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# ORGANOTIN AND TIN(IV) DERIVATIVES OF DIMETHYLDITHIOARSINIC ACID *

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## Summary

Organotin derivatives of dimethyldithioarsinic (dithiocacodylic) acid have been obtained from the appropriate organotin chloride and the sodium salt of the latter. Tin(IV) chloride and $NaS_2AsMe_2 \cdot 2\ H_2O$ yielded only two products, namely $Cl_2Sn(S_2AsMe_2)_2$ and $Sn(S_2AsMe_2)_4$, regardless of the reagent ratio. Spectroscopic characterization of the compounds (infrared and $^1H$ NMR) provides structural information suggesting that the dimethyldithioarsinato group behaves as monodentate (or anisobidentate) ligand in $Me_2Sn(S_2AsMe_2)_2$, $Bu_2Sn(S_2AsMe_2)_2$ and $Cy_3Sn(S_2AsMe_2)$, as bidentate in $Ph_2Sn(S_2AsMe_2)_2$, $Ph_3Sn(S_2AsMe_2)$ and $Cl_2As(S_2AsMe_2)_2$, whereas $Sn(S_2AsMe_2)_4$ contains both mono- and bidentate ligands, presumably in a six-coordinate structure.

## Introduction

The potential biological activity of organometallic derivatives of various dithio acids and the general interest in sulfur-containing ligands stimulates considerable interest in the synthesis and structure of such compounds. Organotin and inorganic tin dithiophosphinates [1—3], dialkyldithiophosphates [4—6] and dithiocarboxylates [7,8] have received more attention than other derivatives of dithioacids, and have been characterized by various structural methods, including several X-ray diffraction determinations [9—12]. Dialkyldithiophosphates in particular, have been found to show remarkably varied coordination patterns [13], acting as monodentate, bidentate or bridging groups. However, derivatives

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* In honor of Professor Henry Gilman, the great man and outstanding scientist, one of the founders of organometallic chemistry to the inspiring teacher who influenced so much the scientific careers of those who had the privilege to work with him.

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of the closely similar dimethyldithioarsinic acid have received much less attention and no organometallic derivative of this or any other dithioarsinic acid has been reported so far, although some transition metal derivatives have been investigated [14—17].

In the present study we have prepared and investigated several organotin derivatives of dimethyldithioarsinic acid, $Me_2As(S)SH$, as well as some inorganic tin(IV) derivatives of the latter.

## Results and discussion

### *Preparation of the compounds*

The organotin and tin(IV) dimethyldithioarsinates described in this paper were prepared by the reaction of the appropriate chlorides with sodium dimethyldithioarsinate dihydrate, $NaS_2AsMe_2 \cdot 2\,H_2O$, in ethanol or benzene/ethanol, at room temperature or under gentle heating. After filtration of sodium chloride, the organotin dimethyldithioarsinates crystallize on concentrating the solution. The dimethyltin derivative can be prepared in an aqueous system.

$$R_{4-n}SnCl_n + n\,NaS_2AsMe_2 \rightarrow R_{4-n}Sn(S_2AsMe_2)_n + n\,NaCl$$

$R = Me, Bu, Ph;\ n = 2$
$R = Ph, Cy \quad n = 1$

The compounds are stable in closed vials and decompose slowly in contact with a humid atmosphere. After one year of storage the compounds were ca. 50% decomposed. All dimethyldithioarsinates are extremely malodorous and presumably toxic. Melting points, colors and analytical data are given in Table 1.

When a benzene solution of tin(IV) chloride was treated with four equivalents

TABLE 1

PROPERTIES AND ANALYTICAL DATA

| Compound | Color | M.p. (°C) | Analytical data found (calcd.) | |
|---|---|---|---|---|
| | | | As | S |
| 1. $Me_2Sn(S_2AsMe_2)_2$ | colorless | 156 | 30.38<br>(30.82) | 26.01<br>(26.30) |
| 2. $Bu_2Sn(S_2AsMe_2)_2$ | colorless | 92 | 28.23<br>(28.69) | 24.70<br>(24.48) |
| 3. $Ph_2Sn(S_2AsMe_2)_2$ | pale yellow | 176 | 24.21<br>(24.56) | 20.63<br>(20.95) |
| 4. $Ph_3Sn(S_2AsMe_2)$ | colorless | 140 | 14.16<br>(14.45) | 12.02<br>(12.33) |
| 5. $Cy_3Sn(S_2AsMe_2)$ [a] | colorless | 96 | 13.45<br>(13.97) | 11.78<br>(11.92) |
| 6. $Cl_2Sn(S_2AsMe_2)_2$ | yellow | 210<br>(dec.) | 26.80<br>(28.42) | 36.12<br>(36.21) |
| 7. $Sn(S_2AsMe_2)_4$ | orange | 74 | 38.03<br>(37.75) | 26.58<br>(26.80) |

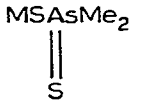
[a] Cy = cyclohexyl.

of sodium dimethyldithioarsinate dissolved in ethanol, a yellow precipitate was formed which analysed as $Cl_2Sn(S_2AsMe_2)_2$. The orange filtrate afforded after evaporation of the solvent the tetrasubstituted derivative, $Sn(S_2AsMe_2)_4$, as an orange microcrystalline solid. The dichloro derivative $Cl_2Sn(S_2AsMe_2)_2$ can also be obtained directly and in good yield by mixing solutions of $SnCl_4$ (in benzene) and $NaS_2AsMe_2 \cdot 2\,H_2O$ (in ethanol) in 1 : 2 molar ratio of the reagents. The use of 1 : 1 or 1 : 3 molar ratios afforded only the two compounds mentioned, and no mono- or tris-(dimethyldithioarsinato)tin(IV) derivative could be obtained.

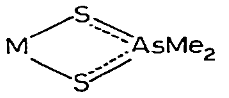
### *Spectra and structure of the compounds*

The compounds prepared have been characterized by infrared and $^1H$ NMR spectra. The resulting data were provided useful structural information.

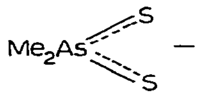
Dithioarsinic derivatives are known to exhibit As—S stretching frequencies in the range 500—300 $cm^{-1}$ [18] and As—C stretching frequencies in the range 650—580 $cm^{-1}$ [19]. The band at 488 $cm^{-1}$present in the spectrum of $Me_2As(=S)SAsMe_2$ has been assigned to $\nu_{as}(As{=}S)$ of the As=S double bond, while the low frequency bands at 399 and 365 $cm^{-1}$ have been assigned to the As—S single-bond stretching [19]. These assignments can thus be correlated with a monodentate structure (A) of the dimethyldithioarsinato ligand. In transition metal complexes the bidentate dithioarsinates (B) exhibit $\nu$(As—S) bands at 460—413 $cm^{-1}$ [14,16,17], thus affording a means to distinguish between the two types of coordination. The dimethyldithioarsinato anion itself (C) exhibits the two $\nu$(As—S) stretching frequencies at 449 and 424 $cm^{-1}$ [14,17], in the same region as the bidentate ligand, in agreement with a delocalized distribution of the $\pi$-electrons over the whole S—As—S fragment.



(A)



(B)



(C)

The spectroscopic data are confirmed by a normal coordinate analysis of the vibrational spectrum of $Me_2AsS_2^-$ anion [20]: the calculated $\nu$(As—S) stretching frequencies are 458 $cm^{-1}$ ($B_2$) and 412 $cm^{-1}$ ($A_1$) with an As—S bond order of 1.20. It should be mentioned that these are pure As—S frequencies, rather than combinations of As—S and As—C vibrations, as found for the phosphorus analogue $Me_2PS_2^-$, where strong coupling between P—S and P—C vibrations was discovered by normal coordinate analysis [21]. Therefore, the $\nu$(As—S) stretching frequencies can be used with more confidence for the interpretation of the structure of dimethyldithioarsinates.

The As—C bond stretching frequencies occur in the range 650—580 $cm^{-1}$ [19]. For the dimethyldithioarsinato anion the As—C frequencies are found at 618 $cm^{-1}$ ($\nu_{as}$) and 600 $cm^{-1}$ ($\nu_s$) [14—16], in agreement with calculated values 613 $cm^{-1}$ ($B_1$) and 605 $cm^{-1}$ ($A_1$), obtained from normal coordinate analysis [20].

The infrared spectra of the compounds reported here are listed in Table 2, where assignments of the observed bands are given. The $\nu_{as}(As{=}S)$ band at 480

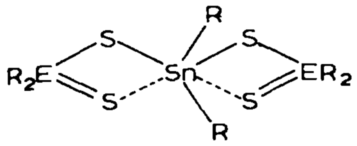
TABLE 2

INFRARED SPECTRA ($L = S_2AsMe_2$)

| $Me_2SnL_2$ | $Bu_2SnL_2$ | $Ph_2SnL_2$ | $Ph_3SnL$ | $Cy_3SnL$ | $Cl_2SnL_2$ | $SnL_4$ | Assignment |
|---|---|---|---|---|---|---|---|
| | | 3070w | 3070w | | | | $\nu$(CH) phenyl |
| | | 3055(sh) | 3055sh | | | | |
| 3010w | 3000 (sh) | 3025w | 3025w | 3015w | 3015m | | $\nu(CH_3)$ |
| 2990w | 2970m | 2995w | 2998w | 2990w | | 2990m | |
| 2920w | 2930m | | | 2930vs | 2930w | 2917m | |
| | 2880m | | | 2855vs | | | $\nu$(CH) |
| | 2865w | | | | | | |
| | | 1582w | 1582w | | | | $\nu$(CC) |
| | 1470ms | 1484ms | 1482ms | 1448vs | | | |
| 1405m | 1403ms | 1440s | 1430s | 1405s | 1403m | 1410ms | $\delta_{as}(CH_3)$ |
| | 1380w | | | | | | |
| | 1365w | 1338m | 1338m | 1350w | | | $\delta$(CH) |
| | 1300 | 1310m | 1308m | 1332m | | | |
| | | | | 1298m | | | |
| 1260ms | 1260m | 1270m | 1270m | 1265s | 1262s | 1260m | $\delta_s(CH_3)$ |
| 1190w | 1180m | 1195w | 1192m | | | | |
| | 1150w | 1170w | 1160m | 1178s | | | |
| | 1080m | 1080s | 1080s | 1090m | | | $\delta$(CH) |
| | | | | 1073m | | | |
| | 1035m | 1030m | 1030m | 1030m | | | |
| | 965m | 1003ms | 1005s | 998vs | | | |
| 920vs | 920s | 920m | 920m | 912s | 930s | 929s | |
| 890vs | 880s | 890m | | 890s | 890s | 889s | $\rho(CH_3)$ |
| | | 860m | 860m | 850m | 855 (sh) | 842ms | |
| 790s | 825w | | | 810w | | | |
| | 750w | 740vs | 740vs | 805w | | | |
| | 705w | 698vs | 700vs | | | | $\pi$(CH) |
| | 685w | 665w | 663mw | 665m | | | |
| 623m | 625m | 640w | 620w | 647w | 635mw | 630m | $\nu_{as}$(As—C) |
| | | | | 620m | | | |
| 603vs | 605s | | | 600s | 600s | 603vs | $\nu_s$(As—C) |
| | | | | | | 583m | |
| 557m | | | | | | 575m | $\nu_{as}$(Sn—C) |
| 525m | | | | | | | $\nu_s$(Sn—C) |
| 480vs | 460s | | | 480vs | | 480ms | |
| | | 450s | 458vs | | 455vs | 455ms | $\nu_{as}$(As—S) |
| | | 445 (sh) | 445s | | | | Ph ring |
| 415vs | 420s | 400m | 400m | 400s | 435vs | 435m | $\nu_s$(As—S) |
| | | | | | | 403m | |

s, strong; vs, very strong; m, medium; w, weak; sh, shoulder.

$cm^{-1}$ is observed in the infrared spectra of $Me_2Sn(S_2AsMe_2)_2$, $Bu_2Sn(S_2AsMe_2)_2$ and $Cy_3Sn(S_2AsMe_2)$, suggesting that the dimethyldithioarsinato ligands are monodentate (A) in these compounds. Additional weak interaction of uncoordinated sulfur atoms may result in anisobidentate behavior. Such a structure was suggested for the phosphorus analogue $Me_2Sn(S_2PMe_2)_2$, with monodentate (or anisobidentate) dithiophosphinato ligands, on the basis of Mössbauer spectrum, dipole moment [3] and X-ray diffraction structure determination [22].



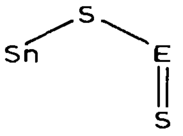
R = Me , E = P , As

The same type of structure was found by X-ray diffraction for dimethyltin bis(dimethyldithiocarbamate) [23], thus indicating similar behavior of all these three sulfur-containing ligands towards dialkyltin moieties.

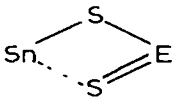
In agreement with the postulated structure, the infrared spectrum $Me_2Sn(S_2AsMe_2)_2$ exhibits two Sn—C stretching frequencies, at 557 and 525 cm$^{-1}$, indicating a distorted tetrahedral (or octahedral) structure; a linear *trans*-Me—Sn—Me arrangement would have resulted in the presence of only one $\nu$(Sn—C) band in the infrared spectrum.

The infrared spectra of compounds $Ph_2Sn(S_2AsMe_2)_2$, $Ph_3Sn(S_2AsMe_2)$ and $Cl_2Sn(S_2AsMe_2)_2$ exhibit bands in the same range as the bidentate $R_2AsS_2$ ligands in transition metal complexes; the $\nu_{as}$(As—S) at 455—460 cm$^{-1}$ (compare with 449 cm$^{-1}$ in the free anion) suggests that the dimethyldithioarsinato ligand is bidentate (B) in these compounds.

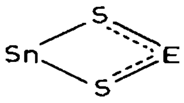
The compound $Sn(S_2AsMe_2)_4$ exhibits in the $\nu$(As—S) region four bands, at 480, 458, 435 and 403 cm$^{-1}$, originating from the presence of both monodentate (480 and 403 cm$^{-1}$) and bidentate (458 and 435 cm$^{-1}$) dimethyldithioarsinato groups. The $^1$H NMR spectrum also shows nonequivalence of the As—$CH_3$ groups, with signals at $\delta$ = 2.05 and 1.95 ppm, thus confirming that two kinds of dimethyldithioarsinato ligands are present in this compound. Therefore, in $Sn(S_2AsMe_2)_4$ the tin atom can be assumed to be six-coordinate (octahedral), with two bidentate and two monodentate ligands. A similar coordination pattern is known for $Sn(S_2CNEt_2)_4$ [24]. The ability of tin to coordinate sulfur ligands as bidentate is demonstrated by an X-ray structure determination of $Ph_2Sn[S_2P(OPr^i)_2]_2$, which contains an octahedral arrangement with a linear *trans*-Ph—Sn—Ph fragment, and bidentate diisopropyldithiophosphato groups, with equal P—S and Sn—S bonds [11] whereas in $Ph_2Sn[S_2P(OEt)_2]_2$ the dithiophosphato ligand is anisobidentate (with short P=S and long P—S bonds; also short Sn—S and long Sn···S bonds) [9]. In $Ph_3Sn—S_2P(OEt)_2$ the dithiophosphate is clearly monodentate [10]. All these facts demonstrate three different possibilities of the tin atom to coordinate anionic disulfur ligands (E = P, As, C), and dimethyldithioarsinates seem to be no exception.



monodentate



anisobidentate



bidentate

The $^1$H NMR spectra of all compounds described here, except $Sn(S_2AsMe_2)_4$, exhibit a single signal for As—$CH_3$ groups, with $\delta$ = 1.98 to 2.05 ppm relative to tetramethylsilane.

Although we are quite confident about the structural assignments made here on the basis of spectroscopic data, we realize that ultimate proof rests upon

X-ray diffraction structure determination, and we hope to be able in the future to provide such data as well, especially to distinguish between possible monodentate and anisobidentate coordination.

## Experimental

The reagents used were commercial products and were used as received. Sodium dimethyldithioarsinate dihydrate $NaS_2AsMe_2 \cdot 2\ H_2O$ was prepared according to literature data [14,15], from dimethylarsinic (cacodylic) acid. The solvents were purified by distillation. Although the products are not air-sensitive, work under nitrogen and especially long storage in inert atmosphere is beneficial.

*Caution:* Dimethyldithioarsinates are extremely malodorous and probably very toxic. All operations must be carried out in a good hood. Contact with skin must be avoided, at least because of the persistent fouling smell, which is difficult to remove even by prolonged washing.

The infrared spectra were recorded in KBr pellets, on a Carl Zeiss, Jena (D.D.R.) UR-20 instrument and $^1H$ NMR spectra on a Tesla BS-487 (Czech-made) spectrometer. Melting points are uncorrected. Analytical data are collected in Table 1.

### *Dimethyltin bis(dimethyldithioarsinate), $Me_2Sn(S_2AsMe_2)_2$*

A solution of 0.90 g (4 mmol) sodium dimethyldithioarsinate dihydrate in 20 ml water was treated with 0.44 g (2 mmol) dimethyltin dichloride in 20 ml ethanol. The mixture was stirred at room temperature for ca 0.5 h. White crystals of $Me_2Sn(S_2AsMe_2)_2$ deposited slowly from the reaction mixture. Yield 0.69 g (71%). IR spectrum: see Table 2. $^1H$ NMR spectrum: $\delta = 2.05$(s) ppm ($As{-}CH_3$) and 1.4 (s) ppm ($Sn{-}CH_3$).

### *Dibutyltin bis(dimethyldithioarsinate), $Bu_2Sn(S_2AsMe_2)_2$*

A solution of 0.45 g (2 mmol) sodium dimethyldithioarsinate dihydrate in 20 ml absolute ethanol was treated with a solution of 0.30 g (1 mmol) $Bu_2SnCl_2$ in 25 ml absolute ethanol. Sodium chloride was filtered after ca 1 h. Concentration of the filtrate deposited 0.50 g (88%) $Bu_2Sn(S_2AsMe_2)_2$, as colorless, needle-like crystals. IR spectrum: see Table 2. $^1H$ NMR spectrum: $\delta = 2.00$ (s) ppm ($As{-}CH_3$), two multiplets centered at 0.9 ppm and 1.31 ppm ($Sn{-}C_4H_9$).

### *Diphenyltin bis(dimethyldithioarsinate), $Ph_2Sn(S_2AsMe_2)_2$*

Two ethanolic solutions of sodium dimethyldithioarsinate dihydrate (0.45 g, 2 mmol in 20 ml ethanol) and diphenyltin dichloride (0.35 g, 1 mmol, in 30 ml ethanol) were mixed and refluxed for 1 h under stirring. The solution turned yellow and sodium chloride precipitated. After filtration and concentration of the filtrate pale yellow crystals of $Ph_2Sn(S_2AsMe_2)_2$ were obtained in 20% yield (0.15 g). IR spectrum: see Table 2. $^1H$ NMR spectrum: $\delta = 1.95$ (s) ppm ($As{-}CH_3$). 5.85 (m) ppm ($Sn{-}C_6H_5$).

### *Triphenyltin dimethyldithioarsinate, $Ph_3Sn(S_2AsMe_2)$*

Sodium dimethyldithioarsinate dihydrate (0.45 g, 2 mmol) in 20 ml ethanol was refluxed with 0.76 g (2 mmol) triphenyltin chloride in 30 ml ethanol, and the mixture was filtered hot after 0.5 h of refluxing. On cooling 0.55 g (54%) $Ph_3Sn(S_2AsMe_2)$ deposited. IR spectrum: see Table 2. $^1H$ NMR spectrum: $\delta = 1.98$ (s) ppm ($As—CH_3$), 5.85 (m) ppm ($Sn—C_6H_5$).

*Tricyclohexyltin dimethyldithioarsinate, $Cy_3Sn(S_2AsMe_2)$*

Prepared as described for the triphenyltin derivative. IR spectrum: see Table 2. $^1H$ NMR spectrum: $\delta = 1.88$ (s) ppm ($As—CH_3$), 1.3 (m) ppm ($Sn—C_6H_{11}$).

*Dichlorobis(dimethyldithioarsinato)tin(IV), $Cl_2Sn(S_2AsMe_2)_2$, and tetrakis-(dimethyldithioarsinato)tin(IV), $Sn(S_2AsMe_2)_4$*

A solution of 0.26 g (1 mmol) tin tetrachloride in 15 ml benzene was treated with 0.88 g (4 mmol) sodium dimethyldithioarsinate dihydrate dissolved in 20 ml absolute ethanol, and the mixture was stirred at room temperature for 15 min. A precipitate of sodium chloride, severely contaminated with a yellow product, deposited and was filtered quickly. The filtrate deposited on standing a yellow precipitate. This was washed with ethanol and dried. Elemental analysis indicated $Cl_2Sn(S_2AsMe_2)_2$.

The filtrate was concentrated on a rotary evaporator, to deposit orange crystals of $Sn(S_2AsMe_2)_4$.

IR spectra: see Table 2. $^1H$ NMR spectra; $Cl_2Sn(S_2AsMe_2)_2$. $\delta = 2.00$ (s) ppm ($As—CH_3$). $Sn(S_2AsMe_2)_4$: $\delta = 2.05$(s) and 1.95(s) ppm ($As—CH_3$).

The dichloro derivative can be obtained in ca. 75% yield by mixing the reagents in 1 : 2 molar ratio. Thus, 0.26 g (1 mmol) tin tetrachloride in 15 ml benzene, treated with 0.45 g (2 mmol) sodium dimethyldithioarsinate, gave 0.39 g (75%) $Cl_2As(S_2Me_2)_2$.

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