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Synthesis and characterisation of tin(IV) and organotin(IV) derivatives 2-{[(2-hydroxyphenyl)imino]methyl}phenol

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Abstract

From the interaction of 2-{[(2-hydroxyphenyl)imino]methyl}phenol($salopH_2$) with tin and organotin(IV) acceptors, the derivatives [SnR_3(salopH)] (R = Me or Bu^n), [SnR_2(salop)] (R = Me, Bu^n, Bu^t, Vin or Ph), [SnRX(salop)(solvent)] (R = Me, Bu^n, Ph or X; X = Cl, Br or I; solvent = CH_3OH or H_2O), [Sn(salop)$_2$], [R_2SnCl_2($salopH_2$)] (R = Me or Bu^n) have been obtained and characterised. The chelates, containing the Schiff base in mono or dianionic form, are generally stable both in the solid state and in solution, whereas the [SnR_2Cl_2($salopH_2$)] adducts slowly decompose in acetone or DMSO yielding [SnR_2(salop)] and releasing HCl. All the [SnR_2(salop)] and [SnRX(salop)(solvent)] complexes are fluxional in solution. The ^{119}Sn NMR chemical shift is a function of the number of R groups. The X-ray single crystal diffraction study of [$SnVin_2$(salop)] shows the metal to be five-coordinate in a distorted square pyramidal environment, Sn–C distances being 2.112(2) and 2.113(2) Å, Sn–O 2.117(2) and 2.125(2) Å and Sn–N 2.227(2) Å. The whole structure consists of molecular units connected by weak intermolecular Sn–O interactions. In the complexes [SnX_2(salop)(CH_3OH)]·CH_3OH complexes (X = Cl or Br), the tin atom is found in a strongly distorted octahedral environment with the Sn–O bond ranging from 1.995(3) to 2.055(2) Å. The Sn–N bond is 2.116(4) Å in the bromide and 2.171(3) Å in the chloride complex. © 2001 Published by Elsevier Science B.V.

Keywords: Tin(IV) compounds; Organotin (IV) complexes; X-ray crystal structures; Schiff base

1. Introduction

Schiff bases still play an important role as ligands in metal coordination chemistry even after almost a century since their discovery [1]. Recently, this class of molecules has been employed as models for biological systems [2] and in the control of the stereochemistry in six-coordinate [(Schiff base)MCl_2] complexes (M = Ti or Zr) which are potential catalysts for alkene polymerisation [3]. Increasing attention has also been devoted to Schiff base complexes of organotin(IV) moieties in view of their potential applications in medicinal chemistry and biotechnology [4]. 2-{[(2-Hydroxyphenyl)imino]methyl}phenol($salopH_2$) is a typical potentially ONO tridentate Schiff base ligand forming stable complexes with many transition and post-transition metal ions [5]. Its coordination chemistry is less developed with respect to that of tetradentate Schiff bases as *N*,*N*′-ethylenbis(salicylaldimine) ($salenH_2$) [6].

Literature on metal–$salopH_2$ complexes of the Group IV elements is rather sparse [7], only three tin(IV) complexes structurally characterised being reported, i.e [$SnMe_2$(Salop)] [8], [$SnPh_2$(salop)] [9] and [Sn(salop)]$_2$ [10]. In addition, the organotin(IV) derivatives reported have not been fully spectroscopically characterised. As a part of our project dealing with the study of the interaction of tin(IV) and organotin(IV) species with *O*-donor and *N*-donor ligands, we report here synthesis and full characterisation of 15 new derivatives containing the schiff base in mono- (salopH)$^-$, di-anionic(salop)$^{2-}$ or neutral form ($salopH_2$). We described here also a new route for the synthesis

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and not-reported spectroscopic features of [$SnMe_2$(salop)] [8], [$SnPh_2$(salop)] [9] and [$Sn(salop)_2$] [10], as well as the X-ray crystal structure of [$SnVin_2$(salop)], [$SnCl_2$(salop)(CH_3OH)]·CH_3OH, [$SnBr_2$(salop)(CH_3OH)]·CH_3OH.

2. Experimental

2.1. Materials

All chemicals and reagents were reagent grade quality and were used as received without further purification. Solvent evaporations were always carried out under vacuum by using a rotavaporator. The samples for microanalysis were dried in vacuo to constant weight (20 °C, ca. 0.1 Torr). All syntheses were carried out under a nitrogen atmosphere. Hydrocarbon solvents were dried by distillation from sodium–potassium; dichloromethane was distilled from calcium hydride; benzene and light petroleum (40–60 °C) were dried by refluxing over freshly cut sodium; methanol was dried over CaO. All solvents were degassed with dry nitrogen prior to use.

2.2. Physical measurements

Elemental analyses (C, H, N) were performed in-house with a Fison's instruments 1108 CHNS-O elemental analyser. IR spectra were recorded from 4000 to 100 cm^{-1} with a Perkin–Elmer system 2000 FT-IR instrument. ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on a VXR-300 Varian instrument and on a Bruker AC 200 spectrometers operating at room temperature (r.t.) (at 300 and 200 MHz for ^1H; 75 and 50 MHz for ^{13}C; and 111.9 MHz for ^{119}Sn). The chemical shifts (δ) are reported in parts per million (ppm) from $SiMe_4$ (^1H and ^{13}C calibration by internal deuterium solvent lock) and $SnMe_4$ (external). The spectral width is 900 ppm (from +200 to −700 ppm). Peak multiplicities are abbreviated: singlet, s; doublet, d; triplet, t; multiplet, m. UV spectra were recorded on a HP-8453 spectrometer. Melting points are uncorrected and were taken on an SMP3 Stuart scientific instrument and on a capillary apparatus. The electrical conductivity measurements (Λ_M, reported as Ω^{-1} cm^2 mol^{-1}) of dichloromethane solutions of complexes **1**–**18** were taken with a Crison CDTM 522 conductimeter at r.t.

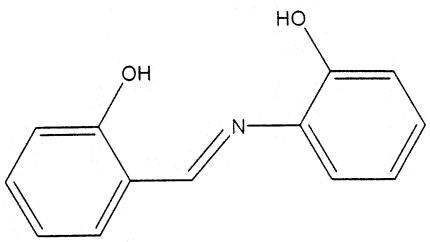


Fig. 1. Structure of the Schiff base salopH_2.

2.3. Synthesis of the donor salopH_2

The 2-{[(2-hydroxyphenyl)imino]methyl}phenol (Fig. 1) has been synthesised by stirring at 60–80 °C a 1:1 molar ratio mixture of salicylaldehyde and 2-hydroxyaniline in refluxing methanol following a reported method [11]. M.p. 187–189 °C. IR (Nujol, cm^{-1}): 2300br, 1800br (OH), 1631s, 1612s, 1593s, 1530s, 1506w (C···C, C···N). ^1H NMR ($CDCl_3$, 293 K): δ, 5.84, 12.28 (s br, OH) 6.93–7.46 (m, 8H, $H_{aromatic}$), 8.66 (m, 1H, CH). ^1H NMR (acetone-d_6, 293 K): δ, 6.88–7.56 (m, 8H, $H_{aromatic}$), 8.56 (s br, OH), 8.92 (m, 1H, CH). ^1H NMR (DMSO-d_6, 293 K): δ, 6.82–7.62 (m, 8H, $H_{aromatic}$), 8.95 (m, 1H, CH), 11.10 (s br, OH). ^{13}C NMR ($CDCl_3$, 293 K): δ, 117.3, 128.7, 119.5, 121.0, 135.9, 119.3, 115.9, 133.7, 118.3, 132.6 (s, $C_{aromatic}$), 149.9, 160.6 (s, CO), 163.9 (s, CN). ^{13}C NMR (acetone-d_6, 293 K): δ, 118.8, 130.0, 121.8, 122.2, 138.1, 120.9, 118.5, 134.9, 120.8, 134.6 (s, $C_{aromatic}$), 152.9, 163.2 (s, CO), 165.0 (s, CN). ^{13}C NMR (DMSO-d_6, 293 K): δ, 116.7, 128.1, 119.6, 119.5, 134.9, 119.5, 116.5, 132.9, 119.6, 132.3 (s, $C_{aromatic}$), 151.1, 160.7 (s, CO), 161.7 (s, CN). UV ($CHCl_3$, λ_{max}, nm): 243, 270, 354.

2.4. Synthesis of complexes

2.4.1. [$SnMe_2$(salop)] (*1*)

To a hot methanol solution (30 ml) of the Schiff base salopH_2 (0.42 g, 2.0 mmol), sodium methoxide was added (0.21 g, 4.0 mmol). When the colour of the solution changed from orange to red, $SnMe_2Cl_2$ (0.42 g, 2.0 mmol) was added. After 3 h stirring, the solvent was removed and the residue was treated with chloroform (15 ml). The solution formed was filtered off to remove the sodium salt and then evaporated to dryness. The red powder was re-crystallised from diethyl ether and shown to be compound **1**. Yield 54%. M.p. 169–170 °C. *Anal.* Calc. for $C_{15}H_{15}NO_2Sn$: C, 50.05; H, 4.20; N, 3.89. Found: C, 49.88; H, 4.30; N, 3.76%. IR (Nujol, cm^{-1}): 3059w (CH), 1606s, 1585s, 1567sh, 1530s, 1514m (C···C, C···N), 528s, 520m (Sn–O), 573m, 545w (Sn–C), 321s (Sn–N). ^1H NMR ($CDCl_3$, 293 K): δ, 0.8 (s, 6H, $^2J(^{119}Sn–^1H)$: 78.1 Hz, $^2J(^{117}Sn–^1H)$: 74.8 Hz, Sn–CH_3) 6.6–6.8 (m), 7.1–7.5 (m) (8H, $H_{aromatic}$), 8.7 (s, 1H, $^3J(^{119/117}Sn–^1H)$: 50.6 Hz, CH_{salop}). ^{13}C NMR ($CDCl_3$, 293 K): δ, 0.99 (s, $^1J(^{119}Sn–^{13}C)$: 660 Hz, Sn–CH_3), 114.66, 116.59, 117.26, 117.79, 118.47, 122.56, 130.24, 135.22, 136.84, 137.12 (s, $C_{aromatic}$), 158.84, 168.85 (s, CO), 161.98 (s, CN). ^{119}Sn NMR ($CDCl_3$, 293 K): δ, −146.4. UV ($CHCl_3$, λ_{max}, nm): 249, 316, 455. Λ_M (DMSO, c (mol l^{-1}) = 1.0×10^{-3}) = 1.3 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2, c (mol l^{-1}) = 0.9×10^{-3}) = 0.1 Ω^{-1} cm^2 mol^{-1}.

*2.4.2. [SnBu$^n_2$(salop)] (**2**)*

Complex **2** (orange) was prepared as **1**. Yield 44%. M.p. 131 °C dec. *Anal.* Calc. for $C_{21}H_{27}NO_2Sn$: C, 56.79; H, 6.13; N, 3.15. Found: C, 56.63; H, 5.97; N, 3.26%. IR (Nujol, cm^{-1}): 3053w (CH), 1607s, 1589sh, 1538m, 1509w (C⋯C, C⋯N), 504vs, 475s (Sn–O), 578s, 534m (Sn–C), 324m (Sn–N). ^1H NMR ($CDCl_3$, 293 K): δ, 0.9–1.1 (m), 1.7–1.8 (m) (18H, Sn–Bu^n), 6.7–7.4 (m, 8H, $H_{aromatic}$), 8.6 (s, 1H, $^3J(^{119/117}Sn–^1H)$: 44.8 Hz, CH_{salop}) ^{13}C NMR ($CDCl_3$, 293 K): δ, 13.49 (s, Sn–Bu^n), 26.37, 26.47, 26.58 (s, Sn–Bu^n), 116.69, 118.02, 118.32, 119.39, 121.18, 129.10, 133.00, 134.56, 136.30, 149.87 (s, $C_{aromatic}$) 159.43, 162.11 (s, CO), 163.35 (s, CN). ^{119}Sn NMR ($CDCl_3$, 293 K): δ, −186.4. UV ($CHCl_3$, λ_{max}, nm): 249, 318, 454. Λ_M (CH_2Cl_2, c (mol l^{-1}) = 1.0×10^{-3}) = 0.1 Ω^{-1} cm^2 mol^{-1}.

*2.4.3. [SnBu$^t_2$(salop)] (**3**)*

Complex **3** was prepared as **1** by using 2.0 mmol of salopH_2, 4.0 mmol of NaOMe and 2.0 mmol of $SnBu^t_2Cl_2$. Yield 45%. M.p. 127–129 °C. *Anal.* Calc. for $C_{21}H_{27}NO_2Sn$: C, 56.79; H, 6.13; N, 3.15. Found: C, 56.55; H, 6.22; N, 3.03%. IR (Nujol, cm^{-1}): 3050w (CH), 1605s, 1584s, 1559sh, 1533s (C⋯C, C⋯N), 525s (Sn–O), 488m, 441w (Sn–C), 318m (Sn–N). ^1H NMR ($CDCl_3$, 293 K): δ, 1.30 (s, 18H, Sn–Bu^t, $^3J(^{119}Sn–^1H)$: 108.4 Hz, $^3J(^{117}Sn–^1H)$: 104.3 Hz), 6.6–7.4 (m, 8H, $H_{aromatic}$), 8.7 (s, 1H, $^3J(^{119/117}Sn–^1H)$: 41.9 Hz, CH_{salop}). ^{13}C NMR ($CDCl_3$, 293 K): δ, 29.85 (s, Sn–C$(CH_3)_3$), 40.68 (s, Sn–C$(CH_3)_3$), 114.67, 115.84, 116.44, 118.49, 122.57, 129.81, 132.23, 135.00, 136.47, 160.36 (s, $C_{aromatic}$), 161.34 (s, CN), 160.36, 170.66 (s, CO). ^{119}Sn NMR ($CDCl_3$, 293 K): δ, −279.2. UV ($CHCl_3$, λ_{max}, nm): 248, 465. Λ_M (CH_2Cl_2, c (mol l^{-1}) = 1.0×10^{-3}) = 0.3 Ω^{-1} cm^2 mol^{-1}.

*2.4.4. [SnVin$_2$(salop)] (**4**)*

Complex **4** was prepared as **2** by using 2.0 mmol of salopH_2, 4.0 mmol of NaOMe and 2.0 mmol of $SnVin_2Cl_2$. Yield 31%. M.p. 133–134 °C. *Anal.* Calc. for $C_{17}H_{15}NO_2Sn$: C, 53.17; H, 3.94; N, 3.65. Found: C, 53.04; H, 4.02; N, 3.76%. IR (Nujol, cm^{-1}): 3050w (CH), 1605s, 1584s, 1567sh, 1535s (C⋯C, C⋯N), 519vs, 489m (Sn–O), 557s, 539m (Sn–C), 328m (Sn–N). ^1H NMR ($CDCl_3$, 293 K): δ, 6.14 (dd) 6.22 (dd) 6.30 (dd) (6H, $J(^1H–^1H)_{gem}$: 3.6 Hz, $J(^1H–^1H)_{cis}$: 11.8 Hz, $J(^1H–^1H)_{trans}$: 19.9 Hz, Sn–C*H*=CH_2), 6.7–7.0 (m) 7.2–7.5 (m) (8H, $H_{aromatic}$), 8.6 (s, 1H, $^3J(^{119/117}Sn–^1H)$: 55.8 Hz, CH_{salop}). ^{13}C NMR ($CDCl_3$, 293 K): δ, 114.67, 116.84, 117.46, 118.75, 122.61, 130.29, 131.10, 136.96, 138.50, (s, $C_{aromatic}$), 135.30 (s, $^2J(^{117/119}Sn–^{13}C)$: 442 Hz, Sn–CH=CH_2), 136.77 (s, $^1J(^{119}Sn–^{13}C)$: 975 Hz, $^1J(^{117}Sn–^{13}C)$: 930 Hz, Sn–CH=CH_2), 161.59 (s, CN), 169.28, 158.84 (s, CO). ^{119}Sn NMR ($CDCl_3$, 293 K): δ, −320.69. UV ($CHCl_3$, λ_{max}, nm): 248, 291, 317, 454. Λ_M (DMSO, c (mol l^{-1}) = 0.9×10^{-3}, Ω^{-1} cm^2 mol^{-1}) = 0.5. Λ_M (CH_2Cl_2, c (mol l^{-1}) = 1.1×10^{-3}) = 0.2 Ω^{-1} cm^2 mol^{-1}.

*2.4.5. [SnPh$_2$(salop)] (**5**)*

To a hot ethanol solution (30 ml) of salopH_2 (2.0 mmol), NaOMe was added (4.0 mmol). After the colour of the solution changed from orange to red. After a few minutes Ph_2SnCl_2 (2.0 mmol) was added and a red precipitate immediately formed. After 3 h stirring, the solid was filtered off, washed with ethanol, dried under reduced pressure to constant weight and shown to be compound **5**. Yield 70%. M.p. 200–201 °C. *Anal.* Calc. for $C_{25}H_{19}NO_2Sn$: C, 62.02; H, 3.96; N, 2.89. Found: C, 62.25; H, 4.06; N, 3.02%. IR (Nujol, cm^{-1}): 3047w (CH), 1605s, 1590s, 1567sh, 1539s, 1506w (C⋯C, C⋯N), 605s, 536vs (Sn–O), 262m, 243m (Sn–C), 334 (Sn–N). ^1H NMR ($CDCl_3$, 293 K): δ, 6.7–7.5 (m, 8H, $H_{aromatic}$ of salop), 7.9–8.0 (m, 10H, $^3J(^{119/117}Sn–^1H)$: 92.0 Hz, Sn–C_6H_5), 8.7 (s, 1H, $^3J(^{119/117}Sn–^1H)$: 59.6 Hz, CH_{salop}). ^{13}C NMR ($CDCl_3$, 293 K): δ, 114.63, 116.86, 117.50, 119.04, 122.81, 125.05, 125.25, 127.84, 128.67, 129.50, 129.72, 130.12, 130.29, 131.13, 131.83, 135.09, 135.38, 136.04, 136.59, 137.00, 137.14, 139.70 (s, C_{salop} + Sn–C_6H_5). 158.96, 169.47 (s, CO), 161.57 (s, CN). ^{119}Sn NMR ($CDCl_3$, 293 K): δ, −328.35. UV ($CHCl_3$, λ_{max}, nm): 246, 318, 454. Λ_M (DMSO, c (mol l^{-1}) = 1.0×10^{-3}, Ω^{-1} cm^2 mol^{-1}) = 0.2. Λ_M (CH_2Cl_2, c (mol l^{-1}) = 1.1×10^{-3}) = 0.1 Ω^{-1} cm^2 mol^{-1}.

*2.4.6. [SnCl$_2$(Salop)(H$_2$O)] (**6**)*

Complex **6** was prepared in methanol as **5** by using 2.0 mmol of salopH_2, 4.0 mmol of NaOMe and 2.0 mmol of $SnCl_4 \cdot 5H_2O$. Yield 74%. M.p. 290 °C dec. *Anal.* Calc. for $C_{13}H_{11}Cl_2NO_3Sn$: C, 37.28; H, 2.65; N, 3.34. Found: C, 37.20; H, 2.73; N, 3.46%. IR (Nujol, cm^{-1}): 3000–3400 (H_2O), 1608s, 1590w, 1557w, 1544m, 1508w (C⋯C, C⋯N), 502s, 490s (Sn–O), 377sh, 366s, 348sh (Sn–Cl). ^1H NMR (acetone-d_6, 293 K): δ, 6.8–7.0 (m) 7.2–7.3 (m) 7.4–7.9 (m) (8H, $H_{aromatic}$), 8.9 (br, 2H, H_2O), 9.2 (s, 1H, CH_{salop}, $^3J(^{119/117}Sn–^1H)$: 86.7 Hz). ^{119}Sn NMR ($CDCl_3$, 293 K): δ, −563.37. UV ($CHCl_3$, λ_{max}, nm): 246, 315, 426. Λ_M (DMSO, c (mol l^{-1}) = 1.1×10^{-3}) = 4.6 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2, c (mol l^{-1}) = 1.0×10^{-3}) = 0.3 Ω^{-1} cm^2 mol^{-1}.

*2.4.7. [SnCl$_2$(salop)(CH$_3$OH)]·CH$_3$OH (**7**)*

Complex **7** was obtained from the mother liquor of complex **6**. M.p. 300 °C dec. *Anal.* Calc. for $C_{15}H_{17}Cl_2NO_4Sn$: C, 38.75; H, 3.69; N, 3.01. Found: C, 38.64; H, 3.46; N, 3.18%. IR (Nujol, cm^{-1}): 3000–3400 (OH), 1607s, 1591w, 1559w, 1543m, 1507w (C⋯C, C⋯N), 501s, 482s (Sn–O), 367m, 353s, 335s (Sn–Cl). ^1H NMR (acetone-d_6, 295 K): δ, 3.3 (s, 3H, CH_3OH), 6.8–7.0 (m) 7.2–7.3 (m) 7.4–7.9 (m) (8H, $H_{aromatic}$), 8.9

(br, 1H, CH_3OH), 9.2 (s, 1H, CH_{salop} $^3J(^{119/117}Sn–^1H)$: 84.2 Hz). ^{119}Sn NMR ($CDCl_3$, 295 K): δ, −542.74, −558.10. ^{119}Sn NMR (acetone-d_6, 295 K): δ, −545br, −562br. Λ_M (DMSO, c (mol l^{-1}) = 1.0×10^{-3}) = 4.0 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2, c (mol l^{-1}) = 1.1×10^{-3}) = 0.2 Ω^{-1} cm^2 mol^{-1}.

2.4.8. $[SnBr_2(salop)(H_2O)]$ (**8**)

Complex **8** was prepared as **6** by using 2.0 mmol of $salopH_2$, 4.0 mmol of NaOMe and 2.0 mmol of $SnBr_4$. Yield 76%. M.p. 218 °C dec. *Anal.* Calc. for $C_{13}H_{11}Br_2NO_3Sn$: C, 30.75; H, 2.18; N, 2.76. Found: C, 30.54; H, 2.22; N, 2.84%. IR (Nujol, cm^{-1}): 3000–3400 (H_2O), 1605s, 1589sh, 1557w, 1543s, 1519w, 1503w (C⋯C, C⋯N), 501s, 485s (Sn–O), 234s, 200vs (Sn–Br). ^1H NMR ($CDCl_3$, 294 K): δ, 3.45 (s br, 2H, H_2O), 6.8–7.1 (m) 7.2–7.5 (m) (8H, $H_{aromatic}$), 8.57 (s, 1H, CH_{salop} $^3J(^{119/117}Sn–^1H)$: 76.6 Hz). ^{119}Sn NMR (acetone-d_6, 293 K): δ, −755.1. UV ($CHCl_3$, λ_{max}, nm): 245, 315, 429. Λ_M (DMSO, c (mol l^{-1}) = 1.1×10^{-3}) = 21.5 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2, c (mol l^{-1}) = 1.1×10^{-3}) = 0.1 Ω^{-1} cm^2 mol^{-1}.

2.4.9. $[SnBr_2(salop)(CH_3OH)]\cdot CH_3OH$ (**9**)

Complex **9** was obtained from the mother liquor of complex **8**. M.p. 230 °C dec. *Anal.* Calc. for $C_{14}H_{13}Br_2NO_3Sn$: C, 32.53; H, 3.09; N, 2.51. Found: C, 32.44; H, 3.12; N, 2.72%. IR (Nujol, cm^{-1}): 3000–3400 (OH), 1605s, 1590sh, 1558w, 1544s, 121w, 1504w (C⋯C, C⋯N), 502s, 497w, 483s (Sn–O), 226s, 203vs (Sn–Br). ^1H NMR (acetone-d_6, 293 K): δ, 3.36 (s, 3H, CH_3OH), 6.8–7.0 (m) 7.2–7.3 (m) 7.4–7.9 (m) (8H, $H_{aromatic}$), 9.22 (s, 1H, CH_{salop}, $^3J(^{119/117}Sn–^1H)$: 75.5 Hz). ^{119}Sn NMR ($CDCl_3$, 293 K): δ, −756.58. Λ_M (DMSO, c (mol l^{-1}) = 1.0×10^{-3}) = 21.9 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2, c (mol l^{-1}) = 1.2×10^{-3}) = 0.1 Ω^{-1} cm^2 mol^{-1}.

2.4.10. $[SnI_2(salop)(CH_3OH)]$ (**10**)

Complex **10** was prepared as **6**, by using 2.0 mmol of $salopH_2$, 4.0 mmol of NaOMe and 2.0 mmol of SnI_4. Yield 85%. M.p. >350 °C. *Anal.* Calc. for $C_{14}H_{13}I_2NO_3Sn$: C, 27.31; H, 2.13; N, 2.28. Found: C, 27.56; H, 2.20; N, 2.40%. IR (Nujol, cm^{-1}): 3000–3400 (CH_3OH), 1602s, 1588s, 1543s (C⋯C, C⋯N), 508m, 481s (Sn–O), 178s, 143m (Sn–I). ^1H NMR ($CDCl_3$, 293 K): δ, 3.51 (s, 3H, CH_3OH), 6.8–7.8 (m, 8H, $H_{aromatic}$), 8.50 (br, 1H, CH_3OH), 8.93 (s, 1H, $^3J(^{119}Sn–^1H)$: 86.7 Hz; $^3J(^{117}Sn–^1H)$: 82.0 Hz, CH_{salop}). ^{13}C NMR (DMSO-d_6, 293 K): δ, 48.59 (s, CH_3OH) 116.00, 116.28, 117.63, 117.99, 118.52, 119.03, 119.19, 119.46, 119.84, 121.93, 128.77, 129.27, 130.57, 130.68, 136.78, 137.16, 153.56, 154.02, 154.16, 154.49 (s, $C_{aromatic}$), 166.40, 165.85, 165.17, 164.42 (s, CO), 162.84, 162.34 (s, CN). ^{119}Sn NMR (DMSO-d_6): δ, −620.9, −622.6, −813.94, −814.99. UV ($CHCl_3$, λ_{max}, nm): 245, 286, 316, 436. Complex **10** can also be obtained by interaction of 2.0 mmol of $salopH_2$ with 2.0 mmol of SnI_4 in refluxing toluene without base. Λ_M (DMSO, c (mol l^{-1}) = 1.0×10^{-3}) = 44.8 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2, c (mol l^{-1}) = 1.0×10^{-3}) = 0.5 Ω^{-1} cm^2 mol^{-1}.

2.4.11. $[SnMeCl(salop)(H_2O)]$ (**11**)

Complex **11** was obtained as **2** by using 2.0 mmol of $salopH_2$, 4.0 mmol of NaOMe and 2.0 mmol of $SnMeCl_3$. Yield 32%. M.p. >350 °C. *Anal.* Calc. for $C_{14}H_{14}ClNO_3Sn$: C, 42.11; H, 3.54; N, 3.51. Found: C, 42.46; H, 3.48; N, 3.23%. IR (Nujol, cm^{-1}): 3000–3400br (H_2O), 1606s, 1586s, 1539s (C⋯C, C⋯N), 579w (Sn–C), 497m, 487s (Sn–O), 269vs (Sn–Cl). ^1H NMR (acetone-d_6, 293 K): δ, 0.95 (s, 3H, Sn–CH_3, $^2J(^{119}Sn–^1H)$: 122.1 Hz, $^2J(^{117}Sn–^1H)$: 111.0 Hz), 3.47 (s, 3H, CH_3OH), 6.7–7.8 (m, 8H, $H_{aromatic}$), 9.03 (s, 1H, $^3J(^{119/117}Sn–^1H)$: 91.7 Hz, CH_{salop}). ^{13}C NMR (acetone-d_6, 293 K): δ, 115.80, 117.30, 117.88, 119.06, 121.25, 123.14, 126.76, 130.21, 132.99, 136.06, 137.69 (s, $C_{aromatic}$), 157.34, 168.69, 173.73, (s, CO), 159.76 (s, CN), resonance of Sn–CH_3 not observed. ^{13}C NMR ($CDCl_3$, 293 K): δ, 115.8, 117.29, 117.88, 119.06, 119.31, 121.24, 123.14, 126.76, 130.21, 130.73, 132.99, 136.06, 136. (s, $C_{aromatic}$), 168.69, 157.34 (s, CO), 159.76 (s, CN). ^{119}Sn NMR (DMSO-d_6, 293 K): δ, −436.44, −442.54. UV ($CHCl_3$, λ_{max}, nm): 252, 286, 312, 430. Λ_M (DMSO, c (mol l^{-1}) = 1.1×10^{-3}) = 2.2 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2, c (mol l^{-1}) = 1.0×10^{-3}) = 0.4 Ω^{-1} cm^2 mol^{-1}.

2.4.12. $[SnBu^nCl(salop)(CH_3OH)]$ (**12**)

To a hot methanol solution (30 ml) of $salopH_2$ (0.21 g, 1.0 mmol), $SnBu^nCl_3$ (0.56 g, 2.0 mmol) was added and a yellow precipitate immediately formed. After 8 h stirring, the solid was filtered off, washed with methanol and shown to be compound **12**. Yield 96%. M.p. 233–235 °C. *Anal.* Calc. for $C_{18}H_{22}ClNO_3Sn$: C, 47.57; H, 4.88; N, 3.08. Found: C, 47.74; H, 4.68; N, 3.20%. IR (Nujol, cm^{-1}): 3000–3400br (OH), 1605s, 1588s, 1568sh, 1539s (C⋯C, C⋯N), 584w (Sn–C), 494m, 481s (Sn–O), 283s, 275s (Sn–Cl). ^1H NMR ($CDCl_3$, 293 K): δ, 0.96, 1.00, 0.9–1.1 (t, 3H, Sn–Bu^n), 1.4–1.6 (m) 1.9–2.1 (m) (6H, Sn–Bu^n), 3.49 (s, 3H, CH_3OH), 6.7–7.4 (m, 8H, $H_{aromatic}$), 8.41 (s, 1H, CH_{salop} $^3J(^{119}Sn–^1H)$: 85.1 Hz, $^3J(^{117}Sn–^1H)$: 81.4 Hz). ^{13}C NMR (DMSO-d_6, 293 K): δ, 13.56 (s, Sn–Bu^n), 26.02 (s, Sn–Bu^n), 27.41 (s, Sn–Bu^n $^2J(^{119/117}Sn–^{13}C)$: 59.7 Hz), 29.64 (s, Sn–Bu^n, $^1J(^{119}Sn–^{13}C)$: 1138.2 Hz, $^1J(^{117}Sn–^{13}C)$: 1070.9 Hz), 50.87 (s, CH_3OH), 113.88, 118.48, 119.34, 120.00, 123.01, 130.38, 134.17, 135.93 (s, $C_{aromatic}$), 154.97, 164.58 (s, CO), 159.03 (s, CN). ^{119}Sn NMR (DMSO-d_6, 293 K): δ, −452.32. UV ($CHCl_3$, λ_{max}, nm): 246, 313, 431. Λ_M (DMSO, c (mol l^{-1}) = 1.0×10^{-3}) = 1.1 Ω^{-1} cm^2 mol^{-1}. Λ_M (CH_2Cl_2, c (mol

$l^{-1}) = 0.9 \times 10^{-3}) = 0.2\ \Omega^{-1}\ cm^2\ mol^{-1}$. Compound **12** has been obtained also from the reaction of $SnBu^nCl_3$ with $salopH_2$ in refluxing toluene, in absence of base.

2.4.13. [SnPhCl(salop)(CH_3OH)] (**13**)

Complex **13** was prepared as **2** by using 2.0 mmol of $salopH_2$, 4.0 mmol of NaOMe and 2.0 mmol of $SnPhCl_3$. Yield 93%. M.p. > 350 °C. *Anal.* Calc. for $C_{20}H_{18}ClNO_3Sn$: C, 50.63; H, 3.82; N, 2.95. Found: C, 50.38; H, 3.88; N, 3.06%. IR (Nujol, cm^{-1}): 3000–3400br (O*H*), 1606s, 1586s, 1538s (C⋯C, C⋯N), 485sbr (Sn–O), 278vs (Sn–Cl), 243s (Sn–C). ^1H NMR ($CDCl_3$, 293 K): δ, 3.48 (s, 3H, CH_3OH), 6.7–7.6 (m, 13H, CH_{salop} + Sn–Ph), 8.91 (s, 1H, CH_{salop}, $^3J(^{119/117}Sn–^1H)$: 88.0 Hz). ^1H NMR (DMSO-d_6, 293 K): δ, 3.41 (s, 3H, CH_3OH), 6.6–8.0 (m, 13H, CH_{salop} + Sn–Ph), 8.97, 9.07 (br, 1H, CH_{salop}). ^{13}C NMR (DMSO-d_6, 293 K): δ, 48.61 (s, CH_3OH), 115.67, 115.83, 116.04, 116.26, 116.88, 117.58, 117.82, 118.21, 118.46, 121.92, 122.21, 127.40, 128.48, 129.11, 129.33, 129.60, 130.40, 134.74, 134.87, 135.12, 135.51, 135.68, 136.02, 146.22 (s, C_{salop} + Sn–Ph), 150.01, 154.82, 156.38, 165.75, 167.42 (s, CO), 157.21, 158.53 (s, CN). ^{119}Sn NMR (DMSO-d_6, 293 K): δ, −497.40, −508.04, −571.96. UV ($CHCl_3$, λ_{max}, nm): 247, 286, 315, 431. Λ_M (DMSO, *c* (mol $l^{-1}) = 1.1 \times 10^{-3}) = 1.9\ \Omega^{-1}\ cm^2\ mol^{-1}$. Λ_M (CH_2Cl_2, *c* (mol $l^{-1}) = 1.0 \times 10^{-3}) = 0.2\ \Omega^{-1}\ cm^2\ mol^{-1}$. Compound **13** has been also obtained by the reaction of $SnPhCl_3$ with $salopH_2$ in methanol, in the absence of base.

2.4.14. [Sn(salop)$_2$] (**14**)

Complex **14** was prepared as **2** by using 2.0 mmol of $SalopH_2$, 4.0 mmol of NaOMe and 1.0 mmol of $SnBr_4$, or by using 2.0 mmol of $SalopH_2$, 4.0 mmol of NaOMe and 1.0 mmol of $SnCl_4{\cdot}H_2O$ or by using 2.0 mmol of $SalopH_2$, 4.0 mmol of NaOMe and 2.0 mmol of Vin_2SnCl_2. Yield 74%. M.p. > 350 °C. *Anal.* Calc. for $C_{26}H_{18}N_2O_4Sn$: C, 57.71; H, 3.35; N, 5.18. Found: C, 57.53; H, 3.41; N, 5.30%. IR (Nujol, cm^{-1}): 1605s, 1586s, 1538s, 1506w (C⋯C, C⋯N), 495m, 485s (Sn–O). ^1H NMR ($CDCl_3$, 293 K): δ, 6.8–7.0 (m), 7.2–7.6 (m) (16H, $H_{aromatic}$), 8.90 (s, 2H, $^3J(^{119/117}Sn–^1H)$: 86.7 Hz, CH_{salop}). ^{13}C NMR ($CDCl_3$, 293 K): δ, 114.55, 118.40, 119.01, 110.50, 123.59, 135.99, 137.25 (s, C_{salop}); the CN and CO resonance were not observed. Λ_M (DMSO, *c* (mol $l^{-1}) = 1.0 \times 10^{-3}) = 1.3\ \Omega^{-1}\ cm^2\ mol^{-1}$. Λ_M (CH_2Cl_2, *c* (mol $l^{-1}) = 1.1 \times 10^{-3}) = 0.2\ \Omega^{-1}\ cm^2\ mol^{-1}$. ^{119}Sn NMR ($CDCl_3$, 293 K): δ, −567.94. UV ($CHCl_3$, λ_{max}, nm): 247, 319, 436.

2.4.15. [SnMe$_3$(salopH)] (**15**)

Derivative **15** was prepared as **2** by using 2.0 mmol of $salopH_2$, 2.0 mmol of NaOMe and 2.0 mmol of $SnMe_3Cl$. Yield 65%. M.p. 141–144 °C. *Anal.* Calc. for $C_{16}H_{19}NO_2Sn$: C, 51.25; H, 4.84; N, 3.73. Found: C, 51.38; H, 4.92; N, 3.85%. IR (Nujol, cm^{-1}): 3061w (C–H), 1606s, 1586s, 1565sh, 1530s, 1512w (C⋯C, C⋯N), 571s, 528s, 520s (Sn–C), 486s, 458s br (Sn–O). ^1H NMR ($CDCl_3$, 293 K): δ, 0.56 (s, 9H, Sn–CH_3, $^2J(^{119}Sn–^1H)$: 57.2 Hz, $^2J(^{117}Sn–^1H)$: 55.0 Hz), 6.6–7.3 (m, 8H, $H_{aromatic}$), 8.67 (s, 1H, CH_{Salop}), 6.05, 12.14, 14.02 (s br, 1H, OH + NH). ^{13}C NMR ($CDCl_3$, 293 K): δ, −2.70(s, $^1J(^{119/117}Sn–^{13}C)$: 400 Hz, Sn–CH_3), 114.8, 119.52, 120.28, 128.1, 131.30, 131.97, 132.69, 133.77, 136.88 (s, $C_{aromatic}$), 163.67, 161.49 (s, *C*O), 162.03 (s, *C*N). ^{119}Sn NMR ($CDCl_3$, 293 K): δ, +50.8. Λ_M (CH_2Cl_2, *c* (mol $l^{-1}) = 1.0 \times 10^{-3}) = 0.05\ \Omega^{-1}\ cm^2\ mol^{-1}$. UV ($CHCl_3$, λ_{max}, nm): 244, 323, 335, 361, 453.

2.4.16. [SnBu$^n_3$(salopH)] (**16**)

Complex **16** was prepared as **1** by using 2.0 mmol of $salopH_2$, 2.0 mmol of NaOMe and 2.0 mmol of $SnBu^n_3Cl$. Yield 72%. M.p. 128–130 °C. *Anal.* Calc. for $C_{25}H_{37}NO_2Sn$: C, 59.78; H, 7.43; N, 2.79. Found: C, 59.53; H, 7.56; N, 2.64%. IR (Nujol, cm^{-1}): 3058w ν(CH), 1617s, 1589s, 1565sh, 1531m (C⋯C, C⋯N), 569m, 526br ν(Sn–C), 472s, 457s ν(Sn–O). ^1H NMR ($CDCl_3$, 293 K): δ, 0.8–1.0 (m, 9H, Sn–Bu^n), 1.1–1.8 (m, 18H, Sn–Bu^n), 6.6–7.4 (m, 8H, $H_{aromatic}$), 8.66, 8.84 (s, 1H, CH_{salop}), 5.90, 12.15, 14.05, (s br, 1H, OH_{salopH} and/or NH_{salopH}). ^{13}C NMR ($CDCl_3$, 293 K): δ, 13.06 (s, Sn–Bu^n), 16.40 (s, Sn–Bu^n), 27.10 (s, $^2J(^{119/117}Sn–^{13}C)$: 45.8 Hz, Sn–Bu^n), 27.73 (s, Sn–Bu^n), 114.83, 116.06, 116.33, 116.94, 117.34, 117.61, 117.93, 118.97, 119.64, 119.87, 120.79, 121.42, 122.50, 127.65, 130.09, 131.73, 132.43, 133.52, 133.76, 135.23, 136.73, 137.03, 139.18 (s, $C_{aromatic}$), 155.68, 159.53, 161.86, 166.46, 196.63 (s, CO), 162.22, 169.51 (s, CN). ^{119}Sn NMR ($CDCl_3$, 293 K): δ, +123.3. Λ_M (CH_2Cl_2, *c* (mol $l^{-1}) = 1.0 \times 10^{-3}) = 0.05\ \Omega^{-1}\ cm^2\ mol^{-1}$.

2.4.17. SnMe$_2$Cl$_2$(salopH$_2$)] (**17**)

To a diethyl ether solution (30 ml) of $salopH_2$ (0.21 g, 1.0 mmol), $SnMe_2Cl_2$ (1.75 g, 8.0 mmol) was added, and a yellow precipitate immediately formed. After 8 h stirring, the solid was filtered off, washed with diethyl ether and shown to be compound **17**. Yield 88%. M.p. 174–177 °C. *Anal.* Calc. for $C_{15}H_{17}Cl_2NO_2Sn$: C, 42.90; H, 4.50; N, 3.13. Found: C, 42.74; H, 4.54; N, 3.24%. IR (Nujol, cm^{-1}): 1633sbr, 1595s, 1528w, 1505s (C⋯C, C⋯N), 576s, 567s (Sn–C), 496sbr, 478s (Sn–O), 299br (Sn–Cl). ^1H NMR (DMSO-d_6, 293 K): δ, 1.02 (s, 6H, $^2J(^{119}Sn–^1H)$: 114.7 Hz, $^2J(^{117}Sn–^1H)$: 109.9 Hz, CH_3), 6.8–7.5 (m, 8H, $H_{aromatic}$), 9.13 (s, 1H, CH_{salopH_2}), 10.24, 10.74 (s br, OH_{salopH_2} and/or NH_{salopH_2}). ^{13}C NMR (DMSO-d_6, 293 K): δ, 23.88 (s, $^1J(^{119/117}Sn–^1H)$: 931.0 Hz, Sn–CH_3), 136.46, 134.62, 133.31, 132.16, 129.12, 124.23, 122.32, 119.17, 118.32, 116.72, (s, C_{arom}), 150.82, 161.07, 161.72, 191.65 (s, CO and CN). ^{119}Sn NMR (DMSO-d_6, 293 K): δ, −241.55. Λ_M

Table 1
Crystallographic data, details of data collection and refinement for complexes **4**, **7** and **9**

Compound	$[SnVI_2(salop)]$ (**4**)	$[SnCl_2(salop)(CH_3OH)]\cdot CH_3OH$ (**7**)	$[SnBr_2(salop)(CH_3OH)]\cdot CH_3OH$ (**9**)
Molecular formula	$C_{17}H_{15}NO_2Sn$	$C_{15}H_{17}Cl_2NO_4Sn$	$C_{15}H_{17}Br_2NO_4Sn$
M	383.99	464.87	553.79
Crystal system	triclinic	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.597(2)	7.642(2)	7.638(2)
b (Å)	10.203(2)	9.162(2)	9.330(3)
c (Å)	10.378(2)	12.897(3)	13.080(4)
α (°)	103.40(3)	92.42(3)	93.91(4)
β (°)	94.56(3)	95.99(3)	96.05(4)
γ (°)	103.16(2)	106.11(3)	105.15(4)
V (Å^3)	754.5(3)	860.4(4)	890.2(5)
Z	2	2	2
D_{calc} (Mg m^{-3})	1.690	1.794	2.066
μ (cm^{-1})	16.96	18.13	59.41
Temperature (K)	180(2)	180(2)	180(2)
θ (max) (°)	26.8	26.8	27.0
Number of reflections collected	5751	4869	7491
Numberof unique reflections	2902	3267	3450
Reflections with $I>2\sigma(I)$	2751	2574	2745
Reflections/parameters in refinement	2875/250	2776/218	3016/236
wR_2(all)	0.0572	0.0623	0.0688
R_1 ($I>2\sigma(I)$)	0.0223	0.0235	0.0282

(DMSO, c (mol l^{-1}) $= 1.0\times10^{-3}$) $= 0.05$ Ω^{-1} cm^2 mol^{-1}. UV ($CHCl_3$, λ_{max}, nm): 243, 270, 354.

2.4.18. $[SnBu^n_2Cl_2(salopH_2)]$ (**18**)

Complex **18** was prepared as **17** by using 1.0 mmol of $salopH_2$ and 5.0 mmol of $SnBu^n{}_2Cl_2$. Yield 76%. M.p. 192–194 °C. *Anal.* Calc. for $C_{21}H_{29}Cl_2NO_2Sn$: C, 48.78; H, 5.65; N, 2.71. Found: C, 48.43; H, 5.58; N, 2.55%. IR (Nujol, cm^{-1}): 3193br (H_2O), 1626s, 1590s, 1508s (C⋯C, C⋯N), 577s, 533m (Sn–C), 502sbr, 475s (Sn–O), 285br (Sn–Cl). ^{1}H NMR (DMSO-d_6, 293 K): δ, 0.84 (t, 6H, Sn–$CH_2CH_2CH_2CH_3$), 1.2–1.3 (m, 8H, Sn–Bu^n), 1.5–1.6 (m, 4H, Sn–Bu^n), 6.8–7.7 (m, 8H, $H_{aromatic}$), 9.16 (s, 1H, CH_{salopH_2}), 10.2, 10.8 (s br, OH_{salopH_2} and/or NH_{salopH_2}). ^{13}C NMR (DMSO-d_6, 293 K): δ, 13.82 (s, Sn–Bu^n), 17.04 (s, Sn–Bu^n), 25.66 (s, Sn–Bu^n), 27.73 (s, Sn–Bu^n), 116.24, 116.63, 116.86, 117.31, 118.19, 118.89, 119.31, 119.44, 119.60, 119.71, 122.32, 124.22, 128.99, 129.34, 131.90, 133.44, 134.74, 136.40 (s, $C_{aromatic}$), 150.79, 155.89, 157.28, 159.65, 160.79, 161.04, 161.70, 167.24, 191.68 (s, CO and CN). ^{119}Sn NMR (DMSO-d_6, 293 K), δ −211.1. Λ_M (DMSO, c (mol l^{-1}) $= 1.1\times10^{-3}$) $= 0.05$ Ω^{-1} cm^2 mol^{-1}. UV ($CHCl_3$, λ_{max}, nm): 243, 270, 355.

2.5. X-ray crystallography

The data for the complexes **4**, **7** and **9** were collected on an Image-Plate diffractometer (IPDS, Stoe) using graphite monochromated Mo Kα radiation. Numerical absorption correction was only applied for structure **9** due to the higher absorption coefficient. The structures were solved by direct methods (SHELXS-86) [12] and refined anisotropically for all non-hydrogen atoms using crystallographic program package SHELXL-93 [13]. Hydrogen atoms of vinyl groups in **4** and that of OH group in methanol molecules in both **7** and **9** were located from the difference Fourier maps and refined isotropically. All other H atoms were included in the calculated positions and refined in a riding mode. In the structure **9**, the bridging N and C(7) atoms of the salop ligand were found to be disordered between two positions with occupancy ratio 80:20, which corresponds to the disorder of the whole salop ligand. The comparatively high residual electron density (about 1 e Å^{-3}), however, without chemical meaning was found for structures **4** and **9** at the distance ~1 Å from the tin atoms.

Crystallographic data and some details of data collection and structures refinement are given in Table 1. The most relevant bond distances and angles in the structures of **4**, **7** and **9** are listed in Table 2. From the recrystallisation of compound **15** we have obtained good-quality crystals of **1** for which a single crystal X-ray study has been previously reported [8]. Our data compare well with those in literature [8] and are inserted in Table 2.

Table 2
Selected bond distances and angles of complexes **1**, **4**, **7** and **9**

Distances/angles	$[SnMe_2(Salop)]$(**1**) [a]	$[SnVi_2(Salop)]$ (**4**)	$[SnCl_2(Salop)(CH_3OH)]\cdot CH_3OH$ (**7**)	$[SnBr_2(Salop)(CH_3OH)]$ (**9**)
Sn–O(1)	2.117(2)	2.117(2)	2.009(2)	2.005(2)
Sn–O(2)	2.139(3)	2.125(2)	2.055(2)	2.056(2)
Sn–N	2.221(3)	2.227(2)	2.171(3)	2.178(5) [b]
Sn–C(14)	2.112(3)	2.112(2)		
Sn–C(16)	2.117(4)	2.113(2)		
Sn–X(1)			2.348(1)	2.506(1)
Sn–X(2)			2.400(1)	2.553(1)
Sn–O(3)			2.182(2)	2.194(3)
C(14)–Sn–C(16)	140.1(1)	138.3(1)		
X(1)–Sn–X(2)			96.18(4)	96.72(3)
O(1)–Sn–O(2)	158.7(1)	158.88(8)	162.6(1)	161.5(1)
O(1)–Sn–N	75.4(1)	75.79(7)	90.0(1)	90.1(1)
O(2)–Sn–N	83.5(1)	83.34(7)	77.55(9)	76.6(1)
O(1)–Sn–O(3)			83.69(9)	83.3(1)
O(2)–Sn–O(3)			82.83(9)	82.3(1)
N–Sn–O(3)			83.76(9)	82.9(1)
C(14)–Sn–O(1)	97.8(1)	98.60(8)		
C(16)–Sn–O(1)	99.3(1)	95.91(8)		
C(14)–Sn–O(2)	87.4(1)	91.00(9)		
C(16)–Sn–O(2)	89.6(1)	89.12(8)		
C(14)–Sn–N	112.3(1)	108.57(9)		
C(16)–Sn–N	106.9(1)	112.81(8)		
X(1)–Sn–O(1)			97.15(7)	97.41(9)
X(1)–Sn–O(2)			93.43(7)	93.72(8)
X(2)–Sn–O(1)			96.00(7)	96.07(9)
X(2)–Sn–O(2)			96.60(7)	97.30(9)
X(1)–Sn–N			168.55(7)	167.5(1)
X(2)–Sn–N			91.91(7)	92.3(1)
X(1)–Sn–O(3)			88.16(6)	88.09(7)
X(2)–Sn–O(3)			175.66(6)	175.19(6)

[a] For $[SnMe_2(Salop)]$, C(15) in the atom list corresponds to C(16) in this table. The data for this compound derived from our determination, more refined with respect to that reported in Ref. [8].
[b] The geometrical parameters are given for the main (80%) component of the disordered Salop ligand.

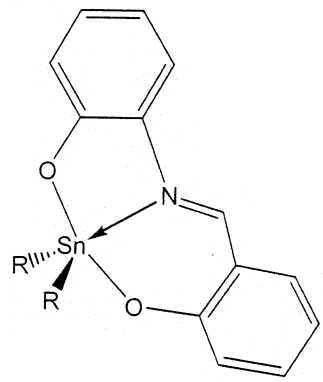
3. Results and discussion

3.1. Synthesis

From the reaction of SnR_2Cl_2 acceptors with an equimolar amount of 2-{[(2-hydroxyphenyl)imino]-methyl}phenol($salopH_2$) in methanol in the presence of bases (KOH, MeONa or NEt_3), the complexes $[SnR_2(Salop)]$ **1**–**5** (R = Me, Ph, Vi, Bu^n, Bu^t), containing the donor in the dianionic tridentate form, have been obtained (Fig. 2). When $SnRX_3$ or SnX_4 acceptors were employed in the same reaction conditions, the complexes $[SnX_2(salop)(S)]$ **6**–**13** (X = Cl, Br, I or R; R = Me, Ph or Bu^n; S = H_2O or MeOH) (Fig. 3) can be easily obtained. Although these reactions seem to be instantaneous when all reactants are mixed, refluxing for approximately 24 h was carried out to ensure complete reaction.

On the other hand the reaction of SnX_4 with 2 mol of $SalopH_2$ and 4 mol of base affords the compound $[Sn(salop)_2]$ **14** in which all halides groups have been substituted by two dianionic tridentate Schiff bases.

With the triorganotin(IV) derivatives SnR_3Cl, the complexes $[SnR_3(salopH)]$ (R = Me or Bu^n) **15** and **16**, containing the monoanionic Schiff base likely coordinate in bidentate fashion, have been prepared.



R = Me, Bu^n, Bu^t, Vi or Ph.

Fig. 2. Structure proposed for the diorganotin(IV) salop derivatives.

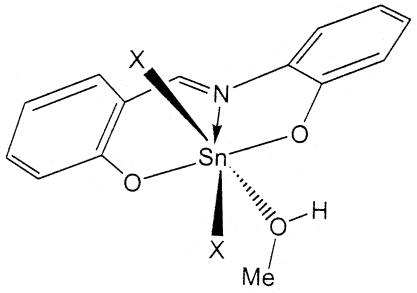


Fig. 3. Structure proposed for the mono- and dihalotin(IV) salop derivatives.

Finally, if the reaction between salopH_2 and SnR_2Cl_2 was carried out in diethyl ether or $CHCl_3$ in the absence of a base, the adducts $[SnR_2Cl_2(salopH_2)]$ **17** and **18** were formed.

Compounds **1**–**13** can be also prepared by refluxing a mixture of the proligand salopH_2 with the tin(IV) acceptors in toluene with azeotropical removal of water.

Under our conditions no derivative was obtained when $SnCy_3Cl$ or $SnPh_3Cl$ were employed.

In some cases, from the reaction of salopH_2 with di and tri organotin(IV) acceptors, the mono-organotin(IV) complexes were obtained due to dissociation of the starting acceptors according to the reaction of Kocheskov [14].

In the presence of moisture the $[SnR_2(salop)]$ and $[SnR_3(salopH)]$ complexes slowly hydrolyse even in $CHCl_3$ solution, yielding the R_2SnO and $(R_3Sn)_2O$ oxides or the hydroxides R_3SnOH [15]. The hydrolysis is faster when $R = Bu^n$. The adducts **17** and **18** are not stable in solution yielding, in quantitative yields after 48 h, complexes **1** and **2**, respectively.

Compounds **1**–**16** are stable under atmospheric conditions and are thermally stable up to their m.p. They all have intense colours (red, orange or yellow) and are soluble in acetone, DMSO and chlorinate solvents in which they are non-electrolytes, thus ruling out ionic structure or displacement of the ligand salop by solvent molecules, with the exception of compounds **8**–**10** for which in DMSO a conductivity value has been found in accordance with the partial ionic dissociation (Eq. (1)).

$$[SnX_2(salop)(CH_3OH)] + x\,DMSO \rightleftharpoons [SnX_{2-n}(salop)(DMSO)_x]^+ + nX^- + CH_3OH \quad (1)$$
$$(n = 1 \text{ or } 2,\ X = Br \text{ or } I)$$

3.2. Spectroscopy

3.2.1. IR

Selected IR data for all complexes are reported in Section 2.

The strong broad band due to ν(O–H), centred in the free donor at approximately 2300 cm^{-1}, disappears in the complexes **1**–**14**, in accordance with complete deprotonation of the ligand and involvement of both phenolate oxygens in bonding to tin. In the triorganotin complexes **15** and **16**, the presence of a broad absorption between 2600 and 2300 cm^{-1} indicates that only one phenolic group is deprotonated, that is in accordance with a bidentate *O*,*N*-coordination of the ligand. In the 3500–2300 cm^{-1} region the spectra of **17** and **18** are similar to that of the free ligand, indicating coordination of salopH_2 in neutral form. In the spectra of di-(**6**–**10**) and mono-halo (**11**–**13**) complexes, new broad absorptions at ca. 3400–3000 cm^{-1}, due to ν(O–H) of MeOH or H_2O bonded to tin, were detected according to the formulations proposed.

In derivatives **1**–**16** the ν(C=N) band, occurring between 1617 and 1567 cm^{-1}, is considerably shifted towards lower frequencies with respect to that of the free Schiff base (1631–1593 cm^{-1}), confirming the coordination of the azomethine nitrogen to the diorganotin(IV) moiety. The stretching frequency is lowered owing to the displacement of electron density from N to Sn atom, thus resulting in the weakening of the C=N bond as reported in the literature [16]. The major shift of C=N is observable in the IR spectrum of the halide derivatives **6**–**13** as compared with that in the triorganotin species **14** and **15**, indicating a strong participation of N atoms of the former in the coordination to the Sn atom. On the other hand, the ν(C=N) remains unchanged in the spectra of adducts **17** and **18** with respect to the free base, whereas a band assignable to ν(C–O) stretching vibration at approximately 1290 cm^{-1} in the ligand is shifted to 1250 cm^{-1} upon adduct formation. Coordination through the phenolic oxygen is confirmed by δ(O–H) absorption deformation, which falls at approximately 1290 cm^{-1} in the spectra of **17** and **18**.

In the spectra of **1**–**16** we have assigned some bands in the region 460–500 cm^{-1} to ν(Sn–O) which in our series seems to be little influenced by the type of halogen bonded to tin, but strongly influenced by the number and type of organic groups. The 20 cm^{-1} increase on going from Me and Bu^n to Ph can be interpreted in terms of the inductive effect of the increasing electron withdrawing power of the corresponding organic groups, which strengthens the Sn–O bonds.

The absorptions at approximately 262 and 243 cm^{-1} (**5**), 577 and 533 cm^{-1} (**2**) and finally 573 and 545 cm^{-1} (**1**) are due to ν(Sn–Ph), ν(Sn–Bu^n) and ν(Sn–Me), respectively [17]. In the case of **3** and **4** (Sn–Bu^t_2 and Sn–Vin_2 derivatives) the assignment of ν(Sn–C) is not certain, due to the overlapping with Sn–O and Whiffen-notation bands. The presence of three absorptions due to Sn–C in the spectra of triorganotin(IV) derivatives **15**–**16** is in accordance with a five-coordinate tbp fac-SnR_3 structure, with two other positions likely occupied by two donor atom from Salop [18].

In the far-IR region of **6**–**10** two ν(Sn–O) and two or more ν(Sn–Cl), ν(Sn–Br) and ν(Sn–I) bands were detected, indicating halogen atoms being in *cis* position in accordance with crystal structures (see above). For Sn–X stretching absorptions, the following trend, typical of dihalide complexes, has been found: $\nu(SnCl) > \nu(SnBr) > \nu(SnI)$ [19].

3.2.2. UV spectra

Details of the electronic spectra (in all cases recorded in $CHCl_3$) are also given in the experimental section. The spectra of **1**–**14** remain unchanged after a few days, confirming the stability of the complexes and remain unaffected by dilution. The spectra of **1**–**16** contain a characteristic band in the region 240–267 nm and two or more intense broad bands in the region 280–456 nm. The band in the region 240–270 nm can be considered a π–π^* benzenoid band, in view of the assignments made by Chatterijee and Douglas [20]. In the UV–Vis spectra of **1**–**5**, all three bands, due to conjugate systems of the coordinated ligand, reveal a red shift with respect to analogue absorptions in the spectrum of free salopH_2. In particular, the absorption at 354 nm, due to C=N system between phenyl rings in salopH_2, undergoes a shift to approximately 454–465 nm.

The replacement of methyl or butyl groups by the more electronegative chloride results in pronounced blue shifts of the long wavelength absorption band of the coordinated dinegative anion, a behaviour previously reported for other tin(IV) derivatives containing schiff bases [21].

The spectra of the adducts **17** and **18** are similar to that of the free ligand, suggesting that in chloroform solution they completely dissociate into starting reagents, as also indicated by NMR data (see below).

3.2.3. NMR spectra

The ^{1}H NMR data for the ligand and its tin(IV) complexes have been reported in Section 2. The choice of the solvent was dictated by the solubility, the order of preference being $CDCl_3$, acetone-d_6 and DMSO-d_6. The absence of the OH proton signals in the complexes **1**–**14** further supports the binding of the tin centre to both ligand oxygen atoms through the replacement of both phenolic hydrogens. Whereas the OH resonance is present in the spectra of the triorganotin(IV) complexes **15** and **16**, in accordance with a partial deprotonation of the ligand, as also in the adducts **17** and **18,** in which the ligand is in the neutral form. The chemical shift values of the ligand protons in **1**–**16** are as expected: a downfield shift in the δ value of azomethine (HC=N) proton resonance upon coordination, supports the ligation of azomethine nitrogen to tin. The Sn–N bond found in the solid state (see below) is retained also in solution. In fact, in the proton NMR spectra of **1**–**16** it is possible to observe the ^3J(Sn–H) coupling involving the azomethine proton, thus indicating direct Sn–N bonding. The magnitude of ^3J(Sn–H) can be employed to evaluate the strenght of Sn–N interaction. It has been found that the values of ^3J(Sn–H) in mono and di-halotin(IV) derivatives are greater than in the triorganotin(IV) complexes **15** and **16**. The ^{1}H NMR spectrum of the adducts **17** and **18** shows the azomethine proton unchanged with respect to the free ligand indicating the absence of coordination of the imine N atom to tin atom.

In the ^{1}H NMR spectra of **1**–**9** and **11**–**13** the HC=N proton is observed as one sharp singlet due to absence of isomers or fluxionality in solution. In the ^{1}H NMR spectrum of the diiodo complex **10** three different signals have been found for the HC=N groups. This multiplicity, also found in the ^{13}C and ^{119}Sn spectra, is in accordance with the occurrence of equilibrium **1**.

The $^2J(^{119}Sn–^1H)$ of dimethyltin derivative **1** has a value of 78.1 Hz, typical of five-coordinated tin species. On the basis of Lockarts's Eq. (2):

$$[Me - Sn - Me] = 0.0161 \times (^2J(^{119}Sn - {}^1H))2 - 1.32 \times {}^2J(^{119}Sn–^1H) + 133.4 \quad (2)$$

the Me–Sn–Me angle is estimated to approximately 128° [22]. The discrepancy between the C–Sn–C angle from X-ray data (see below) and the empirical estimation in solution suggests a change of the structure with the long Sn–O bond interaction being likely broken upon dissolution.

The ^{13}C NMR spectra show a significant downfield shift of all carbon resonances. The shift is a consequence of an electron density transfer from the ligand to the acceptor. The $^nJ(^{119}Sn–^{13}C)$ coupling constants were detected in the case of sufficiently soluble derivatives. In derivatives **1**–**5**, the order of magnitude of the coupling constants is the same as those previously reported for analogous five-coordinate derivatives [23], whereas in the case of derivatives **11**–**13** the $^nJ(^{119}Sn–^{13}C)$ are close to those found for six-coordinate skewed trapezoidal organotin(IV) complexes [19,23]. By using the simple linear relationship between $^1J(^{119}Sn–^{13}C)$ and the C–Sn–C bond angles derived by Lockart [22] and Howard [24] for dimethyltin species a value has been found for compound **1** in the range 130–134° which well agrees with the angle of 138° found in the crystal structure [8].

The ^{119}Sn NMR spectra of **1**–**5** show only one sharp resonance in the range -140 to -330 ppm, typical of five-coordinated diorganotin compounds [23]. As previously reported the ^{119}Sn chemical shift increases with the following order:

$$Me \approx Bu^n < Bu^t < Vin < Ph$$

The ^{119}Sn NMR chemical shift of **6**–**13** is typical of six-coordinate tin(IV) [19,23] and increases also when the R groups are replaced by more electronegative groups such as halides. As previously reported in the case of acylpyrazolonates the trend of chemical shift can be related to the electron-withdrawing inductive effect of the halogens and also to the possibility of additional π-contribution to the SnX bonds which would shield the nucleus to a greater extent. In the ^{119}Sn spectrum of **10** four resonances have been detected, two at approximately −621 ppm likely due to $[Sn(salop)(DMSO)_2(CH_3OH)]^{2+}[I_2]^{2-}$ and two at approximately −814 ppm—due to $[SnI(salop)(DMSO)(CH_3OH)]^{+}[I]^{-}$ species in accordance with equilibrium **1** proposed on the basis of the conductivity measurements which indicate the existence in solution of 1:1 electrolytes.

The ^{1}H and ^{119}Sn NMR spectra of the adducts **17** and **18** are typical of completely dissociated species, all signals being analogous to that of the free ligand and of the solvated organotin species.

3.3. X-ray diffraction study

The single-crystal X-ray diffraction (XRD) study of derivative **4** shows the tin center coordinated by five donor atoms, two O and one N from the salop ligand and two C of the vinyl groups, in a distorted trigonal pyramidal geometry (Fig. 4). The distortion is mainly due to the rigidity of chelate rings, together with the large covalent radius of tin(IV). The nitrogen (Sn–N: 2.227(2) Å) and the carbon atoms (Sn–C: 2.112(2) and 2.113(2) Å) occupy the equatorial plane, whereas the oxygen atoms (Sn–O: 2.117(2) and 2.125(2) Å) are in axial positions, with a O–Sn–O angle of 158.88 (8)°. The vinyl groups, directed above and below the plane defined by Sn, N and both O atoms, adopt a conformation with the terminal C atom bent toward the O2 of salop, the C–Sn–C angle being 138.3(1)°. Each molecular units weakly interact with another one through the O1 atom of salop, which is involved in an interaction with the metal of the second complex molecule (Sn···O:2.748(2)Å). The structure is very similar to that of derivatives **1** and **5**, reported previously [8,9], however, in **5** no Sn···O interactions between the complex molecules were found, and the C–Sn–C angle was less (121.4°) than in **1** and **4**.

The equatorial angles in the structure of **4** are close to that reported for $[SnMe_2(salop)]$ [8], whereas they differ from those reported for diphenyltin derivative [9]. The Sn–O distances are in the range typical for the Sn(IV) derivatives of salop, but are slightly shorter with respect to those reported for $[SnBu^n{}_2(Vanophen)]$ [6 h]. The monomeric $[SnVin_2(salop)]$ units are linked into dimers by weak intermolecular interactions with Sn–O distance being 2.748(2). This is similar to $[SnMe_2(salop)]$ complex [8], in which the value of additional Sn–O bonding is 2.881(8) Å, but differs from $[SnPh_2(salop)]$ [9], in which this interaction is absent likely due to steric factors. The comparison of three structures with R = Me, Vin, Ph shows the $[SnVin_2(salop)]$ derivative being much more similar to methyl-one. On the contrary to **4**, the divinyltin(IV) derivative of *N*-(2-hydroxyacetophenone)glycinate reported recently contains a water molecule coordinated to tin [25]. The coordination of water in this case can be

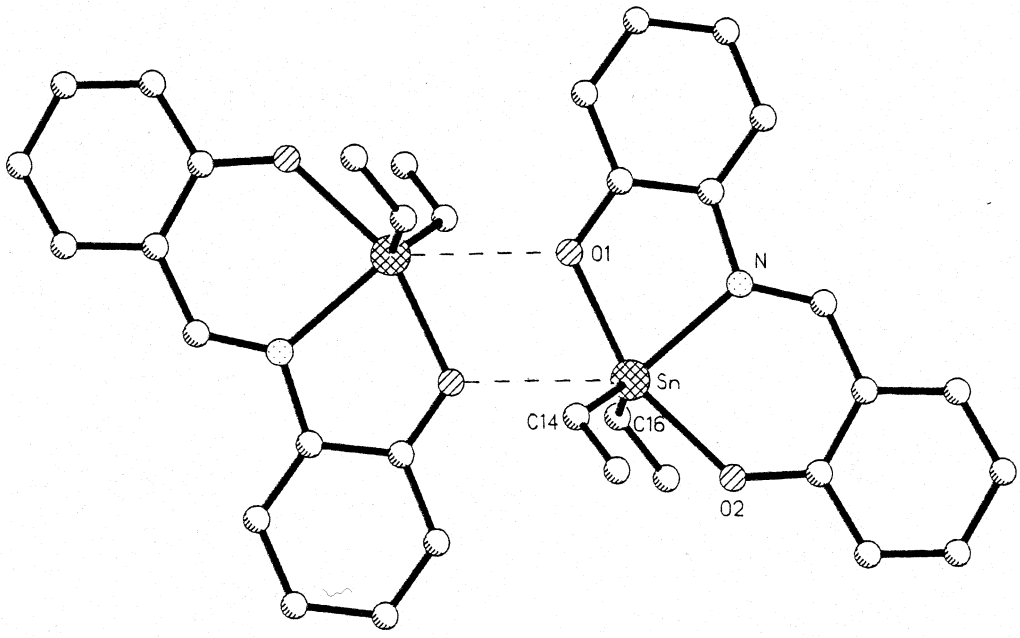


Fig. 4. The molecular structure of **4**.

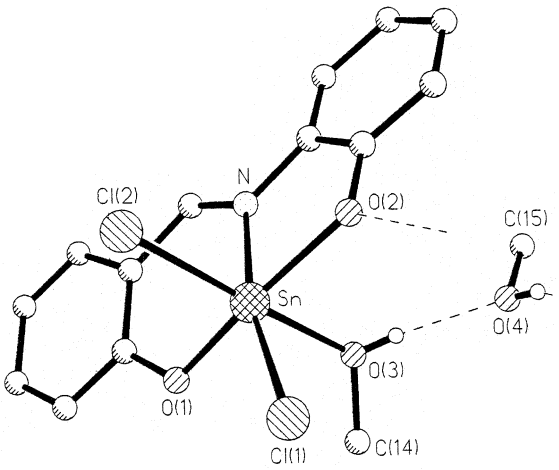


Fig. 5. The molecular structure of **7**. All the hydrogen atoms except those involved in hydrogen bonding are omitted.

easily explained by the intermolecular hydrogen bonding that links separate species in loosely associate dimers [25].

The isotypic structures of derivatives **7** and **9** reveal tin atom in a distorted octahedral geometry. The salop ligand occupies three meridional positions with the O atoms mutually in *trans*, while the halogen atoms are in *cis* with a Cl–Sn–Cl angle of 96.18(4)° and Br–Sn–Br 96.72(3)°. The Sn–O(salop) and Sn–N bonds in **7** and **9** are much more shorter with respect to diorganotin derivatives of salop [8–10] and other Schiff bases [6h] due to more electropositive character of tin centre caused by electron-withdrawing nature of halide atoms. The two Sn–halide distances in both structures are not equivalent, that *trans* to N atom being longer than the other.

The $[SnX_2(salop)(CH_3OH)]\cdot CH_3OH$ molecules are connected with each other via hydrogen bonds to the solvate CH_3OH molecules (with O(4) atom, see Fig. 5). The H-bonding over the solvate CH_3OH molecules results in the formation of the dimeric units $\{[SnX_2Salop(CH_3OH)](CH_3OH)\}_2$. Based on their lengths, the H-bonds O(3) – H(1)···O(4), 2.56–2.57 Å, and O(4)–H(2)···O(2)′, 2.79–2.80 Å, are of the middle strength. The latter H-bond is responsible for 0.05 Å longer Sn–O(2) distances as compared with Sn–(O1) in both **7** and **9**.

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References

[1] (a) L. Sacconi, Coord. Chem. Rev. 1 (1966) 126;
(b) S. Yamada, Coord. Chem. Rev. 1 (1966) 415;
(c) C. Mehrotra, G. Srivastava, B.S. Saraswat, Rev. Si, Ge, Sn, Pb, Compounds 6 (1982) 171;
(d) M. Nath, S. Goyal, Main Group Met. Chem. 19 (1996) 75.
[2] R.S. Collinson, D.E. Fenton, Coord. Chem. Rev. 148 (1996) 19.
[3] J.P. Corden, W. Errington, P. Moore, M.G.H. Wallbridge, Chem. Commun. (1999) 323 and references therein.
[4] (a) I. Belsky, D. Gerther, A. Zilkla, J. Med. Chem. 1 (1968) 92;
(b) R.H. Holm, in: G.L. Eichorn (Ed.), Inorganic Biochemistry, vol. 2, Elsevier, Amsterdam, 1974, p. 1137;
(c) L. Albanus, N.E. Bjorklund, B. Gustafsson, M. Johsson, Acta Pharmacol. Toxicol. Suppl. 36 (1975) 93;
(d) K.C. Joshi, V.N. Pathak, P. Panwar, Agric. Biol. Chem. 41 (1977) 543.
[5] (a) A. Syamal, K.S. Kale, Inorg. Chem. 18 (1979) 992;
(b) B.K. Dwivedi, K. Bhatnagar, A.K. Srivastava, Synth. React. Inorg. Met.-Org. Chem. 16 (1986) 715;
(c) T. Gunduz, O. Atakol, Synth. React. Inorg. Met.-Org. Chem. 19 (1989) 441;
(d) M.R. Maurya, M.N. Jayaswal, V.G. Puranik, P. Chakrabarti, S. Gopinathan, G. Gopinathan, Polyhedron 16 (1997) 3977.
[6] (a) S.J. Gruber, C.M. Harris, E. Sinn, J. Inorg. Nucl. Chem. 30 (1968) 1805;
(b) K. Key, J. Inorg. Nucl. Chem. 30 (1970) 3125;
(c) K. Kawakami, M. Miya-Uchi, T. Tanaka, J. Inorg. Nucl. Chem. 33 (1971) 3773;
(d) M. Calligaris, G. Nardin, L. Randaccio, J. Chem. Soc., Dalton Trans. (1972) 2003;
(e) D.A. Atwood, J.A. Jegier, K.J. Martin, D. Rutherford, Organometallics 14 (1995) 1453;
(f) D.A. Atwood, D. Rutherford, Organometallics 14 (1995) 2880;
(g) H. Chen, P.S. White, M.R. Gagné, Organometallics 17 (1998) 5358;
(h) D. Kumar Dey, M. Kumar Saha, M. Kanti Das, N. Bhartiya, R.K. Bansal, G. Rosair, S. Mitra, Polyhedron 18 (1999) 2687;
(i) D. Agustin, G. Rima, H. Gornitzka, J. Barrau, Eur. J. Inorg. Chem. (2000) 693;
(j) R. Barbieri, G. Alonzo, A. Silvestri, N. Burriesci, N. Bertazzi, G. Stocco, L. Pelleritto, Gazz. Chim. Ital. 104 (1974) 885;
(k) A. van der Bergen, R.J. Cozen, K.S. Murray, J. Chem. Soc. (A) (1970) 3060.
[7] (a) R.H. Herber, R. Barbieri, Gazz. Chim. Ital. 101 (1971) 149;
(b) N.S. Biridar, V.K. Kulkarni, J. Inorg. Nucl. Chem. 33 (1971) 3781;
(c) J.N.R. Ruddick, J.R. Sams, J. Organomet. Chem. 60 (1973) 233;
(d) T.N. Srivastava, A.K.S. Chauhan, M. Agarwal, J. Inorg. Nucl. Chem. 41 (1979) 896.
[8] (a) V.on H. Preut, F. Huber, H.-J. Haupt, R. Cefalù, R. Barbieri, Z. Anorg. Allg. Chem. 410 (1974) 88;
(b) D.L. Evans, B.R. Penfold, J. Cryst. Mol. Struct. 5 (1975) 93.
[9] (a) H. Von, F. Preut, R. Huber, N. Barbieri, Z. Bertazzi, Anorg. Allg. Chem. 423 (1976) 75;
(b) A.A. Diamantis, J.M. Gulbis, M. Manikas, E.R.T. Tiekink, Phosph. Sulf. Silicon 151 (1999) 251.
[10] A. van der Bergen, J.D. Cashion, G.D. Fallon, B.O. West, Aust. J. Chem. 43 (1990) 1559.
[11] D.C. Freeman, C.E. White, J. Am. Chem. Soc. 78 (1956) 2678.
[12] G.M. Sheldrick, SHELXS-86, University of Göttingen, 1986.
[13] G.M. Sheldrick, SHELXS-93, University of Göttingen, 1993.

[14] J.L. Wardell, in: P.G. Harrison (Ed.), Formation and Cleavage of the Tin–Carbon Bond. Chemistry of Tin, Blackie, London, 1989, p. 169 Chapter 5.
[15] A.G. Davies, Organotin Chemistry, VCH, Weinheim, 1997, pp. 138–154 Chapter 10 and references therein.
[16] S.G. Teoh, G.-Y. Yeap, C.C. Loh, L.-W. Foong, S.-B. Teo, H.-K. Fun, Polyhedron 16 (1997) 2213 and references therein.
[17] (a) J.R. May, W.R. McWhinnie, R.C. Poller, Spectrochim. Acta Part A 27 (1971) 96;
(b) A.L. Smith, Spectrochim. Acta Part A 24 (1967) 695;
(c) M.S. Dance, W.R. McWhinnie, R.C. Poller, J. Chem. Soc., Dalton Trans. (1976) 2349;
(d) F. Huber, M. Vornfield, G. Ruisi, R. Barbieri, Appl. Organomet. Chem. 7 (1993) 243 and references therein.
[18] (a) B.Y.K. Ho, J.J. Zuckermann, Inorg. Chem. 12 (1973) 1552;
(b) R. Okawara, D.E. Webster, E.G. Rochow, J. Am. Chem. Soc. 82 (1960) 3287;
(c) G.K. Sandhu, G. Kaur, J. Holecek, A. Lycka, J. Organomet. Chem. 345 (1988) 51.
[19] C. Pettinari, F. Marchetti, A. Cingolani, D. Leonesi, E. Mundorff, M. Rossi, F. Caruso, J. Organomet. Chem. 557 (1998) 187.
[20] K.K. Chatterjee, B.E. Douglas, Spectrochim. Acta 21 (1965) 1625.
[21] (a) T. Labib, T.E. Khalil, M.F. Iskander, L.S. Refaat, Polyhedron 15 (1996) 3697;
(b) T. Labib, T.E. Khalil, M.F. Iskander, L.S. Refaat, Polyhedron 15 (1996) 349.
[22] T.P. Lockhart, W.F. Manders, Inorg. Chem. 25 (1986) 892.
[23] B. Wrackmeyer, Ann. Rep. NMR Spectrosc. 16 (1985) 73.
[24] W.F. Howard Jr., R.W. Crecely, W.H. Nelson, Inorg. Chem. 24 (1985) 2204.
[25] D. Dakternieks, T.S. Basu Baul, S. Dutta, E.R.T. Tiekink, Organometallics 17 (1998) 3058.