C2	0.270(3)	0.506(2)	0.556(2)	11(1)
C3	0.208(2)	0.359(2)	0.506(1)	4.0(8)
C4	0.222(2)	0.523(2)	0.612(2)	4.7(8)
C5	0.619(3)	0.299(2)	0.604(2)	8(1)
C6	0.442(5)	0.231(3)	0.712(3)	4(2)
C6′	0.428(5)	0.161(4)	0.664(3)	6(2)
C7	0.369(3)	0.169(2)	0.711(2)	6(1)
C8	0.460(7)	0.225(4)	0.589(4)	9(1)

^{a} $B_{eq} = (4/3)[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

mixture immediately gave a black precipitate of NiS_x. No other products were observed even after prolonged heating. The same phenomenon was observed when Ph_4PBr was used; however, prolonged heating resulted in the formation of dark brown plates of $(Ph_4P)_2[NiAs_4S_8]$ as the major product with a small amount (5%) of black NiS precipitate.

$(Me_4N)_2[Mo_2O_2As_2S_7]$ (**II**) was prepared by heating MoO_3 with K_3AsS_3 and Me_4NCl in H_2O at 130 °C. Again, several other tetraalkylammonium cations were tried and only Et_4N^+ afforded a crystalline product. However, the poor crystal quality of the Et_4N^+ salt prohibited further characterization. The $(Et_4N)_2[Mo_2O_2As_2Se_7]$ (**III**) was prepared by heating MoO_3 with K_3AsSe_3 and Et_4NBr in H_2O at 110 °C. Reactions with other tetraalkylammonium cations, such as triethylmethylammonium[13a] and tetramethylammonium[13b] afforded crystalline products. A crystal structure was attempted on the triethylmethylammonium salt and revealed the anion to be isostructural to the $[Mo_2O_2As_2Se_7]_n{}^{2n-}$ anion of **III**. The organic cations, however, showed significant disorder, and a weakly diffracting crystal prevented further structural refinement.

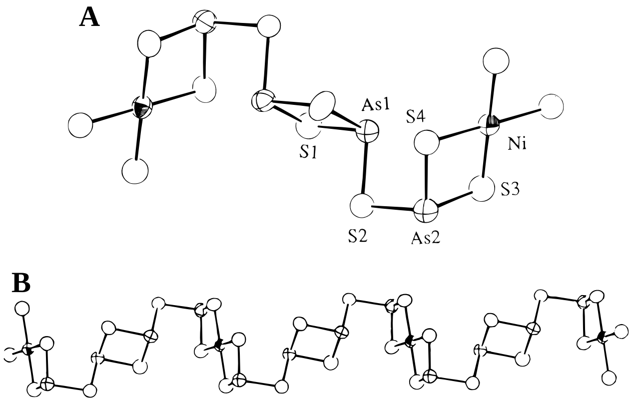

Figure 1. ORTEP representation and labeling scheme of the repeating unit (A) and a long section of a single $[Ni_2As_4S_8]_n{}^{2n-}$ chain (B).

Table 5. Selected Distances (Å) and Angles (deg) in $(Ph_4P)_2[Ni_2As_4S_8]$ with Standard Deviations in Parentheses

Ni−S3	2.222(2)	N1−S4	2.202(2)
As1−S2	2.303(3)	As1−S3	2.208(3)
As1−S4	2.218(2)	As2−S1	2.314(3)
As2−S1	2.250(2)	As2−S2	2.250(2)
S3−Ni−S3	180.00	S3−Ni−S4	88.59(9)
S3−Ni−S4	91.41(9)	S4−Ni−S4	180.00
S2−As1−S3	104.8(1)	S2−As1−S4	99.81(9)
S3−As1−S4	88.51(9)	S1−As2−S1	89.53(9)
S1−As2−S2	95.48(9)	S1−As2−S2	102.5(1)
As2−S1−As2	90.47(9)	As1−S2−As2	93.99(9)
As1−S3−Ni	90.69(9)	As1−S4−Ni	90.97(9)

Structure of $(Ph_4P)_2[Ni_2As_4S_8]$. The $[Ni_2As_4S_8]_n{}^{2n-}$ macroanion has an unusual one-dimensional polymeric structure composed of square planar Ni^{2+} ions and $[As_4S_8]^{4-}$ ligands. The $[As_4S_8]^{4-}$ ligand has not been seen before and is formed by a central core of edge-sharing $[AsS_3]^{3-}$ ligands capped by two corner-sharing pyramidal $[AsS_3]^{3-}$ units, see Figure 1. The $[Ni_2As_4S_8]_n{}^{2n-}$ chains run along the crystallographic *a*-axis and are well separated by Ph_4P^+ cations. The Ni^{2+} resides on an inversion center with Ni−S distances of 2.202(2) and 2.222(2) Å, respectively. Selected bond distances and angles for $(Ph_4P)_2[Ni_2As_4S_8]$ are given in Table 5. The average As−S distance and the average S−As−S angles are well within the normal range found in other arsenic/sulfide compounds.[14] The unique feature of this compound is the $[As_4S_8]^{4-}$ ligand, which can be derived from the condensation of four $[AsS_3]^{3-}$ units. As discussed earlier,[5] the $[AsS_3]^{3-}$ unit exhibits facile condensation reactions resulting in higher nuclearity $[As_xS_y]^{n-}$ ligands. Remarkably, the $[As_4S_8]^{4-}$ unit contains a four-membered As_2S_2 ring with *trans* connection to the other $[AsS_3]^{3-}$ units. In this example of the $[As_xS_y]^{n-}$ anion, the $[AsS_3]^{3-}$ pyramids share

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(13) (a) Crystals of $(Et_3MeN)_2[Mo_2O_2As_2Se_7]$ are orthorhombic *Cmca* (No. 64) with a = 14.989(7) Å, b = 18.086(6) Å, c = 21.125(5) Å, V = 5746(3) Å^3, Z = 4, D_{calc} = 2.682 g/cm^3, μ = 119.47 cm^{-1}, $2\theta_{max}$ = 40.0; R/R_w = 7.5/13.9 %. Single-crystal X-ray diffraction data were collected at −100 °C on a Rigaku AFC6 diffractomer. (b) Hanko, J. A.; Kanatzidis, M. G. Work in progress.

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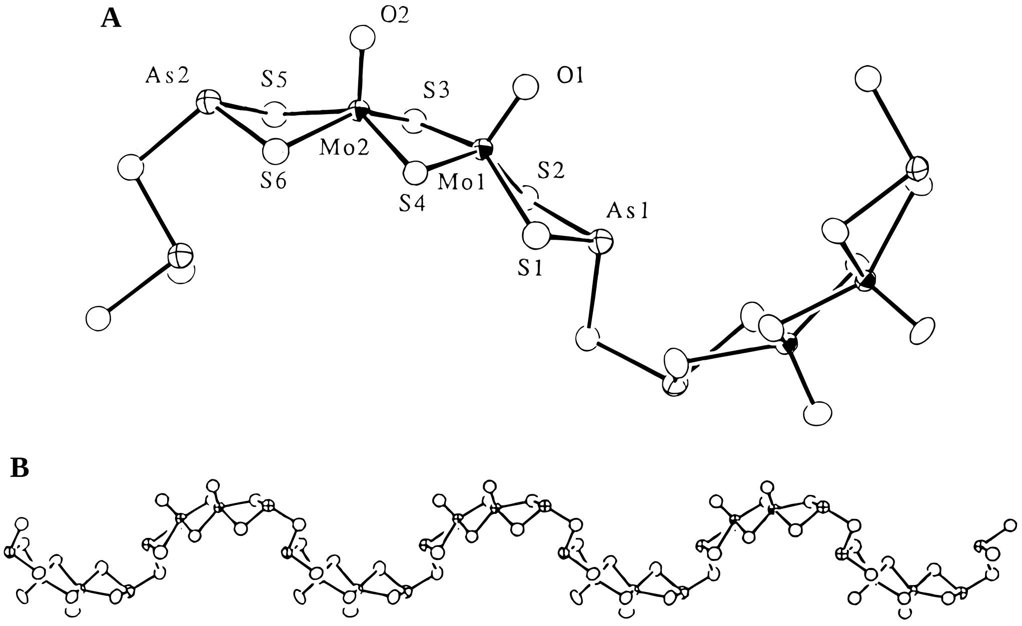


Figure 2. ORTEP representation and labeling scheme of the repeating unit (A) and a long section of a single $[Mo_2O_2As_2S_7]_n^{2n-}$ chain (B).

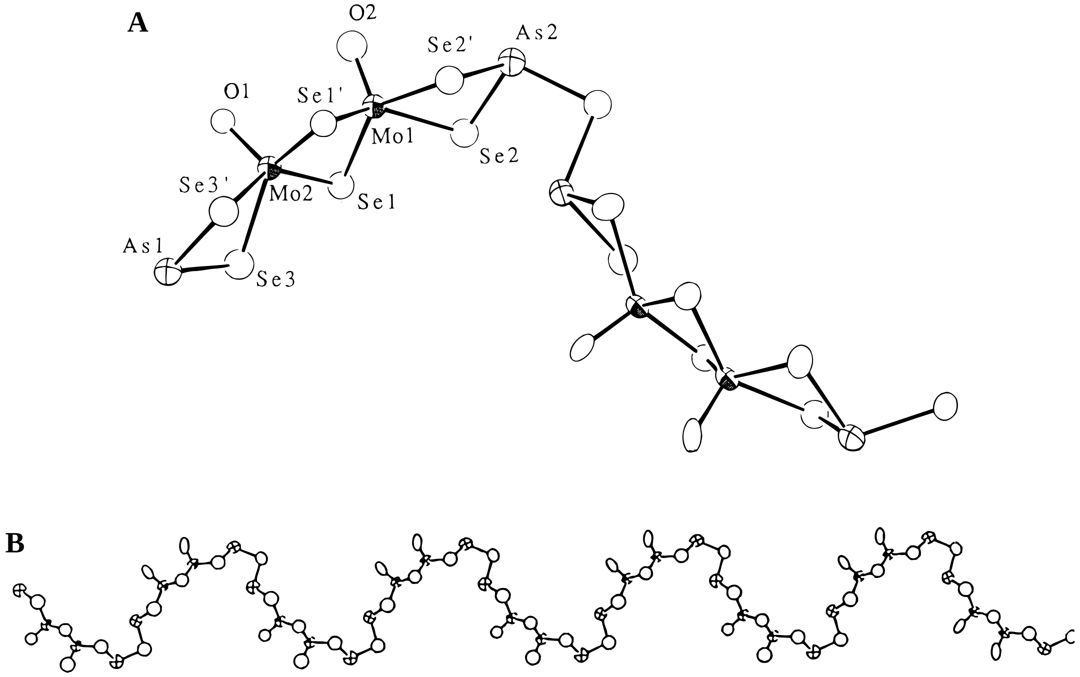
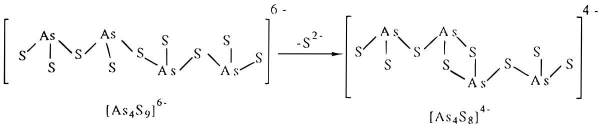


Figure 3. ORTEP representation and labeling scheme of the repeating unit (A) and a long section of a single $[Mo_2O_2As_2S_7]_n^{2n-}$ chain (B).

both corners and edges. A similar four-membered ring in a *cis* connection is found in $[As_6S_{12}]^{6-}$, which exists in the sulfosalt $PbTlAs_3S_6$.[15] The $[As_4S_8]^{4-}$ ligands can also be viewed as the intermolecular condensation product of the $[As_4S_9]^{6-}$ ligands found in $[Hg_2As_4S_9]^{2-}$,[5] see Scheme 1. The $[As_4S_8]^{4-}$ represents a new thioarsenate anion.

Scheme 1



Structure of $(R_4N)_2[Mo_2O_2As_2Q_7]$ (R = CH_3, Q = S and R = CH_3CH_2, Q = Se). The $[Mo_2O_2As_2Q_7]_n^{2n-}$ chains of **II** and **III**, see Figure 2 and Figure 3, consist of $[Mo_2O_2Q_2]^{2+}$ cores linked by $[As_2Q_5]^{4-}$ (Q = S, Se) ligands forming a one-dimensional chain. The $[As_2Q_5]^{4-}$ ligands are formed by two corner-sharing $[AsQ_3]^{3-}$ units. The chains in **II** and **III** run along the crystallographic *b*-axis and are separated by tetramethylammonium cations in **II** and tetraethylammonium cations in **III**. The overall conformation of the chains in **II** and **III** is sinusoidal with a period corresponding to the length of the *b* lattice constant. In **II** the chains run in-phase, while in **III** the chains run both in-phase and out-of-phase with respect to each other. The chain in **III** is situated on a crystallographic mirror plane perpendicular to the *a*-axis.

The $[Mo_2O_2Q_2]^{2+}$ (Q = S, Se) core fragment in **II** and **III** is well-known in molecular Mo−Q (Q = S, Se) chemistry; examples include $[Mo_2O_2S_2(S_2)_2]^{2-}$,[16,17] $[Mo_2O_2S_2(S_3O_2)]^{2-}$,[18] and $[Mo_2O_2Se_2(Se_2)_2]^{2-}$.[19] This is the first example in which the $[Mo_2O_2Q_2]^{2+}$ cores have been incorporated into a polymeric

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Table 6. Selected Distances (Å) and Angles (deg) in $(Me_4N)_2[Mo_2O_2As_2S_7]$ with Standard Deviations in Parentheses

Mo1−Mo2	2.848(2)	As2−S7	2.262(6)
Mo1−S4	2.335(5)	Mo1−S3	2.337(5)
Mo1−S6	2.425(5)	Mo1−S5	2.442(6)
Mo2−S1	2.435(6)	Mo1−O1	1.68(1)
Mo2−S3	2.335(5)	Mo2−S2	2.440(5)
Mo1−O1	1.70(1)	Mo2−S4	2.334(5)
As1−S6	2.236(6)	As2−S1	2.245(6)
As1−S5	2.230(6)	As2−S2	2.240(5)
As1−S7	2.260(6)		

Mo2−Mo1−S3	52.4(1)	Mo1−S5−As1	88.9(2)
Mo2−Mo1−S5	130.7(1)	Mo2−Mo1−S4	52.4(1)
Mo2−Mo1−O1	106.5(4)	Mo2−Mo1−S6	129.4(1)
S3−Mo1−S5	145.9(2)	S3−Mo1−S4	101.1(2)
S3−Mo1−O1	109.3(8)	S3−Mo1−S6	80.1(2)
S4−Mo1−S6	141.6(2)	S4−Mo1−S5	80.1(2)
S5−Mo1−S6	78.7(2)	S4−Mo1−O1	110.9(4)
S6−Mo1−O1	104.6(4)	S5−Mo1−O1	101.9(5)
Mo1−Mo2−S2	126.6(1)	Mo1−Mo2−S1	130.9(2)
Mo1−Mo2−S4	52.4(1)	Mo1−Mo2−S3	52.5(1)
S1−Mo2−S2	78.0(2)	Mo1−Mo2−O2	104.8(4)
S1−Mo2−S4	80.8(2)	S1−Mo2−S3	144.1(2)
S2−Mo2−S3	77.9(2)	S1−Mo1−O2	104.7(5)
S2−Mo2−O2	108.6(4)	S2−Mo2−S4	139.5(2)
S3−Mo2−O2	108.0(5)	S3−Mo2−S4	101.3(2)
S5−As1−S6	87.4(2)	S4−Mo2−O2	110.0(5)
S6−As1−S7	87.4(2)	S5−As1−S7	108.5(2)
S1−As2−S7	104.1(2)	S1−As2−S2	86.3(3)
Mo2−S1−As2	92.5(5)	S2−As2−S7	98.3(2)
Mo1−S3−Mo2	75.1(2)	Mo2−S2−As2	92.5(2)
Mo1−S6−As1	89.2(2)	Mo1−S4−Mo2	75.2(2)

Table 7. Selected Distances (Å) and angles (deg) in $[Me_4N)_2[Mo_2O_2As_2Se_7]$ with Standard Deviations in Parentheses

Mo1−Mo2	2.915(6)	Mo1−Se1	2.468(5)
Mo1−Se2	2.566(5)	Mo1−O2	1.65(3)
Mo2−Se1	2.465(5)	Mo2−Se3	2.572(5)
Mo2−O1	1.65(3)	As1−Se3	2.377(6)
As1−Se4	2.391(8)	As2−Se4	2.398(7)
As2−Se2	2.371(6)		

Mo2−Mo1−Se1	53.6(1)	Se3−Mo2−O1	105(1)
Mo2−Mo1−Se2	130.5(2)	Mo1−Se1−Mo2	72.5(2)
Mo2−Mo1−O2	102(1)	Mo1−Se2−As2	88.9(2)
Se1−Mo1−Se2	78.6(2)	Mo2−Se3−As1	90.5(2)
Se1−Mo1−O2	109.3(8)	As1−Se4−As2	97.3(4)
Se1−Mo1−Se2	142.2(3)	Se3−As1−Se4	102.6(3)
Se2−Mo1−O2	106(1)	Se2−As2−Se4	106.1(3)
Mo1−Mo2−Se1	53.9(2)	Mo1−Mo2−O1	103(1)
Mo1−Mo2−Se3	130.5(2)	Se1−Mo2−Se3	142.4(3)

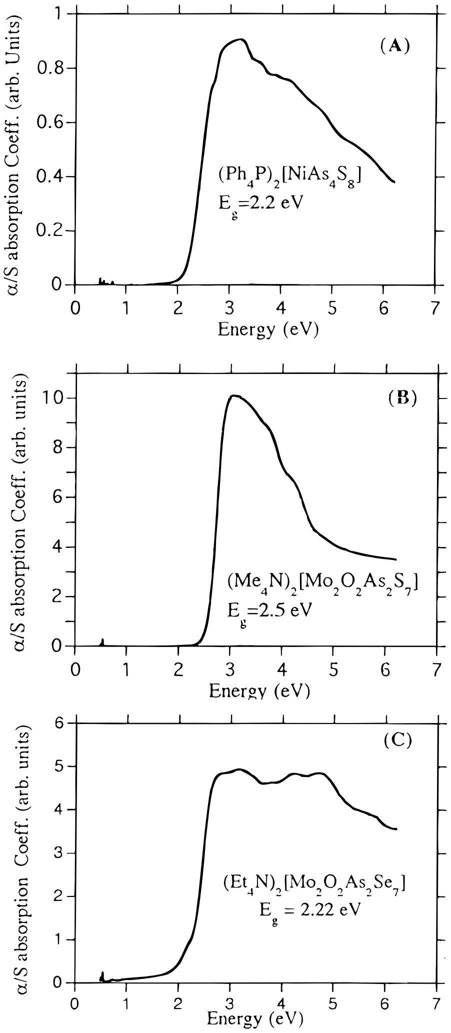

Figure 4. (A) Optical absorption spectrum of $(Ph_4P)_2[Ni_2As_4S_8]$. (B) Optical absorption spectrum of $(Me_4N)_2[Mo_2O_2As_2S_7]$. (C) Optical absorption spectrum of $(Et_4N)_2[Mo_2O_2As_2Se_7]$.

framework. With the introduction of the trivalent As atom, the $[As_xS_y]^{n-}$ ligand's potential connectivity is increased, greatly improving the chances of forming a polymeric compound. The Mo−Mo distances of 2.848(2) and 2.915(6) Å in **II** and **III**, respectively, are similar to those found in the molecular polychalcogenide compounds.[16−19] Selected bond distances and angles for **II** and **III** are given in Tables 6 and 7, respectively. There are two different types of Mo−Q distances in **II** and **III**. In **II** the average Mo−S distance, 2.335(5) Å, inside of the $[Mo_2O_2S_2]^{2+}$ core is significantly shorter than the Mo−S distance, 2.435(5) Å, between the core and the thioarsenate ligands. In **III** a similar trend is observed for the Mo−Se distances. The average Mo−Se distance is 2.467(5) Å within the $[Mo_2O_2Se_2]^{2+}$ core and 2.569(5) Å between the core and the polyselenoarsenate ligand. A comparison of the Mo−Q bond distances of several compounds which contain the $[Mo_2O_2Q_2]^{2+}$ core is given in Table 8. The Mo−Q distances for the polymeric species **II** and **III** compare well with the molecular polychalcogenide counterparts. This trend in alternating Mo−S bond lengths between the $[Mo_2O_2S_2]^{2+}$ core and the bridging polysulfides is also observed in the molecular species $[Mo_2S_{10}]^{2-}$ and to a lesser extent in $[Mo_2S_{12}]^{2-}$.[20] This dramatic shortening may be due to the enhanced $Mo_{d\pi}$−$Q_{p\pi}$ bonding interactions in the $[Mo_2O_2Q_2]^{2+}$ core. This may be attributed to the fact that the monochalcogenides in the core are bridging two Mo^{5+} centers while the chalcogenides of the ligands are bonded to only one. But with a limited number of examples further work will be needed to confirm this observation. Similar trends were observed in $[Mo_2O_2As_4S_{14}]^{2-}$ [8] (see Table 8). It is noteworthy that in the same paper Rauchfuss et al. describes a cyclic structure for $[Mo_4O_4As_4S_{14}]^{4-}$ where two $[As_2S_5]^{4-}$ ligands connect two $[Mo_2O_2S_2]^{2+}$ cores.[8] The compounds reported here are the polymeric analogs of $(Ph_4P)_4[Mo_4O_4As_4S_{14}]$. The $[As_2S_5]^{4-}$ unit of **II** occurs in the sulfosalts $PbTlCuAs_2S_5$ (Wallisite),[21] $PbTlAgAs_2S_5$ (Hatchite),[22]

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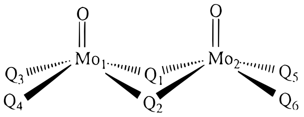
Table 8. Comparison of the Axial and Bridging Bond Distances (Å) and Selected Angles (deg) within Various $[Mo_2O_2Q_2]^{2+}$ Cores in Discrete and Polymeric Complexes[a]



	$[Mo_2O_2S_6]^{2-}$	$[Mo_2O_2As_2S_7]^{2-}$	$[Mo_2O_2As_4S_{14}]^{2-}$	$[Mo_2O_2Se_6]^{2-}$	$[Mo_2O_2As_2Se_7]^{2-}$
Mo_1-Mo_2	2.825(2)	2.848(2)	2.828(3)	2.888(2)	2.915(6)
Mo_1-O	1.670(11)	1.70(1)	1.688(14)	1.672(6)	1.65(3)
Mo_2-O	1.680(9)	1.68(1)	1.718(11)	1.702(6)	1.65(3)
Mo_1-Q_1	2.320(4)	2.337(5)	2.320(5)	2.456(1)	2.468(5)
Mo_1-Q_2	2.372(4)	2.335(5)	2.294(6)	2.445(2)	
Mo_2-Q_1	2.330(4)	2.335(5)	2.301(7)	2.453(2)	2.465(5)
Mo_2-Q_2	2.320(4)	2.334(5)	2.308(4)	2.446(2)	
$Mo-Q_{(av)}$	2.33(1)	2.335(5)	2.305(5)	2.443(5)	2.466(5)
Mo_1-Q3	2.392(5)	2.442(6)	2.441(5)	2.538(2)	2.566(5)
Mo_1-Q4	2.441(5)	2.425(5)	2.447(8)	2.545(2)	
Mo_2-Q5	2.422(5)	2.435(6)	2.455(6)	2.540(2)	2.572(5)
Mo_2-Q6	2.382(6)	2.440(5)	2.448(6)	2.544(2)	
$Mo-Q(av)$	2.41(1)	2.43(1)	2.44(2)	2.54(1)	2.56(3)
$Mo_1-Q_1-Mo_2$	74.8(1)	75.1(1)	75.5(2)	72.1(1)	72.5(2)
$Mo_1-Q_2-Mo_2$	74.9(1)	75.2(2)	75.8(2)	72.4(1)	

[a] Schematic of the common structural fragment with a common labeling scheme is provided at the top of this table.

and $Tl_2MnAs_2S_5$.[23] Examination of the literature for the occurrence of $[As_2Se_5]^{4-}$ observed in **III** revealed only one example, $Tl_2As_2Se_5$.[24]

These compounds are wide band gap semiconductors. The optical absorption spectrum of $(Ph_4P)_2[NiAs_4S_8]$, see Figure 4, spectrum A, exhibits an intense, steep absorption edge, revealing an optical band gap of 2.2 eV. The spectra of $(R_4N)_2[Mo_2O_2As_2Q_7]$ (Q = S, Se) also show a similar absorption edge with a corresponding band gap at 2.5 and 2.2 eV, see Figure 4, spectra B and C. The intense absorptions are probably due to a chalcogen to metal charge-transfer transition.

In conclusion, the $[AsQ_3]^{3-}$ anion produces oligomers which act as bridging units to connect known molecular clusters giving new metal/arsenic/chalcogenide chemistry. Three important factors dominate this chemistry: the condensation equilibria among the thio- and selenoarsenate anions, the nature of counterions (templates), and the coordination preferences of the metal ions. Further investigations will explore the existence of other novel $[As_xQ_y]^{n-}$ anions and the possibility of using them as synthetic building blocks for solid state materials.

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Supporting Information Available: Tables of anisotropic thermal parameters (21 pages). Ordering information is given on any current masthead page.

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