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Transition-metal Schiff-base complexes as ligands in tin chemistry. Part 7. Reactions of organotin(IV) Lewis acids with $[M(L)]_2$ [M = Ni, Cu and Zn; H_2L = *N*,*N*′-bis(3-methoxysalicylidene)benzene-1,3-diamine and its -1,4-diamine analog]

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Abstract

Dinuclear complexes $[M(3MeO\text{-}sal\text{-}m\text{-}phen)(H_2O)]_2$ [M = Cu, Ni and Zn; 3MeO–H_2sal-*m*-phen = *N*,*N*′-bis(3-methoxysalicylidene)benzene-1,3-diamine] and $[M(3MeO\text{-}sal\text{-}p\text{-}phen)(H_2O)]_2$ [M = Cu, Ni and Zn; 3MeO–H_2sal-*p*-phen = *N*,*N*′-bis(3-methoxysalicylidene)benzene-1,4-diamine] were synthesised and reacted with diorganotin(IV) dihalides, dinitrates and dithiocyanates. Only in the case of those reactions involving $[M(3MeO\text{-}sal\text{-}m\text{-}phen)(H_2O)]_2$ with M = Ni or Zn were adducts obtained as the sole products of reaction; the adducts were all tetranuclear complexes. The tetranuclear adduct $\{(SnBu^n_2).[Ni(3MeO\text{-}sal\text{-}m\text{-}phen)(NCS)_2]\}_2\cdot$ 6MeCN results from salicylaldimine ligands, related by a 2-fold axis, adopting bridging roles by co-ordinating to each of the symmetry related nickel atoms through phenolic oxygen and imine nitrogen atoms, while their phenolic and methoxy oxygen atoms form donor bonds to the tin atoms of symmetry related dibutyltin cations. The salicylaldimine ligands, related by inversion, adopt the same bridging role towards the nickel atoms in the adduct $\{[SnBz_2(NO_3)]\cdot[Ni(3MeO\text{-}sal\text{-}m\text{-}phen)(NO_3)]\}_2$.6MeCN (Bz = benzyl), but as a result of the bidentate role of the nitrate co-ordinated to nickel, the arrangement of the phenolic and methoxy oxygens is such that each tin is co-ordinated quite strongly by a bidentate nitrate, a methoxy and two phenolic oxygen atoms while a second methoxy oxygen provides a weak Sn–O interaction, thus resulting in pseudo eight co-ordinate tin. ^{119}Sn Mössbauer parameters indicate that all of the adducts of di- and triorganotin halides are organotin aqua adducts with the donor water engaged in hydrogen bonding with Schiff-base oxygen atoms. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Salicylaldimine; Tin; Nickel; Copper; Mössbauer

1. Introduction

Previous studies in this laboratory [1] have shown that the metal salicylaldimine complexes of Fig. 1(a) with X = H are effective ligands for both inorganic and organotin species. When X becomes a methoxy group, the nature of the metal salicylaldimine complexes as ligands is, not surprisingly, radically altered, transforming them from bidentate to extremely effective tetradentate ligands. Much more surprisingly however is the finding that the behaviour of the complexes as ligands is markedly and dramatically influenced by the nature of the bridging group B of Fig. 1(a). This is well demonstrated by the fact that $SnMe_2(NCS)_2$ reacts with Ni(3MeO-sal1,2pn)[$H_2$3MeO-sal1,2pn = *N*,*N*′-bis(3-methoxysalicylidene)propane-1,2-diamine] to give a brick red diamagnetic 1/1 adduct whereas a similar reaction

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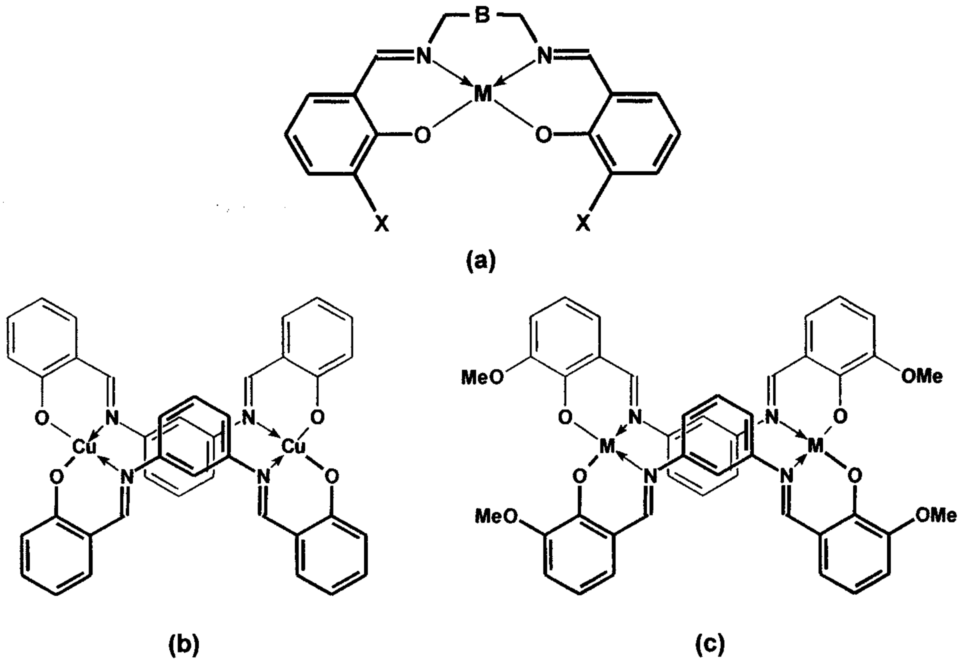

Fig. 1. (a) Divalent metal salicylaldimines; (b) the structure of Cu(sal-*m*-phen) and (c) the ligands of the present study (M = Cu, Ni and Zn).

with Ni(3MeO-sal1,3pn) [$H_2$3MeO-sal1,3pm = *N*,*N*′-bis(3-methoxysalicylidene)propane-1,3-diamine] results in the formation of a deep purple paramagnetic 1/1 adduct. It also became apparent that as the number of carbon atoms linking the imine nitrogen atoms increases beyond three, the effectiveness of the metal salicylaldimines as ligands is greatly reduced. For example, practically no organotin(IV) Lewis acids react with the complex Ni(3MeO-sal1,5pent) [$H_2$3MeO-sal1, 5pent = *N*,*N*′ - bis(3 - methoxysalecylidene)pentane - 1,5 - diamine].

Against this background our attention focused on Cu(sal-*m*-phen) [H_2sal-*m*-phen = *N*,*N*′-bis(salicylidene)benzene-1,3-diamine] and related complexes as potential donor molecules. This complex has a centrosymmetric dimeric structure [2] shown schematically in Fig. 1(b) in which the geometry about the copper atoms is not significantly different to that in the complexes of Fig. 1(a) where M = Cu. Thus, it would reasonably be assumed, though it has not been demonstrated, that the complex would behave as a bidentate donor ligand (through the phenolic oxygens). More specifically, the presence of methoxy substituents in the 3,3′ positions of the Schiff-base [see Fig. 1(c)] should potentially produce tetradentate donor ligands somewhat similar to those which we have previously investigated [1], the important difference being in the complex nature of the imine nitrogen bridge in the present case. In order to investigate the effect of this bridging system, complexes M(3MeO-sal-*m*-phen) and M(3MeO-sal-*p*-phen) [3MeO-H_2sal-*m*-phen = *N*,*N*′-bis(3-methoxysalicylidene)benzene-1,3-diamine; 3MeO-H_2sal-*p*-phen = *N*,*N*′-bis(3-methoxysalicylidene)benzene-1,4-diamine; M = Ni, Cu and Zn] were synthesised and their reactions with organotin(IV) Lewis acids investigated.

2. Experimental details

2.1. Instrumentation

Infrared spectra were recorded on a Perkin Elmer 983G spectrometer. Details of the Mössbauer spectrometer and spectrum curve-fitting program have been published [3].

2.2. Synthesis of complexes [M(3-MeOsal-m-phen).H_2O)]$_2$ and [M(3-MeOsal-p-phen).H_2O]$_2$ (M = Cu, Ni and Zn)

All complexes, with the exception of [Ni(3-MeOsal-*p*-phen).H_2O]$_2$ were prepared by a common procedure. Typically, 0.01 mol of the ligand was dissolved in 150 cm.^{3} of methanol and an equimolar quantity of the metal acetate was added. After refluxing for 3 h and cooling the reaction solution to r.t., the resulting precipitate of the metal complex was isolated by filtration and dried under vacuum. Nickel acetate did not react with $H_2$3-MeOsal-*p*-phen under these conditions but the desired metal complex was obtained when bis(acetylacetenato)nickel(II) was substituted for nickel acetate. Analytical data are in Table 1.

The reaction of nickel acetate with 3MeO-H_2sal-*m*-phen was noteworthy in that a green microcrystalline solid which initially formed, rapidly underwent a colour change to yellow in the course of isolation; accompany-

Table 1
Analytical data[a]

	C	H	N	Hal
[Ni(3MeO-sal-*m*-phen)(H_2O)]$_2$	58.90 (58.58)	4.61 (4.47)	6.16 (6.21)	
[Ni(3MeO-sal-*p*-phen)(H_2O)]$_2$	59.29 (58.58)	4.00 (4.47)	6.52 (6.21)	
[Cu(3MeO-sal-*m*-phen)(H_2O)$_2$]$_2$	55.74 (55.75)	4.33 (4.68)	5.60 (5.91)	
[Cu(3MeO-sal-*p*-phen)(H_2O)]$_2$	58.35)57.95)	4.34 (4.42)	6.23 (6.14)	
[Zn(3MeO-sal-*m*-phen)(H_2O)]$_2$	57.32 (57.72)	4.61 (4.40)	5.79 (6.12)	
[Zn(3MeO-sal-*p*-phen)(H_2O)]$_2$	56.61 (57.72)	4.72 (4.40)	5.94 (6.12)	
{SnBu^n_2.[Ni(3MeO-sal-*m*-phen)(NCS)$_2$]}$_2$	48.25 (49.14)	4.72 (4.64)	7.24 (7.16)	
{SnBu^n_2.[Ni(3MeO-sal-*m*-phen)(NCS)$_2$].H_2O}$_2$	47.51 (48.03)	4.62 (4.79)	6.90 (7.00)	
{[$SnBz_2$(NO_3)].[Ni(3MeO-sal-*m*-phen)(NO_3)]}$_2$	49.08 (50.39)	4.26 (3.76)	6.41 (6.53)	
{[SnBu^n_2(NO_3)].[Ni(3MeO-sal-*m*-phen)(NO_3)].H_2O}$_2$	43.80 (44.59)	4.75 (4.74)	6.56 (6.93)	
{[SnBu^n_2(NO_3)].[Zn(3MeO-sal-*m*-phen)(NO_3)].H_2O}$_2$	43.19 (44.25)	4.80 (4.70)	6.55 (6.88)	
{[$SnPh_2$(NO_3)].[Ni(3MeO-sal-*m*-phen)(NO_3)].H_2O}$_2$	47.44.(48.16)	3.67 (3.57)	6.38 (6.61)	
{[$SnPh_2$(NO_3)].[Zn(3MeO-sal-*m*-phen)(NO_3)].H_2O}$_2$	47.37 (47.78)	3.77 (3.54)	6.10 (6.58)	
{[$SnMe_2$(NO_3)$_2$]$_3$.[Ni(3MeO-sal-*m*-phen)]2}.H_2O	35.95 (35.32)	4.78 (3.30)	9.47 (8.24)	
{[Sn$Bu^n_2$$Cl_2$].[Ni(3MeO-sal-*m*-phen)].2H_2O}$_2$	46.48 (46.62)	5.33 (5.22)	3.23 (3.62)	9.79 (9.17)
{[Sn$Bu^n_2$$Cl_2$].[Zn(3MeO-sal-*m*-phen)].2H_2O}$_2$	47.03 (46.22)	5.23 (5.17)	3.65 (3.59)	10.15 (9.10)
{[$SnBz_2Cl_2$].[Ni(3MeO-sal-*m*-phen)].2H_2O}$_2$	51.11 (51.42)	4.70 (4.32)	3.84 (3.33)	9.24 (8.43)
{[$SnBz_2Cl_2$].[Zn(3MeO-sal-*m*-phen)].2H_2O}$_2$	51.23 (51.01)	4.19 (4.28)	3.44 (3.30)	9.28 (8.36)
{[$SnPh_2Br_2$].[Ni(3MeO-sal-*m*-phen)].2H_2O}$_2$	44.91 (45.28)	3.66 (3.58)	2.91 (3.12)	17.86 (17.72)
{[$SnPh_3Cl$].[Ni(3MeO-sal-*m*-phen)].2H_2O}$_2$	56.39 (56.22)	4.66 (4.36)	4.73 (3.28)	4.27 (4.15)
{SnBu^n_2.[Ni(3MeO-sal-*p*-phen)(NCS)$_2$].H_20}$_2$	48.66 (48.03)	3.86 (4.79)	6.92 (7.00)	

[a] All melting points (with decomposition) of new complexes >200°C.

ing this colour change there was a loss of crystallinity. Recrystallisation of the yellow powder from methanol yielded, once again, the unstable green crystalline material. All data reported are for the stable yellow complex. Crystals of the green complex proved to be unsuitable for an X-ray structure determination.

2.3. Synthesis of the adducts

All of the organotin(IV) halide and thiocyanate adducts of Table 1 were prepared by a common procedure. Typically, 0.5 g. of the Metal Schiff-base complex and an equimolar quantity of the tin Lewis acid were stirred in acetonitrile (≈ 50 cm^3) for 3 h at r.t., after which time the solid adduct was isolated by filtration and dried under vacuum.

Samples of {SnBu^n_2.[Ni(3-MeOsal-*m*-phen)(NCS)$_2$}$_2$ from different reactions had colours ranging from emerald green to yellow. Green samples exhibited no bands in their infrared spectra in the region 3000–4000 cm^{-1} whereas yellow samples exhibited a band at 3387 cm^{-1}. On standing in the solid state, green samples became yellow, but on crystallisation from acetonitrile the yellow solids yielded green crystals which gave identical infrared spectra to those of the initially formed green powders. A suitable green crystal for a crystallographic study was obtained from a crystallisation in acetonitrile. Due to the instability of the green crystals when dried, the crystal selected for the crystallographic study was sealed in a capillary containing residual solvent.

The only other organotin(IV) chloride or thiocyanate adduct which yielded crystals suitable for crystallography was {$SnPh_3Cl \cdot H_2O \cdot$[Ni(3-MeO-*m*-phen)$\cdot H_2O$]}$_2$. Green crystals of the complex were obtained from acetonitrile. However, these crystals were extremely unstable out of solution and, furthermore, diffracted very weakly. As a result, the crystal structure was not successfully determined.

The organotin nitrate adducts were isolated using a common procedure. Typically, 0.5 g. of the diorganotin(IV) dihalide were dissolved in dry acetone and a 2 M equivalent of silver nitrate added to the solution in a dry nitrogen atmosphere (in order to avoid the formation of stannoxane). The solution was refluxed for 1 h and the sodium chloride removed by filtration (under nitrogen). An equimolar quantity (to that of the tin Lewis acid) of the metal Schiff-base complex was added to the acetone solution and the resulting reaction mixture stirred at r.t. for 3 h, after which time the resulting solid adduct was isolated by filtration and dried under vacuum. Only one nitrate adduct, {SnBz(NO_3).[Ni(3-MeOsal-*m*-phen)(NO_3)]}2, yielded crystals which were suitable for a crystallographic study. The crystals, which were grown in acetonitrile, were unstable when removed from the solvent and thus the crystal selected for the crystallographic study was sealed in a capillary containing residual solvent.

2.4. X-ray crystallography

Crystallographic details are in Table 2. Both structures were solved by direct methods, SHELX 86 [4], and refined by full-matrix least squares, SHELX 93 [5]. Data were corrected for Lorentz and polarisation effects but not for absorption. In the case of **A**, one of the terminal carbon atoms of a butyl group was disordered over three positions and co-ordinates for these [C(30), C(130) and C(230)] are included in Table 3; only C(30) is shown in Fig. 2. Hydrogen atoms were included in calculated positions in final refinement cycles. All non-hydrogen atoms were refined anisotropically. Calculations were carried out on a VAX 6610 computer. The programs ORTEP[6] and ORTEX [7] were used to produce the drawings of Figs. 2 and 3.

Table 2
Crystallographic data[a]

	A	**B**
Empirical formula	$C_{38}H_{45}N_7O_4S_2NiSn$	$C_{42}H_{41}N_7O_{10}NiSn$
M	905.328	981.27
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a (Å)	32.844(2)	11.390(4)
b (Å)	14.432(2)	11.529(2)
c (Å)	25.208(3)	17.360(3)
α (°)	90.0	72.200(14)
β (°)	133.738(12)	88.70(2)
γ (°)	90.0	90.53(2)
V (Å^3)	8633(2)	2139.9(10)
Z	8	2
D_{calc} (g cm^{-3})	1.393	1.523
Absorption coefficient (mm^{-1})	1.168	1.089
$F(000)$	3712.0	1000.0
Crystal size (mm)	$0.2\times0.23\times0.25$	$0.25\times0.23\times0.28$
θ Range (°)	2.24–23.97	2.16–28.23
Index ranges	$0\leq h\leq 34$ $0\leq k\leq 16$ $-27\leq l\leq 27$	$0\leq h\leq 11$ $-11\leq k\leq 11$ $-17\leq l\leq 17$
Reflections collected	3348	6765
Independent reflections (R_{int})	3161 (0.0265)	6599 (0.0402)
Data/restraints/parameters	3161/0/507	6599/0/556
Goodness-of-fit on F^2	0.912	0.959
Final R indicies ($I>2\sigma I$)		
R	0.0347	0.0605
R'	0.0922	0.1602
Final R indicies (all data)		
R	0.0365	0.0906
R'	0.0944	0.1751
Largest difference peak, hole (eÅ^{-3})	0.539, -0.743	1.320, -1.340

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[a] Details in common: T (K) 293(2); λ(Mo–K$_\alpha$ = 0.71069 Å); refinement, full-matrix least squares on F^2; $R=(\Sigma||F_o|-|F_c||)/\Sigma|F_o|$ (based on F); $R'=[\Sigma w\ (|F_o-F_c|)^2]^{1/2}/[\Sigma w(|F_o|)^2]^{\frac{1}{2}}$ (based on F^2); $w=1/[(\sigma F_o)^2+(0.1{*}P)^2]$ for **A** and $1/[(\sigma F_o)^2+(0.11{*}P)^2]$ for **B**. Goodness-of-fit $=[\Sigma w\ (|F_o^2|-|F_c^2|)^2/(N_{obs}-N_{parameters})]^{\frac{1}{2}}$.

Table 3
Selected bond lengths (Å) and angles (°) for **A**

Sn(1)–O(1)	2.100(4)	Sn(1)–O(2)	2.085(4)
Sn(1)–O(3)	2.493(5)	Sn(1)–O(4)	2.517(5)
Sn(1)–C(23)	2.122(7)	Sn(1)–C(27)	2.119(11)
Ni(1)–O(1)	2.088(4)	Ni(1)–O(2)	2.091(4)
Ni(1)–N(1)	2.104(5)	Ni(1)–N(2)	2.083(5)
Ni(1)–N(3)	2.050(6)	Ni(1)–N(4)	2.041(6)
S(1)–C(31)	1.626(7)	C(31)–N(3)	1.128(10)
S(2)–C(32)	1.617(8)	C(32)–N(4)	1.149(10)
O(1)–C(1)	1336(8)	O(2)–C(20)	1.339(8)
O(3)–C(19)	1.381(8)	O(4)–C(2)	1.383(9)
N(1)–C(7)	1.275(8)	N(1)–C(8)	1.465(7)
N(2)–C(12)	1.431(9)	N(2)–C(14)	1.265(9)
C(1)–C(6)	1.404(10)	C(1)–C(2)	1.425(8)
C(2)–C(3)	1.354(10)	C(3)–C(4)	1.372(12)
C(4)–C(5)	1.374(9)	C(5)–C(6)	1.392(9)
C(6)–C(7)	1.455(8)	C(8)–C(9)	1.360(11)
C(8)–C(13)	1.381(10)	C(9)–C(10)	1.399(9)
C(10)–C(11)	1.384(11)	C(11)–C(12)	1.360(11)
C(12)–C(13)	1.391(8)	C(14)–C(15)	1.459(11)
C(15)–C(20)	1.393(9)	C(15)–C(16)	1.411(11)
C(16)–C(17)	1.351(13)	C(17)–C(18)	1.393(12)
C(18)–C(19)	1.368(11)	C(19)–C(20)	1.415(11)
C(27)–Sn(1)–C(23)	143.0(3)	O(2)–Sn(1)–O(1)	75.8(2)
O(1)–Sn(1)–O(4)	68.13(14)	O(1)–Sn(1)–C(23)	109.1(3)
C(27)–Sn(1)–O(1)	100.4(3)	O(2)–Sn(1)–O(3)	68.8(2)
O(2)–Sn(1)–C(23)	100.0(2)	C(27)–Sn(1)–O(2)	108.7(3)
O(3)–Sn(1)–O(4)	148.8(2)	C(23)–Sn(1)–O(3)	88.6(3)
C(27)–Sn(1)–O(3)	80.8(3)	C(23)–Sn(1)–O(4)	81.2(2)
C(27)–Sn(1)–O(4)	89.8(3)	O(1)–Ni(1)–O(2)	75.9(2)
O(1)–Ni(1)–N(1)	88.6(2)	N(3)–Ni(1)–O(1)	85.3(2)
N(4)–Ni(1)–O(1)	88.7(2)	N(2)–Ni(1)–O(2)	88.8(2)
N(3)–Ni(1)–O(2)	90.8(2)	N(4)–Ni(1)–O(2)	85.4(2)
N(2)–Ni(1)–N(1)	106.7(2)	N(3)–Ni(1)–N(2)	92.7(2)
N(4)–Ni(1)–N(2)	92.5(2)	N(3)–Ni(1)–N(1)	90.6(2)
N(4)–Ni(1)–N(1)	91.6(2)	N(3)–Ni(1)–N(4)	173.6(2)
N(3)–C(31)–S(1)	179.8(6)	C(31)–N(3)–Ni(1)	165.3(6)
N(4)–C(32)–S(2)	176.9(8)	C(32)–N(4)–Ni(1)	170.8(6)

Material available from the Cambridge Crystallographic Data Centre comprises atom co-ordinates, thermal parameters and remaining bond lengths and angles.

3. Results and discussion

With the exception of [Ni(3-MeOsal-*p*-phen).H$_2$O]$_2$ which was prepared from the reaction of the bis(acetylacetenato)nickel complex with the Schiff-base ligand, the other metal complexes were readily prepared from the reaction of the metal acetate with the appropriate ligand. In the light of the crystallographic data previously presented for [Cu(sal-*m*-phen)]$_2$.2(CHCl$_3$) [2] and the crystallographic data of the present study, the complexes are given dimeric formulations. Infrared data clearly establish that all of the complexes are hydrates. However, the unstable green crystals obtained from crystallisation of yellow [Ni(3MeO-*m*-phen)(H$_2$O)]$_2$ and which rapidly revert to the yellow hydrate (see Section 2), are quite likely those of the anhydrous complex.

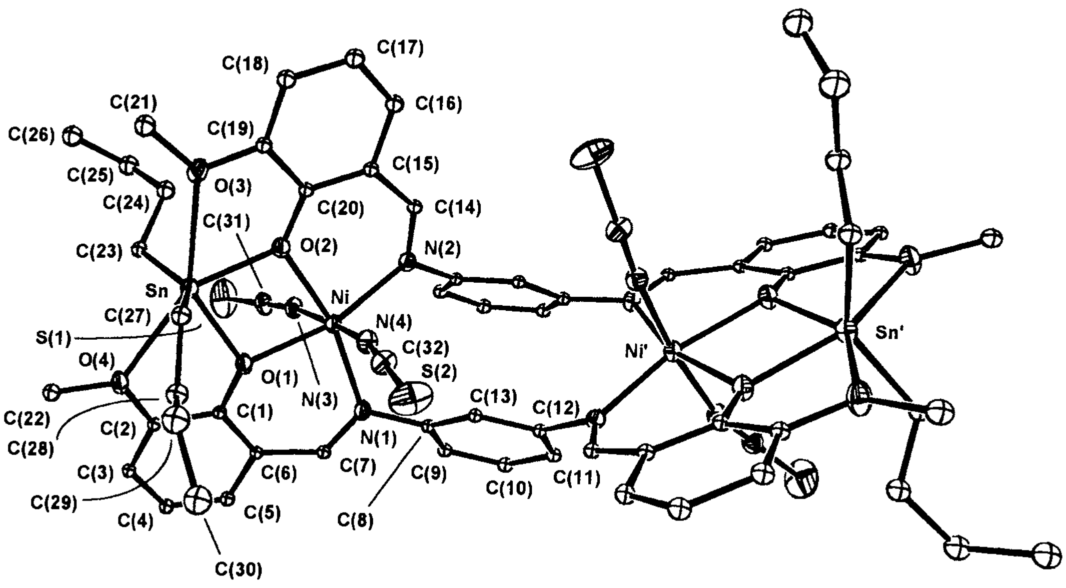

Fig. 2. The dimeric structure of **A**.

Magnetic moments of the nickel complexes (see Table 5) are compatible with either five or six co-ordinated nickel(II). Unfortunately, bands resulting from d–d transitions in the reflectance spectra of the copper and nickel complexes were rather poorly defined as a result of tailing of charge transfer bands into the visible region and this prevented reliable structural conclusions being made from reflectance spectra; this problem has previously been noted in the case of the reflectance spectrum of [Cu(sal-*m*-phen)]$_2$ [2]. However, the magnetic data for the nickel complexes make it clear that at least one water molecule is co-ordinated to each nickel. In view of the extremely pronounced tendency for this co-ordinated water to be involved in hydrogen bonding interactions with the methoxy and phenolic oxygens of neighbouring molecules [8], it is highly likely that this is the situation in the present complexes thus giving hydrogen bonded dimers or chains.

On the assumption that the disposition of the methoxy and phenolic oxygens in the present complexes is similar to that in, for example, Ni(3MeO-sal1,3pn). H_2O [9] [3MeO-H2sal1,3pn = *N*,*N*′-bis(3-methoxysalicylidene)propane-1,3-diamine], there are two ways in which organotin(IV) Lewis acids can potentially react with them. The water molecule involved in hydrogen bonding with the Schiff-base oxygens may at the same time form a donor bond to tin, as in the case of $SnPh_3Cl.H_2O$/Ni(3MeO-sal1,3pn) (1/1) [10], or alternatively, this water may be displaced while tin becomes involved in donor bond formation with the Schiff-base oxygens, as in the case of $SnBu_2$.[Ni(3MeO-sal1,3pn)(NCS)$_2$] [9].

In actual fact, the diorganotin Lewis acids SnR_2X_2 (R = benzyl, Ph, Me or Bu^n; X = nitrate, halide or thiocyanate) reacted with all of the new nickel(II), copper(II) and zinc(II) Schiff-base complexes. However, the Schiff-base ligands proved to be somewhat more labile than those in complexes M(3-MeOsal1,3pn) (though less labile then those in divalent metal complexes with bidentate Schiff-base ligands) with the result that there was a tendency for reactions to proceed beyond adduct formation. Analytical data suggested that in most cases 1/1 (i.e. one tin per nickel centre) addition complexes were being formed but only in the case of the complexes listed in Table 1 were the adducts reasonably free of impurities from further reactions. Thus, reactions with copper complexes led more frequently than in the case of nickel analogs to reactions other than simple straightforward 1/1 adduct formation. Furthermore, greater success in obtaining relatively pure 1/1 addition complexes was achieved with the *m*-phenylene than with the *p*-phenylene imine nitrogen bridged-Schiff-base complexes.

The adduct formed between SnBu$^n_2$(NCS)$_2$ and [Ni3-MeOsal-*m*-phen) (H_2O)]$_2$ has a green anhydrous form and a yellow hydrated form (see Section 2). A crystallographic study of the anhydrous adduct confirmed it to be the interesting tetranuclear complex {SnBu$^n_2$.[Ni3-MeOsal-*m*-phen)(NCS)$_2$]}$_2$ (**A**) (the crystal contains three molecules of lattice acetonitrile per asymmetric unit).

The dimeric structure of **A** (with the six associated lattice acetonitrile molecules omitted) is shown in Fig. 2. Selected molecular parameters are in Table 3. The Schiff-base ligands adopts the same bridging role as that displayed by the ligands in [Cu(sal-*m*-phen)]$_2$.2($CHCl_3$), the essential difference being that, while the ligands in the latter are related by a centre of inversion, they are related by a 2-fold axis in **A**. The mode of co-ordination of tin is the same as that in the

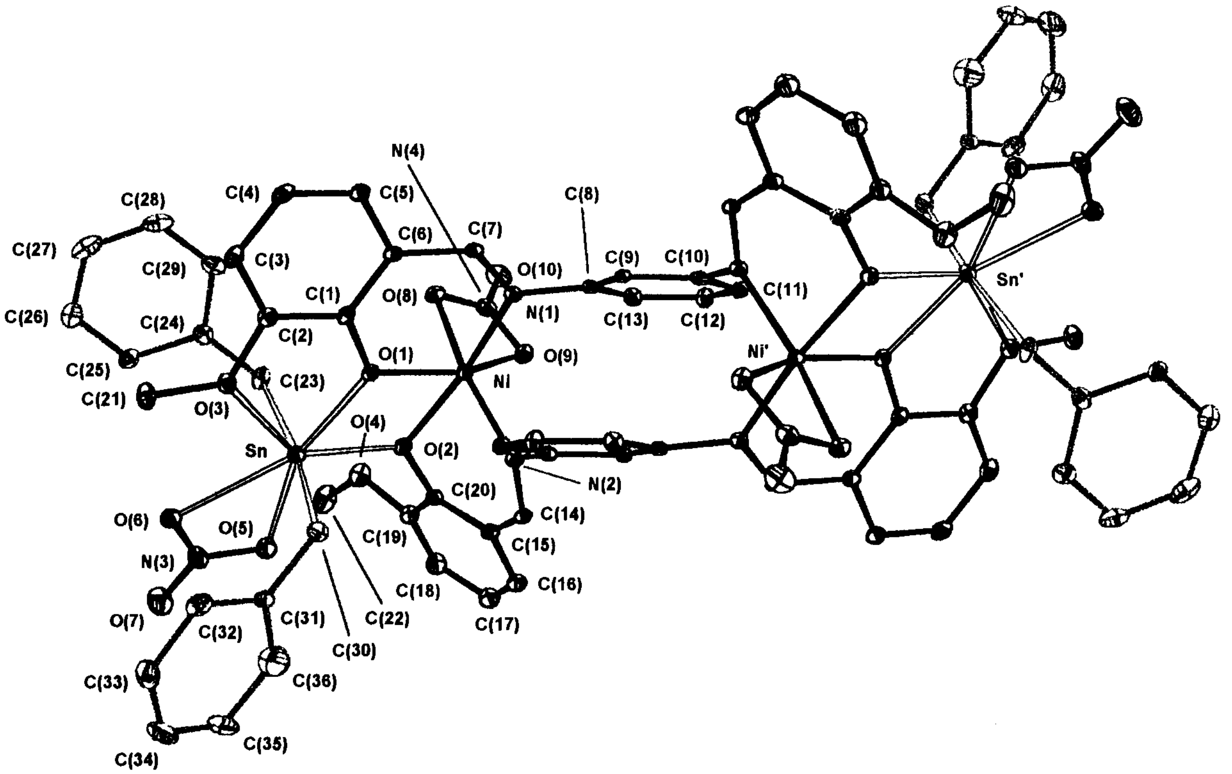

Fig. 3. The dimeric structure of **B**.

bimetallic complex SnBu^n_2.[Ni(3MeO-sal1,3pn)(NCS)$_2$] [9] and, in fact, the skew trapezoidal bipyramidal co-ordination geometry about the tin is remarkably similar for the two complexes. This is emphasised by the fact that both the C–Sn–C bond angle and the bond angles within the plane defined by the Schiff-base oxygen atoms in the present complex differ by no more than 3° from analogous angles in SnBu^n_2.[Ni(3-MeOsal1,3pn) (NCS)$_2$]. The Sn–O bond lengths, involving the phenolic oxygens, for the two complexes agree within experimental error, but the Sn–O bond lengths, involving the methoxy oxygens, in **A** [2.493(5) and 2.517(5) Å] are significantly shorter than those for SnBu^n_2.[Ni(3-MeOsal1,3pn)(NCS)$_2$] [2.567(4) and 2.603(3) Å]. The differences in the bond lengths involving the methoxy oxygens can be related to the manner in which the two halves of the Schiff-base ligands pivot about nickel in the two complexes.

Despite the marked similarity in the tin co-ordination geometries in **A** and SnBu^n_2.[Ni(3-MeOsal1,3pn) (NCS)$_2$], the complexes differ significantly in their reactions with dimethylformamide (dmf). SnBu^n_2.[Ni(3-MeOsal1,3pn)(NCS)$_2$] and its dimethyltin analog readily reacted with dimethylformamide to give seven co-ordinated tin adducts [9] whereas **A** reacted with dmf to give Ni(NCS)$_2$(dmf)$_4$ and dibutyltin Schiff-base complexes. This latter reaction again emphasises the more labile nature of the Schiff-base ligands in **A**.

The adduct {[SnBz$_2$(NO$_3$)].[Ni(3MeO-sal-*m*-phen) (NO$_3$)]}$_2$ (**B**) displays significant structural differences to **A**. The dimeric structure of this adduct (excluding three lattice molecules of acetonitrile per asymmetric unit) is shown in Fig. 3 while selected molecular parameters are in Table 4. The salicylaldimine ligands have the same bridging role as the ligands in **A** and in [Cu(3-MeO-sal-*m*-phen)]$_2$ and, as in the case of the latter complex, they are related by a centre of inversion.

Contrasting with the situation in **A** where two thiocyanate groups migrated to nickel, in the case of **B** only one nitrate thus migrates. That one nitrate should remain coordinated to tin is predictable since, in bimetallic complexes of the present type, there seems to be no tendency to generate cations (SnR$_2$)$^{2+}$ where R is phenyl or benzyl. What most significantly distinguishes the structure of **B** from the structures of adducts of diorganotin dinitrates with M(3MeO-sal1,3pn) (M = Ni, Co or Zn) [1] is the fact that, in the latter adducts, nitrate acts as a monodentate ligand to nickel, cobalt and zinc, whereas in **B** it is co-ordinated to nickel in a clearly bidentate fashion thus giving rise to Ni–O bond lengths of 2.035(4) and 2.139(5) Å. The flexibility of the ligands in their bisbidentate bridging role in **B** apparently makes it energetically more favourable for the nitrate to act as a bidentate ligand to nickel than it would in adducts of Ni(3-MeOsal1,3pn) where the relatively short 1,3-propylene bridging group has a constraining influence on nickel coordination geometry.

The most significant effect of the bidentate nitrate group is to prevent the usual co-planarity (or approximately so) of the imine nitrogen and phenolic oxygen atoms. As a result, the two halves of the salicylaldimine ligands, encapsulating nickel in **B,** pivot about the metal in a very different manner to the way in which they do so in **A,** thus providing a much greater methoxy oxygen separation in **B** (the methoxy oxygen separations in **A** and **B** are 4.823 and 5.521 Å, respectively). This makes it possible for the nitrate remaining on tin to adopt a bidentate role, contrasting with its monodentate role in the complex [SnBz$_2$(NO$_3$)].[Co(3MeO-sal1,3pn)(NO$_3$)] [10]. The tin coordination geometry in **B** approximates (rather poorly) pentagonal bipyramidal geometry with the phenolic oxygens, O(1) and O(2), two nitrate oxygens, O(5) and O(6), and a methoxy oxygen, O(3), defining the equatorial plane and the axially located carbon atoms subtending an angle of 170.8(3)° at tin. However, the remaining methoxy oxygen, O(4), is only 3.315 Å from tin, a distance which is within the sum of the van der Waal's radii of tin(IV) and oxygen and if this interaction is recognised, the tin coordination number can be considered as eight (in the case of the 1/1 adduct of dimethyltin dichloride with salicylaldehyde there is clear evidence for an intermolecular Sn–O bond at a length of 3.336 Å [11]). This coordination number has only once being encountered in a diorganotin(IV) complex, namely in the anion [SnPh$_2$(NO$_3$)$_3$]$^-$ in which tin has well defined hexagonal bipyramidal geometry [12].

Table 4
Bond lengths (Å) and angles [°] for **B**

Sn(1)–O(1)	2.280(4)	Sn(1)–O(2)	2.131(4)
Sn(1)–O(3)	2.391(4)	Sn(1)–O(5)	2.300(5)
Sn(1)–O(6)	2.579(5)	Sn(1)–C(23)	2.120(7)
Sn(1)–C(30)	2.114(7)	Ni(1)–O(1)	1.958(4)
Ni(1)–O(2)	2.071(4)	Ni(1)–O(8)	2.139(5)
Ni(1)–O(9)	2.035(4)	Ni(1)–N(1)	2.055(5)
Ni(1)–N(2)	2.064(5)	O(1)–C(1)	1.291(7)
O(2)–C(20)	1.313(7)	N(1)–C(7)	1.230(7)
N(1)–C(8)	1.475(8)	N(2)–C(10)	1.368(7)
N(2)–C(14)	1.259(7)	C(1)–C(2)	1.424(9)
C(1)–C(6)	1.462(9)	C(2)–C(3)	1.332(9)
C(3)–C(4)	1.460(11)	C(4)–C(5)	1.358(10)
C(5)–C(6)	1.373(9)	C(6)–C(7)	1.483(9)
C(8)–C(13)	1.314(8)	C(8)–C(9)	1.333(8)
C(9)–C(10)	1.425(8)	C(10)–C(11)	1.310(9)
C(11)–C(12)	1.321(9)	C(12)–C(13)	1.408(9)
C(14)–C(15)	1.404(8)	C(15)–C(16)	1.354(9)
C(15)–C(20)	1.399(9)	C(16)–C(17)	1.302(10)
C(17)–C(18)	1.395(11)	C(18)–C(19)	1.320(10)
C(19)–C(20)	1.349(9)	O(5)–N(3)	1.291(8)
O(6)–N(3)	1.209(8)	O(7)–N(3)	1.258(9)
O(8)–N(4)	1.228(8)	O(9)–N(4)	1.264(7)
O(10)–N(4)	1.198(8)		
O(2)–Sn(1)–O(1)	65.76(14)	O(1)–Sn(1)–O(3)	68.03(14)
C(23)–Sn(1)–O(1)	93.5(3)	C(30)–Sn(1)–O(1)	88.6(2)
O(3)–Sn(1)–O(6)	82.6(3)	C(23)–Sn(1)–O(3)	82.6(2)
C(30)–Sn(1)–O(3)	89.9(3)	O(6)–Sn(1)–O(5)	50.3(3)
O(6)–Sn(1)–C(23)	85.4(3)	O(6)–Sn(1)–C(30)	88.3(3)
O(2)–Sn(1)–O(5)	93.9(2)	C(23)–Sn(1)–O(5)	95.2(3)
C(30)–Sn(1)–O(5)	85.9(3)	C(23)–Sn(1)–O(2)	93.4(2)
C(30)–Sn(1)–O(2)	95.7(3)	C(30)–Sn(1)–C(23)	170.8(3)
O(1)–Ni(1)–O(2)	73.0(2)	O(1)–Ni(1)–N(1)	97.4(2)
O(1)–Ni(1)–N(2)	103.1(2)	O(1)–Ni(1)–O(8)	92.6(2)
O(9)–Ni(1)–N(1)	93.9(2)	N(1)–Ni(1)–N(2)	98.2(2)
N(1)–Ni(1)–O(8)	87.3(2)	O(9)–Ni(1)–O(2)	94.6(2)
O(9)–Ni(1)–N(2)	101.2(2)	O(9)–Ni(1)–O(8)	61.5(2)
N(2)–Ni(1)–O(2)	84.4(2)	O(2)–Ni(1)–O(8)	92.9(2)
N(2)–Ni(1)–O(8)	162.4(2)		

The mutual arrangements of the *m*-phenylene rings in [Cu(sal1,3-*m*-phen)]$_2$, **A** and **B** are significant. In the case of the copper complex, the close approach of the phenylene groups was considered to result in steric repulsion, a reasonable assumption since the ring separation is only 3.05 Å. However, in view of the now much greater understanding of $\pi-\pi$ interactions, this assumption needs further consideration. Fig. 4 shows the arrangements of the bridging phenylene groups in all three complexes, from which it is apparent that the arrangements of these groups in the copper complex and in **B** are very similar (in each structure the phenylene groups are related by a centre of inversion) but quite different to the arrangement in **A** in which the groups are related by a 2-fold axis. If the rings in the copper complex and in **B** (the rings are parallel in each structure) were arranged face to face there would indeed be a net repulsive interaction between the π-systems. However, the rings are well offset laterally with respect to each other (see Fig. 4) and this offset geometry leads to a marked increase in the attractive forces between the π-systems to the extent that they can become more significant than the repulsive forces [13]. Thus, the arrangements of the phenylene groups may well be resulting in net attraction rather than repulsion.

In the case of **A**, one ring is rotated relative to the other in a manner very similar to that found in the solid state structure of *p*-benzoquinone [14] and this type of arrangement can also result in the attractive forces offsetting the repulsive forces. Furthermore, in the case of **A**, one ring is tilted relative to the other (this is clearly apparent from the C–C contacts quoted in Fig. 4) and this represents yet another way of maximising the attractive forces between the two ring systems [13]. There is thus the suggestion that, in all three complexes, the *m*-phenylene rings are arranged such as to give rise to net $\pi-\pi$ attraction.

While recording the ^{119}Sn Mössbauer spectrum of **A** at low temperature, the sample assumed a yellowish green colour thus indicating that some hydration had occurred (see Section 2). However, the lines in the Mössbauer spectrum did not show any significant broadening as a result of this change and furthermore, the spectrum was identical to that recorded for the

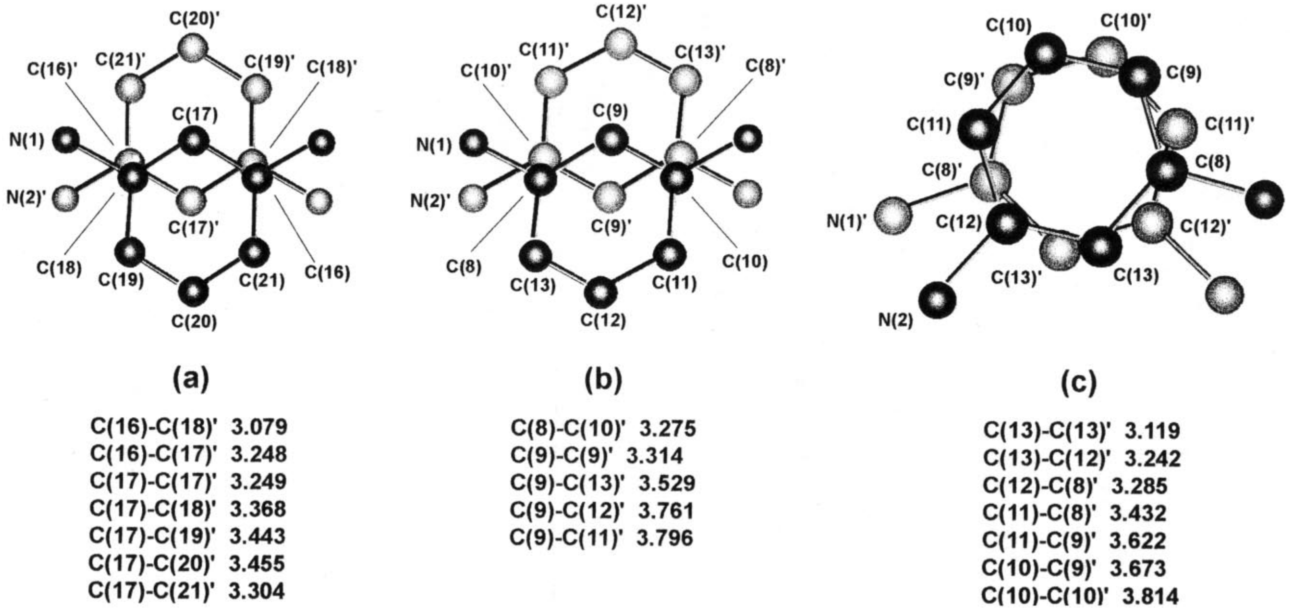

Fig. 4. Significant C–C separations (Å) between symmetry related *meta*-phenylene groups in (a) [Cu(3MeOsal-*m*-phen)]$_2$; (b) complex **B** and (c) complex **A**.

hydrated form. It must thus be assumed that the water is lattice water. This was further suggested by the fact that the infrared spectra of the green and yellow forms of the complex were almost identical if the water related bands were ignored. The extremely similar Mössbauer parameters for **A** and its *p*-phenylene analog (see Table 5) suggests that the compounds are isostructural.

The dibutyl- and diphenyltin nitrate adducts all have Mössbauer quadrupole splitting values which are consistent with tin being coordinated by the Schiff-base oxygens as in **A** and **B** [9]. In view of the structural data available from both this study and the previous study [10], it can be reasonably assumed that, in all cases, one nitrate is co-ordinated to nickel or zinc. However, the mode of co-ordination of this nitrate is not evident from infrared data since nitrate related vibrations tend to be obscured by ligand vibrations. Useful information regarding metal co-ordination geometry could not be obtained from UV–vis spectra for the reasons outlined earlier in the discussion of the structures of the parent salicylaldimine complexes.

The compound formulated as $[SnMe_2(NO_3)_2]_3$.[Ni(3MeO-sal-*m*-phen)]$_2$.H$_2$O in Table 5 may, in fact, be the ionic compound {SnMe$_2$.[Ni(3MeO-sal-*m*-phen)(NO$_3$)]}$_2$[SnMe$_2$(NO$_3$)$_4$].H$_2$O in which two nitrate groups of the anion act as bridging groups to tin atoms of the bimetallic cations, thereby completing pentagonal bipyramidal geometry with *trans* methyl groups (thus accounting for the large quadrupole splitting of 4.13 mm s^{-1} [9]) for these latter tin atoms. This type of structure would closely parallel that of [SnMe$_2$.Ni(3MeO-sal1,3pn)(H$_2$O)Cl]$_2$[SnMe$_2$Cl$_4$] [15] in which chlorine atoms of the anion form close contacts with the cationic tin atoms. The suggested structure for the nitrate complex would feature two tin environments and although this is not apparent from the normal line widths in the ^{119}Sn Mössbauer spectrum, neither was it in the case of the chloride complex (in the latter case the structure was confirmed crystallographically).

The quadrupole splitting of 3.84 mm s^{-1} for {SnBz$_2$Cl$_2$.[Zn(3MeO-sal-*m*-phen)].H$_2$O}$_2$ is consistent with tin being located between the Schiff-base oxygens as was found in **A** and **B,** and since there appears to be little tendency for the formation of either the dibenzyl- or diphenyltin cations in adducts of this general type, it is highly probable that one chloride remains coordinated to tin thus completing pentagonal bipyramidal tin coordination geometry as was found in a number of other related structures. Thus, the complex should probably be formulated as {[SnBz$_2$Cl].[Zn(sal-*m*-phen)Cl].H$_2$O}$_2$.

In contrast to the quadrupole splitting of 3.84 mm s^{-1} for the above complex, the analogous adduct with nickel salicylaldimine as donor ligand has a dramatically reduced quadrupole splitting of 3.03 mm s^{-1}, while the adduct of diphenyltin dibromide with the same metal salicylaldimine has an even smaller quadrupole splitting of 2.67 mm s^{-1}. These latter quadrupole splitting values are unquestionably too small to be considered to arise from six coordinated tin and thus pose the interesting question as to the precise nature of the adducts. The key to their structures is probably provided by the adduct of triphenyltin chloride with Ni(3-MeO-sal-*m*-phen). It has become increasingly clear from studies in this laboratory that triphenyltin

Table 5
Sn-119 Mössbauer, selected infrared and magnetic data

	δ (mm s^{-1})	Δ (mm s^{-1})	ν(C–O) (cm^{-1})	μ (BM)
$[\text{Ni(3MeO-sal-}m\text{-phen)(H}_2\text{O)}]_2$			1536	2.80
$[\text{Ni(3MeO-sal-}p\text{-phen)(H}_2\text{O)}]_2$			1536	2.79
$[\text{Cu(3MeO-sal-}m\text{-phen)(H}_2\text{O)}_2]_2$			1535	1.81
$[\text{Cu(3MeO-sal-}p\text{-phen)(H}_2\text{O)}]_2$			1535	1.83
$[\text{Zn(3MeO-sal-}m\text{-phen)(H}_2\text{O)}]_2$			1537	
$[\text{Zn(3MeO-sal-}p\text{-phen)(H}_2\text{O)}]_2$			1538	
$\{\text{SnBu}^n_2[\text{Ni(3MeO-sal-}m\text{-phen)(NCS)}_2]\cdot\text{H}_2\text{O}\}_2$	1.59	3.74	1547	3.30
$\{[\text{SnBz}_2(\text{NO}_3)]\cdot[\text{Ni(3MeO-sal-}m\text{-phen)(NO}_3)]\}_2$	1.57	3.83	1555	3.04
$\{[\text{SnBu}^n_2(\text{NO}_3)]\cdot[\text{Ni(3MeO-sal-}m\text{-phen)(NO}_3)]\cdot\text{H}_2\text{O}\}_2$	1.45	3.51	1547	3.14
$\{[\text{SnBu}^n_2(\text{NO}_3)]\cdot[\text{Zn(3MeO-sal-}m\text{-phen)(NO}_3)]\cdot\text{H}_2\text{O}\}_2$	1.49	3.57	1554	
$\{[\text{SnPh}_2(\text{NO}_3)]\cdot[\text{Ni(3MeO-sal-}m\text{-phen)(NO}_3)]\cdot\text{H}_2\text{O}\}_2$	1.33	3.36	1547	3.36
$\{[\text{SnPh}_2(\text{NO}_3)]\cdot[\text{Zn(3MeO-sal-}m\text{-phen)(NO}_3)]\cdot\text{H}_2\text{O}\}_2$	1.34	3.35	1545	
$\{[\text{SnMe}_2(\text{NO}_3)_2]_3\cdot[\text{Ni(3MeO-sal-}m\text{-phen)}]_2\cdot\text{H}_2\text{O}$	1.43	4.13	1548	
$\{[\text{SnBu}^n_2\text{Cl}_2]\cdot[\text{Ni(3MeO-sal-}m\text{-phen)}]\cdot2\text{H}_2\text{O}\}_2$	1.51	3.29	1548	3.77
$\{[\text{SnBu}^n_2\text{Cl}_2]\cdot[\text{Zn(3MeO-sal-}m\text{-phen)}]\cdot2\text{H}_2\text{O}\}_2$	1.45	3.20	1552	
$\{[\text{SnBz}_2\text{Cl}_2]\cdot[\text{Ni(3MeO-sal-}m\text{-phen)}]\cdot2\text{H}_2\text{O}\}_2$	1.49	3.03	1554	3.43
$\{[\text{SnBz}_2\text{Cl}_2]\cdot[\text{Zn(3MeO-sal-}m\text{-phen)}]\cdot2\text{H}_2\text{O}\}_2$	1.75	3.84	1554	
$\{[\text{SnPh}_2\text{Br}_2]\cdot[\text{Ni(3MeO-sal-}m\text{-phen)}]\cdot2\text{H}_2\text{O}\}_2$	1.29	2.67	1554	3.10
$\{[\text{SnPh}_3\text{Cl}]\cdot[\text{Ni(3MeO-sal-}m\text{-phen)}]\cdot2\text{H}_2\text{O}\}_2$	1.34	2.92	1552	3.78
$\{\text{SnBu}^n_2\cdot[\text{Ni(3MeO-sal-}p\text{-phen)(NCS)}_2]\cdot\text{H}_20\}_2$	1.58	3.78	1565	3.12

chloride is incapable of forming donor bonds with either the methoxy or phenolic oxygens of salicylaldimine complexes. Where apparent adducts were formed, it has been confirmed that, in fact, monoaqua adducts of triphenyltin chloride were formed with the donor water molecule held by hydrogen bonds to the Schiff-base oxygens [10]. Monoaqua adducts of dimethyltin dichloride have likewise been shown to engage in hydrogen bonding interactions with nickel salicylaldimine complexes [8]. Almost certainly, the triphenyltin chloride, diphenyltin dibromide and dibenzyltin dichloride complexes under discussion are monoaqua adducts of this type with five co-ordinated tin. The quadrupole splittings of 3.20 and 3.29 mm s^{-1} for the dibutyltin dichloride adducts (see Table 5) may reflect the fact that the tin atoms have pseudo octahedral co-ordination geometries as a result of weak intermolecular Sn–Cl interactions such as exist in $\text{SnMe}_2\text{Cl}_2.\text{H}_2\text{O}$/Ni(3-MeOsal1,3pn) (1/1) [8].

4. Summary

Complexes $\text{M(3MeO-sal-}m\text{-phen)(H}_2\text{O)}]_2$ are effective donor ligand to organotin(IV) Lewis acids, behaving in some cases like complexes M(3MeO-salen) in that they result in the formation of aqua adducts of tin with the donor water linked to the metal salicylaldimine through hydrogen bonding, and in other cases like complexes M(3MeO-sal1,3pn) where they react to give intimate ion-paired adducts. They show a greater flexibility about the metal M than that in either the complexes M(3MeO-salen) or M(3MeO-sal1,3pn) thus allowing for significantly different geometries about tin and M to those encountered in adducts with the latter complexes.

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