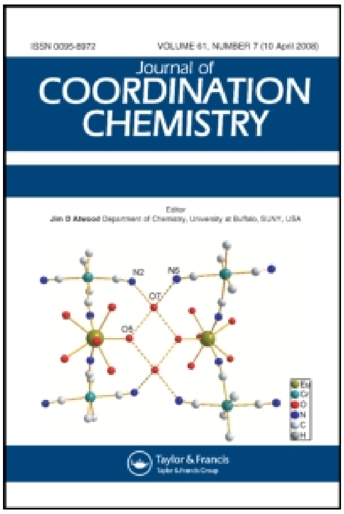

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THE PREPARATION AND CRYSTAL STRUCTURE OF DIMETHYL [[N-(PENTANONE-4-(2-MERCAPTOPHENYL)IMINATO](2-)- N,O,S]TIN(IV)

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THE PREPARATION AND CRYSTAL STRUCTURE OF DIMETHYL[[*N*-(PENTANONE-4-(2-MERCAPTOPHENYL)IMINATO](2-)-*N,O,S*]TIN(IV)

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The reaction of dimethyltin(IV) with 2-pentanone-4-(2-benzothiazolinyl) results in the formation of dimethyl[[*N*-(2-pentanone-4-(2-mercaptophenyl)iminato](2−)-*N,O,S*]tin(IV) which crystallizes in the monoclinic crystal system, space group $P2_1/n$, $Z = 4$, $a = 7.489(1)$, $b = 13.164(1)$ and $c = 15.028(2)$ Å; $\beta = 103.32(1)°$ and $V = 1441.7(3)$ Å^3. Refinement converged to $R = 0.021$ and $R_w = 0.022$ based on 2515 reflections with $I > 3\sigma(I)$. The ligand functions as a terdentate dianion coordinating to the tin atom through the imine nitrogen, oxygen and sulphur to give a distorted trigonal bipyramidal arrangement.

Keywords: 2-Pentanone-4-(2-benzothiazolinyl), dimethyltin(IV) dichloride, trigonal bipyramidal coordination, X-ray structure

INTRODUCTION

Condensation of 2-aminothiophenol with a carbonyl-containing compound has been known to give rise to the formation of a benzothiazoline, the nature of which depends on the carbonyl compound and the reaction conditions.[1–5] Upon reaction with a metal ion, the benzothiazoline rearranges to the corresponding Schiff base and the metal complex of the Schiff base can be isolated.[6,7]

Complexes of Schiff bases derived from benzothiazolines with a number of transition metal ions have been investigated[8–12] and in recent years, the study has been extended to complexes of mono-organotin(IV) and diorganotin(IV) with benzothiazolines derived from the condensation of 2-aminothiophenol with salicylaldehyde and acetylacetone.[5,10,12–14]

Our attention has been drawn to the fact that in the formation of 2-pentanone-4-(2-benzothiazolinyl), **1**, by the condensation of 2-aminothiophenol with acetylacetone, only one carbonyl group of the latter has been utilized.

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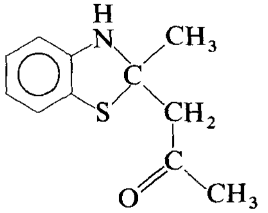

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In this paper, we report the synthesis and a full X-ray structural analysis of the dimethyltin(IV) complex of **1**.

EXPERIMENTAL

Synthesis of ligand, 1

A solution of 2,4-pentanedione (20 mmol) in 20 cm^3 of methanol was added to a methanolic solution of 2-aminothiophenol (20 mmol). The mixture was stirred for 2 hrs and then chilled. The colourless crystals which appeared were filtered and recrystallized from methanol. Yield 85%; m.p. 85–87°C. Anal.: Calcd. for $C_{11}H_{13}NOS$: C, 63.78; H, 6.32; N, 6.76%. Found: C, 63.55; H, 6.32; N, 6.70%. IR (KBr): ν, 3340 (NH), 1705 (C=O); NMR (^1H, $CDCl_3$ 25°C): δ, 1.83, 2.20 (s, 6H, $2CH_3$); 3.11 (s, 2H, CH_2); 5.09 (m, 1H, NH); 6.62–7.29 (m, 5H aromatic) ppm.

Synthesis of dimethyl[[N-(2-pentanone-4-(2-mercaptophenyl)iminato](2−)-N,O,S]tin(IV), $C_{13}H_{17}NOSSn$

A reaction mixture consisting of **1** (5 mmol), sodium methoxide (10 mmol) and dimethyltin(IV) dichloride (5 mmol) in 50 cm^3 of methanol was stirred for 3 hrs at room temperature under nitrogen. The sodium chloride which precipitated was filtered off and on standing yellow crystals were formed from the filtrate. Yield 72%; m.p. 110–112°C. Anal.: Calcd. for $C_{13}H_{17}NOSSn$: C, 44.10; H, 4.84; N, 3.96; Sn, 33.52%. Found: C, 43.98; H, 4.78; N, 3.96; Sn, 33.50%. IR (KBr): ν, 1540–1515 (C=N, delocalized); NMR (^1H, $CDCl_3$, 25°C): δ, 0.73 (s, 3H, Sn–CH_3); 2.05, 2.16 (s, 3H, CH_3); 5.38 (m, 2H, CH_2); 6.9–7.4 (m, 5H, aromatic) ppm.

The carbon, hydrogen and nitrogen analyses were carried out on a Control Equipment Corporation 240 XA elemental analyzer at the School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia. The tin analysis was performed using an Instrumental Laboratory aa/ee 357 atomic absorption spectrophotometer. IR data were recorded using a Beckman IR 4250 spectrophotometer in the frequency range 4000–250 cm^{-1}. Samples were prepared as KBr discs. ^1H spectra were recorded on a Bruker 300 MHz AC-P NMR spectrometer.

Determination of crystal structure of $C_{13}H_{17}NOSSn$

An air-stable crystal of dimensions 0.3 × 0.3 × 0.2 mm was mounted on a thin glass fibre on an Enraf-Nonius CAD4 diffractometer. Accurate cell dimensions and space

TABLE I
Crystal data and refinement details for $C_{13}H_{17}NOSSn$

Formula	$C_{13}H_{17}NOSSn$
Formula weight	354.04
Crystal system	Monoclinic
Space group	$P2_1/n$
Cell constants	$a = 7.489(1)$ Å
	$b = 13.164(1)$ Å
	$c = 15.028(2)$ Å
	$V = 1441.7(3)$ Å^3
	$\beta = 103.32(1)^\circ$
Z	4
$F(000)$	704
Density, ρ_c	1.631 g cm^{-3}
μ	19.02 cm^{-3}
Radiation	MoK$_\alpha$ ($\lambda = 0.71073$ Å)
Temperature	27°C
Collection range	$2 \leqslant 2\theta \leqslant 50^\circ$; $\sin\theta/\lambda_{max} = 0.5940$ Å^{-1}
Range of $h\ k\ l$	$h: 0 \rightarrow 8$; $k: 0 \rightarrow 15$; $l: -17 \rightarrow 17$
Intensity reflections	1 5 6, 0 5 7, 0 1 8
Intensity variation	−0.1143%/hr
Orientation reflections	0 1 10, 0 10 0, 5 0 $\bar{5}$
No. of unique reflections	2515
No. of observed reflections	2056
No. of variables	222
R	0.021
R_W	0.022; $w = 1/[\sigma F^2 + (0.02F)^2 + 1]$
Max. s/σ	0.19
Err. weight	1.033
Fourier difference	max. 0.475 e/Å^3; min. −0.312 e/Å^3

TABLE II
Positional parameters and their estimated standard deviations

Atom	x/a	y/b	z/c	B_{eq} (Å^2)
Sn1	0.72067(3)	0.20849(2)	0.71742(2)	3.019(4)
S1	0.5424(1)	0.11695(8)	0.81693(6)	4.08(2)
O1	0.7795(3)	0.2745(2)	0.5939(2)	3.85(5)
N1	0.4819(4)	0.1595(2)	0.6180(2)	3.32(6)
C1	0.4284(4)	0.0364(3)	0.7287(3)	3.38(7)
C2	0.3592(5)	−0.0576(3)	0.7478(3)	4.7(1)
C3	0.2738(5)	−0.1214(3)	0.6784(4)	5.8(1)
C4	0.2624(5)	−0.0948(4)	0.5897(4)	6.0(1)
C5	0.3283(5)	−0.0027(4)	0.5689(3)	4.9(1)
C6	0.4067(4)	0.0650(3)	0.6381(2)	3.50(8)
C7	0.3889(5)	0.2253(3)	0.5578(2)	3.99(8)
C8	0.1839(5)	0.2155(4)	0.5250(3)	5.7(1)
C9	0.4710(5)	0.3084(3)	0.5256(3)	4.26(9)
C10	0.6566(5)	0.3265(3)	0.5393(2)	3.83(8)
C11	0.7279(6)	0.4095(4)	0.4887(3)	5.4(1)
C12	0.7062(6)	0.3548(3)	0.7728(3)	5.3(1)
C13	0.9571(6)	0.1186(4)	0.7301(3)	5.3(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)*[a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3) + ab(\cos \text{gamma})*B(1,2) + ac(\cos \text{beta})*B(1,3) + bc(\cos \text{alpha})*B(2,3)]$.

group data were obtained from 25 strong reflections in the 28° $< 2\theta <$ 32° shell. A total of 2859 reflections were collected and processes. Lorentz-polarization and linear decay corrections were applied. Absorption correction was not included as an attempt using the program DIFABS[23] did not show any improvement.

The structure was solved by Direct methods (MULTAN) and all the hydrogen atoms were located from subsequent difference Fourier maps. All non-hydrogen atoms were refined anisotropically (hydrogen atoms isotropically). A Killean-Lawrence weighting scheme was employed throughout refinement. Analytic expressions of neutral atom scattering factors were employed and anomalous dispersion corrections were incorporated.[16] Computer programs used were in the MolEN package[24] and all calculations were performed using a MicroVAX II minicomputer. The parameters used in data collection and processing as well as the final discrepancy factors at the conclusion of the refinement are given in Table I. Fractional atomic coordinates and their equivalent isotropic displacement parameters are given in Table II and bond distances and angles in Table III. The asymmetric unit of $C_{13}H_{17}NOSSn$ with atom labelling is shown in Figure 1.

TABLE III

Selected bond distances (Å) and angles (°) with e.s.d.'s in parentheses for non-hydrogen atoms

Sn1-S1	2.528(1)	S1-Sn1-O1	158.39(6)
Sn1-O1	2.184(3)	S1-Sn1-N1	78.45(8)
Sn1-N1	2.148(3)	S1-Sn1-C12	96.9(1)
Sn1-C12	2.111(4)	S1-Sn1-C13	103.1(1)
Sn1-C13	2.102(4)	O1-Sn1-N1	80.0(1)
S1-C1	1.757(4)	O1-Sn1-C12	90.6(1)
O1-C10	1.282(4)	O1-Sn1-C13	88.3(1)
N1-C6	1.425(5)	N1-Sn1-C12	116.0(1)
N1-C7	1.328(5)	N1-Sn1-C13	116.3(1)
C1-C2	1.397(6)	C12-Sn1-C13	126.6(2)
C1-C6	1.386(3)	Sn1-S1-C1	94.1(1)
C2-C3	1.377(6)	Sn1-O1-C10	120.1(2)
C3-C4	1.362(8)	Sn1-N1-C6	114.9(2)
C4-C5	1.371(7)	Sn1-N1-C7	120.0(2)
C5-C6	1.392(6)	C6-N1-C7	122.0(3)
C7-C8	1.506(5)	S1-C1-C2	121.2(3)
C7-C9	1.395(6)	S1-C1-C6	120.3(3)
C9-C10	1.378(5)	C2-C1-C6	118.5(3)
C10-C11	1.498(6)	C1-C2-C3	121.0(4)
		C2-C3-C4	119.9(4)
		C3-C4-C5	120.4(4)
		C4-C5-C6	120.6(4)
		N1-C6-C1	118.8(3)
		N1-C6-C5	121.3(3)
		C1-C6-C5	119.5(4)
		N1-C7-C8	120.2(4)
		N1-C7-C9	123.0(3)
		C8-C7-C9	116.8(3)
		C7-C9-C10	126.4(3)
		O1-C10-C9	123.7(4)
		O1-C10-C11	115.3(3)
		C9-C10-C11	121.0(3)

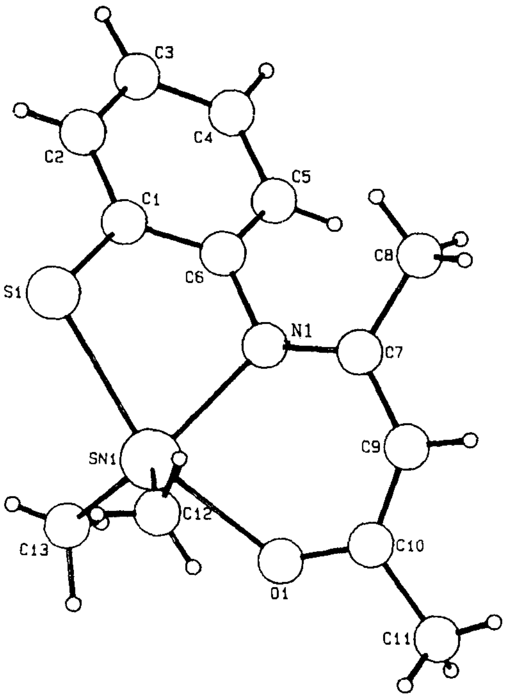

FIGURE 1 The molecular structure of $C_{13}H_{17}NOSSn$.

RESULTS AND DISCUSSION

As shown in Figure 1, the structure of dimethyl[[*N*-(2-pentanone-4-(2-mercaptophenyl)(2−)-*N*,*O*,*S*]tin(IV) is a distorted trigonal bipyramid about the Sn atom with two methyl groups and an azomethine nitrogen atom in the equatorial positions while the more electronegative sulphur and oxygen atoms occupy the axial positions. The ligand, **1**, functions as a terdentate dianion coordinating to $(CH_3)_2Sn^{IV}$ through the imine nitrogen and sulphur atom of the benzothiazoline ring and the oxygen atom of the carbonyl group. Such an *O*,*N*,*S*-mode of coordination to dialkyltin(IV) is also exhibited by benzothiazolines (*e.g.*, (2-hydroxyphenyl)benzothiazoline) containing an additional functional oxygen atom available for chelation[5,12,13,17] but not by those which do not possess the additional feature.[18–20]

The ligand, **1**, seems to impose a rigid "planar" configuration to the coordinated base[15] but in the complex it is not planar but folded. Here, a nearly sp^2 hybridized tin(IV) atom can bind two methyl carbon atoms and the N atom of the azomethine group which are thus located in the trigonal plane. The highly polar SSnO bonds are considerably bent (S1–Sn1–O1 angle is 158.38(6)°) thus resulting in a "*quasi*" trigonal bipyramidal structure.

The C12–Sn1–C13 angle is 126.6(2)° and the Sn1–S1, Sn1–O1 and Sn1–N1 distances are comparable with those observed in diorganotin(IV) compounds of (2-hydroxyphenyl)benzothiazoline.[12,17]

It is found that both the ν_{N-H} peak at 3360 cm^{-1} and $\nu_{C=O}$ peak at 1705 cm^{-1} in

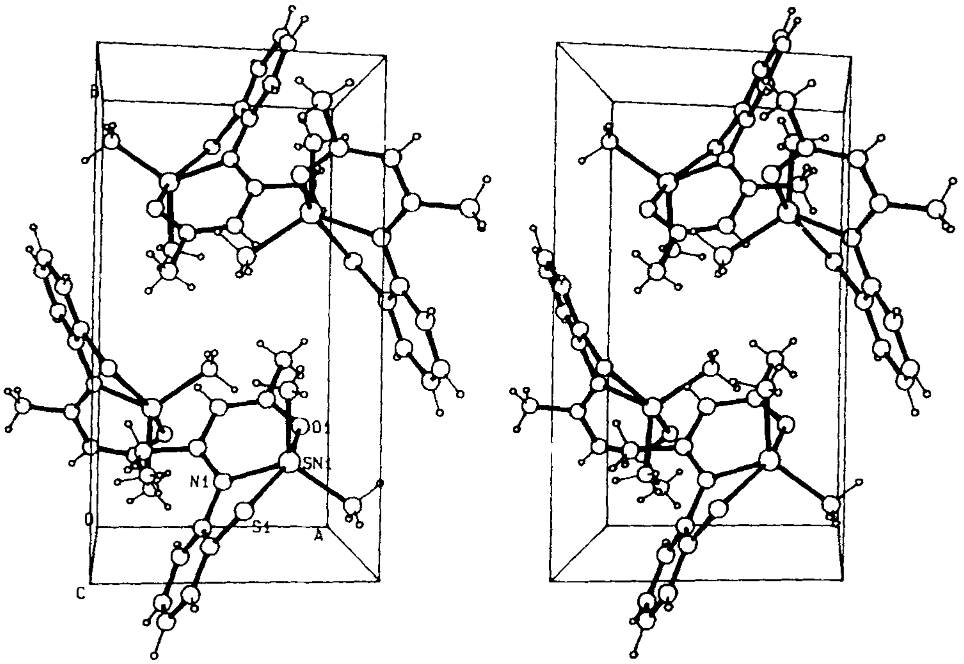

FIGURE 2 Diagram showing the unit cell packing of $C_{13}H_{17}NOSSn$.

the IR spectrum of the ligand disappear upon complexation with $(CH_3)_2SnCl_2$. The N-H deformation at 1580 cm^{-1} also disappears and a new sharp doublet appears at 1540-1515 cm^{-1}. The doublet may be due to the expected C=N, C=C and C=O stretching vibrations which lose their double bond character in the tin-containing '*quasi*' aromatic six-membered ring. Cefalu *et al.*[5] had assigned the absorption at ~1500 cm to $\nu_{C=N}$, consistent with an aromatic CN π bond, since it corresponds to the value observed in pyridine.[22] This is further corroborated by a shortening of the CN bond (C7-N1 = 1.328(5) Å, *c.f.* 1.463(3) Å in **1**[15]).

The ^1H NMR spectrum of the ligand shows an N-H signal at $\delta = 5.09$ ppm which disappears upon complexation while a new peak is observed at $\delta = 5.38$ ppm. Such an observation seems to indicate the presence of a vinyl hydrogen whilst the presence of non-equivalent methyl groups in the NMR spectrum is consistent with the structure shown in Figure 1. It may be pertinent to note that the coordinated ligand exists in the enol form as indicated by the double bond character of the C9-C10 bond (bond length 1.378(5) Å; *c.f.* 1.493(3) Å for the single bond found in the ligand[15]).

The packing of the title compound is shown in Figure 2 and the closest intermolecular contact is 3.513(5) (between O1 and C8).

SUPPLEMENTARY MATERIAL

Tables of hydrogen coordinates and their corresponding atomic displacement parameters, anisotropic atomic displacements for the non-hydrogen atoms and structure factors are available from C.W.

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