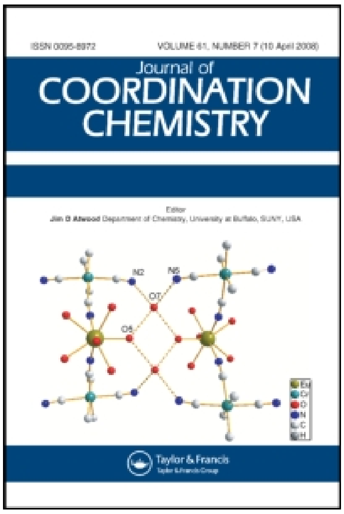

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

SYNTHESIS AND CHARACTERISATION OF TIN(IV) AND ORGANOTIN(IV) COMPLEXES OF [N'-2-HYDROXYPHENYL-6-METHYLPYRIDINE-2-CARBALDIMINE. X-RAY CRYSTAL STRUCTURES OF *n*-BUTYLDICHLORO[N'-2-HYDROXYPHENYL-6-METHYLPYRIDINE-2-CARBALDIMINATO(1-)*N,N',O*]TIN(IV) AND DIPHENYLCHLORO [*N'*-2-HYDROXYPHENYL-6-METHYL-PYRIDINE-2-CARBALDIMINATO(1-) *N,N',O*]TIN(IV)

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To cite this Article Teo, Soon-Beng , Teo, Hui-Shan , Chang, Seng-Teong , Yeow, Liang-Ming and Tiekink, Edward R. T.(2000) 'SYNTHESIS AND CHARACTERISATION OF TIN(IV) AND ORGANOTIN(IV) COMPLEXES OF [N'-2-HYDROXYPHENYL-6-METHYLPYRIDINE-2-CARBALDIMINE. X-RAY CRYSTAL STRUCTURES OF *n*-BUTYLDICHLORO[N'-2-HYDROXYPHENYL-6-METHYLPYRIDINE-2-CARBALDIMINATO(1-)*N,N',O*]TIN(IV) AND DIPHENYLCHLORO [*N'*-2-HYDROXYPHENYL-6-METHYL-PYRIDINE-2-CARBALDIMINATO(1-) *N,N',O*]TIN(IV)', Journal of Coordination Chemistry, 49: 4, 269 — 280

To link to this Article: DOI: 10.1080/00958970008022237

URL: http://dx.doi.org/10.1080/00958970008022237

J. Coord. Chem., 2000, Vol. 49, pp. 269–280
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Printed in Malaysia.

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(Received 16 February 1999)

The reactions of *N*′-2-hydroxyphenyl-6-methylpyridine-2-carbaldimine (LH) with tin(IV) chloride and organotin(IV) chlorides result in the formation of the corresponding tin(IV) and organotin(IV) complexes in which LH behaves as a uninegative tridentate ligand coordinating to the central tin atom *via* an *N*,*N*,*O* donor set. Crystal structure determinations of two of the compounds, *n*-butyldichloro[*N*′-2-hydroxyphenyl-6-methylpyridine-2-carbaldiminato(1-)*N*,*N*′,*O*]-tin(IV) ($BuSnCl_2.L$) and diphenylchloro[*N*′-2-hydroxyphenyl-6-methylpyridine-2-carbaldiminato(1-)*N*,*N*′,*O*]tin(IV) ($Ph_2SnCl.L$), have been performed and both structures feature distorted octahedral geometries about the tin centres. Systematic differences in the Sn-ligand separations are rationalised in terms of the reduced Lewis acidity of tin in $Ph_2SnCl.L$.

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[*] Corresponding author.

Keywords: Tin(IV) and organotin(IV) complexes; *N*′-2-hydroxyphenyl-6-methylpyridine-2-carbaldimine; X-ray structures; *n*-butyldichloro[*N*′-2-hydroxyphenyl-6-methylpyridine-2-carbaldiminato(1-*N*,*N*′,*O*]tin(IV); diphenylchloro[*N*′-2-hydroxyphenyl-6-methyl-pyridine-2-carbaldiminato(1-)*N*,*N*′,*O*]tin(IV)

INTRODUCTION

A variety of Schiff bases are formed by the condensation of 6-methylpyridine-2-carboxaldehyde with various amines.[1,2] These 6-methylpyridine-2-carboxaldehyde *N*-substituted imine ligands have been found to coordinate to transition metals *via* the *N*-pyridyl and the aminic or iminic nitrogen atom.[1,2] In this paper, we report the synthesis *N*′-2-hydroxyphenyl-6-methylpyridine-2-carbaldimine, LH by condensing 6-methylpyridine-2-carboxaldehyde with 2-aminophenol. The Schiff base ligand so obtained was then reacted in turn with inorganic tin(IV) chloride and various organotin(IV) chlorides ($BuSnCl_3$, $PhSnCl_3$, Me_2SnCl_2 and Ph_2SnCl_2) resulting in the formation of the respective tin(IV) and organotin(IV) complexes, which were characterised by X-ray structural analysis (for the monobutyltin(IV) and diphenyltin(IV) complexes) and other physical measurements. The results of these analyses together with the modes of coordination in these complexes are discussed below.

EXPERIMENTAL

Reagents

Tin(IV) chloride and all organotin(IV) chlorides ($BuSnCl_3$, $PhSnCl_3$, Me_2SnCl_2 and Ph_2SnCl_2) were obtained from Aldrich Chemical Company. 6-Methylpyridine-2-carboxaldehyde was obtained from Fluka Chemie AG and 2-aminophenol was obtained from Acros Organics.

Preparation of Ligand: *N*′-2-Hydroxyphenyl-6-methylpyridine-2-carbaldimine (*LH*)

A 10 cm^3 ethanolic solution of 2-aminophenol (10 mmol) was added to a solution of 6-methylpyridine-2-carboxaldehyde (10 mmol) in the same solvent. The mixture was then stirred for 2 h whereupon the yellow precipitate which formed was filtered and subsequently recrystallised from methanol. Yield: 1.68 g (79%). *Anal.*: Calcd. for $C_{13}H_{12}N_2O$ (%). C, 73.56; H, 5.70;

N, 13.20. Found: C, 73.65; H, 5.72; N, 13.20. IR (KBr): ν, 3300–3150 (O–H); 1581 (C=N); 1244 (C–O) cm^{-1}. NMR (^{1}H, DMSO, 25°C): δ, 7.157 (s, CH=N); 7.682 (s, OH); 2.492 (s, CH_3); 6.883–7.992 (m, aromatic H) ppm. NMR (^{13}C, DMSO, 25°C): δ, 138.00 (s, CH=N) ppm.

Preparation of Tin(IV) and Organotin(IV) Complexes

All the complexes were prepared by refluxing the appropriate tin compounds with LH. The preparation of $BuSnCl_2.L$ is described as an example.

A 10 cm^3 dry methanolic solution of the ligand (3 mmol) was added to butyltin(IV) trichloride (3 mmol) in 10 cm^3 of dry dichloromethane. The mixture was stirred for 2 h and on standing at room temperature, red crystals were formed. Recrystallisation was performed in a mixture of methanol and dichloromethane. Yield: 0.95 g (80%). *Anal.*: Calcd. for $C_{17}H_{20}N_2O$-$SnCl_2$ (%): C, 44.58; H, 4.40; N, 6.12; Sn, 25.91. Found: C, 44.79; H, 4.30; N, 5.97; Sn, 25.69. IR (KBr): ν, 1602 (C=N); 1260 (C–O); 551 (Sn–O) cm^{-1}. NMR (^{1}H, DMSO, 25°C): δ, 9.587 (s, CH=N); 2.502 (s, CH_3); 6.803–8.403 (m, aromatic H) ppm. NMR (^{13}C, DMSO, 25°C): δ, 142.58 (s, CH=N) ppm.

Anal. for $SnCl_3.L$: Calcd. for $C_{13}H_{11}N_2OSnCl_3$ (%): C, 35.78; H, 2.54; N, 6.42; Sn, 27.20. Found: C, 35.37; H, 2.33; N, 6.28; Sn, 27.67. IR (KBr): ν, 1600 (C=N); 1254 (C–O); 525 (Sn–O) cm^{-1}. NMR (^{1}H, DMSO, 25°C): δ, 9.705 (s, CH=N); 2.593 (s, CH_3); 6.635–8.673 (m, aromatic H) ppm. NMR (^{13}C, DMSO, 25°C): δ, 151.77 (s, CH=N) ppm.

Anal. for $PhSnCl_2.L$: Calcd. for $C_{19}H_{16}N_2OSnCl_2$(%): C, 47.74; H, 3.37; N, 5.86; Sn, 24.83. Found: C, 47.59; H, 3.29; N, 5.76; Sn, 24.67. IR (KBr): ν, 1604 (C=N); 1256 (C–O); 550 (Sn–O) cm^{-1}. NMR (^{1}H, DMSO, 25°C): δ, 9.698 (s, CH=N); 2.503 (s, CH_3); 6.875–8.387 (m, aromatic H) ppm. NMR (^{13}C, DMSO, 25°C): δ, 148.19 (s, CH=N) ppm.

Anal. for $Me_2SnCl.L$: Calcd. for $C_{15}H_{17}N_2OSnCl$ (%): C, 45.55; H, 4.33; N, 7.08; Sn, 30.01. Found: C, 45.54; H, 4.18; N, 7.22; Sn, 29.09. IR (KBr): ν, 1592 (C=N); 1258 (C–O); 533 (Sn–O) cm^{-1}. NMR (^{1}H, DMSO, 25°C): δ, 8.625 (s, CH=N); 2.607 (s, CH_3); 6.836–8.656 (m, aromatic H) ppm. NMR (^{13}C, DMSO, 25°C): δ 147.30 (s, CH=N) ppm.

Anal. for $Ph_2SnCl.L$: Calcd. for $C_{25}H_{21}N_2OSnCl$ (%): C, 57.78; H, 4.07; N, 5.39; Sn, 22.84. Found: C, 54.90; H, 3.85; N, 4.98; Sn, 22.38. IR (KBr): ν, 1589 (C=N); 1268 (C–O); 550 (Sn–O) cm^{-1}. NMR (^{1}H, DMSO, 25°C): δ, 9.615 (s, CH=N); 2.506 (s, CH_3); 6.712–8.058 (m, aromatic H) ppm. NMR (^{13}C, DMSO, 25°C): δ, 146.07 (s, CH=N) ppm.

Characterisation of Compounds

Microanalyses were carried out at the School of Chemical Sciences, Universiti Sains Malaysia. Infrared absorption spectra were recorded using a Perkin Elmer FTIR spectrophotometer in the frequency range 4000–450 cm^{-1}. Samples were prepared as KBr discs. ^{1}H and ^{13}C NMR spectra were recorded using a Brüker 300 MHz AC-P NMR spectrometer with chemical shifts reported in ppm relative to Me_4Si. The samples were dissolved in DMSO-d_6.

Crystal Structure Determination of *n*-Butyldichloro[*N*′-2-hydroxyphenyl-6-methylpyridine-2-carbaldiminato(1-)*N*,*N*′,*O*]tin(IV) ($BuSnCl_2.L$), $C_{17}H_{20}N_2OSnCl_2$ and Diphenylchloro[*N*′-2-hydroxyphenyl-6-methylpyridine-2-carbaldiminato(1-)*N*,*N*′,*O*]tin(IV) ($Ph_2SnCl.L$), $C_{25}H_{21}N_2OSnCl$

Intensity data for the crystals were collected at room temperature on a Rigaku AFC6R diffractometer employing MoK_α radiation ($\lambda = 0.71073$ Å) and the $\omega/2\theta$ scan technique such that θ_{max} was 27.5°; the data sets were corrected for Lorentz and polarisation effects[3] as well as for absorption employing an empirical procedure.[4] The structures were solved by direct methods[5] and each refined by a full-matrix least-squares procedure based on F.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were included in the model at their calculated positions (C–H 0.97 Å). In the structure of $BuSnCl_2.L$ which has two molecules in the crystallographic asymmetric unit, there is some disorder in the *n*-butyl groups, in particular for molecule *a*. Attempts to model these over multiple sites were unsuccessful. The refinement was continued until convergence in each case employing sigma weights.[3] Crystal data and final refinement details are given in Table I while fractional atomic coordinates for $BuSnCl_2.L$ and $Ph_2SnCl.L$ are given in Tables II and III, respectively. The crystallographic numbering schemes for $BuSnCl_2.L$ and $Ph_2SnCl.L$ are shown in Figures 1 and 2 which were drawn using ORTEP[6] at 40% and 30% probability levels, respectively. Bond lengths and angles are listed in Table IV. Lists of atomic coordinates, thermal parameters and, observed and calculated structure factors are available on request from the authors.

RESULTS AND DISCUSSION

The molecular structure $BuSnCl_2.L$ is shown in Figure 1 and selected interatomic parameters are given in Table IV. There are two molecular

TABLE I Crystal data and refinement details for $BuSnCl_2.L$ and $Ph_2SnCl.L$

	$BuSnCl_2.L$	$Ph_2SnCl.L$
Formula	$C_{17}H_{20}Cl_2N_2OSn$	$C_{25}H_{21}ClN_2OSn$
Formula weight	458.0	519.6
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	17.483(9)	10.014(2)
b (Å)	12.840(6)	17.316(2)
c (Å)	18.410(10)	12.567(2)
β (°)	117.38(3)	93.42(1)
V (Å^3)	3669(3)	2175.3(5)
Z	8	4
Crystal size (mm)	0.16 × 0.16 × 0.24	0.13 × 0.24 × 0.48
D_c (g cm^{-1})	1.658	1.586
$F(000)$	1824	1040
μ (cm^{-1})	16.88	13.16
transmission factors	0.979–1.000	0.969–1.000
No. of data collected	8683	5506
θ_{max} (°)	27.5	27.5
No. of unique data	8405	5223
No. of reflections with $I \geq 3\sigma(I)$	3629	3532
R	0.041	0.031
R_w	0.040	0.032
Residual ρ_{max} (e Å^{-3})	0.44	0.35

entities comprising the crystallographic asymmetric unit, labelled molecules *a* and *b*, respectively. The tin atom is six-coordinate, existing in a distorted octahedral geometry with the equatorial plane being defined by an *N,N,O* donor set derived from the tridentate, uninegative ligand LH and a carbon atom of the *n*-butyl group; above and below the plane are two chloride atoms. The major distortion from the ideal geometry is manifested in the N(1)–Sn–N(2) chelate angle of 72.6(2)° for molecule *a* (71.9(2)° for molecule *b*). The mode of coordination of the tridentate ligand results in the formation of two five-membered rings each being essentially planar and within each molecule, coplanar. There are no major differences between the two independent molecules with most of the angles subtended at the tin atoms having values within a few degrees of each other. The Sn(1)–Cl(a) distance of 2.495(2) Å is significantly longer than the other three Sn–Cl distances (range: 2.472(3)–2.474(2) Å) at the 5σ level. The reason for this elongation is not obvious and in this context it is noted that the closest non-hydrogen intermolecular contact in the lattice occurs between the C(4b) and C(11a)′ atoms of 3.339(8) Å (symmetry operation: $0.5-x$, $0.5+y$, $1.5-z$); the closest contact involving a chloride is Cl(2)···H(7a)′ of 2.833 Å (Cl(2)···C(7a)′ is 3.339(8) Å).

The molecular structure of $Ph_2SnCl.L$ is illustrated in Figure 2 and important parameters are listed in Table IV. The tin atom exists in a

TABLE II Fractional atomic coordinates for $BuSnCl_2.L$

Atom	*x/a*	*y/b*	*z/c*
Sn(1)	0.41799(4)	0.21723(4)	0.65538(3)
Sn(2)	−0.14299(4)	0.26560(4)	0.57942(3)
Cl(1a)	0.5351(1)	0.1738(2)	0.7942(1)
Cl(1b)	−0.2894(2)	0.2395(2)	0.4658(1)
Cl(2a)	0.3128(1)	0.2168(2)	0.5085(1)
Cl(2b)	−0.0014(1)	0.3286(2)	0.6843(1)
O(1a)	0.3245(4)	0.2390(4)	0.6931(3)
O(1b)	−0.1786(4)	0.2177(4)	0.6667(3)
N(1a)	0.3748(4)	0.0586(5)	0.6614(3)
N(1b)	−0.1942(4)	0.4074(5)	0.6069(4)
N(2a)	0.4949(4)	0.1050(5)	0.6157(4)
N(2b)	−0.1339(4)	0.3995(5)	0.4986(4)
C(1a)	0.2846(5)	0.1526(6)	0.6996(5)
C(1b)	−0.2142(5)	0.2893(7)	0.6933(5)
C(2a)	0.2215(6)	0.1588(7)	0.7251(5)
C(2b)	−0.2437(6)	0.2651(7)	0.7504(5)
C(3a)	0.1823(6)	0.0688(9)	0.7322(6)
C(3b)	−0.2806(6)	0.3393(9)	0.7768(5)
C(4a)	0.2058(6)	−0.0276(7)	0.7160(6)
C(4b)	−0.2913(6)	0.4397(9)	0.7474(6)
C(5a)	0.2683(6)	−0.0344(7)	0.6915(5)
C(5b)	−0.2637(6)	0.4665(7)	0.6908(5)
C(6a)	0.3090(5)	0.0556(6)	0.6836(4)
C(6b)	−0.2257(5)	0.3918(6)	0.6642(5)
C(7a)	0.4150(6)	−0.0183(6)	0.6507(5)
C(7b)	−0.1908(5)	0.4936(6)	0.5738(5)
C(8a)	0.4841(5)	0.0043(7)	0.6288(4)
C(8b)	−0.1575(5)	0.4932(6)	0.5141(4)
C(9a)	0.5536(5)	0.1297(7)	0.5904(5)
C(9′a)	0.5600(5)	0.2399(8)	0.5692(5)
C(9b)	−0.1042(5)	0.3946(6)	0.4428(5)
C(9′b)	−0.0810(6)	0.2902(7)	0.4230(5)
C(10a)	0.6037(6)	0.0542(9)	0.5803(5)
C(10b)	−0.0976(6)	0.4825(7)	0.4029(5)
C(11a)	0.5942(6)	−0.0473(9)	0.5963(5)
C(11b)	−0.1227(6)	0.5773(7)	0.4189(5)
C(12a)	0.5323(6)	−0.0750(7)	0.6189(5)
C(12b)	−0.1532(5)	0.5826(6)	0.4753(5)
C(13a)	0.4606(6)	0.3752(7)	0.6665(5)
C(13b)	−0.0934(6)	0.1220(7)	0.5596(6)
C(14a)	0.4134(7)	0.4498(9)	0.5968(8)
C(14b)	−0.1085(10)	0.0317(9)	0.5959(8)
C(15a)	0.4662(15)	0.5489(11)	0.5923(10)
C(15b)	−0.0709(8)	−0.0703(8)	0.5858(7)
C(16a)	0.4940(14)	0.6019(12)	0.6515(11)
C(16b)	−0.1053(7)	−0.1057(8)	0.5039(8)

distorted octahedral geometry with the equatorial plane being defined by the three donor atoms of the tridentate ligand and the solitary chloride atom; the phenyl groups occupy positions *trans* to each other. The restricted bite angle of the N(1)–Sn–N(2) chelate is more acute at 69.7(1)° than that

TABLE III Fractional atomic coordinates for $Ph_2SnCl.L$

Atom	*x/a*	*y/b*	*z/c*
Sn	0.22736(3)	0.40286(1)	0.21955(2)
Cl(1)	0.1149(1)	0.53373(6)	0.19768(9)
O(1)	0.4059(2)	0.4435(1)	0.2894(2)
N(1)	0.3494(3)	0.2942(2)	0.2156(2)
N(2)	0.0978(3)	0.2876(2)	0.1581(2)
C(1)	0.5000(4)	0.3901(2)	0.3176(3)
C(2)	0.6265(4)	0.4120(2)	0.3620(3)
C(3)	0.7205(4)	0.3571(3)	0.3914(4)
C(4)	0.6933(4)	0.2787(3)	0.3782(4)
C(5)	0.5721(4)	0.2554(2)	0.3345(3)
C(6)	0.4760(4)	0.3107(2)	0.3019(3)
C(7)	0.3005(4)	0.2280(2)	0.2266(3)
C(8)	0.1674(4)	0.2212(2)	0.1745(3)
C(9)	−0.0273(4)	0.2838(3)	0.1134(3)
C(9′)	−0.1046(5)	0.3568(3)	0.1005(4)
C(10)	−0.0820(5)	0.2130(3)	0.0802(4)
C(11)	−0.0106(5)	0.1474(3)	0.0965(4)
C(12)	0.1161(5)	0.1497(2)	0.1453(3)
C(13)	0.1431(4)	0.3878(2)	0.3715(3)
C(14)	0.1605(4)	0.4466(2)	0.4456(3)
C(15)	0.1220(5)	0.4377(3)	0.5495(3)
C(16)	0.0664(4)	0.3701(3)	0.5803(3)
C(17)	0.0484(4)	0.3108(3)	0.5091(4)
C(18)	0.0870(4)	0.3197(2)	0.4049(3)
C(19)	0.2885(4)	0.4111(2)	0.0595(3)
C(20)	0.2049(4)	0.4346(3)	−0.0258(3)
C(21)	0.2518(5)	0.4429(3)	−0.1273(3)
C(22)	0.3833(6)	0.4287(3)	−0.1430(4)
C(23)	0.4692(5)	0.4055(3)	−0.0595(4)
C(24)	0.4214(4)	0.3961(2)	0.0419(3)

found in $BuSnCl_2.L$ and is responsible for the major distortion from ideal geometry. In the lattice the closest non-hydrogen contact of 3.418(7) Å occurs between the C(3) and C(12)′ atoms (symmetry operation: $0.5+x$, $0.5-y$, $0.5+z$). The structure of $Ph_2SnCl.L$ is readily derived from that of $BuSnCl_2.L$ in that, for the axial positions, the two phenyl groups have replaced the chloride atoms and in the equatorial plane, the chloride has substituted for the *n*-butyl group. Such a substitution pattern influences the extent of interaction of the ligand, LH with the tin centre.

Generally, the principal bond lengths and angles found in both $BuSnCl_2.L$ and $Ph_2SnCl.L$ are comparable to those observed for organotin(IV) and transition metal complexes of pyridine-2-carbaldimine and their substituted analogues.[7–11] However, the Sn–N(1) bond length (2.192(6) Å for molecule *a* and 2.189(6) Å for molecule *b* in $BuSnCl_2.L$ and 2.267(3) Å in $Ph_2SnCl.L$) is shorter than the Sn–N(2) distance (2.308(6) Å for molecule *a* and

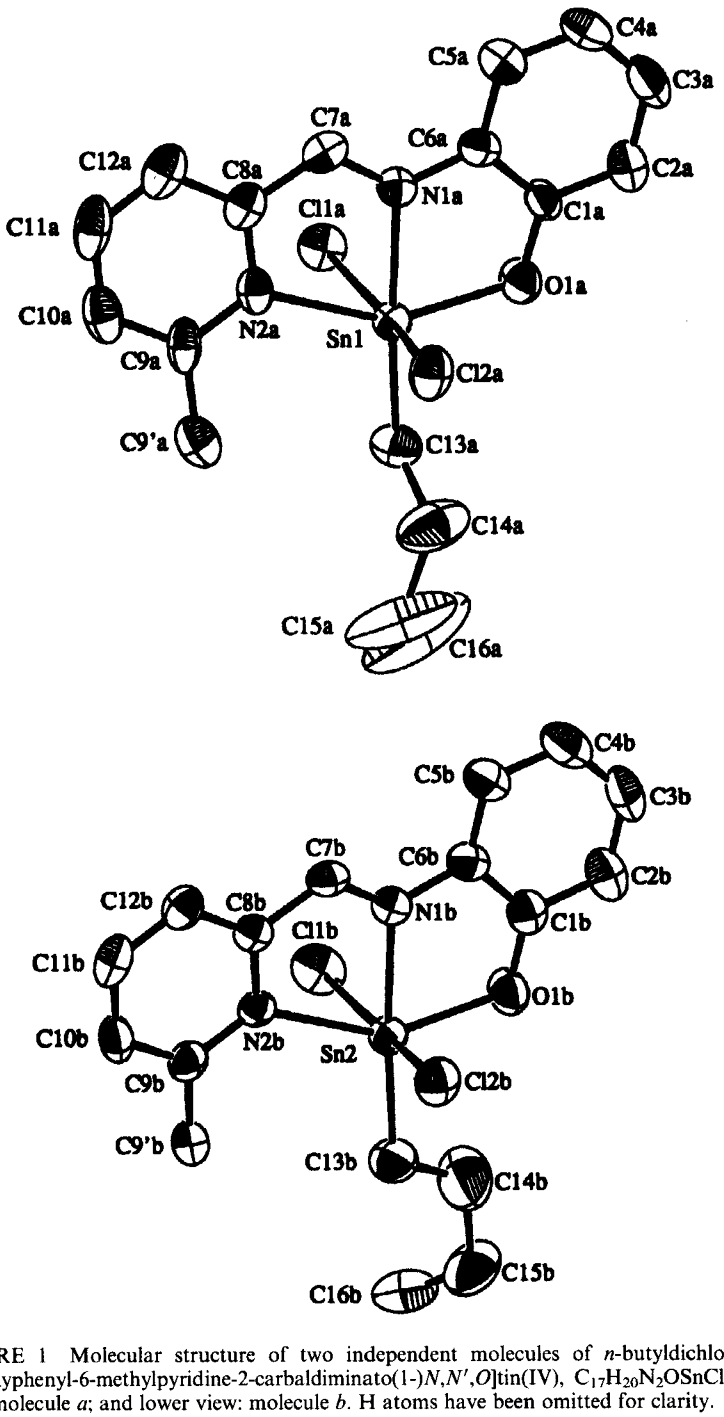

FIGURE 1 Molecular structure of two independent molecules of *n*-butyldichloro[*N*′-2-hydroxyphenyl-6-methylpyridine-2-carbaldiminato(1-)*N*,*N*′,*O*]tin(IV), $C_{17}H_{20}N_2OSnCl_2$; upper view: molecule *a*; and lower view: molecule *b*. H atoms have been omitted for clarity.

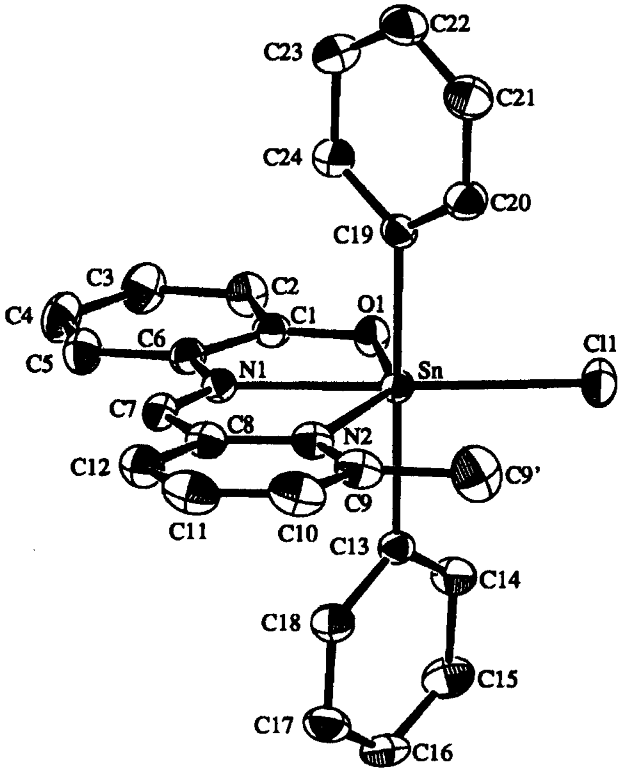

FIGURE 2 Molecular structure of diphenylchloro[*N*′-2-hydroxyphenyl-6-methylpyridine-2-carbaldiminato(1-)*N*,*N*′,*O*]tin(IV), $C_{25}H_{21}N_2OSnCl$. H atoms have been omitted for clarity.

2.326(6) Å for molecule *b* in $BuSnCl_2.L$ and 2.478(3) Å in $Ph_2SnCl.L$), a reverse of that observed in the latter complexes.[7–11] Such a reversal could be attributed to the presence of the 6-methyl substituent in the pyridine ring of LH Chattopadhyay[8] has pointed out that Sn–N distance is sensitive to electronic effects. In fact, the presence of a methyl substituent in the pyridine ring of a large planar system has been found to cause a substantial change in the spectrum of its copper(II) complex.[2] In the present case, it is found that the 6-methyl substituent, while exerting the electronic effect, does not cause steric inhibition to coordination with the metal (tin) centre.[12]

Comparing the derived interatomic parameters describing the tin atom in the two structures reveals that in $Ph_2SnCl.L$ the Sn-ligand separations are systematically longer than the comparable parameters in the $BuSnCl_2.L$ structure. This observation can be rationalised in terms of the reduced Lewis acidity of the tin atom in the *trans*-$Ph_2SnCl.L$ entity compared with

TABLE IV Selected bond distances (Å) and angles (deg) for $BuSnCl_2.L$ and $Ph_2SnCl.L$

	$BuSnCl_2.L$ $Y = Cl(2)$		$Ph_2SnCl.L$
	Molecule a	*Molecule b*	
Sn–Cl(1)	2.495(2)	2.473(3)	2.538(1)
Sn–O(1)	2.068(5)	2.066(5)	2.098(2)
Sn–N(1)	2.192(6)	2.189(6)	2.267(3)
Sn–N(2)	2.308(6)	2.326(6)	2.478(3)
Sn–C(13)	2.138(9)	2.139(9)	2.149(4)
Sn–Y	2.474(2)	2.472(3)	2.142(4)
O(1)–C(1)	1.344(9)	1.325(9)	1.328(4)
N(1)–C(6)	1.389(9)	1.410(9)	1.412(4)
N(1)–C(7)	1.278(9)	1.279(9)	1.277(5)
N(2)–C(8)	1.345(9)	1.345(9)	1.354(5)
N(2)–C(9)	1.345(9)	1.350(9)	1.344(5)
C(7)–C(8)	1.47(1)	1.46(1)	1.455(5)
Cl(1)–Sn–O(1)	95.1(2)	93.0(2)	96.61(7)
Cl(1)–Sn–N(1)	83.1(2)	86.2(2)	172.50(8)
Cl(1)–Sn–N(2)	82.0(2)	84.7(2)	117.69(8)
Cl(1)–Sn–C(13)	91.6(3)	94.7(3)	90.5(1)
Cl(1)–Sn–Y	165.17(8)	168.52(8)	89.4(1)
O(1)–Sn–N(1)	76.4(2)	76.5(2)	76.0(1)
O(1)–Sn–N(2)	148.9(2)	148.3(2)	145.7(1)
O(1)–Sn–C(13)	97.7(3)	99.6(3)	92.7(1)
O(1)–Sn–Y	93.6(2)	92.4(2)	94.6(1)
N(1)–Sn–N(2)	72.6(2)	71.9(2)	69.7(1)
N(1)–Sn–C(13)	171.6(3)	176.0(3)	88.7(1)
N(1)–Sn–Y	87.3(2)	85.2(2)	92.4(1)
N(2)–Sn–C(13)	113.3(3)	112.0(3)	87.3(1)
N(2)–Sn–Y	84.3(2)	85.4(2)	86.3(1)
C(13)–Sn–Y	99.1(3)	94.4(3)	172.7(1)
Sn–O(1)–C(1)	116.2(5)	116.3(5)	116.1(2)
Sn–N(1)–C(6)	113.1(5)	113.4(5)	111.8(6)
Sn–N(1)–C(7)	119.0(6)	119.7(7)	120.4(2)
Sn–N(2)–C(8)	113.1(5)	114.1(5)	112.4(2)
Sn–N(2)–C(9)	127.6(6)	128.0(5)	128.9(3)
C(6)–N(1)–C(7)	127.7(7)	126.9(5)	127.8(3)
C(8)–N(2)–C(9)	118.8(7)	117.8(7)	118.7(4)
N(1)–C(7)–C(8)	118.0(7)	118.6(7)	120.7(3)

that of *trans*-$BuSnCl_2.L$.[7] Further, the Sn–Cl(1) distance of 2.538(1) Å in $Ph_2SnCl.L$ is longer than the Sn–Cl distance in $BuSnCl_2.L$, a result that may be related to the *trans* influence exerted by the N(1) atom.

A band assignable to the stretching vibration of C=N at 1581 cm^{-1} in the IR spectrum of LH was found to be shifted to 1602 and 1589 cm^{-1} upon reaction of the ligand with butyltin(IV) trichloride and diphenyltin(IV) dichloride, respectively, indicating the participation of the azomethine N atoms in the coordination to the Sn atom. The shift in frequency is due to the displacement of electron density from N to the Sn atom.[13] A comparison between the IR spectrum of the complexes and LH also shows that a band characteristic of ν_{C-O} at 1244 cm^{-1} is shifted significantly to 1260 and 1268 cm^{-1}, respectively, suggesting that the phenolic O atoms also participate in coordination to the Sn atom. ^{1}H NMR data show that a peak attributed to the hydroxyl proton (OH) in the uncoordinated ligand LH disappears after reaction with the tin compounds, again indicating the involvement of the phenolic O atoms in coordination to Sn atom. IR and ^{1}H NMR spectra of the $SnCl_3$.L, $PhSnCl_2$.L and Me_2SnCl.L are similar to those of $BuSnCl_2$.L and Ph_2SnCl.L and as such these species have been postulated to have similar structures and coordination modes to tin as the latter two compounds. This is supported by microanalytical data.

A similar *N*,*N*,*O* coordination mode to that found in the present study has been observed for iron(III) complexes of *N*′-2-hydroxyphenyl-pyridine-2-carbaldimine.[14] However, *N*′-2-hydroxy-4-methylphenyl-pyridine-2-carbaldimine coordinates to platinum(II) *via* an *N*,*N* donor set despite having a hydroxy group substituted at position two of the amine ring.[15] On the other hand, the pyrrole analogue, *N*′-methylsubstitute-pyrrole-2-carbaldimine, coordinates to zinc(II) *via* the azomethine *N* and *O* atoms only.[16]

Acknowledgements

S.-B. Teo would like to thank the Malaysian Government and Universiti Sains Malaysia for the R&D grant No. 190/9609/3407. E.R.T. Tiekink thanks the Australian Research Council for the financial support for the crystallographic facility.

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