product (>90%). The solvent was removed under vacuum and the residue recrystallized from benzene to give $FeH(S\text{-}t\text{-}Bu)(DMPE)_2$ as an orange crystalline solid, mp 142-143 °C dec. Anal. Calcd for $C_{16}H_{42}FeP_4S$: C, 43.06; H, 9.49. Found: C, 43.0; H, 9.8. *trans*-$FeH(S\text{-}t\text{-}Bu)(DMPE)_2$ (*trans*-**3e**): ^1H NMR (benzene-d_6, 298 K) δ 2.18-2.38 (br m, 4 H, 4 × PC*H*H-), 1.86 (br s, 12 H, 4 × CH_3P-), 1.76 (s, 9 H, (CH_3)$_3$C-), 1.58-1.73 (br m, 4 H, 4 × PCH*H*-), 1.29 (br s, 12 H, 4 × CH_3P-), -27.6 (quintet, 1 H, J_{PH} = 52.5 Hz, Fe-*H*); $^{13}C\{P,H\}$ NMR (benzene-d_6, 298 K) δ 39.58 ((*C*H$_3$)$_3$C-), 38.86 ((CH$_3$)$_3$*C*-), 32.97 (P*C*H$_2$-), 28.98 (*C*H$_3$P-), 18.22 (*C*H$_3$P-). Even on prolonged warming with excess *tert*-butyl mercaptan, the disubstituted product, $Fe(S\text{-}t\text{-}Bu)_2(DMPE)_2$, was not formed in a detectable quantity.

Thiophenol. Reaction of thiophenol with $FeH_2(DMPE)_2$ was significantly more rapid than that of alkanethiols. The cis and trans thiolate hydrides formed over the space of 1 h, and the reaction to form dithiolate complexes was effectively complete after 24 h (see Figure 1). After 24 h at room temperature, the solvent was removed under vacuum and the residue recrystallized from petroleum ether. $Fe(SPh)_2(DMPE)_2$ was obtained as a green crystalline solid, mp 170 °C dec. Anal. Calcd for $C_{24}H_{42}FeP_4S_2$: C, 50.18; H, 7.40; P, 21.57. Found: C, 49.9; H, 7.4; P, 21.4. *trans*-$Fe(SPh)_2(DMPE)_2$ (*trans*-**4a**): $^{13}C\{P,H\}$ NMR (THF-d_8, 315 K) δ 153.08 (Ar C_{ipso}), 139.48, 129.12 (Ar C_{ortho}, Ar C_{meta}), 124.27 (Ar C_{para}), 32.70 (P*C*H$_2$-), 17.53 (*C*H$_3$P-); ^1H NMR (benzene-d_6, 300 K) δ 7.64-7.56 (m, 4 H, Ar H_{ortho}), 7.23-7.16 (m, 2 H, Ar H_{para}), 7.12-7.04 (m, 4 H, Ar H_{meta}), 2.23 (br s, 8 H, 4 × PCH_2-), 1.61 (br s, 24 H, 8 × CH_3P-).

1,2-Ethanedithiol. A solution of $FeH_2(DMPE)_2$ (ca. 60 mg) in dry, oxygen-free THF was treated with 1,2-ethanedithiol (400 μL, 1.5 M in THF), and the mixture was left to stand at room temperature. $\overline{SCH_2CH_2S}Fe(DMPE)_2$ (**5**) crystallized from the reaction mixture over a period of 10 days. The solid was removed, washed with pentane, and dried under high vacuum to give the product as deep red plates, mp 236-237 °C dec. Anal. Calcd for $C_{14}H_{36}FeP_4S_2$: C, 37.51; H, 8.09. Found: C, 37.8; H, 8.4. ^1H NMR (benzene-d_6, 298 K): δ 3.00-2.91 (br m, 2 H, 2 × SC*H*H-), 2.63-2.52 (br m, 2 H, 2 × SCH*H*-), 1.64 (m, 6 H, 2 × CH_3P-), 1.56-1.42 (br m, 4 H, 4 × PC*H*H-), 1.32 (m, 6 H, 2 × CH_3P-), 1.23 (m, 6 H, 2 × CH_3P-), 1.21-1.09 (br m, 2 H, 2 × PC*H*H-), 1.09-0.97 (br m, 2 H, 2 × PCH*H*-), 0.75 (m, 6 H, 2 × CH_3P-). $^{13}C\{H,P\}$ NMR (benzene-d_6, 298 K): δ 35.01 (S*C*H$_2$-), 33.69 (P*C*H$_2$-), 28.96 (P*C*H$_2$-), 20.66 (*C*H$_3$P-), 17.92 (*C*H$_3$P-), 16.90 (*C*H$_3$-P), 13.25 (*C*H$_3$P-). Slow recrystallization from toluene afforded orange plates suitable for X-ray crystallography.

1,3-Propanedithiol. Reaction of 1,3-propanedithiol was analogous to that of 1,2-ethanedithiol. $\overline{SCH_2CH_2CH_2S}Fe(DMPE)_2$ (**6**) crystallized from the reaction mixture over a period of 10 days. The solid was removed, washed with pentane, and dried under high vacuum to give the product as deep red plates, mp 208-210 °C dec. Anal. Calcd for $C_{15}H_{38}FeP_4S_2$: C, 38.97; H, 8.29. Found: C, 39.1; H, 8.7. ^1H NMR (benzene-d_6, 302 K): δ 2.66-2.60 (br m, 4 H, 2 × SCH_2-), 2.37-2.30 (br m, 2 H, SCH_2-), 2.04 (m, 6 H, 2 × CH_3P-), 1.77-1.62 (br m, 4 H, 4 × PC*H*H-), 1.43 (m, 6 H, 2 × CH_3P-), 1.43-1.28 (br m, 2 H, 2 × PC*H*H-), 1.25 (m, 6 H, 2 × CH_3P-), 1.11-0.96 (br m, 2 H, 2 × PC*H*H-), 0.76 (m, 6 H, 2 × CH_3P-). $^{13}C\{H,P\}$ NMR (benzene-d_6, 302 K): δ 33.4 (S*C*H$_2$-), 33.4 (P*C*H$_2$-), 29.1 (P*C*H$_2$-), 23.6 (SCH$_2$*C*H$_2$-), 20.6 (*C*H$_3$P-), 17.0 (*C*H$_3$P-), 16.0 (*C*H$_3$P-), 13.2 (*C*H$_3$P-).

1,4-Bis(mercaptomethyl)benzene. A solution of $FeH_2(DMPE)_2$ (ca. 100 mg) in dry, oxygen-free THF (50 mL) was treated with 1,4-bis(mercaptomethyl)benzene (24 mg, 0.5 equiv), and the mixture was left to stand at room temperature for 4 weeks. $HFe(DMPE)_2(SCH_2C_6H_4CH_2S)FeH(DMPE)_2$ crystallized directly from the reaction mixture on slow evaporation of the solvent. ^1H NMR (benzene-d_6, 302 K): δ 7.8 (s, 4 H, Ar *H*), 3.35 (s, 4 H, 2 × SCH_2-), 2.10-1.95 (br m, 4 H, 4 × PC*H*H-), 1.73 (br s, 24 H, 8 × CH_3P-), 1.73-1.55 (br m, 8 H, 8 × PC*H*H-), 1.31 (br s, 24 H, 8 × CH_3P-), -25.2 (quintet, 2H, $^1J_{PH}$ = 50.2 Hz, 2 × Fe-*H*). $^{13}C\{H,P\}$ NMR (benzene-d_6, 315 K): δ 144.9 (Ar C_{ipso}), 128.7 (Ar *C*), 39.2 (S*C*H$_2$-), 32.6 (P*C*H$_2$), 26.2 (*C*H$_3$P-), 16.6 (*C*H$_3$P-). Cis isomers were present only to <5%.

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Supplementary Material Available: Tables of crystallographic data, thermal parameters, and hydrogen positional and thermal parameters for **5** (3 pages); tables of calculated and observed structure factors for **5** (8 pages). Ordering information is given on any current masthead page.

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Chemistry of Organometalloid Complexes with Potential Antidotes: Structure of an Organoarsenic(III) Dithiolate Ring

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The reactions of several arylarsenic dichlorides with the vicinal dithiols $HSCH_2CH(SH)CH_2OH$ (British Anti-Lewisite, BAL) and *meso*-HOOCCH(SH)CH(SH)COOH (dimercaptosuccinic acid, DMSA) were investigated. They readily formed five-membered rings with the dithiolate groups chelated to the arsenic(III) center. The complexes were characterized by a variety of spectroscopic techniques, which indicate that the dithiolates chelate tightly to the arsenic(III) through the sulfur atoms. The complex between tolylarsenic dichloride and BAL was characterized by single-crystal X-ray diffraction. The cell is monoclinic, of space group $P2_1/n$, with a = 13.343 (2) Å, b = 5.116 (1) Å, c = 17.196 (3) Å, β = 96.66 (1)°, Z = 4, V = 1166.0 (6) Å^3, R = 0.039, and R_w = 0.048. The structure contains a five-membered arsenic(III) dithiolate with pyramidal geometry around the arsenic atom. Though both syn and anti isomers are possible, only the anti isomer is isolated. The lone pairs on the oxygen atoms do not appear to be involved in bonding.

Introduction

There is a great deal of concern about the toxicity of post-transition-element ions and their organometallic complexes.[2,3] Despite this, there has been relatively little research done on antidotes to metalloid poisoning in the United States. In fact, the antidote which is most commonly prescribed in the United States is still British Anti-Lewisite, which was developed by the British at the beginning of World War II to counteract anticipated German poison gas attacks.[4]

We have recently initiated a program to investigate the chemistry, spectroscopy, and structure of complexes between heavy p-block elements and their potential antidotes.[5,6] We are initially interested in antidotes to trivalent organoarsenical toxins, such as Lewisite ($ClCH{=}CHAsCl_2$). The mechanism of toxic action of organoarsenic(III) compounds is not well understood, but is believed to arise from the affinity of As(III) for enzyme sulfhydryl groups.[7-9] The presence of organic groups makes the arsenic

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compound permeable to cell membranes.

Most antidotes to organoarsenicals contain a vicinal dithiol group to complex the arsenical, as well as a polar group to make the antidote water soluble.[10] The most common antidote is 2,3-dimercaptopropanol, or British Anti-Lewisite (BAL). This has been used for many years, but it has several serious limitations. It has poor water solubility, has a dreadful stench, is toxic itself, and is not amenable to oral administration. Recently, several other compounds have been investigated as possible antidotes for organo–heavy metal poisoning. Most promising are dimercaptosuccinic acid (DMSA), sodium 2,3-dimercaptopropanesulfonate (DMPS),[11-13] and *N*-(2,3-dimercaptopropyl)phthalamidic acid (DMPA).[14] These compounds are more water soluble and considerably less toxic than BAL. Also, they are crystalline solids that can be administered orally.[15]

In this paper we report the preparation and spectroscopic characterization of BAL and DMSA complexes of several organoarsenic(III) compounds. Also, we report the crystal structure of tolylarsenic 2,3-dimercaptopropanolate. This is the first crystal structure of a BAL complex, as well as the first structure of any dithioarsenic(III) complex.

Experimental Section

General Considerations. All manipulations involving the organoarsenic chlorides were performed under an atmosphere of dry argon to prevent hydrolysis. All solvents were dried over activated molecular sieves prior to use. Precursors were purchased from Aldrich Corp. and used as received. IR spectra either as Nujol mulls or as KBr pellets were obtained on a Nicolet 5D FT IR spectrometer. NMR spectra were obtained in acetone-d_6 solutions on a JEOL FX90Q instrument using the solvent peaks as a reference. Mass spectral data were obtained on a Hewlett Packard 5985 instrument using an EI beam of 70 eV. Elemental analysis were performed by Atlantic Microlabs, Atlanta, GA. *Caution! All of the organosarsenic halides are powerful vessicants, which cause severe irritation and blistering if allowed to come into contact with skin.* Precautions should include use of rubber gloves when the organoarsenic halides are handled.

Synthesis of Phenyldichloroarsine (PDA), $C_6H_5AsCl_2$. PDA was prepared by a modification of a literature method.[16] A flask was charged with 2 g of phenylarsonic acid, 60 mL of HCl added, and the mixture stirred for 1 h to dissolve the arsenic compound. Sulfur dioxide was slowly bubbled into the solution for 2 h to reduce the arsenic complex. The solution was allowed to stand overnight, after which droplets of viscous yellow oil formed in the flask. The solution was carefully decanted and the yellow oil isolated. This crude PDA was vacuum-distilled to give a clear refractive oil. IR (neat): 3057 (s), 1433 (s), 1072 (s), 998 (m), 736 (s), 607 cm^{-1} (s). Bp: 252–254 °C.

Synthesis of Tolyldichloroarsine (TDA), $CH_3C_6H_4AsCl_2$. TDA was prepared by a modification of the above procedure. Tolylarsonic acid, 2 g, was added to a flask with 60 mL of concentrated HCl. The mixture was stirred for 1 h at 25 °C. The flask was exposed to vacuum briefly three times during this period to remove HCl vapor. Sulfur dioxide was slowly bubbled into the flask for 2 h. The solution was allowed to sit at room temperature for 24 h, during which pale yellow crystalline needles of TDA precipitated. These were isolated, dried, and stored at 4 °C. Mp: 31 °C. IR (Nujol): 1591 (s), 1073 (m), 800 cm^{-1} (m). MS: *m/e* 236/238, 201, 91.

Synthesis of $C_6H_5As\overline{SCH_2CHSCH_2OH}$ (PDA–BAL). Phenyldichloroarsine (PDA), 0.526 g (2.36 mmol), was dissolved in 40 mL of acetone, and 0.293 g (2.36 mmol) of 2,3-dimercaptopropanol (BAL) was added slowly. The solution was stirred for 1 h. Crystalline product was obtained by addition of 20 mL of H_2O followed by slow evaporation of solvent. The product was recrystallized in the same fashion to yield long white needles, 0.388 g (yield 60%). IR (Nujol): 1009 (s), 732 (s), 694 cm^{-1} (s). MS: *m/e* 274 (parent), 216 (Ph–AsS_2), 165 (As–$S_2C_2H_2$), 151 (Ph–As), 107 (As–S). Mp: 86 °C. Anal. Calcd for $C_9H_{11}OAsS_2$: C, 39.41; H, 4.04. Found: C, 39.52; H, 4.05.

Table I

chemical formula $C_{10}H_{13}OAsS_2$	$Z = 4$
fw 288.3	$T = 20$ °C
space group $P2_1/n$, monoclinic	$\lambda = 0.71073$ Å
$a = 13.343$ (2) Å	density 1.64 g cm^{-3}
$b = 5.116$ (1) Å	$\mu = 32.2$ cm^{-1}
$c = 17.196$ (3) Å	$R = 0.039$
$\beta = 96.66$ (1)°	$R_w = 0.048$
$V = 1166.0$ (6) Å	

Synthesis of $CH_3C_6H_4As\overline{SCH_2CHSCH_2OH}$ (TDA–BAL). The compound was prepared by a procedure similar to that for PDA–BAL. In a typical reaction, 0.552 g (2.33 mmol) of TDA was dissolved in 30 mL of acetone. After the solution was stirred for 15 min, 0.296 g (2.38 mmol) of BAL was added and the solution stirred overnight. Water, 20 mL, was added, and a yellow oil precipitated overnight. Crystallization from acetone/water produced white crystals, 0.214 g (yield 32%). Mp: 78 °C. IR (KBr): 3370 (m), 3037 (s), 2934 (s), 1006 (m), 805 cm^{-1} (m). MS: *m/e* 288 (parent), 230 ($CH_3C_6H_4AsS_2$), 215 ($C_6H_4AsS_2$), 197 (As–BAL), 165 ($AsS_2C_2H_3$), 91 ($CH_3C_6H_4$). Anal. Calcd for $C_{10}H_{13}OAsS_2$: C, 41.66; H, 4.54. Found: C, 41.67; H, 4.59.

Synthesis of $C_6H_5As\overline{SC(COOH)HCHSCOOH}\cdot H_2O$ (PDA–DMSA). In a typical preparation, 0.327 g (1.47 mmol) of phenyldichlorarsine was dissolved in 40 mL of acetone and 0.273 g (1.50 mmol) of dimercaptosuccinic acid (DMSA) was added in three parts over 30 min. As the DMSA dissolved, the solution began to turn pale yellow. The solution was stirred for 90 min and filtered. Water, 20 mL, was added, and a pale yellow solid formed upon standing. Recrystallization from acetone/water produced 0.359 g (yield 72%) of product. IR (KBr): 3484 (m), 3049 (s), 1720 (s), 1203 (s), 749 (m), 687 cm^{-1} (m). MS: *m/e* 261 (HOOCCCH), 229 (PhAsSSCH), 152 (PhAS), 77 (Ph). Mp: 165 °C. Anal. Calcd for $C_{10}H_{11}O_5AsS_2$: C, 34.29; H, 3.16. Found: C, 34.58; H, 3.19.

Synthesis of $CH_3C_6H_4As\overline{SC(COOH)HCHSCOOH}$ (TDA–DMSA). In a typical reaction, 0.227 g (0.958 mmol) of tolyldichloroarsine (TDA) was dissolved in 40 mL of acetone with stirring. DMSA, 0.173 g (0.958 mmol), was added as above and the solution stirred for 24 h. Water, 20 mL, was added, and crude product precipitated overnight. The white powder was recrystallized from acetone/water to produce pale yellow thin needles, 0.232/g (yield 70%). IR (KBr): 3404 (m), 1707 (s), 1280 (m), 798 cm^{-1} (m). MS: *m/e* 197 ($CH_3C_6H_4AsS$), 166 ($CH_3C_6H_4As$), 91 ($CH_3C_6H_4$). Mp: 196 °C. Anal. Calcd for $C_{11}H_{11}O_4AsS_2$: C, 38.15; H, 3.20. Found: C, 38.27; H, 3.25.

X-ray Crystallography of $CH_3C_6H_4As\overline{SCH_2CHSCH_2OH}$ (TDA–BAL). Suitable clear needles were grown by slow evaporation of an acetone/water solution. A parallelepiped of dimensions 0.22 × 0.18 × 0.64 mm was sealed in epoxy resin and mounted on an Enraf-Nonius CAD-4 diffractometer with molybdenum radiation. Intensities were measured by using ω–2θ scans of 4–16° min^{-1} in 2θ. The unit cell was determined by least-squares analysis of 25 well-centered reflections with $20° < 2\theta < 26°$. The choice of space group was confirmed by unambiguous systematic absences and the use of TRACER. The lattice constants and other crystallographic data are listed in Table I. Full crystallographic data are given in the supplementary material. The analytical absorption correction based on crystal shape varied from 0.82 to 1.00. Data were collected to 45° in 2θ, for $0 < h < 17$, $-6 < k < 0$, $-22 < l < 22$. Four standard reflections decreased 1.4% over 25.3 h of data collection. The structure was solved by direct methods using MULTAN11/82 and Fourier methods with minimized full-matrix least-squares values using the standard Enraf-Nonius SDP 1982 package. All non-hydrogen atoms were refined anisotropically, and the hydrogen on the OH group was located on a difference map and constrained to that position. All other hydrogen atoms were idealized. Atomic scattering factors and anomalous dispersion corrections were taken from reference 17. Atomic coordinates, selected bond distances and angles, and anisotropic thermal parameters are listed in Tables II and III and in the

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Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å²) for the Atoms[a]

	x	y	z	B_{eq}
As	0.17620 (3)	0.4705 (1)	0.34186 (3)	3.265 (9)
S(1)	0.04340 (9)	0.5993 (2)	0.39913 (8)	3.45 (2)
S(2)	0.08286 (9)	0.1816 (3)	0.26312 (7)	3.51 (2)
O	−0.2067 (2)	0.4045 (7)	0.2636 (2)	4.16 (8)
C(1)	−0.0298 (3)	0.3033 (9)	0.3848 (2)	2.68 (8)
C(2)	−0.0402 (3)	0.2132 (8)	0.2991 (3)	2.55 (8)
C(3)	−0.1058 (3)	0.3889 (9)	0.2439 (3)	3.16 (9)
C(4)	0.2390 (3)	0.2184 (9)	0.4192 (3)	2.95 (9)
C(5)	0.3202 (4)	0.084 (1)	0.3980 (3)	4.1 (1)
C(6)	0.3700 (4)	−0.098 (1)	0.4474 (3)	4.5 (1)
C(7)	0.3405 (4)	−0.150 (1)	0.5210 (3)	3.4 (1)
C(8)	0.2607 (4)	−0.011 (1)	0.5426 (3)	3.7 (1)
C(9)	0.2094 (3)	0.173 (1)	0.4932 (3)	3.5 (1)
C(10)	0.3941 (4)	−0.352 (1)	0.5736 (3)	4.8 (1)
H(11)	−0.238	−0.285	0.244	

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[(a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

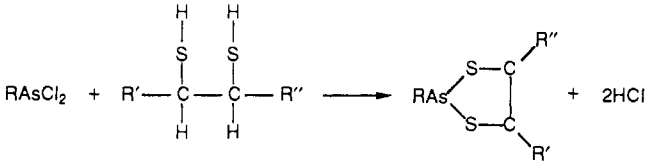
Table III. Selected Bond Distances (Å) and Bond Angles (deg)

As-S(1)	2.225 (1)	C(1)-C(2)	1.535 (5)
As-S(2)	2.276 (1)	C(2)-C(3)	1.511 (5)
As-C(4)	1.968 (4)	C(7)-C(10)	1.500 (6)
S(1)-C(1)	1.803 (4)	C-C(ph) range	1.367-1.396
S(2)-C(2)	1.828 (4)	C-C(ph) mean	1.383
O-C(3)	1.428 (5)	O···O′	2.823
O-H(11)	0.79	O···H(11)	2.08
S(1)-As-S(2)	92.68 (4)	S(2)-C(2)-C(3)	108.5 (3)
S(1)-As-C(4)	101.2 (1)	C(1)-C(2)-C(3)	114.0 (3)
S(2)-As-C(4)	97.9 (1)	C(2)-C(3)-O	112.2 (4)
As-S(1)-C(1)	97.9 (1)	C-C-C(Ph) range	117.4-121.3
As-S(2)-C(2)	101.1 (1)	C-C-C(Ph) mean	120.0
S(1)-C(1)-C(2)	111.7 (3)	O···H(11)···O	156
S(2)-C(2)-C(1)	111.5 (3)		

supplementary material, respectively.

Results and Discussion

Syntheses. The organodichloroarsinicals were prepared by standard methods of forming chlorides from arsonic acids in HCl, followed by reduction to As(III) with SO_2 as the reductant. These compounds react readily with vicinal dithiols with displacement of HCl and formation of five-membered rings containing chelating dithiolates.



These are extremely stable and form the basis of the antidotal properties of these compounds. None of the molecules seem to show any tendency to adopt higher coordination numbers. Addition of excess dithiol only results in no further reaction. Also, in the crystal lattice of PDA-BAL, the hydroxy group of BAL shows no tendency toward inter- or intramolecular coordination.

It was observed qualitatively that the BAL adducts seem more stable than the DMSA adducts. The BAL complexes survive multiple recrystallizations and show no other peaks in the NMR over weeks in solution. However, the DMSA complexes usually show unidentified peaks in the NMR spectrum after several days.

Structural Studies. A suitable single crystal of the adduct between $CH_3C_6H_4AsCl_2$ and $HSCH_2CH(SH)CH_2OH$ was obtained by recrystallization from acetone/water. The structure solution was straightforward, and the details are listed in the Experimental Section. The structure contains a five-membered ring with both sulfur atoms chelated to the arsenic (see Figure 1). The As-S bond lengths are 2.225 (1) and 2.276 (1) Å, and the S-As-S bite angle is 92.68 (4)° (see Table II). The geometry

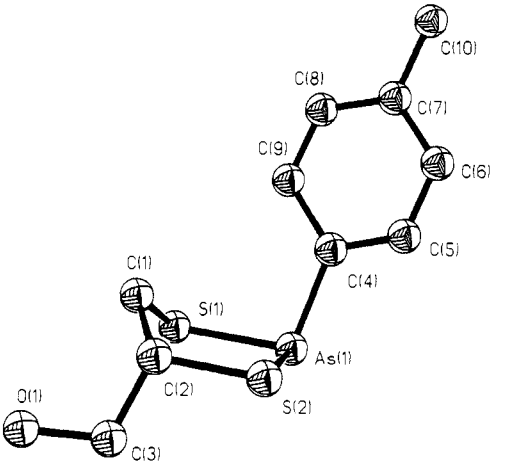


Figure 1. ORTEP view of the PDA-BAL molecule with ellipsoids at 50% probability and hydrogens omitted for clarity. The view clearly shows the anti conformation.

about the arsenic atom is pyramidal as expected for As(III). To our knowledge, this is the first arsenic(III) dithio complex characterized structurally. The As-S distances are somewhat shorter but comparable to other As^{III}-S distances.[18]

There has been a complex characterized that contains phenylarsenic(III) chelated by two dithiophosphate groups.[19] In this complex the arsenic is in a distorted-square-pyramidal coordination geometry, with one of the sulfur atoms on each of the chelating ligands considerably farther from the arsenic than the other. The authors point out that this is a result of the tendency of arsenic(III) to adopt a three-coordinate environment. The As-S distance in our molecule is shorter than the shortest distance in the dithiophosphate complex (2.276 Å versus 2.310 Å), as expected. The two As-S-C bond angles are 97.9 (1) and 101.1 (1)°. The various carbon bond lengths and angles are within normal range. Weak hydrogen bonds link the molecules about the screw axis in the *y* direction.

The five-membered ring adopts an envelope configuration with the hydroxymethyl group located on a hinge of the envelope anti to the phenyl group of the arsenic. This is because the inversion of pyramidal arsenic is expected to be slow, and it should be possible to observe two isomers. There is NMR evidence that there is a small amount of the syn isomer in solution (vide infra), but this is not observed in the isolated solid. The As-S(1)-S(2)-C(2) fragment of the ring is planar to within 0.04 Å with C(1) 0.73 Å out of the plane.

Spectroscopy of BAL Adducts. In addition to the X-ray crystallography, the arylarsenical adducts of BAL were characterized by a variety of physical methods. Mass spectra of the adducts show the parent ion as well as several recognizable fragments. The ^{13}C NMR spectrum of uncomplexed BAL shows three aliphatic peaks as expected, with the resonance of the carbon attached to the hydroxyl group being farthest downfield. Upon coordination, the resonances of the two carbons attached to the sulfurs shift downfield by 13-15 ppm (see Table IV). From work with a variety of related systems, this appears to be a characteristic shift and can be used as a diagnostic for coordination of these thiols to arsenic.

The ^1H NMR spectrum is complex, with resonances of five chemically distinct aliphatic protons. The second-order spectrum has been investigated by two-dimensional techniques and fully discussed in a previous communication.[8] We do observe other resonances when BAL is added directly to a solution of the organoarsenic chloride in a sample tube, and we attribute these to a small amount of the syn isomer in solution. Under our experimental conditions the anti is clearly the preferred isomer.[20]

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Table IV. ^{13}C NMR Chemical Shifts of BAL and DMSA Adducts (ppm)[a]

carbon atoms	TDA–BAL	PDA–BAL	BAL
CH_3	21.2		
CH_2	43.15	40.47	30.07
CH	59.5	58.83	45.56
CH_2OH	64.36	63.93	65.64
phenyl	130.0	129.2	
	131.5	130.6	
		132.0	
carbon atoms	TDA–DMSA	PDA–DMSA	DMSA[b]
CH_3	21.21		
CH	59.5	59.23	49.75
COOH	170.2	169.9	179.8
phenyl	130.2	129.31	
	131.6	130.1	
	139.7	131.3	
	140.4	142.9	

[a] Chemical shifts are downfield from Me_4Si. [b] Sample dissolved in H_2O at pH ~ 3.0.

Spectroscopy of DMSA Adducts. Although we were unable to grow single crystals of the DMSA adducts suitable for X-ray diffraction, there can be little doubt as to their identity. The infrared spectra of the adducts clearly show the OH groups of the acid as well as the C=O stretch of the acid. Also, the stretches due to substituted phenyl groups can be clearly seen. The mass spectra also show the presence of various recognizable fragments, although the parent ions are not observed, most likely due to facile CO_2 loss.

The NMR spectra are also informative. The ^{13}C NMR spectrum again displays the characteristic downfield shift of the resonances of the carbons attached to the sulfur atoms, upon coordination to arsenic. They shift from 49 to 59 ppm. The proton NMR spectrum is not straightforward. Since we are using only the meso form of DMSA, the proton NMR spectrum should only contain one singlet. However, we have had considerable difficulty observing this. It is impossible to completely remove all traces of water from the compounds, and it appears to cause some complexity in the spectrum. The aliphatic proton resonance is weak and broad, and this is probably due to exchange caused by the acid groups or water. In addition, other peaks appear sporadically, suggesting that there is some decomposition occurring in solution.

Summary

The ligating properties of several vicinal dithiols toward arylarsenic dichlorides was investigated. These compounds readily chelate to organoarsenic(III) compounds, forming stable five-membered rings with pyramidal arsenic. The arsenic shows no tendency to adopt higher coordination environments, preferring only three-coordination. The stable crystalline adducts can be isolated and their properties studied. The shift of the resonances of the carbons attached to the sulfurs in the ^{13}C NMR spectrum was found to be most indicative of coordination.

Supplementary Material Available: Tables of crystallographic data and anisotropic thermal parameters (2 pages); a listing of structure factor amplitudes (18 pages). Ordering information is given on any current masthead page.

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Syntheses and Structures of K_3MQ_4 (M = Nb, Ta; Q = S, Se)

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The four tetrachalcogenometalates K_3NbS_4, K_3NbSe_4, K_3TaS_4, and K_3TaSe_4 have been obtained by direct reaction among the elements at 850 °C. The structures of K_3NbS_4 and K_3NbSe_4 have been determined by single-crystal X-ray diffraction methods. K_3TaS_4 and K_3TaSe_4 are isostructural with K_3NbS_4 and K_3NbSe_4, as determined from X-ray Guinier photographs. All of them crystallize with four formula units in space group D_{2h}^{16}-*Pnma* of the orthorhombic system in cells of dimensions a = 9.214 (8), b = 10.484 (6), and c = 9.319 (7) Å for K_3NbS_4, a = 9.599 (2), b = 11.042 (3), and c = 9.660 (2) Å for K_3NbSe_4, a = 9.283 (2), b = 10.806 (3), and c = 9.387 (2) Å for K_3TaS_4,and a = 9.682 (3), b = 11.276 (4), and c = 9.712 (3) Å for K_3TaSe_4. The final refinements of 43 variables lead to R and R_w values of 0.106 and 0.115 for K_3NbS_4 and 0.069 and 0.083 for K_3NbSe_4. These structures are of the K_3VS_4 type and contain discrete K^+ and tetrahedral MQ_4^{3-} ions. In K_3NbS_4 the Nb–S distances range from 2.241 (8) to 2.258 (8) Å and the S–Nb–S angles range from 108.3 (2) to 111.6 (3)°. In K_3NbSe_4 the Nb–Se distances range from 2.387 (1) to 2.403 (1) Å and Se–Nb–Se angles range from 108.49 (3) to 111.68 (5)°.

Introduction

Among the tetrachalcogenometalates MQ_4^{3-} (M = V, Nb, Ta; Q = S, Se, Te) only the VS_4^{3-} ion has been synthesized by wet-chemical methods.[1] Attempts to prepare MS_4^{3-} (M = Nb, Ta) from $M(OEt)_5$ and $S(SiMe_3)_2$ in acetonitrile led to the polynuclear cage anions $M_6S_{17}^{4-}$.[2] Similarly, a number of other synthetic strategies involving wet-chemical methods have failed to afford the $NbSe_4^{3-}$ or $TaSe_4^{3-}$ ions.[3] Hence, synthesis via solid-state reactions of the alkali-metal tetrachalcogenometalates A_3MQ_4 (M = Nb, Ta; Q = S, Se) and their subsequent dissolution might be a route to such ions. By direct combination of the constituent elements, some of these ions have been synthesized in the solid state. Thus Tl_3MQ_4[4] (M = V, Nb, Ta; Q = S, Se) and Cu_3MQ_4[5] (M = V, Nb, Ta; Q = S, Se, Te) have been obtained; these compounds adopt a cubic structure built from MQ_4^{3-} tetrahedra in which there are significant anion–cation interactions.

Table I. Crystal Data for K_3NbS_4 and K_3NbSe_4

formula	K_3NbS_4	K_3NbSe_4
fw	338.45	526.05
a, Å	9.214 (8)	9.599 (2)
b, Å	10.484 (6)	11.042 (3)
c, Å	9.319 (7)	9.660 (2)
V, Å^3	900.2	1023.8
Z	4	4
t, °C	−150	−150
d_{calcd}, g/cm^3	2.497	3.412
space group	D_{2h}^{16}-*Pnma*	D_{2h}^{16}-*Pnma*
μ, cm^{-1}	34.05	163.51
R on F_o	0.106	0.069
R_w on F_o	0.115	0.083

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