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SYNTHESES AND SPECTROSCOPIC STUDIES OF INORGANIC TIN AND ORGANOTIN DERIVATIVES OF 1-[(4-METHYLPHENYLIMINO)METHYL]-2-NAPHTHOL. CRYSTAL STRUCTURE OF CHLOROTRIMETHYL {1-[(4-METHYLPHENYLIMINO)METHYL]-2-NAPHTHOL}TIN(IV)

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Abstract—The reactions of $SnCl_2$, $SnCl_4$, $RSnCl_3$, R_2SnCl_2 and R_3SnCl (where R = Me and Ph) with 1-[(4-methylphenylimino)methyl]-2-naphthol (L) resulted in the formation of a series of adducts of which the tin : ligand ratio was either 1 : 1 or 1 : 2. The $Ph_3SnCl \cdot 3/2L$ adduct contains an additional uncoordinated ligand co-crystallized between two tin moieties. All adducts exhibit Sn—O coordination, whilst the divalent tin adduct is further stabilized by an additional Sn—N bond. An X-ray crystal structure analysis of the trimethyltin(IV) derivative is reported.

Although a considerable number of six-coordinate tin(IV) adducts derived from the interaction of inorganic tin(IV) and organotin(IV) halides with 2-hydroxynaphthalidene and related Schiff bases have been documented, five-coordinate tin(IV) adducts have been scarcely reported.[1–6] The observation that the chlorotriphenyltin(IV) adducts are invariably five-coordinate rather than six-coordinate has been attributed to steric crowding by the organic groups attached to the tin atom.[6] Our recent structural study on the adduct prepared from the reaction of trimethyltin(IV) chloride with 1-[(4-methoxyphenylimino)methyl]-2-naphthol, however, has revealed that the electronic effect outweighs the steric effect in the formation of the five-coordinate trimethyltin(IV) adduct.[7] In this paper we report the synthesis and characterization of a series of adducts derived from the reactions of 1-[(4-methoxyphenylimino)methyl]-2-naphthol with $SnCl_2$, $SnCl_4$, monoorganotin(IV), diorganotin(IV) and triorganotin(IV) chlorides. An X-ray structural study has been carried out on the five-coordinate trimethyltin(IV) adduct, chlorotrimethyl{1-[(4-methylphenylimino)methyl]-2-naphthol}tin(IV).

EXPERIMENTAL

Reagents

p-Methylaniline and 2-hydroxy-1-naphthaldehyde were purchased from Fluka Chemie AG, whilst inorganic tin(II), tin(IV) and organotin(IV) chlorides were obtained from Aldrich Chemical Company.

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Preparation of ligand, 1-[(4-*methylphenylimino*) *methyl*]-2-*naphthol,* $[HOC_{10}H_6CH:NC_6H_4CH_3]$

The ligand was prepared by adding an equimolar amount of *p*-methylaniline to 2-hydroxy-1-naphthaldehyde in a mixed (1 : 1) dichloromethane–96% ethanol solvent.

Preparation of adducts

All the adducts were obtained by the reactions of the various tin compounds with the ligand. The preparation of $Me_3SnCl \cdot [HOC_{10}H_6CH:NC_6H_4CH_3]$ is described as an example.

The synthesis was carried out by adding trimethyltin chloride (0.60 g, 3 mmol), dissolved in dichloromethane, into the solution of the ligand (1.57 g, 6 mmol) in the same solvent. The mixture was stirred under nitrogen at room temperature and then left standing overnight, whereupon yellowish crystals were obtained.

Characterization

Microanalyses. All microanalyses were carried out on a Control Equipment Corporation model 240 XA elemental analyser at the School of Chemical Sciences, Universiti Sains, Malaysia. The results, along with melting points, are shown in Table 1.

IR spectral analysis. The spectra of the ligands and complexes were measured on a Beckman IR 20A spectrophotometer in the frequency range 4000–250 cm^{-1} with the samples prepared as KBr discs. The data are shown in Table 2.

^1H *NMR spectral analysis.* The data were recorded on a Bruker AC-P 300 MHz NMR spectrometer. $CDCl_3$ and DMSO-d_6 were used as solvents, depending on the solubility of the sample, with TMS as the internal standard. Selected ^1H NMR peaks are presented in Table 3.

Table 2. Selected IR frequencies (cm^{-1}) for ligand and adducts

Compound	ν(C=N)	ν(C—O)		ν(Sn—O)
L	1618	1290		—
$SnCl_2 \cdot L$	1630	1298	1275	560
$SnCl_4 \cdot 2L$	1618	1295	1275	512
$MeSnCl_3 \cdot 2L$	1615	1298	1280	510
$PhSnCl_3 \cdot 2L$	1620	1305	1278	518
$Me_2SnCl_2 \cdot 2L$	1620	1308	1290	518
$Ph_2SnCl_2 \cdot 2L$	1620	1298	1275	520
$Me_3SnCl \cdot L$	1615	1302	1290	540
$Ph_3SnCl \cdot 3/2L$	1620	1300	1275	522

Mössbauer spectral analysis. The spectra (Table 4) were recorded with a constant-acceleration microprocessing spectrometer using $Ca^{119m}SnO_3$ as the source. The samples were compressed within Perspex discs and cooled to 80 K.

Crystallography: determination of X-ray crystal structure of chlorotrimethyl{1-[(4-*methylphenylimino*)*methyl*]-2-*naphthol*}*tin*(IV), $Me_3SnCl \cdot [HOC_{10}H_6CH:NC_6H_4CH_3]$

Intensity data for a crystal with dimensions 0.5 × 0.3 × 0.2 mm were measured at room temperature on a Syntex $P2_1$ diffractometer fitted with graphite monochromated Mo-K_α radiation, $\lambda = 0.71069$ Å. The Θ–2θ scan was employed to measure a total of 4698 reflections such that $\theta_{max} \leqslant 26°$. Corrections were applied for Lorentz and polarization effects but not for absorption.

Table 1. Melting points (°C) and microanalytical data (%) for ligand and adducts

Compound	Melting point (°C)	Calculated (%)				Found (%)			
		Sn	C	H	N	Sn	C	H	N
L	104–106	—	82.7	5.8	5.4	—	82.5	5.8	5.3
$SnCl_2 \cdot L$	230	26.3	47.9	3.4	3.1	26.2	46.8	3.2	3.0
$SnCl_4 \cdot 2L$	280	15.2	55.2	3.9	3.6	15.5	54.7	4.0	3.3
$MeSnCl_3 \cdot 2L$	258	15.6	58.3	4.4	3.7	15.5	57.8	4.3	3.6
$PhSnCl_3 \cdot 2L$	240	14.4	61.2	4.3	3.4	13.9	61.0	4.0	3.3
$Me_2SnCl_2 \cdot 2L$	172–174	16.0	61.4	4.9	3.8	15.6	61.4	4.7	3.6
$Ph_2SnCl_2 \cdot 2L$	170–172	13.7	66.5	4.7	3.2	13.9	66.3	4.5	3.0
$Me_3SnCl \cdot L$	108–110	25.8	54.8	5.3	3.0	25.3	54.3	5.1	3.2
$Ph_3SnCl \cdot 3/2L$	129–131	15.3	69.5	4.9	2.7	15.1	69.2	4.6	2.6

Table 3. Selected ^{1}H NMR chemical shifts (ppm) for ligand and adducts

	δ(OH)		δ(C=NH)	
Compound	in $CDCl_3$	in DMSO-d_6	in $CDCl_3$	in DMSO-d_6
L	15.82	13.76	9.40	9.85
$SnCl_2 \cdot L$	[a]	15.83[b]	[a]	9.85
$SnCl_4 \cdot 2L$	[a]	15.82[b]	[a]	9.80
$MeSnCl_3 \cdot 2L$	[a]	15.83[b]	[a]	9.85
$PhSnCl_3 \cdot 2L$	[a]	15.82[b]	[a]	9.85
$Me_2SnCl_2 \cdot 2L$	15.82[b]	13.78	9.40	9.85
$Ph_2SnCl_2 \cdot 2L$	15.83[b]	13.76	9.40	9.85
$Me_3SnCl \cdot L$	15.82[b]	13.75	9.40	9.85
$Ph_3SnCl \cdot 3/2L$	15.83[b]	13.76	9.40	9.82

[a] Insoluble.
[b] Broadened.

Table 4. Mössbauer data for adducts (mm s^{-1})

Compound	δ	ΔE_Q
$SnCl_2 \cdot L$	3.29	1.25
$SnCl_4 \cdot 2L$	0.34	—
$MeSnCl_3 \cdot 2L$	0.93	2.01
$PhSnCl_3 \cdot 2L$	0.85	1.97
$Me_2SnCl_2 \cdot 2L$	1.54	3.77
$Ph_2SnCl_2 \cdot 2L$	1.33	3.63
$Me_3SnCl \cdot L$	1.36	3.60
$Ph_3SnCl \cdot 3/2L$	1.32	3.06

Table 5. Crystal data and details of structure refinement for $Me_3SnCl \cdot L$

Formula	$C_{21}H_{24}NOClSn$
Formula weight	460.64
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	9.675(2)
b (Å)	16.815(3)
c (Å)	12.457(2)
β (°)	94.87(1)
V (Å^3)	2019(1)
Z	4
D_x (Mg m^{-3})	1.515
μ (mm^{-1})	1.287
F(000)	928
R	0.056
R_w	0.059
w	$k/[\sigma^2(F_o)+gF_o^2]$
k	2.3112
g	0.001428
$(\Delta\rho)_{max}$	0.87 (near tin atom)

There were 4447 unique data, of which 3648 satisfied the $I \geqslant 2.5\sigma(I)$ criterion of observability and were used in the subsequent analysis. The structure was solved by using SHELXS86[8] and refined by a full matrix least squares procedure based on F using SHELX76.[9] All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in their idealized positions (C—H = 0.96 Å) and refined isotropically. A weighting scheme of the form $w = k/[\sigma^2(F)+gF^2]$ was used and the refinement continued to final $R = 0.056$, $R_w = 0.059$ for $k = 2.3112$ and $g = 0.001428$. The analysis of variance showed no special features and the maximum residual electron density peak in the final difference map was 0.87 e Å^{-3}. The scattering factors for all the atoms were used as incorporated in SHELX76. Crystal data and refinement parameters are summarized in Table 5 and bond lengths and angles in Table 6. Lists of atomic coordinates, thermal parameters and observed and calculated structure factors have been deposited as supplementary material with the Cambridge Crystallographic Data Centre, from whom copies are available on request.

RESULTS AND DISCUSSION

The molecular structure of $Me_3SnCl \cdot L$ derived from the reaction of Me_3SnCl and the ligand L in the neutral form (Fig. 1) consists of the ligand bound to the tin atom in the trimethyltin(IV) chloride moiety via the phenolic oxygen atom. A chlorine atom and the phenolic oxygen of the ligand occupy the axial positions, whilst the three methyl groups lie in the equatorial plane as reported for chlo-

Table 6. Bond distances (Å) and angles (°) with e.s.d.s in parentheses for non-hydrogen atoms

Cl(1)—Sn	2.494(2)	C(14)—C(9)	1.381(8)
C(1)—Sn	2.112(7)	C(11)—C(10)	1.365(9)
C(2)—Sn	2.130(6)	C(12)—C(11)	1.394(9)
C(3)—Sn	2.121(7)	C(13)—C(12)	1.369(9)
O(1)—Sn	2.441(4)	N(1)—C(14)	1.306(7)
C(4)—O(1)	1.269(7)	C(15)—N(1)	1.403(7)
C(5)—C(4)	1.429(8)	C(16)—C(15)	1.383(7)
C(9)—C(4)	1.437(8)	C(20)—C(15)	1.363(8)
C(6)—C(5)	1.335(8)	C(17)—C(16)	1.360(8)
C(7)—C(6)	1.404(8)	C(18)—C(17)	1.373(9)
C(8)—C(7)	1.411(8)	C(19)—C(18)	1.389(8)
C(10)—C(7)	1.406(8)	C(21)—C(18)	1.510(8)
C(9)—C(8)	1.444(7)	C(20)—C(19)	1.376(8)
C(13)—C(8)	1.402(8)		

C(1)—Sn—Cl(1)	93.7(2)	C(13)—C(8)—C(9)	123.2(5)
C(2)—Sn—Cl(1)	94.9(2)	C(8)—C(9)—C(4)	119.9(5)
C(3)—Sn—Cl(1)	95.7(2)	C(14)—C(9)—C(4)	118.8(5)
C(2)—Sn—C(1)	122.0(3)	C(14)—C(9)—C(8)	121.3(5)
C(3)—Sn—C(1)	119.1(3)	C(11)—C(10)—C(7)	121.8(6)
C(3)—Sn—C(2)	116.8(3)	C(12)—C(11)—C(10)	118.8(6)
O(1)—Sn—Cl(1)	176.6(1)	C(13)—C(12)—C(11)	120.9(6)
O(1)—Sn—C(1)	86.0(2)	C(12)—C(13)—C(8)	121.2(6)
O(1)—Sn—C(2)	88.1(2)	N(1)—C(14)—C(9)	125.7(5)
O(1)—Sn—C(3)	81.5(2)	C(15)—N(1)—C(14)	127.5(5)
C(4)—O(1)—Sn	131.3(4)	C(16)—C(15)—N(1)	123.7(5)
C(5)—C(4)—O(1)	120.9(5)	C(20)—C(15)—N(1)	118.4(5)
C(9)—C(4)—O(1)	121.6(5)	C(20)—C(15)—C(16)	117.8(5)
C(9)—C(4)—C(5)	117.5(5)	C(17)—C(16)—C(15)	121.1(6)
C(6)—C(5)—C(4)	121.6(5)	C(18)—C(17)—C(16)	121.8(5)
C(7)—C(6)—C(5)	122.5(5)	C(19)—C(18)—C(17)	117.1(5)
C(8)—C(7)—C(6)	119.5(5)	C(21)—C(18)—C(17)	121.6(6)
C(10)—C(7)—C(6)	121.3(5)	C(21)—C(18)—C(19)	121.4(6)
C(10)—C(7)—C(8)	119.1(6)	C(20)—C(19)—C(18)	121.0(6)
C(9)—C(8)—C(7)	118.7(5)	C(19)—C(20)—C(15)	121.2(5)
C(13)—C(8)—C(7)	118.1(5)		

rotrimethyl{1-[(4-methoxyphenylimino)methyl]-2-naphthol}tin(IV).[7]

The C—Sn—C angles between the three equatorial methyl groups, C(2)—Sn—C(1) [122.0(3)°], C(3)—Sn—C(1) [119.1(3)°], C(3)—Sn—C(2) [116.8(3)°] and the axial O(1)—Sn—Cl(1) angle [176.6(1)°] show that the tin atom possesses a slightly distorted trigonal bipyramidal geometry. However, its Sn—Cl(1) distance [2.494(2) Å] is shorter than that reported in chlorotriphenyl{1-[(3-methylphenylimino)methyl] - 2 - phenol}tin(IV) [2.535(1) Å].[10]

As in the case of chlorotrimethyl{1-[(4-methoxyphenylimino)methyl]-2-naphthol}tin(IV), the phenolic proton in the structure has migrated to the imine nitrogen atom via an intramolecular hydrogen bond, which forms part of the stable six-membered ring.

The IR spectral data (Table 2) show that a band attributed to the presence of a C═N stretching vibration at 1618 cm^{-1} in the free ligand is almost unchanged upon adduct formation. This observation may be ascribed to the non-coordination of the imino nitrogen atom to the tin atom. However, a remarkable shift of this band is observed in the spectrum of the adduct obtained from the reaction of SnCl$_2$ with the ligand, indicating that the nitrogen atom is involved in the coordination. A band which is assignable to the C—O stretching vibration at 1290 cm^{-1} in the ligand is shifted to 1275–1290 cm^{-1}, coupled with deformation of O—H at 1295–1308 cm^{-1} for all the adducts. Hence, all the adducts possess a unidentate Sn—O coordination mode, except the tin(II) adduct, which possesses bidentate Sn—O and Sn—N coordination modes.

The ^{1}H NMR spectra of the adducts were

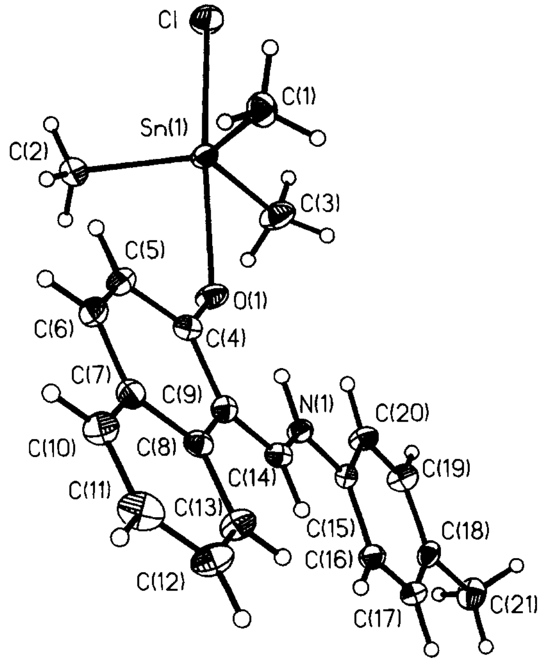

Fig. 1. Molecular structure of chlorotrimethyl{1-[(4-methylphenylimino)methyl]-2-naphthol}tin(IV).

obtained in comparision with the ligand in two different solvents due to the differences in solubility of the adducts. The ^1H NMR data (Table 3) show that the signal at 9.40 (in $CDCl_3$) and 9.80 ppm (in DMSO-d_6), assigned to the azomethine proton of the free ligand, remains unaltered upon adduct formation, indicating that the nitrogen atom is not involved in the coordination to the tin atom.

The Mössbauer spectrum (Table 4) of $SnCl_4 \cdot 2L$ exhibits a band at 0.34 mm s^{-1}, indicating that the tin exists as tin(IV), consistent with the values of 0.24–0.34 mm s^{-1} reported by Greenwood and Ruddick,[11] Cusack *et al.*[12] and Yeats *et al.*[13] The absence of quadrupole splitting suggests that this adduct possesses *cis*-octahedral geometry, as has been observed by Gustavson and Zuckerman[14] for similar complexes owing to unresolved quadrupole splitting. The $SnCl_2 \cdot L$ adduct with δ 3.29 mm s^{-1} contains tin(II), as this value lies within the range 3.10–3.60 mm s^{-1} of previously reported tin(II) adducts in which the structural variety of the complexes, with the tin(II) lone pair occupying one site, encompasses square pyramidal structures, as well as the trigonal bipyramidal forms.[15–17] The compound $MeSnCl_3 \cdot 2L$ exhibits a band at δ 0.93 mm s^{-1}, which is within the range of 0.80–1.21 mm s^{-1} reported by Barbieri *et al.*[18] for similar compounds. The quadrupole splitting for this adduct (2.01 mm s^{-1}) is found to be consistent with that of a six-coordinate tin(IV) compound.[19] The δ (1.54 mm s^{-1}) and ΔE_Q (3.77 mm s^{-1}) values of $Me_2SnCl_2 \cdot 2L$ are readily attributed to tin(IV) octahedral complexes.[19,20] In the case of $Ph_2SnCl_2 \cdot 2L$, the X-ray structure of which is known,[21] the smaller δ (1.33 mm s^{-1}) and ΔE_Q (3.63 mm s^{-1}) values compared with those obtained for $Me_2SnCl_2 \cdot 2L$ may be ascribed to the electron withdrawing properties of the phenyl group, resulting in the reduction of *s* electron density at the tin nucleus. Parish and Platt[22] have reported that in octahedral $R_2SnX_2 \cdot 2L$ systems, the majority of *trans*-R_2 complexes possess δ greater than 1.2 mm s^{-1}, whereas very few *cis*-R_2 compounds exhibit δ greater than 1.0 mm s^{-1}. Hence, the structure of the present $R_2SnCl_2 \cdot 2L$ is consistent with the *trans* R_2 configuration.

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REFERENCES

1. N. S. Biradar and V. H. Kulkarni, *J. Inorg. Nucl. Chem.* 1971, **33**, 2451.
2. J. N. R. Ruddick and J. R. Sams, *J. Organomet. Chem.* 1973, **60**, 233.
3. T. N. Srivastava and A. K. S. Chauhan, *J. Inorg. Nucl. Chem.* 1977, **39**, 371.
4. L. E. Khoo and F. E. Smith, *Polyhedron* 1982, **1**, 213.
5. M. E. Kamwaya and L. E. Khoo, *Acta Cryst.* 1985, **C41**, 1027.
6. J. R. Charland, F. L. Lee, E. J. Gabe, L. E. Khoo and F. E. Smith, *Inorg. Chim. Acta* 1987, **128**, 139.
7. S. G. Teoh, S. B. Teo, G. Y. Yeap, H. K. Fun and P. J. Smith, *J. Organomet. Chem.* 1993, **454**, 73.
8. G. M. Sheldrick, SHELXS86, A Program for Crystal Structure Determination. University of Gottingen, Germany (1986).
9. G. M. Sheldrick, SHELX76, A Program for Crystal Structure Determination and Refinement. University of Cambridge, U.K. (1976).
10. H. K. Fun, S. B. Teo, S. G. Teoh, G. Y. Yeap and T. S. Yeoh, *Acta Cryst.* 1991, **C47**, 1824.
11. N. N. Greenwood and J. N. R. Ruddick, *J. Chem. Soc.* (*A*) 1967, 1679.
12. P. A. Cusack, B. N. Patel, P. J. Smith, D. W. Allen and I. W. Nowell, *J. Chem. Soc., Dalton Trans.* 1984, 1239.
13. P. A. Yeats, J. R. Sams and F. Aubke, *Inorg. Chem.* 1970, **9**, 740.
14. W. A. Gustavson and J. J. Zuckerman, *Synth. React. Inorg. Met. Org. Chem.* 1981, **11**, 47.
15. A. M. van den Bergen, J. D. Cashion, G. D. Fallon and B. O. West, *Aust. J. Chem.* 1990, **43**, 1559.
16. R. H. Herber and E. Smelkinson, *Inorg. Chem.* 1977, **16**, 953.

17. P. F. R. Ewings, P. G. Harrison and A. Mangia, *J. Organomet. Chem.* 1976, **114**, 35.
18. R. Barbieri, L. Pellerito, N. Bertazzi and G. C. Stocco, *Inorg. Chim. Acta* 1974, **11**, 173.
19. B. W. Fitzsimmons, N. J. Seeley and A. W. Smith, *J. Chem. Soc.* (*A*) 1969, 143.
20. R. Barbieri, A. Silvestri, L. Pellerito, A. Gennaro, M. Petrera and N. Burriesci, *J. Chem. Soc., Dalton Trans.* 1980, 1983.
21. H. K. Fun, S. B. Teo, S. G. Teoh and G. Y. Yeap, *Acta Cryst.* 1991, **C47**, 1602.
22. R. V. Parish and R. H. Platt, *Inorg. Chim. Acta* 1970, **4**, 589.