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INTERACTION OF DIMETHYLTIN SULFIDE WITH 1,2-DIBROMOETHANE. CRYSTAL STRUCTURE OF THE DIMETHYLTIN DIBROMIDE/1,4-DITHIANE COMPLEX.

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Summary

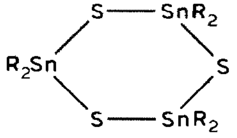
Reaction between trimeric dimethyltin sulfide and 1,2-dibromoethane at 140 °C results in a complex of dimethyltin dibromide with 1,4-dithiane formulated as: $Me_2SnBr_2 \cdot SC_2H_4C_2H_4S \cdot Me_2SnBr_2$. X-ray analysis of the crystal structure of this complex has been performed.

Introduction

The reactivity of trialkyl- and dialkyltin sulfides is due to the tin–sulphur bonds in such compounds. Trialkyltin sulfides (type I compounds) are acyclic compounds, dialkyltin sulfides (type II compounds) are cyclic trimers:

$R_3Sn—S—SnR_3$

(I)



(II)

Despite having different structures, sulfides of these two types react in a similar fashion across the Sn–S bond with some desulphurizing agents. Thus reactions of compounds I and II with an excess of methyl iodide result in trimethyl- or dimethyltin iodides and, in both cases, the sulphonium salt [1]:

$$(Me_3Sn)_2S \xrightarrow[40\,^\circ C]{MeI,} 2\ Me_3SnI + Me_2S \cdot MeI$$

$$(Me_2SnS)_3 \xrightarrow[40\,^\circ C]{MeI,} 3\ Me_2SnI_2 + 3\ Me_2S \cdot MeI$$

But reactions of compounds I and II with other desulphurizing agents proceeds differently, probably owing to the dissimilar structures of the original organotin sulfides.

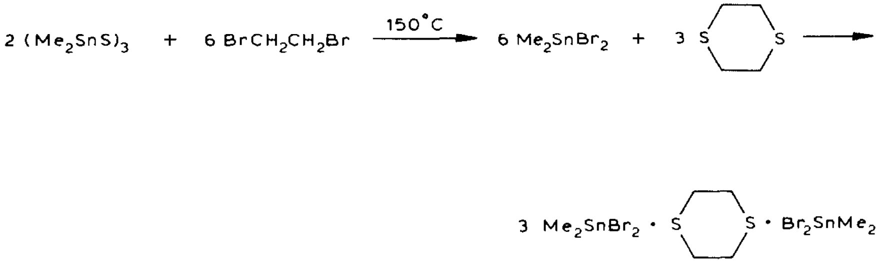
This article reports on such a reaction, viz. the reaction of dimethyltin sulfide (type II compound) with 1,2-dibromoethane. The products of this reaction significantly differ from those of the analogous reaction of type I organotin sulfides.

Results and discussion

It is known [2], that triethyltin sulfide (a type I compound) reacts with an excess of 1,2-dibromoethane at 150 °C giving ethylene and elemental sulphur:

$$(Et_3Sn)_2S \xrightarrow[150\,^\circ C]{BrCH_2CH_2Br,} 2\ Et_3SnBr + CH_2{=}CH_2 + 1/8\ S_8$$

We have found that trimeric dimethyltin sulfide, under identical conditions, also reacts with 1,2-dibromoethane resulting in the splitting of tin–sulphur bonds. However, 1,4-dithiane is formed along with dimethyltin dibromide; and ethylene or elemental sulphur are not released. With a further rise in reaction temperature these primary products interact producing a complex formulated as: $Me_2SnBr_2 \cdot SC_2H_4C_2H_4S \cdot Me_2SnBr_2$, as pretty, colourless crystals which are highly light refracting.



Complexes of composition $Me_2SnX_2 \cdot 0.5S(C_2H_4C_2H_4)S$, where X = Br (III), Cl (IV), were otherwise prepared by heating 1,4-dithiane with the corresponding dimethyltin dihalogenide in a sealed tube. Compounds III and IV can be sublimated in vacuo at 70 °C/1 mmHg without decomposition, but dissociates into initial components when dissolved in various organic solvents. Pyridine or HMPT can quantitatively replace 1,4-dithiane in complexes III and IV.

From elemental analysis data for complex III the emperical formula was found to be $C_4H_{10}Br_2SSn$. We originally formulated this product as: $Me_2Sn(Br)SCH_2CH_2Br$ [1]. But when the molecular mass of this product was cryoscopically determined in benzene, we always obtained the values which were three times less than expected.

This led to an additional study of product III using physico-chemical analysis.

The IR absorption bands of complex III, are representative of dimethyltin dibromide and 1,4-dithiane. The following characteristic absorption bands were observed: $(Sn{-}Br)_s$ 220; $(Sn{-}Br)_{as}$ 245; $(Sn{-}C)_s$ 510; $(Sn{-}C)_{as}$ 560; (C–H) (rock. in CH_3) 785; (C–H) (in CH_2 in dithiane cycle) 1400, 1360, 900, 660 cm^{-1}.

Complex III was also studied using mass spectrometry. Fragment ions representative of dimethyltin dibromide and 1,5-dithiane were present in the mass spectrum. The following fragments were identified based on the available groups of ion lines:

$$m/e \left.\begin{array}{l} 316, 314, \\ 312, 310, \\ 308, 306, \\ 304 \end{array}\right\} Me_2SnBr_2^{+\cdot} \qquad m/e \left.\begin{array}{l} 301, 299, \\ 297, 295, \\ 293, 291, \\ 289 \end{array}\right\} MeSnBr_2^{+} \qquad m/e \left.\begin{array}{l} 124, \\ 122, \\ 121, \\ 120 \end{array}\right\} C_4H_8S_2^{+\cdot}$$

A large number of ions for each fragment is accounted for by a natural abundance of tin, bromine and sulphur isotopes. The analytical data from the mass spectra correspond to the relation between the isotopes of these elements.

To determine the structure of complex III we carried out X-ray crystal structure analysis. The crystal structure projection along the *b* axis is shown in Fig. 1. The major bond lengths and valence angles are shown in the Fig. 2. As can be seen from Fig. 1, crystals of III have a polymeric structure. The 1,4-dithiane molecule links the two molecules of dimethyltin dibromide owing to the formation of intermolecular (secondary) Sn–S bonds, the $Me_2Br_2Sn \cdot S(CH_2CH_2)_2S \cdot SnBr_2Me_2$ dimer is symmetrical. These dimers, in turn, are joined end to end by intermolecular secondary Sn···Br(1)' and Br(1)···Sn' bonds, to form chains along the *a* axis. Only the Br(1) atoms are involved in the formation of these chains as the Br(2) atoms remain terminal. Thus the coordination about the Sn atom in the crystal structure becomes octahedral owing to the S and Br atoms of the neighbouring molecules of 1,4-di-

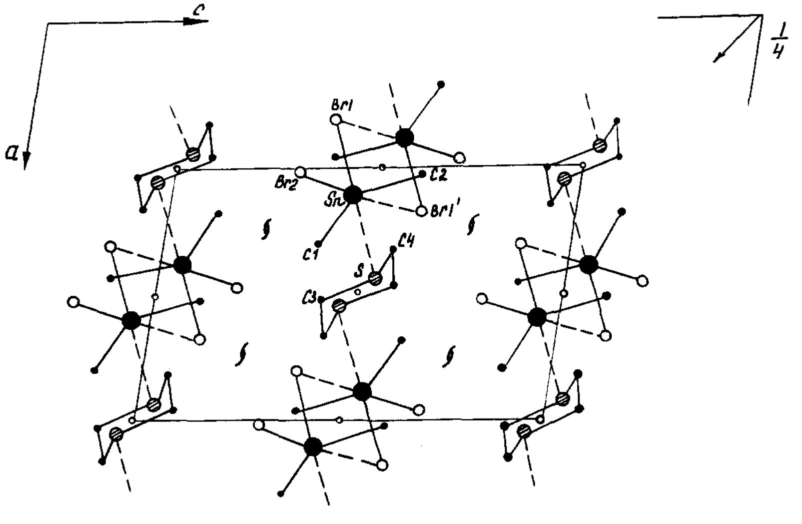


Fig. 1. Crystal structure projection of complex III along the *b* axis. H atoms are not shown.

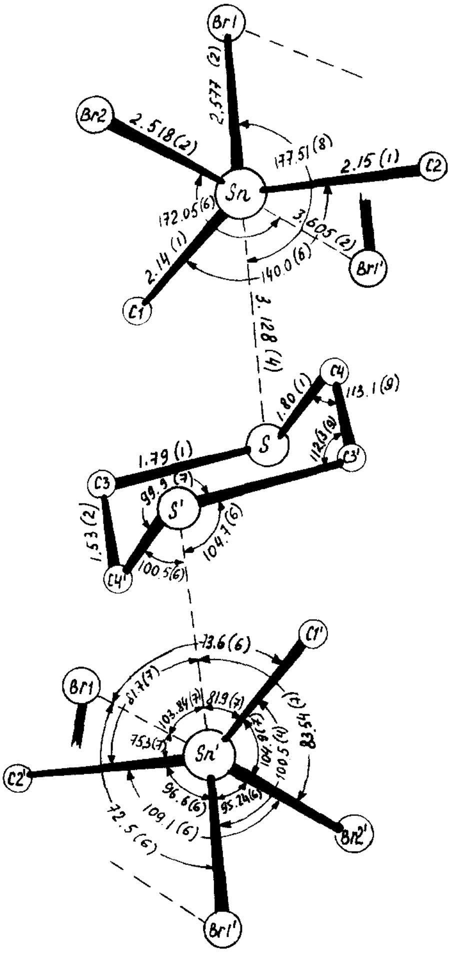


Fig. 2. Crystal structure fragments of complex III with bond lengths and valence angles.

thiane and dimethyltin dibromide. In this case the Sn ··· S and Sn ··· Br(1)′ distances are 3.128 and 3.605 Å respectively and are appreciably less than the sum of the Van der Waals radii of 4.00 and 4.05 Å; $r_W(Sn) = 2.20$Å [4], $r_W(Br) = 1.85$Å, $r_W(S) = 1.80$Å [5]. The tin atom in complex III has a strongly distorted octahedral coordination which is representative of the complexes $Me_nSnX_{4-n} \cdot 2B$ (X = Cl, B = base) [6,7]. The Br(1) and S atoms are located in the axial and the C(1), C(2), Br(2), Br(1)′ in the equatorial positions. The S–Sn–Br(1) 177.51(8)° and Br(1)′–Sn–Br2 172.05(6)° angles between *trans*-ligands deviate less from the ideal value of 180° than the C(1)–Sn–C(2) angle of 140.0(6)°. The values of valence angles between the equatorial and axial ligands also deviate appreciably from the ideal value of 90°: S–Sn–C(1) 81.9(7)°, S–Sn–C(2) 81.7(7)°, S–Sn–Br(2) 83.54(7)°, S–Sn–Br(1) 103.84(7)°, see Fig. 2. The Sn–C(Me) bond lengths of 2.14(1) and 2.15(1) Å are usual for this bond (see, for example, [8]). The axial Sn–Br(1) bond (2.577(2) Å) is 0.06 Å longer than the equatorial Sn–Br(2) bond (2.518(2) Å). It is also slightly less (0.1 Å) than the elongation of axial Sn–Halogen bonds normally observed in the octahedral tin complexes compared with the analogous equatorial bonds [7].

The molecule of 1,4-dithiane situated at the centre of symmetry has the chair conformation. The torsion angles of C(4)′–C(3)–S–C(4) 59,9° and C(3)–S–C(4)–C(3)′ 60,5° are close to the ideal value of 60° but the S–C(4)–C(3)′–S′ 67,9° angle is appreciably greater. The angle between the C(3)–S–C(4) and C(3)–C(4)–C(3)′–C(4)′ planes is 53.2°. The S–C, 1.79(1), 1.80(1); and the C–C, 1.53(2) Å bond lengths, as well as the C–S–C, 99.9(7)°; S–C–C 112.3(9)° and 113.1(9)° valence angles (Fig. 2) are close to the corresponding values of the crystal structure of 1,4-dithiane itself [9]. With regard to the intermolecular S ··· Sn interaction, the S atom has a trigonal-pyramidal coordination.

Experimental

IR spectra were obtained on a Perkin–Elmer 577 instrument (a thin film in vaseline oil, CsI).

Mass spectra were recorded with an MI-1305 isotopic mass spectrometer with acceleration voltage of 2 kV, an electronic energy of 70 eV, an emission current of 1.5 mA and a resolution of 500 at a level of 10% from the peak height. X-ray crystal analysis was performed with an automatic diffractometer Syntex P2$_1$ (λMo-K_α, $\theta/2\theta$ scanning in the range $2 \leqslant 2\theta \leqslant 56°$, 1971 independent reflections with $|F| > 2\sigma(F)$. Since crystals of III are highly volatile they were investigated at −110°C. Absorption was not taken into account (μ(Mo-K_α) = 116.3 cm^{-1}).

Crystals of III are monoclinic; at −110°C a 7.444(2); b 11.130(4); c 11.722(3) Å; β 99.3(2)°; $Z = 4$; d_{calc} 2.56 g/cm^3, space group $P2_1/n$.

The structure was determined by the heavy-atom method. The position of tin atom was found using the Paterson function, the positions of all other non-hydrogen atoms were revealed by subsequent electron-density syntheses. The structure was refined by a full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. The H atoms were identified from difference synthesis but their positions and isotopic temperature factors (assumed to be equal to 4.0 Å^2) were not refined. Finally, the R values were calculated as $R = 0{,}053$, $R_w = 0{,}068$. The coordinates of the atoms and their anisotropic thermal parameters are given in Table 1. All calculations were performed using INEXTL programmes [3] by Eclipse S/200 computer.

1. Reaction of trimeric dimethyltin sulfide with 1,2-dibromoethane

4.00 g (0.0074 mol) of dimethyltin sulfide dissolved in 10-fold excess of 1,2-dibromoethane (19 ml) were heated at 140°C for 35 h until the reaction mixture darkened slightly. The excess of 1,2-dibromoethane was removed in vacuum at room temperature and the residue was sublimated at 70°C into an air condenser connected to a trap cooled with liquid nitrogen. 1,4-dithiane was qualitatively found in the trap contents by means of chromatography. 1.23 g (0.0040 mol) of dimethyltin dibromide were found sublimed in the upper part of the air condenser (yield 18%). The lower part of the air condenser contained 4.72 g of sublimated crystals with m.p. 96–98°C which turned out to be complex III (yield 58%). Found: C, 13.23; H,

TABLE 1

COORDINATES OF ATOMS ($\times 10^4$) AND THEIR ANISOTROPIC THERMAL PARAMETERS ($\times 10^2$): $T = \exp[-1/4(B_{11}h^2a^{\star 2} + \ldots)]$

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Sn	1068(1)	1961(1)	4486(1)	18(4)	48(3)	79(3)	1(3)	−7(3)	1(3)
Br(1)	−1804(2)	710(1)	3761(1)	51(6)	104(6)	133(6)	−53(5)	−46(5)	10(5)
Br(2)	274(2)	3648(1)	3063(1)	80(6)	80(6)	100(5)	8(5)	−33(5)	35(4)
S	4444(5)	3570(3)	5394(3)	76(16)	57(14)	113(14)	−21(12)	−6(13)	14(11)
C(1)	3085(23)	931(14)	3812(14)	125(71)	124(65)	281(79)	48(59)	133(63)	−44(58)
C(2)	325(21)	2466(13)	6116(10)	119(65)	158(63)	2(46)	48(56)	24(47)	4(16)
C(3)	5349(22)	3982(13)	4125(13)	113(63)	67(60)	129(60)	−78(55)	42(52)	−72(50)
C(4)	3335(24)	4950(15)	5662(12)	101(66)	119(64)	91(61)	−30(54)	37(57)	−56(50)
H(11)	3790	1060	3105						
H(12)	3780	950	4510						
H(13)	2500	250	3750						
H(21)	−500	2000	6250						
H(22)	−160	3380	5960						
H(23)	970	1980	6580						
H(31)	5800	3390	4030						
H(32)	4320	3930	3130						
H(41)	2590	5100	5180						
H(42)	3410	5200	6320						

2.87; Sn *, 32.90; S **, 8.60; Br ***, 44.00. $C_8H_{20}Br_4S_2Sn_2$ calc: C, 13.02; H, 2.71; Sn, 32.19; S, 8.68; Br, 43.40%. The solid residue (1.45 g) which was not volatile in vacuum (0.5–1.0 mmHg) contained 0.0025 mol (11%) of tin.

2. *Reaction of dimethyltin dibromide with 1,4-dithiane*

3.19 g (0.013 mol) of dimethyltin dibromide and 0.62 g (0.0051 mol) of 1,4-dithiane were dissolved in 15 ml of 1,2-dibromoethane and heated at 140°C for 6 h until the reaction mixture began to darken. 2.93 g (0.0040 mol) of complex III were separated from the mixture. The product had a m.p. of 96–98°C/subl., yield 78%.

3. *Reaction of dimethyltin dichloride with 1,4-dithiane*

1.97 g (0.0089 mol) of dimethyltin dichloride and 0.53 g (0.0044 mol) of 1,4-dithiane were heated at 140°C in a sealed tube in a vacuum for 12 h. Sublimating the contents of tube at 70°C/0.5 mmHg we separated 2.22 g of colourless crystals with a m.p. of 112.5–116°C, which proved to be complex IV and was formulated as: $Me_2SnCl_2 \cdot SC_2H_4C_2H_4S \cdot Me_2SnCl_2$. The product yield was 90%. Found: C, 17.50; H, 3.50; Cl, 25.86; S, 11.75; Sn, 42.08. $C_8H_{20}Cl_2S_2Sn_2$ calc: C, 17.16; H, 3.58; Cl, 25.38;, S, 11.44; Sn, 42.44%. The analyses for tin, halogen and sulphur were performed as described in the footnotes, see below.

4. *Reaction of the complex III with pyridine and hexamethyl phosphotriamide*

0.85 g (0.0106 mol) of pyridine was added to 1.95 g (0,0026 mol) of the complex III, the reaction was exothermic. The reaction mixture was washed with ether (3 × 5 ml) and the solid residue was recrystallized from heptane. Thus we obtained 2.4 g of a complex of composition $Me_2SnBr_2 \cdot 2Py$ with m.p. of 179–181°C/heptane (173°C [10], 164–166°C [11]). The product yield was 99%.

While treating complex III and with HMPT under identical conditions we obtained the complex, $Me_2SnBr_2 \cdot 2HMPT$, m.p. 141–143°C (142–143°C [11]). The yield was quantitative.

Acknowledgements

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* Tin was determined gravimetrically in the form of SnO_2 by wet combustion of the sample in concentrated sulphuric acid. Hydrogen peroxide was added to the mixture and the non-organic residue was then subjected to calcination.

** Sulphur was determined using Schöniger's method.

*** Halogen was determined in the following way. A sample of complex III was saponified at 50°C for 3–4 hours in a sealed tube by a 5% aqueous solution of NaOH (10 ml). The resulting precipitate of dimethyltin oxide was filtered off, washed with water and then with ether. The combined aqueous filtrates were neutralized with 5% nitric acid and analyzed argentometrically for halogen contents. From the ether extract we separated 1,4-dithiane, m.p. 110–113°C/pentane in the ratio of 1 mole of 1,4-dithiane per 2 moles of dimethyltin dibromide.

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