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SYNTHESES AND CHARACTERIZATION OF SOME INORGANIC TIN AND ORGANOTIN(IV) ADDUCTS OF *N-p*-METHOXYPHENYLPYRIDINE-2-CARBALDIMINE

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Abstract—The reactions of *N-p*-methoxyphenylpyridine-2-carbaldimine with $SnCl_2$, $SnCl_4$, n-$BuSnCl_3$ and Me_2SnCl_2 led to the formation of their respective adducts which possess tin—nitrogen bonds formed by the coordination of the pyridyl and imino nitrogen atoms of the ligand. An X-ray structure analysis was performed on the adduct n-$BuSnCl_3 \cdot [C_5H_4N C(H)=NC_6H_5OCH_3$-*p*] and the results along with those of a variety of physical measurements for the adducts are discussed.

Extensive studies have been carried out on organotin compounds possessing NN chelating ligands[1–3] owing to the link between the Sn—N bond length and the anti-tumour activity of such compounds.[4,5] In this paper, we report the reactions of the ligand, *N-p*-methoxyphenylpyridine-2-carbaldimine (**1**) with $SnCl_2$, $SnCl_4$, n-$BuSnCl_3$ and Me_2SnCl_2, which result in the formation of their respective adducts. All the complexes were characterized by a variety of physical methods, including the crystallographic analysis of n-$BuSnCl_3 \cdot [C_5H_4NC(H)=NC_6H_5 OCH_3$-*p*], and the results are presented herein.

EXPERIMENTAL

Synthesis of ligand N-p-*methoxyphenylpyridine-2-carbaldimine* (**1**)

A 20 cm^3 dry ethanolic solution of pyridine-2-carboxaldehyde (60 mmol) was added to a solution of *p*-anisidine (60 mmol) in 20 cm^3 of the same solvent. The reaction mixture was stirred for 30 min after which the solvent was removed *in vacuo*. The product was distilled at 136°C under low pressure to yield a yellow liquid.

Synthesis of the adducts

All the adducts were prepared by the reactions of the ligand (**1**) with the respective tin compounds ($SnCl_2$, $SnCl_4$, n-$BuSnCl_3$ and Me_2SnCl_2). The preparation of trichloro-n-butyl-*p*-methoxyphenylpyridine-2-carbaldimine-*N,N'* (**2**) is described as an example.

A solution of the ligand **1** (3 mmol) in a 30 cm^3 mixture of CH_2Cl_2 and CCl_4 (2 : 1) was added to a solution of n-$BuSnCl_3$ (3 mmol) in 10 cm^3 CH_2Cl_2. The mixture was stirred for 30 min and, on standing, yellow crystals were formed.

Physical measurements

Microanalyses were carried out at the School of Chemical Sciences, Universiti Sains Malaysia,

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Penang, Malaysia. Determination of tin was carried out using an aa IL357 atomic absorption spectrophotometer. IR absorption spectra (frequency range 4000–250 cm^{-1}) of the compounds were recorded on a Perkin–Elmer FTIR 1650 spectrophotometer with the samples as KBr discs. The ^1H NMR spectra were obtained with a Bruker 300 MHz AC-P NMR spectrometer with the samples dissolved in DMSO-d_6. ^{119}Sn Mössbauer spectra were recorded on a constant-acceleration microprocessing spectrometer with $Ca^{119m}SnO_3$ as the source. The samples were compressed between Perspex discs and cooled to 80 K.

Crystal structure determination of n-$BuSnCl_3$·[$C_5H_4NC(H)$=$NC_6H_5OCH_3$-*p*] (**2**)

Intensity data for a yellow crystal of **2** with dimensions 0.03 × 0.24 × 0.24 mm were measured at room temperature on a Rigaku AFC6R diffractometer fitted with graphite monochromated Mo-K_α radiation, λ = 0.71073 Å, up to a maximum Bragg angle of 27.5°. The $\omega:2\theta$ scan technique was employed to measure a total of 5104 reflections. The data set was corrected for Lorentz and polarization effects and an empirical absorption correction was applied.[6] There were 4904 unique data of which 2973 satisfied the $I \geqslant 3\sigma(I)$ criterion of observability and were used in the subsequent analysis.

The structure was solved by direct methods[7] and refined by a full-matrix least-squares procedure[8] based on *F*. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in the model at their calculated positions (C—H = 0.97 Å). Sigma weights were employed in the refinement which was continued to final R = 0.030 and R_w = 0.028. The crystal data and refinement details are listed in Table 1. Selected bond lengths and angles are given in Table 2.

Lists of atomic coordinates, thermal parameters and observed and calculated structure factors have been deposited as supplementary material with the Editor from whom copies are available on request.

Table 1. Crystal data and refinement details for **2**, n-$BuSnCl_3$[$C_5H_4NC(H)$=$NC_6H_5OCH_3$-*p*]

Formula	$C_{17}H_{21}Cl_3N_2OSn$
Formula weight	494.4
Crystal system	Monoclinic
Crystal size (mm)	0.03 × 0.24 × 0.24
Space group	$P2_1/c$
a (Å)	13.436(2)
b (Å)	11.194(1)
c (Å)	13.543(2)
β (°)	106.42(1)
V (Å^3)	1953.9(4)
Z	4
ρ_{calc} (g cm^{-3})	1.681
$F(000)$	984
μ (cm^{-1})	17.24
Transmission coefficients	0.905–1.022
No. of data collected	5104
No. of unique data	4904
R_{amal}	0.034
No. of unique data with $I \geqslant 3\sigma(I)$	2973
R	0.030
R_w	0.028
Max. residual density (e Å^{-3})	0.43

RESULTS AND DISCUSSION

Figure 1 shows the molecular structure of n-$BuSnCl_3$·[$C_5H_4NC(H)$=NC_6H_5OMe-*p*] obtained by the reaction of the ligand **1** with n-$BuSnCl_3$. The crystal structure contains well separated molecules, there being no major intermolecular contacts; the closest non-hydrogen contact occurs between the Cl(3) and C(8)′ atoms (symmetry operation: x, $0.5-y$, $-0.5-z$) at 3.415(4) Å.

In the molecule, the ligand **1** coordinates to the central tin atom *via* the *N,N′* donor atoms; the tin atom exists in a distorted octahedral geometry defined by the C atom of the n-butyl group, the three Cl atoms and two N donor atoms [N(1) and N(2)] derived from the chelating ligand. The greatest deviations from the ideal octahedral angle are found for the Cl(2)—Sn—N(2) and N(1)—Sn—N(2) angles of 160.45(8) and 71.3(1)°, respectively; i.e. reflecting the restricted bite distance of the chelate. The Sn—N(1) and Sn—N(2) bond distances [2.243(3) and 2.322(3) Å, respectively] are significantly different from each other reflecting the relative *trans* effects of C(1) and Cl(2) atoms such that the shorter Sn—N(1) bond has the N(1) atom occupying a position approximately *trans* to the organic substituent. These Sn—N distances are comparable with those found in trichloro-n-butyl[*N*-phenylpyridine-2-carbaldimine-*N,N′*)tin(IV),[5] dichlorodibutylbis(pyrazole)tin(IV)[9] and dibromo(*N,N′*-dimethyl-2,2′-biimidazole)dimethyltin(IV).[10] The Sn—Cl bond distances are also disparate with the Sn—Cl(2) bond distance [i.e. *trans* to the N(2) atom] being the shortest at 2.399(1) Å. The Sn—Cl(3) bond distance of 2.456(1) Å is significantly longer than the Sn—Cl(1) bond distance [2.423(1) Å] which may be explained in terms of a weak intermolecular contact between the Cl(3) atom and H(5)″ (symmetry operation: $1-x$, $0.5+y$, $0.5-z$) of 2.74 Å.

The five-membered chelate ring consisting of Sn,

Table 2. Selected bond distances (Å) and bond angles (°) for **2**

Sn—Cl(1)	2.423(1)	Sn—Cl(2)	2.399(1)
Sn—Cl(3)	2.456(1)	Sn—N(1)	2.243(3)
Sn—N(2)	2.322(3)	Sn—C(1)	2.120(4)
N(1)—C(5)	1.319(5)	N(1)—C(9)	1.329(5)
N(2)—C(10)	1.259(5)	N(2)—C(11)	1.421(5)
C(9)—C(10)	1.443(6)		
Cl(1)—Sn—Cl(2)	93.67(4)	Cl(1)—Sn—Cl(3)	165.94(4)
Cl(1)—Sn—N(1)	86.11(8)	Cl(1)—Sn—N(2)	85.91(8)
Cl(1)—Sn—C(1)	97.8(1)	Cl(2)—Sn—Cl(3)	90.37(4)
Cl(2)—Sn—N(1)	89.20(9)	Cl(2)—Sn—N(2)	160.45(8)
Cl(2)—Sn—C(1)	101.4(1)	Cl(3)—Sn—N(1)	80.47(8)
Cl(3)—Sn—N(2)	85.80(8)	Cl(3)—Sn—C(1)	94.6(1)
N(1)—Sn—N(2)	71.3(1)	N(1)—Sn—C(1)	168.3(2)
N(2)—Sn—C(1)	98.0(2)	Sn—N(1)—C(5)	124.7(3)
Sn—N(1)—C(9)	116.8(3)	C(5)—N(1)—C(9)	118.3(4)
Sn—N(2)—C(10)	113.9(3)	Sn—N(2)—C(11)	125.0(2)
C(10)—N(2)—C(11)	120.8(4)	N(2)—C(10)—C(9)	120.7(4)

N(1), C(9), C(10) and N(2) atoms is essentially planar with the maximum deviation from the least-square plane through these atoms being 0.094(4) Å for the C(9) atom; the N(1)—C(9)—C(10)—N(2) torsion angle being −0.6(6)°. The chelating ligand itself is not planar, however, with the C_6H_4OMe group being twisted with respect to the remaining ligand as shown in the torsion angle of −52.3(6)° for C(10)—N(2)—C(11)—C(12).

Analytical data for all adducts are listed in Table 3. The IR spectrum (Table 4) of the free ligand shows a band at 1625 cm^{-1} which is assigned to $\nu_{C=N}$. Shifts from the $\nu_{C=N}$ of the free ligand are observed when the tin compounds are coordinated

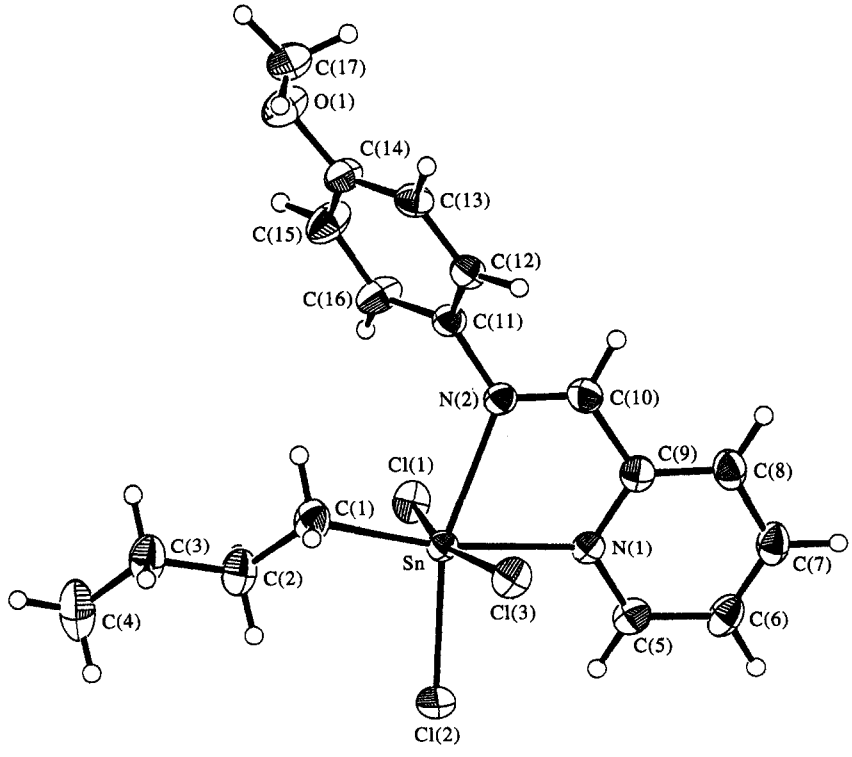

Fig. 1. Molecular structure with atom labelling for n-$BuSnCl_3[C_5H_4NC(H)=NC_6H_5OCH_3$-*p*].

Table 3. Analytical data for the adducts of **1**

Compound	M.p. (°C)	Found (calc.) (%) Sn	C	H	N
$SnCl_2 \cdot L$	176 (dec.)	29.1 (29.5)	38.4 (38.9)	3.0 (3.0)	6.8 (7.0)
$SnCl_4 \cdot L$	150 (dec.)	23.8 (24.1)	32.2 (33.0)	2.5 (2.6)	5.6 (5.9)
$n\text{-}BuSnCl_3 \cdot L$	204–206	22.9 (23.0)	41.1 (41.3)	4.4 (4.3)	5.6 (5.6)
$Me_2SnCl_2 \cdot L$	185	27.4 (27.5)	41.7 (41.7)	4.3 (4.2)	6.4 (6.5)

L = *N*-*p*-methoxyphenylpyridine-2-carbaldimine.

Table 4. Selected IR frequencies and NMR chemical shifts for **1** and its adducts

Compound	IR ($\nu_{C=N}$) (cm^{-1})	$\delta_{C=N\underline{H}}$ (ppm)
L	1625	8.64
$SnCl_2 \cdot L$	1630	8.90
$SnCl_4 \cdot L$	1635	8.84
$n\text{-}BuSnCl_3 \cdot L$	1638	9.92
$Me_2SnCl_2 \cdot L$	1620	9.03

L = *N*-*p*-methoxyphenylpyridine-2-carbaldimine.

to the ligand via the nitrogen atom of the imino group. Similarly, the ^1H NMR data (Table 4) show that the signal at 8.64 ppm (in DMSO-d_6) assigned to the azomethine proton of the free ligand is shifted downfield upon adduct formation indicating that the imino N atom is involved in the coordination to the tin atom.

The ^{119}Sn Mössbauer data for the adducts are listed in Table 5. The Mössbauer parameters of $n\text{-}BuSnCl_3 \cdot L$ complex are consistent with the X-ray crystal structure of the molecule. The isomer shift, $\delta = 1.04$ mm s^{-1}, is significantly lower than $n\text{-}BuSnCl_3$ itself ($\delta = 1.38$ mm s^{-1})[11] and this decrease indicates a change to higher coordination for the tin atom (from sp^3 to sp^3d^2 hybridization)

Table 5. ^{119}Sn Mössbauer data for the adducts of **1**

Compound	δ (mm s^{-1})	ΔE_Q (mm s^{-1})
$SnCl_2 \cdot L$	3.43	1.29
$SnCl_4 \cdot L$	0.47	0.00
$n\text{-}BuSnCl_3 \cdot L$	1.04	1.70
$Me_2SnCl_2 \cdot L$	1.49	3.99

L = *N*-*p*-methoxyphenylpyridine-2-carbaldimine.

reflecting the reduction of the *s*-electron density at the nucleus. The six-coordinate structure assigned to the $n\text{-}BuSnCl_3 \cdot L$ complex is further supported by the value of the quadrupole splitting at 1.70 mm s^{-1} lying within the range 1.6–2.3 mm s^{-1} which is observed for six-coordinated mono-organotin(IV) complexes.[11,12]

The $SnCl_2L$ adduct contains tin(II) since its isomer shift ($\delta = 3.43$) falls within the range 2.70–3.60 mm s^{-1} which is observed for tin(II) complexes as reported by Bergen *et al.*,[13] Herber and Smelkinson[14] and Ewings *et al.*[15] The quadrupole splitting at 1.29 mm s^{-1} conforms with the value observed for *N*,*N*′-(4,5-dimethyl-1,2-phenylene) bis(2-hydroxybenzalideneaminato)tin(II) ($\delta = 1.32$ mm s^{-1})[13] in which the tin atom is five-coordinate and possesses a trigonal bipyramidal geometry. The isomer shift ($\delta = 0.47$ mm s^{-1}) of $SnCl_4 \cdot L$ lies close to the values observed for $SnCl_4$(2,2′-bipyridyl) ($\delta = 0.42$ mm s^{-1}) and $SnCl_4$(8-hydroxyquinoline) ($\delta = 0.45$ mm s^{-1}) indicating the presence of six-coordinate configuration.[16] The absence of quadrupole splitting suggests further that the $SnCl_4 \cdot L$ possesses a *cis* octahedral geometry about the tin(IV) atom as noted by Gustavson and Zuckerman for similar compounds.[17]

The Mössbauer data for the $Me_2SnCl_2 \cdot L$ complex ($\delta = 1.49$ mm s^{-1}; $\Delta E_Q = 3.99$ mm s^{-1}) lie close to the values observed for Me_2SnCl_2(2,2′-bipyridyl) ($\delta = 1.43$ mm s^{-1}; $\Delta E_Q = 4.12$ mm s^{-1}) and Me_2SnCl_2(1,10-phenanthroline) ($\delta = 1.36$ mm s^{-1}; $\Delta E_Q = 4.23$ mm s^{-1}) indicating the presence of six-coordinate configuration.[18] The quadrupole splitting lying close to 4 mm s^{-1} indicates *trans*-R_2SnX_4 configuration while that lying close to 2 mm s^{-1} indicates *cis*-R_2SnCl_4 configuration as observed by Crowe and Smith.[18] Sham and Bancroft[19] suggested that the quadrupole splitting for

trans-R_2SnX_4 compounds decreases further away from 4 mm s^{-1} as the regular octahedral geometry becomes more distorted. It would be expected that the $Me_2SnCl_2 \cdot L$ complex adopts a *trans*-methyl arrangement with a slightly distorted octahedral geometry about tin.

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