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# Reactions of 8-methoxyquinoline [$C_{10}H_9ON$] and diorganotin dichlorides. Crystal structures of [$C_{10}H_9ON \cdot H]_2Ph_2SnCl_4$ and [$C_{10}H_9ON \cdot H \cdot NOH_9C_{10}]Ph_2SnCl_3$

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**Abstract**

The reactions of 8-methoxyquinoline ($C_{10}H_9ON$) with $R_2SnCl_2$ (R = Ph, Me, *n*-Bu) have been investigated. All these reactions yielded the corresponding distannoxanes, $[(R_2SnCl)_2O]_2$, 8-methoxyquinolinium chloride for R = *n*-Bu and organostannate salts for R = Ph, Me. The central tin atom of the stannate salts is not bonded to the two N and O donor atoms of the ligand species. X-ray structural analysis was performed on the complexes, $[C_{10}H_9ON \cdot H \cdot NOH_9C_{10}]Ph_2SnCl_3$ and $[C_{10}H_9ON \cdot H]_2Ph_2SnCl_4$, and the results along with those obtained from a variety of physical measurements for these products are discussed. In addition, it was found that the $Ph_2SnCl_3^-$ moiety present in $[C_{10}H_9ON \cdot H \cdot NOH_9C_{10}]Ph_2SnCl_3$ disproportionated into $Ph_2SnCl_2$ and $Ph_2SnCl_4^{2-}$.


*Keywords:* 8-Methoxyquinoline; Diorganotin dichlorides; Distannoxanes; Crystal structure of organostannate salts of 8-methoxyquinoline

## 1. Introduction

It has been previously reported [1–3] that the 1:1 adducts formed between diorganotin di(pseudo)halides and ligands with a N–C–C–N skeleton structure like 2-aminomethylpyridine and 1,10-phenanthroline possessed anti-tumour activity. However, organotin adduct formation reactions with ligands having an N–C–C–O skeleton structure, like 8-quinolinol and 8-methoxyquinoline, have not been examined. This is due to the fact that almost all the organotin derivatives of 8-hydroxyquinoline were derived from its deprotonated form [4–6]. And, to the best of our knowledge, there were no reports on complexes of 8-methoxyquinoline with organotin compounds even though the product of 8-methoxyquinoline with $CuSO_4$ was reported to have pesticidal properties [7]. Thus, as a continuation in our efforts to coax the potentially bidentate N–C–C–N and N–C–C–O ligands to form adducts [8–10], 8-methoxyquinoline was prepared and its behaviour towards diorganotin dichlorides studied.

## 2. Experimental

### 2.1. Materials and instrumentation

Diorganotin dichlorides, 8-hydroxyquinoline and methyl iodide were used as supplied. 8-Methoxyquinoline was prepared according to published procedures [5,11,12]. Organic solvents were dried with 3 Å molecular sieve. The NMR spectra for ligands and complexes were recorded on a JEOL FX90 MHz NMR spectrometer at a temperature of 297 K with 20 ~ 50 scans for a proton spectrum and about 20000 scans for a $^{13}C$ spectrum. Depending on the solubility of the sample, $CDCl_3$ and/or DMSO-$d_6$ with TMS as the internal

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Table 1
Spectroscopic data of 8-methoxyquinoline ($C_{10}H_9ON$) and its deriveratives, **1–4**

| | $C_{10}H_9ON$ 8-methoxyquinoline | $C_{10}H_9ON\cdot HCl\cdot H_2O$ **1** | $[C_{10}H_9ON\cdot H]_2$ $Me_2SnCl_4$ **2** | $[C_{10}H_9ON\cdot H]_2$ $Ph_2SnCl_4$ **3** | $[C_{10}H_9ON\cdot H\cdot NOH_9C_{10}]$ $Ph_2SnCl_3$ **4** |
|---|---|---|---|---|---|
| IR ($cm^{-1}$)[a] | | | | | |
| $\nu_{NH+}$ | — | 2805br,m | Not observed | 2818br,s | 2634br, 1980br |
| $\delta_{NH+}$ | — | 1548s | 1549 | 1553s | 1553s |
| $\nu_{ArOMe}$ | 1264s | 1275m | 1270 | 1271m | 1270s |
| Other bands | — | 3400br,s ($\nu_{H_2O}$) | 577m, 491m ($\nu_{SnMe}$) | 746s, 698m ($\delta_{Ph}$) | 728s, 694s ($\delta_{Ph}$) |
| $^1$H-NMR $\delta$ (ppm) $J$(c/s)[b] | | | | | |
| H2 ($J_{23}$, $J_{24}$) | 8.92q (4.2, 1.8) | 9.22s | 9.20s | 9.13d (8.2, —) | 8.99d (4.8, —) |
| H4 ($J_{34}$, $J_{24}$) | 8.14d (8.4, —) | 9.15s | 9.11s | 9.11d (1.7, —) | 8.75q (8.4, 1.6) |
| H3, H5, H6 | 7.56–7.29m | 8.19–7.59m | 8.17–7.85m | 8.07–7.85m | 8.05–7.37m |
| H7 ($J_{57}$, $J_{67}$) | 7.04q (2.6, 6.6) | — | 7.66d (—, 4.7) | 7.66d (—, 4.4) | — |
| $NH^+$ | — | Not observed | Not observed | Not observed | 6.70br |
| $R_2Sn$ ($J_{SnCH_3}$) | — | — | 1.10s (112.5) | 7.31–7.22m | 7.48–7.25m |
| $CH_3O$ | 4.09s | 4.14s | 4.15s | 4.15s | 4.06s |
| $^{13}$C-NMR $\delta$ (ppm) | | | | | |
| C2 | 149.24 | 145.45 | 145.13 | 145.17 | 147.12 |
| C3 | 121.67 | 129.41 | 129.41 | 129.74 | 122.30 |
| C4 | 135.89 | 145.13 | 145.22 | 145.17 | 140.16 |
| C5, C6 | 107.58, 126.73 | 112.59, 122.77 | 112.47, 122.69 | 112.47, 122.69 | 110.27, 128.19 |
| C7 | 119.56 | 119.92 | 119.96 | 119.92 | 119.68 |
| C8 | 155.43 | 150.06 | 150.18 | 150.14 | 152.78 |
| C9, C10 | 140.24, 129.37 | 129.82, 129.41 | 130.18, 129.18 | 130.14, 129.37 | 135.15, 129.13 |
| MeO | 55.95 | 56.72 | 56.68 | 56.68 | 56.11 |
| $R_2Sn$ | | | 25.04 | 157.18, 134.87, 127.06, 126.60 | 156.37, 134.79, 127.33, 126.85 |

[a] IR: s, strong; m, medium; br, broad.
[b] $^1$H-NMR: s, singlet; d, doublet; q, quartet; m, multiplet; br, broad.

standard were used. The IR spectra for ligands and complexes, prepared as KBr discs or neat on NaCl windows, were measured on a Perkin-Elmer Model 1725 FT-IR spectrometer in the 4000–400 $cm^{-1}$ frequency range. The IR spectrum was acquired usually after two to ten scans. Elemental (C, H, N) analysis for ligands and complexes was performed in-house on a LECO CHNS-932 microanalyser.

## 2.2. Preparation of 8-methoxyquinolinium hyrochloride monohydrate, *1*

A stream of HCl gas, produced by dropwise addition (one drop every 2 s) of concentrated $H_2SO_4$ into a solution of HCl (500 ml), was bubbled through an etheral solution of 8-methoxyquinoline (4.0 g, 25 mmol) for 1 h to yield a white solid. The filtered solid, after three washings with ether (3 × 10 ml), was dissolved in 15 ml of warmed absolute ethanol. On cooling to room temperature (r.t.), 10 ml of diethylether was added to it and the resulting solution was kept in the freezer overnight to yield a white product, (2.51 g, 47% yield, m.p. 180–183°C), identified as protonated 8-methoxyquinoline. Elemental analysis of the compound [observed (calculated): C 56.12(56.24); H 5.70(5.66); N 6.95(6.56)%] confirmed a formula of $C_{10}H_9ON\cdot HCl\cdot H_2O$ for **1**, indicating that it is a monohydrate hydrochloride salt of 8-methoxyquinoline. The spectral data for **1** are summarised in Table 1.

## 2.3. Reactions of 8-methoxyquinoline with $Bu_2SnCl_2$ in chloroform/cyclohexane

A solution of 8-methoxyquinoline (0.48 g, 3 mmol) in 2 ml of chloroform was added to a solution of $Bu_2SnCl_2$ (0.91 g, 3 mmol) in 2 ml of chloroform. The mixture was heated to boiling for ca. 5 min on a hot plate. The solution was then evaporated to dryness using a rotary evaporator and the residue was extracted with ether (5 × 15 ml). The non-extracted solid (0.38 g, 59% yield, m.p. 152–170°C) was recrystallised from absolute ethanol/diethylether to give a white compound identical to **1**. The etheral extracts were evaporated to dryness under vacuum and the residue was recrystallised twice using hexanes to afford a white solid of 1,3-dichloro-1,1,3,3-tetrabutyldistannoxane dimers, $[(Bu_2SnCl)_2O]_2$, m.p. 98–102°C (112.5°C [13]).

The same products, **1** and $[(Bu_2SnCl)_2O]_2$, were also isolated when the above reaction was carried out in cyclohexane.

### 2.4. Reaction of 8-methoxyquinoline with $Me_2SnCl_2$ in chloroform

A 2 ml chloroform solution of $Me_2SnCl_2$ (0.70 g, 3.2 mmol) was added to a solution of 8-methoxyquinoline (0.51 g, 3.2 mmol) in 2 ml of chloroform. The mixture was heated to boiling within 5 min on a hot plate. On cooling, ca. 3 ml of petroleum ether (40–60°C) was added dropwise until the solution turned turbid before allowing it to stand in a freezer and the light yellow solid which formed overnight was filtered. Recrystallisation of the solid (0.69 g, 80% yield, m.p. 173–178°C) in $CHCl_3$:MeOH:petroleum ether (10:1:2) yielded crystals (m.p. 177–180°C) of bis(8-methoxyquinolinium)tetrachlorodimethylstannate(IV), $(C_{10}H_9ON\cdot H)_2$-$Me_2SnCl_4$, **2**. Anal. found: C, 42.92; H, 4.45; N, 4.71. Calc. for $C_{22}H_{26}N_2O_2Cl_4Sn$: C, 43.25; H, 4.29; N, 4.59%. The spectral data of **2** are listed in Table 1.

An additional 4 ml of petroleum ether (40–60°C) was added to the above filtrate and, on cooling in a freezer for 2 h, the filtrate afforded a solid (0.20 g, 33% yield, m.p. 230–240°C) upon filtration. Recrystallisation of this solid in benzene yielded white crystals of 1,3-dichloro-1,1,3,3-tetramethyldistannoxane dimers, $[(Me_2SnCl)_2O]_2$, m.p. > 300°C (300°C dec [13]).

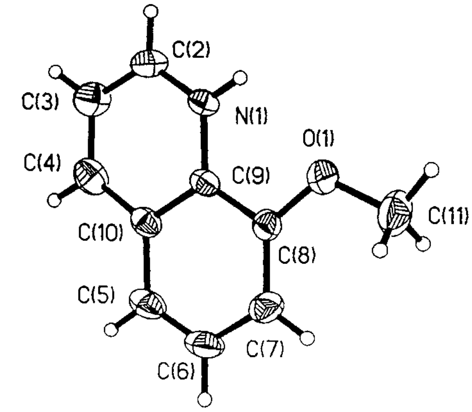


Fig. 1. An ORTEP drawing with atom-numbering scheme for the 8-methoxyquinolium cation.

Table 2
Crystal and structure refinement data for **3** and **4**

| | **3** | **4** |
|---|---|---|
| Empirical formula | $C_{32}H_{30}Cl_4N_2O_2Sn$ | $C_{32}H_{29}Cl_3N_2O_2Sn$ |
| Formula weight | 735.07 | 698.61 |
| Temperature (K) | 295(2) | 295(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/n$ | $P\bar{1}$ |
| Lattice parameters | | |
| $a$ (Å) | 11.842(3) | 11.078(6) |
| $b$ (Å) | 9.570(2) | 11.309(6) |
| $c$ (Å) | 14.136(4) | 13.695(7) |
| $\alpha$ (°) | 90 | 92.36(2) |
| $\beta$ (°) | 103.775(12) | 107.18(2) |
| $\gamma$ (°) | 90 | 107.26(3) |
| $V$ (Å$^3$) | 1556.0(6) | 1550(2) |
| $Z$ | 2 | 2 |
| $D_{calc.}$ (g cm$^{-3}$) | 1.569 | 1.497 |
| Absorption coefficient (mm$^{-1}$) | 1.197 | 1.114 |
| $F$(000) | 740 | 704 |
| Crystal size (mm) | $0.4\times0.3\times0.2$ | $0.5\times0.4\times0.4$ |
| $\theta$ Range for data collection (°) | 2.0–24.00 | 1.9–25.00 |
| Limiting indices: | $-1\le h\le 13$<br>$-1\le k\le 10$<br>$-16\le l\le 15$ | $-1\le h\le 13$<br>$-13\le k\le 12$<br>$-16\le l\le 15$ |
| Reflections collected | 3223 | 6352 |
| Independent reflections ($R_{int}$) | 2450 (0.0416) | 5436 (0.0115) |
| Absorption correction | Semi-empirical from Ψ-scans | |
| Max/min transmission | 1.0000/0.9022 | 0.9753/0.8352 |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data/restraints/parameters | 2450/0/187 | 5404/0 /362 |
| Goodness-of-fit on $F^2$ | 0 947 | 1.036 |
| Final $R$ indices [$I>2\sigma(I)$] | $R_1=0.0235$,<br>$wR_2=0.0561$ | $R_1=0.0215$<br>$wR_2=0.0587$ |
| $R$ indices (all data) | $R_1=0.0300$<br>$wR_2=0.0573$ | $R_1=0.0236$<br>$wR_2=0.0607$ |
| Extinction coefficient | | 0.0130(5) |
| Largest difference peak and hole (e Å$^{-3}$) | 0.956 and −0.400 | 0.384 and −0.242 |

### 2.5. Reactions of 8-methoxyquinoline with $Ph_2SnCl_2$ in chloroform

A solution of $Ph_2SnCl_2$ (1.03 g, 3 mmol) in 3 ml of chloroform was added to a solution of 8-methoxyquinoline (0.48 g, 3 mmol) in 2 ml of chloroform. The mixture was heated to boiling within 5 min on a hot plate. On cooling, ca. 3 ml of petroleum ether (40–60°C) was added dropwise to the mixture until the solution turned turbid before allowing it to remain in a freezer overnight. On filtration, the precipitate (0.28 g, 37% yield, m.p. 168–174°C), identical to 1,3-dichloro-1,1,3,3-tetraphenyldistannoxane dimers ($[Ph_2SnCl)_2$-$O_2]_2$, m.p. 194–196°C [14]), was obtained.

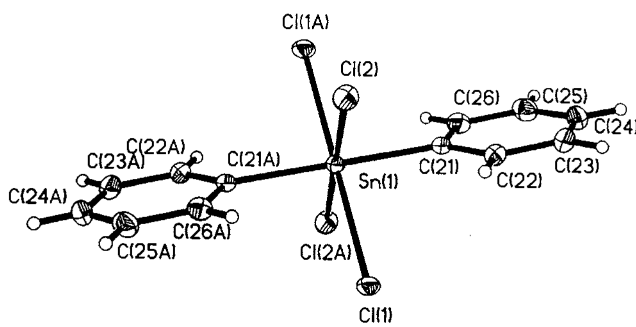


Fig. 2. An ORTEP drawing of the $Ph_2SnCl_4^{2-}$ dianion showing the atomic labelling scheme.

To the filtrate, another 2 ml of petroleum ether (40–60°C) was added. It was then cooled in a freezer for 6 h to yield a solid which was isolated upon filtration. Recrystallisation of this solid (0.65 g, 59% yield, m.p. 155–62°C) in MeOH:$CHCl_3$:petroleum ether (1:10:2) yielded yellowish crystals (mp. 166–169°C) of bis(8-methoxyquinolinium)tetrachlorodiphenylstannate(IV), $(C_{10}H_9ON \cdot H)Ph_2SnCl_4$, **3**. Anal. found: C, 51.77; H, 4.31; N, 3.94. Calc. for $C_{32}H_{30}N_2O_2Cl_4Sn$: C, 52.29; H, 4.11; N, 3.81%. The spectroscopic data of **3** are listed in Table 1.

### 2.6. Reactions of 8-methoxyquinoline with $Ph_2SnCl_2$ in cyclohexane

To a solution of 8-methoxyquinoline (0.48 g, 3 mmol) dissolved in 6 ml of cyclohexane, was added 10 ml of cyclohexane solution of $Ph_2SnCl_2$. The mixture was heated to boiling within 5 min on a hot plate. On cooling to r.t., a precipitate (0.64 g, m.p. 100–120°C) appeared. After filtering off the precipitate, the filtrate was concentrated to dryness and the residue (0.23 g, m.p. 150–160°C) collected was identified as $[(Ph_2SnCl)_2O]_2$ from its IR spectrum [14].

The isolated precipitate was dissolved in 30 ml of dried, warmed benzene. On cooling to r.t., the solution yielded a solid (0.10 g, m.p. 167–170°C) which was identified to be **3** from its IR spectrum. The benzene filtrate was then concentrated to ca. 15 ml and after allowing it to cool slowly to r.t., two types of crystals were visible. These crystals, when isolated and dried, could be separated manually. The first kind of crystals (0.123 g, combined yield 20%, m.p. 168–171°C) was identified as **3** and the second kind of light yellow crystals (0.342 g, 34% yield, m.p. 107–109°C) was found to be suitable for X-ray structural study which identified them to be a complex salt with the formula $(C_{10}H_9ON \cdot H \cdot NOH_9C_{10})Ph_2SnCl_3$, **4**. Anal. found: C, 55.16; H, 4.58; N, 4.14. Calc. for $C_{32}H_{29}N_2O_2Cl_3Sn$: C, 55.01; H, 4.18; N, 4.01%. The spectral details of **4** are summarised in Table 1.

Table 3
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Sn(1) | 0 | 0 | 0 | 28(1) |
| Cl(1) | 138(1) | −1469(1) | 1579(1) | 40(1) |
| Cl(2) | 2179(1) | −376(1) | 111(1) | 43(1) |
| O(1) | −593(2) | −2191(2) | 3732(2) | 56(1) |
| N(1) | −1061(2) | 306(2) | 2947(2) | 41(1) |
| C(2) | −1273(3) | 1512(3) | 2505(2) | 51(1) |
| C(3) | −1775(3) | 2595(4) | 2908(2) | 57(1) |
| C(4) | −2079(3) | 2385(4) | 3772(2) | 54(1) |
| C(5) | −2104(3) | 803(4) | 5171(2) | 53(1) |
| C(6) | −1840(3) | −457(4) | 5585(2) | 56(1) |
| C(7) | −1321(3) | −1526(4) | 5147(2) | 50(1) |
| C(8) | −1066(2) | −1290(3) | 4260(2) | 40(1) |
| C(9) | −1323(2) | 32(3) | 3822(2) | 36(1) |
| C(10) | −1852(2) | 1091(3) | 4262(2) | 40(1) |
| C(11) | −322(3) | 3582(3) | 4082(3) | 71(1) |
| C(21) | −421(2) | −1877(3) | −857(2) | 31(1) |
| C(22) | 223(2) | −3088(3) | −611(2) | 38(1) |
| C(23) | 32(3) | −4281(3) | −1187(2) | 48(1) |
| C(24) | −932(3) | −4269(3) | −2010(2) | 51(1) |
| C(25) | −1587(3) | −3078(3) | −2265(2) | 50(1) |
| C(26) | −1337(2) | −1880(3) | −1691(2) | 41(1) |

[a] $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

Table 4
Selected bond lengths (Å) and angles (°) for 3

| Bond lengths (Å) | | | |
|---|---|---|---|
| Sn(1)–C(21) | 2.158(2) | Sn(1)–Cl(2) | 2.5727(8) |
| Sn(1)–C(11) | 2.6099(8) | O(1)–C(8) | 1.347(3) |
| O(1)–C(11) | 1.430(4) | N(1)–C(2) | 1.309(4) |
| N(1)–C(9) | 1.370(4) | C(2)–C(3) | 1.383(4) |
| C(3)–C(4) | 1.368(5) | C(4)–C(10) | 1.413(4) |
| C(5)–C(6) | 1.345(5) | C(5)–C(10) | 1.414(4) |
| C(6)–C(7) | 1.410(5) | C(7)–C(8) | 1.376(4) |
| C(8)–C(9) | 1.409(4) | C(9)–C(10) | 1.411(4) |
| C(21)–C(22) | 1.385(4) | C(21)–C(26) | 1.399(4) |
| C(22)–C(23) | 1.393(4) | C(23)–C(24) | 1.378(4) |
| C(24)–C(25) | 1.378(5) | C(25)–C(26) | 1.395(4) |
| **Bond angles (°)** | | | |
| C(21A)–Sn(1)–C(21) | 180.0 | Cl(2)–Sn(1)–Cl(2A) | 180.0 |
| Cl(1)–Sn(1)–Cl(1A) | 180.0 | C(21)–Sn(1)–Cl(2) | 90.70(7) |
| C(21)–Sn(1)–Cl(1) | 89.47(2) | Cl(2)–Sn(1)–Cl(1) | 90.83(2) |
| C(8)–O(1)–C(11) | 119.5(3) | C(2)–N(1)–C(9) | 122.8(3) |
| N(1)–C(2)–C(3) | 121.1(3) | C(4)–C(3)–C(2) | 119.2(3) |
| C(3)–C(4)–C(10) | 120.4(3) | C(6)–C(5)–C(10) | 119.5(3) |
| C(5)–C(6)–C(7) | 122.7(3) | C(8)–C(7)–C(6) | 119.6(3) |
| O(1)–C(8)–C(7) | 127.6(3) | O(1)–C(8)–C(9) | 114.0(2) |
| C(7)–C(8)–C(9) | 118.4(3) | N(1)–C(9)–C(8) | 119.8(2) |
| N(1)–C(9)–C(10) | 118.6(3) | C(8)–C(9)–C(10) | 121.6(3) |
| C(9)–C(10)–C(4) | 117.8(3) | C(9)–C(10)–C(5) | 118.2(3) |
| C(4)–C(10)–C(5) | 124.0(3) | C(22)–C(21)–C(26) | 118.7(2) |
| C(22)–C(21)–Sn(1) | 121.1(2) | C(26)–C(21)–Sn(1) | 120.2(2) |
| C(21)–C(22)–C(23) | 120.6(3) | C(24)–C(23)–C(22) | 120.2(3) |
| C(23)–C(24)–C(25) | 120.2(3) | C(24)–C(25)–C(26) | 120.0(3) |
| C(25)–C(26)–C(21) | 120.4(3) | | |

### 2.7. Decomposition reaction of $(C_{10}H_9ON \cdot H \cdot NOH_9C_{10})Ph_2SnCl_3$, **4**

A solution of **4** (0.26 g, 0.40 mmol) in 6 ml of commercial chloroform was heated to boiling on a hot plate for 5 min. On cooling, petroleum ether (40–60°C) was added dropwise (8 ml) to the solution until it turned turbid. The white precipitate (0.093 g, 37% yield, m.p. 166–174°C) formed was filtered off and identified to be $[(Ph_2SnCl)_2O]_2$ from its IR spectrum [14].

The filtrate was then placed in a freezer after another 5 ml of petroleum ether (40–60°C) was added to it. Overnight, it yielded a solid (0.089 g, 30% yield, m.p.

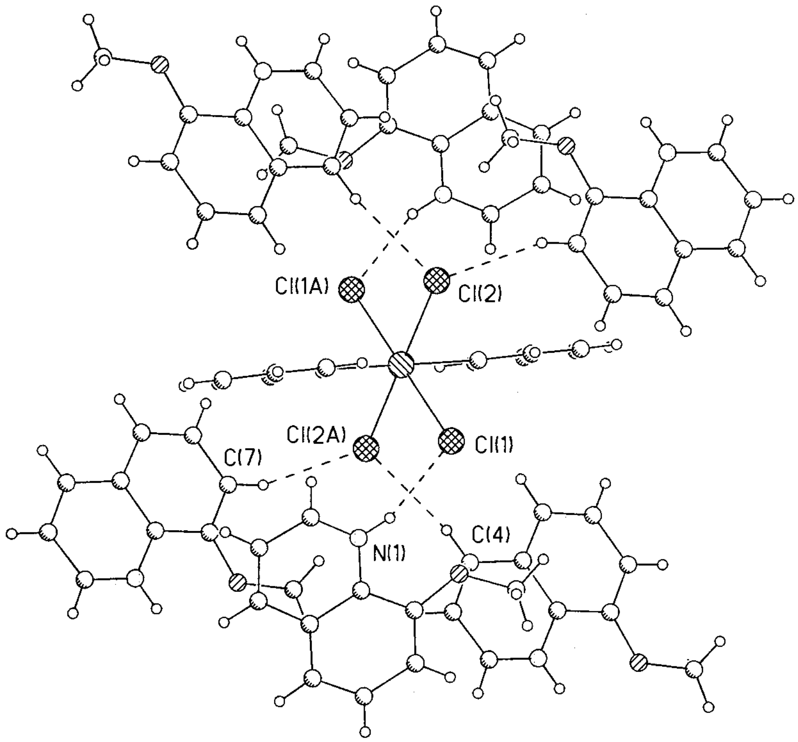


Fig. 3. Perspective drawing of the crystal structure of **3**. Symmetry codes: $x+1$, $y+1$, $z$ for C(4)H···Cl(2A) and $x+1$, $y$, $z$ for C(4)H···Cl(2A).

165–169°C). The IR spectrum of this solid was found to superimpose with that of **3**.

The remaining filtrate was checked with TLC using chloroform as the eluant. A spot ($R_f = 0.6$), identical with **1** ($R_f = 0.63$), was observed.

### 2.8. Crystal structure determination of 3 and 4

The crystallographic data were collected on a single crystal of **3** ($0.4 \times 0.3 \times 0.2$ mm) and **4** ($0.5 \times 0.4 \times 0.4$ mm), using the Siemens P4 X-ray diffractometer with Mo–$K_\alpha$ radiation by $\theta/2\theta$ scan. The intensity data were reduced, and corrected for Lorentz, polarization and extinction factors. Absorption correction was applied based on $\Psi$-scan data using the applied program [15]. The crystal structures were solved by using the direct method [16] and refined with the full-matrix least-squares on $F^2$ using the applied program [15]. The crystal data and the details of the data collection and refinement for **3** and **4** are shown in Table 2. Non-H atoms are refined anisotropically. All H atoms are placed at calculated positions and refined with fixed displacement parameters of 1.2 times for all the C, N and H atoms. These data and supplementary material comprising positional isotropic thermal parameters for H atoms, anisotropic thermal parameters and structural factor data have been deposited with the editors and are also available from the corresponding author.

## 3. Results and discussion

### 3.1. Reactions of 8-methoxyquinoline with $R_2SnCl_2$

It was found that when 8-methoxyquinoline ($C_{10}H_9ON$) reacted with $R_2SnCl_2$ (R = Bu, Me and Ph) it gave, instead of adducts, the corresponding dimeric stannoxanes, $[(R_2SnCl)_2O]_2$, and different type of products depending on R and the solvent used. These products, like **1** and the complex stannate salts, **2–4**, isolated from the reactions of $R_2SnCl_2$ with $C_{10}H_9ON$ are summarised in the equations below.

$$C_{10}H_9ON + Bu_2SnCl_2 \xrightarrow[CHCl_3/c-C_6H_{12}]{} C_{10}H_9ON\cdot HCl\cdot H_2O\ \mathbf{1} + [(Bu_2SnCl)_2O]_2 \quad (1)$$

$$C_{10}H_9ON + Me_2SnCl_2 \xrightarrow[CHCl_3]{} (C_{10}H_9ONH)_2Me_2SnCl_4\ \mathbf{2} + [(Me_2SnCl)_2O]_2 \quad (2)$$

$$C_{10}H_9ON + Ph_2SnCl_2 \xrightarrow[CHCl_3]{} (C_{10}H_9ONH)_2Ph_2SnCl_4\ \mathbf{3} + [(Ph_2SnCl)_2O]_2 \quad (3)$$

$$C_{10}H_9ON + Ph_2SnCl_2 \xrightarrow[c-C_6H_{12}]{} \mathbf{3} + [C_{10}H_9ON\cdot H\cdot NOH_9C_{10}]Ph_2SnCl_3\ \mathbf{4} + [(Ph_2SnCl)_2O]_2 \quad (4)$$

The molecular structures of **1–4** were characterised with a variety of physical methods including X-ray

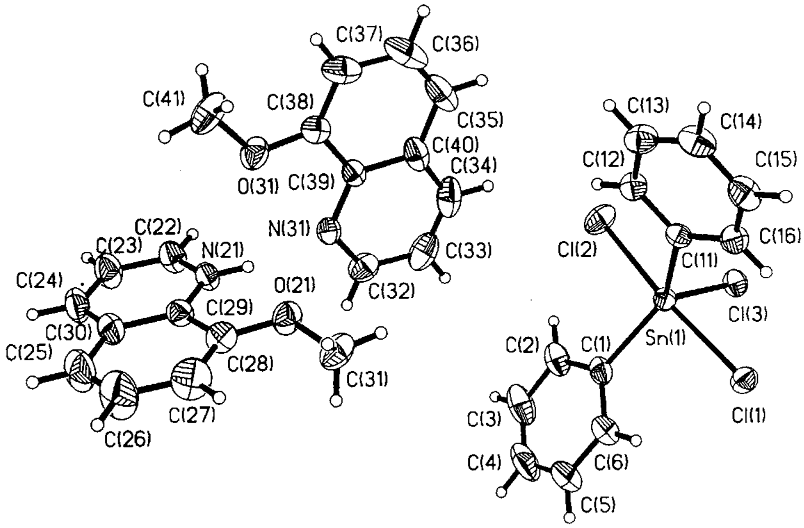


Fig. 4. The molecular structure and atom numbering for **4**.

diffraction structural study for **3** and **4**. Spectroscopic (IR, $^{1}$H- and $^{13}$C-NMR) interpretations, satisfactory elemental analysis and spectroscopic comparison with authentic sample isolated from the reaction of 8-methoxyquinoline with gaseous HCl confirmed that **1** is 8-methoxyquinolinium chloride monohydrate with the formula $C_{10}H_9ON \cdot HCl \cdot H_2O$. Structural elucidation on **2** and **3** reveals that each of the two ligands involved in **2** and **3** is protonated at the pyridyl N atom and the organotin moiety exists as $R_2SnCl_4^{2-}$ stannates with octahedral geometry for the tin atom. In **4**, a ligand pair cation, $(C_{10}H_9ON \cdot H \cdot NOH_9C_{10})^+$, was found to coexist with the pentacoordinated $Ph_2SnCl_3^-$ anion. In addition, **4** was found to decompose to **1**, **3** and $[(Ph_2SnCl)_2O]_2$ upon heating in chloroform, suggesting that its anionic fragment, $Ph_2SnCl_3^-$, disproportionated into $Ph_2SnCl_2$ and $Ph_2SnCl_4^{2-}$. It has been reported that the five-coordinated anion, $PhSnCl_4^-$, easily disproportionates to $Ph_2SnCl_2$ and $SnCl_6^{2-}$ in polar solvent [17,18]. Thus, the finding that the $Ph_2SnCl_3^-$ anion in **4** disproportionated into $Ph_2SnCl_2$ and $Ph_2SnCl_4^{2-}$ is expected.

Formation of $[(R_2SnCl)_2O]_2$, have been reported for reactions of $R_2SnCl_2$ with potassium ethylxanthate [19], 2-aminobenzothiazole [20] and 8-aminoquinoline [8]. Thus, given that 8-methoxyquinoline is a weaker donor than 8-aminoquinoline, the isolation of dimeric stannoxanes in its reactions with diorganotin dihalides is to be expected. There are reports [14,21–23] indicating that, in commercial solvent and in the presence of a ligand, $R_2SnCl_2$ is easily hydrolysed to HCl and $R_2Sn(OH)Cl$, which dehydrated to the more stable $[(R_2SnCl)_2O]_2$. Subsequently, the newly formed protonated ligand will compete with the water, arising from the dehydration process or present in the solvent, for $R_2SnCl_2$ to yield, respectively, complex salts (organostannates) or $[(R_2SnCl)_2O]_2$ [21]. The yield of these two products will depend on the rate of the two reactions. It has also been implicated [22] that the increasing rate of hydrolysis of $R_2SnCl_2$ is in the order $Ph_2SnCl_2 < Me_2SnCl_2 < Bu_2SnCl_2$. The present study is in agreement with the proposed relative hydrolytic rate as the reaction of 8-methoxyquinoline with $Bu_2SnCl_2$ failed to yield organostannates (Eqs. (1)–(4)).

### *3.2. Characterisation of $(C_{10}H_9ON \cdot H)_2R_2SnCl_4$, ($R = Me$ **2**, $Ph$ **3**)*

Single crystal X-ray crystallographic study on **3** reveals that it consists of two 8-methoxyquinolinium cations and tetrachlorodiphenylstannate, a dinegatively charged anion. The asymmetric unit and the atom-labelling scheme of **3** are shown in Figs. 1 and 2. The fractional atomic coordinates and the equivalent isotropic displacement parameters for **3** are listed in Table 3 while its selected bond lengths and angles are shown in Table 4.

For the 8-methoxyquinolinium cation (Fig. 1), the quinoline ring, which is protonated at the pyridyl N atom, is nearly planar with 0.0091 Å deviation from its least-square plane. The N–C bond distances of the quinoline ring in the cations are N(1)–C(2) 1.309 and N(1)–C(9) 1.370 Å and are similar to those (1.328 and 1.378 Å, respectively) reported for 8-aminoquinolinium chloride [8].

For the $Ph_2SnCl_4^{2-}$ anion (Fig. 2), the tin atom lies on a centre of symmetry and is bonded to four Cl atoms and two phenyl groups to give an octahedral *trans*-$Ph_2SnCl_4$ geometry with the phenyl groups lying above and below the plane formed by the four chlorine atoms. Consequently, though the coordination angles between each respective *trans* groups are exactly 180°, the phenyl rings are not precisely perpendicular to the plane [C(21A)–Sn(1)–Cl(2) 89.30, C(21)–Snl–Cl(2) 90.70°], thus making the geometry of the $Ph_2SnCl_4^{2-}$ dianion slightly deviated from a standard octahedron. The two Sn–C(phenyl) bond distances are equal (2.158 Å) and are within the expected range [17,23–26]. There are two short and two long Sn–Cl bond distances (2.5727(8) and 2.6099(8) Å, respectively) which are close to those reported for $(HOC_6H_4CH{=}NHC_6H_4OCH_3)_2Ph_2SnCl_4$ [17] and are shorter than those reported for complexes containing the $Me_2SnCl_4$ and $Et_2SnCl_4$ dianionic species [23–26]. Nevertheless, the Sn–C1 bonds in **3** are longer than those found in **4**, presumably owing to the lower percentage of $\sigma$ (and $\pi$) character per Sn–Cl bonds [17].

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4**

| Atom | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Sn(1) | 7416(1) | 7631(1) | 6747(1) | 37(1) |
| Cl(1) | 5346(1) | 7875(1) | 7033(1) | 52(1) |
| Cl(2) | 9672(1) | 7555(1) | 6698(1) | 62(1) |
| Cl(3) | 8558(1) | 8510(1) | 8528(1) | 49(1) |
| O(21) | 5277(2) | 3517(2) | 669(1) | 58(1) |
| O(31) | 8381(2) | 4948(2) | 379(1) | 58(1) |
| N(21) | 7164(2) | 2408(2) | 662(1) | 45(1) |
| N(31) | 8133(2) | 4405(2) | 2183(1) | 42(1) |
| C(1) | 6628(2) | 5625(2) | 6579(2) | 48(1) |
| C(2) | 7460(3) | 4901(2) | 6703(2) | 68(1) |
| C(3) | 6940(4) | 3605(3) | 6643(3) | 93(1) |
| C(4) | 5608(5) | 3041(3) | 6454(3) | 97(1) |
| C(5) | 4781(4) | 3749(3) | 6322(3) | 93(1) |
| C(6) | 5285(3) | 5038(2) | 6384(2) | 70(1) |
| C(11) | 7464(2) | 9018(2) | 5719(1) | 39(1) |
| C(12) | 8198(2) | 9094(2) | 5054(2) | 47(1) |
| C(13) | 8243(2) | 9987(2) | 4389(2) | 57(1) |
| C(14) | 7548(3) | 10806(2) | 4383(2) | 61(1) |
| C(15) | 6811(3) | 10746(2) | 5035(2) | 61(1) |
| C(16) | 6773(2) | 9862(2) | 5708(2) | 50(1) |
| C(22) | 8086(2) | 1878(2) | 716(2) | 58(1) |
| C(23) | 7874(3) | 871(3) | −1(2) | 70(1) |
| C(24) | 6698(3) | 438(3) | −775(2) | 68(1) |
| C(25) | 4436(3) | 555(3) | −1623(2) | 88(1) |
| C(26) | 3529(3) | 1118(4) | −1617(3) | 106(1) |
| C(27) | 3777(3) | 2115(3) | −868(2) | 84(1) |
| C(28) | 4984(2) | 2563(2) | −104(2) | 53(1) |
| C(29) | 5955(2) | 1994(2) | −97(2) | 46(1) |
| C(30) | 5697(2) | 976(2) | −849(2) | 59(1) |
| C(31) | 4385(3) | 3983(3) | 836(2) | 69(1) |
| C(32) | 7987(3) | 4129(3) | 3073(2) | 59(1) |
| C(33) | 8467(3) | 5020(3) | 3956(2) | 76(1) |
| C(34) | 9108(3) | 6209(3) | 3906(2) | 74(1) |
| C(35) | 9902(3) | 7812(3) | 2840(3) | 81(1) |
| C(36) | 10001(3) | 8071(3) | 1920(3) | 92(1) |
| C(37) | 9506(3) | 7144(3) | 1057(3) | 72(1) |
| C(38) | 8898(2) | 5927(2) | 1143(2) | 47(1) |
| C(39) | 8766(2) | 5616(2) | 2111(2) | 40(1) |
| C(40) | 9272(2) | 6571(2) | 2971(2) | 57(1) |
| C(41) | 8420(3) | 5167(3) | −639(2) | 77(1) |

[a] $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* a_i a_j$.

The dinegative anion, $Ph_2SnCl_4^{2-}$, and the two 8-methoxyquinolinium cations in **3** are held together by electrostatic force and hydrogen bonding. The two Cl atoms, Cl(1) and Cl(1A), which are *trans* to one another and have the shorter Sn–Cl bond distance in $Ph_2SnCl_4^{2-}$, formed two NH···Cl hydrogen bonds with two cations (Fig. 3). The N(1)H···Cl(1) distance of 3.154 Å and bond angle of 174.7° ($-x$, $-y$, $-z$) are typical for the NH···Cl hydrogen bond [23–26]. In this configuration, each of the other two *trans* chlorine atoms, Cl(2) and Cl(2A), in $Ph_2SnCl_4^{2-}$ formed another two C(sp$^2$)H···Cl intermolecular hydrogen bonds with two neighbouring cations, one bond at the C(4)H ($x+1$, $y+1$, $z$) and another at the C(7)H ($x+1$, $y$, $z$) atom of the 8-methoxyquinolinium cation (Fig. 3). These two weak interactions, C(4)H···Cl(2A) (3.653 Å and 175.7°) and C(7)H···Cl(2A) (3.450 Å and 119°), are caused by the protonation of the pyridyl N atom which increases the acidity of the proton attached to the C(4) and C(7) atoms in the quinoline ring [27,28]. The existence of such a C(sp$^2$)H···Cl interaction has recently been reported for 4,6-dimethylpyrimidine-2-thione hydrochloride monohydrate (3.562 Å, 165°) [29]. These weak interactions (C(sp$^2$)H···Cl and NH···Cl), as well as the electrostatic force between the cations and the dianion, permit **3** to be a closely packed 3D crystalline solid.

The IR and NMR spectral data interpretations for **3** (Table 1) are in agreement with the structure determined by X-ray crystallography. The observed broad band, centred at 2818 cm$^{-1}$ and assigned as $NH^+$ stretching vibration in the IR spectrum of **3**, suggests that the ligand moiety is protonated and the organotin species exists as a counter anion. That the ligand moiety is indeed protonated is further evidenced from the similarity observed in the $^1$H- and $^{13}$C-NMR spectra of **3**, **1** and 8-methoxyquinoline. Elemental analysis and $^1$H-NMR integration further reveal that **3** is a complex salt where the charges of the two protonated 8-methoxyquinoline are balanced by the dinegative $Ph_2SnCl_4^{2-}$ anion, to yield a $(C_{10}H_9ON \cdot H)_2Ph_2SnCl_4$ molecule.

In view of the results of the elemental analysis of **2** and the fact that its spectral data (Table 1) are very similar to that of **1** and **3**, it can be concluded that **2** is a dimethyltin analogue of **3**.

### 3.3. Characterisation of $(C_{10}H_9ON \cdot H \cdot NOH_9C_{10})Ph_2SnCl_3$, **4**

The X-ray structure and atom-numbering scheme for **4** are shown in Fig. 4 and its crystal data and structural refinement parameters are listed in Table 2. While the fractional atomic coordinates with equivalent isotopic displacement parameters for **4** are listed in Table 5, its bond lengths and angles are collected in Table 6.

Table 6
Selected bond lengths (Å) and angles (°) for **3**

| Bond lengths (Å) | | | | | |
|---|---|---|---|---|---|
| Sn(1)–C(1) | 2.150(2) | Sn(1)–C(1) | 2.150(2) | Sn(1)–Cl(1) | 2.5276(14) |
| Sn(1)–Cl(2) | 2.546(2) | Sn(1)–Cl(3) | 2.4010(14) | O(21)–C(28) | 1.352(3) |
| O(21)–C(31) | 1.421(3) | O(31)–C(38) | 1.351(3) | O(31)–C(41) | 1.436(3) |
| N(21)–C(22) | 1.316(3) | N(21)–C(29) | 1.363(3) | N(31)–C(32) | 1.313(3) |
| N(31)–C(39) | 1.363(3) | C(1)–C(6) | 1.376(4) | C(1)–C(2) | 1.383(3) |
| C(2)–C(3) | 1.396(4) | C(3)–C(4) | 1.361(5) | C(4)–C(5) | 1.364(5) |
| C(5)–C(6) | 1.387(4) | C(11)–C(12) | 1.380(3) | C(11)–C(16) | 1.387(3) |
| C(12)–C(13) | 1.387(3) | C(13)–C(14) | 1.367(4) | C(14)–C(15) | 1.370(4) |
| C(15)–C(16) | 1.387(3) | C(22)–C(23) | 1.389(3) | C(23)–C(24) | 1.351(4) |
| C(24)–C(30) | 1.397(4) | C(25)–C(26) | 1.342(5) | C(25)–C(30) | 1.411(4) |
| C(26)–C(27) | 1.397(5) | C(27)–C(28) | 1.366(4) | C(28)–C(29) | 1.407(3) |
| C(29)–C(30) | 1.414(3) | C(32)–C(33) | 1.401(4) | C(33)–C(34) | 1.336(4) |
| C(34)–C(40) | 1.406(4) | C(35)–C(36) | 1.333(5) | C(35)–C(40) | 1.415(4) |
| C(36)–C(37) | 1.404(5) | C(37)–C(38) | 1.367(3) | C(38)–C(39) | 1.423(3) |
| C(39)–C(40) | 1.418(3) | | | | |

| Bond angles (°) | | | |
|---|---|---|---|
| C(11)–Sn(1)–C(1) | 135.80(8) | C(11)–Sn(1)–Cl(3) | 113.08(6) |
| C(1)–Sn(1)–Cl(3) | 111.10(6) | C(11)–Sn(1)–Cl(1) | 91.53(6) |
| C(1)–Sn(1)–Cl(1) | 92.16(7) | C(13)–Sn(1)–C(11) | 86.57(4) |
| C(11)–Sn(1)–Cl(2) | 90.33(6) | C(1)–Sn(1)–Cl(2) | 91.71(7) |
| Cl(3)–Sn(1)–Cl(2) | 85.83(4) | Cl(1)–Sn(1)–Cl(2) | 172.30(2) |
| C(28)–O(21)–C(31) | 117.8(2) | C(38)–O(31)–C(41) | 119.0(2) |
| C(22)–N(21)–C(29) | 121.7(2) | C(32)–N(31)–C(39) | 118.6(2) |
| C(6)–C(1)–C(2) | 118.6(2) | C(6)–C(1)–Sn(1) | 120.3(2) |
| C(2)–C(1)–Sn(1) | 121.1(2) | C(1)–C(2)–C(3) | 120.3(3) |
| C(4)–C(3)–C(2) | 120.2(3) | C(3)–C(4)–C(5) | 119.7(3) |
| C(4)–C(5)–C(6) | 120.7(3) | C(1)–C(6)–C(5) | 120.5(3) |
| C(12)–C(11)–C(16) | 118.2(2) | C(12)–C(11)–Sn(1) | 120.3(2) |
| C(16)–C(11)–Sn(1) | 121.5(2) | C(11)–C(12)–C(13) | 120.9(2) |
| C(14)–C(13)–C(12) | 120.1(2) | C(13)–C(14)–C(15) | 119.9(2) |
| C(14)–C(15)–C(16) | 120.(2) | C(11)–C(16)–C(15) | 120.6(2) |
| N(21)–C(22)–C(23) | 121.5(2) | C(24)–C(23)–C(22) | 119.0(2) |
| C(23)–C(24)–C(30) | 120.8(2) | C(26)–C(25)–C(30) | 119.4(3) |
| C(25)–C(26)–C(27) | 122.6(3) | C(28)–C(27)–C(26) | 120.4(3) |
| O(21)–C(28)–C(27) | 127.4(2) | O(21)–C(28)–C(29) | 114.4(2) |
| C(27)–C(28)–C(29) | 118.1(2) | N(21)–C(29)–C(28) | 119.7(2) |
| N(21)–C(29)–C(30) | 118.9(2) | C(28)–C(29)–C(30) | 121.4(2) |
| C(24)–C(30)–C(25) | 123.8(2) | C(24)–C(30)–C(29) | 118.1(2) |
| C(25)–C(30)–C(29) | 118.1(3) | N(31)–C(32)–C(33) | 123.0(3) |
| C(34)–C(33)–C(32) | 119.4(3) | C(33)–C(34)–C(40) | 120.4(2) |
| C(36)–C(35)–C(40) | 120.1(3) | C(35)–C(36)–C(37) | 122.2(3) |
| C(38)–C(37)–C(36) | 120.1(3) | O(31)–C(38)–C(37) | 126.1(2) |
| O(31)–C(38)–C(39) | 114.5(2) | C(37)–C(38)–C(39) | 119.3(2) |
| N(31)–C(39)–C(40) | 121.6(2) | N(31)–C(39)–C(38) | 118.9(2) |
| C(40)–C(39)–C(38) | 119.5(2) | C(34)–C(40)–C(35) | 124.2(3) |
| C(34)–C(40)–C(39) | 117.0(2) | C(35)–C(40)–C(39) | 118.8(3) |

The assymmetric unit of **4** consists of an isolated $Ph_2SnCl_3^-$ anion and a ligand pair cation, $(C_{10}H_9ON \cdot H \cdot NOH_9C_{10})^+$, with no inter-atomic distance of $< 6$ Å. This means that these discrete ions are held together mainly by electrostatic force.

In the cationic species of **4**, the two 8-methoxyquinoline species are mainly held together by a proton which forms hydrogen bonds with the two pyridyl N atoms. Thus the proton is situated between the two pyridyl N atoms, making an almost linear N(21)H···N(31) angle of 165.6° and a N(21)···N(31) bond distance of 2.729 Å. This distance is shorter than that (2.961 Å) reported for the adduct of bis(3-methyladenine)dimethyldichlorotin [10]. The short distance, is also caused by the presence of an additional N(21)H···O(31) hydrogen bond (2.884 Å, 104.9°) observed in **4**. The closeness of the two 8-methoxyquinoline molecules in the cationic ligand pair thus prevents any formation of Sn–N and/or Sn–O bonds.

An analogous cationic ligand pair for the complex salt $(L_2H)[Ph_3Sn(NCS)_2]$, where L = 1-(salicylideneimino)-2-methoxybenzene has been reported [30]. The two L ligands in this complex were coplanar and held together by a proton between the phenolic O atoms of the two ligands. However, in **4**, the two quinoline rings, which are nearly planar individually (0.0452 and 0.010 Å deviation from its respective least-square plane), are almost vertical (92.7°) to each other. This is due to the steric hindrance posed by the presence of the methoxy group in the ligand.

The tin atom in the anionic species of **4**, is five-coordinated and is bonded to three chlorine atoms and two carbon atoms of the phenyl rings. This tin atom adopts a trigonal bipyramid geometry, with C(1), C(11) and Cl(3) sitting on the equatorial plane while the other two chlorine atoms, Cl(1) and C1(2), occupying the axial positions of the bipyramid (Fig. 4). This trigonal bipyramid geometry is distorted as shown by the following bond angles: C(1)–Sn(1)–C(11) 135.78(8), C(11)–Sn(1)Cl(3) 113.08(6), Cl(3)–Sn(1)–C(1) 92.14(7) and Cl(1)–Sn(1)–Cl(2) 172.31(7)°. Bond distances (2.5267(14) and 2.546(2) Å) between the tin atom and the two axial chlorine atoms are significantly longer than the equatorial Sn–Cl(3) bond (2.4010(14) Å). The Sn–C bonds (2.150 Å) are in the normal range of Sn–C (Ph) distances (2.105–2.16 Å) [10].

Similar anionic structures have been reported in $(Et_4N)Ph_2SnCl_3$ [31]. As expected, all the bond lengths and bond angles that are involved in the anionic structure of **4** are very similar in magnitude to those recorded for $(Et_4N)Ph_2SnCl_3$. Furthermore, all the three Sn–Cl bonds in **4** and in $(Et_4N)Ph_2SnCl_3$ are shorter than those of the $Me_2SnCl_3$ or $Et_2SnCl_3$ anions found in the complex salts of $(C_9H_8N)Me_2SnCl_3$ [32], $[Pt(S_2N_2H)(PEt_3)_2]Me_2SnCl_3$ [33], $(TTF)_3Me_2SnCl_3$ (TTF = tetrathiafalvalen) [34], $(MeOC_{10}H_6CH{=}NHC_6H_4OMe)_2[Me_4Sn_2Cl_6](H_2O)_2$ [35] and $[SnEt_2(H_2dapin')]_2(Et_2SnCl_3)Cl_3 \cdot H_2O$ [$H_2$dapin′ = 2,6-diacetylpyridine-bis(isonicotinoylhydrazone)] [36]. This may be due to the fact that, to-date, only the dimeric structures of $Me_2SnCl_3$ and $Et_2SnCl_3$ anions have been characterised [32–36]. Thus it can be inferred that the bulky phenyl groups are responsible for the non-dimerisation of the $Ph_2SnCl_3$ anion.

The assignment of IR characteristic absorption frequencies of **4** has been made by comparison with the IR spectrum of **1**, **2** and **3** (Table 1). The broad band centred at 2634 $cm^{-1}$, and assigned as $NH^+$ stretching vibration, is lower than the corresponding band observed for **1** (2805 $cm^{-1}$) and for **3** (2818 $cm^{-1}$). Another broad band located at 1980 $cm^{-1}$ in the spectrum of **4**, is attributed to the stretching vibration of a very weak N–H bond. From these observations it is concluded that the two ligand species are bonded through the N(H)···N hydrogen bond with their respective pyridyl N atom present in the 8-methoxyquinoline ring.

The $^1$H-NMR spectrum of **4** shows the expected integration and peak multiplicities. The broad signal at $\delta$ 6.7 ppm is ascribed to the proton attached to the pyridyl N atom in ligand moieties of **4**. This interpretation is further substantiated by the shifts in the $\delta$ values observed between the H2, H4 and other aromatic protons attached to the free 8-methoxyquinoline, **1**, **2** and **3** (Table 1). In addition, the $\delta$ chemical shifts observed in the $^1$H- and $^{13}$C-NMR spectra of **4** are intermediate in magnitude between the free and protonated (**1** and **3**) 8-methoxyquinoline (Table 1), thus confirming the existence of a united ligand pair with a N(H)···N hydrogen bond as suggested by X-ray structural crystallographic study.

## 4. Conclusions

Unlike 8-aminoquinoline, which formed 1:1 adduct with $Ph_2SnCl_2$ [8] and $Me_2SnCl_2$ [9], it is very hard to coax 8-methoxyquinoline to form 1:1 adduct with $R_2SnCl_2$. The factors preventing 8-methoxyquinoline from behaving as a strong bidentate donor are the electronegativity of the methoxy O atom, the possibility of conjugation between the electron pair of the O atom in the methoxy group and the quinoline ring, and the C–O bond rotation of the bulky methoxy group affecting the electron donating ability of the pyridyl N atom in 8-methoxyquinoline. Since an organotin adduct-formation reaction with 8-methoxyquinoline is unfavourable, competing reactions, like hydrolysis of $R_2SnCl_2$, occur, and depending on the rate of hydrolysis of $R_2SnCl_2$, resulting in the formation of $[(R_2SnCl)_2O]_2$ and/or organostannates. The isolation of **3** and **4** in the reaction mixture of $Ph_2SnCl_2$ with 8-methoxyquinoline in cyclohexane suggests that the formation of $Ph_2SnCl_4^{2-}$ arises from the disproportionation reaction of $Ph_2SnCl_3^-$ rather than from the reaction, $Ph_2SnCl_3^- + Cl^- \rightarrow Ph_2SnCl_4^{2-}$.

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