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PREPARATION AND PROPERTIES OF SOME ORGANOTIN DIMETHYL- AND DIPHENYL-DITHIOARSINATES. THE CRYSTAL STRUCTURE OF $(CH_3)_2Sn[S_2As(CH_3)_2]_2$

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Summary

Alkyl- and aryl-tin(IV) diphenyldithioarsinates, $R_nSn[S_2As(C_6H_5)_2]_{4-n}$, where $n = 2$, $R = CH_3$, C_4H_9, C_6H_5; $n = 3$, $R = CH_3$, C_6H_{11}, C_6H_5 were prepared in good yields by the reaction of the appropriate organotin halides and the sodium salt of diphenyldithioarsinic acid. The IR spectra of the dialkyl- and trialkyl-tin species, are consistent with four coordination, while the phenyltin derivatives seem to be six coordinate. The molecular structure of $(CH_3)_2Sn[S_2As(CH_3)_2]_2$ was determined by X-ray diffraction; the compound crystallizes in the orthorhombic, D_{2h}^{17}-*Ccmm* space group with *a* 6.310(1), *b* 11.324(3), *c* 23.160(6) Å, *V* 1655 Å^3, $Z = 4$. The dimethyldithioarsinate ligand is monodentate, with single (As–S 2.171 Å) and double (As=S 2.089 Å) arsenic–sulphur bonds. The tin atom is four coordinate, nearly tetrahedral.

Introduction

Among organotin derivatives with sulphur-containing ligands, dithiocarbamates, dithiophosphates and dithiophosphinates have been investigated in considerable detail [1], but little attention has been paid to organotin dithioarsinates. We have recently reported the synthesis of some organotin dimethyldithioarsinates [2] and their infrared and ^1H NMR spectra. On the basis of these spectral data we suggested that in $(CH_3)_2Sn[S_2As(CH_3)_2]_2$ the dimethyldithioarsinate ligand is monodentate,

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with individual single (As–S) and double (As=S) bonds. An X-ray diffraction structure determination confirmed this conclusion and is presented here, along with an account of the synthesis of trimethyltin dimethyldithioarsinate, which also contains a monodentate ligand, and several diphenyldithioarsinates. Interesting comparisons can be made with the structures of dimethyltin dimethyldithiophosphinate, $(CH_3)_2Sn[S_2P(CH_3)_2]_2$ [3] and other organotin diorganodithiophosphates [4–7].

Experimental

The organotin compounds used were commercial products and used without purification. Bis(diphenylarsine)oxide was prepared as by a published method [8]. The solvents were distilled before use. Infrared spectra were recorded on a SPECORD 75 IR C. Zeiss-Jena (DDR) in KBr pellets, in the range 4000–400 cm^{-1}. ^1H NMR spectra were recorded in $CDCl_3$ solutions (TMS standard) on a TESLA B-487 spectrometer operating at 80 MHz. Carbon-hydrogen microanalyses were performed with a Perkin–Elmer 240 B microanalyser.

Sodium diphenyldithioarsinate, $NaS_2As(C_6H_5)_2$

An aqueous solution of bis(diphenylarsine)oxide, $[(C_6H_5)_2As]_2O$, (15 g in 100 ml water) was treated with 3 ml 30% hydrogen peroxide. The diphenylarsinic acid separated as white crystals, m.p. 169°C. Yield 15.7 g (96%).

The diphenylarsinic acid formed was dissolved in 60 ml of 75% ethanol and 2.4 g NaOH were added. A stream of hydrogen sulphide was passed through for 2 h. The black solid which separated on concentration was filtered off. The sodium diphenyldithioarsinate separated out from the filtrate on cooling. After recrystallization from a mixture of acetone and carbon tetrachloride (1/1), white crystals of sodium diphenyldithioarsinate were obtained. Yield: 15.1 g (80%). The product is very hygroscopic.

^1H NMR: δ 7.20–7.90 ppm (m, As-C_6H_5). Anal. Found: C, 45.18; H, 3.02; As, 23.41. $C_{12}H_{10}AsS_2Na$ calcd.: C, 45.56; H, 3.16; As, 23.73%.

Dimethyltin(IV) bis(diphenyldithioarsinate). $(CH_3)_2Sn[S_2As(C_6H_5)_2]_2$

A solution of 0.88 g (4 mmol) dichlorodimethyltin in 20 ml acetone was treated with 2.52 g (8 mmol) sodium diphenyldithioarsinate in 25 ml acetone. After 30 min the sodium chloride was filtered off and the filtrate was concentrated in vacuum to give white-yellowish crystals of title compound, m.p. 126°C, yield 1.10 g (75%).

^1H NMR: δ 1.40 (s, Sn-CH_3), 7.30–7.95 ppm (m, As-C_6H_5). Anal. Found: C, 42.21; H, 3.26; As, 20.16. $C_{26}H_{26}As_2S_4Sn$ calcd.: C, 42.46; H, 3.53; As, 20.41%.

Trimethyltin(IV) diphenyldithioarsinate, $(CH_3)_3SnS_2As(C_6H_5)_2$

A mixture of a solution of 0.6 g (3 mmol) chlorotrimethyltin in 20 ml carbon tetrachloride with a solution of 0.95 g (3 mmol) sodium diphenyldithioarsinate in 20 ml carbon tetrachloride was stirred at room temperature for 40 min. The sodium chloride was filtered off and the solution concentrated in vacuum, to give light yellow crystals, m.p. 108°C, yield 0.9 g (59%).

^1H NMR: δ 0.72 (s, Sn-CH_3), 7.28–7.92 ppm (m, As-C_6H_5). Anal. Found: C, 39.16; H, 4.28; As, 16.11. $C_{15}H_{19}AsS_2Sn$ calcd.: C, 39.41; H, 4.16; As, 16.42%.

Dibutyltin(IV) bis(diphenyldithioarsinate), $(C_4H_9)_2Sn[S_2As(C_6H_5)_2]_2$

A solution of 0.6 g (2 mmol) dibutyldichlorotin in 20 ml acetone was mixed with 1.26 g (4 mmol) sodium diphenyldithioarsinate in 30 ml acetone. After 1 h of stirring at room temperature the sodium chloride was filtered off and the solution concentrated to give white needles, m.p. 86°C, yield 0.92 g (56%).

^{1}H NMR: δ 0.8–1.4 (m, Sn-C_4H_9), 7.30–7.95 ppm (m, As-C_6H_5)). Anal. Found: C, 46.71; H, 4.43; As, 18.06. $C_{32}H_{38}As_2S_4Sn$ calcd.: C, 46.90; H, 4.64; As, 18.32%.

Tricyclohexyltin(IV) diphenyldithioarsinate, $(C_6H_{11})_3SnS_2As(C_6H_5)_2$

A solution of chlorotricyclohexyltin(IV) (0.8 g, 2 mmol) in 20 ml benzene was stirred for 1 h with 0.64 g (2 mmol) sodium diphenyldithioarsinate in 20 ml acetone. The sodium chloride was filtered off and the solution concentrated in vacuum to give white crystals; m.p. 105°C, yield 0.9 g (68%).

^{1}H NMR: δ 0.8–1.3 (m, Sn-C_6H_{11}), 7.15–7.90 ppm (m, As-C_6H_5). Anal. Found: C, 54.16; H, 6.31; As, 11.01. $C_{30}H_{43}AsS_2Sn$ calcd.: C, 54.48; H, 6.50; As, 11.35%.

Diphenyltin(IV) bis(diphenyldithioarsinate), $(C_6H_5)_2Sn[S_2As(C_6H_5)_2]_2$

Dichlorodiphenyltin(IV) (0.7 g, 2 mmol) in 20 ml CCl_4 was added to a solution of sodium diphenyldithioarsinate (1.35 g, 4 mmol in 20 ml acetone) and the mixture was stirred for 30 min. The sodium chloride was filtered off and the solution was concentrated in vacuum, to give crystals of the title compound. M.p. 168°C, yield 0.79 g (48%).

^{1}H NMR: δ 7.15–7.95 ppm (m, Sn-C_6H_5; As-C_6H_5). Anal. Found: C, 50.06; H, 3.22; As, 17.17. $C_{36}H_{30}As_2S_4Sn$ calcd.: C, 50.30; H, 3.49; As, 17.47%.

Triphenyltin(IV) diphenyldithioarsinate, $(C_6H_5)_3SnS_2As(C_6H_5)_2$

A mixture of chlorotriphenyltin(IV) (0.77 g, 2 mmol) and sodium diphenyldithioarsinate (0.64 g, 2 mmol) in 40 ml acetone was stirred for 30 min, at room temperature. The sodium chloride was filtered off and the solution concentrated in vacuum to give white crystals, m.p. 114°C, in 57% yield (0.73 g).

^{1}H NMR: δ 7.15–7.95 (m, Sn-C_6H_5; As-C_6H_5). Anal. Found: C, 55.83; H, 3.53; As, 11.31. $C_{30}H_{25}AsS_2Sn$ calcd.: C, 56.01; H, 3.88; As, 11.67%.

Trimethyltin(IV) dimethyldithioarsinate, $(CH_3)_3SnS_2As(CH_3)_2$

A solution of 0.6 g (3 mmol) of chlorotrimethyltin(IV) in 20 ml acetone was mixed with 0.66 (3 mmol) sodium dimethyldithioarsinate dihydrate in 30 ml ethanol. After 30 min, of stirring at 50°C the sodium chloride was filtered off and the

TABLE 1

ATOMIC COORDINATES ($\times 10^4$) (with e.s.d's in parentheses)

Atom	x	y	z	U
Sn	4772(1)	1/2	3/4	356(2)
As	3419(1)	1/2	5988(1)	387(2)
S(1)	1778(3)	1/2	6812(1)	586(8)
S(2)	6714(3)	1/2	6078(1)	690(9)
C(1)	6400(14)	6626(8)	3/4	656(35)
C(2)	2335(11)	6332(6)	5581(3)	704(26)

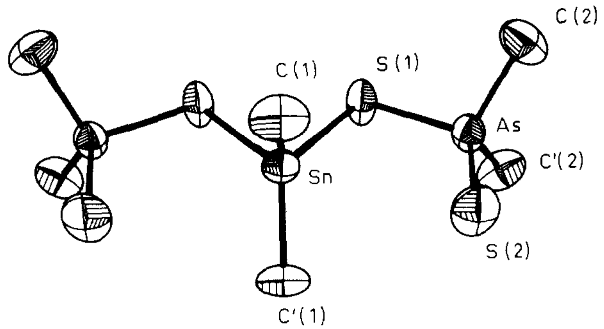


Fig. 1. The molecular structure of $(CH_3)_2Sn[S_2As(CH_3)_2]_2$.

solution concentrated in vacuum to leave an oil, which crystallized in a refrigerator but melted again at room temperature. Yield 0.71 g (72%).

^{1}H NMR: δ 0.70 (s, Sn-CH_3), 2.06 ppm (As-CH_3) Anal. Found: C, 17.78; H, 4.34; As, 22.18. $C_5H_{15}AsS_2Sn$ calcd.: C, 18.03; H, 4.50; As, 22.54%.

Determination of the crystal structure

The unit cell parameters were obtained by least-squares refinement of the respective angular settings of 25 reflections. Intensity measurements were performed on a Syntex R3 diffractometer (Mo-K_α radiation, θ–2θ scans) up to $2\theta = 65°$. Reflections with $I < 2.5\delta(I)$ were regarded as unobserved, leaving 1121 independent reflexions for the calculations. They were corrected for Lorentz and polarisation factors, and an empirical absorption correction was carried out.

Crystal data. $C_6H_{18}As_2S_4Sn$, mol.wt. 486.69; orthorhombic, space group D_{2h}^{17}-*Ccmm*, *a* 6.310(1), *b* 11.324(3), *c* 23.160(6) Å; *V* 1655 Å^3; $Z = 4$.

Structure determination

The structure was solved by Patterson and Fourier synthesis, using the SHELXTL

TABLE 2

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) (with e.s.d's in parantheses) IN $(CH_3)_2Sn[S_2As(CH_3)_2]_2$

Sn–C(1)	2.108(9)
Sn–S(1)	2.471(2)
Sn ··· S(2)	3.515(2)
S(1)–As	2.171(2)
As–S(2)	2.089(2)
As–C(2)	1.905(7)
C(1)–Sn–C'(1)	121.8(5)
S(1)–Sn–S'(1)	80.3(1)
C(1)–Sn–S(1)	111.8(2)
Sn–S(1)–As	101.7(1)
S(1)–As–S(2)	112.8(1)
S(1)–As–C(2)	105.3(2)
S(2)–As–C(2)	114.0(2)
C(2)–As–C'(2)	104.6(4)

program. The hydrogen atoms were fixed at 0.96 Å from the C atoms. Anisotropic refinement for all atoms and isotropic refinement for hydrogen produced convergence at $R = 0.045$ ($R_w = 0.042$). The final atomic coordinates are given in Table 1.

The molecule lies on two perpendicular planes, with the tin atom at their intersection. The C(1) atom is in one of the planes, while the arsenic and sulphur atoms are in the second plane. The molecular structure is shown in Fig. 1. The interatomic distances and bond angles are given in Table 2.

Results and discussion

Sodium diphenyldithioarsinate was prepared by oxidizing bis(diphenylarsine)oxide, $[(C_6H_5)_2As]_2O$ (prepared from As_2O_3 and C_6H_5MgBr [8]) to diphenylarsinic acid, followed by treatment with hydrogen sulphide in ethanol [9]. The stoichiometric amounts of organotin chlorides and sodium diphenyldithioarsinate were stirred in an organic solvent, at room temperature, and the organotin diphenyldithioarsinates were isolated by evaporating the solvent:

$$R_{4-n}SnCl_n + nNaS_2As(C_6H_5)_2 \rightarrow R_{4-n}Sn[S_2As(C_6H_5)_2]_n + nNaCl$$

$$(n = 1, R = CH_3, C_6H_{11}, C_6H_5;$$
$$n = 2, R = CH_3, C_4H_9, C_6H_5)$$

To complete the series of dimethyldithioarsinates, the trimethyltin derivative $(CH_3)_2SnS_2As(CH_3)_2$, not reported in our previous paper [2], was also prepared.

The pure compounds are air stable, but a nitrogen atmosphere is preferable for prolonged storage to avoid decomposition.

Infrared and ^1H NMR spectra

The infrared spectra were recorded in order to provide information about the dithioarsinate ligand. In diphenyldithioarsinates, the As–S stretching vibrations are expected to be in the range 500–350 cm^{-1} [10], as in the spectra of dimethyldithioarsinates, due to lack of coupling between As–S and As–C vibrations [11]. The important frequencies observed in the infrared spectra are listed in Table 3.

The presence of two Sn–C stretching frequencies in $(CH_3)_2Sn[S_2As(C_6H_5)_2]_2$, at 557 and 514 cm^{-1}, indicate distorted tetrahedral coordination around tin [2,12]. Accordingly, the dithioarsinato ligand is assumed to be monodentate; a six coordinated tin compound, with bidentate dithioarsinato groups and linear CH_3–Sn–CH_3

TABLE 3

INFRARED SPECTRA [a] (cm^{-1})

Compound	ν(As=S)	ν(As–S)	ν(Sn–C)	
$(CH_3)_2Sn[S_2As(C_6H_5)_2]_2$	484ms	416m	557m	514m
$(CH_3)_3SnS_2As(C_6H_5)_2$	485ms	420m	550m	513m
$(C_4H_9)_2Sn[S_2As(C_6H_5)_2]_2$	485ms	418m	625m	538m
$(C_6H_{11})_3SnS_2As(C_6H_5)_2$	484ms	416m	665m	645m
$(C_6H_5)_2Sn[S_2As(C_6H_5)_2]_2$	460ms	426m	–	–
$(C_6H_5)_3SnS_2As(C_6H_5)_2$	465ms	420m	–	–
$(CH_3)_3SnS_2As(CH_3)_2$	480s	405m	550m	515m

[a] For all diphenyldithioarsinic derivatives: ν(As–C_6H_5) 685s; 1080s; 1030s cm^{-1}.

arrangement around an octahedral tin atom would exhibit only one Sn–C stretching frequency. The two bands, at 484 and 416 cm^{-1} are, therefore, assigned to ν(As=S) and ν(As–S) stretchings, respectively.

Monodentate coordination, deduced from infrared spectral data for this compound and for $(CH_3)_2Sn[S_2As(CH_3)_2]_2$ described in our previous paper [2], is confirmed by the X-ray molecular structure determination for the later (see below).

Assuming that the two stretching frequencies just discussed are indicative of monodentate diphenyldithioarsinate ligands, it is obvious from the data in Table 3, that all the alkyltin(IV) diphenyldithioarsinates reported here contain four-coordinate (tetrahedral) tin and monodentate dithio ligands. This is also consistent with the presence of two Sn–C stretchings.

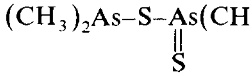
In the infrared spectra of diphenyltin- and triphenyltin-dithioarsinates (Table 3) the bands shifted to ca. 460 cm^{-1} and ca. 420 cm^{-1} can be best assigned to $\nu_{asym}(AsS_2)$ and $\nu_{sym}(AsS_2)$ in a bidentate dithioarsinate ligand. This assignment is made by comparison with the spectra of transition metal diphenyldithioarsinates, in which the ligand is clearly bidentate [9].

The ^1H NMR spectra do not show any peculiarities and are in agreement with the proposed structures. The chemical shifts for individual compounds are given in the Experimental section.

The molecular structure of $(CH_3)_2Sn[S_2As(CH_3)_2]_2$

The structure suggested in our previous paper [2], involving monodentate dithioarsinato ligands, is now confirmed by the X-ray diffraction data. This compound is isostructural with the analogous dimethyltin bis(dimethyldithiophosphinate), $(CH_3)_2Sn[S_2P(CH_3)_2]_2$ [3]. The coordination at tin can be described as distorted tetrahedral (C–Sn–S 111.8(2)°; S–Sn–S 80.3(1)°; C–Sn–C 121.8(5)°). The bond angles are very similar to those in the related dimethyldithiophosphinate (C–Sn–C 109.2(5)°, S–Sn–S 79.9(2)°; C–Sn–C 122.6(8)°) [3]. The dimethyldithioarsinato group in $(CH_3)_2As{-}S{-}As(S)(CH_3)_2$ shows similar parameters: As–S 2.214, As=S 2.075 Å, S–As–S 113.3, S–As–C 106.2 and 115.7° [13].

In the dithioarsinato ligand, long (single) As–S bonds (2.171(2) Å) and short (double) As=S (2.089(2) Å) can be distinguished, suggesting that the ligand can be regarded as monodentate. Alternatively, if the other two sulphur atoms are considered, the geometry can be described as strongly distorted octahedral, with anizobidentate ligands. In any case, the unsymmetrical coordination of the ligand, with two nonequivalent arsenic–sulphur bonds, confirms the assignment of infrared spectral data suggested in ref. 2.

The non-bonded Sn–S(2) distances in both $(CH_3)_2Sn[S_2As(CH_3)_2]_2$ (3.515 Å; this work) and $(CH_3)_2Sn[S_2P(CH_3)_2]_2$ (3.334 Å) [3] are shorter than the sum of the Van der Waals radii (4.0 Å) of tin and sulphur. This may be due to the small bite of the dithio ligands, which brings the second sulphur atom S(2) close to the tin coordination center, but such a short contact probably involves some charge transfer interaction. It is surprising that the dithio ligands do not adopt a monodentate coordination, as in $Ph_3Sn{-}S_2P(OC_2H_5)_2$ [6]. It is noteworthy that in  $(CH_3)_2As{-}S{-}\underset{\underset{S}{\|}}{As}(CH_3)_2$ [13] the similar nonbonded As ··· S distance, calculated by us from the published atomic coordinates is 3.19 Å, i.e. also shorter than the sum of Van der Waals radii.

In view of the fact that this is one of the few X-ray structure determinations for dithioarsinato metal derivatives (the only other compound containing a dimethyldithioarsinato group investigated by X-ray diffraction being $(CH_3)_2As{-}S{-}As(S)(CH_3)_2$ [13]), the structural analogy between the As-containing and P-containing dithio ligands is notable. The other As- and P-analogous dithio compounds investigated by X-ray diffraction, $(C_6H_5)_2SbS_2E(C_6H_5)_2$ (E = P, As), were also found to be isostructural [14].

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