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A complex salt formed in reactions of $^{n}BuSnCl_3$ with 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)-2-ketones

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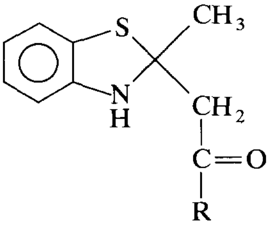
Abstract

The reaction of $^{n}BuSnCl_3$ with 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)-2-ketones (ketone = propanone, methyl phenyl ketone) involves cleavage of the exocyclic ketonyl group to give the complex salt $[(C_8H_8NS)^+]_2[(C_4H_9Sn(OH)Cl_3)_2]^{2-} \cdot 2[C_8H_7NS]$. An X-ray diffraction study of the complex has revealed the first example of true hydrogen bonding involving an Sn–Cl bond.

1. Introduction

The condensation of acetylacetone and benzoylacetone with 2-aminothiophenol is known to give rise to the formation of the respective 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)-2-ketone (1) [1–3].



1a $R = CH_3$
1b $R = C_6H_5$

(1)

The reactions of 1 with the appropriate tin compounds in a basic medium (e.g. methanol containing sodium methoxide) give tin(II) and organotin(IV) complexes in which the tin is coordinated to the ligand via the ONS donor atoms [2–8]. Up to now there has been no report of such reactions carried out in the absence of base.

We have now examined the reactions of **1a** and **1b** with $^{n}BuSnCl_3$ in the absence of added base. In both cases, cleavage of the exocyclic ketonyl group of the ligand occurs, and the complex salt $[(C_8H_8NS)^+]_2$-$[(C_4H_9Sn(OH)Cl_3)_2]^{2-} \cdot 2[C_8H_7NS]$ (**2**) is formed. An X-ray structural investigation of **2** has been carried out, and the results are presented along with other physical data.

2. Experimental details

Acetylacetone, benzoylacetone and $^{n}BuSnCl_3$ were purchased from the Aldrich Chemical Company, and 2-aminothiophenol from Fluka Chemie AG.

Microanalyses were carried out at the School of Chemical Sciences, Universiti Sains Malaysia. The IR spectra were recorded on a Beckman IR 20A spectrophotometer in the frequency range 4000–250 cm^{-1} with samples as KBr discs. The ^1H NMR spectra were recorded on a Brüker AC-P 300 MHz NMR spectrometer; $CDCl_3$ or DMSO-d_6 were used as solvents with TMS as internal standard. Tin analysis was carried out with an Instrumental Laboratory Model aa/ee atomic absorption spectrometer. The mass spectra (at 70 eV) were obtained with a Hewlett Packard 5989A mass spectrometer. Tin-119m Mössbauer isomer shifts (δ), and quadrupole splittings (ΔR_Q) at 78 K were determined with a Cryophysics constant acceleration spectrometer operating in the saw-tooth wave mode. The velocity calibration was based on the room temperature spectrum of natural iron with calcium stannate as the zero-velocity reference.

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2.1. Preparation of 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)-2-propanone (1a)

A solution of acetylacetone (2.0 g, 20 mmol) in 20 cm^3 of methanol was added to a methanolic solution of 2-aminothiophenol (2.5 g, 20 mmol) and the mixture was stirred for 2 h and then chilled. The colourless crystals that separated were filtered off and recrystallized from methanol. Yield 85%; m.p. 85–87°C. Anal. Found: C, 63.5; H, 6.32; N, 6.70. $C_{11}H_{13}NOS$ calc.: C, 63.8; H, 6.32; N, 6.76%. IR: ν(NH) 3360, ν(C=O) 1710 cm^{-1}. ^{1}H NMR: 1.83, 2.20 (s, 2CH$_3$); δ 3.11 (s, CH$_2$); δ 5.09 (m NH); δ 6.62–7.29 (m, aromatic) ppm. MS (70 eV): m/z 207 (M, 20%); 150 (100), 149 (78).

2.2. Preparation of 1-(2-methyl-2,3-dihydrobenzothiazol-2-yl)-methyl phenyl ketone (1b)

This compound was prepared in a similar manner to **1a** from addition of benzoylacetone (16.2 g, 0.1 mol) to 2-aminothiophenol (12.5 g, 0.1 mol). The colourless solid obtained was recrystallized from methanol. Yield 88%; m.p. 62–64°C. Anal. Found; C, 71.4; H, 5.51; N, 5.20. $C_{16}H_{15}NOS$ calc.: C, 71.3; H, 5.61; N, 5.19%. IR: ν(NH) 3375, ν(C=O) 1680 cm^{-1}. ^{1}H NMR: δ 2.20 (s, CH$_3$); δ 2.86 (s, CH); δ 4.10 (m, NH); δ 6.20 (m, CH$_2$); δ 7.40–7.90 (m, aromatic) ppm. MS (70 eV): m/z 269 (M, 13%); 150 (100), 149 (80).

TABLE 1. Crystal data and details of the structure refinement for $[C_{20}H_{25}Cl_3N_2OS_2Sn]_2$ (2)

Empirical formula	$C_{20}H_{25}Cl_3N_2OS_2Sn$
Formula weight	598.6
Crystal system	Triclinic
Space group	$P\bar{1}$
a(Å)	9.493(6)
b(Å)	12.021(7)
c(Å)	12.291(8)
α(°)	65.81(5)
β(°)	76.15(5)
γ(°)	75.04(5)
V(Å^3)	1221.8(13)
Z	2
D_c (mg cm^{-3})	1.627
F(000)	600
μ (mm^{-1})	1.559
Data collected	4737
Unique data	4397
Data with $F > 4.0(F)$	3821
R	0.071
R_w	0.077
w^{-1}	$\sigma^2(F)+0.0031F^2$
k	1
g	0.0031
ρ_{max}(e Å^{-3})	2.59 (near Sn atom)

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$)

	x	y	z	U_{eq} ^{a}
Sn(1)	199(1)	1431(1)	−195(1)	38(1)
Cl(1)	2924(3)	787(2)	−437(2)	57(1)
Cl(2)	−2258(7)	1724(5)	120(5)	152(3)
Cl(3)	86(3)	2161(2)	1392(2)	60(1)
O(1)	−27(6)	305(4)	−1058(3)	41(2)
C(1)	29(12)	3164(9)	−1678(8)	73(4)
C(2)	1260(12)	3361(8)	−2717(7)	64(4)
C(3)	1159(15)	4672(9)	−3644(9)	85(5)
C(4)	2344(16)	4798(11)	−4706(10)	99(6)
C(5)	4436(9)	−5386(7)	1971(6)	43(3)
C(6)	5737(9)	−5905(7)	1374(6)	43(3)
C(7)	6865(9)	−5213(8)	790(7)	52(4)
C(8)	6706(12)	−4059(9)	795(9)	66(4)
C(9)	5427(11)	−3564(8)	1402(8)	58(4)
C(10)	4290(10)	−4241(8)	2007(8)	55(4)
S(1)	3239(3)	−6416(2)	2555(2)	54(1)
N(1)	5732(7)	−7079(6)	1417(6)	47(3)
C(11)	4521(9)	−7449(7)	1989(7)	48(3)
C(12)	4145(12)	−8646(9)	2164(10)	67(5)
C(13)	−1337(10)	1842(7)	−5129(6)	46(3)
C(14)	−1523(10)	1495(6)	−3884(6)	44(3)
C(15)	−2907(12)	1559(8)	−3232(7)	60(4)
C(16)	−4073(12)	2042(10)	−3837(10)	75(5)
C(17)	−3872(14)	2420(10)	−5093(10)	79(6)
C(18)	−2527(13)	2316(10)	−5743(8)	67(5)
S(2)	537(3)	1590(2)	−5687(2)	59(1)
N(2)	−183(8)	1038(6)	−3410(5)	48(3)
C(19)	909(10)	1051(7)	−4222(6)	50(3)
C(20)	2518(12)	593(11)	−3985(4)	89(6)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

2.3. Preparation of complex 2

A solution of ^{n}BuSnCl$_3$ (1.1 g, 4 mmol) in dichloromethane was added with stirring to a solution of the ligand (8 mmol of **1a** or **1b**) in the same solvent. Slow evaporation of the solvent at room temperature afforded colourless crystals. Yield 70%; m.p. 96–98°C. Anal. Found: C, 40.6; H, 4.45; N, 4.68; Sn, 19.6. $C_{40}H_{50}Cl_6N_4O_2S_4Sn_2$ calc.: C, 40.2; H, 4.21; N, 4.67; Sn, 19.8%. IR: ν(NH) 3370; ν(Sn–O) 530, ν(Sn–Cl) 430 cm^{-1}. ^{1}H NMR: δ 0.95–1.60 (m, butyl); δ 2.85 (s, CH$_3$); δ 5.80 (m, NH), δ 7.50–8.20 (m, aromatic) ppm. Mössbauer: δ 0.76; (ΔE_Q) 3.80 mm s^{-1}.

2.4. Crystallography

The X-ray diffraction data were collected on a Siemens P4 diffractometer using monochromated Mo Kα radiation, $\lambda = 0.71073$ Å. All calculations were performed with Siemens SHELXTL PLUS (PC version). The unit parameters were calculated from the setting angles of 25 reflections with $15 \leq 2\theta < 35°$.

The intensities of 4397 independent reflections were measured by the 2θ–θ scan technique. The structure was solved by direct methods and refined by using a full-matrix least squares technique. All hydrogen atoms except H(N(1)) were located from the difference Fourier map. The (N(1)) atom was placed in its calculated position and included in the refinement. The inclusion of this proton was based on the IR and ^{1}H NMR data which suggest the presence of NH and on the slightly longer N(1)–C(11) bond compared with the N(2)–C(19) bond. Furthermore, the intermolecular N(1) ··· Cl(2) distance of 2.695(8) Å is ideal for the formation of a hydrogen bond.

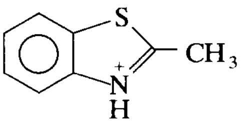
TABLE 3. Selected bond distances (Å) and angles (°), with e.s.d.s in parentheses

Sn(1)–Cl(1)	2.483(3)	Cl(1)–Sn(1)–Cl(2)	171.9(2)
Sn(1)–Cl(2)	2.229(6)	Cl(1)–Sn(1)–Cl(3)	94.2(1)
Sn(1)–Cl(3)	2.418(3)	Cl(2)–Sn(1)–Cl(3)	89.0(2)
Sn(1)–O(1)	2.107(6)	Cl(1)–Sn(1)–O(1)	92.1(2)
Sn(1)–C(1)	2.131(8)	Cl(2)–Sn(1)–O(1)	82.5(2)
Sn(1)–O(1A)	2.043(4)	Cl(3)–Sn(1)–O(1)	159.9(1)
C(1)–C(2)	1.495(13)	Cl(2)–Sn(1)–C(1)	87.5(3)
C(2)–C(3)	1.514(12)	Cl(3)–Sn(1)–C(1)	99.2(3)
C(3)–C(4)	1.488(16)	O(1)–Sn(1)–C(1)	98.6(4)
C(5)–C(6)	1.413(10)	Cl(1)–Sn(1)–O(1A)	88.8(2)
C(5)–C(10)	1.366(13)	Cl(2)–Sn(1)–O(1A)	83.7(2)
C(5)–S(1)	1.717(9)	C1(3)–Sn(1)–O(1A)	90.2(2)
C(6)–C(7)	1.399(12)	O(1)–Sn(1)–O(1A)	70.8(2)
C(6)–N(1)	1.391(12)	C(1)–Sn(1)–O(1A)	167.0(4)
C(7)–C(8)	1.359(16)	Sn(1)–O(1)–Sn(1A)	109.2(2)
C(8)–C(9)	1.393(14)	Sn(1)–C(1)–C(2)	118.6(6)
C(9)–C(10)	1.398(14)	C(1)–C(2)–C(3)	115.1(8)
S(1)–C(11)	1.741(9)	C(2)–C(3)–C(4)	113.0(9)
N(1)–C(11)	1.278(11)	C(6)–C(5)–C(10)	120.8(8)
C(11)–C(12)	1.489(15)	C(6)–C(5)–S(1)	108.5(6)
C(13)–C(14)	1.391(10)	C(10)–C(5)–S(1)	130.7(6)
C(13)–C(18)	1.376(15)	C(5)–C(6)–C(7)	118.9(8)
C(13)–S(2)	1.742(9)	C(5)–C(6)–N(1)	114.4(7)
C(14)–C(15)	1.367(12)	C(7)–C(6)–N(1)	126.6(7)
C(14)–N(2)	1.411(12)	C(6)–C(7)–C(8)	120.4(8)
C(15)–C(16)	1.351(16)	C(7)–C(8)–C(9)	120.2(10)
C(16)–C(17)	1.398(17)	C(8)–C(9)–C(10)	120.7(10)
C(17)–C(18)	1.340(16)	C(5)–C(10)–C(9)	118.9(8)
S(2)–C(19)	1.736(8)	C(5)–S(1)–C(11)	90.3(4)
N(2)–C(19)	1.254(10)	C(6)–N(1)–C(11)	111.7(7)
C(19)–C(20)	1.539(14)	S(1)–C(11)–N(1)	115.0(7)
		S(1)–C(11)–C(12)	119.8(6)
		N(1)–C(11)–C(12)	125.2(8)
		C(14)–C(13)–C(18)	121.3(8)
		C(14)–C(13)–S(2)	109.4(7)
		C(18)–C(13)–S(2)	129.3(6)
		C(13)–C(14)–C(15)	120.4(8)
		C(13)–C(14)–N(2)	113.5(7)
		C(15)–C(14)–N(2)	126.1(7)
		C(14)–C(15)–C(16)	118.2(8)
		C(15)–C(16)–C(17)	120.9(10)
		C(16)–C(17)–C(18)	121.7(12)
		C(13)–C(18)–C(17)	117.4(9)
		C(13)–S(2)–C(19)	88.7(4)
		C(14)–N(2)–C(19)	111.8(7)
		S(2)–C(19)–N(2)	116.6(7)
		S(2)–C(19)–C(20)	119.5(5)
		N(2)–C(19)–C(20)	123.9(7)

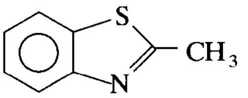
A weighting scheme of the form $w^{-1} = \sigma^2(F) + 0.0031F^2$ was employed and the refinement continued to final $R = 0.071$, $R_w = 0.077$ for $k = 1$ and $g = 0.0031$. Crystal data and refinement parameters are summarized in Table 1. Fractional coordinates are listed in Table 2 and bond lengths and angles in Table 3. Additional data, including hydrogen atomic coordinates, anisotropic temperature factors and lists of observed and calculated structure factors are available from the authors.

3. Results and discussion

The molecular structure of the complex salt, **2**, formed by the reaction of either **1a** or **1b** with $^{n}BuSnCl_3$ is shown in Fig. 1. It is an outer-sphere complex in which the central tin-containing unit, $[C_4H_9Sn(OH)Cl_3]_2^{2-}$, is surrounded by four 2-methylbenzothiazole molecules, two of which are in the protonated forms, **3a**, and the other two, **3b**, in the non-protonated form.



(3a)



(3b)

The C=N bond in **3a** (N(1)–C(11), 1.278(11) Å) is slightly longer than that in **3b** (N(2)–C(19), 1.254(10) Å), in accord with the longer length of C=$\overset{+}{\mathrm{N}}$H bonds [9,10]. The above C=N bonds, however, are shorter than the analogous C–N single bond in **1a** (*cf.* C–N bond length 1.463(3)°) [8]. The presence of the imino protons in the **3a** moieties is supported by the observation of the =NH peak at 3370 cm^{-1} in the IR spectrum of **2** and a sharp peak at δ 5.80 ppm in its ^{1}H NMR spectrum.

Formation of the moieties **3a** and **3b** necessitate the loss of ketonyl groups from the parent ligand. Both the mass spectra of **1a** and **1b** show base peaks at m/z 150 and a peak of significant intensity (~ 80%) at m/z 149 corresponding to the fragments **3a** and **3b**, respectively. The fragmentation patterns are in excellent agreement with those found in the mass spectra of similar compounds [11] and Elias and Giles [12] have shown that the formation of such stable species as **3a** and **3b** is characteristic of the mass spectra of *ortho*-substituted aromatic Schiff bases.

Counterbalancing the two positively charged species, **3a** is the centrosymmetric doubly negatively charged central tin-containing unit. The structure is built up

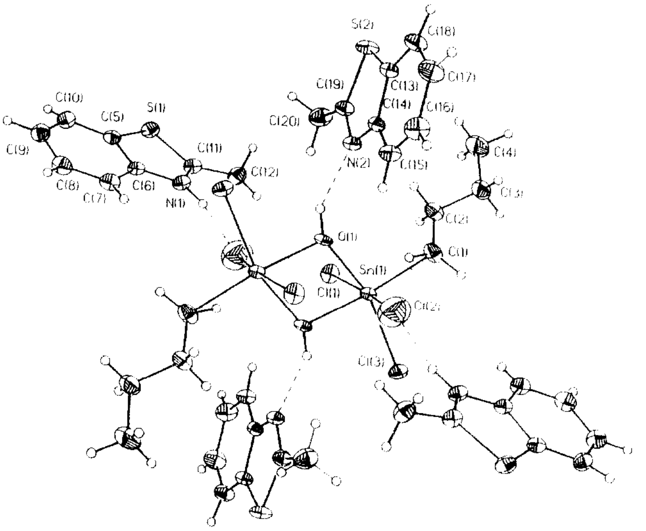


Fig. 1. Molecular structure of $[(C_8H_8NS)^+]_2[(C_4H_9Sn(OH)Cl_3)_2]^{2-} \cdot 2[C_8H_7NS]$.

around a planar Sn_2O_2 distannoxane unit with Sn(1)–O(1)–Sn(1A) angle of 109.2(2)° and O(1)–Sn(1)–O(1A) angle of 70.8(2)°. These angles are in the range found for similar distannoxane units [13–16] and so are the Sn–O distances [13,17].

Each tin atom in the dimeric formation possesses a grossly distorted octahedral geometry and is coordinated to the n-butyl group, three chlorine atoms and two bridging oxygen atoms from the two hydroxyl groups. The isomer shift (δ 0.73 mm s^{-1}) and quadrupole splitting ($\Delta E_Q = 2.16$ mm s^{-1}) values of the Mössbauer spectrum of **2** are indicative of the presence of tin(IV) consistent with the six-coordinated tin environment [18]. The n-butyl group is *trans* to one of the bridging hydroxyl groups (C(1)–Sn(1)–O(1A) bond angle, 167.0(4)°) while two of the chlorine atoms (Cl(1), Cl(2)) are *trans* with respect to each other. The Sn(1)–Cl(1) and Sn(1)–Cl(3) bond lengths are within the range of 2.30–2.45 Å found for Sn–Cl bonds [13] whereas the Sn–Cl(2) bond (2.229(6) Å) is slightly shorter. It can be seen from Fig. 1 that Cl(2) interacts with a protonated **3a** moiety; similar interaction occurs between Cl(2A) and another **3a** moiety. As the H(N(1)) ··· Cl(2A) distance is 1.755(6) Å, such strong interactions give rise to partially charged positive and negative centres at the tin and the Cl(1) and Cl(2A) atoms, respectively, increasing the strength of the Sn–Cl bond, so accounting for the slightly shorter Sn(1)–Cl(2) (also the Sn(1A)–Cl(2A)) bond. The Cl(2) atom exhibits rather high thermal parameters, comparable in magnitude with those of the C(3) and C(4) atoms of the butyl group arising from free rotation about the C–C bonds. The disorder of the Cl(2) atom could be due to softness of the position of the chlorine atom between the H and Sn(1) atoms $(\overset{\delta+}{\mathrm{H}} \cdots \overset{\delta-}{\mathrm{Cl}} \cdots \overset{\delta+}{\mathrm{Sn}})$.

Similarly short Sn–Cl bonds to that in complex **2** have been found in the dimeric trihalogenostannic acid ester, $SnCl_3OCH_3 \cdot CH_3OH$, which has Sn–Cl bond lengths of ~ 2.2 Å [19].

The hydrogen bonding in **2** is, to the best of our knowledge, the first example involving an Sn–Cl bond. In the crystal structure of $[Cl_3(H_2O)Sn\text{–}OH\text{–}]_2 \cdot 4H_2O$ [20], there are H ··· Cl(Sn) distances of ~ 2.90 Å; those interactions must be very weak and cannot be considered as indicating true hydrogen bonding.

There is also hydrogen bonding between the two bridged hydroxyl groups and the two **3b** moieties; the H(O(1))–N(2) bond distance of 1.809(7) Å agrees well with those of other similar bonds [21].

The type of outer-sphere complex exemplified by **2** in which the ligands are not coordinated directly to the tin atom but are held in position by hydrogen bonds has been reported for phenanthroline and bipyridine complexes of triphenyltin chloride [22].

Dimeric structures containing the distannoxane ring, Sn_2O_2, with an octahedral arrangement of ligands about tin(IV) are known for $[SnCl_3(OH)(OH_2)]_2 \cdot 3C_4H_8O_2$ [17] and $[SnCl_3(OMe)(MeOH)]_2$ [19]. Hydrolysis of ^{n}BuSnCl$_3$ has given the species $[^{n}BuSn(OH)(OH_2)Cl_2]_2$ [13] in which the central tin-containing moiety is similar to that in **2** except for the replacement of one of the chlorine atoms of ^{n}BuSnCl$_3$ by a water molecule. In the present study, however, all the chlorine atoms of ^{n}BuSnCl$_3$ have been been retained. Neither the IR nor ^{1}H NMR spectra of **2** show any water peak, and the requirement for electrical neutrality precludes the presence of a water molecule.

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