

Synthesis and characterization of a rare arsenic trithiolate with an organic disulfide linkage and 2-chloro-benzo-1,3,2-dithiastibole

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Abstract

The synthesis and structural characterization of bis(2-(1,3,2-benzodithiarsol-2ylsulfanyl)-benzenesulfide) (**1**) and 2-chloro-benzo-1,3,2-dithiastibole (**2**) are reported. Both compounds contain a five-membered ring with sulfur bound to the central group 15 atom. In compound **1**, the centroidal distance between each opposing arene is 3.819 Å. An alternating arene sandwich structure is created in the solid state with an intramolecular centroid distance between each set of stacked rings of 5.467 Å. Compound **2** is an example of a three coordinate antimony dithiolate. It does not possess any of the secondary interactions seen in **1**. Compound **2** demonstrates trigonal bipyramidal geometry around the antimony if secondary interactions are considered.

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1. Introduction

Arsenic thiolates have been of interest since World War II with the treatment of Lewisite poisoning ($\text{Cl}_2\text{AsCH}=\text{CHCl}$) with the dithiol 2,3-dimercaptopropanol more commonly known as British Anti-Lewisite (BAL) [1]. BAL has several undesired side effects; it causes hypertension and tachycardia as well as headache, nausea, vomiting, salivation, and pain. It is generally given by intramuscular injection. The most common oral chelate in use today for arsenic poisoning is *meso*-2,3-dimercaptosuccinic acid.

A safe and easy method for the disposal of Lewisite and other arsenic based “war gases” was sought. The addition of 1,2-ethanedithiol to arsenic trichloride was shown to quantitatively yield 2-chloro-dithiarsolane and two equivalents of HCl [1]. The same synthetic technique was used to synthesize the compounds discussed here.

Bis(2-(1,3,2-benzodithiarsol-2ylsulfanyl)-benzenesulfide) is the first published arsenic trithiolate which includes an

organic disulfide linkage elsewhere in the molecule. There are several known arsenic compounds with disulfide linkages in the molecule. However, the compounds are typically arsenic–sulfur clusters or cage compounds lacking any organic moieties.

Recent interest in arsenic thiolates as building blocks in self-assembled macrocycles [2,3] along with a lack of single crystal X-ray structural analysis of relatively simple arsenic thiolates has prompted our work on the synthesis and characterization of several arsenic dithiolates [4]. These are of the general formula RS_2AsX where R is an organic group connecting the sulfurs and $\text{X} = \text{Cl}$ or I. The coordination environment of the As atoms in these compounds demonstrates the overall characteristics of the series with the common feature being an axial placement of terminal halides in the heterocyclic rings. Thus, the anomeric effect dominates placement of the terminal halides in these compounds. This is well established for six-membered rings and can be seen in the two compounds reported here as well [5]. The present work will add to the understanding of group 15 dithiolate compounds with the structure and characterization of bis(2-(1,3,2-benzodithiarsol-2ylsulfanyl)-benzenesulfide) (**1**) and 2-chloro-benzo-1,3,2-dithiastibole (**2**) [4].

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2. Experimental

Caution. Arsenic compounds are toxic and should be handled with care.

2.1. General methods

AsF₃ was purchased from SynQuest laboratories and SbCl₃ was obtained from Aldrich. AsF₃ is highly toxic and carcinogenic and along with any byproducts must be handled and disposed of as hazardous. The dithiols were obtained from Aldrich and used as delivered without further purification. All manipulations were carried out using standard inert atmosphere techniques under a nitrogen atmosphere. NMR spectra were obtained at room temperature in CDCl₃ on Varian Gemini 200 or Varian Innova 400 NMR spectrometers. Chemical shifts are reported in ppm, relative to tetramethylsilane. FT-IR spectra were recorded as KBr pellets on a Varian Spec 9800. Melting points were obtained on a Mel-Temp melting point apparatus.

2.2. Preparation of bis(2-(1,3,2-benzodithiarsol-2-ylsulfanyl)-benzenesulfide) (1)

Arsenic trifluoride (1.02 g, 7.74 mmol) was added dropwise to 1,2-benzenedithiol (1.00 g, 7.03 mmol) at room temperature. The solvents CCl₄ (10 mL) and CH₂Cl₂ (10 mL) were added and the reaction was stirred overnight and cooled to –20 °C and kept for a week under an ambient atmosphere. Yellow block-like crystals formed in the solution. The solvent was then removed yielding 0.45 g of a crystalline solid was obtained (yield 36.0%); m.p.: 158–160 °C. ¹H NMR (CDCl₃, ppm): δ 7.60 (phenyl, q, 2H), δ 7.47 (phenyl, q, 2H), δ 7.45 (phenyl, q, 4H), δ 7.22 (phenyl, q, 2H) δ 7.11 (phenyl, q, 2H), δ 7.08 (phenyl, q, 4H). ¹³C NMR (CDCl₃, ppm): δ 143.75 (–phenyl–), δ 139.99 (–phenyl–), δ 135.57 (–phenyl–), δ 128.92 (–phenyl–), δ 127.00 (–phenyl–), δ 1125.81 (–phenyl–). IR (ν, cm^{–1}, KBr): 3430.61 (vwb), 3048.05 (m), 1627.75 (mb), 1444.02 (s), 1436.66 (s), 1418.31 (w), 1384.42 (m), 1271.38 (w), 1246.87 (w), 1105.89 (m), 1032.19 (m), 800.57 (s), 737.29 (vs), 658.78 (w), 479.23 (w), 424.50 (w). Mass spectra (GC-MS): 215 (AsSC₆H₄S)⁺, 108 (SC₆H₄)⁺.

2.3. Preparation of 2-chloro-benzo-1,3,2-dithiastibole (2)

1,2-benzenedithiol (1.00 g, 7.03 mmol) in benzene (10 mL) was added dropwise to antimony trichloride (1.60 g, 7.01 mmol) in benzene (30 mL) at room temperature. The solution turned yellow upon addition and was stirred for an hour under a nitrogen atmosphere. The solid present was dissolved by the addition of 15 mL of methanol. Approximately 10 mL of solvent was then removed by vacuum. Crystals formed shortly thereafter and were kept at room temperature. The solution was filtered and 0.99 g of crystalline material was obtained (yield 47.4%);

m.p.: 170.0–172.0 °C. ¹H NMR(CDCl₃, ppm): δ 7.560 (benzene, m, 2H), δ 7.092 (benzene, m, 2H). ¹³C NMR (CDCl₃, ppm): δ 130.23 (=CH–), δ 125.77 (=CH–). IR (ν, cm^{–1}, KBr): 3045.79 (w), 1942.56 (w), 1909.15 (w), 1790.01 (w), 1603.65 (w), 1549.47 (w), 1442.79 (vs), 1429.02 (w), 1421.04 (s), 1249.39 (m), 1100.26 (m), 1028.58 (m), 940.61 (w), 744.93 (vs), 650.13 (m), 463.08 (m), 426.67 (m). Mass spectra (GC-MS): 261 (SbSC₆H₄S)⁺, 185 (SbS₂)⁺, 153 (Sb–S)⁺.

2.4. X-ray crystallographic analysis

X-ray diffraction data were collected at 90 K on a Nonius Kappa CCD diffractometer unit using Mo Kα radiation from colorless regular shaped crystals mounted in Paratone-N oil on glass fibers. Initial cell parameters were obtained using DENZO from 1° frames and were refined by least-squares using all data-collection frames (SCALEPACK) [6]. The structures were solved by direct methods (SHELXL-97) and completed by difference Fourier methods (SHELXL-97) [7]. Refinement was performed against *F*² by weighted full-matrix least-squares method. Hydrogen atoms were placed at calculated positions using suitable riding models with isotropic displacement parameters derived from their carrier atoms. Non-hydrogen atoms were refined with anisotropic displacement parameters. Atomic scattering factors were taken from the International Tables for Crystallography volume C [8]. Details of crystal data, data collection, and structure refinement are listed in Table 1. Table 2 lists selected bond lengths and bond angles.

3. Discussion

Compound **1** was synthesized by direct addition of AsF₃ to 1,2-benzenedithiol. Upon addition, a brown viscous

Table 1
Crystallographic data for compounds **1** and **2**

	1	2
Empirical formula	C ₂₄ H ₁₆ As ₂ S ₈	C ₆ H ₄ ClS ₂ Sb
Formula weight	710.69	297.41
Space group	C2/c	Pbca
<i>a</i> (Å)	24.3415(4)	8.8985(6)
<i>b</i> (Å)	12.8324(2)	10.0884(8)
<i>c</i> (Å)	8.7729(2)	18.7374(15)
<i>α</i> (°)	90.0	90.0
<i>β</i> (°)	109.440(1)	90.0
<i>γ</i> (°)	90.0	90.0
<i>V</i> (Å ³)	2584.08(8)	1682.1(2)
<i>Z</i>	4	8
Density (g/cm ³)	1.827	2.349
Absorption coefficient (mm ^{–1})	9.366	4.011
Reflections collected	16482	12586
Unique reflections	2327	1928
<i>R</i> ₁ ^a	0.0265	0.0284
<i>wR</i> ₂ ^a	0.0662	0.0620

^a Final *R* indices [*I* > 2σ(*I*)].

Table 2
Selected bond distances (Å) and bond angles (°) for compounds **1** and **2**

	1 (M = As)	2 (M = Sb)
M(1)–S(1)	2.2465(7)	2.4118(9)
M(1)–S(2)	2.2331(6)	2.4037(10)
M(1)–S(3)	2.2930(7)	
M(1)–Cl(1)		2.4563(9)
C(1)–C(6) centroid to C(7)–C(12) centroid	3.819	
M(1)–Cl(1) intermolecular		3.356
M(1)–Cl(1) intermolecular		3.359
S(1)–M(1)–S(2)	91.86(2)	88.39(3)
S(1)–M(1)–S(3)	102.99(3)	
S(2)–M(1)–S(3)	103.61(2)	
S(1)–M(1)–Cl(1)		93.84(3)
S(2)–M(1)–Cl(1)		93.41(3)

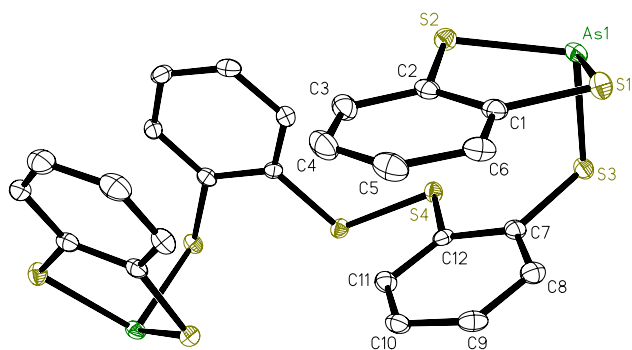


Fig. 1. Thermal ellipsoid plot (50%) of bis(2-(1,3,2-benzodithiarsol-2ylsulfanyl)-benzenesulfide) (**1**). Hydrogen atoms have been omitted for clarity.

substance formed. CCl_4 was then added to the viscous oil and the solid turned bright yellow in color. CH_2Cl_2 was added to the solution shortly thereafter and stirred, resulting in the crystallization of compound **1** as pale yellow crystals.

Compound **1** has six signals corresponding to the phenyl protons in the ^1H NMR and six signals in the ^{13}C NMR which is consistent with six magnetic environments available to the carbon atoms. This signifies that the compound is locked in conformation in solution. The carbons with no protons are not seen due to a lack of the NOE effect. Compound **1** displays the characteristic IR bands seen in organo-arsenic thiolates [9,10]. The band at 659 cm^{-1} is indicative of C–S bonds and the peaks although weak at 479 and 425 cm^{-1} are in the correct range for the As–S bonds in the ring.

Structurally, the bond lengths seen in **1** for As–S bonds are consistent with previously published compounds, for example 1,2-bis-dithiarsolan-2-ylmercapto-ethane [4]. The As–S bonds in **1** range from 2.23 Å to 2.29 Å. There are no intramolecular As– π interactions, despite the fact that As– π interactions are a well known characteristic of As-aromatic systems [3].

Compound **1** is also interesting because of an approximate (3°) variance from a 90° turn angle between the arene stacks within the molecule. The molecular structure and packing diagram of **1** can be found in Figs. 1 and 2, respectively. If **1** were used as a synthon for a larger supramolecular assembly, this could lead to a slow rotation within a two- or three-dimensional structure. Also, the gap between the opposing arene rings is 3.819 Å. This is close enough to

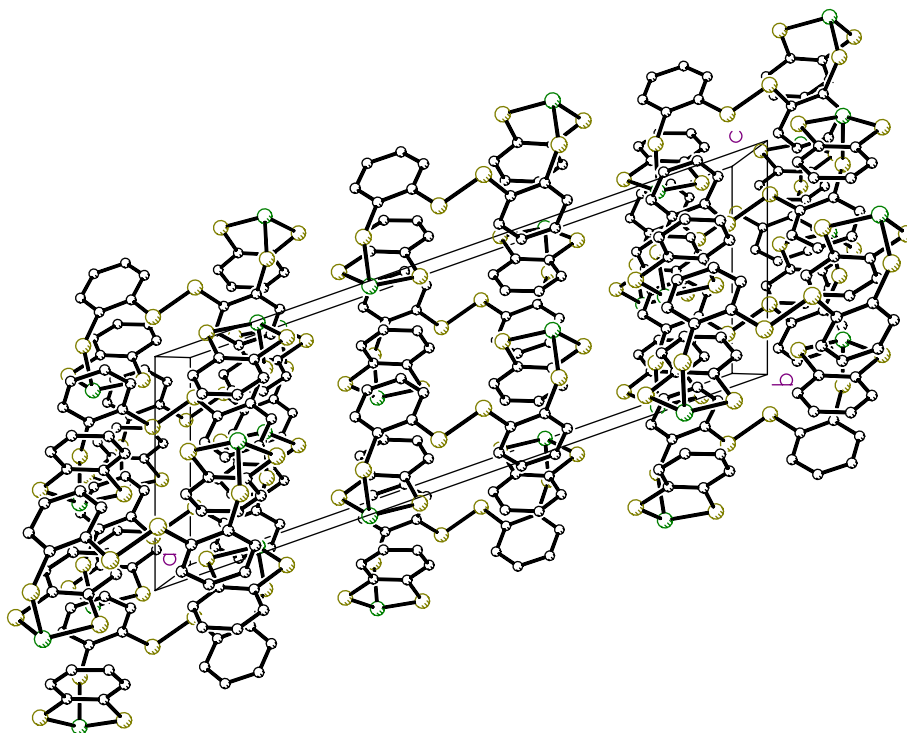


Fig. 2. Packing diagram of bis(2-(1,3,2-benzodithiarsol-2ylsulfanyl)-benzenesulfide) (**1**). Hydrogen atoms have been omitted for clarity.

accommodate a large transition metal cation; for example Ru(II), which has an average centroid distance from an arene to Ru(II) of 1.678 Å [11–13]. A Ru (II) cation would seemingly be a good choice for the synthesis of larger 2D and 3D systems.

To better understand the structure and bonding of **1**, it is compared to the published compound 1,2-bis-dithiarso-lan-2-ylmercapto-ethane (**3**) shown in Fig. 3 [4]. In comparison with **3**, the arsenic–sulfur bonds in **1** are almost identical with As1–S1, As1–S2, and As1–S3 having 2.2315 Å, 2.2472 Å, and 2.2610 Å bond lengths, respectively. In terms of the bond angles surrounding the arsenic center, the S1–As1–S2, S1–As1–S3, and S2–As1–S3 average bond angles are similar to the angles found in **3**. However, the bond angles around As in **1** are slightly wider than those in **3**. This is most likely due to the difference in the length of the hydrocarbon backbones in the two compounds.

Compound **2** was **1** synthesized by addition of 1,2-benzenedithiol to SbCl₃ in benzene. The solution turned yellow upon addition and HCl gas was evolved. Ethanol was added and stirred for 30 min and then approximately 75% of the solvent was removed under vacuum. Yellow crystals subsequently formed. The compound is soluble in most organic solvents. Compound **2** displays two proton signals in the ¹H NMR due to the symmetry of the molecule. In the ¹³C spectrum, the lack of protons on the carbons attached to the sulfurs, prohibit the NOE effect and thus those carbons are not seen. The IR spectrum of **2** shows the corresponding C–S stretches at 650 cm⁻¹, and Sb–S stretches at 463 cm⁻¹ and 427 cm⁻¹, respectively. A close arsenic analog of **2** has been used for derivatization with among others dialkylthiocarbamates and dialkyldi-

thiophosphates [14,15]. This is the first structural elucidation of **2** and its structure is shown in Fig. 4.

A similar reaction yielded an antimony (V) derivative bound to three benzenedithiol ligands which has been structurally characterized [16]. The Sb–S bond lengths in **2** are between 2.40 Å and 2.41 Å. This is the expected range for Sb–S bonds. The Sb–Cl bond length is approximately 2.46 Å. Sb has two close contacts at within 0.3 Å of the Sb–S Van der Waals radius which gives it a distorted trigonal bipyramidal molecular geometry if secondary interactions are considered. In comparison to **1** and **3**, the Sb–S bonds in **2** are approximately 0.2 Å longer. The bond angles are considerably narrower in **2** than in **1** as can be seen in Table 2.

4. Conclusion

As a coordinating ligand through the arsenic lone pairs, or as a basis for metallocenes in molecular self assembly, **1** opens several options for future compounds. The intramolecular π -stacking observed in the solid state suggests the possibility of η^2 -coordination of transition metals to form metallocenes. Thus **1** may have use as a linkage in supramolecular self assembly. However, the reactivity of the disulfide linkage would have to be considered.

Another remarkable possibility for further investigation of compound **1** is in the synthesis of a helical structure with rotation around the disulfide bond with the ability of the As lone pairs to donate to soft Lewis acids.

On the other hand, **2** is an example of an antimony (III) dithiolate with short intermolecular contacts but without π -stacking in the solid state. The secondary interactions give a distorted trigonal bipyramidal molecular environment around the antimony. Due to intermolecular interactions from two chlorines on near molecules, this interaction is apparently stronger than the π -interactions.

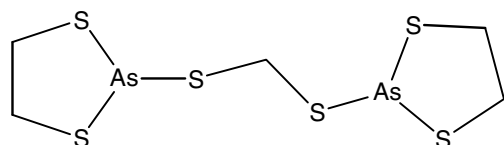


Fig. 3. 1,2-Bis-dithiarso-lan-2-ylmercapto-ethane (**3**).

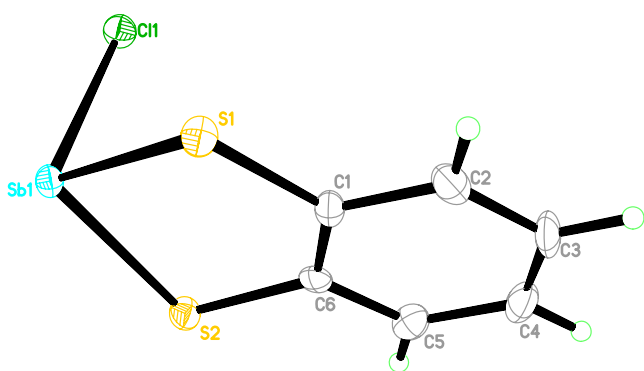


Fig. 4. Thermal ellipsoid plot (50%) of 2-chloro-benzo-1,3,2-dithiastibole (**2**).

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Appendix A. Supporting Information Available

CCDC 603073 and 603074 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article

can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.06.031](https://doi.org/10.1016/j.jorganchem.2006.06.031).

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