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## SHORT PAPER

# Complexes of diorganotin(IV) dihalides with diphosphoryl compounds and their Mössbauer spectra

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## INTRODUCTION

Many complexes of organotin(IV) compounds with donor ligands have now been synthesized and their molecular structures investigated by various spectroscopic methods, including Mössbauer spectroscopy.[1,2] Various types of ligands are employed in coordination with tin, but the literature indicates that in spite of convenience for spectroscopic studies only a few adduct types with phosphoryl and diphosphoryl compounds (namely alkyl (aryl) phosphine oxides and bis(diphenylphosphoryl)-alkanes or -alkenes) have been obtained and investigated so far.

$[Ph_2P(O)]_2CH_2$ and *cis*-$[Ph_2P(O)CH]_2$ are bidentate chelating ligands providing monomeric adducts with diorganotin(IV) derivatives in most cases.[3–6] At the same time $[Ph_2P(O)CH_2]_2$ and *trans*-$[Ph_2P(O)CH]_2$ are bidentate bridging ligands providing polymeric or binuclear complexes. Recent X-ray data for $Me_2SnCl_2$–$[(EtO)_2P(O)]_2CHNMe_2$ [8] reveal that it is an unusual binuclear dimeric complex with two bridging ligands *cis*-linking octahedral organotin units. As confirmed by X-ray data, octahedral diorganotin(IV) complexes possess *trans*-$R_2SnX_4$ configuration in all cases.

This paper deals with the synthesis and identification of potentially antitumor active[9] complexes of dialkyl- and diphenyl-tin(IV) dihalides with a number of diphosphoryl compounds. Some of these complexes were investigated by Mössbauer spectroscopy.

## EXPERIMENTAL

### Preparation of complexes with ligands of the type $[RO(R')P{=}O]_2CH_2$ ($L^1$: R = Et, R' = $(EtO)_2CH$; $L^2$: R = $Pr^i$; R' = Me)

Adducts of organotin(IV) dihalides with bidentate methylenediphosphinates were synthesized by addition of *ca.* 1 mmol of the donor ligand to a boiling solution of an equimolar amount of the organometallic compound in 5 cm$^3$ of pentane or petroleum ether. After it had been stirred for several minutes the reaction mixture was gradually cooled to 0 °C. After a period for crystallization, the white crystals formed were filtered, washed with cold pentane and dried. In the case of $Bu_2SnCl_2 \cdot L^1$, $Bu_2SnCl_2 \cdot L^2$ and $Bu_2SnBr_2 \cdot L^2$, which occur at room temperature as colourless viscous liquids, heavy transparent layer appeared, which was separated, washed with pentane and dried. The composition of these adducts was 1:1, as indicated by elemental analyses and integration of $^1H$ NMR spectra. Melting points and elemental analysis data are listed in Table 1.

### Preparation of complexes with ligands of the type $[(RO)_2P{=}O)]_2CHR'$ ($L^3$:R = Et, R' = H; $L^4$: R = iPr; R' = $NMe_2$)

Molecular complexes of organotin dihalides with tetra-alkyl methylene diphosphonates were obtained as described for the previous group of adducts. These colourless compounds have 1:1 composition according to elemental analysis data and $^1H$ NMR spectra, with the exception of adducts of dimethyltin dihalides with $L^4$ having a 2:1 composition independent of the initial molar ratio of the components. Melting points and analysis data are given in Table 2.

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**Table 1** Molecular complexes of L$^1$ and L$^2$

| Complex | M.p. (°C) | Analysis: Found (calcd) (%) C | H |
|---|---|---|---|
| $Me_2SnCl_2 \cdot L^1$ | 79–82 | 32.9 (32.7) | 6.4 (6.4) |
| $Me_2SnBr_2 \cdot L^1$ | 86–88 | 28.5 (28.6) | 5.7 (5.6) |
| $Et_2SnCl_2 \cdot L^1$ | 63–65 | 35.1 (35.0) | 6.8 (6.8) |
| $Et_2SnBr_2 \cdot L^1$ | 56–58 | 30.8 (30.8) | 6.0 (6.0) |
| $Bu_2SnCl_2 \cdot L^1$ | Oil | 36.5 (39.0) | 7.0 (7.3) |
| $Bu_2SnBr_2 \cdot L^1$ | 48–50 | 34.9 (34.6) | 7.0 (6.5) |
| $Ph_2SnCl_2 \cdot L^1$ | 76–78 | 42.0 (43.3) | 5.8 (5.9) |
| $Et_2SnCl_2 \cdot L^2$ | 87–88 | 30.3 (31.0) | 6.4 (6.4) |
| $Et_2SnBr_2 \cdot L^2$ | 85–87 | 26.3 (26.3) | 5.5 (5.4) |
| $Ph_2SnCl_2 \cdot L^2$ | 138–139 | 41.3 (42.0) | 5.3 (5.3) |
| $Bu_2SnCl_2 \cdot L^2$ | Oil | 36.0 (36.4) | 7.1 (7.1) |
| $Bu_2SnBr_2 \cdot L^2$ | Oil | 31.6 (31.4) | 6.4 (6.2) |

### Preparation of complexes with tetraethyl ethylene-1,2-diphosphonate (L$^5$=[(EtO)$_2$P(O)CH$_2$]$_2$)

Complexes of dialkyltin dihalides with L$^5$ were synthesized in a similar manner to the previous groups of complexes. These adducts appear as colourless crystals having 1:1 composition according to elemental analysis and $^1$H NMR spectra. Data are listed in Table 3.

The preparation of the ligands is described elsewhere.[10–13] Diorganotin(IV) dihalides were obtained by known procedures.

Mössbauer spectra were obtained using a 185 MBq Ba$^{119}$SnO$_3$ source and absorber (8.3 mg Sn cm$^{-2}$) in a liquid-helium cryostat and with a 512 multichannel analyser. IR spectra were recorded using a Perkin–Elmer 983G spectrometer in nujol.

**Table 2** Molecular complexes with L$^3$ and L$^4$

| Complex | M.p. (°C) | Analysis: Found (calcd) (%) C | H |
|---|---|---|---|
| $Me_2SnCl_2 \cdot L^3$ | 32–37 | 25.6 (26.0) | 5.4 (5.5) |
| $Me_2SnBr_2 \cdot L^3$ | Oil | 21.6 (22.1) | 4.7 (4.7) |
| $Et_2SnCl_2 \cdot L^3$ | 33–35 | 29.0 (29.1) | 5.9 (6.0) |
| $Et_2SnBr_2 \cdot L^3$ | 37–40 | 25.1 (25.0) | 5.1 (5.1) |
| $Bu_2SnCl_2 \cdot L^3$ | Oil | 33.9 (34.4) | 6.8 (6.8) |
| $Bu_2SnBr_2 \cdot L^3$ | Oil | 30.8 (30.0) | 6.4 (5.9) |
| $(Me_2SnCl_2)_2 \cdot L^4$ | 63–65 | 27.3 (27.6) | 5.8 (5.7) |
| $(Me_2SnBr_2)_2 \cdot L^4$ | 105–107 | 22.3 (22.7) | 4.9 (4.7) |
| $Bu_2SnCl_2 \cdot L^4$ | Oil | 38.9 (39.9) | 7.6 (7.7) |
| $Bu_2SnBr_2 \cdot L^4$ | Oil | 35.0 (35.4) | 6.4 (6.8) |

**Table 3** Molecular complexes with L$^5$

| Complex | M.p. (°C) | Analysis: Found (calcd) (%) C | H |
|---|---|---|---|
| $Me_2SnCl_2 \cdot L^5$ | 30 | 28.0 (27.6) | 5.7 (5.8) |
| $Me_2SnBr_2 \cdot L^5$ | 56 | 22.8 (23.6) | 4.9 (4.9) |
| $Et_2SnCl_2 \cdot L^5$ | 57–58 | 30.7 (30.6) | 6.2 (6.2) |
| $Et_2SnBr_2 \cdot L^5$ | 59–60 | 26.2 (26.3) | 5.4 (5.3) |

## RESULTS AND DISCUSSION

$^{119m}$Sn Mössbauer isomer shifts ($\delta$) and quadrupole splittings ($\Delta E$) of some of the adducts prepared are given in Table 4. The isomer shifts $\delta$ (mm s$^{-1}$) are typical of dialkyltin(IV) complexes. The experimental nuclear quadrupole splittings, $\Delta E$ (mm s$^{-1}$) of all the complexes except $(Me_2SnHa_2)_2 \cdot L^4$, are fully consistent with the occurrence of octahedral *trans*-R$^2$

**Table 4** Mössbauer data of some selected (L$^1$–L$^5$)-diorganotin dihalide complexes

| No. | Complex | $\delta$ (mm s$^{-1}$)$^a$ | $\Delta E$ (mm s$^{-1}$)$^b$ |
|---|---|---|---|
| **1** | $Me_2SnCl_2 \cdot L^1$ | 1.33 | 4.29 |
| **2** | $Me_2SnBr_2 \cdot L^1$ | 1.39 | 4.38 |
| **3** | $Et_2SnBr_2 \cdot L^1$ | 1.60 | 4.32 |
| **4** | $Bu_2SnCl_2 \cdot L^1$ | 1.49 | 3.90 |
| **5** | $Bu_2SnBr_2 \cdot L^1$ | 1.70 | 3.91 |
| **6** | $Ph_2SnCl_2 \cdot L^1$ | 1.20 | 3.74 |
| **7** | $Et_2SnCl_2 \cdot L^2$ | 1.56 | 4.29 |
| **8** | $Bu_2SnCl_2 \cdot L^2$ | 1.46 | 3.85 |
| **9** | $Bu_2SnBr_2 \cdot L^2$ | 1.54 | 3.95 |
| **10** | $Ph_2SnCl_2 \cdot L^2$ | 1.30 | 3.72 |
| **11** | $Me_2SnBr_2 \cdot L^3$ | 1.43 | 4.11 |
| **12** | $Bu_2SnCl_2 \cdot L^3$ | 1.52 | 3.97 |
| **13** | $(Me_2SnBr_2)_2 \cdot L^4$ | 1.30 | 3.28 |
| **14** | $Bu_2SnBr_2 \cdot L^4$ | 1.50 | 3.67 |
| **15** | $(Me_2SnCl_2)_2 \cdot L^4$ | 1.36 | 3.38 |
| **16** | $Me_2SnCl_2 \cdot L^5$ | 1.44 | 4.09 |
| **17** | $Et_2SnCl_2 \cdot L^5$ | 1.56 | 4.29 |
| **18** | $Bu_2SnCl_2 \cdot L^5$ | 1.58 | 4.14 |

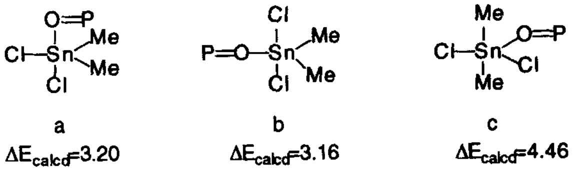
[a] Isomer shift with respect to BaSnO$_3$ at room temperature.
[b] Nuclear quadrupole splitting.

structures,[4,7,14–16] with some distortion. The experimental $\Delta E$ values for all the octahedral complexes, have then been rationalized according to the point-charge model formalism, to calculate the C–Sn–C angles, which ranged from 158 (complex **14** in Table 4) to 180 (complexes **1–3**, **7**, **17** in Table 4). The agreement between $\Delta E_{exp}$ and $\Delta E_{calcd}$ would appear to confirm the proposed structures. The negative shifts of the $\nu$(P=O) bands in all compounds suggest the coordination of the phosphoryl oxygen atom to tin, and their values (10–42 $cm^{-1}$) are similar to those reported earlier.[7]

The $\nu$(SnO), $\nu$(SnCl) and $\nu$(SnC) assignments are uncertain because of the presence of other absorptions in the respective spectral regions. However, as far as the coordination of the ligand at the tin atom in complexes with $L^1$–$L^4$ is concerned, no information can be drawn from Mössbauer data, since possible chelate,[4] open-chained polymer[7] or cyclic oligomer[8] with *trans*-$R_2SnX_4$ configurations have similar $\delta$ and $\Delta E$ values.

Diorganotin(IV) complexes with $L^5$ may have a polymeric structure, as does the complex of $Bu_2SnCl_2$ with 1,2-bis(diphenylphosphoryl)-ethane.[7] This information (on the monomeric or polymeric nature of the investigated complexes in the solid state) can be obtained from variable-temperature Mössbauer studies that are being continued.

The significantly lower $\Delta E$ value for $(Me_2SnHal_2)_2 \cdot L^4$ indicates the formation of a pentacoordinate complex with the ligand $L^4$ bridging two $Me_2SnHal_2$ units. The calculated $\Delta E$ values for $(Me_2SnCl_2) \cdot L^4$, 3.20 and 3.16 mm $s^{-1}$, according to the point-charge formalism, by using tabulated alkyl and chloride p.q.s. for the idealized structures of Fig. 1 (respectively **a** and **b**), are in good agreement with the experimental $\Delta E$ (see Table 4). {P=O}p.q.s. have been calculated from the $\{Me_2SnCl_2 \cdot Me_2NCH[(EtO)_2P(O)]_2\}_2$ $\Delta E$ value the structure of this complex has been well established by X-ray analysis.[8]



a $\Delta E_{calcd}$=3.20 b $\Delta E_{calcd}$=3.16 c $\Delta E_{calcd}$=4.46

**Figure 1**

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