Zwitterionic Forms of Salicylaldimine Donor Ligands in Unusual Adduct Formation with Organotin(IV) Lewis Acids

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The focus of this investigation was on adduct formation, and its consequences, between organotin(IV) Lewis acids and the tetradentate salicylaldimine ligands $H_2$3-MeOsalen [*N*,*N*′-bis(3-methoxysalicylidine)1,2-ethane diamine] and $H_2$3-MeOsalbiphen [*N*,*N*′-bis(3-methoxysalicylidine)2,2′-biphenyl diamine]. $SnBu^n_2Cl_2$ reacted with $H_2$3-MeOsalen to give a 1/1 adduct, **A**, containing a dangling salicylaldimine ligand but failed to yield a solid state adduct with $H_2$3-MeOsalbiphen, even though it exists in dynamic equilibrium with the latter ligand in solution. The stronger Lewis acids $SnPh_2Cl_2$ and $SnBu^nCl_3$ yielded 2/1 solid state adducts **D** and **E**, respectively, with $H_2$3-MeOsalbiphen in each of which the ligand bridges to six-coordinated tin centers and donor bonds are via phenolic and methoxy oxygen atoms. $SnBu^n_2(NCS)_2$ reacted with $H_2$3-MeOsalen to give an adduct, **B**, having a solid state ionic structure of formulation $\{[SnBu^n_2(NCS)(H_2\text{3-MeOsalen})]_2(\mu\text{-}H_2\text{3-MeOsalen})\}[SnBu^n_2(NCS)_4]$. The cation of **B** displays both bridging and dangling ligands and seven-coordinated tin. The ionic structure gives way to a nonionic symmetric cyclic trimeric structure of formulation $[SnBu^n_2(NCS)_2(\mu\text{-}H_2\text{3-MeOsalen})]_3$ in solution. The latter reacted with NaCl and $SnBu^n_2Cl_2$ to yield a new adduct, **C**, which in the solid state has an the ionic formulation $[SnBu^n_2Cl(\mu\text{-}H_2\text{3-MeOsalen})]_2[SnBu^n_2(NCS)_4]$, the cation of which has a centrosymmetric structure and seven-coordinated tin. The solid state ionic structure of **C** is not retained in solution. Crystallographic data are also reported for the free ligands $H_2$3-MeOsalen and $H_2$3-MeOsalbiphen (two crystal modifications of the latter were identified). The structural data clearly identify that donor bond formation through the salicylaldimine phenolic oxygen has the concomitant effect of phenolic hydrogen transfer to the imine nitrogen, a process that accounts for the imine hydrolysis which frequently occurs when the salicylaldimine ligands react with Lewis acids. Salicylaldehyde does not assume a zwitterionic form in its 1/1 adduct, **F**, with $SnMe_2Cl_2$ (the structure of this adduct was reinvestigated in the present study), and consequently the role of the phenolic oxygen is reduced to that of a very weak donor, participating merely in secondary bonding.

Introduction

Transition metal salicylaldimine complexes have been intensively investigated. They are complexes that display a wide diversity of properties embracing such important phenomena as high-spin−low-spin equilibrium and reversible uptake of both dioxygen and carbon dioxide.[1] Their ability to act as chiral oxidation catalysts is of greatest current interest, prime examples being Jacobson's manganese(III) salicylaldimine chiral epoxidation catalysts.[2] Significantly less attention has focused on p-block salicylaldimine complexes.[3] One of the attractive features of the salicylaldimine complexes is their ease of synthesis, generally from the metal acetate, acetylacetonate, or, in some cases, the freshly precipitated hydroxide. A number of synthetic methods have been employed for the synthesis of diorganotin complexes, but problems have been encountered that are attributed to tin hydrolysis resulting in stannoxane formation.[4−10] The use of a diorganotin dihalide in the presence of a HCl scavenger is generally not an appropriate synthetic route since the Lewis-base scavenger can catalyze stannoxane formation. In the absence of the base, simple adducts of 1/1 stoichiometry are formed, and several such adducts were isolated.[4] Closely related adducts $SnR_2Cl_2{\cdot}H_2$acacen [H_2acacen = *N*,*N*′-bis(acetylecetenato)ethane 1,2-diamine] have also been isolated and their structures studied in detail by Mössbauer

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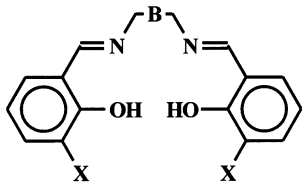
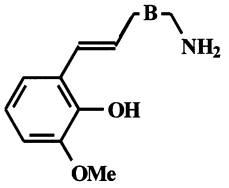
Scheme 1. Salicylaldimine Ligands



B = ethylene; X = H. **H_2salen**
B = ethylene; X = methoxy. **$H_2$3-MeOsalen**
B = 1,2propylene; X = methoxy. **$H_2$3-MeOsal1,2pn**
B = 2,2'-biphenyl; X = methoxy. **$H_2$3-MeOsalbiphen**
B = phenylene; X = methoxy. **$H_2$3-MeOsalphen**



B= ethylene; **H3-MeOsalenNH$_2$**
B = 1,2propylene; **H3-MeOsal1,2pnNH$_2$**

spectroscopy, from which it was concluded that they possessed chain polymeric structures with bridging H_2-acacen ligands and *trans* alkyl octahedral tin coordination geometries.[11−13] The structure of $SnMe_2Cl_2$·H_2salen (see Scheme 1 for ligand nomenclature) was subsequently determined, and although the data were of low quality (due to crystal twinning), they confirmed this type of polymeric structure.[14] No further interest has been expressed in adducts of this type. Interest in this laboratory in salicylaldimine complexes having methoxy substituents in the 3,3′-positions led to the investigation of adducts of organotin tin species with $H_2$3-MeOsalen and related ligands (see Scheme 1). The study revealed an unexpected and fascinating structural chemistry as well as important zwitterionic behavior of salicylaldimine ligands, the latter behavior accounting for the catalytic role of Lewis acids in the hydrolysis of the imine functional group.

Experimental Section

Infrared spectra, recorded on a Perkin-Elmer 1600 spectrophotometer, were obtained for Nujol mulls between KBr plates. NMR spectra were recorded on a JEOL Lambda 400 spectrometer. Sn-119 Mössbauer spectra were recorded on a spectrometer supplied by J & P Engineering, Reading, U.K. Spectra were recorded with the sample at liquid nitrogen temperature and the source, $Ca^{119}SnO_3$ (the Radiochemical Centre Amersham, U.K), at room temperature. Spectra were analyzed using the program Peakfit (Jandel Scientific). Molecular weights in chloroform (distilled from calcium hydride immediately before use) were determined using a Perkin-Elmer 115 molecular weight machine employing the vapor pressure (isopiestic) method. Naphthalene was employed as calibrant. Conductivity measurements in solution were determined using a conductivity meter (EDT instruments).

Butyltin halides (Aldrich Chemical Co.) were used as supplied. Diphenyltin dichloride (Aldrich Chemical Co.) was recrystallized prior to use. $SnBu^n_2(NCS)_2$ was prepared as in the literature.[15] Salicylaldehyde, ethylenediamine, and 1,3-diaminopropane (Aldrich Chemical Co.) and 3-methoxy salicylaldehyde (Jannsen Chimica) were used as supplied. 2,2′-Diaminobiphenyl was obtained from the reduction of 2,2′-dinitrobiphenyl.[16]

Synthesis of Salicylaldimine Ligands and Crystallization of $H_2$3-MeOsalen (G) and $H_2$3-MeOsalbiphen (H). The salicylaldimine ligands were prepared by standard procedures.[17] Crystals of $H_2$3-MeOsalen (mp 170−172 °C) were grown from an acetonitrile solution that had been saturated at a temperature approximately 5 °C higher than room temperature. Ruby red needlelike crystals of $H_2$3-MeOsalbiphen (**H**) (mp 178−180 °C) can be grown likewise. Crystals of the same polymorph were obtained from an acetonitrile solution containing $SnBu^nCl_2$ and $H_2$3-MeOsalbiphen in equimolar quantities, and from this solution slightly paler colored crystals (mp 184−186 °C) with a more blocklike morphology belonging to another crystal modification were also obtained.

Synthesis and Crystallization of $SnBu^n_2Cl_2$·$H_2$3-MeOsalen (A). $SnBu^n_2Cl_2$ (1.21 g) was dissolved in 40 cm^3 of acetonitrile. An equimolar quantity of $H_2$3-MeOsalen was added and the resulting solution stirred over gentle heat for 1 h. On cooling, the yellow 1/1 adduct precipitated (yield 80%). After removal of the solid by filtration, the solution was left to stand for approximately 12 h, after which time good quality crystals were obtained (dec at ca. 170 °C). The crystals had limited lifetime in solution and were totally unstable out of solution. A crystal for the crystal structure determination was sealed in a capillary tube, with residual solvent and data collection was undertaken without delay. Anal. Calcd for $C_{26}H_{38}N_2O_4Cl_2Sn$: C, 49.40; H, 6.06; N, 4.43. Found for initial precipitate: C, 49.74; H, 5.83; N, 4.85. Found for the crystals: C, 49.51; H, 5.84; N, 4.61.

Synthesis and Crystallization of {[$SnBu^n_2$(NCS)($H_2$3-MeOsalen)]$_2$(μ-$H_2$3-MeOsalen)}[$SnBu^n_2$(NCS)$_4$] (B). To a solution of 1.4 g (4 mmol) of $SnBu^n_2(NCS)_2$ in methanol (40 cm^3) was added an equimolar quantity of $H_2$3-MeOsalen. The suspension was stirred over gentle heat for 1 h to yield a clear yellow solution. On cooling, the microcrystalline adduct was obtained (yield 70%). Recrystallization from acetonitrile gave air-stable crystals (dec at ca. 170 °C) suitable for crystallography. Anal. Calcd for $C_{84}H_{114}N_{12}O_{12}S_6Sn_3$: C, 49.64; H, 5.65; N, 8.27. Found for the microcrystalline material: C, 49.36; H, 5.26; N, 8.03. Found for the crystals: C, 49.43; H, 5.54; N, 8.11.

Synthesis and Crystallization of [$SnBu^n_2Cl$(μ-$H_2$3-MeOsalen)]$_2$[$SnBu^n_2$(NCS)$_4$] (C). To a solution of 3.1 g (1.5 mmol) of **B** in methanol (60 cm^3) was added equimolar quantities of $SnBu^n_2Cl_2$ and NaCl. After stirring over gentle heat for 3 h a clear yellow solution was obtained. On cooling, **C** was obtained as a yellow solid (yield 60%). Crystallization of the yellow solid from acetonitrile yielded crystals of **C** (dec at ca. 160 °C). Anal. Calcd for $C_{64}H_{94}N_8O_8S_4Cl_2Sn_3$: C, 46.34; H, 5.71; N, 6.76. Found for the precipitate: C, 45.89; H, 5.13; N, 6.23. Found for the crystals: C, 46.11; H, 5.45; N, 6.63.

Synthesis and Crystallization of ($SnPh_2Cl_2$)$_2$·$H_2$3-MeOsalbiphen (D). To a solution of 0.96 g (2.1 mmol) of H_2-MeOsalbiphen in acetonitrile (20 cm^3) was added 1.46 g (4.2 mmol) of $SnPh_2Cl_2$. The resulting orange solution was left aside for 1 day, after which time air-stable orange crystals of the adduct **D** were obtained (yield 60%). Anal. Calcd for $C_{52}H_{44}N_2O_4Cl_4Sn_2$: C, 54.78; H, 3.87; N, 2.46. Found for the crystals: C, 54.65; H, 3.81; N, 2.39.

Synthesis and Crystallization of ($SnBu^nCl_3$)$_2$·$H_2$3-MeOsalbiphen (E). To a solution of 2.44 g (5 mmol) of $H_2$3-MeOsalbiph in acetonitrile (20 cm^3) was added 3.05 g (10

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mmol) of $SnBu^nCl_3$. A yellow precipitate of the adduct rapidly formed in the resulting orange solution (yield 85%). A saturated solution of the yellow solid in acetonitrile at approximately 40 °C yielded crystals of adduct **E** after slow cooling. Anal. Calcd for $C_{36}H_{42}N_2O_4Cl_6Sn_2$: C, 42.52; H, 4.16; N, 2.75. Found for the precipitate: C, 42.11; H, 3.74; N, 2.52. Found for the crystals: C, 42.44; H, 3.78; N, 2.61.

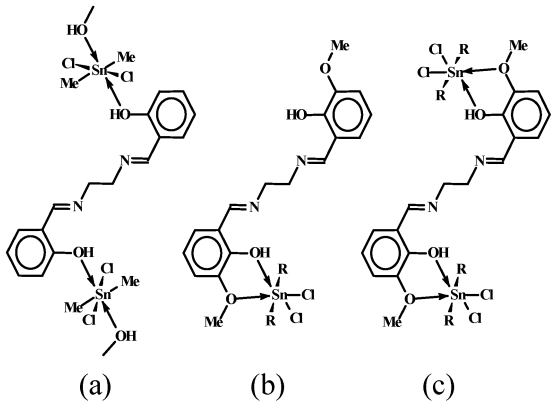
Synthesis and Crystallization of $SnMe_2Cl_2$·salicylaldehyde (F). A large excess of salicylaldehyde was added to a hot solution of $SnMe_2Cl_2$ (1.0 g) in hexane (40 cm^3). On cooling, crystals of $SnMe_2Cl_2$ formed. When 1.0 g of $SnMe_2Cl_2$ was dissolved in 15 cm^3 of hot salicylaldehyde and the resulting solution allowed to cool, crystals of $SnMe_2Cl_2$·salicylaldehyde were obtained (yield 90%). Anal. Calcd for $C_9H_{12}O_2Cl_2Sn$: C, 31.63; H, 3.54. Found: C, 31.44; H, 3.50.

Crystallography. Crystal data are in Table 1. Diffraction data for **A**, **B**, **F**, **G**, and **H** were collected on an image plate (Marr Research). Data for **C**, **D**, and **E** were collected on a four-circle diffractometer (Enraf-Nonius CAD 4). Unit cell parameters, in all cases, were determined from four-circle diffractometer data. Data were corrected for Lorentz and polarization effects but not for absorption. All structures were solved by direct methods, SHELXS-97,[18] and refined by full matrix least squares using SHELXL-97.[19] SHELX operations were automated using ORTEX, which was also used to obtain the drawings.[20] The non-hydrogen atoms were refined anisotropically. With the exception of the phenolic hydrogen, all other hydrogen atoms were included in calculated positions with thermal parameters 30% larger than the atom to which they were attached. At this point of refinement, the difference map in each case, with the exception of that for **C**, revealed a peak close to either the phenolic oxygen or the imine nitrogen. Generally these peaks were the highest intensity peaks in the difference maps (in the case of **E** higher intensity peaks were found around the butyl group, which did not refine very satisfactorily, and in the case of **D**, high-intensity peaks were found very close to tin, thus accounting for the high residual electron density following final refinement). In no case was a peak found close to both the nitrogen and oxygen. In the case of **C** a peak was found close to nitrogen at one end of the ligand, but no peak was found at the other end. In the case of $H_2$3-MeOsalen, data were collected for a second crystal from a different crystallization, and in this case the peak in the difference map was found close to the phenolic oxygen precisely as it was found in the first structure determination. These peaks were taken to represent the positions of the phenolic hydrogens, and in the final refinement the positions were refined isotropically. All calculations were performed on a Pentium PC.

Results and Discussion

$SnMe_2Cl_2$·H_2salen has a chain polymeric structure resulting from the formation of *trans* phenolic oxygen donor bonds to tin, as shown schematically in Scheme 2a.[14] In this way tin achieves octahedral geometry with *trans* methyl groups. A noteworthy feature is the lack of participation of the imine nitrogen in donor bond formation; the lack of participation of the nitrogen atoms necessitated the involvement of all of the phenolic oxygen atoms in bonding such as to produce six-coordinated tin in the polymeric structure. The introduction of methoxy groups in the 3,3′-positions provides alternative bonding possibilities. Polymeric structures such as that observed in $SnMe_2Cl_2$·H_2salen may still result with little or no participation of the methoxy oxygens. On the other hand, their likely involvement in bonding to tin may result in simple monomeric structures of either 1/1 or 2/1 stoichiometry (Scheme 2b and 2c, respectively), in which tin achieves a coordination number of six without recourse to a polymeric structure. In fact, it would be anticipated that a 2/1 adduct would form if sufficient tin Lewis acid (e.g., $SnBu^n_2Cl_2$) was available.

Scheme 2. Possible Structures of Diorganotin Dichloride Adducts with Salicylaldimine Ligands



As it transpires, the reaction of $SnBu^n_2Cl_2$ with $H_2$3-MeOsalen led exclusively to the formation of a 1/1 addition complex (**A**), irrespective of the quantity of $SnBu^n_2Cl_2$ used in the synthesis, and this suggested that an adduct of type 2a was being formed. The crystal structure of the adduct (see Figure 1 and Table 2) however revealed that the salicylaldimine ligand was acting as a dangling ligand with only one phenolic and one methoxy oxygen coordinating to tin, thus giving an adduct of type b in Scheme 2. An examination of the lattice structure did not reveal any bonding features that would tend to add stability to the lattice and hence favor a 1/1 rather than a 2/1 adduct. For example, there are no intermolecular hydrogen-bonding interactions involving the free end of the ligands and the phenyl rings are not involved in significant π-interactions.

^{119}Sn NMR solution state spectra suggest that the failure to isolate the 2/1 adduct is largely, if not totally, a consequence of ligand hydrolysis reactions, which become more extensive as the acid/base ratio increases. A dry chloroform solution of adduct **A** gave a ^{119}Sn NMR spectrum displaying two tin signals, a broad peak (peak width of 638 Hz at half peak height) at −115.6 and a sharp peak at −185.5 ppm. The ratio of the integrated intensities of broad peak to sharp peak was approximately 3.1. These are not attributable to the $ClSnBu^n_2OSnBu^n_2Cl$ or $ClSnBu^n_2OSnBu^n_2OH$, nor is either peak attributable to the presence of the free tin Lewis acid. The broad peak is attributable to a tin that is involved in dynamic behavior on the NMR time scale. Progressive addition of further dibutyltin dichloride had the effect of shifting this latter peak to lower field (as expected) while the sharp peak position remained static. Furthermore, with addition of the extra tin Lewis acid, the intensity of the sharp peak increased very significantly relative to that of the broad peak. When a solution containing excess dibutyltin dichloride was left aside for a number of hours, a precipitate fell from solution. This precipitate contained some of the 1/1 adduct but also contained a complex (or complexes) that gave rise to a

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Table 1. Crystallographic Data

	A	B	C	D	E	F	G	H
empirical formula	$C_{26}H_{38}Cl_2N_2O_4Sn$	$C_{42}H_{57}N_6O_6S_3Sn_{1.50}$	$C_{32}H_{47}ClN_4O_4S_2Sn_{1.50}$	$C_{26}H_{22}Cl_2NO_2Sn$	$C_{36}H_{42}Cl_6N_2O_4Sn_2$	$C_9H_{12}Cl_2O_2Sn$	$C_9H_{10}NO_2$	$C_{56}H_{48}N_4O_8$
fw	316.09	1016.15	829.34	570.04	1016.80	341.78	164.18	904.98
cryst syst	triclinic	triclinic	triclinic	monoclinic	triclinic	orthorhombic	monoclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$
unit cell dimens	$a = 11.065(2)$ Å	$a = 11.8427(14)$ Å	$a = 10.2080(9)$ Å	$a = 27.041(3)$Å	$a = 12.0011(18)$ Å	$a = 6.9027(17)$ Å	$a = 8.663(2)$ Å	$a = 11.914(5)$ Å
	$b = 11.412(3)$ Å	$b = 12.479(3)$ Å	$b = 13.3280(10)$ Å	$b = 9.9112(10)$ Å	$b = 12.113(3)$ Å	$b = 10.3651(11)$ Å	$b = 10.8412(18)$ Å	$b = 12.9241(12)$ Å
	$c = 13.989(2)$ Å	$c = 18.090(2)$ Å	$c = 15.3710(10)$ Å	$c = 17.9541(10)$ Å	$c = 16.878(2)$ Å	$c = 17.488(3)$ Å	$c = 8.823(3)$ Å	$c = 15.642(3)$ Å
	$\alpha = 69.594(17)°$	$\alpha = 80.286(12)°$	$\alpha = 107.440(10)°$	$\alpha = 90°$	$\alpha = 84.055(15)°$	$\alpha = 90°$	$\alpha = 90°$	$\alpha = 88.155(11)°$
	$\beta = 69.925(15)°$	$\beta = 83.393(10)°$	$\beta = 103.400(10)°$	$\beta = 102.430(10)°$	$\beta = 77.920(12)°$	$\beta = 90°$	$\beta = 93.98(3)°$	$\beta = 82.28(2)°$
	$\gamma = 67.293(17)°$	$\gamma = 66.869(14)°$	$\gamma = 90.030(10)°$	$\gamma = 90°$	$\gamma = 60.310(14)°$	$\gamma = 90°$	$\gamma = 90°$	$\gamma = 81.416(19)°$
volume (Å^3)	1482.1(5)	2419.9(7)	1935.3(3)	4699.0(8)	2084.2(6)	1251.2(4)	826.6(4)	2359.8(11)
Z	2	2	2	8	2	4	4	2
density (calc) (Mg/m^3)	1.417	1.395	1.423	1.612	1.620	1.814	1.319	1.274
abs coeff (mm^{-1})	1.074	0.958	1.190	1.339	1.622	2.443	0.094	0.086
$F(000)$	648	1044	846	2280	1012	664	348	952
cryst size (mm)	0.46 × 0.32 × 0.20	0.36 × 0.32 × 0.15	0.50 × 0.40 × 0.20	0.50 × 0.40 × 0.20	0.50 × 0.40 × 0.20	0.46 × 0.27 × 0.20	0.31 × 0.24 × 0.20	0.61 × 0.34 × 0.27
θ range (deg)	1.60 to 20.86	1.79 to 21.20	2.06 to 27.97	2.19 to 27.96	2.14 to 27.97	2.28 to 20.86	2.98 to 20.77	1.59 to 20.83
index ranges	$-10 \le h \le 10$	$-11 \le h \le 11$	$0 \le h \le 13$	$-7 \le h \le 35$	$-1 \le h \le 12$	$-6 \le h \le 6$	$-8 \le h \le 8$	$-11 \le h \le 11$
	$-11 \le k \le 11$	$-12 \le k \le 12$;	$-17 \le k \le 17$	$-5 \le k \le 13$	$-12 \le k \le 12$	$-10 \le k \le 10$	$-10 \le k \le 10$	$-12 \le k \le 12$
	$-13 \le l \le 13$	$-18 \le l \le 18$	$-20 \le l \le 19$	$-23 \le l \le 23$	$-17 \le l \le 17$	$-17 \le l \le 16$	$-8 \le l \le 8$	$-15 \le l \le 15$
no. of reflns coll	5702	10 590	10 122	5939	8695	5123	3254	7710
no. of indep reflns	2780	4925	9330	5647	8012	1265	845	4512
no. of reflns obsd ($>2\sigma$)	2533	4306	8072	5008	6936	1258	783	3568
no. of data/restraints/ params	2780/0/328	4925/0/517	9330/0/412	5647/0/294	8012/0/453	1265/0/133	845/0/114	4512/0/621
goodness-of-fit on F^2	1.047	1.099	1.076	1.044	1.044	1.157	0.836	0.981
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0532$.	$R_1 = 0.0347$	$R_1 = 0.0500$	$R_1 = 0.0502$	$R_1 = 0.0374$	$R_1 = 0.0261$	$R_1 = 0.0464$	$R_1 = 0.0560$
	$wR_2 = 0.1306$	$wR_2 = 0.0904$	$wR_2 = 0.1486$	$wR_2 = 0.1527$	$wR_2 = 0.1021$	$wR_2 = 0.0609$	$wR_2 = 0.1094$	$wR_1 = 0.1360$
R indices (all data)	$R_1 = 0.0576$	$R_1 = 0.0415$	$R_1 = 0.0576$	$R_1 = 0.0545$	$R_1 = 0.0428$	$R_1 = 0.0264$	$R_1 = 0.0491$	$R_1 = 0.0738$
	$wR_2 = 0.1340$	$wR_2 = 0.0935$	$wR_2 = 0.1663$	$wR_2 = 0.1566$	$wR_2 = 0.1050$	$wR_2 = 0.0610$	$wR_2 = 0.1125$	$wR_2 = 0.1475$
largest diff peak and hole (e·Å^{-3})	0.332 and −0.484	0.415 and −0.404	1.223 and −1.208	1.247 and −2.617	0.983 and −1.343	0.299 and −0.607	0.257 and −0.345	0.211 and −0.281

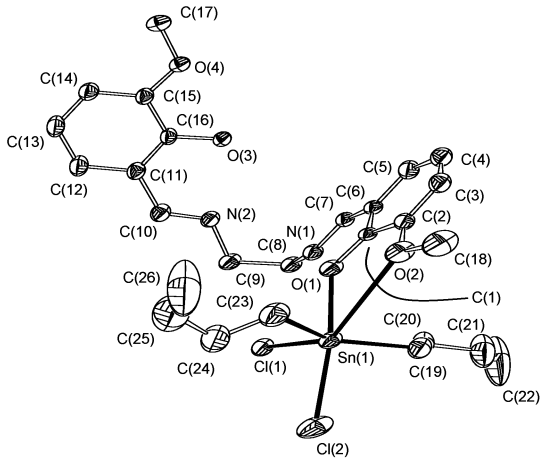


Figure 1. ORTEX[20] view **A** (30% ellipsoids).

Table 2. Selected Bond Lengths (Å) and Angles (deg) for A

Sn(1)−O(1)	2.293(4)	Sn(1)−O(2)	3.177(4)
Sn(1)−Cl(1)	2.4252(17)	Sn(1)−Cl(2)	2.527(2)
Sn(1)−C(19)	2.122(7)	Sn(1)−C(23)	2.130(8)
C(19)−Sn(1)−C(23)	145.1(3)	C(19)−Sn(1)−O(1)	87.6(3)
C(23)−Sn(1)−O(1)	89.3(3)	C(19)−Sn(1)−Cl(1)	107.5(2)
C(23)−Sn(1)−Cl(1)	105.8(3)	O(1)−Sn(1)−Cl(1)	78.53(10)
C(19)−Sn(1)−Cl(2)	94.4(2)	C(23)−Sn(1)−Cl(2)	96.7(2)
O(1)−Sn(1)−Cl(2)	166.23(11)	Cl(1)−Sn(1)−Cl(2)	87.89(6)
C(19)−Sn(1)−O(2)	79.0(2)	C(23)−Sn(1)−O(2)	70.7(2)
O(1)−Sn(1)−O(2)	55.66(13)	Cl(1)−Sn(1)−O(2)	133.74(9)
Cl(2)−Sn(1)−O(2)	138.09(10)		

strong band at 2060 cm^{-1} and other weaker bands at 2282, 2441, and 2519 cm^{-1} in the infrared spectrum. These bands do not occur in the spectrum of the adduct but are typically observed in adducts of ethylenediamine and in complexes containing the partially hydrolyzed salicylaldimine ligand H3-MeOsalenNH_2 (see Scheme 1). They are found, for example, in the spectrum of $SnBu^n_2Cl_2$(3-MeOsalenNH_2), which has been characterized crystallographically in this laboratory.[21] The complexities of the ^{119}Sn NMR spectra are thus almost certainly a consequence of ligand hydrolysis, which will introduce 3-methoxysalicylaldehyde, ethylenediamine (resulting from total hydrolysis), and/or H3-MeOsalenNH_2 (resulting from partial hydrolysis) as potential donor ligands. Since the ethylenediamine adduct of dibutyltin dichloride is insoluble in chloroform, its involvement in solution is ruled out. Furthermore, a ^{119}Sn NMR spectrum of an equimolar chloroform solution of dibutyltin dichloride and 3-methoxysalicylaldehyde showed a single sharp peak that was only 5 ppm upfield from the peak due to dibutyltin dichloride, and thus the involvement of the free 3-methoxysalicylaldehyde is also eliminated. This leaves the presence of H3-MeOsalenNH_2 as the most likely source of the NMR complexities. Chelation between H3-MeOsalenNH_2 and $SnBu^n_2Cl_2$ could account for the sharp peak that remains invariant at −185.5 ppm [$SnBu^nCl_2$(salenNH_2) shows a single sharp peak in its ^{119}Sn NMR spectrum], whereas the other peak may be attributable to a dynamic interaction between $SnBu^n_2Cl_2$ and the phenolic oxygen of $H_2$3-MeOsalen. The loss of intensity of this latter peak, occurring on increasing the concentration of $SnBu^n_2Cl_2$, relative to that of the stationary peak at −185.5 ppm is explicable on the basis of increased hydrolysis of the salicylaldimine ligand.

Ligand hydrolysis was also observed in other reactions. For example, the ^{119}Sn NMR spectrum of a solution containing equimolar quantities of $SnBu_2Cl_2$ and $H_2$3-MeOsal1,3pn again showed a broad peak (at −123.0 ppm) and the sharp peak (at 188.0 ppm), but in this case the intensity of the latter peak (resulting from ligand hydrolysis) was very low. Reaction of Bu^nSnCl_3 with $H_2$3-MeOsalen in chloroform yielded an oily product, which was not identified, but a product from the reaction of $SnBu^nCl_3$ with $H_2$3-MeOsal1,3pn was isolated and identified as 1,3propylenediamine bishydrochloride, showing that in this case complete hydrolysis of the ligand occurs. Reaction of $SnBu^nCl_3$ with $H_2$3-MeOsal1,2pn in ethanol at room temperature resulted in the precipitation of $SnBu^nCl_2$(3-MeOsal1,2pnNH_2) in high yield.[21] However, ligand hydrolysis was not observed when $H_2$3-MeOsalphen and $H_2$3-MeOsalbiphen were employed as donor ligands. A chloroform solution containing $SnBu^n_2Cl_2$ and $H_2$3-MeOsalphen, in 1:1 molar ratio, showed only a broad peak at −44.08 ppm, and the position of this peak moved with increasing ratio of Lewis acid to base. Likewise, a chloroform solution containing $SnBu^n_2Cl_2$ and H_2salbiphen showed a single broad peak, the position of which was dictated by the acid/base ratio.

Ligand hydrolysis had not been considered in early synthetic studies or in ^{13}C and ^{1}H NMR studies of complex formation between organotin Lewis acids and salicylaldimine ligands. On the other hand, the possibility of hydrolysis of the organotin Lewis acid leading to stannoxane formation was clearly recognized.[6,9] In actual fact, if solutions of $SnBu^n_2Cl_2$ and $H_2$3-MeOsalen are not rigorously protected from water, two extra sharp bands located at −90 and −140 ppm due to $ClSnBu^n_2$-$OSnBu^n_2Cl$ are found in the NMR spectrum.

Reaction of $SnBu_2(NCS)_2$ with $H_2$3-MeOsalen again leads exclusively to the formation of what appears from analytical data to be a 1/1 addition complex (complex **B**). However, the crystallographic study revealed a considerably more complicated structure than that of **A**. It is an ionic adduct having the formulation {[$SnBu_2$(NCS)($H_2$3-MeOsalen)]$_2$(μ-$H_2$3-MeOsalen)}-[$SnBu_2(NCS)_4$]; analytical data correspond to those expected for a simple 1/1adduct formulation. The structure of the centrosymmetric ditin cation is shown in Figure 2a and that of the anion in Figure 2b. Selected bonding parameters are in Table 3. The presence of dangling ligands is again a surprising feature.

The ^{119}Sn Mössbauer spectrum of the complex revealed the existence of two tin environments with quadrupole splitting values of 4.59 and 3.69 $mm.s^{-1}$ and associated isomer shifts of 2.30 and 1.85 $mm.s^{-1}$, respectively. The larger quadrupole splitting is clearly associated with the anionic tin with the much greater C−Sn−C bond angle.[22] Rather surprisingly, however, the ^{119}Sn NMR spectrum of **B** (measured in dry chloroform) showed a single sharp signal at −294 ppm, and furthermore, the ^{13}C NMR spectrum was simple, showing evidence for only one type of salicylaldimine ligand and

(21) Timmins, B. Ph.D. Degree Thesis, National University of Ireland, 1995.

(22) Bancroft, T. M.; Platt, R. H. *Adv. Inorg. Radiochem.* **1972**, *15*, 159.

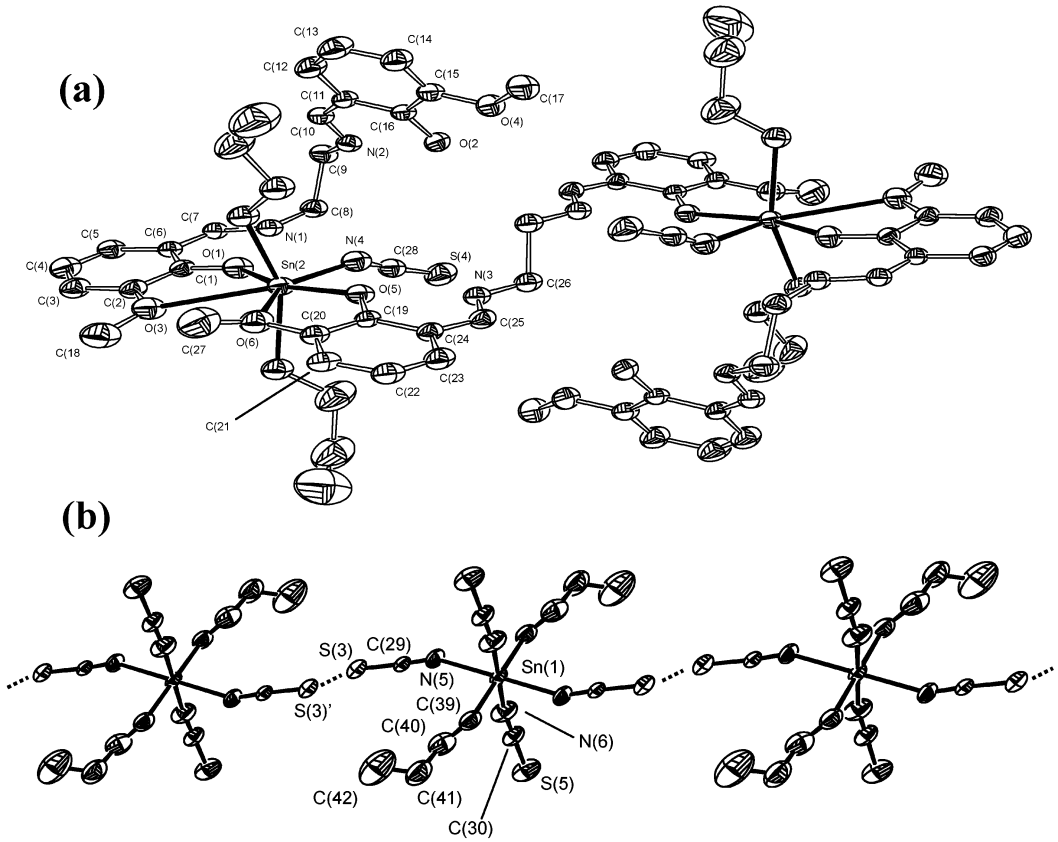


Figure 2. Structure of **B**. (a) Centrosymmetric ditin cation. (b) Chain arrangement of the anions resulting from short S−S contacts of 3.4 Å (30% ellipsoids).

Table 3. Selected Bond Lengths (Å) and Angles (deg) for B

Sn(1)−C(39)	2.134(7)	Sn(1)−N(5)	2.271(5)
Sn(1)−N(6)	2.284(7)	Sn(2)−C(31)	2.121(3)
Sn(2)−C(35)	2.097(4)	Sn(2)−O(1)	2.193(3)
Sn(2)−O(3)	2.913(3)	Sn(2)−O(5)	2.205(3)
Sn(2)−O(6)	2.946(3)	Sn(2)−N(4)	2.139(5)
C(39)−Sn(1)−N(5)	90.9(2)	C(39)−Sn(1)−N(6)	87.7(3)
N(5)−Sn(1)−N(6)	91.3(2)	C(35)−Sn(2)−C(31)	149.2(2)
C(35)−Sn(2)−N(4)	106.49(17)	C(35)−Sn(2)−O(1)	91.40(14)
C(35)−Sn(2)−O(3)	80.22(12)	C(35)−Sn(2)−O(5)	95.60(13)
C(35)−Sn(2)−O(6)	76.94(13)	C(31)−Sn(2)−N(4)	104.30(17)
C(31)−Sn(2)−O(1)	94.36(14)	C(31)−Sn(2)−O(3)	76.23(12)
C(31)−Sn(2)−O(5)	91.50(12)	C(31)−Sn(2)−O(6)	80.92(13)
N(4)−Sn(2)−O(1)	78.06(14)	O(1)−Sn(2)−O(3)	61.21(11)
O(3)−Sn(2)−O(6)	83.54(10)	O(5)−Sn(2)−O(6)	59.94(10)
N(4)−Sn(2)−O(5)	77.55(13)		

this being a ligand symmetrically involved in bonding interactions. The conductivity of chloroform and acetonitrile was only marginally altered by the addition of the complex. For example, the conductivity of a 0.003 M chloroform solution was 0.0 μs, and that of a 0.012 M solution 0.9 μs. It can thus be safely concluded that the ionic structure does not persist in solution. Molecular weight measurements in chloroform solutions were consistent with the existence of trimeric units of $SnBu_2(NCS)_2 \cdot H_2$3-MeOsalen. For example, measured molecular weights for 1.11, 1.44, and 2.16 M (based on the monomeric formulation) chloroform solutions were 1828.2, 1817.0, and 1755.3, respectively, and these values compare with a theoretical molecular weight of 1780.14 for a trimeric formulation. Taken as a whole, the data point to the existence of a complex of formula $[SnBu_2(NCS)_2(\mu\text{-}H_2$3-MeOsalen)$]_3$ in chloroform having a symmetrical cyclic structure such as that in Scheme 4.

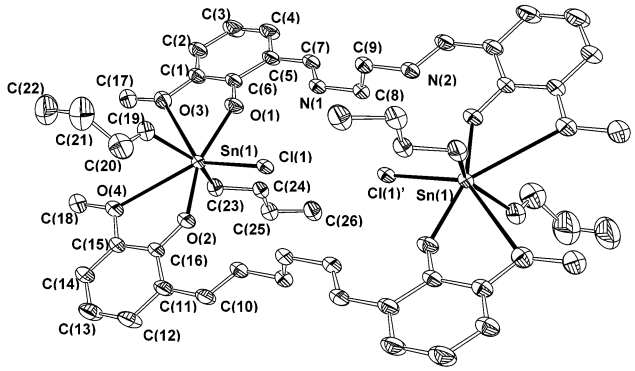
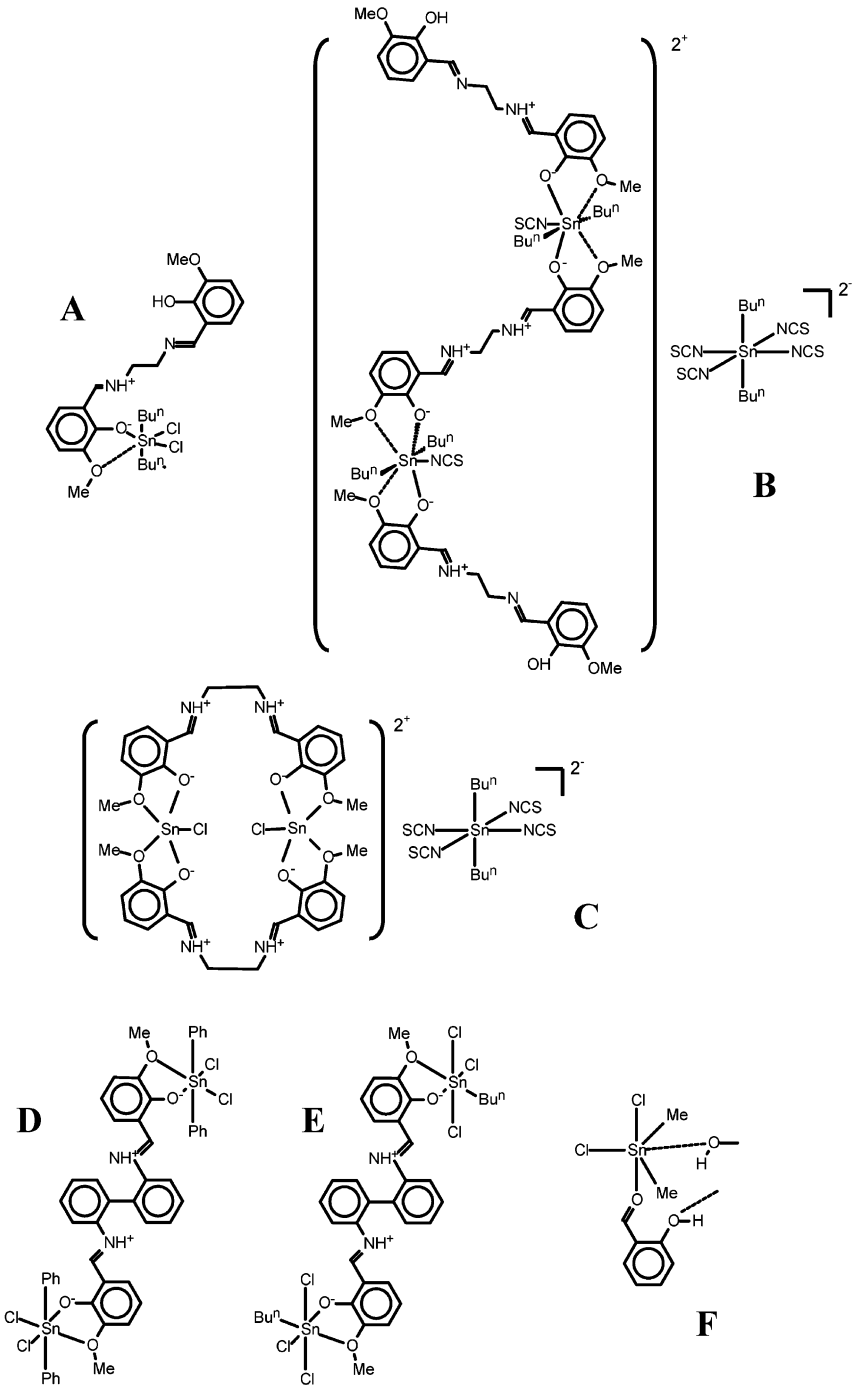


Figure 3. Centrosymmetric ditin cation of **C** (30% ellipsoids).

When equimolar quantities of $\{[SnBu_2(NCS)(H_2$3-MeOsalen)$]_2(\mu\text{-}H_2$3-MeOsalen)$SnBu_2\}[SnBu_2(NCS)_4]$, $SnBu_2Cl_2$, and NaCl are stirred together in warm methanol (approximately 50 °C), a new complex **C** is obtained which can be crystallized from acetonitrile. This is also an ionic adduct and has the formulation $[SnBu_2Cl(\mu\text{-}H_2$3-MeOsalen$)]_2[SnBu_2(NCS)_4]$. The interesting cyclic centrosymmetric ditin cation of this complex is in Figure 3, and selected bonding parameters are in Table 4. In this instance there are no dangling salicylaldimine ligands. As in the case of **B**, its addition to chloroform or acetonitrile had essentially no impact on conductivity measurements, and a ^{119}Sn NMR spectrum of a chloroform solution showed two signals, a sharp intense band at −182.5 ppm and a very broad low-intensity band at −294 ppm. A major difficulty associated with the interpretation of the NMR spectrum

Scheme 3. Schematic Representations of the Solid State Structures of A−F



in this instance stems from the ratio of tin to ligands; to every three tin atoms in solution there are two chloride, four thiocyanate, and two salicylaldimine ligands.

Although $SnBu^n_2Cl_2$ is involved in dynamic equilibrium with both $H_2$3-MeOsalphen and $H_2$3-MeOsalbiphen in solution (see earlier discussion), it did not prove possible to isolate adducts in the solid state. Acetonitrile and chloroform solutions of $SnBu^n_2Cl_2$ and $H_2$3-MeOsalphen (equimolar quantities) yielded intractable oils after slow removal of solvent. Acetonitrile and chloroform solutions containing either $SnBu^n_2Cl_2$ or $SnBu^n_2(NCS)_2$, along with $H_2$3-MeOsalbiphen, invariably yielded crystals of the free ligand. On the other hand, this latter ligand readily yielded the 2/1 adducts $(SnPh_2Cl_2)_2\cdot H_2$3-MeOsalbiphen (**D**) and $(SnBu^nCl_3)_2\cdot H_2$3-MeOsalbiphen (**E**). For each adduct, crystallographic data confirmed straightforward bisbidentate behavior of the ligand as in Scheme 2c, with the phenolic and methoxy atoms alone involved in donation to tin (see Figures 4 and 5 for views of the asymmetric units and Tables 5 and 6 for selected bonding parameters).

There are several features of the crystallographic structural data that merit comment. The cationic tin species of **B** and **C** have very similar tin coordination geometries. Methoxy and phenolic oxygen atoms from two separate salicylaldimine ligands form donor bonds to tin of a dibutyltin monothiocyanato cation in **B** and to a dibutyltin monochloro cation in **C**. The phenolic oxygen donor bonds to tin are strong, whereas the

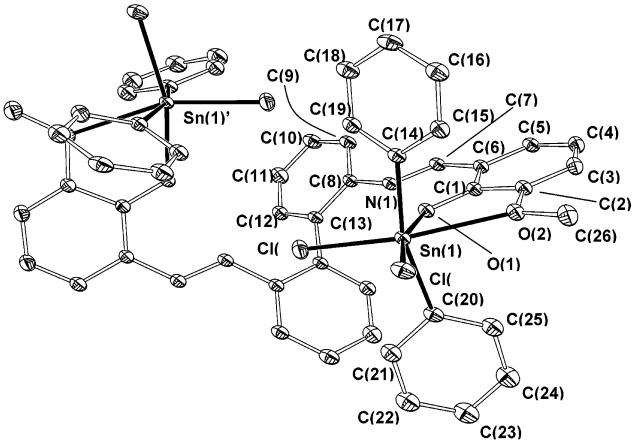


Figure 4. ORTEX[20] view of **D** (30% ellipsoids).

Scheme 4. Solution State Structure for $[SnBu^n_2(NCS)_2{\cdot}H_2$3-MeOsalen$]_3$ Consistent with Molecular Weight and NMR Data

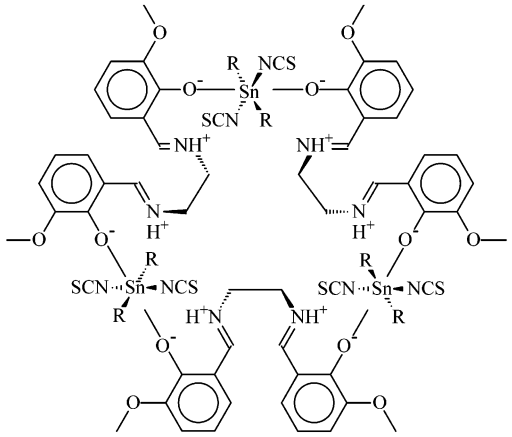


Table 4. Selected Bond Lengths (Å) and Angles (deg) for the Cation of C

Sn(1)−C(19)	2.096(4)	Sn(1)−C(23)	2.105(4)
Sn(1)−O(1)	2.232(3)	Sn(1)−O(2)	2.155(3)
Sn(1)−O(3)	3.150(4)	Sn(1)−O(4)	3.035(3)
Sn(1)−Cl(1)	2.4233(8)		
C(19)−Sn(1)−C(23)	144.2(2)	C(19)−Sn(1)−O(1)	91.1(2)
C(19)−Sn(1)−O(2)	96.5(2)	C(19)−Sn(1)−O(3)	74.3(2)
C(19)−Sn(1)−O(4)	76.74(19)	C(19)−Sn(1)−Cl(1)	107.09(18)
C(23)−Sn(1)−O(1)	94.0(2)	C(23)−Sn(1)−O(2)	92.2(2)
C(23)−Sn(1)−O(3)	79.23(19)	C(23)−Sn(1)−O(4)	78.01(16)
C(23)−Sn(1)−Cl(1)	108.68(13)	O(1)−Sn(1)−O(3)	56.45(9)
O(4)−Sn(1)−O(3)	86.53(9)	O(2)−Sn(1)−O(4)	59.50(10)
O(2)−Sn(1)−Cl(1)	79.16(8)	O(1)−Sn(1)−Cl(1)	78.40(7)

methoxy oxygens bonds to tin are very weak (contrasting with the much stronger methoxy-tin interactions in **D** and **E**); essentially they are van der Waals interactions. When the latter are considered, the coordination geometry about tin in each case is most aptly described as distorted pentagonal bipyramidal with axial alkyl groups. Within the equatorial plane the largest angle subtended at tin is by the methoxy oxygens, and not surprisingly, as a result of this and the weakness of the methoxy oxygen−tin interactions, the butyl groups fall away from the true axial positions toward the methoxy oxygens. In the case of the centrosymmetric ditin cation of **C**, the tin and chlorine atoms are essentially collinear and chlorine−chlorine separation within the ring is 3.99 Å.

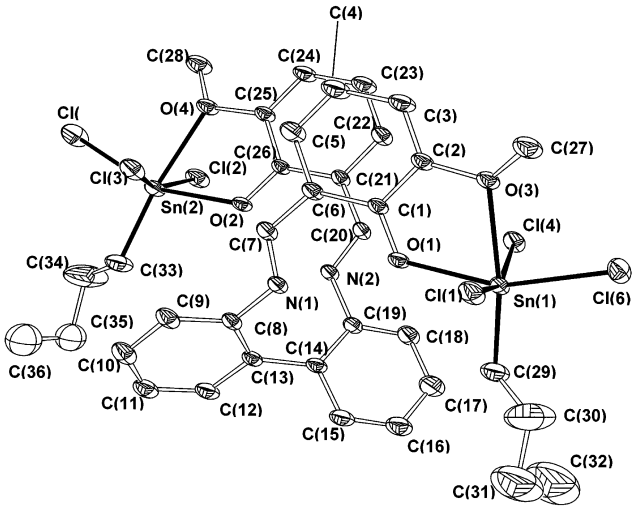


Figure 5. ORTEX[20] view of **E** (30% ellipsoids). Phenyl rings C(1)−C(6) and C(21)−C(26) are nonparallel, having a centroid−centroid separation of 3.95 Å and a closest C−C contact of 3.36 Å.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for D

Sn(1)−C(14)	2.140(3)	Sn(1)−C(20)	2.148(3)
Sn(1)−O(1)	2.206(2)	Sn(1)−O(2)	2.594(3)
Sn(1)−Cl(1)	2.3999(10)	Sn(1)−Cl(2)	2.5287(10)
C(14)−Sn(1)−C(20)	164.40(15)	C(14)−Sn(1)−O(1)	87.45(12)
C(20)−Sn(1)−O(1)	89.07(12)	C(14)−Sn(1)−Cl(1)	97.79(10)
C(20)−Sn(1)−Cl(1)	97.54(11)	O(1)−Sn(1)−Cl(1)	92.45(7)
C(14)−Sn(1)−Cl(2)	90.65(10)	C(20)−Sn(1)−Cl(2)	88.80(10)
C(14)−Sn(1)−O(2)	80.31(11)	C(20)−Sn(1)−O(2)	84.32(12)
O(1)−Sn(1)−O(2)	67.34(9)	Cl(1)−Sn(1)−Cl(2)	102.47(4)
Cl(2)−Sn(1)−O(2)	97.75(6)		

Table 6. Selected Bond Lengths (Å) and Angles (deg) for E

Sn(1)−C(29)	2.131(5)	Sn(1)−O(1)	2.116(2)
Sn(1)−O(3)	2.447(3)	Sn(1)−Cl(1)	2.4215(12)
Sn(1)−Cl(4)	2.4748(11)	Sn(1)−Cl(6)	2.3888(11)
Sn(2)−C(33)	2.124(4)	Sn(2)−O(2)	2.115(2)
Sn(2)−O(4)	2.444(3)	Sn(2)−Cl(2)	2.4209(12)
Sn(2)−Cl(3)	2.4710(11)	Sn(2)−Cl(5)	2.3888(11)
O(1)−Sn(1)−C(29)	100.23(15)	C(29)−Sn(1)−Cl(6)	104.01(14)
O(1)−Sn(1)−Cl(1)	86.18(7)	C(29)−Sn(1)−Cl(1)	104.83(16)
Cl(6)−Sn(1)−Cl(1)	91.12(4)	O(1)−Sn(1)−O(3)	71.22(9)
C(29)−Sn(1)−O(3)	170.70(15)	Cl(6)−Sn(1)−O(3)	84.34(7)
Cl(1)−Sn(1)−O(3)	78.74(7)	O(1)−Sn(1)−Cl(4)	83.89(7)
C(29)−Sn(1)−Cl(4)	96.39(16)	Cl(6)−Sn(1)−Cl(4)	89.78(4)
O(3)−Sn(1)−Cl(4)	79.33(7)	O(2)−Sn(2)−C(33)	100.80(15)
O(2)−Sn(2)−Cl(5)	155.31(7)	O(2)−Sn(2)−Cl(2)	86.19(7)
O(2)−Sn(2)−O(4)	70.94(9)	O(2)−Sn(2)−Cl(3)	83.86(7)
C(33)−Sn(2)−Cl(5)	103.62(14)	C(33)−Sn(2)−Cl(3)	96.62(16)
C(33)−Sn(2)−Cl(2)	104.62(16)	Cl(2)−Sn(2)−O(4)	78.70(7)
Cl(5)−Sn(2)−Cl(2)	91.07(4)	O(4)−Sn(2)−Cl(3)	79.40(7)
Cl(5)−Sn(2)−O(4)	84.46(7)	Cl(5)−Sn(2)−Cl(3)	89.80(4)

Both **B** and **C** contain centrosymmetric dibutyltetrathiocyanato tin(IV) anions. The geometries of the anions do not differ in any significant manner, but in the case of **B**, but not **C**, they are arranged in linear arrays in the lattice as in Figure 2b such that there are very short S−S contacts of 3.4 Å. S−S interactions are found in many structures,[23] but they are particularly noteworthy

(23) See for example: Turner, S. S.; Day, P.; Gelbrich, T.; Hursthouse, M. B. *J. Solid State Chem.* **2001**, *159*, 385. Or: Kepert, C. J.; Kurmoo, M.; Truter, M. R.; Day, P. *J. Chem. Soc., Dalton Trans.* **1997**, 607.

Table 7. Phenolic C−O and Imine C−N Bond Lengths (Å) for $H_2$3-MeOsalen, $H_2$3-MeOsalbiphen, and Their Adducts

	uncomplexed end of ligand		complexed end of ligand	
complex	C−O	C−N	C−O	C−N
G	1.349(2)	1.266(3)		
A	1.351(7)	1.267(8)	1.296(7)	1.285(8)
B	1.341(5)	1.260(6)	1.311(5)	1.287(6)
			1.307(5)	1.290(6)
C			1.302(4)	1.290(5)
			1.312(4)	1.289(5)
L[a]			1.286(6)	1.300(7)
H[b]	1.352(4)	1.280(4)		
	1.352(4)	1.281(4)		
	1.355(4)	1.284(4)		
	1.357(4)	1.272(4)		
D			1.304(4)	1.295(5)
E			1.322(4)	1.301(4)
			1.310(4)	1.294(4)
F			1.365(8)	

[a] L = $[La(H_2salen)(NO_3)_3(MeOH)_2]_n$ (see ref 23). [b] The first two and last two rows of data are for molecules 1 and 2, respectively (see Figure 7).

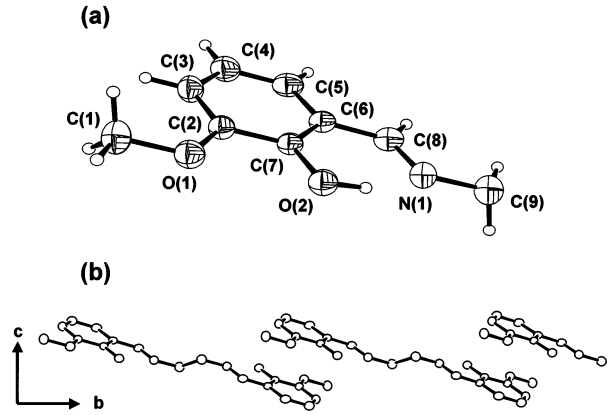


Figure 6. Structure of **G**. (a) Asymmetric unit (30% ellipsoids). The phenolic hydrogen is positioned as found. (b) Aromatic π-stacking of molecules. Opposing phenyl ring planes are parallel with a centroid−centroid separation of 3.73 Å.

in the present case where they have the effect of shortening the separation between the doubly charged anions.

The ability of salicylaldimine ligands to exist in zwitterionic forms in their adducts with lanthanide metals has already been demonstrated both by NMR spectroscopy and crystallographically.[24−26] In the case of $Dy(LH)_3(NO_3)_3$ (LH = 4-methoxy-*N*-*n*-butyl-2-hydroxybenzaldimine) the phenolic hydrogen was located bonded to the imine nitrogen and hydrogen-bonded to the phenolic oxygen; this is probably the case also for the Nd(III) and Tb(III) analogues.[25] In the case of $La(H_2salen)(NO_3)_3(MeOH)_2]_n$ the crystallographic data did not reveal the position of the phenolic hydrogen, but the transfer of this hydrogen to the imine nitrogen was suggested on the basis of the shortened C−O bond length compared to that of the C−O bond length in a related free ligand.[26]

The present crystallographic data provide the most complete description of zwitterion formation since crystallographic data are included for the free ligands as well as those for their adducts. Furthermore, in practically all cases the phenolic hydrogen position was clearly identified from the difference maps.

Crystallographic data for **A**, **B**, and **G** ($H_2$3-MeOsalen) revealed the positions of all phenolic hydrogen atoms. In the case of **G**, these hydrogens, as expected, are bonded to the phenolic oxygens. Both **A** and **B** have dangling salicylaldimine ligands, and at the free end of these ligands the phenolic hydrogen atoms were also located bonded to the phenolic oxygens. However, at the complexed end of the ligands the phenolic hydrogens were located bonded to the imine nitrogen atoms. The effect of zwitterion formation is clearly evident from the phenolic C−O and imine C=N bond lengths (see Table 7). At the uncomplexed end of the dangling ligands the bond distances under consideration are very similar to those of the free ligand (**G**). At the complexed end of the ligands the C−O bond lengths are considerably shorter (despite the fact that the oxygen forms a bond to tin) and the C=N bond distances considerably longer than the corresponding uncomplexed ligand bond lengths. It is now clear from the data in Table 7 that in the case of $La(H_2salen)(NO_3)_3(MeOH)_2]_n$ not only is the phenolic C−O bond length shortened as a result of adduct formation (as previously suggested) but the imine C=N bond length is lengthened as observed in the present case. In the case of **C**, only one of the phenolic hydrogens was located with certainty from the difference map. Significantly, it is bonded to the imine nitrogen, and in general C−O and C=N bond lengths point clearly to the presence of zwitterionic forms of the ligands.

Acetonitrile solutions containing $SnBu^n_2Cl_2$ and $H_2$3-MeOsalbiphen yielded crystals of two triclinic polymorphs of $H_2$3-MeOsalbiphen. One polymorph, **H**, contained two slightly different molecules per asymmetric unit, whereas the other contained only one molecule per asymmetric unit. The only significant difference between the molecules existing in these polymorphs is seen in the angle between phenyl planes of the biphenyl bridge. In the case of **H**, the angles are 62.6° and 63.3° (these compare with angles of 60.3° and 57.4° in **D** and **E**, respectively, the latter smaller angle probably being a consequence of the aromatic interactions indicated in Figure 5), whereas for the other polymorph the angle is 71.6°. It should be noted that neither of the structures feature the strong aromatic interactions that dictate the lattice structure of $H_2$3-MeOsalen (see Figure 6).

Corresponding bond lengths were virtually identical for the molecules of the two crystal modifications of $H_2$3-MeOsalbiphen. The data in Table 7 are for the structure with two molecules per asymmetric unit (see Figure 7). In general, while there does not appear to be a significant difference between the phenolic C−O bond lengths of $H_2$3-MeOsalen and $H_2$3-MeOsalbiphen, the C=N bond lengths of the latter are longer than those of the former, an observation that can clearly be related to the delocalization of the C=N bonds next to the phenyl groups. On formation of the adducts **D** and **E**, the C−O bond lengths decrease quite dramatically, whereas the

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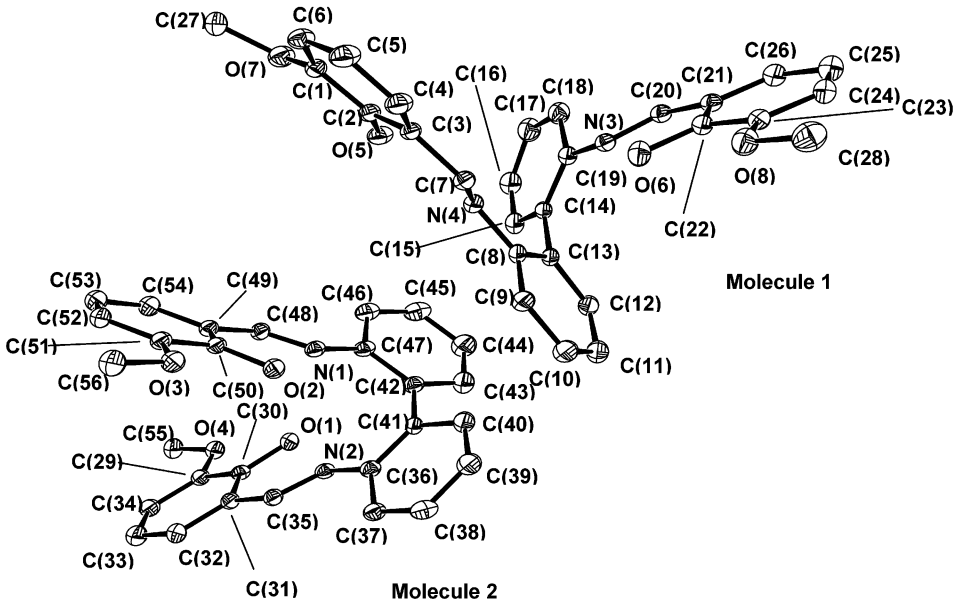

Figure 7. ORTEX[20] view of the asymmetric unit of **H** (30% ellipsoids).

C═N bond lengths increase, and this, once again, is indicative of zwitterion formation (in the cases of **D** and **E** all of the phenolic hydrogen atoms were located bonded to the imine nitrogen atoms).

It would appear that on adduct formation, salicylaldimine ligands, in general, assume zwitterionic forms. The catalytic role of tin(IV) Lewis acids and $FeCl_3$ (see ref 27) in promoting ligand hydrolysis can clearly be related to the protonation of the imine nitrogen, thus facilitating electrophilic attack of the imine carbon by water as the initial hydrolysis step.

In an attempt to observe the extent to which phenolic hydrogen transfer to the imine nitrogen would occur in the presence of a weak tin Lewis acid, trimethyltin chloride and $H_2$3-MeOsalen were added in equimolar quantities to warm acetonitrile. However, as the solution cooled, the only crystals that grew from solution were those of the starting materials.

In light of zwitterion formation by the salicylaldimine ligands, attention is drawn to the behavior of salicylaldehyde as a ligand, the latter differing from salicylaldimines in having a carbonyl group in place of the imine group. Preliminary details of the crystal structure of the adduct $SnMe_2Cl_2$·salicylaldehyde based on Weissenberg data have been reported.[28] The structure was redetermined in the course of the present study using image plate data, and this yielded much more accurate structural parameters. Furthermore, the phenolic hydrogen was located in the difference map.

The most significant feature of the structure of this adduct (**F**) (see Figure 8 for a view of the structure and Table 8 for selected bonding parameters) is the fact that it is the carbonyl oxygen rather than the phenolic oxygen that forms the intramolecular donor bond to tin, and this is a very weak bond [Sn−O = 2.702(4) Å]. The formation of a weak donor bond through the carbonyl group rather than a strong donor bond through the phenolic oxygen, as occurs in all of the salicylaldimine adduct structures, is a result of the fact that zwitterion formation does not occur; the phenolic hydrogen was located bonded to the phenolic oxygen. The inability to form the zwitterion also accounts for the fact that, whereas the salicylaldimine ligands exist in dynamic equilibrium with $SnBu^n_2Cl_2$ in solution, there is essentially no such interaction between either salicylaldehyde or 3-methoxysalicylaldehyde and $SnBu^n_2Cl_2$.

The phenolic C−O bond length [1.365(8) Å] is longer than that of $H_2$3-MeOsalen [1.349(2) Å] (presumably this latter bond length is very similar to that of free salicylaldehyde), this being a consequence of the fact that the phenolic oxygen forms a weak intermolecular donor bond to a neighboring tin [Sn−O = 3.383(5) Å], thus generating the chain structure of Figure 8. Within the chain, the phenyl groups are perfectly coplanar and

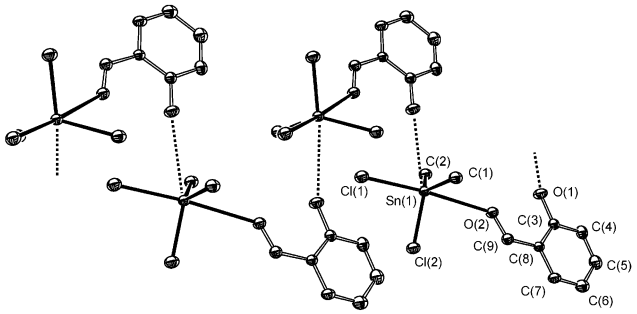

Figure 8. Section of a chain in the crystal structure of **F** (30% ellipsoids). Phenyl groups within each chain are coplanar. Each phenyl group is flanked by two phenyl groups from neighboring chains giving rise to centroid−centroid separations of 3.64 Å.

Table 8. Selected Bond Lengths (Å) and Angles (deg) for F

Sn(1)−C(1)	2.097(7)	Sn(1)−C(2)	2.110(6)
Sn(1)−Cl(1)	2.4028(16)	Sn(1)−Cl(2)	2.3522(16)
Sn(1)−O(2)	2.702(4)		
C(1)−Sn(1)−C(2)	132.0(3)	C(1)−Sn(1)−Cl(1)	101.30(19)
C(1)−Sn(1)−Cl(2)	110.65(19)	C(1)−Sn(1)−O(2)	81.2(2)
C(2)−Sn(1)−Cl(1)	101.22(18)	C(2)−Sn(1)−Cl(2)	108.91(19)
C(2)−Sn(1)−O(2)	79.70(19)	Cl(2)−Sn(1)−Cl(1)	95.02(6)
Cl(2)−Sn(1)−O(2)	80.34(9)	Cl(1)−Sn(1)−O(2)	175.29(10)

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each is flanked on each side by phenyl groups of neighboring chains. In this fashion each chain is zipped to four neighboring chains via significant aromatic π-interactions.

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Supporting Information Available: Tables giving details of crystal data, data collection and structure refinement, atomic coordinates, isotropic and anisotropic thermal parameters, and all bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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