The crystal structure of the salts [Hthiamine] [SnMe₂(H₂O)Cl₃]Cl and [Hthiamine][SnPh₂Cl₄]H₂O: competition between water and chloride for coordination to diorganotin dihalides

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Abstract

Reaction of thiamine chloride hydrochloride (TCl · HCl) (vitamin B_1 hydrochloride) with $SnMe_2Cl_2$ and $SnPh_2Cl_2$ in 9:1 v/v ethanol–water afforded the salts $(HT)[SnMe_2(H_2O)Cl_3]Cl$ (I) and $(HT)[SnPh_2Cl_4]H_2O$ (II) respectively. Both compounds were characterized by mass spectrometry and by IR and Raman spectroscopy, and the crystal structures of both were determined by X-ray diffraction. I crystallizes in the monoclinic space group $P2_1/n$; the thiaminium cation adopts the F conformation, and in the anion the tin atom co-ordinates to two trans C atoms of methyl groups, three Cl atoms and the O atom of a water molecule in a distorted octahedral arrangement. II crystallizes in the triclinic space group $P\bar{1}$; the thiaminium cation adopts the S conformation, and there are two kinds of $[SnPh_2Cl_4]^{2-}$ anion, one placed between two cations with its phenyl groups stacking over their pyridine rings, and the other without a close relationship with any cation. The two Sn atoms lie on a crystallographic inversion centre and have a separation of (0.5, 0.5, 0.0). Several hydrogen bonds are present in both structures, as well as S · · · O electrostatic interactions in II.

Keywords: Tin; X-ray structure; Thiamine; Dimethyltin compounds; Competition between ligands

1. Introduction

The widespread use of organotin(IV) compounds [1] and the biological significance of some of their complexes [2] have prompted investigation of their behaviour in aqueous solution, including identification of hydrates and hydrolysates. Although direct total hydrolysis of dialkyltin dihalides yields the corresponding oxides, R_2SnO [3], this process can be limited to a partial hydrolysis by using moist organic solvents. One experimental approach involves the presence of a base (B) [4,5]. For example, initial hydrolysis of $SnMe_2Cl_2$ produces HCl which reacts with B to give BH^+, so releasing Cl^- ions which can compete with water and remaining B for coordination to the metal [4]. By means of this approach, the following anionic or neutral dimethyltin(IV) compounds have been isolated and structurally characterized: in order of increasing water–

chloride ratio in the coordination sphere of the metal, $[SnMe_2Cl_4]^{2-}$ [4a,b], $[Sn_2Me_4Cl_6]^{2-}$ (a dimer formed of two $[SnMe_2Cl_3]^-$ units that co-crystallize with a water molecule which is not directly bonded to the tin atoms) [6], $[SnMe_2(H_2O)Cl_2][4c,d]$, $[SnMe_2(H_2O)Cl_2]_2$ [4e] and $[SnMe_2(H_2O)_2Cl_2]$ [4f]. For the halide $SnPh_2Cl_2$, a more complex mechanism has been proposed [5]: initial acid–base adduct formation, followed successively by partial hydrolysis to dichlorostannoxane and B hydrochloride, further hydrolysis of dichlorostannoxane to hydroxydistannoxane and additional B hydrochloride, and finally, reaction of B hydrochloride and $SnPh_2Cl_2$ to afford diphenyltetrachlorostannate anions.

To compare the formation of aqua–chloro complexes by the methyl and phenyl derivatives under the same conditions, we have reacted $SnMe_2Cl_2$ and $SnPh_2Cl_2$ in 9:1 ethanol–water with the base vitamin B_1, thiamine chloride hydrochloride (formally TCl · HCl, although thiaminium chloride, $HT^{2+}2Cl^-$, might be a more realistic formulation). This base was chosen be-

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cause of its biological implications. The reactions with SnMe$_2$Cl$_2$ afforded the compound (HT)[SnMe$_2$(H$_2$O)Cl$_3$]Cl (I), which was isolated and characterized. As far as we are aware, no crystallographic study of any species containing [SnMe$_2$(H$_2$O)Cl$_3$]$^-$ has previously been reported, although [SnR$_2$Cl$_3$]$^-$ anions are known to co-crystallize with occluded H$_2$O [6,7]. Co-crystallization with H$_2$O was in fact the result of the reaction with SnPh$_2$Cl$_2$, which afforded (HT)[SnPh$_2$Cl$_4$]H$_2$O (II).

2. Experimental

Dimethyltin dichloride (Aldrich), diphenyltindichloride (Aldrich) and thiamine chloride hydrochloride (Merck) were used as supplied. Solvents were purified by the usual methods. Mass spectra were recorded on a Kratos MS50TC spectrometer connected to a DS90 system and operating under EI conditions (direct insertion probe, 70 eV, 250°C); ions were identified by DS90 software and the normal values for the metallated peaks were calculated using the isotope ^{120}Sn. Elemental analyses were performed with a Carlo Erba 1108 apparatus. Melting points were measured on a Büchi apparatus. IR

spectra were recorded in Nujol mulls or KBr discs on Perkin–Elmer 1330 or Mattson Cygnus 100 spectrophotometers, and Raman spectra were obtained with a Dilor Omars 89 spectrometer (argon ion laser, 5145 Å) using powdered samples in capillary tubes. Conductivities were measured in a WTW LF-3 conductivity meter.

2.1. Synthesis of (HT)[SnMe$_2$(H$_2$O)Cl$_3$]Cl

1.09 g (5 mmol) of solid SnMe$_2$Cl$_2$ were added to a solution of 3.37 g (10 mmol) of TCl · HCl in 9:1 v/v ethanol–water. Upon slow concentration, the colourless solution afforded crystals suitable for X-ray study. Anal. Found: C, 29.4; H, 4.1; N, 9.8. C$_{14}$H$_{26}$Cl$_4$N$_4$O$_2$SSn. Calc.: C, 29.2; H, 4.5; N, 9.7%. M.p. 213°C. The EI mass spectrum showed metallated peaks at m/e (ion, intensity) 120(Sn, 16.7); 155(SnCl, 49.8); 185(SnMe$_2$Cl, 24.1); 205(SnMeCl$_2$, 100). Λ_M (DMSO), 41.7 S cm^2 mol^{-1}.

2.2. Synthesis of (HT)[SnPh$_2$Cl$_4$]H$_2$O

1.72 g (5 mmol) of solid SnPh$_2$Cl$_2$ were added to a solution of 3.37 g (10 mmol) of TCl · HCl in 9:1 v/v ethanol–water. After 6 h stirring the white solid formed

Table 1
Crystal data, data collection and structure refinement parameters

	I	II
Crystal shape	prismatic	prismatic
Size (mm^3)	0.30 × 0.25 × 0.30	0.05 × 0.25 × 0.65
Chemical formula	C$_{14}$H$_{26}$Cl$_4$N$_4$O$_2$SSn	C$_{48}$H$_{60}$Cl$_8$N$_8$O$_4$S$_2$Sn$_2$
Formula weight	574.95	1398.20
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$
Unit cell dimensions		
a (Å)	7.422(1)	17.273(3)
b (Å)	31.756(2)	10.776(1)
c (Å)	9.735(1)	7.877(1)
α (deg)	90.00(−)	87.91(1)
β (deg)	96.93(1)	86.74(1)
γ (deg)	90.00(−)	79.31(1)
Volume of unit cell (Å^3)	2277.5(3)	1437.9(5)
Z	4	1
D_x (g cm^{-3})	1.677	1.615
$F(000)$	1152	1368
Linear absorption coefficient (mm^{-1})	1.70	1.36
Total No. of refl. measured, θ range (deg)	5459, 3–27	7840, 3–29
No. of unique reflections; R_{int}	4705, 0.017	7320, 0.036
No. of observed reflections	3820	3779
Criterion for observed reflections	$I > 3\sigma(I)$	$I > 3\sigma(I)$
Weighting scheme	$1/\sigma^2(F)$	$1/\sigma^2(F)$
Parameters refined	236	467
Value of R	0.029	0.044
Value of wR	0.036	0.050
Ratio of max. LS shift to e.s.d. (Δ/σ)	0.001	0.001
Max. $\Delta\rho$ in final difference electron density map (e Å^{-3})	0.521	0.604
Error in an observation of unit weight	1.840	1.969
Secondary extintion coefficient	1.337 × 10^{-7}	7.591 × 10^{-8}

was filtered off. Slow concentration of the filtrate afforded crystals subsequently used in the X-ray study. Anal. Found: C, 41.1; H, 4.1; N 7.9. $C_{24}H_{30}Cl_4N_4O_2$-SSn. Calc.: C, 41.2; H, 4.3; N, 8.0%. M.p. 198°C. The EI mass spectrum showed metallated peaks at m/e – (ion, intensity) 120(Sn, 20.5); 155(SnCl, 100); 232(SnPhCl, 38.6); 267(SnPhCl$_2$, 22.0); 309(SnPh$_2$Cl, 13.4); 344(SnPh$_2$Cl$_2$, 19.4). Λ_M(DMSO), 30.0 S cm^2 mol^{-1}.

2.3. X-ray data collection and reduction

Crystals of (HT)[SnMe$_2$(H$_2$O)Cl$_3$]Cl (**I**) and (HT)[SnPh$_2$Cl$_4$]H$_2$O (**II**) were mounted on glass fibres and used for data collection in an Enraf–Nonius CAD4 automatic diffractometer. Cell constants and an orientation matrix for data collection were obtained by least squares refinement of the diffraction data from 25 reflections in the range $8 < \theta < 12°$ (**I**) or $6 < \theta < 12°$ (**II**) [8]. Data were collected at 293 K using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and the ω–2θ scan technique, and were corrected for Lorentz and polarization effects. An empirical absorption correction was also made [9]. Table 1 summarizes the crystal data, experimental details and refinement results.

2.4. Structure solution and refinement

The structures were solved by direct methods [10], which revealed the positions of all non-hydrogen atoms, and refined on F by a full-matrix least squares procedure; anisotropic displacement parameters were used for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map (except O-bonded H atoms in **II**) and were added to the structure factor calculations as fixed contributions ($B_{iso} = 4.0$ Å), but their positional parameters were not refined. A secondary extinction correction was applied [11]. Atomic scattering factors were taken from *International Tables for X-Ray Crystallography* [12]. Molecular graphics were produced with SCHAKAL [13]. Tables 2 and 3 list the positional and thermal parameters of **I** and **II** respectively.

3. Results and discussion

3.1. Description of the structures

The structure of **I** is shown in Fig. 1 together with the adopted numbering scheme. The crystal consists of thiaminium cations, aquotrichlorodimethylstannate(IV) anions and chloride anions.

Table 2
Positional and thermal parameters of I, and their e.s.d.s

Atom	x	y	z	B_{eq} [a]
Sn	0.42112(4)	0.34691(1)	0.33156(3)	2.274(5)
Cl(1)	0.4540(2)	0.41036(4)	0.1531(1)	3.09(2)
Cl(2)	0.1168(2)	0.33182(4)	0.2048(1)	3.12(2)
Cl(3)	0.3816(2)	0.28829(5)	0.5063(1)	4.63(3)
Cl(4)	0.8681(2)	0.44263(5)	0.6202(1)	4.09(3)
S(1)	−0.3051(2)	0.32165(4)	−0.1539(1)	3.81(2)
O(1)	0.7204(5)	0.3645(1)	0.4433(4)	4.84(9)
O(5γ)	−0.0450(5)	0.3022(1)	−0.4911(3)	4.05(7)
N(1′)	−0.1536(5)	0.4572(1)	0.2951(3)	2.61(7)
N(3′)	−0.2876(5)	0.5004(1)	0.1190(4)	2.49(7)
N(3)	−0.0811(4)	0.3787(1)	−0.0873(3)	2.01(6)
N(4α)	−0.2517(5)	0.4884(1)	−0.1063(4)	3.09(8)
C(2′)	−0.2578(6)	0.4900(1)	0.2495(4)	2.43(8)
C(2)	−0.2520(6)	0.3688(2)	−0.0811(5)	3.05(9)
C(2′α)	−0.3406(7)	0.5154(2)	0.3537(5)	4.0(1)
C(4′)	−0.2134(5)	0.4763(1)	0.0245(4)	2.25(7)
C(4)	0.0163(5)	0.3489(1)	−0.1525(4)	2.39(7)
C(4α)	0.2103(6)	0.3561(2)	−0.1690(5)	3.9(1)
C(5)	−0.0869(6)	0.3149(1)	−0.1932(4)	2.58(8)
C(5′)	−0.0984(5)	0.4417(1)	0.0671(4)	2.16(7)
C(5α)	−0.0287(7)	0.2747(2)	−0.2567(4)	3.08(9)
C(5β)	−0.0996(7)	0.2690(2)	−0.4074(5)	3.17(9)
C(6′)	−0.0732(6)	0.4333(1)	0.2053(4)	2.63(8)
C(10)	0.5701(7)	0.3080(2)	0.2134(6)	4.2(1)
C(20)	0.3364(8)	0.3915(2)	0.4672(5)	4.6(1)
C(3, 5′)	0.0076(5)	0.4179(1)	−0.0295(4)	2.31(8)

[a] $B_{eq} = 4/3\Sigma_{ij}B_{ij}(a_i \cdot a_j)$

Table 3
Positional and thermal parameters of **II**, and their e.s.d.s

| Atom	x	y	z	B_{eq} [a]
Sn(1)	0.000	0.500	0.000	2.44(1)
Sn(2)	−0.500	0.000	0.000	2.64(1)
Cl(11)	−0.1155(1)	0.4575(2)	0.2009(3)	3.78(4)
Cl(12)	0.0981(1)	0.3443(2)	0.1740(3)	4.16(4)
Cl(21)	−0.5739(1)	−0.0430(2)	0.2892(3)	3.93(4)
Cl(22)	−0.3908(1)	0.0687(2)	0.1605(3)	4.58(4)
S(1)	−0.1756(1)	−0.0157(2)	0.1282(3)	4.26(5)
O	0.2974(4)	0.7425(6)	0.2216(9)	5.9(2)
O(5γ)	−0.2190(4)	0.2617(6)	0.0852(8)	5.3(2)
N(1′)	−0.4260(4)	−0.2175(5)	0.4604(8)	3.2(1)
N(3′)	−0.3891(4)	−0.4163(5)	0.5866(8)	3.4(1)
N(3)	−0.1926(3)	−0.1701(6)	0.3636(8)	3.0(1)
N(4′α)	−0.2598(4)	−0.5044(6)	0.6108(8)	4.1(1)
C(2)	−0.1788(4)	−0.1631(8)	0.197(1)	3.9(2)
C(2′α)	−0.5283(5)	−0.3308(8)	0.565(1)	4.5(2)
C(2′)	−0.4437(4)	−0.3225(7)	0.5369(9)	3.4(2)
C(4′)	−0.3128(4)	−0.4052(6)	0.5628(9)	2.9(1)
C(4)	−0.2003(4)	−0.0547(6)	0.4440(9)	2.7(1)
C(4α)	−0.2123(5)	−0.0493(7)	0.634(1)	3.7(2)
C(5α)	−0.1991(5)	0.1772(7)	0.369(1)	4.4(2)
C(5)	−0.1928(4)	−0.0401(7)	0.3303(9)	3.1(1)
C(5β)	−0.2533(5)	0.2646(8)	0.257(1)	4.4(2)
C(5′)	−0.2907(4)	0.2959(6)	0.4818(9)	2.8(1)
C(6′)	−0.3498(4)	−0.2042(6)	0.4333(9)	3.1(1)
C(11)	0.0146(4)	0.6540(6)	0.1516(9)	2.8(1)
C(12)	0.0275(5)	0.7676(7)	0.078(1)	3.6(2)
C(13)	0.0371(5)	0.8678(7)	0.178(1)	3.9(2)
C(14)	0.0333(5)	0.8548(8)	0.353(1)	4.4(2)
C(15)	0.0208(5)	0.7410(9)	0.429(1)	4.6(2)
C(16)	0.0113(5)	0.6423(8)	0.329(1)	3.9(2)
C(21)	−0.5642(4)	0.1890(6)	−0.0108(9)	2.8(1)
C(22)	−0.6456(4)	0.2137(7)	0.025(1)	3.3(2)
C(23)	−0.6879(5)	0.3368(8)	0.010(1)	4.9(2)
C(24)	−0.6497(6)	0.4343(8)	−0.039(1)	5.4(2)
C(25)	−0.5704(6)	0.4113(7)	−0.073(1)	5.1(2)
C(26)	−0.5265(5)	0.2881(7)	−0.057(1)	3.7(2)
C(3, 5′)	−0.2050(4)	−0.2882(7)	0.453(1)	3.7(2)

[a] $B_{eq} = 4/3 \Sigma_{ij} B_{ij}(a_i \cdot a_j)$.
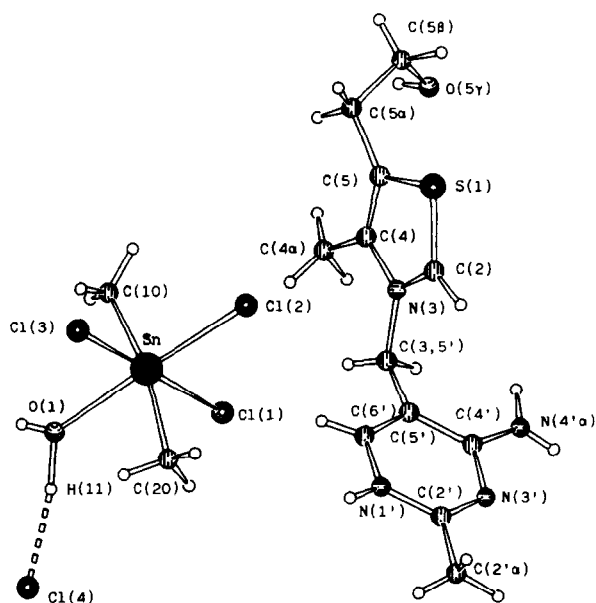
Fig. 1. The crystal structure of **I**, showing the numbering scheme.

In the $[SnMe_2(H_2O)Cl_3]^-$ anion the tin atom is co-ordinated to the two methyl C atoms, three Cl atoms and the O atom of a water molecule in a distorted octahedral arrangement (the C–Sn–C angle, 165.8°, is the most distorted geometrical parameter). The two Sn–C bond distances (Table 4) are practically equal, and are shorter than in other octahedral dimethyltin(IV) chlorocomplexes, such as $[SnMe_2Cl_4]^{2-}$ (2.119(2) Å [4a], 2.115(6) Å [4b]) or $[SnMe_2(H_2O)_2Cl_2]$ (2.112(7) Å) [4f]. The mean length of the two Sn–Cl bonds adjacent to the Sn–O bond (Sn–Cl(1) and Sn–Cl(3)) is close to that found in $[SnMe_2(H_2O)_2Cl_2]$ (2.591(1) Å) [4f]; and the trans bond Sn–Cl(2) is shorter than the trans-bond in $[SnMe_2(H_2O)Cl_2]$ (2.559(2) Å) [4c]. The Sn–O(1) bond is longer than in these previously isolated aquochloro complexes (2.235(4) Å [4f], 2.407(9) Å [4c]). Comparison of the structural parameters of $[SnMe_2(H_2O)Cl_3]^-$ with those of $[SnMe_2Cl_3]^-$ [14] shows that co-ordination to water does not significantly change the Sn–C bond distances, but does lengthen the

Table 4
Bond lengths (Å) and angles (deg) in I, with e.s.d.s

Sn–Cl(1)	2.690(1)	Cl(2)–Sn–C(10)	97.0(1)
Sn–Cl(2)	2.486(1)	Cl(2)–Sn–C(20)	96.9(2)
Sn–Cl(3)	2.562(1)	Cl(3)–Sn–O(1)	92.4(2)
Sn–O(1)	2.418(4)	Cl(3)–Sn–C(10)	92.7(2)
Sn–C(10)	2.092(6)	Cl(3)–Sn–C(20)	90.3(2)
Sn–C(20)	2.084(6)	O(1)–Sn–C(10)	82.3(2)
S(1)–C(2)	1.683(6)	O(1)–Sn–C(20)	83.6(2)
S(1)–C(5)	1.722(5)	C(10)–Sn–C(20)	165.8(2)
O(5γ)–C(5β)	1.421(7)	C(2)–S(1)–C(5)	91.5(2)
N(1′)–C(2′)	1.342(5)	C(2′)–N(1′)–C(6′)	120.4(3)
N(1′)–C(6′)	1.350(6)	C(2′)–N(3′)–C(4′)	118.7(4)
N(3′)–C(2′)	1.305(5)	C(2)–N(3)–C(4)	114.6(4)
N(3′)–C(4′)	1.363(6)	C(2)–N(3)–C(3, 5′)	124.6(4)
N(3)–C(2)	1.315(5)	C(4)–N(3)–C(3, 5′)	120.8(3)
N(3)–C(4)	1.390(5)	N(1′)–C(2′)–N(3′)	122.8(4)
N(3)–C(3, 5′)	1.487(5)	N(1′)–C(2′)–C(2′α)	117.7(4)
N(4α)–C(4′)	1.328(5)	N(3′)–C(2′)–C(2′α)	119.4(4)
C(2′)–C(2′α)	1.486(7)	S(1)–C(2)–N(3)	111.8(3)
C(4′)–C(5′)	1.421(6)	N(3′)–C(4′)–C(5′)	120.9(4)
C(4)–C(4α)	1.486(6)	N(4α)–C(4′)–C(5′)	123.7(4)
C(4)–C(5)	1.356(6)	N(3)–C(4)–C(4α)	120.6(4)
C(5)–C(5α)	1.504(6)	N(3)–C(4)–C(5)	111.7(4)
C(5′)–C(6′)	1.363(6)	C(4α)–C(4)–C(5)	127.7(4)
C(5′)–C(3, 5′)	1.501(6)	S(1)–C(5)–C(4)	110.4(3)
C(5α)–C(5β)	1.509(6)	S(1)–C(5)–C(5α)	121.5(3)
Cl(1)–Sn–Cl(2)	88.38(4)	C(4)–C(5)–C(5α)	128.0(4)
Cl(1)–Sn–Cl(3)	177.79(4)	C(4′)–C(5′)–C(6′)	116.5(4)
Cl(1)–Sn–O(1)	88.2(1)	C(4′)–C(5′)–C(3, 5′)	123.3(3)
Cl(1)–Sn–C(10)	89.5(2)	C(6′)–C(5′)–C(3, 5′)	119.9(4)
Cl(1)–Sn–C(20)	87.6(2)	C(5)–C(5α)–C(5β)	114.6(4)
Cl(2)–Sn–Cl(3)	91.12(5)	O(5γ)–C(5β)–C(5α)	112.3(4)
Cl(2)–Sn–O(1)	176.5(2)	N(1′)–C(6′)–C(5′)	120.7(4)
		N(3)–C(3, 5′)–C(5′)	114.7(3)

Sn–Cl bonds (especially those corresponding to the equatorial Cl and to one of the axial Cl atoms of $[SnMe_2Cl_3]^-$) and widen the C–Sn–C angle from 140(2) to 165.8(2)° (Table 4).

The thiaminium cation is protonated at N(1′), as in other structures containing protonated thiamine [15], and has a C(2′)–N(1′)–C(6′) angle of 120.4°, typical of such structures [15]. The pyrimidine and thiazolium rings are both practically planar ($\chi^2 = 35.8$ and 31.4 respectively). The angles $\phi_T[C(5′)–C(3, 5′)–N(3)–C(2)]$ and $\phi_P[N(3)–C(3, 5′)–C(5′)–C(4′)]$ [16] are 13.7 and $-96.4°$, i.e. the cation adopts the F conformation. The values for the angles C(2)–N(3)–C(3, 5′) and C(4)–N(3)–C(3, 5′), 124.6 and 120.8° respectively, are also those expected for the F form, as are all bond lengths and remaining angles [15]. The torsion angles $\phi_{5α}[S(1)–C(5)–C(5α)–C(5β)]$ and $\phi_{5β}$ [C(5)–C(5α)–C(5β)–O(5γ)], which describe the conformation of the hydroxyethyl side chain [17], are 74.05 and 58.74°; thus the electrostatic interaction between the electronegative O(5γ) and the electron-deficient S atom of the thiazolium ring, which is possible if $\phi_{5α}$ is less than $+70°$ and $\phi_{5β}$ is negative [18], does not occur in this case.

Stability and compactness are lent to the crystal by hydrogen bonds. Besides the hydrogen bond shown in Fig. 1, the N(1′)–H, O(5γ)–H, O(1)–H and N(4′α)–H groups and the Cl(4), Cl(3) and O(5γ) atoms are all involved in such bonds (Table 5).

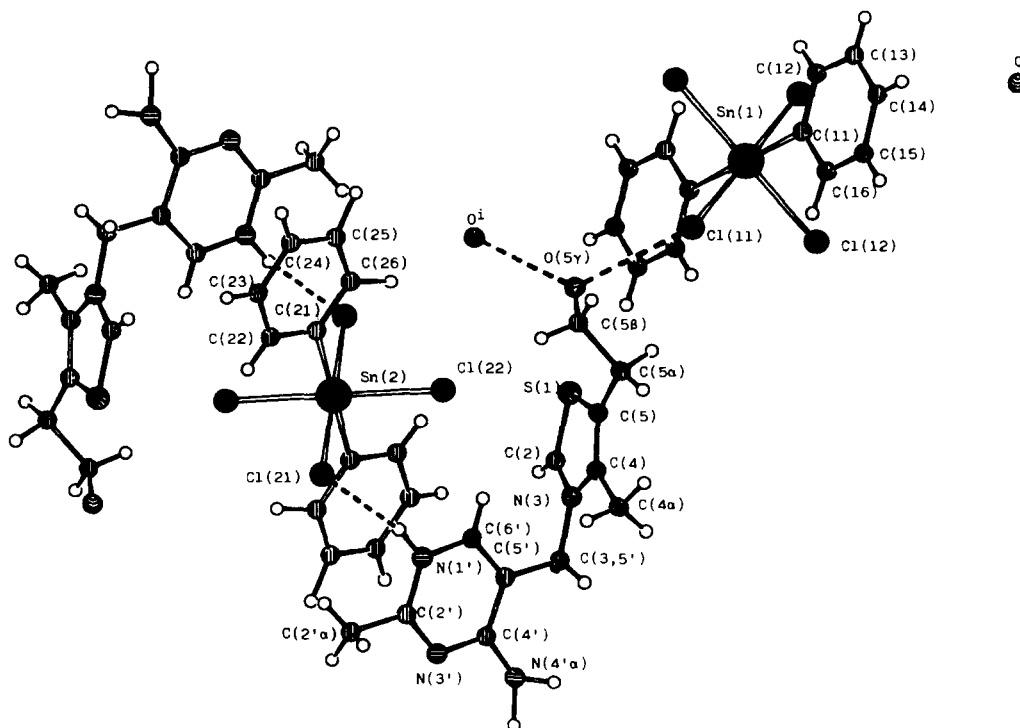The structure of II is shown in Fig. 2 together with the numbering scheme used. Interatomic distances and

Fig. 2. The crystal structure of II, showing the numbering scheme.

Table 5
Hydrogen bonding in **I**

A–H ⋯ B	AH (Å)	H ⋯ B (Å)	A ⋯ B (Å)	A–H–B (deg)
N(1')–H(1') ⋯ Cl(4) [a]	0.95(7)	2.25(7)	3.182(4)	167(6)
O(5γ)–H(5γ) ⋯ Cl(3) [b]	0.76(7)	2.44(7)	3.200(4)	174(7)
O(1)–H(11) ⋯ Cl(4)	1.13(7)	2.03(7)	3.141(4)	168(6)
O(1)–H(12) ⋯ O(5γ) [c]	0.67(7)	2.01(7)	2.661(5)	161(8)
N(4'α)–H(4'α1) ⋯ Cl(4) [d]	0.92(7)	2.33(7)	3.252(4)	169(6)

Symmetry codes: [a] $x - 1$, y, z; [b] x, y, $z - 1$; [c] $1 + x$, y, $1 + z$; [d] $x - 1$, y, $z - 1$.

Table 6
Bond lengths (Å) and angles (deg) in **II**, with e.s.d.s

Sn(1)–Cl(11)	2.573(2)	C(4)–C(4α)	1.501(10)
Sn(1)–Cl(12)	2.571(2)	C(4)–C(5)	1.353(10)
Sn(1)–C(11)	2.140(7)	C(5α)–C(5)	1.503(11)
Sn(2)–Cl(21)	2.616(2)	C(5α)–C(5β)	1.502(12)
Sn(2)–Cl(22)	2.562(2)	C(5')–C(6')	1.345(9)
Sn(2)–C(21)	2.132(6)	C(5')–C(3, 5')	1.502(11)
S(1)–C(2)	1.668(9)	C(11)–C(12)	1.386(10)
S(1)–C(5)	1.712(7)	C(11)–C(16)	1.398(10)
O(5γ)–C(5β)	1.444(11)	C(12)–C(13)	1.402(12)
N(1')–C(2')	1.340(10)	C(13)–C(14)	1.376(12)
N(1')–C(6')	1.356(10)	C(14)–C(15)	1.392(13)
N(3')–C(2')	1.314(9)	C(15)–C(16)	1.383(13)
N(3')–C(4')	1.348(10)	C(21)–C(22)	1.395(10)
N(3)–C(2)	1.325(10)	C(21)–C(26)	1.379(11)
N(3)–C(4)	1.397(9)	C(22)–C(23)	1.396(1)
N(3)–C(3, 5')	1.477(10)	C(23)–C(24)	1.373(14)
N(4'α)–C(4')	1.330(9)	C(24)–C(25)	1.358(14)
C(2'α)–C(2')	1.485(12)	C(25)–C(26)	1.406(10)
C(4')–C(5')	1.422(9)		
Cl(11)–Sn(1)–Cl(11) [a]	180.00(0)	Cl(22)–Sn(2)–Cl(22) [b]	180.00(0)
Cl(11)–Sn(1)–Cl(12)	90.77(6)	Cl(22)–Sn(2)–C(21)	91.36(20)
Cl(11)–Sn(1)–Cl(12) [a]	89.23(6)	Cl(22)–Sn(2)–C(21) [b]	88.64(20)
Cl(11)–Sn(1)–C(11)	90.49(19)	Cl(22) [b]–Sn(2)–C(21)	88.64(20)
Cl(11)–Sn(1)–C(11) [a]	89.51(19)	Cl(22) [b]–Sn(2)–C(21) [b]	91.36(20)
Cl(11) [a]–Sn(1)–Cl(12)	89.23(6)	C(21)–Sn(2)–C(21) [b]	180.00(0)
Cl(11) [a]–Sn(1)–Cl(12) [a]	90.77(6)	C(2)–S(1)–C(5)	91.9(4)
Cl(11) [a]–Sn(1)–C(11)	89.51(19)	C(2')–N(1')–C(6')	120.3(6)
Cl(11) [a]–Sn(1)–C(11) [a]	90.49(19)	C(2')–N(3')–C(4')	118.7(6)
Cl(12)–Sn(1)–Cl(12) [a]	180.00(0)	C(2)–N(3)–C(4)	114.1(6)
Cl(12)–Sn(1)–C(11)	91.38(18)	C(2)–N(3)–C(3, 5')	112.2(7)
Cl(12)–Sn(1)–C(11) [a]	88.62(18)	C(4)–N(3)–C(3, 5')	123.4(6)
Cl(12) [a]–Sn(1)–C(11)	88.62(18)	S(1)–C(2)–N(3)	111.9(6)
Cl(12) [a]–Sn(1)–C(11) [a]	91.38(18)	N(1')–C(2')–N(3')	122.3(8)
C(11)–Sn(1)–C(11) [a]	180.00(0)	N(1')–C(2')–C(2'α)	117.9(6)
Cl(21)–Sn(2)–Cl(21) [b]	180.00(0)	N(3')–C(2')–C(2'α)	119.9(7)
Cl(21)–Sn(2)–Cl(22)	90.13(7)	N(3')–C(4')–N(4'α)	116.3(6)
Cl(21)–Sn(2)–Cl(22) [b]	89.87(7)	N(3')–C(4')–C(5')	121.3(6)
Cl(21)–Sn(2)–C(21)	90.79(18)	N(4'α)–C(4')–C(5')	122.3(7)
Cl(21)–Sn(2)–C(21) [b]	89.21(18)	N(3)–C(4)–C(4α)	120.0(6)
Cl(21) [b]–Sn(2)–Cl(22)	89.87(7)	N(3)–C(4)–C(5)	111.2(6)
Cl(21) [b]–Sn(2)–Cl(22) [b]	90.13(7)	C(4α)–C(4)–C(5)	128.8(6)
Cl(21) [b]–Sn(2)–C(21)	89.21(18)	C(5)–C(5α)–C(5β)	113.5(7)
Cl(21) [b]–Sn(2)–C(21) [b]	90.79(18)	S(1)–C(5)–C(4)	110.9(5)
S(1)–C(5)–C(5α)	122.8(6)	C(11)–C(12)–C(13)	120.9(7)
C(4)–C(5)–C(5α)	126.3(7)	C(12)–C(13)–C(14)	120.2(8)
O(5γ)–C(5β)–C(5α)	109.3(6)	C(13)–C(14)–C(15)	119.6(9)
C(4')–C(5')–C(6')	116.6(7)	C(14)–C(15)–C(16)	120.1(7)
C(4')–C(5')–C(3, 5')	119.9(6)	C(11)–C(16)–C(15)	121.1(8)
C(6')–C(5')–C(3, 5')	123.6(6)	C(22)–C(21)–C(26)	119.1(6)
N(1')–C(6')–C(5')	120.8(7)	C(21)–C(22)–C(23)	120.1(7)
C(12)–C(11)–C(16)	118.2(8)		

Symmetry codes: [a] $-x$, $1 - y$, $-z$; [b] $-1 - x$, $-y$, $-z$.

angles are given in Table 6. The structure consists of thiaminium cations, tetrachlorodiphenylstannate(IV) anions and water molecules so arranged that the compound may be described crystallographically as $[(HT)_2SnPh_2Cl_4]SnPh_2Cl_4 \cdot 2H_2O$. The asymmetric unit consists of one thiaminium cation, halves of two $[SnPh_2Cl_4]^{2-}$ anions with Sn atoms occupying special positions, and one water molecule; the whole $[(HT)_2SnPh_2Cl_4]SnPh_2Cl_4 \cdot 2H_2O$ unit is generated by inversion.

The two $[SnPh_2Cl_4]^{2-}$ anions are located in different crystallographic environments, although in both the tin atom is coordinated to two phenyl C atoms and four Cl atoms in an octahedral arrangement, and both have parameters similar to those reported previously [19].

As in I, the thiaminium cation is protonated at N(1') and the pyrimidine and thiazolium rings are both practically planar ($\chi^2 = 2.4$ and 1.2 respectively). The C(2')–N(1')–C(6') angle is 120.3°. The angles ϕ_T and ϕ_P (95.6 and −178.5° respectively) show S conformation [16]. The values of the angles C(2)–N(3)–C(3, 5') and C(4)–N(3)–C(3, 5'), 122.2 and 123.4° respectively, are close to those found in other thiaminium compounds with S conformation [20,21]. The torsion angles $\phi_{5\alpha}$ and $\phi_{5\beta}$, respectively 48.6 and −68.1°, allow an S $\cdots$ O interaction confirmed by the S(1)–O(5γ) distance (Table 7), which is shorter than the sum of the Van der Waals radii and falls within the reported range for this type of interaction (2.88–3.06 Å) [15].

The mutual arrangement of anions and cations is such that the phenyl groups of one of the tetrachlorodiphenylstannate anions stack over the pyrimidine rings of the cations. The distance between the centre of each pyrimidine ring and its corresponding phenyl ring is 4.25 Å, the shortest interatomic distance being 3.56 Å (C(21)–N(1')) and the dihedral angle between the pyrimidine and phenyl ring planes 17.7°. These figures suggest that some inter-ring interaction occurs, although the distances are greater and the dihedral angles less favourable than in other thiamine derivatives [16,22]. As in I (but through different groups) several hydrogen

bonds lend the crystal stability and compactness (Table 7).

3.2. IR and Raman spectroscopy

The main features of the IR spectra of I and II in the range 4000–600 cm^{-1} recall the spectrum of thiamine chloride hydrochloride and are due to the thiaminium cation, whose bands largely mask those due to the co-ordinated or occluded water. In the range 600–200 cm^{-1} the IR spectrum of I shows a band at 580 cm^{-1} for ν_{as}(Sn–C) and bands at 285, 270 sh, 260 and 240 cm^{-1} for ν(Sn–Cl), while the Raman spectrum (of low quality owing to fluorescence problems) shows a strong band at 522 cm^{-1} (ν_{sym}(Sn–C)); in the IR spectrum ν_{sym}(Sn–C) is probably masked by a thiaminium band at 520 cm^{-1}. The positions of the ν(Sn–Cl) bands in the IR spectrum are close to those found in the complex trichloro(1-methyl-2(3H)-imidazolinethione)dimethyl-stannate(IV) [23], and when compared with their positions in the spectrum of $[SnMe_2Cl_3]^-$ (313, 256 and 242 cm^{-1}) [24] are in keeping with the increased co-ordination number of tin and the abovementioned lengthening of the Sn–Cl bond lengths. In the phenyl derivative $[SnPh_2Cl_4]^{2-}$, ν(Sn–C) and ν(Sn–Cl) IR bands are located at 290 and 260 cm^{-1}, practically the same positions as in other salts of this anion [25] and near to the position found in other octahedral complexes of type $[SnPh_2Cl_2L_2]$ [26].

3.3. Behaviour in solution

The molar conductivities of $(HT)[SnMe_2(H_2O)Cl_3]Cl$ (41.7 S cm^2 mol^{-1}) and $(HT)[SnPh_2Cl_4]H_2O$ (30.0 S cm^2 mol^{-1}) in DMSO (10^{-3} M solutions) do not differ significantly, as would be expected for uni–divalent and di–divalent electrolytes [15,27], and are in both cases low even for 1 : 1 electrolytes [28]. The similarity of the two values is probably due to the partial chloride–water interchange in the tin coordination sphere of the methyl derivative that has also been detected in

Table 7
Hydrogen bonding and electrostatic interactions in II

A–H $\cdots$ B	A–H (Å)	H $\cdots$ B (Å)	A $\cdots$ B (Å)	A–H–B (deg)
Hydrogen bonds				
N(1')–H(1')–Cl(21)	0.968(6)	2.275(2)	3.209(6)	161.9(4)
N(4α)–H(4α)–O^i ^{a}	1.133(6)	1.960(7)	3.004(9)	151.4(4)
O(5γ) $\cdots$ O ^{b}			2.843(9)	
O(5γ) $\cdots$ Cl(11)			3.193(9)	
Electrostatic interactions				
S(1) $\cdots$ O(5γ)	2.957 Å			

Symmetry codes: ^{a} $-x, -y, 1-z$; ^{b} $-x, 1-y, -z$.

other ionic diorganotin complexes [29]; their low magnitudes are attributable to the low ionic mobility of the ions [28].

Acknowledgement

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