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Synthesis and characterization of *N,N*-diethyldithiocarbamate complexes of 2-alkoxycarbonylethyltin trichloride

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***N,N*-Diethyldithiocarbamate complexes of 2-alkoxycarbonylethyltin trichloride, $ROCOCH_2CH_2SnCl_{3-x}[S_2CNEt_2]_x$ (R = CH_3 (a); CH_3CH_2 (b); $CH_2{=}CHCH_2$ (c); $CH_3CH_2CH_2$ (d); $CH_3CH_2CH_2CH_2$ (e); $x = 1$ (1), 2 (2)) were synthesized and characterized by means of elemental analysis, IR, and NMR (^1H, ^{13}C and ^{119}Sn) spectra. The crystal structure of 1b (i.e. R = CH_3CH_2, $x = 1$) was determined and shows that the tin atom adopts a distorted octahedral geometry with both a five-membered chelate ring, formed via carbonyl coordination to tin, and a four-membered chelate ring, formed by the bidentate dithiocarbamate. The spectral data and *ab initio* calculations indicate that intramolecular carbonyl-oxygen to tin coordination in 1a–1e persists, but not in 2a–2e, owing to the preference of the dithiocarbamate ligands to chelate the tin centre. Copyright © 2005 John Wiley & Sons, Ltd.**

KEYWORDS: crystal structure; 2-alkoxycarbonylethyltin trichloride; *N,N*-diethyldithiocarbamate; organotin complex; NMR; *ab initio* calculation

INTRODUCTION

Interest in dithiocarbamate complexes of organotin species arises because of their variety of structures and biological activities.[1–14] On the basis of crystallographic studies of the dithiocarbamate complexes of organotin, a variety of coordination environments around the central tin atom, ranging from tetrahedral to pentagonal bipyramidal, with ligands having anisobidentate or monodentate character, have been reported.[1–13] 2-Alkoxycarbonylethyltin trichlorides, $ROCOCH_2CH_2SnCl_3$, so-called estertin trichloride, which are synthesized directly from $SnCl_2$ and acrylates in high yields, have received considerable attention owing to the variety of coordination geometries about the tin atom.[6,7,13,15–28] To date, many investigations have been reported about the compounds derived from the reaction of 2-alkoxycarbonylethyltin trichlorides with simple Lewis bases and the ligands containing nitrogen, oxygen and sulfur atoms.[6,13,17–28] Jung *et al.*[6,7] have reported the syntheses and structures of 2-methoxycarbonylethyltin complexes with *N,N*-dimethyldithiocarbamate, $MeOCOCH_2CH_2SnCl_{3-x}[S_2CNMe_2]_x$ ($x = 1, 2, 3$). As a continuation of the investigation of the coordination chemistry of 2-alkoxycarbonylethyltin trichloride with dithiocarbamate ligands, we have synthesized and characterized complexes derived from the reaction of some 2-alkoxycarbonylethyltin trichloride with *N,N*-diethyldithiocarbamate.

EXPERIMENTAL

Materials and physical measurements

2-Alkoxycarbonylethyltin trichlorides were prepared by a published procedure.[15] All chemicals were of reagent grade and were used without further purification. Carbon, hydrogen and nitrogen analyses were obtained using a Perkin Elmer 2400 Series II elemental analyser. Melting points were measured on an X-4 microscopic melting point apparatus. IR spectra were recorded on a Nicolet 470 FT-IR spectrophotometer using KBr discs in the range 4000–400 cm^{-1}. ^1H and ^{13}C NMR spectral data were collected using a Bruker Avance DMX500 FT-NMR spectrometer with $CDCl_3$ as solvent and tetramethylsilane as internal standard. ^{119}Sn NMR spectra were recorded in $CDCl_3$ on

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a Varian Mercury Vx300 FT-NMR spectrometer using Me_4Sn as internal reference.

Synthesis of 2-Alkoxycarbonylethyltin dithiocarbamates

A solution of $NaS_2CNEt_2 \cdot 3H_2O$ (1.35 g, 6 mmol) dissolved in 50 ml of dry acetone was added dropwise to an appropriate stoichiometric amount solution of 2-alkoxycarbonylethyltin trichloride (6 or 3 mmol) in 30 ml of the same solvent at room temperature. The reaction mixture was stirred for about an hour under reflux, and then cooled to about 0 °C. The NaCl formed was removed by filtration. The filtrate, after distilling off the excess solvent, yielded a crystalline solid or oil, which was recrystallized from dichloromethane–*n*-hexane (1 : 1, v/v) and dried in vacuum.

$CH_3OCOCH_2CH_2SnCl_2[S_2CN(CH_2CH_3)_2]$ (**1a**)

White solid, 74.2% yield, m.p. 79–80 °C. Anal. Found: C, 25.39; H, 3.82; N, 3.23. Calc. for $C_9H_{17}Cl_2NO_2S_2Sn$: C, 25.44; H, 4.03; N, 3.30%. ^1H NMR δ: 4.02 (3H, s, CH_3O), 3.72 (4H, q, $J = 7.2$ Hz, $N(CH_2CH_3)_2$), 2.89 (2H, t, $J = 7.5$ Hz, $^3J(^{119/117}Sn{-}^1H) = 222/217$ Hz, $COCH_2$), 1.86 (2H, t, $J = 7.5$ Hz, $^2J(^{119/117}Sn{-}^1H) = 112/107$ Hz, CH_2Sn), 1.36 (6H, t, $J = 7.2$ Hz, $2CH_3$). ^{13}C NMR δ: 194.51 (C=S), 180.57 (C=O), 54.89 (CH_3O), 52.07 (NCH_2), 32.90 ($SnCH_2$, $^1J(^{119/117}Sn{-}^{13}C) = 981/940$ Hz), 29.11 (CH_2CO, $^2J(^{119}Sn{-}^{13}C) = 77$ Hz), 12.16 (CH_3). ^{119}Sn NMR δ: −382.31. IR (cm^{-1})ν: 1664 (vs, C=O), 1520 (vs, C–N), 994 (s, C–S).

$CH_3CH_2OCOCH_2CH_2SnCl_2[S_2CN(CH_2CH_3)_2]$ (**1b**)

White solid, 81.3% yield, m.p. 101–102 °C. Anal. Found: C, 27.38; H, 4.29; N, 3.20. Calc. for $C_{10}H_{19}Cl_2NO_2S_2Sn$: C, 27.36; H, 4.36; N, 3.19%. ^1H NMR δ: 4.46 (2H, q, $J = 6.8$ Hz, CH_2O), 3.72 (4H, q, $J = 7.2$ Hz, $N(CH_2CH_3)_2$), 2.92 (2H, t, $J = 7.4$ Hz, $^3J(^{119/117}Sn{-}^1H) = 221/216$ Hz, $COCH_2$), 1.89 (2H, t, $J = 7.4$ Hz, $^2J(^{119/117}Sn{-}^1H) = 111/106$ Hz, CH_2Sn), 1.39 (3H, t, $J = 7.2$ Hz, CH_3), 1.36 (6H, t, $J = 7.2$ Hz, $2CH_3$). ^{13}C NMR δ: 194.71 (C=S), 180.62 (C=O), 64.43 (CH_2O), 52.03 (NCH_2), 32.85 ($SnCH_2$, $^1J(^{119/117}Sn{-}^{13}C) = 976/935$ Hz), 29.07 (CH_2CO, $^2J(^{119}Sn{-}^{13}C) = 76$ Hz), 14.32 (CH_3), 12.17 (CH_3). ^{119}Sn NMR δ: −381.66. IR (cm^{-1})ν: 1662 (vs, C=O), 1528 (vs, C–N), 999 (s, C–S).

$CH_2{=}CHCH_2OCOCH_2CH_2SnCl_2[S_2CN(CH_2CH_3)_2]$ (**1c**)

Colourless oil, 70.7% yield. Anal. Found: C, 29.31; H, 4.12; N, 2.98. Calc. for $C_{11}H_{19}Cl_2NO_2S_2Sn$: C, 29.29; H, 4.25; N, 3.11%. ^1H NMR δ: 5.95–6.03 (1H, m, =CH), 5.42, 5.33 (2H, dd, $^2J = 0.74$ Hz, $J_{trans} = 17.2$ Hz, $J_{cis} = 10.3$ Hz, $CH_2{=}$), 4.87 (2H, d, $J = 5.8$ Hz, CH_2O), 3.73 (4H, q, $J = 7.1$ Hz, $N(CH_2CH_3)_2$), 2.96 (2H, t, $J = 7.3$ Hz, $^3J(^{119}Sn{-}^1H) = 221$ Hz, $COCH_2$), 1.92 (2H, t, $J = 7.3$ Hz, $^2J(^{119}Sn{-}^1H) = 108$ Hz, CH_2Sn), 1.37 (6H, t, $J = 7.2$ Hz, $2CH_3$). ^{13}C NMR δ: 194.03 (C=S), 180.35 (C=O), 130.88 (=CH), 120.19 ($CH_2{=}$), 68.58 (CH_2O), 52.06 (NCH_2), 32.77 ($SnCH_2$, $^1J(^{119/117}Sn{-}^{13}C) = 973/930$ Hz), 29.00 (CH_2CO, $^2J(^{119}Sn{-}^{13}C) = 77$ Hz), 12.13 (CH_3). ^{119}Sn NMR δ: −380.92. IR (cm^{-1})ν: 1670 (vs, C=O), 1518 (vs, C–N), 989 (s, C–S).

$CH_3CH_2CH_2OCOCH_2CH_2SnCl_2[S_2CN(CH_2CH_3)_2]$ (**1d**)

White solid, 76.5% yield, m.p. 65–66 °C. Anal. Found: C, 29.18; H, 4.69; N, 3.12. Calc. for $C_{11}H_{21}Cl_2NO_2S_2Sn$: C, 29.16; H, 4.67; N, 3.09%. ^1H NMR δ: 4.36 (2H, t, $J = 6.7$ Hz, CH_2O), 3.72 (4H, q, $J = 7.2$ Hz, $N(CH_2CH_3)_2$), 2.92 (2H, t, $J = 7.3$ Hz, $^3J(^{119}Sn{-}^1H) = 216$ Hz, $COCH_2$), 1.89 (2H, t, $J = 7.3$ Hz, $^2J(^{119/117}Sn{-}^1H) = 111/107$ Hz, CH_2Sn), 1.77 (2H, sextet, $J = 7.2$ Hz, CH_2) 1.36 (6H, t, $J = 7.1$ Hz, $N(CH_2CH_3)_2$), 1.00 (3H, t, $J = 7.4$ Hz, CH_3). ^{119}Sn NMR δ: −381.27. IR (cm^{-1})ν: 1654 (vs, C=O), 1521 (vs, C–N), 988 (s, C–S).

$CH_3CH_2CH_2CH_2OCOCH_2CH_2SnCl_2[S_2CN(CH_2CH_3)_2]$ (**1e**)

Colourless oil, 73.2% yield. Anal. Found: C, 30.66; H, 4.89; N, 3.02. Calc. for $C_{12}H_{23}Cl_2NO_2S_2Sn$: C, 30.86; H, 4.96; N, 3.00%. ^1H NMR δ: 4.39 (2H, t, $J = 7.0$ Hz, CH_2O), 3.71 (4H, q, $J = 7.0$ Hz, $N(CH_2CH_3)_2$), 2.89 (2H, t, $J = 7.4$ Hz, $^3J(^{119}Sn{-}^1H) = 219$ Hz, $COCH_2$), 1.88 (2H, t, $J = 7.4$ Hz, $^2J(^{119}Sn{-}^1H) = 104$ Hz, CH_2Sn), 1.68 (2H, quin, $J = 7.2$ Hz, CH_2), 1.41 (2H, m, $J = 7.5$ Hz, CH_2), 1.36 (6H, t, $J = 7.2$ Hz, $N(CH_2CH_3)_2$), 0.94 (3H, t, $J = 7.4$ Hz, CH_3). IR (cm^{-1})ν: 1660 (vs, C=O), 1525 (vs, C–N), 995 (s, C–S).

$CH_3OCOCH_2CH_2SnCl[S_2CN(CH_2CH_3)_2]_2$ (**2a**)

White solid, 69.2% yield, m.p. 98–99 °C. Anal. Found: C, 31.18; H, 5.02; N, 5.20. Calc. for $C_{14}H_{27}ClN_2O_2S_4Sn$: C, 31.27; H, 5.06; N, 5.21%. ^1H NMR δ: 3.74 (8H, q, $J = 7.2$ Hz, $2N(CH_2CH_3)_2$), 3.67 (3H, s, CH_3O), 2.80 (2H, t, $J = 8.5$ Hz, $^3J(^{119/117}Sn{-}^1H) = 148/142$ Hz, $COCH_2$), 2.15 (2H, t, $J = 8.5$ Hz, $^2J(^{119}Sn{-}^1H) = 96$ Hz, CH_2Sn), 1.34 (12H, t, $J = 7.0$ Hz, $4CH_3$). ^{13}C NMR δ: 198.07 (C=S), 174.26 (C=O), 51.68 (CH_3O), 51.31 (NCH_2), 39.24 ($SnCH_2$, $^1J(^{119/117}Sn{-}^{13}C) = 956/914$ Hz), 31.52 (CH_2CO, $^2J(^{119}Sn{-}^{13}C) = 73$ Hz), 12.17 (CH_3). ^{119}Sn NMR δ: −592.23. IR (cm^{-1})ν: 1728 (vs, C=O), 1518 (vs, C–N), 990 (s, C–S).

$CH_3CH_2OCOCH_2CH_2SnCl[S_2CN(CH_2CH_3)_2]_2$ (**2b**)

White solid, 62.8% yield, m.p. 79–80 °C. Anal. Found: C, 32.48; H, 5.27; N, 5.06. Calc. for $C_{15}H_{29}ClN_2O_2S_4Sn$: C, 32.65; H, 5.30; N, 5.08%. ^1H NMR δ: 4.13 (2H, q, $J = 7.1$ Hz, CH_2O), 3.74 (8H, q, $J = 7.2$ Hz, $2N(CH_2CH_3)_2$), 2.78 (2H, t, $J = 8.5$ Hz, $^3J(^{119/117}Sn{-}^1H) = 145/139$ Hz, $COCH_2$), 2.13 (2H, t, $J = 8.5$ Hz, $^2J(^{119}Sn{-}^1H) = 95$ Hz, CH_2Sn), 1.34 (12H, t, $J = 7.1$ Hz, $2N(CH_2CH_3)_2$), 1.26 (3H, t, $J = 7.1$ Hz, CH_3). ^{13}C NMR δ: 198.01 (C=S), 174.14 (C=O), 60.82 (CH_2O), 51.83 (NCH_2), 39.17 ($SnCH_2$, $^1J(^{119/117}Sn{-}^{13}C) = 952/911$ Hz), 31.25 (CH_2CO, $^2J(^{119}Sn{-}^{13}C) = 74$ Hz), 14.12 (CH_3), 12.19 (CH_3). ^{119}Sn NMR δ: −591.68. IR (cm^{-1})ν: 1731 (vs, C=O), 1508 (vs, C–N), 992 (s, C–S).

$CH_3CH_2CH_2CH_2OCOCH_2CH_2SnCl[S_2CN(CH_2CH_3)_2]_2$ (**2e**)

Colourless oil, 76.3% yield. Anal. Found: C, 35.03; H, 5.62; N, 4.78. Calc. for $C_{17}H_{33}ClN_2O_2S_4Sn$: C, 35.21; H, 5.74; N, 4.83%. ^{1}H NMR δ: 4.07 (2H, t, $J = 6.7$ Hz, CH_2O), 3.76 (8H, q, $J = 7.0$ Hz, $2N(CH_2CH_3)_2$), 2.77 (2H, t, $J = 8.4$ Hz, $^3J(^{119}Sn-^1H) = 144$ Hz, $COCH_2$), 2.11 (2H, t, $J = 8.4$ Hz, $^2J(^{119}Sn-^1H) = 95$ Hz, CH_2Sn), 1.61 (2H, quin, $J = 7.4$ Hz, CH_2), 1.37 (2H, m, $J = 7.6$ Hz, CH_2), 1.34 (12H, t, $J = 7.4$ Hz, $2N(CH_2CH_3)_2$), 0.93 (3H, t, $J = 7.4$ Hz, CH_3). ^{13}C NMR δ: 197.43 (C=S), 174.40 (C=O), 64.66 (CH_2O), 51.24 (NCH_2), 39.56 ($SnCH_2$, $^1J(^{119/117}Sn-^{13}C) = 945/904$ Hz), 31.34 (CH_2CO, $^2J(^{119}Sn-^{13}C) = 72$ Hz), 30.91 (CH_2), 19.36 (CH_2), 13.94 (CH_3), 12.20 (CH_3). ^{119}Sn NMR δ: −591.43. IR (cm^{-1})ν: 1731 (vs, C=O), 1507 (vs, C–N), 991 (s, C–S).

Crystal structure determination of (1b)

Intensity data for a colourless crystal with dimensions $0.30 \times 0.30 \times 0.35$ mm^3 were measured on a Bruker P4 four-circle diffractometer with graphite monochromated Mo Kα (0.71 073 Å) at 293(2) K so that θ_{max} was 25.0°.[29] Crystal data: $C_{10}H_{19}Cl_2NO_2S_2Sn$, $M = 438.97$, monoclinic, space group $P2_1/c$, $a = 14.881(3)$, $b = 9.5127(10)$, $c = 12.9323(14)$ Å, $\beta = 110.282(6)°$, $V = 1717.1(4)$ Å^3, $Z = 4$, $D_c = 1.698$ g cm^{-3}, μ(Mo Kα) = 2.036 mm^{-1}. The structure was resolved by direct methods and refined by full-matrix least-squares methods on F^2 using SHELXTL.[30] Anisotropic displacement parameters were employed for non-hydrogen atoms and hydrogen atoms were included in the model at their calculated positions. The refinement converged to final $R = 0.031$ (for 2520 reflections with $I > 2\sigma(I)$), $wR = 0.083$ (all 3014 data). One ethyl group (C4 and C5) in the dithiocarbamate ligand was found to be disordered and, from refinement, the two components were refined with 50% site occupancy factors. CCDC deposition number: 168 458.

Computational method

All geometry optimizations were performed on an IBM compatible PC by using the Gaussian 98w software package.[31] All calculations were carried out at the Hartee–Fock and density functional (B3LYP) levels of theory using 3-21G* and Lanl2DZ basis sets.

RESULTS AND DISCUSSION

The reaction of $ROCOCH_2CH_2SnCl_3$ with sodium *N*,*N*-diethyldithiocarbamate in appropriate molar ratios, followed by recrystallization, afforded the products. The reaction equation was as follows:

$$ROCOCH_2CH_2SnCl_3 + xNaS_2CNEt_2 \longrightarrow$$

$$ROCOCH_2CH_2SnCl_{3-x}(S_2CNEt_2)_x + xNaCl$$

$$R = Me, Et, Allyl, n\text{-}Pr, n\text{-}Bu;\ x = 1, 2$$

2-Alkoxycarbonylethyltin *N*,*N*-diethyldithiocarbamate complexes are crystalline solids with sharp melting points or colourless oils, which are soluble in benzene and in polar organic solvents (e.g. chloroform, dichloromethane, ethanol, acetone and tetrahydrofuran), but insoluble in water and in saturated aliphatic hydrocarbons.

IR spectra

Among the stretching modes, the carbonyl band ν(C=O) in the 1650–1750 cm^{-1} region is known to depend on the nature of the coordination of the carbonyl oxygen to tin.[17] The ν(C=O) bands of **2a**–**2e** (1730 cm^{-1}) is in the same region as that of the free fat ester, in which the carbonyl group is not coordinated, whereas the bands of compounds **1a**–**1e** (1665 cm^{-1}) exhibit a remarkable red shift from that of the free fat ester. These results clearly indicate that the carbonyl is coordinated to the tin atom[15–17] in compounds **1a**–**1e**, but such a coordination is broken to accommodate two potentially bidentate dithiocarbamate ligands in compounds **2a**–**2e**. The type of bonding between the dithiocarbamate ligand and the tin atom was deduced using the ν(C–N) and ν(C–S) vibrations. The IR spectra of the complexes show a single ν(C–S) absorption at ~990 cm^{-1}, whereas the free ligand shows a doublet (962 and 987 cm^{-1}). This difference is strongly indicative of the bidentate behaviour of the ligand in the complexes.[32] The appearance of a strong band for the complexes at 1510–1530 cm^{-1}, which may be assigned to ν(C–N), gives further confirmation of the above suggested behaviour.[33] Thus, we deduce that these compounds have six-coordinated tin.

NMR spectra

The ^{1}H and ^{13}C NMR data also support the presence of carbonyl-oxygen to tin coordination in compounds **1a**–**1e**. The δ values of alkoxyl CH_nO (n = 2, 3) in **1a**–**1e** show a downfield shift ($\Delta\delta \approx 0.35$) compared with those in **2a**–**2e**, and the $\delta(^{13}C)$ values of C=O and CH_nO ($n = 2$, 3) in **1a**–**1e** are deshielded by $\Delta\delta \approx 6$ and $\Delta\delta \approx 4$ respectively relative to those of **2a**–**2e** because the coordination of carbonyl to tin causes the deshielding of CH_nOCO. However, when the coordination is broken by another dithiocarbamate ligand, the shielding of CH_nOCO is recovered again. The assignments of ^{1}H and ^{13}C of the CH_2Sn in these complexes were made from the lower $^2J(^{119}Sn-^1H)$ (95–112 Hz) and $^2J(^{119}Sn-^{13}C)$ (72–77 Hz) compared with the corresponding $^3J(^{119}Sn-^1H)$ (144–222 Hz) and $^1J(^{119}Sn-^{13}C)$ (945–981 Hz) respectively. The $^2J(^{119}Sn-^1H)$, $^3J(^{119}Sn-^1H)$, $^1J(^{119}Sn-^{13}C)$ and $^2J(^{119}Sn-^{13}C)$ coupling constants in complexes **1a**–**1e** are lower than those in the corresponding complexes **2a**–**2e**, which are in agreement with those reported in the literature.[19]

^{119}Sn NMR spectroscopy is very useful for the elucidation of the nature of coordination in the dithiocarbamatotin(IV) complexes.[6,8,10,34,35] Even for compounds with the same coordination number, a wide range of ^{119}Sn chemical shift values are observed; depending on the different organic and dithiocarbamate groups attached to the tin atom, there is an approximate relationship between the ^{119}Sn chemical shift values and the coordination numbers of the tin atoms.[6] The ^{119}Sn chemical shift values were found to be in the ranges of

−380.92 to −382.31 ppm for the complexes **1a**–**1e** and −591.46 to −592.23 ppm for the complexes **2a**–**2e**. The appearance of chemical shift values in this region indicates that there is a hexa-coordinated environment around the tin atom in these complexes,[6] which implies that both the dithiocarbamate and ester groups act as chelating ligands in complexes **1a**–**1e** and in complexes **2a**–**2e** two dithiocarbamate groups are bidentate. Although all complexes have the hexa-coordinated tin atom, the ^{119}Sn chemical shifts in complexes **2a**–**2e** appear much further unfield than those in complexes **1a**–**1e** owing to the partial change of donor atoms coordinated to tin(IV).

Crystal structure of 1b

The molecular geometry of **1b** is shown in Fig. 1, and selected bond lengths and bond angles are given in Table 1. The results of X-ray single crystal diffraction of **1b** are completely in agreement with the above spectral analysis. The complex exists as a discrete molecule, containing a five-membered chelate ring, formed via carbonyl coordination to tin, and a four-membered chelate ring, formed by the bidentate dithiocarbamate ligand. The central tin atom is in a distorted octahedral geometry with the narrow bite angles (69.95(4)° for S1–Sn–S2 and 76.82(13)° for O1–Sn–C6) of the ligands being, in part, responsible for the distortion from the ideal octahedral geometry. The dithiocarbamate ligand in complex **1b** is anisobidentically chelated to the tin atom, with one longer and one shorter Sn–S bond; the average Sn–S bond distance is 2.5582(12) Å, which is similar to those in $MeOCOCH_2CH_2Sn(S_2CNEt_2)Cl_2$[6] and $BuSn(S_2CNEt_2)Cl_2$,[9] and those collated in reviews by Tiekink.[1,2] The intramolecular Sn–O1 distances (2.394(3) Å) is slightly longer than the sum of the covalent radii of tin and oxygen (2.13 Å) and much shorter than the sum of the Van de Waals' radii (3.70 Å),

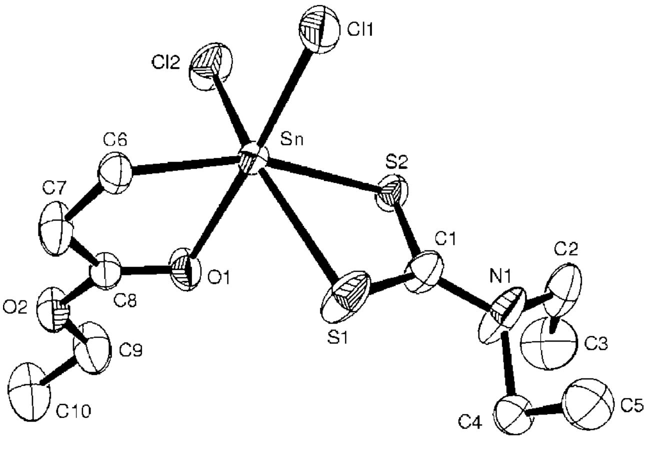

Figure 1. Molecular structure of complex **1b**. For clarity, only one component of the disordered C4–C5 ethyl group is shown and hydrogen atoms are omitted.

Table 1. Selected bond lengths (Å) and angles (°) of the X-ray and optimized structure of **1b**

Parameter	X-ray	HF/Lanl2DZ	B3LYP/Lanl2DZ	HF/3-21G*	B3LYP/3-21G*
Sn–O1	2.394(3)	2.28	2.35	2.25	2.32
Sn–C6	2.137(4)	2.14	2.16	2.19	2.20
Sn–Cl1	2.4082(13)	2.43	2.45	2.41	2.43
Sn–Cl2	2.4231(13)	2.42	2.46	2.42	2.44
Sn–S1	2.6371(12)	2.85	2.81	2.67	2.70
Sn–S2	2.4792(11)	2.54	2.61	2.54	2.56
S1–C1	1.711(4)	1.77	1.78	1.73	1.73
S2–C1	1.725(4)	1.80	1.81	1.74	1.75
S1–Sn–C6	99.66(13)	91.3	93.2	94.8	94.4
S1–Sn–Cl1	94.86(6)	98.4	98.9	93.3	96.9
S1–Sn–Cl2	157.24(5)	159.3	157.5	160.0	159.0
S1–Sn–S2	69.95(4)	68.0	68.9	68.9	69.2
S1–Sn–O1	87.47(9)	82.3	81.9	85.5	83.9
O1–Sn–C6	76.82(13)	77.2	77.2	77.3	77.2
O1–Sn–Cl1	176.54(7)	176.5	177.3	175.9	177.4
O1–Sn–Cl2	82.61(9)	85.8	84.4	85.5	85.1
O1–Sn–S2	87.01(7)	84.4	83.4	86.9	85.3
S2–Sn–Cl1	96.18(4)	99.0	99.2	96.3	97.3
S2–Sn–Cl2	89.06(4)	94.1	91.9	92.8	92.2
S2–Sn–C6	161.32(12)	154.1	155.4	158.3	157.3
Cl1–Sn–C6	100.24(12)	102.5	100.2	100.5	100.2
Cl2–Sn–C6	97.94(13)	99.4	101.1	99.0	100.5
Cl1–Sn–Cl2	96.09(6)	94.5	95.6	96.9	94.8

and, again, is comparable to those intramolecular Sn–O bonds reported in other six-coordinated $ROCOCH_2CH_2Sn$ compounds.[6,13,21,24–28,36]

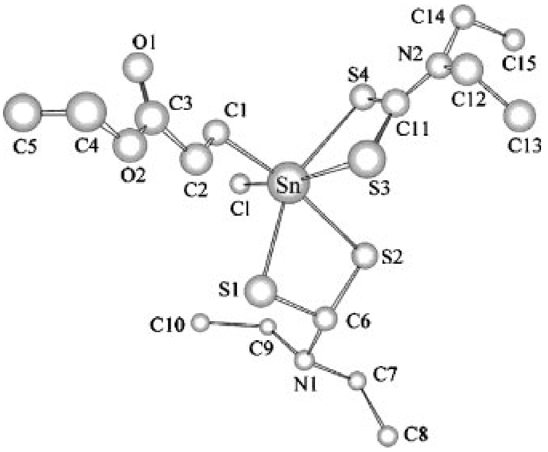

Figure 2. Optimized geometry for **2b**.

Ab intio calculations

We could not obtain crystal of good quality of the compounds **2a**–**2e** to solve the structure by X-ray methods; therefore, *ab intio* calculations were performed in order to determine an equilibrium molecular geometry for **2b**. To allow a comparison with experimental data obtained from the X-ray investigation, *ab initio* calculations were also carried out on **1b**. The molecular geometry was optimized at the HF/3-21G*, HF/Lanl2DZ, B3LYP/3-21G* and B3LYP/Lanl2DZ levels of theory using the Gaussian 98w software package.[31] The data obtained for compounds **1b** and **2b** are listed in Tables 1 and 2. The data in Table 1 show that the geometric parameters obtained from the *ab initio* calculations on **1b** were slightly different from parameters obtained from the X-ray crystallographic study and that the tin–ligand distances tend to be shorter in the crystal structure than in the optimized structure, which is consistent with Tiekink and co-workers' conclusion from organotin systems.[37] The differences between the crystal structure and theoretical structure can be ascribed in part to the influences of intermolecular forces or crystal packing effects operating in the former. In the crystal of **1b**, although there are no non-hydrogen contacts less than 3.6 Å in the lattice, there are five X···H contacts less than 3.0 Å: $Cl1\cdots H2B^{i}$ (symmetry operation i: $1-x, -y, 1-z$) 2.77 Å, $Cl1\cdots H7A^{ii}$ (ii: $2-x, \frac{1}{2}+y, \frac{3}{2}-z$) 2.82 Å, $Cl2\cdots H6A^{iii}$ (iii: $x, \frac{1}{2}-y, \frac{1}{2}+z$) 2.89 Å, $O2\cdots H7B^{iv}$ (iv: $2-x, 1-y, 2-z$) 2.82 Å, and $O1\cdots H5A^{v}$ (v: $1-x, -\frac{1}{2}+y, \frac{3}{2}-z$) 2.98 Å. The geometric structures for the organotin compounds can be predicted by *ab initio* methods, although there are differences between the X-ray structural parameters and the optimized geometric parameters.[5,37,38] The optimized structure of **2b** is shown in Fig. 2. As seen in Table 2 and Fig. 2, the centre tin atom in complex **2b** has a distorted octahedral geometry with the ester group C1 and Cl atoms occupying

Table 2. Selected bond lengths (Å) and angles (°) obtained from *ab initio* calculations for **2b**

Parameter	HF/3-21G*	B3LYP/3-21G*	HF/Lanl2DZ	B3LYP/Lanl2DZ
Sn–C1	2.18	2.20	2.14	2.16
Sn–S1	2.62	2.64	2.70	2.71
Sn–S2	2.47	2.42	2.64	2.69
Sn–S3	2.68	2.70	2.82	2.80
Sn–S4	2.58	2.60	2.61	2.66
Sn–Cl	2.44	2.45	2.44	2.47
Sn···O1	5.00	5.02	4.97	5.02
C1–Sn–Cl	95.9	96.3	97.8	96.6
C1–Sn–S4	101.9	102.4	101.8	103.0
C1–Sn–S3	91.4	91.5	89.6	92.3
C1–Sn–S1	97.5	97.0	97.2	100.3
C1–Sn–S2	168.2	168.0	165.6	165.5
Cl–Sn–S4	93.9	94.6	94.5	93.7
Cl–Sn–S3	161.8	162.9	162.1	161.6
Cl–Sn–S1	101.0	101.4	101.1	102.0
Cl–Sn–S2	89.5	90.0	84.9	86.4
S4–Sn–S3	68.3	68.8	67.9	68.5
S4–Sn–S1	154.2	153.2	153.5	150.1
S4–Sn–S2	88.1	87.3	92.1	90.9
S3–Sn–S1	94.5	92.7	94.2	92.2
S3–Sn–S2	86.5	85.3	92.0	89.0
S1–Sn–S2	71.2	71.6	68.5	65.2

mutually cis positions. The distance between tin and O1 (carbonyl oxygen) optimized by HF/3-21G*, HF/Lanl2DZ, B3LYP/3-21G* and B3LYP/Lanl2DZ in **2b** is 5.00 Å, 4.97 Å, 5.02 Å, 5.02 Å respectively, which is much longer than the sum of van der Waals' radii for tin and oxygen (3.70 Å).[39] The Sn–O1 distance from the theoretical study further supports the results of spectral analysis of these compounds: intramolecular carbonyl-oxygen to tin coordination in **1a**–**1e** persists but not in **2a**–**2e**.

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