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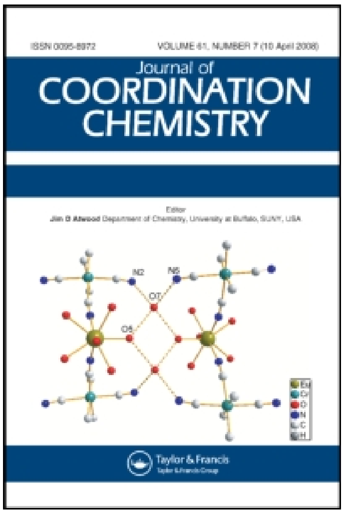

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Complex Salts Derived from the Reactions of Organotin(IV) with 6-Methylpyridine-2-Carboxaldehyde Phenylhydrazone: X-Ray Crystal Structure of BIS[6-Methylpyridine- 2-Carboxaldehydehydrazodium]-Tetrachlorodimethylstannate(IV)

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COMPLEX SALTS DERIVED FROM THE REACTIONS OF ORGANOTIN(IV) WITH 6-METHYLPYRIDINE-2-CARBOXALDEHYDE PHENYLHYDRAZONE: X-RAY CRYSTAL STRUCTURE OF BIS[6-METHYLPYRIDINE-2-CARBOXALDEHYDEHYDRAZODIUM]-TETRACHLORODIMETHYLSTANNATE(IV)

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Reactions of organotin(IV) chloride (Me_2SnCl_2, $PhSnCl_3$ and n-$BuSnCl_3$) with the Schiff base 6-methylpyridine-2-carboxaldehyde phenylhydrazone (**L**) result in the formation of organotin(IV) anionic complexes. Me_2SnCl_2 reacts with **L** in dichloromethane to form $[\mathbf{L}H^+]_2[Me_2SnCl_4]^{2-}$. X-ray structural analysis has been carried out on the complex salt bis[6-methylpyridine-2-carboxaldehydehydrazodium]tetrachlorodimethylstannate(IV), $[\mathbf{L}H^+]_2[Me_2SnCl_4]^{2-}$ wherein the tin moieties exist as monomers. Reactions of $PhSnCl_3$ and n-$BuSnCl_3$ with **L** form the complexes $[\mathbf{L}H^+]_2[PhSnCl_5]^{2-}$ and $[\mathbf{L}H^+]_2[n\text{-}BuSnCl_5]^{2-}$. Compounds were also characterized by FTIR, ^1H and ^{13}C NMR spectroscopy.

Keywords: Schiff base; 6-Methylpyridine-2-carboxaldehyde phenylhydrazone; Organotin(IV) anionic complexes; Organotin(IV) chloride

INTRODUCTION

Extensive studies have been carried out on reactions of hydrazone derivatives with transition metals [1,2] and organotin(IV) [3] resulting in formation of complexes wherein coordination occurs through the iminic or aminic nitrogen to the metal. In a previous paper, we reported that 6-methylpyridine-2-carboxaldehyde phenylhydrazone, **L**, reacted with Ph_2SnCl_2 with unprecedented formation of the protonated ligand outer-sphere complex, $[\mathbf{L}H^+]_2[Ph_2SnCl_4]^{2-}$ [4]. In this article, we report reactions of a series

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of organotin(IV) chlorides (Me_2SnCl_2, $PhSnCl_3$ and *n*-$BuSnCl_3$) with **L**, resulting in the formation of $[\mathbf{L}H^+]_2[Me_2SnCl_4]^{2-}$, $[\mathbf{L}H^+]_2[PhSnCl_5]^{2-}$ and $[\mathbf{L}H^+]_2[n\text{-}BuSnCl_5]^{2-}$, along with an X-ray structural analysis of bis[6-methylpyridine-2-carboxaldehydehydrazodium]tetrachlorodimethylstannate(IV), $[\mathbf{L}H^+]_2[Me_2SnCl_4]^{2-}$.

EXPERIMENTAL

Reagents

6-Methylpyridine-2-carboxyaldehyde and all organotin(IV) chlorides (Me_2SnCl_2, $PhSnCl_3$ and *n*-$BuSnCl_3$) were obtained as commercial grade chemicals from Aldrich Chemical Company. Phenylhydrazine was supplied by Fluka Chemie AG and used without further purification.

Characterization

Microanalyses were carried out on a Control Equipment Corporation 240 XA instrument at the School of Chemical Sciences, Universiti Sains Malaysia. Tin analyses were carried out on an Instrument Laboratory 357 atomic absorption spectrophotometer. IR spectra were recorded on a Perkin Elmer FTIR spectrophotometer in the range 4000–450 cm^{-1} with samples in KBr discs. ^1H NMR spectra were recorded on a Bruker AC-P 300 MHz NMR spectrometer; DMSO-d_6 was used as solvent with TMS as internal standard.

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6-Methylpyridine-2-carboxaldehyde Phenylhydrazone (L)

The ligand **L** was prepared by dropwise addition of 10 cm^3 of a dry ethanolic solution of phenylhydrazine (1.08 g, 10 mmol) to an ethanolic solution of 6-methylpyridine-2-carboxyaldehdye (1.22 g, 10 mmol). The reaction mixture was stirred for 2 h whereupon the yellowish crystals that separated were filtered off and recrystallized from ethanol. Yield, 1.60 g (75%); m.p. 194–196°C. *Anal*.: Calcd. for $C_{13}H_{13}N_3$ (%): C, 73.91; H, 6.20; N, 19.89. Found: C, 73.08; H, 6.23; N, 19.54. IR (KBr): ν, 3213 (N–H), 1604 (C=N) cm^{-1}; NMR (^1H, DMSO-d_6, 25° C): δ, 6.77–7.74 (m, aromatic H); 7.84 (s, NH); 10.62 (s, CH=N) ppm. NMR (^{13}C, DMSO-d_6, 25° C): δ, 137.05 (C=N) ppm.

Organotin(IV) Complexes

All complexes were prepared by stirring the appropriate tin compounds with **L**. The preparation involving the reaction of Me_2SnCl_2 with **L** is described below as an example

A solution of dimethyltin dichloride (0.66 g, 3 mmol) in 10 cm^3 of dry dichloromethane was added to 6-methylpyridine-2-carboxyaldehyde phenylhydrazone (1.26 g, 6 mmol) in 20 cm^3 of the same solvent. The reaction mixture was stirred for 2 h and was then left to stand at room temperature for a day, whereupon yellow crystals were obtained. The product was then recrystallized from dry ethanol. Yield: 1.89 g (88.3%); m.p. 126–128°C. *Anal*.: Calcd. for $Cl_4N_6C_{28}H_{34}Sn$ (%): C, 47.02; H, 4.75; N, 11.75; Sn, 16.60. Found: C, 47.08; H, 4.73; N, 11.74; Sn, 16.56. IR (KBr): ν, 3272

(N–H+), 3177 (N–H), 1644 (C=N) cm^{-1}; NMR (^{1}H, DMSO-d^6, 25° C): δ, 6.77–7.74 (m, aromatic H); 7.83 (s, N–NH); 10.63 (s, CH=N) ppm. NMR (^{13}C, DMSO-d_6, 25°C): δ, 143.08 (C=N) ppm.

Anal. for $[\mathbf{L}H^+]_2[n\text{-BuSnCl}_5]^{2-}$: Calcd. for $C_{30}H_{37}Cl_5N_6Sn$ (%): C, 46.34; H, 4.80; N, 10.81; Sn, 15.26. Found C, 46.32; H, 4.83; N, 10.89; Sn, 15.24. IR (KBr): ν, 3435 (N–H+), 3273 (N–H), 1632 (C=N) cm^{-1}; NMR (^{1}H, DMSO-d_6, 25° C): δ, 6.78–7.76 (m, aromatic H); 7.84 (s, NH); 10.67 (s, CH=N) ppm. NMR (^{13}C, DMSO-d_6, 25° C): δ, 144.69 (C=N) ppm.

Anal. for $[\mathbf{L}H^+]_2[PhSnCl_5]^{2-}$: Calcd. for $C_{32}H_{33}Cl_5N_6Sn$ (%): C, 48.19; H, 4.17; N, 10.53; Sn, 14.88. Found: C, 48.02; H, 4.13; N, 10.54; Sn, 14.90. IR (KBr): ν, 3415 (N-H+), 3240 (N-H), 1644 (C=N) cm^{-1}; NMR (^{1}H, DMSO-d_6, 25° C): δ, 6.92–7.14 (m, aromatic H); 8.14 (s, NH); 11.76 (s, CH=N) ppm. NMR (^{13}C, DMSO-d_6, 25° C): δ, 144.06 (C=N) ppm.

Crystal Structure of Bis[6-methylpyridine-2-carboxaldehydehydrazodium] Tetrachlorodimethylstannate(IV), $[\mathbf{L}H^+]_2[Me_2SnCl_4]^{2-}$

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Intensity data for a yellowish crystal was collected at room temperature on a Rigaku AFC-5 diffractometer employing MoK_α radiation ($\lambda = 0.710714$ Å). Accurate cell dimensions and space group data were obtained from 25 reflections in the $8.3° < 2\theta < 28.8°$ shell. Lorentz–polarization and linear decay corrections were applied. The structure was solved by direct methods and refined by full-matrix least-squares procedures based on *F*. All non-hydrogen atoms were refined anisotropically (hydrogen atoms isotropically). The final *R* and R_w values were 0.058 and 0.072, respectively. Crystal data and structure refinement details are listed in Table I. Atomic coordinates in $[\mathbf{L}H^+]_2[Me_2SnCl_4]^{2-}$ are listed in Table II and interatomic bond distances and angles in Table III. The crystallographic numbering scheme for $[\mathbf{L}H^+]_2[Me_2SnCl_4]^{2-}$ is shown in Fig. 1, which was drawn using ORTEP.

TABLE I Crystal data and structure refinement details for $[\mathbf{L}H^+]_2[Me_2SnCl_4]^{2-}$

Formula	$SnCl_4N_6C_{28}H_{34}$
Formula weight	715.1
Crystal system	Triclinic
Space group	P_1
a (Å)	10.4050(31)
b (Å)	10.6652(53)
c (Å)	8.4375(27)
α (°)	94.291(38)
β (°)	108.917(24)
γ (°)	111.007(28)
Z	1
No. measured reflections	21459
No. independent reflections	3300
$2\theta_{max}$ (°)	100
μ (mm^{-1})	1.3410
R	0.058
R_w	0.072
$\Delta\rho_{min,\ max}$ (eÅ^{-3})	− 3.08, 1.68
σ (Δρ)(eÅ^{-3})	0.17
S	1.857
Minimum, maximum transmission	0.857, 0.859

TABLE II Fractional atomic coordinates for non-hydrogen atoms in $[LH^+]_2[Me_2SnCl_4]^{2-}$

Atom	*x/a*	*y/b*	*z/c*
Sn	1.00000	0.00000	1.00010
C(0)	0.8823(12)	0.0126(12)	0.7574(16)
Cl(1)	1.0373(3)	0.2503(2)	1.1257(4)
Cl(3)	0.7502(3)	−0.0998(2)	1.0553(4)
C(11)	0.6828(10)	0.3539(8)	0.5555(11)
C(12)	0.8190(10)	0.3775(9)	0.5399(12)
C(13)	0.8283(12)	0.2688(11)	0.4452(14)
C(14)	0.7098(13)	0.1456(10)	0.3714(13)
C(15)	0.5741(13)	0.1240(9)	0.3865(13)
C(16)	0.5620(10)	0.2302(9)	0.4815(12)
N(1)	0.6773(8)	0.4650(7)	0.6513(10)
N(2)	0.5521(8)	0.4462(7)	0.6799(9)
C(3)	0.5560(9)	0.5547(8)	0.7681(11)
C(31)	0.4256(9)	0.5379(8)	0.8097(11)
N(32)	0.4353(7)	0.6537(6)	0.9014(9)
C(33)	0.3239(9)	0.6572(8)	0.9527(11)
C(331)	0.3558(11)	0.7936(10)	1.0572(13)
C(34)	0.2002(10)	0.5409(10)	0.9113(13)
C(35)	0.1863(10)	0.4203(9)	0.8198(14)
C(36)	0.2996(10)	0.4183(8)	0.7669(12)

TABLE III Selected interatomic distances (Å) and angles (°) for $[LH^+]_2[Me_2SnCl_4]^{2-}$

Sn–C(0)	2.060(12)	C(11)–C(12)	1.400(16)
C(11)–C(16)	1.374(10)	C(11)–N(1)	1.413(13)
C(12)–C(13)	1.409(17)	C(13)–C(14)	1.362(13)
C(14)–C(15)	1.40(2)	C(15)–C(16)	1.405(16)
N(1)–N(2)	1.349(13)	N(2)–C(3)	1.309(12)
C(3)–C(31)	1.463(15)	C(31)–N(32)	1.360(12)
C(31)–C(36)	1.379(10)	N(32)–C(33)	1.374(14)
C(33)–C(331)	1.508(14)	C(33)–C(34)	1.348(11)
C(34)–C(35)	1.384(15)	C(35)–C(36)	1.396(17)
C(1)–Sn–C(0)	180.0000	C(12)–C(11)–C(16)	121.9(10)
C(12)–C(11)–N(1)	115.9(7)	C(16)–C(11)–N(1)	122.3(10)
C(11)–C(12)–C(13)	117.3(8)	C(12)–C(13)–C(14)	121.5(12)
C(13)–C(14)–C(15)	120.5(12)	C(14)–C(15)–C(16)	119.2(8)
C(11)–C(16)–C(15)	119.6(11)	C(11)–N(1)–N(2)	118.8(6)
N(1)–N(2)–C(3)	114.8(6)	N(2)–C(3)–C(31)	116.9(7)
C(3)–C(31)–N(32)	114.6(6)	C(3)–C(31)–C(36)	126.3(9)
N(32)–C(31)–C(36)	119.1(10)	C(31)–N(32)–C(33)	122.8(6)
N(32)–C(33)–C(331)	115.3(7)	N(32)–C(33)–C(34)	118.6(9)
C(331)–C(33)–C(34)	126.0(11)	C(33)–C(34)–C(35)	120.6(11)
C(34)–C(35)–C(36)	120.3(8)	C(31)–C(34)–C(35)	118.7(9)

RESULTS AND DISCUSSION

The molecular structure of the complex salt $[LH^+]_2[Me_2SnCl_4]^{2-}$, formed by the reaction of **L** with Me_2SnCl_2, is shown in Fig. 1. It is clearly seen that there are no intermolecular contacts between the central tin-containing moiety and the Schiff base. The dinegatively charged tetrachlorodimethyltin(IV) anionic moiety exists as a monomer sandwiched between two positively charged molecular ions $[LH^+]$. The presence of the tin-containing anionic species has earlier been observed in the tetrachlorodiphenylstannate(IV) salt, $[LH^+]_2[Ph_2SnCl_4]^{2-}$ [5]. The charge on the Schiff base is presumed to be brought about by protonation of the pyridine nitrogen

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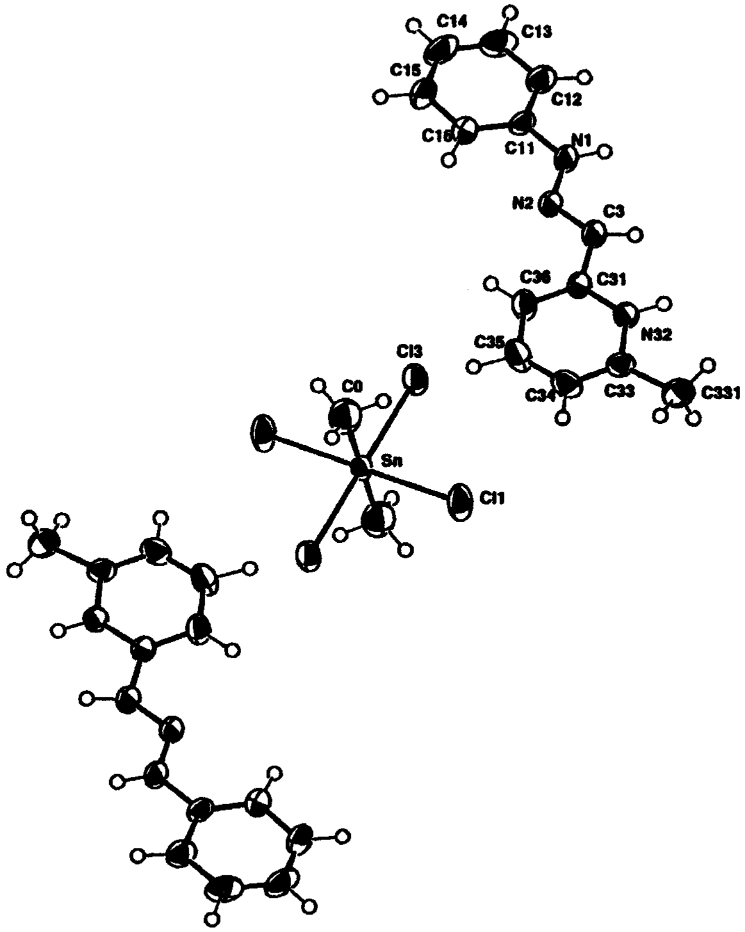

FIGURE 1 Molecular structure of bis[6-methylpyridine-2-carboxyaldehyde hydrazonium] dichlorodimethylstannate(IV), $[LH^+]_2[Me_2SnCl_4]^{2-}$, showing the atom numbering scheme.

atom via a series of stepwise equilibium and disproportionation reactions as reported by Jones *et al.* [6].

The central tin atom possesses two methyl groups occupying *trans* axial positions and four chlorides in the equatorial plane. The Sn–Cl bond distances 2.642(3) and 2.639(3) Å are in good accord with those found in various outer-sphere complex salts of tin(IV) [4,7]. However, the Sn–Cl bond distances in the title complex are longer than the normal Sn–Cl bond of 2.30–2.48 Å as reported in the literature. Elongation of the Sn–Cl bonds can be attributed to the presence of hydrogen bonding interactions [8]. The Sn–C(0) separation (2.060(12) Å) is slightly shorter than that in the complex salt, $[LH^+]_2[Ph_2SnCl_4]^{2-}$ wherein the Sn–C(1) distance was reported as 2.146(3) Å [4]. The short Sn–C distance in the title compound can be ascribed to less steric hindrance resulting from methyl groups as compared to phenyl groups.

The bond distance C(33)–N(32) of 1.374(14) Å is slightly longer than C(31)–N(32), 1.360(12) Å. This observation conforms with that reported for the complex salt $[LH^+]_2[Ph_2SnCl_4]^{2-}$ [C(15)–N(3), 1.351(4) Å and C(14)–N(3), 1.346(4) Å] [4]. One of the reasons which can explain the difference between the distances of these two adjacent endocyclic C–N bonds is the steric hindrance resulting from the methyl group C(331) in the present compound. The bond length C(33)–N(32) of 1.374(14) Å is also slightly longer than other C=N bonds reported in the literature [C(3)–N(2), 1.309(12) Å] [4,9–11].

It has previously been reported that Me_2SnCl_3 anion exists as a loosely associated dimer in $[Pt(S_2N_2H)(PEt_3)_2][Me_2SnCl_3]$ [12] and $[C_9H_8N][Me_2SnCl_3]$ [13], and not as a monomeric five- or six-coordinate species. In the present study, however, the anion exists as a monomeric, six-coordinate species $[Me_2SnCl_6]^{2-}$, counteracted by two protonated Schiff bases. A noticeable feature of the cations in this complex salt is that protonation occurs at the endocyclic N atom instead of the C=N group.

The crystal structure of the present compound $[\mathbf{L}H^+]_2[Me_2SnCl_4]^{2-}$ is reflected in the IR data wherein a band assignable to C=N stretching is observed at 1644 cm^{-1}. Evidence relating to the protonated endocyclic N atom (N–H+) can also be seen in the band at 3272 cm^{-1}. The ^{1}H NMR spectrum of $[\mathbf{L}H^+]_2[Me_2SnCl_4]^2$ shows diagnostic peaks at $\delta = 10.63$ and 7.83 ppm, indicating the presence of azomethine (CH = N) and hydrozonyl (NH) protons, respectively. However, the peak due to the proton on the endocyclic N atom is not observed in the same ^{1}H NMR spectrum leading to the suggestion that this proton is very mobile in the organic solvent. Inspection of ^{13}C NMR data shows that a peak assignable to the azomethine carbon in the Schiff base at $\delta = 137.05$ ppm is shifted to 143.08 ppm upon reaction with Me_2SnCl_2 [14]. The shift can be rationalized by the long range inductive effect wherein the π electron density on the C=N bond is essential for stabilizing the protonated endocyclic N atom.

Similar characteristics are inferred by the IR data for the complexes derived from reactions of **L** with $BuSnCl_3$ and $PhSnCl_3$, respectively. A band attributed to C=N stretching was found to be shifted to 1632 and 1644 cm^{-1} upon complexation with *n*-$BuSnCl_3$ and $PhSnCl_3$, respectively. ^{1}H NMR spectra of $[\mathbf{L}H^+]_2[PhSnCl_5]^{2-}$ and $[\mathbf{L}H^+]_2[n\text{-}BuSnCl_5]^{2-}$ show similar features as those observed in the ^{1}H NMR spectrum of $[\mathbf{L}H^+]_2[Me_2SnCl_4]^{2-}$. The peak attributed to the azomethine (C=N) carbon in the ^{13}C NMR of the ligand ($\delta = 137.05$ ppm) was shifted remarkably upon reaction with $PhSnCl_3$ and *n*-$BuSnCl_3$. As such, the structures of these complexes could be postulated as complex salts similar to the complex $[\mathbf{L}H^+]_2[Me_2SnCl_4]^{2-}$ whereby the anionic tin moieties were counteracted by two protonated ligands.

Studies to further investigate the protonation of the endocyclic N atom is underway and will be reported elsewhere.

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