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**Preparation and Properties of Sodium
Dimethyldithioarsinate Dihydrate, $\text{Me}_2\text{AsS}_2\text{Na} \cdot 2\text{H}_2\text{O}$,
and Palladium(II) Dimethyldithioarsinate,
 $(\text{Me}_2\text{AsS}_2)_2\text{Pd}$**

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**Preparation and Properties of
Sodium Dimethyldithioarsinate Dihydrate,
Me₂AsS₂Na·2H₂O,
and Palladium(II) Dimethyldithioarsinate, (Me₂AsS₂)₂Pd**

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Preparation and Properties of
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and Palladium(II) Dimethyldithioarsinate, $(\text{Me}_2\text{AsS}_2)_2\text{Pd}$

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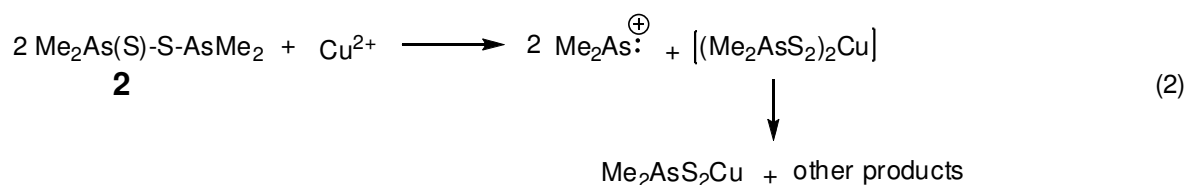
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7 **Abstract.** Palladium(II) acetate in non-deaerated chloroform splits Bunsen's cacodyl
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9 disulfide, $\text{Me}_2\text{As}(\text{S})\text{-S-AsMe}_2$, giving the slightly-chloroform-soluble complex $(\text{Me}_2\text{AsS}_2)_2\text{Pd}$
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11 and the arsonium ion Me_2As^+ . However, after a few minutes the complex reacted giving
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13 $\text{Me}_2\text{As}(\text{S})\text{-O-As}(\text{S})\text{Me}_2$ and other unidentified compound(s). Therefore, the complex
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15 $(\text{Me}_2\text{AsS}_2)_2\text{Pd}$ was prepared from sodium dimethyldithioarsinate dihydrate,
16
17 $\text{Me}_2\text{AsS}_2\text{Na}\cdot 2\text{H}_2\text{O}$, and palladium(II) acetate. $(\text{Me}_2\text{AsS}_2)_2\text{Pd}$ reacts with Pd^{II} and Ph_3P in a
18
19 different way compared to other $(\text{Me}_2\text{AsS}_2)_x\text{M}$ (M = heavy metal cation) and $(\text{Me}_2\text{PS}_2)_2\text{Pd}$.
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21 The reaction of equimolar quantities of $\text{Me}_2\text{AsS}_2\text{Na}\cdot 2\text{H}_2\text{O}$ and Ph_3P under argon involved
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23 four consecutive reactions with $\text{Me}_2\text{As-O-AsMe}_2$ and $\text{Me}_2\text{AsS}_2\text{Na}$ as the final products. The
24
25 salt $\text{Me}_2\text{AsS}_2\text{Na}\cdot 2\text{H}_2\text{O}$ has been structurally characterized: triclinic, $P\bar{1}$, $a = 6.0285(2) \text{ \AA}$, $b =$
26
27 $6.5552(2) \text{ \AA}$, $c = 12.1480(4) \text{ \AA}$, $\alpha = 98.282(2)^\circ$, $\beta = 93.994(3)^\circ$, $\gamma = 115.951(3)^\circ$, $V =$
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29 $422.38(3) \text{ \AA}^3$, $Z = 2$, $R_1 = 0.0207$, $wR_2 = 0.0414$.
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58 **Keywords:** Sodium dimethyldithioarsinate; Dimethylarsino dimethylthioarsinate (Bunsen's
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60 cacodyl disulfide); Palladium(II) dimethyldithioarsinate; Triphenylphosphine.

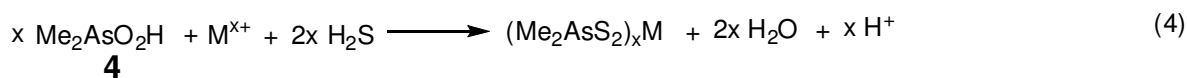
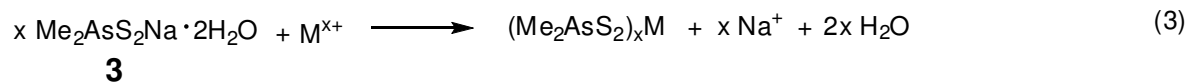
Introduction

Derivatives of P^V having the $>P(S)S^-$ group are of interest both for practical (agricultural and industrial) and theoretical (mode of coordination to metal cations) reasons [1-3].

Derivatives of As^V such as $(RO)_2AsS_2^-$ and $(RO)R'AsS_2^-$ cannot be prepared because of the hydrolytic instability of the $RO-As^V$ bond [4] but those of $Ph_2AsS_2^-$ and $Me_2AsS_2^-$ are known. For example, *Bunsen* [5] prepared salts (complexes) of the unknown [6] $Me_2As(S)SH$, LH, **1** with Au^I , Cu^I , Pb^{II} , Sb^{III} , and Bi^{III} by reacting the so-called Bunsen's cacodyl disulfide, $Me_2As(S)-S-AsMe_2$ **2** with metal salts according to the simplified equations (1) and (2). The complexes L_2Hg and LAg have also been prepared using the reaction of equation (1) and possible mechanisms for the reactions of equations (1) and (2) have been proposed [7].



Casey et al. [8] prepared the L_xM complexes with $M = Cr^{III}$, Mn^{II} , Co^{II} , Ni^{II} , Cu^I , Zn^{II} , Cd^{II} , and In^{III} according to equations (3) and (4).

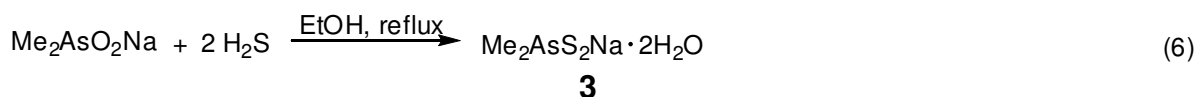
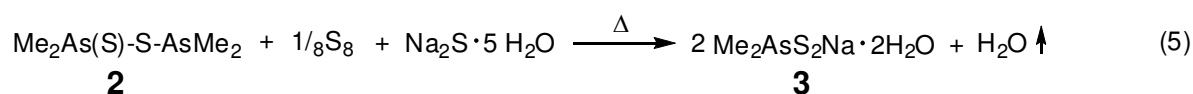


At the same time Förster et al. [9] prepared the L_xM complexes with $M = \text{Cr}^{\text{III}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Zn}^{\text{II}}$, and Cd^{II} , while the Sn^{IV} was prepared later on [10], both using the reaction of equation (3).

The $\text{Me}_2\text{AsS}_2^-$, L^- , anion is a ligand for organometallic derivatives of Sn^{IV} [10], Sb^{III} [11], Si^{IV} , Ge^{IV} and Pb^{IV} [12], Pt^{IV} [13], and V^{IV} [14] as well as for the carbonyls of Mn^{I} and Re^{I} [15].

The crystal structures of $LK \cdot 2\text{H}_2\text{O}$ [16], $L_3\text{Bi}$ [17], $L_3\text{In}$ [18], $L_3\text{Cr}$ [19], Ph_2SbL [20] and Me_2SnL_2 [21] have been reported as well as the solid state IR spectra [8] and magnetic properties [9] of some complexes. The thermal behaviour of the complexes prepared by Bunsen was studied by him in addition to a few chemical properties [5], and we have studied the same as well [7].

The key salt, $\text{Me}_2\text{As(S)S}^-\text{Na}^+ \cdot 2\text{H}_2\text{O}$ **3**, has been prepared according to equations (5) [8] and (6) [9].



We prepared Bunsen's cacodyl disulfide **2** [5, 22] and studied its *electrophilic* character towards Lewis bases of group 15 [6] and *nucleophilic* character towards Lewis acids: heavy metal cations [7] and molecular halides and thallium(III) acetate of group 13

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4 [23]. Heavy metal salts, split **2** into two parts, equations (1) and (2), i.e. to the complexes L_xM
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6 and to arsenium ion Me_2As^+ [7, 23].
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10 Since arsenium ions are reactive species, we wanted to find a salt of M^{x+} soluble in
11 non-polar solvents in order to react with **2** to give, preferably, an insoluble L_xM and a soluble
12 Me_2As^+ . This strategy would allow us to study the properties of Me_2As^+ in greater detail
13
14 than previously done [7]. Palladium acetate is soluble in chloroform, has a diamagnetic Pd^{II} ,
15
16 its reaction with **2** can be studied by 1H NMR, and we expected L_2Pd to be insoluble in
17
18 chloroform as were the other L_xM complexes prepared so far.
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24 In this paper we present our results on the reaction of palladium(II) acetate with **2**
25
26 which proved to be complicated and did not afford $(Me_2AsS_2)_2Pd$ **5**. The complex **5** was,
27
28 however, prepared from **3**, equation (3). Because **3** prepared according to equation (5) had a
29
30 melting point 222-224 °C (this work) while when prepared according to equation (6) had a
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32 melting point 181-182 °C [9] and >200 °C [24], we determined its structure by X-ray analysis.
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38 **Results and discussion**

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Table 1. ^1H NMR values of methyl and phenyl groups in CDCl_3 and CD_3OD , and ^{31}P NMR values of phosphorus compounds encountered in this work. Our δ values for the methyl protons have a range of less than ± 0.002 ppm of the quoted values (s = singlet, m = multiplet).

CDCl_3			CD_3OD		
Compound	δ , ppm	Compound	δ , ppm		
	$\text{Pd}(\text{OAc})_2$	1.997s	(3) ^b	$\text{Me}_2\text{AsS}_2\text{Na}\cdot 2\text{H}_2\text{O}$	1.907s
	AcOH	2.069s	(4)	$\text{Me}_2\text{AsO}_2\text{H}$	1.920s [7]
(2)	$\text{Me}_2\text{As}(\text{S})\text{-S-AsMe}_2$	2.164s, 1.544s [6]	(7·Na ⁺)	$\text{Me}_2\text{As-SNa}$	1.233s
(5) ^a	$(\text{Me}_2\text{AsS}_2)_2\text{Pd}$	2.212s	(8)	$\text{Me}_2\text{As-AsMe}_2$	~ 1.25s
(6)	$\text{Me}_2\text{As-S-AsMe}_2$	1.399s [6]	(9)	$\text{Me}_2\text{As}(\text{S})\text{ONa}$	1.736s
(7)	$\text{Me}_2\text{As-S}^-$	1.980→1.891s [6]	(10) ^c	$\text{Me}_2\text{AsO}_2\text{Na}\cdot 3\text{H}_2\text{O}$	1.557s
(8)	$\text{Me}_2\text{As-AsMe}_2$	1.1 [35]	(10) ^d	$\text{Me}_2\text{AsO}_2\text{Na}\cdot 3\text{H}_2\text{O}$	1.628s
(15)	$\text{Me}_2\text{As-SS-AsMe}_2$	1.399 [6]	(4) ^d	$\text{Me}_2\text{AsO}_2\text{H}$	1.923s
(16)	$\text{Me}_2\text{As}(\text{S})\text{-O-As}(\text{S})\text{Me}_2$	2.247 [7]	(11)	$\text{Me}_2\text{As-O-AsMe}_2$	1.275s, 1.270s [7]
	Ph_3P	7.30s		Ph_3P	7.25m, 7.33m
	$\text{Ph}_3\text{P=O}$	7.47m, 7.55m, 7.68m		$\text{Ph}_3\text{P=O}$	7.55m, 7.46m
	$\text{Ph}_3\text{P=S}$	7.44m, 7.50m, 7.72m [6]		$\text{Ph}_3\text{P=S}$	7.50m, 7.58m, 7.60m
	a: 2.250s in $[\text{D}_6]\text{DMSO}$			Ph_3P	-5.58, +8 [25]
	b: 1.993s, 1.95 [22], 1.99 [24] in D_2O			$\text{Ph}_3\text{P=O}$	+32.64, -27 [25]
	c: 0.1 M			$\text{Ph}_3\text{P=S}$	+43.27, -42.6 [25]
	d: mixture, both 0.1 M				

To simplify the text, in Table 1 we summarize the ^1H and ^{31}P NMR chemical shifts, in various solvents, of the compounds encountered in this work.

Preparation and physical properties of $\text{Me}_2\text{AsS}_2\text{Na}\cdot 2\text{H}_2\text{O}$ (3) and $(\text{Me}_2\text{AsS}_2)_2\text{Pd}$ (5)

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4 Casey et al. [8] prepared the salt **3**, equation (5), using the dihydrate, $\text{Na}_2\text{S}\cdot 2\text{H}_2\text{O}$, a rare
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6 compound [26] (but see ref. [27]). For the same reaction we used the pentahydrate,
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8 $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ [28, 29]. The nonahydrate, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, does not allow a satisfactory
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10 homogenization of the solid reactants because it melted [27] during the grinding. The smaller
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12 the scale (e.g. 0.5 mmol) the better the yields (~95%) because of the better heating of the
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14 solid mixture. The preparation of **3** from **2** according to equation (5) evidently involves the
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16 ring opening of S_8 by S^{2-} [30] to give $\text{S-S}_7\text{S}^-$. Then, this nucleophile reacts with **2**, most
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18 likely at the As=S sulfur [6], giving, after successive cycles, the salt **3**.
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24 The complex **5** was prepared from **3** by a stepwise replacement of the acetate groups
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26 of the trimeric [31, 32] palladium(II) acetate, $[\text{Pd}(\text{OAc})_2]_3$, under conditions [7] which
27
28 prevented the interaction of Pd^{II} with the formed **5**. The complex **5** keeps tenaciously MeOH,
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30 AcOH and probably H_2O (by IR and ^1H NMR) and prolonged drying over concentrated
31
32 sulfuric acid [5, 7] was necessary for satisfactory elemental analyses. While **3** melted, **5** upon
33
34 heating decomposed at ~ 195 °C to PdS and the foul-smelling $\text{Me}_2\text{As-S-AsMe}_2$ **6** indicating
35
36 that the formation of heavy metal sulfides, M_2S_x , is the driving force for such a decomposition
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38 [5, 7, 23]. The poor solubility of **5** points towards a polymeric structure. A saturated solution
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40 of **5** in CDCl_3 resonated at 2.212 ppm, Table 1, quite close (2.246 ppm) to the chloroform-
41
42 soluble $\text{Me}_2\text{AsS}_2^- \text{Me}_2\text{AsS-NEt}_3^+$ [6]. Its IR (KBr) spectrum showed the bands found [7, 8]
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44 and assigned [8] in other $(\text{Me}_2\text{AsS}_2)_x\text{M}$ complexes.
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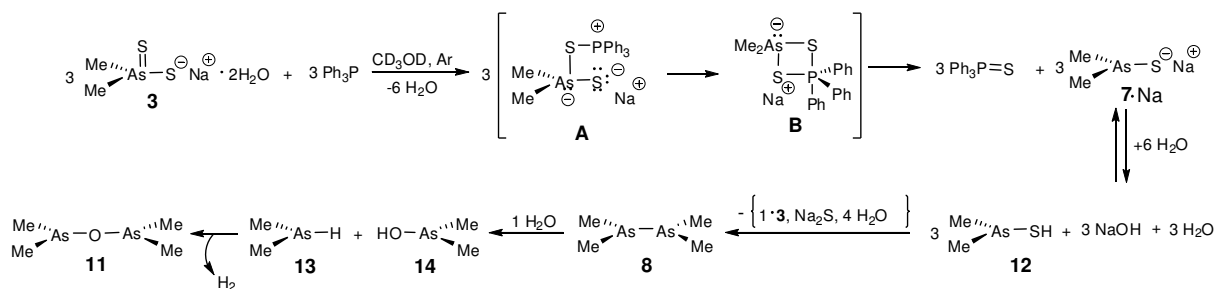
52 *Chemical properties of $\text{Me}_2\text{AsS}_2\text{Na}\cdot 2\text{H}_2\text{O}$ (**3**) and $(\text{Me}_2\text{AsS}_2)_2\text{Pd}$ (**5**)*

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57 Attempted desulfurization of $(\text{Me}_2\text{AsS}_2)_x\text{M}$ (M = heavy metal cation) by Ph_3P [or $(\text{MeO})_3\text{P}$]
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59 did not give the salts $(\text{Me}_2\text{AsS})_x\text{M}$ with the desired [33] thiolato ligand $\text{Me}_2\text{As-S}^-$ **7** but
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 $\text{Ph}_3\text{P=S}$ [or $(\text{MeO})_3\text{P=S}$] together with the metal sulfide M_2S_x and $\text{Me}_2\text{As-S-AsMe}_2$ **6** due to

the affinity of these cations to sulfur [7]. Since Na^+ does not have such an affinity, we tried to desulfurize **3** with Ph_3P hoping to get $\text{Me}_2\text{AsS}^-\text{Na}^+$, **7**· Na^+ . However, the course of the desulfurization was unexpected because 4 consecutive reactions took place.

Upon dissolution of an equimolar quantity of Ph_3P and **3** in CD_3OD under argon the ^1H NMR showed practically no binding of Ph_3P to **3**. In 1 h $\text{Ph}_3\text{P}=\text{S}$ started precipitating and the ^1H NMR spectrum of the supernatant showed the presence of **3** that had not yet reacted and a singlet due to **7**· Na^+ . In 20 h the supernatant contained **3**, $\text{Me}_2\text{As}-\text{AsMe}_2$ **8**, $\text{Me}_2\text{As}(\text{S})\text{O}^-\text{Na}^+$ **9**, and $\text{Me}_2\text{As}(\text{O})\text{O}^-\text{Na}^+$ **10** with a mole ratio of 1.00:1.60:0.04:0.03. The singlet at 1.736 was attributed to $\text{Me}_2\text{As}(\text{S})\text{O}^-\text{Na}^+$ **9** because the free acid $\text{Me}_2\text{As}(\text{S})\text{OH}$ in $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ 3:1 resonated at 2.056 ppm [6]. Triphenylphosphine was totally consumed in 48 h by which time the ^{31}P NMR spectrum showed $\text{Ph}_3\text{P}=\text{S}$ and very little $\text{Ph}_3\text{P}=\text{O}$, while the ^1H NMR spectrum showed **3**, $\text{Me}_2\text{As}-\text{O}-\text{AsMe}_2$ **11**, **9**, and **10** with a mole ratio of 1.00:1.20:0.06:0.04. After 5 days the ratio remained unchanged while a disagreeable odor, due to **11**, developed resembling that of **6** [7].



Scheme 1

These observations can be rationalized as in Scheme 1. Binding of Ph_3P to **3** was absent or very weak because the intermediate **A** has vicinal negatively charged atoms. However, the production of $\text{Ph}_3\text{P}=\text{S}$ must arise from the pentacoordinated intermediate **B**, and the production of $\text{Ph}_3\text{P}=\text{O}$ is discussed below. The product first formed must be **7**· Na^+ which

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4 will be in equilibrium with the unstable (but see [34]) thioarsinous acid **12**. This acid suffers
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6 disproportionation as *Tani* et al. [33] suggested giving **3**, **8**, and Na₂S. The highly reactive
7
8 diarsine **8** resonated at ~1.25 ppm (1.1 ppm in CDCl₃ [35]) and by reaction with H₂O should
9
10 give **13** and **14** [36]. The dimethylarsine, being a strong reducing agent [37], must react with
11
12 the dimethylarsinous acid **14** to give the anhydride **11** and dihydrogen.
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16 Admitting dioxygen to the solution, expelled some **11** and the rest was slowly
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18 oxidized in the presence of the waters of **3** to cacodylic acid **4** which, in the presence of the
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20 hydrolysable Na₂S, gave the salt **10**. The production of the salt **9** is more difficult to explain:
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22 it probably arises from the oxidation of S²⁻ to "S" which is then captured by an As^{III} atom.
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25
26 Running the desulfurization of **3** by Ph₃P in air we found the same final arsenic-
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28 containing compounds but, now, the production of Ph₃P=O was significant due to the reaction
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30 of **8** with dioxygen which should give [38] Me₂As-OO-AsMe₂ which, in turn, will be
31
32 deoxygenated by Ph₃P.
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36 These attempts at the preparation of the Me₂As-S⁻ anion **7** as well as those tried earlier
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38 [7], show that **7** can be produced but it seems that it is not stable.
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41 A suspension of **5** in CDCl₃ reacted with Ph₃P (1:2 mole ratio) giving, by ¹H NMR,
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43 Ph₃P=S and a prominent singlet attributable to unstable [22, 23] Me₂As-SS-AsMe₂ **15** and not
44
45 to the putrid **6** [6], which diminished with time giving a complex ¹H NMR spectrum in the
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47 region of 1.26-2.00 ppm. PdS was not produced. Thus, the reaction of **5** with Ph₃P is not in
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49 line with the other similar reactions of (Me₂AsS₂)_xM [7] and is not amenable to a simple
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51 interpretation. The behaviour of **5** also contrasts the behaviour of (Me₂PS₂)₂Pd with
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53 phosphines, e.g. (Me₂PS₂)₂Pd adds one and two Ph₃P ligands to give new complexes [39,
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55 40].
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59 The complex **5** dissolved, at RT, in pyridine was recovered intact by precipitation with
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Et₂O indicating that pyridine does not coordinate to the complexed Pd^{II}. When the pyridine

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4 solution was heated at 80 °C for 3 h, and cooled at -20 °C [31], a very small amount of a
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6 brown-black solid was formed. The reaction was not studied further.
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9 While heavy metal complexes, e.g. $(\text{Me}_2\text{AsS}_2)_2\text{Pb}$, react in non-deaerated methanol
10 with their own cations, e.g. Pb^{II} , to give PbS and a solution of cacodylic acid **4** plus
11 $\text{Me}_2\text{As}(\text{S})\text{-O-As}(\text{S})\text{Me}_2$ **16** [7], the reaction of **5** with $\text{Pd}(\text{OAc})_2$ (1:1 mole ratio) in non-
12 deaerated chloroform gave an *amorphous* black solid and a solution containing only acetic
13 acid implying that all added Pd^{II} and all $\text{Me}_2\text{As-}$ groups have been incorporated in the solid.
14 With twice the amount of $\text{Pd}(\text{OAc})_2$ over **5**, the black solid was formed and the orange
15 supernatant contained AcOH and the excess of $\text{Pd}(\text{OAc})_2$. Finally, the black solid was formed
16 when a chloroform solution of $\text{Pd}(\text{OAc})_2$ was added to an equimolar quantity of **3** in methanol
17 where the formed **5** reacted with the excess Pd^{II} . The identity of the, insoluble in all common
18 solvents, black precipitates could not be established from the elemental analyses and the
19 weights. Being amorphous, the quality of the powder X-ray diffraction spectrum was poor. Its
20 IR (KBr) spectrum was similar to that of **5**, but its bands were somewhat broader and the
21 intensity of the As-S stretching of the AsS_2Pd ring at 454 cm^{-1} [8] was much weaker than that
22 of **5**.
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45 *The reaction of Bunsen's cacodyl disulfide (2) with $\text{Pd}(\text{OAc})_2$*

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49 In all, so far studied, reactions of **2** with heavy metal cations [equations (1) and (2)] the
50 chloroform-soluble Me_2As^+ did not react with the insoluble L_xM complexes but it gave
51 cacodylic acid **4** [7]. The reaction of **2** with $\text{Pd}(\text{OAc})_2$ under a 1:1 stoichiometry in CDCl_3
52 gave the black solid described in the previous subsection, indicating that **2** does produce **5**
53 which then reacts with the excess of $\text{Pd}(\text{OAc})_2$. However, the dark red supernatant contained,
54 by ^1H NMR, apart from AcOH , two other prominent singlets at 1.434 and 2.180 ppm
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4 belonging to unknown compound(s) probably arising from the reaction of Me_2As^+ with **5** and
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6 with **2**. The singlets are not due to $\text{CH}_3\text{COO-AsMe}_2$ because, in CDCl_3 , its methyl groups
7
8 resonate at 2.47 and 1.84 ppm [41]. It seems, therefore, that when Pd^{II} is in excess, Pd^{II} , in
9
10 preference to Me_2As^+ , acts on the formed **5** giving the black solid. With stoichiometric
11
12 amounts of the reactants, equation (1), a small amount (visually) of **5** was initially formed and
13
14 then reacted giving a clear solution (without the black solid) containing by ^1H NMR: free
15
16 AcOH plus another unknown compound (both resonating at 2.082 ppm), $\text{Me}_2\text{As(S)-O-}$
17
18 As(S)Me_2 **16** [7], and smaller amounts of **2**, **5**, and **15**. The latter was produced at the early
19
20 stages and remained unchanged. Thus, when there is no Pd^{II} in the system, then Me_2As^+
21
22 attacks on the insoluble L_2Pd **5**, most likely on As=S sulfur, leading to the production of **15**
23
24 which is unstable when not complexed [22, 23]. The oxidation of **15** to the main product **16**
25
26 probably involves activated dioxygen [7] and an activator can be Pd^{II} for it is known that Pd^{II}
27
28 can catalyse the air oxidation of secondary alcohols to ketones [42, 43]. Finally, under a 3:1
29
30 stoichiometry, the dark red-brown solution had very little **2** (although it was in excess) and the
31
32 stronger singlets were due to **16**, implying a catalytic conversion of **2** to **16**, and free AcOH
33
34 plus the unknown compound (resonating at 2.082 ppm). In the last two cases it is not known
35
36 how Pd^{II} is kept in solution.
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47 Summarizing, in Bunsen's cacodyl disulfide $\text{Me}_2\text{As(S)-S-AsMe}_2$ **2** and in the complexes
48
49 $(\text{Me}_2\text{AsS}_2)_x\text{M}$, the As=S sulfur is the atom on which nucleophiles and electrophiles attack.
50
51 But the behaviour of the palladium(II) complex **5** towards nucleophiles and electrophiles is
52
53 exceptional compared to the other L_xM studied so far and this can be due to it being a planar
54
55 d^8 complex.
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The crystal structure of $\text{Me}_2\text{AsS}_2\text{Na}\cdot 2\text{H}_2\text{O}$ (3)

Table 2. Crystal data and structure refinement for Me₂AsS₂Na·2H₂O (**3**)

Formula	C ₂ H ₁₀ AsNaO ₂ S ₂
Molecular weight /g mol ⁻¹	228.13
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Unit cell dimensions	
<i>a</i> /Å	6.0285(2)
<i>b</i> /Å	6.5552(2)
<i>c</i> /Å	12.1480(4)
α /deg	98.282(2)
β /deg	93.994(3)
γ /deg	115.951(3)
Volume /Å ³	422.38(3)
<i>Z</i> , <i>D</i> _{calc} /(<i>Mg</i> /m ³)	2, 1.794
Absorption coefficient /mm ⁻¹	4.496
<i>F</i> (000)	228
Crystal size /mm	0.14 × 0.11 × 0.08
θ range for data collection /deg	3.43 to 28.50
Reflections collected / unique	7358 / 2117 (<i>R</i> _{int} = 0.0295)
Index ranges	-8 ≤ <i>h</i> ≤ 8, -8 ≤ <i>k</i> ≤ 8, -15 ≤ <i>l</i> ≤ 16
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/ restraints /parameters	2117 / 4 / 87
Goodness-of-fit on <i>F</i> ²	0.983
<i>R</i> ₁ , <i>wR</i> ₂ indices [<i>I</i> > 2σ(<i>I</i>)]	0.0207, 0.0414
<i>R</i> ₁ , <i>wR</i> ₂ indices (all data)	0.0275, 0.0422
Largest diff. peak and hole /e Å ⁻³	0.653 and -0.328

Table 3. Atomic coordinates^{a)} and thermal displacement parameters^{b)} for Me₂AsS₂Na·2H₂O.

Atom	x	y	z	U_{eq} (Å ²)
As	0.10406(3)	0.43900(3)	0.701426(15)	0.00969(6)
C1	0.3310(4)	0.3832(4)	0.61353(16)	0.0160(4)
C2	-0.2073(4)	0.1660(3)	0.65079(17)	0.0164(4)
S1	0.22176(9)	0.46255(8)	0.87539(4)	0.01113(10)
S2	0.07530(9)	0.73526(8)	0.66564(4)	0.01332(11)
Na	-0.17689(13)	0.15187(13)	0.98329(6)	0.01291(17)
O1	-0.5651(2)	0.0840(2)	0.89047(11)	0.0138(3)
H11	-0.626(4)	0.176(3)	0.8844(18)	0.021
H12	-0.644(4)	-0.007(3)	0.8287(14)	0.021
O2	-0.1765(2)	-0.1912(2)	0.88900(11)	0.0144(3)
H21	-0.324(3)	-0.292(3)	0.8847(19)	0.022
H22	-0.128(4)	-0.208(4)	0.8260(13)	0.022

^{a)} Estimated standard deviations of the last significant digits in parenthesis.

^{b)} U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Selected structural data for Me₂AsS₂Na·2H₂O.

<i>Bond lengths (Å) and bond angles (°)</i>				
As–C1	1.9169 (18)	Na–O1	2.3503 (14)	
As–C2	1.920 (2)	Na–O2	2.3732 (15)	
As–S1	2.1435 (5)	Na–O1 ⁱⁱⁱ	2.4641 (16)	
As–S2	2.1255 (5)	Na–O2 ⁱⁱ	2.4403 (15)	
S1–Na	2.9267 (9)	Na–Na ⁱ	4.0461 (15)	
S1–Na ⁱ	2.9701 (8)	Na–Na ⁱⁱ	3.5364 (13)	
		Na–Na ⁱⁱⁱ	3.6014 (15)	
C1–As–C2	103.74 (9)	As–S1–Na	112.74 (2)	
C1–As–S2	109.64 (6)	As–S1–Na ⁱ	110.28 (2)	
C2–As–S2	110.48 (6)	Na–S1–Na ⁱ	86.65 (2)	
C1–As–S1	108.96 (6)	S1–Na–O1 ⁱⁱⁱ	166.93 (4)	
C2–As–S1	109.30 (6)	O2–Na–S1 ⁱ	171.35 (5)	
S1–As–S2	114.201 (19)	O1–Na–O2 ⁱⁱ	167.98 (6)	
<i>Hydrogen bonds (Å and °)</i>				
D–H...A	D–H	H...A	D...A	D–H...A
O1–H11...S1 ^{iv}	0.841 (13)	2.436 (13)	3.2758 (13)	176 (2)
O1–H12...S2 ^v	0.846 (13)	2.391 (13)	3.2285 (14)	171 (2)
O2–H21...S1 ^v	0.838 (13)	2.478 (13)	3.3078 (15)	171 (2)
O2–H22...S2 ^{vi}	0.849 (13)	2.439 (14)	3.2766 (14)	169 (2)

Symmetry codes: (i) $-x, 1-y, 2-z$; (ii) $-x, -y, 2-z$; (iii) $-1-x, -y, 2-z$; (iv) $-1+x, y, z$; (v) $-1+x, -1+y, z$; (vi) $x, -1+y, z$.

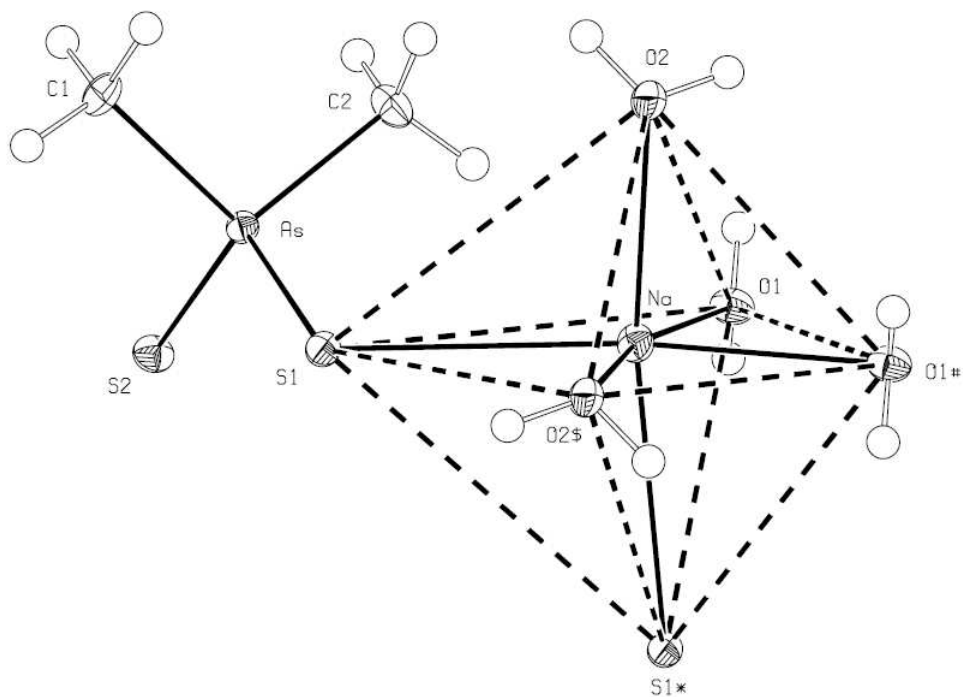


Figure 1. The basic unit of compound **3** showing the coordination about the potassium ion (distorted octahedral) and the numbering scheme (thermal ellipsoids at the 50% probability level).

Symmetry codes: (*) $-x, 1-y, -z$; (\$) $-x, 2-y, -z$; (#) $1-x, 2-y, -z$.

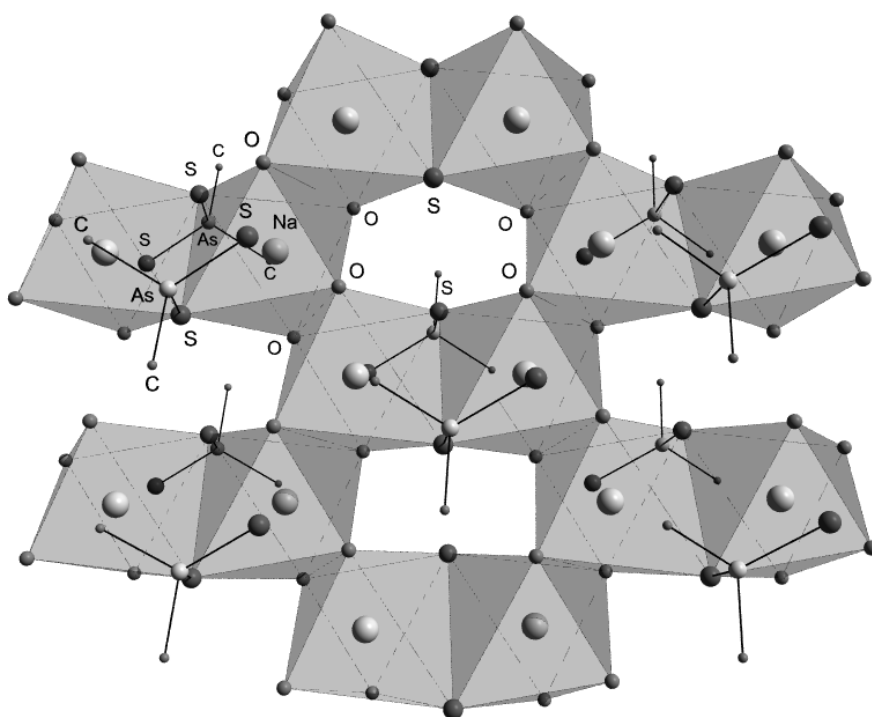


Figure 2. View of the layer structure of **3** in the *ab* plane showing the NaO_4S_2 octahedra. Hydrogen atoms have been omitted for clarity. The drawing was prepared with the *DIAMOND* [50] software.

Crystal data, details of data collection and structure refinement are listed in Table 2. Atomic coordinates and thermal displacement parameters are given in Table 3 and selected bond lengths and angles in Table 4. Figure 1 illustrates the molecular structure with the atom numbering scheme. The coordination environment around the arsenic atom in the Me_2AsS_2 group is distorted tetrahedral; the S-As-S angle of $114.20(2)^\circ$ is noticeably larger and the C-As-C angle of $103.74(9)^\circ$, smaller than the tetrahedral angle. The two As-S bonds have similar lengths [$2.1435(5) \text{ \AA}$ to S1 and $2.1255(5) \text{ \AA}$ to S2] and are intermediate between a single (*ca.* 2.21 \AA) and a double (*ca.* 2.07 \AA) bond, implying delocalization of the negative

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4 charge over the AsS₂ moiety of the structure. Similar delocalization has also been observed in
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6 similar crystal structures e.g., piperidinium diphenyldithioarsinate [33], potassium
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8 dimethyldithioarsinate dihydrate [16], tris(dimethyldithioarsinate)chromium(III) [19], and
9
10 phenylantimony(III) dimethyldithioarsinate [20]. The fact that S1 atom is coordinated to Na⁺
11
12 ions while S2 makes no major contacts accounts for the small difference observed among the
13
14 As–S bonds.
15
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19 Each sodium ion is surrounded by two sulfur and four water oxygen atoms forming a
20
21 distorted octahedron in which the sulfurs occupy *cis*-positions. The deviation from the
22
23 octahedral geometry is evidenced by the values of *trans* angles of the polyhedron [166.93 (4)
24
25 to 171.35 (5)°]. The ranges of Na–S and Na–O distances are 2.9267(9) – 2.9701(8) and
26
27 2.3503(14) – 2.4641(16) Å, respectively.
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29

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31 The NaO₄S₂ octahedra are linked together by edge-sharing, resulting in the formation
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33 of layers in the *ab* plane with every third octahedron missing, Figure 2. The stability within
34
35 each layer is enhanced by a network of weak O–H...S bonds involving hydrogens of the two
36
37 water molecules and the two sulfur atoms (see Table 4). It is noteworthy that the water
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39 molecules contribute actively - through coordination and hydrogen bonds - towards the
40
41 supramolecular organization of the structure. To complete the picture, the NaO₄S₂ octahedra
42
43 constitute the major part of the structure, while the Me₂AsS₂ groups are arranged on either
44
45 side of each layer. The packing (layer structure) of the present compound **3** is very similar to
46
47 that of sodium diethyldithiophosphate dihydrate [44] and potassium dimethyldithioarsinate
48
49 dihydrate [16]. However, the latter structure contains two symmetry-independent potassium
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51 ions which have the same atoms coordinated about them but their spatial arrangement is
52
53 different (the sulfur atoms are at *cis* and *trans* positions).
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Experimental Section

General

Cacodylic acid (Serva), sodium cacodylate trihydrate (Fluka), and sodium sulfide hydrate ($\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$) (Ferak) were used. Triphenylphosphine was recrystallized from methanol, m.p. 80-81 °C. Palladium(II) acetate (Merck) m.p. 204-206 °C dec. (lit. [31] 205 °C), ^1H NMR (CDCl_3 , TMS), δ : 1.997 singlet with small singlets at 1.894, 1.972, 2.030, and 2.100, was used without further purification. AR grade solvents were used, while dichloromethane was dried over A_4 molecular sieves. CDCl_3 and CD_3OD were not dried nor de-aerated. For experiments under argon, CD_3OD (C. E. Saclay, Gif-Sur-Yvette, France) packaged under argon was further purged with Ar. Silica gel 60 H (Merck) was used for thin layer chromatography (TLC). Spots on TLCs were made visible by iodine vapours.

IR spectra were obtained on a Perkin-Elmer model 16PC FT-IR spectrometer. ^1H NMR (400 MHz) and ^{31}P NMR (162 MHz) spectra were recorded on a DPX Avance Spectrometer in CDCl_3 , CD_3OD or $[\text{D}_6]\text{DMSO}$ with internal TMS (0.000) as standard, D_2O with DSS (2,2-dimethyl-2-silapentane-5-sulfonate, sodium salt) (0.000) as standard while the ^{31}P spectra were referenced to 85% aqueous H_3PO_4 in D_2O (0.00 ppm). Downfield shifts are positive while upfield shifts are negative in both cases. When needed, the NMR tubes were tumbled on a test tube rotator. Powder X-ray spectrum was recorded on a Siemens powder X-ray diffractometer model D5000. Elemental analyses were obtained through the Center of Instrumental Analyses, University of Patras, Patras, Greece.

Preparation of sodium sulphide pentahydrate, $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$

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4 Sodium sulphide nonahydrate, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$, was obtained from $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ (20 g) and water
5
6 (10 ml) prewarmed to 50 °C [45], cooled to -20 °C till solidification and then left at +4 °C for
7
8 1 h. Filtration, washing with absolute ethanol (1x10 ml) and ether, and brief (30 min) drying
9
10 in vacuum gave the nonahydrate (8.2 g) as needles, m.p. 52 °C shrinks but does not melt (lit.
11
12 [27] ~50 °C). By heating and stirring at 100 °C a quantity of $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in a round-bottomed
13
14 flask connected to a water aspirator gave the expected weight of the pentahydrate as an off-
15
16 white solid.
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24 *Preparation of sodium dimethyldithioarsinate dihydrate, $\text{Me}_2\text{AsS}_2\text{Na}\cdot 2\text{H}_2\text{O}$ (3)*

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26
27

28 A mixture of Bunsen's cacodyl disulfide **2** (548 mg, 2 mmol), sodium sulphide pentahydrate
29
30 (337 mg, 2 mmol) and octasulfur (64 mg, 2 mmol sulfur atoms) was grounded and mixed
31
32 intimately in an agate mortar. The powder was transferred to a flattened-bottom glass
33
34 evaporating basin preheated at 105 °C. At once a dark yellow mass formed which, in seconds,
35
36 solidified to an off-white solid. Heating was continued for 3 h grinding occasionally with a
37
38 flattened glass rod. To the cooled solid, 95% ethanol (15 ml) was added, boiled and the hot
39
40 yellow solution filtered (Pasteur pipette plugged with cotton). Upon cooling, the solution
41
42 became colorless and crystallized. After overnight cooling at +4 °C, centrifugation and drying
43
44 in vacuum gave the salt **3** as white plates (not suitable for X-rays) (642 mg, 70%), m.p. 222-
45
46 224 °C (lit. [9] 181-182 °C, [24] >200 °C). Its IR (KBr) spectrum was as published [8]. ^1H
47
48 NMR (CD_3OD , TMS), δ : 1.907 (s, 6H), 4.814 (s, 4H for H_2O); ^1H NMR (D_2O , DSS), δ :
49
50 1.993 (s), Table 1.
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59 *Preparation of palladium(II) dimethyldithioarsinate or*
60 *bis(dimethyldithioarsinato)palladium(II), $(\text{Me}_2\text{AsS}_2)_2\text{Pd}$ (5)*

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6
7 To a vigorously stirred solution of **3** (137 mg, 0.6 mmol) in methanol (7 ml) was added
8
9 dropwise during 2 h, a solution of palladium(II) acetate (45 mg, 0.2 mmol) in chloroform (1
10
11 ml). The dark brown suspension was stirred at RT for 2 h, centrifuged, washed with methanol
12
13 (1x2 ml) leaving to settle at RT for 2 h before centrifuging and dried in vacuum to give the
14
15 product **5** (67.5 mg, 76%) as a dark brown powder. It did not melt but decomposed at ~195 °C
16
17 giving off Me₂As-S-AsMe₂ **6**. It is insoluble in Et₂O, sparingly soluble in CHCl₃ and even
18
19 less soluble in MeOH and Me₂CO, and soluble in pyridine giving a dark red solution from
20
21 which **5** precipitates by adding Et₂O. It keeps tenaciously AcOH, MeOH, and possibly H₂O
22
23 (by ¹H NMR) which are removed by keeping it over concentrated sulfuric acid [5] for more
24
25 than two weeks. C₄H₁₂S₄As₂Pd (*M_r* 444.64); C 10.92 (calc. 10.80), H 2.55 (2.72), S 28.40
26
27 (28.85)%. IR (KBr) : 3418 vw, broad, 2982 w, 2090 w, 1610 w, 1394 s, 1250 m, 908 vs, 862
28
29 vs, 750 m, 596 s, 452 vs. ¹H NMR (CDCl₃), δ : 2.212 (s) and very small singlets at 1.679 and
30
31 2.459 ppm; ([D₆]DMSO); δ: 2.250 ppm, Table 1.
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40 *Reaction of Ph₃P with Me₂AsS₂Na·2H₂O (3) and with (Me₂AsS₂)₂Pd (5)*

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43
44
45 In NMR tubes were added **3** (50 μmol), Ph₃P (50 μmol) and purged with argon. Then, argon-
46
47 packaged CD₃OD (0.6 ml) was added in each tube. By shaking for 30 min the slightly soluble
48
49 in methanol triphenylphosphine was dissolved and the progress was followed by ¹H and ³¹P
50
51 NMR for 5 days. Then, dioxygen was admitted and the progress of the oxidation was
52
53 followed by ¹H NMR for another 5 days. Other experiments were conducted without
54
55 exclusion of air. The results are described in the Results Section.
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4 To a suspension of **5** (45 μmol) in CDCl_3 (0.6 ml), Ph_3P (90 μmol) was added and shaken for
5
6
7 4 h. A very dark brown solution resulted after 10 min. The results of the ^1H NMR analyses
8
9 are described in the Results Section.
10

11 12 13 *Reaction of $\text{Pd}(\text{OAc})_2$ with $(\text{Me}_2\text{AsS}_2)_2\text{Pd}$ (**5**)*

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18 In an NMR tube were added **5** (50 μmol), $\text{Pd}(\text{OAc})_2$ (50 μmol) and CDCl_3 (0.6 ml) and
19
20 shaken for 2 h. The pale orange supernatant contained only free acetic acid and traces of
21
22 $\text{Pd}(\text{OAc})_2$. Centrifugation and washing with chloroform gave a supernatant (3.3 mg of a
23
24 brownish film) and a black solid (26 mg) having the attributes described in the following
25
26 experiment.
27
28
29
30
31
32

33 To a solution of **3** (0.1 mmol) in methanol (1 ml) in a centrifuge tube was added dropwise,
34
35 while stirring, a solution of $\text{Pd}(\text{OAc})_2$ (0.1 mmol) in chloroform (2 ml). When half of the Pd^{II}
36
37 has been added a brown suspension of **5** was formed which, thereafter, became black. Stirring
38
39 was continued for 2 h. Centrifugation and washing with methanol (2x2 ml) gave clear
40
41 colorless supernatants and an amorphous black solid (23.3 mg; expected for equimolar PdS
42
43 and, e.g., $\text{Me}_2\text{As}(\text{O})\text{-S-Pd-S-As}(\text{S})\text{Me}_2$: 28.4 mg). The black solid did not melt up to 250 $^\circ\text{C}$,
44
45 and was insoluble in CHCl_3 , Me_2CO , MeOH , DMF , pyridine, H_2O . For the mixture
46
47 $\text{PdS}\cdot\text{C}_4\text{H}_{12}\text{OS}_3\text{As}_2\text{Pd}$ (M_r 138.46 + 428.57); C 9.02 (calc. 8.47), H 1.85 (2.13), S 21.86
48
49 (22.61)%. **IR** (KBr) : 2982 w, 2918 mw, 2852 w, 1640 w, 1570 w, 1392 ms, 1244 mw, 906 s,
50
51 860 vs, 742 w, 594 m, 454 m. The powder X-ray diffraction spectrum showed two not so
52
53 strong peaks matching those of $(\text{MeOCS}_2)_2\text{Pd}$ and very weak peaks attributable to PdS
54
55 (vysotskite) and Pd_{16}S_7 . The black solid suspended in CHCl_3 did not react with excess of **2**,
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4 nor with Ph_3P (by TLC [6], ^1H and ^{31}P [25] NMR). PdS was also inert towards a chloroform
5
6 solution of excess **2**.
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11 *The reaction of Bunsen's cacodyl disulfide (2) with $\text{Pd}(\text{OAc})_2$ under various stoichiometries*
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16 In an NMR tube containing a solution of non-equilibrated [22] **2** (50 μmol) in CDCl_3 (0.3 ml)
17
18 was added portion-wise, while shaking the tube, a solution $\text{Pd}(\text{OAc})_2$ (50 μmol) in CDCl_3 (0.3
19
20 ml). At once a very dark brown solution was formed and traces of a black solid appeared.
21
22 After 24 h the dark orange supernatant contained, by ^1H NMR, free AcOH, some $\text{Pd}(\text{OAc})_2$
23
24 and unknown compound(s) showing singlets at 1.434 and 2.180 ppm. Centrifugation gave the
25
26 black solid (11.5 mg) having the same attributes as described previously. In a preparative run
27
28 in dry dichloromethane the sum of the weights of the precipitate and the dried supernatant
29
30 was less by 2 mol of AcOH per mol of $\text{Pd}(\text{OAc})_2$ than the sum of the weights of the reactants.
31
32
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37
38 To a solution of non-equilibrated [22] **2** (50 μmol) in CDCl_3 (0.3 ml) in an NMR tube was
39
40 added at once a solution of $\text{Pd}(\text{OAc})_2$ (25 μmol) in CDCl_3 (0.3 ml). A dark orange-red
41
42 solution was formed and after 5 min the ^1H NMR spectrum showed the presence of **16**, **2**, **5**,
43
44 **15** with a mole ratio of 1 : 0.78 : 0.27 : 0.14, free AcOH plus an unknown molecule
45
46 resonating at 2.082 ppm, and two very small singlets at 1.773 and 1.716 ppm. The integration
47
48 did not change with time. The production of the insoluble **5** and its subsequent reaction, the
49
50 production of **16** (corresponding to ~30% consumption of **2**), and the loss of 2 mol of AcOH
51
52 per mol of $\text{Pd}(\text{OAc})_2$ were verified in a preparative run. The ether soluble **16** was
53
54 characterized by ^1H NMR [7], IR [46] and TLC (Et_2O) : R_f 0.40 [7].
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4 Under a 3:1 mole ratio the composition of the solution was again **16**, **2**, **5**, **15** but with a mole
5
6 ratio of 1 : 0.5 : 0.12 : 0.08, and it contained free AcOH plus the unknown compound (singlet
7
8 at 2.082 ppm).
9

10 11 12 13 14 *X-ray crystallographic study of Me₂AsS₂Na·2H₂O (3)* 15 16

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18
19 Needles of **3** suitable for X-rays were obtained either by dissolving **3** (as white plates) in
20
21 warm 95% aqueous ethanol and cooling at -20 °C for 3-4 days or by dissolving **3** in 95%
22
23 aqueous ethanol at room temperature, layering ether and, after 2 h, cooling the homogeneous
24
25 solution at -20 °C for 24 h. A colorless prismatic crystal covered with Paraton N oil was
26
27 mounted on the tip of a glass capillary. X-ray diffraction data were collected with an Oxford
28
29 Diffraction Xcalibur diffractometer in 0.6° increment ω -scans under a flow of nitrogen gas at
30
31 100 (2) K with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Data collection
32
33 and reduction were performed with CrysAlis CCD and RED software [47], respectively. The
34
35 reflection intensities were corrected for absorption by the multi-scan method. The structure
36
37 was solved by direct methods with SIR92 [48] and refined by full-matrix least-squares on F^2
38
39 using SHELXL-97 [49]. All of the water H-atoms (involved in H-bonding) were located from
40
41 difference Fourier syntheses and their positions were refined freely with $U_{\text{iso}}(\text{H})$ equal to
42
43 $1.5U_{\text{eq}}$ of their parent atoms. The methyl H-atoms were constrained to an ideal geometry [C–
44
45 H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$] but were allowed to rotate freely about the C–As bond.
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52 The main crystal, collection and structure refinement data are summarized in Table 2.
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57 **Supplementary material.** Crystallographic data for structure **3** have been deposited with the
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59 Cambridge Crystallographic Data Centre as supplementary publication (CCDC 720421).
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Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (<http://www.ccdc.cam.ac.uk>).

Supporting information. Additional colour illustrations of Figures 1 and 2 are available on the WWW as Electronic Supporting Information.

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Legends to Figures

Figure 1. The basic unit of compound **3** showing the coordination about the potassium ion (distorted octahedral) and the numbering scheme (thermal ellipsoids at the 50% probability level).

Symmetry codes: (*) $-x, 1-y, -z$; (\$) $-x, 2-y, -z$; (#) $1-x, 2-y, -z$.

Figure 2. View of the layer structure of **3** in the ab plane showing the NaO_4S_2 octahedra. Hydrogen atoms have been omitted for clarity. The drawing was prepared with the *DIAMOND* [50] software.