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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  
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and Palladium(II) Dimethyldithioarsinate, (Me<sub>2</sub>AsS<sub>2</sub>)<sub>2</sub>Pd**

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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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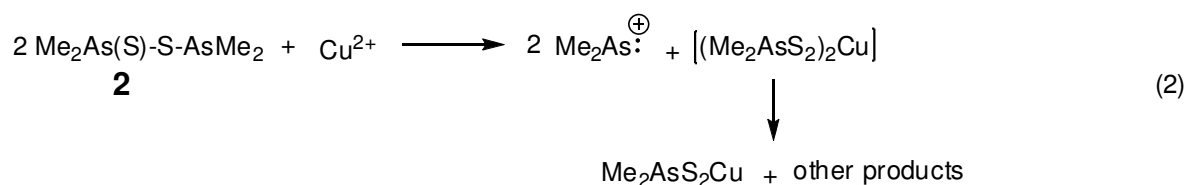
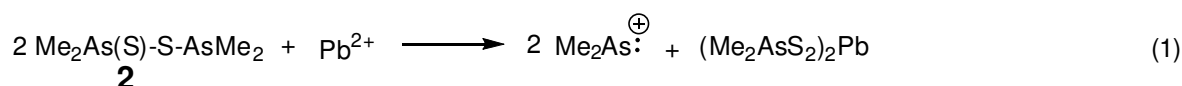
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7 **Abstract.** Palladium(II) acetate in non-deaerated chloroform splits Bunsen's cacodyl  
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9 disulfide,  $\text{Me}_2\text{As}(\text{S})\text{-S-AsMe}_2$ , giving the slightly-chloroform-soluble complex  $(\text{Me}_2\text{AsS}_2)_2\text{Pd}$   
10  
11 and the arsonium ion  $\text{Me}_2\text{As}^+$ . However, after a few minutes the complex reacted giving  
12  
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  $\text{Pd}^{\text{II}}$  and  $\text{Ph}_3\text{P}$  in a  
18  
19 different way compared to other  $(\text{Me}_2\text{AsS}_2)_x\text{M}$  (M = heavy metal cation) and  $(\text{Me}_2\text{PS}_2)_2\text{Pd}$ .  
20  
21 The reaction of equimolar quantities of  $\text{Me}_2\text{AsS}_2\text{Na}\cdot 2\text{H}_2\text{O}$  and  $\text{Ph}_3\text{P}$  under argon involved  
22  
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  $6.5552(2) \text{ \AA}$ ,  $c = 12.1480(4) \text{ \AA}$ ,  $\alpha = 98.282(2)^\circ$ ,  $\beta = 93.994(3)^\circ$ ,  $\gamma = 115.951(3)^\circ$ ,  $V =$   
28  
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.

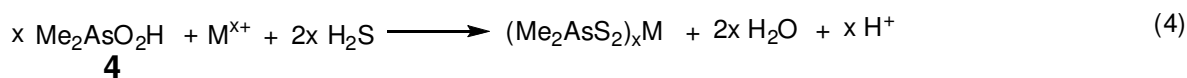
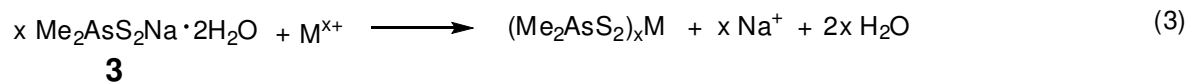
## Introduction

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).

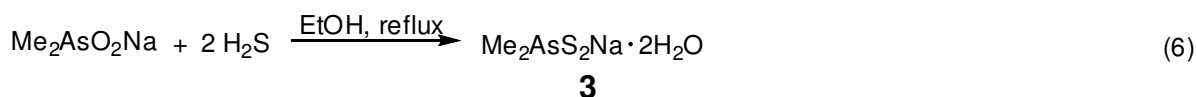
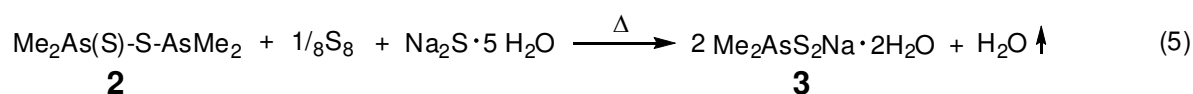


At the same time *Förster* et al. [9] prepared the  $L_xM$  complexes with  $M = \text{Cr}^{\text{III}}, \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Zn}^{\text{II}}$ , and  $\text{Cd}^{\text{II}}$ , while the  $\text{Sn}^{\text{IV}}$  was prepared later on [10], both using the reaction of equation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

The  $\text{Me}_2\text{AsS}_2^-$ ,  $L^-$ , anion is a ligand for organometallic derivatives of  $\text{Sn}^{\text{IV}}$  [10],  $\text{Sb}^{\text{III}}$  [11],  $\text{Si}^{\text{IV}}$ ,  $\text{Ge}^{\text{IV}}$  and  $\text{Pb}^{\text{IV}}$  [12],  $\text{Pt}^{\text{IV}}$  [13], and  $\text{V}^{\text{IV}}$  [14] as well as for the carbonyls of  $\text{Mn}^{\text{I}}$  and  $\text{Re}^{\text{I}}$  [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],  $\text{Ph}_2\text{SbL}$  [20] and  $\text{Me}_2\text{SnL}_2$  [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  
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14 than previously done [7]. Palladium acetate is soluble in chloroform, has a diamagnetic  $Pd^{II}$ ,  
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16 its reaction with **2** can be studied by  $^1H$  NMR, and we expected  $L_2Pd$  to be insoluble in  
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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**  
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26 which proved to be complicated and did not afford  $(Me_2AsS_2)_2Pd$  **5**. The complex **5** was,  
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28 however, prepared from **3**, equation (3). Because **3** prepared according to equation (5) had a  
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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.**  $^1\text{H}$  NMR values of methyl and phenyl groups in  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$ , and  $^{31}\text{P}$  NMR values of phosphorus compounds encountered in this work. Our  $\delta$  values for the methyl protons have a range of less than  $\pm 0.002$  ppm of the quoted values (s = singlet, m = multiplet).

$\text{CDCl}_3$			$\text{CD}_3\text{OD}$		
Compound	$\delta$ , ppm	Compound	$\delta$ , ppm		
	$\text{Pd}(\text{OAc})_2$	1.997s	(3) <sup>b</sup>	$\text{Me}_2\text{AsS}_2\text{Na}\cdot 2\text{H}_2\text{O}$	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 <sup>+</sup> )	$\text{Me}_2\text{As-SNa}$	1.233s
(5) <sup>a</sup>	$(\text{Me}_2\text{AsS}_2)_2\text{Pd}$	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) <sup>c</sup>	$\text{Me}_2\text{AsO}_2\text{Na}\cdot 3\text{H}_2\text{O}$	1.557s
(8)	$\text{Me}_2\text{As-AsMe}_2$	1.1 [35]	(10) <sup>d</sup>	$\text{Me}_2\text{AsO}_2\text{Na}\cdot 3\text{H}_2\text{O}$	1.628s
(15)	$\text{Me}_2\text{As-SS-AsMe}_2$	1.399 [6]	(4) <sup>d</sup>	$\text{Me}_2\text{AsO}_2\text{H}$	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]
	$\text{Ph}_3\text{P}$	7.30s		$\text{Ph}_3\text{P}$	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 $[\text{D}_6]\text{DMSO}$			$\text{Ph}_3\text{P}$	-5.58, +8 [25]
	b: 1.993s, 1.95 [22], 1.99 [24] in $\text{D}_2\text{O}$			$\text{Ph}_3\text{P=O}$	+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  $^1\text{H}$  and  $^{31}\text{P}$  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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*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 compound [26] (but see ref. [27]). For the same reaction we used the pentahydrate,  $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$  [28, 29]. The nonahydrate,  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ , does not allow a satisfactory homogenization of the solid reactants because it melted [27] during the grinding. The smaller the scale (e.g. 0.5 mmol) the better the yields (~95%) because of the better heating of the solid mixture. The preparation of **3** from **2** according to equation (5) evidently involves the ring opening of  $\text{S}_8$  by  $\text{S}^{2-}$  [30] to give  $\text{S-S}_7\text{S}^-$ . Then, this nucleophile reacts with **2**, most likely at the As=S sulfur [6], giving, after successive cycles, the salt **3**.

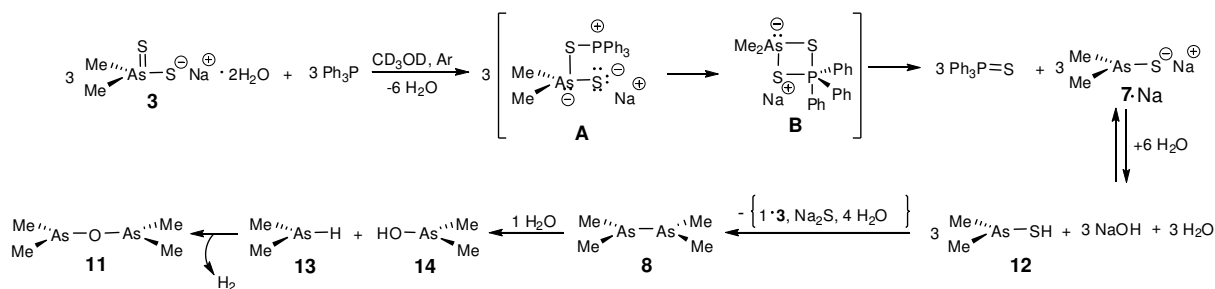
The complex **5** was prepared from **3** by a stepwise replacement of the acetate groups of the trimeric [31, 32] palladium(II) acetate,  $[\text{Pd}(\text{OAc})_2]_3$ , under conditions [7] which prevented the interaction of  $\text{Pd}^{\text{II}}$  with the formed **5**. The complex **5** keeps tenaciously MeOH, AcOH and probably  $\text{H}_2\text{O}$  (by IR and  $^1\text{H}$  NMR) and prolonged drying over concentrated sulfuric acid [5, 7] was necessary for satisfactory elemental analyses. While **3** melted, **5** upon heating decomposed at  $\sim 195$  °C to PdS and the foul-smelling  $\text{Me}_2\text{As-S-AsMe}_2$  **6** indicating that the formation of heavy metal sulfides,  $\text{M}_2\text{S}_x$ , is the driving force for such a decomposition [5, 7, 23]. The poor solubility of **5** points towards a polymeric structure. A saturated solution of **5** in  $\text{CDCl}_3$  resonated at 2.212 ppm, Table 1, quite close (2.246 ppm) to the chloroform-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] and assigned [8] in other  $(\text{Me}_2\text{AsS}_2)_x\text{M}$  complexes.

### ***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**)***

Attempted desulfurization of  $(\text{Me}_2\text{AsS}_2)_x\text{M}$  (M = heavy metal cation) by  $\text{Ph}_3\text{P}$  [or  $(\text{MeO})_3\text{P}$ ] 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  $\text{Ph}_3\text{P=S}$  [or  $(\text{MeO})_3\text{P=S}$ ] together with the metal sulfide  $\text{M}_2\text{S}_x$  and  $\text{Me}_2\text{As-S-AsMe}_2$  **6** due to

the affinity of these cations to sulfur [7]. Since  $\text{Na}^+$  does not have such an affinity, we tried to desulfurize **3** with  $\text{Ph}_3\text{P}$  hoping to get  $\text{Me}_2\text{AsS}^-\text{Na}^+$ ,  $\mathbf{7}\cdot\text{Na}^+$ . However, the course of the desulfurization was unexpected because 4 consecutive reactions took place.

Upon dissolution of an equimolar quantity of  $\text{Ph}_3\text{P}$  and **3** in  $\text{CD}_3\text{OD}$  under argon the  $^1\text{H}$  NMR showed practically no binding of  $\text{Ph}_3\text{P}$  to **3**. In 1 h  $\text{Ph}_3\text{P}=\text{S}$  started precipitating and the  $^1\text{H}$  NMR spectrum of the supernatant showed the presence of **3** that had not yet reacted and a singlet due to  $\mathbf{7}\cdot\text{Na}^+$ . 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  $^{31}\text{P}$  NMR spectrum showed  $\text{Ph}_3\text{P}=\text{S}$  and very little  $\text{Ph}_3\text{P}=\text{O}$ , while the  $^1\text{H}$  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  $\text{Ph}_3\text{P}$  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  $\mathbf{7}\cdot\text{Na}^+$  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 Na<sub>2</sub>S. The highly reactive  
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8 diarsine **8** resonated at ~1.25 ppm (1.1 ppm in CDCl<sub>3</sub> [35]) and by reaction with H<sub>2</sub>O should  
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10 give **13** and **14** [36]. The dimethylarsine, being a strong reducing agent [37], must react with  
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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 Na<sub>2</sub>S, 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 S<sup>2-</sup> to "S" which is then captured by an As<sup>III</sup> atom.  
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26 Running the desulfurization of **3** by Ph<sub>3</sub>P in air we found the same final arsenic-  
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28 containing compounds but, now, the production of Ph<sub>3</sub>P=O was significant due to the reaction  
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30 of **8** with dioxygen which should give [38] Me<sub>2</sub>As-OO-AsMe<sub>2</sub> which, in turn, will be  
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32 deoxygenated by Ph<sub>3</sub>P.  
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36 These attempts at the preparation of the Me<sub>2</sub>As-S<sup>-</sup> 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 CDCl<sub>3</sub> reacted with Ph<sub>3</sub>P (1:2 mole ratio) giving, by <sup>1</sup>H NMR,  
42  
43 Ph<sub>3</sub>P=S and a prominent singlet attributable to unstable [22, 23] Me<sub>2</sub>As-SS-AsMe<sub>2</sub> **15** and not  
44  
45 to the putrid **6** [6], which diminished with time giving a complex <sup>1</sup>H NMR spectrum in the  
46  
47 region of 1.26-2.00 ppm. PdS was not produced. Thus, the reaction of **5** with Ph<sub>3</sub>P is not in  
48  
49 line with the other similar reactions of (Me<sub>2</sub>AsS<sub>2</sub>)<sub>x</sub>M [7] and is not amenable to a simple  
50  
51 interpretation. The behaviour of **5** also contrasts the behaviour of (Me<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>Pd with  
52  
53 phosphines, e.g. (Me<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>Pd adds one and two Ph<sub>3</sub>P ligands to give new complexes [39,  
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60 40].

The complex **5** dissolved, at RT, in pyridine was recovered intact by precipitation with Et<sub>2</sub>O indicating that pyridine does not coordinate to the complexed Pd<sup>II</sup>. 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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8

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.  $\text{Pb}^{\text{II}}$ , to give  $\text{PbS}$  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  $\text{Pd}^{\text{II}}$  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  $\text{AcOH}$  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  $\text{Pd}^{\text{II}}$ . 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  $\text{AsS}_2\text{Pd}$  ring at  $454\text{ cm}^{-1}$  [8] was much weaker than that  
22 of **5**.  
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#### 45 *The reaction of Bunsen's cacodyl disulfide (2) with Pd(OAc)<sub>2</sub>*

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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  $\text{Me}_2\text{As}^+$  did not react with the insoluble  $\text{L}_x\text{M}$  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  $\text{CDCl}_3$   
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  $^1\text{H}$  NMR, apart from  $\text{AcOH}$ , 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  $\text{Me}_2\text{As}^+$  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  $\text{CDCl}_3$ , its methyl groups  
7  
8 resonate at 2.47 and 1.84 ppm [41]. It seems, therefore, that when  $\text{Pd}^{\text{II}}$  is in excess,  $\text{Pd}^{\text{II}}$ , in  
9  
10 preference to  $\text{Me}_2\text{As}^+$ , 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  $^1\text{H}$  NMR: free  
15  
16 AcOH plus another unknown compound (both resonating at 2.082 ppm),  $\text{Me}_2\text{As(S)-O-}$   
17  
18  $\text{As(S)Me}_2$  **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  $\text{Pd}^{\text{II}}$  in the system, then  $\text{Me}_2\text{As}^+$   
21  
22 attacks on the insoluble  $\text{L}_2\text{Pd}$  **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  $\text{Pd}^{\text{II}}$  for it is known that  $\text{Pd}^{\text{II}}$   
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  $\text{Pd}^{\text{II}}$  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  
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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  $\text{L}_x\text{M}$  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 Me<sub>2</sub>AsS<sub>2</sub>Na·2H<sub>2</sub>O (**3**)

Formula	C <sub>2</sub> H <sub>10</sub> AsNaO <sub>2</sub> S <sub>2</sub>
Molecular weight /g mol <sup>-1</sup>	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)
$\alpha$ /deg	98.282(2)
$\beta$ /deg	93.994(3)
$\gamma$ /deg	115.951(3)
Volume /Å <sup>3</sup>	422.38(3)
<i>Z</i> , <i>D</i> <sub>calc</sub> /( <i>Mg</i> /m <sup>3</sup> )	2, 1.794
Absorption coefficient /mm <sup>-1</sup>	4.496
<i>F</i> (000)	228
Crystal size /mm	0.14 × 0.11 × 0.08
$\theta$ range for data collection /deg	3.43 to 28.50
Reflections collected / unique	7358 / 2117 ( <i>R</i> <sub>int</sub> = 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> <sup>2</sup>
Data/ restraints /parameters	2117 / 4 / 87
Goodness-of-fit on <i>F</i> <sup>2</sup>	0.983
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> indices [ <i>I</i> > 2σ( <i>I</i> )]	0.0207, 0.0414
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> indices (all data)	0.0275, 0.0422
Largest diff. peak and hole /e Å <sup>-3</sup>	0.653 and -0.328

**Table 3.** Atomic coordinates<sup>a)</sup> and thermal displacement parameters<sup>b)</sup> for Me<sub>2</sub>AsS<sub>2</sub>Na·2H<sub>2</sub>O.

Atom	x	y	z	$U_{eq}$ (Å <sup>2</sup> )
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

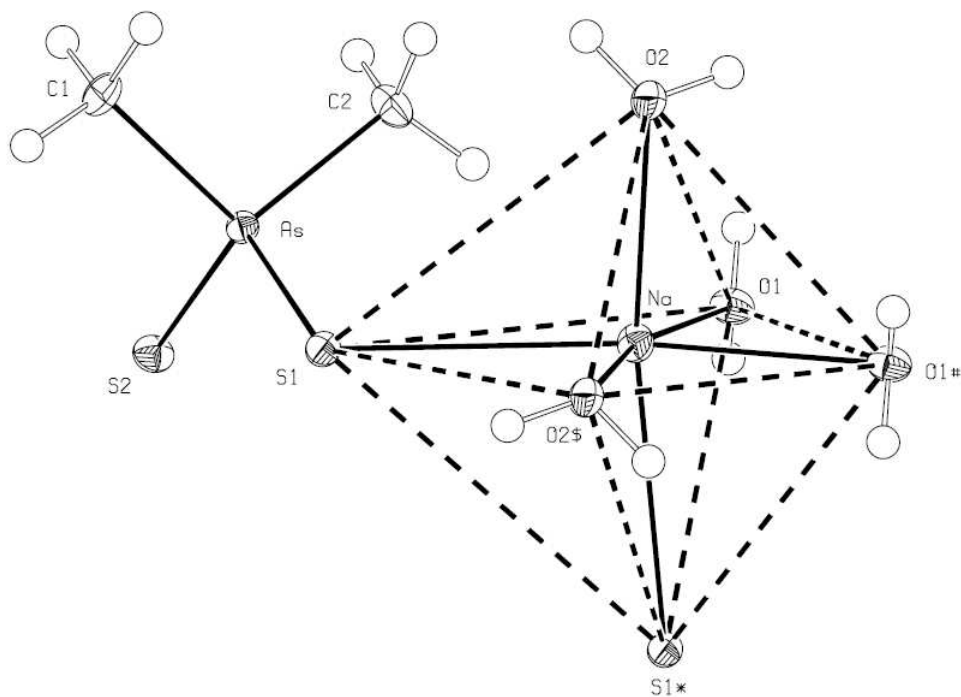
<sup>a)</sup> Estimated standard deviations of the last significant digits in parenthesis.

<sup>b)</sup>  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

**Table 4.** Selected structural data for Me<sub>2</sub>AsS<sub>2</sub>Na·2H<sub>2</sub>O.

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

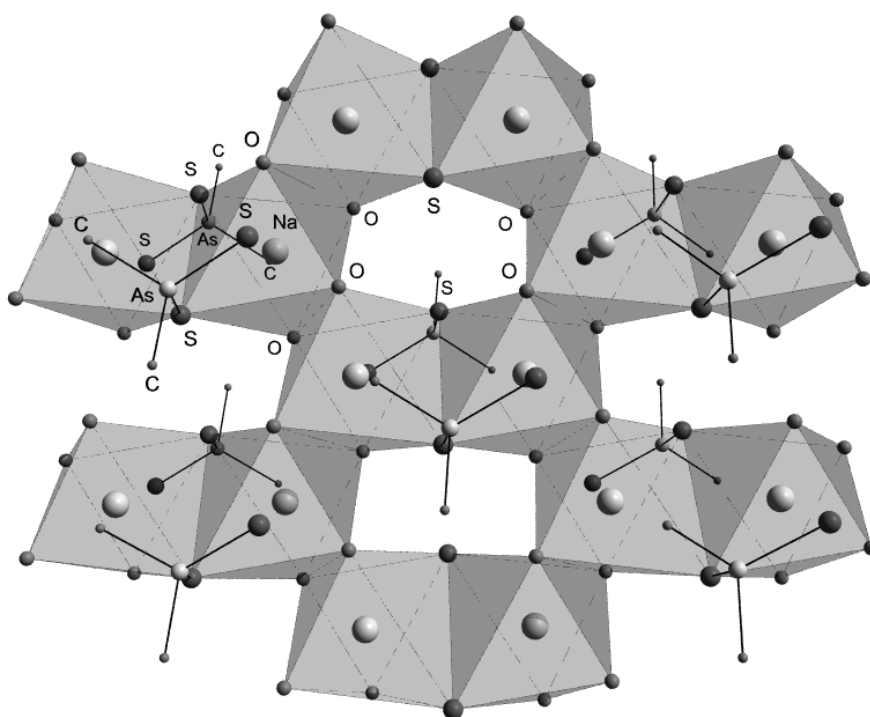
Symmetry codes: (i)  $-x, 1-y, 2-z$ ; (ii)  $-x, -y, 2-z$ ; (iii)  $-1-x, -y, 2-z$ ; (iv)  $-1+x, y, z$ ; (v)  $-1+x, -1+y, z$ ; (vi)  $x, -1+y, z$ .



**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  $\text{NaO}_4\text{S}_2$  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  $\text{Me}_2\text{AsS}_2$  group is distorted tetrahedral; the  $\text{S-As-S}$  angle of  $114.20(2)^\circ$  is noticeably larger and the  $\text{C-As-C}$  angle of  $103.74(9)^\circ$ , smaller than the tetrahedral angle. The two  $\text{As-S}$  bonds have similar lengths [ $2.1435(5) \text{ \AA}$  to  $\text{S1}$  and  $2.1255(5) \text{ \AA}$  to  $\text{S2}$ ] and are intermediate between a single (*ca.*  $2.21 \text{ \AA}$ ) and a double (*ca.*  $2.07 \text{ \AA}$ ) bond, implying delocalization of the negative

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4 charge over the  $\text{AsS}_2$  moiety of the structure. Similar delocalization has also been observed in  
5  
6 similar crystal structures e.g., piperidinium diphenyldithioarsinate [33], potassium  
7  
8 dimethyldithioarsinate dihydrate [16], tris(dimethyldithioarsinate)chromium(III) [19], and  
9  
10 phenylantimony(III) dimethyldithioarsinate [20]. The fact that S1 atom is coordinated to  $\text{Na}^+$   
11  
12 ions while S2 makes no major contacts accounts for the small difference observed among the  
13  
14 As–S bonds.  
15  
16  
17

18  
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.  
28  
29

30  
31 The  $\text{NaO}_4\text{S}_2$  octahedra are linked together by edge-sharing, resulting in the formation  
32  
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  
38  
39 molecules contribute actively - through coordination and hydrogen bonds - towards the  
40  
41 supramolecular organization of the structure. To complete the picture, the  $\text{NaO}_4\text{S}_2$  octahedra  
42  
43 constitute the major part of the structure, while the  $\text{Me}_2\text{AsS}_2$  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  
50  
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),  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , TMS),  $\delta$ : 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  $\text{A}_4$  molecular sieves.  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$  were not dried nor de-aerated. For experiments under argon,  $\text{CD}_3\text{OD}$  (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.  $^1\text{H}$  NMR (400 MHz) and  $^{31}\text{P}$  NMR (162 MHz) spectra were recorded on a DPX Avance Spectrometer in  $\text{CDCl}_3$ ,  $\text{CD}_3\text{OD}$  or  $[\text{D}_6]\text{DMSO}$  with internal TMS (0.000) as standard,  $\text{D}_2\text{O}$  with DSS (2,2-dimethyl-2-silapentane-5-sulfonate, sodium salt) (0.000) as standard while the  $^{31}\text{P}$  spectra were referenced to 85% aqueous  $\text{H}_3\text{PO}_4$  in  $\text{D}_2\text{O}$  (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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3  
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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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].  $^1\text{H}$   
47  
48 NMR ( $\text{CD}_3\text{OD}$ , TMS),  $\delta$  : 1.907 (s, 6H), 4.814 (s, 4H for  $\text{H}_2\text{O}$ );  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ , DSS),  $\delta$  :  
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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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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 Me<sub>2</sub>As-S-AsMe<sub>2</sub> **6**. It is insoluble in Et<sub>2</sub>O, sparingly soluble in CHCl<sub>3</sub> and even  
18  
19 less soluble in MeOH and Me<sub>2</sub>CO, and soluble in pyridine giving a dark red solution from  
20  
21 which **5** precipitates by adding Et<sub>2</sub>O. It keeps tenaciously AcOH, MeOH, and possibly H<sub>2</sub>O  
22  
23 (by <sup>1</sup>H NMR) which are removed by keeping it over concentrated sulfuric acid [5] for more  
24  
25 than two weeks. C<sub>4</sub>H<sub>12</sub>S<sub>4</sub>As<sub>2</sub>Pd (*M<sub>r</sub>* 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. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ : 2.212 (s) and very small singlets at 1.679 and  
30  
31 2.459 ppm; ([D<sub>6</sub>]DMSO); δ: 2.250 ppm, Table 1.  
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#### 40 *Reaction of Ph<sub>3</sub>P with Me<sub>2</sub>AsS<sub>2</sub>Na·2H<sub>2</sub>O (3) and with (Me<sub>2</sub>AsS<sub>2</sub>)<sub>2</sub>Pd (5)*

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42  
43  
44  
45 In NMR tubes were added **3** (50 μmol), Ph<sub>3</sub>P (50 μmol) and purged with argon. Then, argon-  
46  
47 packaged CD<sub>3</sub>OD (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 <sup>1</sup>H and <sup>31</sup>P  
50  
51 NMR for 5 days. Then, dioxygen was admitted and the progress of the oxidation was  
52  
53 followed by <sup>1</sup>H NMR for another 5 days. Other experiments were conducted without  
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55 exclusion of air. The results are described in the Results Section.  
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To a suspension of **5** (45  $\mu\text{mol}$ ) in  $\text{CDCl}_3$  (0.6 ml),  $\text{Ph}_3\text{P}$  (90  $\mu\text{mol}$ ) was added and shaken for 4 h. A very dark brown solution resulted after 10 min. The results of the  $^1\text{H}$  NMR analyses are described in the Results Section.

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

In an NMR tube were added **5** (50  $\mu\text{mol}$ ),  $\text{Pd}(\text{OAc})_2$  (50  $\mu\text{mol}$ ) and  $\text{CDCl}_3$  (0.6 ml) and shaken for 2 h. The pale orange supernatant contained only free acetic acid and traces of  $\text{Pd}(\text{OAc})_2$ . Centrifugation and washing with chloroform gave a supernatant (3.3 mg of a brownish film) and a black solid (26 mg) having the attributes described in the following experiment.

To a solution of **3** (0.1 mmol) in methanol (1 ml) in a centrifuge tube was added dropwise, while stirring, a solution of  $\text{Pd}(\text{OAc})_2$  (0.1 mmol) in chloroform (2 ml). When half of the  $\text{Pd}^{\text{II}}$  has been added a brown suspension of **5** was formed which, thereafter, became black. Stirring was continued for 2 h. Centrifugation and washing with methanol (2x2 ml) gave clear colorless supernatants and an amorphous black solid (23.3 mg; expected for equimolar  $\text{PdS}$  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  $^\circ\text{C}$ , and was insoluble in  $\text{CHCl}_3$ ,  $\text{Me}_2\text{CO}$ ,  $\text{MeOH}$ ,  $\text{DMF}$ , pyridine,  $\text{H}_2\text{O}$ . For the mixture  $\text{PdS}\cdot\text{C}_4\text{H}_{12}\text{OS}_3\text{As}_2\text{Pd}$  ( $M_r$  138.46 + 428.57); C 9.02 (calc. 8.47), H 1.85 (2.13), S 21.86 (22.61)%. **IR** (KBr) : 2982 w, 2918 mw, 2852 w, 1640 w, 1570 w, 1392 ms, 1244 mw, 906 s, 860 vs, 742 w, 594 m, 454 m. The powder X-ray diffraction spectrum showed two not so strong peaks matching those of  $(\text{MeOCS}_2)_2\text{Pd}$  and very weak peaks attributable to  $\text{PdS}$  (vysotskite) and  $\text{Pd}_{16}\text{S}_7$ . The black solid suspended in  $\text{CHCl}_3$  did not react with excess of **2**,

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4 nor with  $\text{Ph}_3\text{P}$  (by TLC [6],  $^1\text{H}$  and  $^{31}\text{P}$  [25] NMR). PdS was also inert towards a chloroform  
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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  $\mu\text{mol}$ ) in  $\text{CDCl}_3$  (0.3 ml)  
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18 was added portion-wise, while shaking the tube, a solution  $\text{Pd}(\text{OAc})_2$  (50  $\mu\text{mol}$ ) in  $\text{CDCl}_3$  (0.3  
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20 ml). At once a very dark brown solution was formed and traces of a black solid appeared.  
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22 After 24 h the dark orange supernatant contained, by  $^1\text{H}$  NMR, free AcOH, some  $\text{Pd}(\text{OAc})_2$   
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24 and unknown compound(s) showing singlets at 1.434 and 2.180 ppm. Centrifugation gave the  
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26 black solid (11.5 mg) having the same attributes as described previously. In a preparative run  
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28 in dry dichloromethane the sum of the weights of the precipitate and the dried supernatant  
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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.  
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38 To a solution of non-equilibrated [22] **2** (50  $\mu\text{mol}$ ) in  $\text{CDCl}_3$  (0.3 ml) in an NMR tube was  
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40 added at once a solution of  $\text{Pd}(\text{OAc})_2$  (25  $\mu\text{mol}$ ) in  $\text{CDCl}_3$  (0.3 ml). A dark orange-red  
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42 solution was formed and after 5 min the  $^1\text{H}$  NMR spectrum showed the presence of **16**, **2**, **5**,  
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44 **15** with a mole ratio of 1 : 0.78 : 0.27 : 0.14, free AcOH plus an unknown molecule  
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46 resonating at 2.082 ppm, and two very small singlets at 1.773 and 1.716 ppm. The integration  
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48 did not change with time. The production of the insoluble **5** and its subsequent reaction, the  
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50 production of **16** (corresponding to ~30% consumption of **2**), and the loss of 2 mol of AcOH  
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52 per mol of  $\text{Pd}(\text{OAc})_2$  were verified in a preparative run. The ether soluble **16** was  
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54 characterized by  $^1\text{H}$  NMR [7], IR [46] and TLC ( $\text{Et}_2\text{O}$ ) :  $R_f$  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  
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6 ratio of 1 : 0.5 : 0.12 : 0.08, and it contained free AcOH plus the unknown compound (singlet  
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8 at 2.082 ppm).  
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### 11 12 13 *X-ray crystallographic study of Me<sub>2</sub>AsS<sub>2</sub>Na·2H<sub>2</sub>O (3)* 14 15 16

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18 Needles of **3** suitable for X-rays were obtained either by dissolving **3** (as white plates) in  
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20 warm 95% aqueous ethanol and cooling at -20 °C for 3-4 days or by dissolving **3** in 95%  
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22 aqueous ethanol at room temperature, layering ether and, after 2 h, cooling the homogeneous  
23  
24 solution at -20 °C for 24 h. A colorless prismatic crystal covered with Paraton N oil was  
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26 mounted on the tip of a glass capillary. X-ray diffraction data were collected with an Oxford  
27  
28 Diffraction Xcalibur diffractometer in 0.6° increment  $\omega$ -scans under a flow of nitrogen gas at  
29  
30 100 (2) K with graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data collection  
31  
32 and reduction were performed with CrysAlis CCD and RED software [47], respectively. The  
33  
34 reflection intensities were corrected for absorption by the multi-scan method. The structure  
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36 was solved by direct methods with SIR92 [48] and refined by full-matrix least-squares on  $F^2$   
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38 using SHELXL-97 [49]. All of the water H-atoms (involved in H-bonding) were located from  
39  
40 difference Fourier syntheses and their positions were refined freely with  $U_{\text{iso}}(\text{H})$  equal to  
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42  $1.5U_{\text{eq}}$  of their parent atoms. The methyl H-atoms were constrained to an ideal geometry [C–  
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44 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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56 **Supplementary material.** Crystallographic data for structure **3** have been deposited with the  
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58 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  $\text{NaO}_4\text{S}_2$  octahedra. Hydrogen atoms have been omitted for clarity. The drawing was prepared with the *DIAMOND* [50] software.