A METHANOL-SOLVATE ADDUCT OF CHLOROTRIPHENYLTIN(IV) WITH 4-BROMO-2-[(DIMETHYLAMINOETHYL)AMINOMETHYL]PHENOL

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Figure 1. ORTEP plot of $(C_6H_5)_3SnCl \cdot O-C_6H_4Br-2-CH_2NH_2CH_2CH_2N(CH_3)_2CH_3OH$ at the 50% probability level. Hydrogen atoms are drawn as spheres of arbitrary radii. Selected bond distances and angles: $Sn1-C1 = 2.122(4)$, $Sn1-C7 = 2.139(5)$, $Sn1-C13 = 2.130(5)$, $Sn1-O1 = 2.176(3)$, $Sn1-Cl1 = 2.586(2)$ Å; $Cl1-Sn1-C7 = 116.1(2)$, $Cl1-Sn1-C13 = 129.6(2)$, $Cl1-Sn1-O1 = 85.8(2)$, $Cl1-Sn1-Cl1 = 86.4(1)$, $C7-Sn1-C13 = 114.4(2)$, $C7-Sn1-O1 = 94.2(2)$, $C7-Sn1-Cl1 = 94.5(1)$, $C13-Sn1-O1 = 90.6(2)$, $C13-Sn1-Cl1 = 90.0(1)$, $O1-Sn1-Cl1 = 170.2(1)^\circ$.

Discussion

The Schiff-base phenol, 1-[(4'-tolylimino)methyl]-2-naphthol, forms a 1/1 adduct with triphenyltin chloride in which the two moieties are linked by a tin-oxygen interaction [$Sn-O = 2.391(3)$ Å] [1] that is considered a dative bond. The adduct of diphenyltin dichloride with a similar Schiff base, 1-[(4'-anisylimino)methyl]-2-naphthol, displays a shorter interaction [$Sn-O = 2.228(3)$ Å], but the complex is assigned a zwitterionic formulation as the phenolic proton has been transferred from the oxygen atom to the imino nitrogen atom [2]. The Mannich base, 4-bromo-2-[(dimethylaminoethyl)aminomethyl]phenol [3], possesses two basic sites that are capable of accepting the phenolic proton; in the 1/1 adduct with triphenyltin chloride, m.p. 66-72°C, the proton is transferred to the *sec*-nitrogen atom, the *tert*-nitrogen atom electing to interact instead with a lattice solvent molecule [$N^{\cdots}O = 2.734(5)$ Å]. The hydrogen bonds give rise to the formation of a dinuclear compound.

4-Nitro-2-[(dimethylaminoethyl)aminomethyl]phenol exists as a zwitterionic compound in which the *sec*-ammonium nitrogen atom is intra-molecularly bonded to the negatively-charged oxygen atom [4]; the phenoxy oxygen atom retains the proton in the 4-chloro analogue [5]. The unusually short tin-oxygen

bond found in the triphenyltin chloride complex of the 4-bromo derivative can be attributed to the availability of the zwitterionic form that places the negative charge on the oxygen atom.

Experimental

A benzene solution of triphenyltin chloride (1.93 g, 5 mmole) was added to a benzene solution of 4-bromo-2-[(dimethylaminoethyl)aminomethyl]phenol (1.37 g, 5 mmole). The mixture was heated briefly, and on cooling, hexane was added. The white solid that deposited (2.65 g, 80% yield) was isolated and recrystallized in methanol to furnish colorless crystal (mp 130-131 °C) suitable for X-ray analysis. CH&N elemental analysis for $C_{30}H_{36}BrClN_2O_2Sn$. Calc (Found) : C, 52.17 (52.64); H, 5.25 (4.82); 4.06 (4.36). 1H NMR ($CDCl_3$): 2.22(s), 6H (NMe_2); 2.44m, 2.68m, 4H ($-CH_2CH_2-N$); 3.93d, 5H (CH_2 ; CH_3O-); 5.52br, 3H (NH/OH); 6.63-7.73 m, 18H (aromatic) ppm.

Table 1. Crystal data for $(C_6H_5)_3SnCl \cdot O-C_6H_3Br-2-CH_2NH_2CH_2CH_2N(CH_3)_2 \cdot CH_3OH$

Formula	$C_{30}H_{36}BrClN_2O_2Sn$	Crystal system	monoclinic
Formula weight	690.66	Space group	$C2/c$
<i>a</i>	23.500(6) Å	<i>b</i>	11.461(3) Å
<i>c</i>	22.191(7) Å	β	91.49(2)°
<i>Z</i>	8	Temperature	25°C
Density _{calc}	1.536 g cm ⁻³	μ (Mo-K α)	2.311 mm ⁻¹
<i>F</i> (000)	2784	Diffraction	Siemens <i>P4</i>
θ_{max}	25°	Reflns measured	6297
Unique reflns	5250 ($R_{int} = 0.029$)	Trans factors	0.147 - 0.191
Reflns with $I > 2\sigma(I)$	3883	<i>R</i> (<i>wR</i>)	0.037 (0.077)
Goodness-of-fit	1.014	Range of ρ	-0.66 to 0.40 eÅ ⁻³
Programs used	<i>SHELXTL-Plus</i> [6] <i>SHELXL-97</i> [7]	Deposition number	CCDC 144886

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