Transition Metal Schiff-base Complexes as Ligands in Tin Chemistry. Part 2.[1] A Tin-119 Mössbauer Spectroscopic Investigation of the Adducts $SnBu^n{}_xCl_{3-x}(OR)\cdot ML$ (x = 0 or 1; R = H or Alkyl; M = Cu^{II} or Ni^{II}; L = Quadridentate Schiff-base ligand)

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The compound $SnCl_3(OEt)\cdot EtOH$ reacts with the complexes ML [M = Cu^{II} or Ni^{II}; H_2L = *N,N'*-ethylenebis(salicylideneimine), *N,N'-o*-phenylenebis(salicylideneimine), or derivatives of these] to give the adducts $SnCl_3(OEt)\cdot ML$. Hydrolysis of the ethoxo adducts in chloroform under ambient conditions yields the adducts $SnCl_3(OH)\cdot ML$. Chloroform solutions of the adducts $SnCl_4\cdot ML$ gives similar hydroxo adducts under ambient conditions when M = Cu^{II} but not when M = Ni^{II}. The compound $SnBu^nCl_2(OH)\cdot H_2O$ reacts with ML at −10 °C to give 1:1 adducts, but at higher temperatures $SnBu^nCl(OH)_2\cdot H_2O$ and $SnBu^nCl_3\cdot ML$ are formed. The compound $SnBu^nCl_2(OMe)\cdot MeOH$ reacts with ML in chloroform to yield the adducts $SnBu^nCl_2(OMe)\cdot ML$. The replacement of chloride by hydroxide or alkoxide in either $SnBu^nCl_3$ or $SnCl_4$ results in a reduction of the Lewis acidity at tin. Mössbauer quadrupole-splitting data for $SnBu^nCl_2(OH)\cdot ML$ and $SnBu^nCl_2(OMe)\cdot ML$ were analysed in terms of the point-charge model from which it was established that the donor oxygen and carbon atoms practically always adopt *fac* geometry about tin; this contrasts with the *mer* geometry preferred by many adducts $SnBu^nCl_3\cdot ML$.

We have recently reported[1] that in the case of adducts $SnRCl_3\cdot ML$ (R = Ph or Bu^n, M = Cu^{II} or Ni^{II}, H_2L = quadridentate Schiff-base ligand) a fine balance exists between the stabilities of *mer* and *fac* isomers with the *mer* isomer being favoured by the adducts containing the stronger Lewis bases. In two instances it proved possible to isolate both the *mer* and *fac* isomers in the solid state. As part of our ongoing studies of *mer–fac* isomerism in monoorganotin adducts, the effect of replacing chloride in the above bimetallic adducts by other halides and pseudohalides is under investigation. The present paper considers, in particular, the interesting chemical and structural consequences of replacing one chloride by a hydroxide or alkoxide ion.

Experimental

Starting Materials and Instrumentation.—Tin(IV) chloride (Aldrich) and *n*-butyltin chloride (Fluka) were distilled prior to use, $SnCl_3(OEt)\cdot EtOH$, $SnBu^nCl_2(OH)\cdot H_2O$ and $SnBu^nCl_2(OMe)\cdot MeOH$ were prepared by literature methods.[2–4] The Schiff-base ligands and their metal complexes were prepared by literature methods.[5]

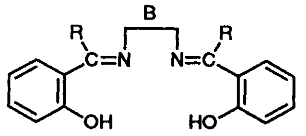
Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrometer, and tin-119 Mössbauer spectra on a constant-acceleration Mössbauer spectrometer (J & P Engineering, Reading) using a calcium stannate source (Radiochemical Centre, Amersham). The spectrometer was calibrated regularly from the positions of the four inner lines of natural iron. The spectra were computer fitted using a least-squares procedure.[6]

Preparation of the Salicylideneimine Adducts.—Adducts $SnCl_4\cdot ML$ were prepared as described previously.[1] Each was stirred in chloroform under ambient conditions for 12 h. The solids isolated by filtration after this time were $SnCl_3(OH)\cdot ML$ when M = Cu^{II}, but when M = Ni^{II} the unhydrolysed adducts were recovered. Similar observations were made when reactions were attempted in refluxing chloroform. Adducts $SnCl_3(OEt)\cdot ML$ were prepared in dry chloroform under a dry nitrogen atmosphere. Typically, $SnCl_3(OEt)\cdot EtOH$ (0.01 mol) was added as a solid to a solution (*ca.* 100 cm^3) or suspension of the metal Schiff-base complex (0.01 mol). Following the addition, stirring was continued for several hours. The solid product was filtered off under dry nitrogen and dried under vacuum. All manipulations of the adducts were carried out in a dry-box. These adducts were hydrolysed as described for the tin(IV) tetrahalide adducts, yielding the adducts $SnCl_3(OH)\cdot ML$.

Adducts $SnBu^nCl_2(OH)\cdot ML$ and $SnBu^nCl_2(OMe)\cdot ML$ were prepared at −10 °C from $SnBu^nCl_2(OH)\cdot H_2O$ and $SnBu^nCl_2(OMe)\cdot MeOH$ respectively using identical procedures to those described for the preparation of $SnCl_3(OEt)\cdot ML$, but in the case of the hydroxy adducts precautions against hydrolysis were unnecessary. Attempted preparation of the hydroxy adducts at 20 °C resulted in the coprecipitation of $SnBu^nCl_2(OH)\cdot ML$ and $SnBu^nCl_3\cdot ML$. The latter precipitated almost exclusively from reactions carried out in refluxing chloroform. It was possible to isolate adducts $SnBu^nCl_2(OMe)\cdot ML$ from reactions in refluxing chloroform.

Reactions of $SnBu^nCl_2(OH)\cdot H_2O$ *with Pyridine, and Dimethylformamide.*—A solution of pyridine (py) (0.03 mol) in chloroform (5 cm^3) was added dropwise to a solution of $SnBu^nCl_2(OH)\cdot H_2O$ (0.03 mol) in chloroform (30 cm^3). The precipitate which formed immediately was filtered off and dried under vacuum. On the basis of elemental analysis and infrared spectroscopy it would appear that the product contained $SnBu^nCl_3\cdot 2py$ contaminated possibly with $SnBu^nCl_2(OH)\cdot py$. Similar results were obtained when the reaction was conducted in benzene, and also at −10 °C in chloroform.

A solution of dimethylformamide (dmf) (0.03 mol) in benzene (5 cm^3) was added to a solution of $SnBu^nCl_2(OH)\cdot H_2O$ (0.03 mol) in benzene (30 cm^3) and the resulting solution was maintained at approximately 50 °C for 0.5 h. At this stage droplets of water which were visible were separated from the benzene solution by decantation. On addition of light petroleum to the benzene solution a precipitate of $SnBu^nCl_2(OH)\cdot dmf$ formed, and this was filtered off and dried under



R	B	
H	$(CH_2)_2$	*N,N'*-Ethylenebis(salicylideneimine) (H_2salen)
H	CH_2CHMe	*N,N'*-Propylenebis(salicylideneimine) (H_2salpn)
H	$(CH_2)_3$	*N,N'*-Trimethylenebis(salicylideneimine) (H_2saltm)
H	C_6H_4-*o*	*N,N'*-*o*-phenylenebis(salicylideneimine) (H_2salphen)
H	MeC_6H_4-*o*	*N,N'*-*o*-(4-methylphenylene)bis(salicylideneimine) (H_2salmphen)
Me	$(CH_2)_2$	*N,N'*-Ethylenebis(α-methylsalicylideneimine) (α,α'-Me_2H_2salen)

Table 1 Analytical data (%) for the adducts *

Adduct	C	H	N	Cl
$SnCl_3(OEt)\cdot Cu(salen)$	35.30 (36.00)	2.75 (3.15)	5.30 (4.65)	18.15 (17.75)
$SnCl_3(OH)\cdot Cu(salen)$	34.45 (33.60)	3.10 (2.60)	5.15 (4.90)	19.35 (18.65)
$SnCl_3(OEt)\cdot Ni(salen)$	35.80 (36.30)	3.40 (3.20)	4.95 (4.70)	17.20 (17.90)
$SnCl_3(OH)\cdot Ni(salen)$	33.20 (33.85)	3.15 (2.65)	4.75 (4.95)	18.35 (18.80)
$SnCl_3(OEt)\cdot Ni(salphen)$	40.85 (41.05)	2.90 (2.95)	4.75 (4.35)	16.80 (16.55)
$SnCl_3(OH)\cdot Ni(salphen)$	39.65 (39.05)	2.50 (2.45)	4.90 (4.55)	17.70 (17.30)
$SnCl_3(OEt)\cdot Ni(salpn)$	33.75 (33.50)	2.85 (3.45)	4.35 (4.60)	17.85 (17.50)
$SnCl_3(OH)\cdot Ni(salpn)$	34.85 (35.10)	2.60 (2.95)	4.65 (4.80)	18.75 (18.35)
$SnCl_3(OEt)\cdot Ni(saltm)\cdot H_2O$	35.75 (36.35)	3.65 (3.65)	4.35 (4.45)	17.20 (17.00)
$SnCl_3(OH)\cdot Ni(saltm)\cdot H_2O$	34.60 (35.10)	3.30 (2.90)	4.55 (4.80)	18.80 (18.35)
$SnCl_3(OEt)\cdot Ni(\alpha,\alpha'\text{-}Me_2\text{-}salen)$	38.00 (38.55)	3.10 (3.70)	4.25 (4.50)	17.75 (17.10)
$SnCl_3(OH)\cdot Ni(\alpha,\alpha'\text{-}Me_2\text{-}salen)$	35.80 (36.30)	3.45 (3.20)	4.50 (4.70)	18.10 (17.90)
$SnBu^nCl_2(OH)\cdot Cu(salen)$	40.20 (40.45)	4.00 (4.05)	4.95 (4.70)	11.80 (11.95)
$SnBu^nCl_2(OMe)\cdot Cu(salen)$	41.20 (41.50)	3.90 (4.30)	4.35 (4.60)	11.25 (11.65)
$SnBu^nCl_2(OH)\cdot Ni(salen)$	40.45 (40.80)	4.35 (4.10)	4.55 (4.75)	12.05 (12.05)
$SnBu^nCl_2(OMe)\cdot Ni(salen)$	41.50 (41.85)	3.95 (4.35)	4.25 (4.65)	11.55 (11.75)
$SnBu^nCl_2(OH)\cdot Ni(salphen)$	44.35 (45.25)	3.60 (3.75)	4.85 (4.40)	10.80 (11.15)
$SnBu^nCl_2(OH)\cdot Cu(salmphen)$	45.75 (45.80)	3.75 (3.95)	4.05 (4.25)	10.30 (10.85)
$SnBu^nCl_2(OH)\cdot Ni(salmphen)$	45.55 (46.15)	3.70 (4.00)	3.95 (4.30)	11.15 (10.90)
$SnBu^nCl_2(OH)\cdot Cu(salpn)$	40.85 (41.50)	4.60 (4.30)	4.30 (4.60)	12.35 (11.70)
$SnBu^nCl_2(OH)\cdot Ni(salpn)$	40.95 (41.85)	4.10 (4.30)	4.75 (4.65)	12.40 (11.80)
$SnBu^nCl_2(OH)\cdot Ni(\alpha,\alpha'\text{-}Me_2\text{-}salen)$	42.15 (42.85)	4.80 (4.55)	4.30 (4.55)	11.25 (11.50)

* Calculated data are in parentheses.

vacuum. When the dmf adduct was refluxed in benzene for 24 h both $SnBu^nCl_3\cdot 2dmf$ and $SnBu^nCl(OH)_2\cdot H_2O$ were recovered from solution. Under similar conditions $SnBu^nCl_2(OH)\cdot H_2O$ yielded exclusively $SnBu^nCl(OH)_2\cdot H_2O$.

Table 2 Ligand–oxygen stretching frequency data for adducts of tin(IV) Lewis acids

Complex	ν(MO)/ cm^{-1}	Complex	ν(MO)/ cm^{-1}
dmf	1685	$SnCl_3(OEt)\cdot C_5H_5NO$ [a]	1190
$SnCl_4\cdot 2dmf$	1612 [b]	PPh_3O	1190
$(SnPhCl_4\cdot dmf)^-$	1630 [c]	$SnCl_4\cdot 2PPh_3O$ [d]	1120
$(SnBu^nCl_4\cdot dmf)^-$	1642 [c]	$SnCl_3(OEt)\cdot PPh_3O$ [a]	1130
$SnBu^nCl_3\cdot 2dmf$	1642 [e]	$P(OPh)_3O$	1296
$SnBu^nCl_2(OH)\cdot dmf$	1655 [e]	$SnCl_4\cdot P(OPh)_3O$ [d]	1212
C_5H_5NO	1245	$P(OMe)_3O$	1275
$SnCl_4\cdot C_5H_5NO$	1195 [d]	$SnCl_3(OEt)\cdot P(OMe)_3O$ [a]	1230

[a] Ref. 10. [b] Ref. 13. [c] Ref. 14. [d] Ref. 15. [e] Present study.

Results and Discussion

In common with $SnCl_3(OH)\cdot H_2O$, $SnEtCl_2(OH)\cdot H_2O$ and $SnCl_3(OEt)\cdot EtOH$ whose structures have been confirmed crystallographically,[7–9] $SnBu^nCl_2(OH)\cdot H_2O$ and $SnBu^nCl_2(OMe)\cdot MeOH$ almost certainly possess dimeric structures in which octahedral geometry about tin is completed by the formation of a donor bond with a solvent molecule. The presence of the donor bond confirms that all of the mono-hydroxy and -alkoxy tin species possess Lewis-acid character, but the extent of this has not been subjected to thorough investigation. A limited series of adducts $SnCl_3(OR)\cdot L$ have been isolated which appear to retain dimeric structures with μ-alkoxy ligands when L is a monodentate donor group but become monomeric when it is a bidentate group,[10] and more recent crystallographic studies confirm that tetrahydrofuran (thf) and [CoCl(salen)] (see diagram for ligand nomenclature) act as donor ligands to tin in $[SnCl_2Br(OH)(thf)]_2 2thf$ and $SnBu^n(OMe)Cl_2\cdot CoCl(salen)$ respectively.[11,12]

The previous lack of attention to the Lewis acidity of monoorganotin(IV) hydroxide halides prompted us initially to treat $SnBu^nCl_2(OH)\cdot H_2O$ with pyridine and dimethylformamide. Although pyridine readily reacted with the tin complex, it did not yield $SnBu^nCl_2(OH)\cdot py$, but instead what appeared to be a mixture of $SnBu^nCl_3\cdot 2py$ and possibly the hydroxy adduct (see Experimental section). However, the reaction with dmf in benzene yielded the adduct $SnBu^nCl_2(OH)\cdot dmf$.

Several features of the infrared spectrum of this new dmf adduct are noteworthy. It exhibits a strong band, with a sharp maximum at 508 cm^{-1}, which is absent in the spectrum of $SnBu^nCl_3\cdot 2dmf$ and is thus almost certainly attributable to an Sn–O–Sn stretching mode.[10,11] The implicated di-μ-hydroxo-ditin structure, similar to that of $SnBu^nCl_2(OH)\cdot H_2O$, is further suggested by the fact that the ν(OH) stretching mode appearing at 3420 cm^{-1} in the spectrum of $SnBu^nCl_2(OH)\cdot dmf$ corresponds with a band (appearing as a strong shoulder) in the spectrum of $SnBu^nCl_2(OH)\cdot H_2O$. Finally, the appearance of a strong band centred at 1655 cm^{-1} in the spectrum of $SnBu^nCl_2(OH)\cdot dmf$ not only confirms the donor role of dmf, but by reference to Table 2 also confirms that, in this instance, $SnBu^nCl_2(OH)$ is behaving as a weaker Lewis acid than $SnBu^nCl_3$, a point which will be further elaborated in the course of the discussion.

The compound $SnCl_3(OEt)\cdot EtOH$ readily forms 1 : 1 adducts with all of the metal salicylideneimine complexes of the present study. These adducts are relatively air stable as dry solids but readily undergo hydrolysis in solution to give the adducts $SnCl_3(OH)\cdot ML$. These latter adducts are also obtained by the air hydrolysis of chloroform solutions of the adducts $SnCl_4\cdot ML$ when $M = Cu^{II}$, but rather surprisingly when $M = Ni^{II}$ the adducts are resistant to hydrolysis under the same conditions. It is also noteworthy that in no case did hydrolysis proceed beyond that of one tin–chlorine bond (see Experimental section).

Initial attempts to prepare adducts $SnBu^nCl_2(OH)\cdot ML$ in chloroform at room temperature resulted in the isolation of solids which in all cases gave ^{119}Sn Mössbauer spectra indicating the presence of two tin environments. This observation prompted the investigation of the reactions at both higher and lower temperatures. At −10 °C the adducts $SnBu^nCl_2(OH)\cdot ML$ were isolated as pure species, whereas in refluxing chloroform $SnBu^nCl_3\cdot ML$ were precipitated in relatively pure form. Following this observation it was shown that $SnBu^nCl_2(OH)\cdot dmf$ undergoes reaction (1) in both refluxing chloroform

$$2SnBu^nCl_2(OH)\cdot dmf \longrightarrow SnBu^nCl(OH)_2\cdot H_2O + SnBu^nCl_3\cdot 2dmf \quad (1)$$

and benzene. The compound $SnBu^nCl_2(OH)\cdot H_2O$, in refluxing benzene, yielded $SnBu^nCl(OH)_2\cdot H_2O$ (this species has previously been isolated through an alternative procedure).

The compound $SnBu^nCl_2(OMe)\cdot MeOH$ readily reacted with [Ni(salen)] and [Cu(salen)] in chloroform at room temperature and at solvent reflux temperature to give 1:1 adducts $SnBu^nCl_2(OMe)\cdot M(salen)$ (M = Cu or Ni), and no scrambling reactions, such as those observed for $SnBu^nCl_2(OH)\cdot H_2O$, occurred. Reactions of the methoxotin complex with the other Schiff-base complexes of this study were not investigated.

Table 3 Mössbauer spectroscopic, phenolic C–O stretching frequency, and magnetic data for inorganic tin(IV) adducts[a]

Complex	Δ/ mm s^{-1}	δ/ mm s^{-1}	ν(C–O)/ cm^{-1}	η_{eff}
$SnCl_3(OEt)\cdot EtOH$	0.66	0.32		
$SnCl_4\cdot Cu(salen)$	0.49	0.47	1560	1.85
$SnCl_3(OEt)\cdot Cu(salen)$	0.43	0.33	1540	1.80
$SnCl_3(OH)\cdot Cu(salen)$	0.51	0.24	1555	1.73
$SnCl_4\cdot Ni(salen)$	0.60	0.55	1565	*b*
$SnCl_3(OEt)\cdot Ni(salen)$	0.53	0.17	1545	*b*
$SnCl_3(OH)\cdot Ni(salen)$	0.58	0.11	1550	2.80
$SnCl_4\cdot Ni(salphen)$	0.45	0.43	1552	*b*
$SnCl_3(OEt)\cdot Ni(salphen)$	0.53	0.45	1535	*b*
$SnCl_3(OH)\cdot Ni(salphen)$	0.51	0.35	1550	2.70
$SnCl_4\cdot Ni(salpn)$	0.51	0.37	1564	*b*
$SnCl_3(OEt)\cdot Ni(salpn)$	0.53	0.38	1555	*b*
$SnCl_3(OH)\cdot Ni(salpn)$	0.50	0.35	1560	2.70
$SnCl_3(OEt)\cdot Ni(saltm)\cdot H_2O$	0.47	0.13	1560	3.00
$SnCl_3(OH)\cdot Ni(saltm)\cdot H_2O$	0.37	0.31	1570	3.15
$SnCl_4\cdot Ni(\alpha,\alpha'-Me_2-salen)$	0.49	0.37	1553	*b*
$SnCl_3(OEt)\cdot Ni(\alpha,\alpha'-Me_2-salen)$	0.45	0.32	1550	*b*
$SnCl_3(OH)\cdot Ni(\alpha,\alpha'-Me_2-salen)$	0.53	0.31	1555	2.50

[a] Data for adducts $SnCl_4\cdot ML$ are from ref. 1. [b] Diamagnetic.

It is well established that a band in the 1600–1700 cm^{-1} region of the infrared spectra of salicylideneimine complexes, which is attributed to the phenolic C–O stretching frequency, is sensitive to the participation of the phenolic oxygens in donor bond formation, tending to move to higher frequencies as the donor–acceptor interaction increases in strength.[16] Thus, the phenolic C–O stretching frequency data in Tables 3 and 4 almost consistently suggest that the replacement of a chloride of either $SnCl_4$ or $SnBu^nCl_3$ by a hydroxide results in loss of Lewis acidity, and this is consistent with the conclusion drawn from the data in Table 2 for the dmf adducts. Furthermore, the phenolic C–O stretching frequency data in Table 3 generally support the suggestion that $SnCl_3(OH)$ is a stronger Lewis acid than is $SnCl_3(OEt)$.

Apart from the data of this present work, there are only very limited data otherwise available which permit a comparison to be made between the Lewis acidity of $SnCl_4$ and $SnCl_3(OR)$ (R = H or organo group). These data (see Table 2) do not always support the general conclusions of the present study. For example, the co-ordination of pyridine *N*-oxide (C_5H_5NO) to $SnCl_4$ results in a reduction of the N–O stretching frequency by 50 cm^{-1} whereas co-ordination to $SnCl_3(OEt)$ causes a somewhat greater reduction of 55 cm^{-1}. However, co-ordination of triphenylphosphine oxide (PPh_3O) to $SnCl_4$ results in a reduction of the P–O stretching frequency by 70 cm^{-1}, whereas co-ordination to $SnCl_3(OEt)$ results in a lesser reduction of 60 cm^{-1}. Furthermore, co-ordination of triphenyl phosphate $[P(OPh)_3O]$ to $SnCl_4$ results in a reduction of the P–O stretching frequency by 84 cm^{-1}, whereas co-ordination of the stronger base trimethyl phosphate to $SnCl_3(OEt)$ results in a much lesser reduction of this frequency by 45 cm^{-1}. Thus, the data for the pyridine *N*-oxide adducts are in conflict with the data of this study, whereas the data for the phosphine oxide and phosphate adducts support them.

The tin(IV) tetrahalide adducts in Table 3 which have nickel donor ligands are diamagnetic thus confirming the retention of square-planar nickel (or approximately so) on adduct formation. Since the adducts $SnCl_3(OEt)\cdot NiL$ (excluding the adduct

Table 4 Mössbauer spectroscopic and phenolic C–O stretching frequency data for monoorganotin(IV) adducts*

	Δ	δ	Δ_{calc}		
	mm s^{-1}				ν(C–O)/
Complex			*mer*	*fac*	cm^{-1}
$SnBu^nCl_3\cdot Cu(salen)$	1.67	0.99	1.67	2.35	1550
$SnBu^nCl_2(OH)\cdot Cu(salen)$	2.19	0.98	1.67	2.35	1540
$SnBu^nCl_2(OMe)\cdot Cu(salen)$	2.18	0.96	1.67	2.35	1550
$SnBu^nCl_3\cdot Ni(salen)$	1.53	1.05	1.64	2.46	1555
$SnBu^nCl_2(OH)\cdot Ni(salen)$	2.13	0.92	1.64	2.46	1540
$SnBu^nCl_2(OMe)\cdot Ni(salen)$	1.53	1.06	1.64	2.64	1550
mer-$SnBu^nCl_3\cdot Ni(salphen)$	1.48	1.05	1.68	2.31	1548
fac-$SnBu^nCl_3\cdot Ni(salphen)$	2.13	1.21	1.68	2.31	1548
$SnBu^nCl_2(OH)\cdot Ni(salphen)$	2.14	0.97	1.68	2.31	1530
$SnBu^nCl_3\cdot Cu(salmphen)$	1.70	1.04	1.68	2.31	1549
$SnBu^nCl_2(OH)\cdot Cu(salmphen)$	2.08	1.15	1.68	2.31	1550
mer-$SnBu^nCl_3\cdot Ni(salmphen)$	1.53	1.08	1.68	2.31	1549
fac-$SnBu^nCl_3\cdot Ni(salmphen)$	2.18	1.15	1.68	2.31	1549
$SnBu^nCl_2(OH)\cdot Ni(salmphen)$	2.18	0.87	1.68	2.31	1530
$SnBu^nCl_3\cdot Cu(salpn)$	1.69	1.00	1.70	2.26	1551
$SnBu^nCl_2(OH)\cdot Cu(salpn)$	2.13	0.87	1.70	2.26	1545
$SnBu^nCl_3\cdot Ni(salpn)$	1.50	0.99	1.66	2.37	1554
$SnBu^nCl_2(OH)\cdot Ni(salpn)$	1.58	1.01	1.66	2.37	1560
$SnBu^nCl_3\cdot Ni(\alpha,\alpha'-Me_2-salen)$	1.49	0.96	1.67	2.35	1554
$SnBu^nCl_2(OH)\cdot Ni(\alpha,\alpha'-Me_2-salen)$	2.17	0.92	1.67	2.35	1540

* All data for adducts of *n*-butyltin trichloride are from ref. 1.

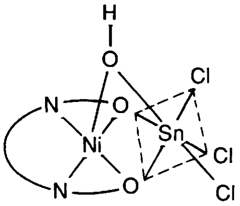
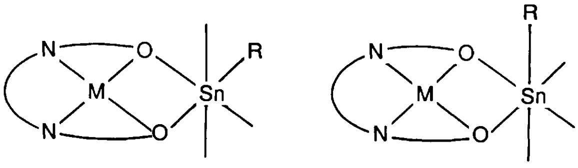


Fig. 1 Schematic representation of the structure of adducts $SnCl_3(OH)\cdot NiL$



mer *fac*

Fig. 2 The *mer* and *fac* isomers of adducts $SnBu^nCl_3\cdot ML$

where L = saltm) are likewise diamagnetic it is surprising that their hydroxo analogues are paramagnetic. The paramagnetic behaviour is most realistically accounted for on the assumption that the hydroxo groups act as metal–metal bridging ligands as shown diagrammatically in Fig. 1, *i.e.* they assume a similar role to that of methoxide in the structure of $SnBu^nCl_2(OMe)\cdot CoCl(salen)$.[12] However, such a role would result in five-co-ordinate nickel, whereas the magnetic moments of $SnCl_3(OH)\cdot Ni(salen)$, $SnCl_3(OH)\cdot Ni(salphen)$, and $SnCl_3(OH)\cdot Ni(salpn)$ are more typical of octahedral nickel. However, the magnetic moment of 2.5 for $SnCl_3(OH)\cdot Ni(\alpha,\alpha'\text{-}Me_2\text{-}salen)$ is too low for a magnetically dilute high-spin nickel(II) complex and may thus indicate the presence of a diamagnetic impurity. If this is true there is a reasonable probability that the other three complexes are likewise contaminated, thus reducing their magnetic moments from the more usual five-co-ordinate nickel(II) values.

The adduct $SnCl_3(OEt)\cdot Ni(saltm)\cdot H_2O$ is exceptional among the ethoxide adducts in that it is paramagnetic with a magnetic moment of 3.0. However, the paramagnetic behaviour does not imply ethoxide bridging in this instance since the water which is co-ordinated to nickel in $[Ni(saltm)]\cdot H_2O$ (thus producing five-co-ordinated nickel[17]) appears to maintain this role in the adduct (this is suggested by the fact that the water associated band at approximately 3360 cm^{-1} in the infrared spectrum of the parent nickel adduct is unmoved on adduct formation). All of the monoorganotin adducts which have nickel salicylideneimines as donor ligands are diamagnetic and thus hydroxide bridging to nickel certainly does not occur in these instances.

An analysis of the Mössbauer quadrupole-splitting data in Tables 3 and 4 reveals that, while the replacement of a chloride in adducts $SnCl_4\cdot ML$ by hydroxide or alkoxide has little effect on the quadrupole splitting, this is not necessarily the case for the monoorganotin adducts in Table 4. In those instances where adducts $SnBu^nCl_3\cdot ML$ have *fac* geometry (see Fig. 2) replacement of chloride by hydroxide results in relatively small changes in quadrupole-splitting values, but for the adducts possessing *mer* geometry there generally is a substantial change in quadrupole splitting. The latter changes can clearly be related to a change from *mer* to *fac* octahedral geometry about tin as a result of ligand replacement.

The fact that chloride replacement by hydroxide or alkoxide in the case of adducts $SnCl_4\cdot ML$ results in little or no change in quadrupole splitting implies that the partial quadrupole splitting (p.q.s.) parameters for chloride, hydroxide and alkoxide are extremely similar. Since we have previously demonstrated that p.q.s. values derived from tin(IV) halide adducts transfer accurately to monoorganotin(IV) adducts,[1,14] the data in Table 3 thus imply that the calculated quadrupole-splitting data[1] for any adduct $SnBu^nCl_3\cdot ML$ in Table 4 apply equally well to both its monohydroxo and methoxo analogues. As had been the case for the adducts $SnBu^nCl_3\cdot ML$, the level of agreement between the experimental quadrupole-splitting value for each 1 : 1 adduct of the present study and one of the calculated values is sufficiently good to allow the geometry about tin to be assigned with an extremely high degree of confidence.

In the case of the adducts $SnBu^nCl_3\cdot ML$ a delicate balance exists between the stabilities of the *mer* and *fac* isomers, with the stronger donor ligands favouring the *mer* isomer. In the case of the hydroxo and methoxo adducts this balance has clearly been tipped in favour of the *fac* isomer. This is clearly evident from the fact that, of the six adducts $SnBu^nCl_3\cdot ML$ in Table 4 which have *mer* geometry, five revert to *fac* geometry in their monohydroxo analogues. Furthermore, while *mer* and *fac* isomers of $SnBu^nCl_3\cdot Ni(salphen)$ and $SnBu^nCl_3\cdot Ni(salmphen)$ could be isolated, only the *fac* isomers of their monohydroxo analogues were obtained. There are only two examples of *mer* geometry being retained in methoxo or hydroxo adducts, these being $SnBu^nCl_2(OMe)\cdot Ni(salen)$ and $SnBu^nCl_2(OH)\cdot Ni(salpn)$. There is no case where *fac* geometry in a butyltin trihalide adduct gives way to *mer* geometry in its monomethoxo or monohydroxo analogue. There is no ready explanation for the *fac* geometry preference in the case of the hydroxo and methoxo adduct, but it may be that it is dictated by the hydroxo and methoxo groups showing the greatest preference to be *trans* to the organo group where bonding-orbital overlap involves an s-electron rich sp-hybrid orbital of tin. Although it may be fortuitous, it is interesting that this *trans* relationship exists in $SnEtCl_2(OH)\cdot H_2O$,[8] $SnMeCl_2(OMe)\cdot MeOH$[9] and $SnBu^nCl_2(OMe)\cdot CoCl(salen)$.[12]

Although the quadrupole splitting is essentially insensitive to the replacement of chloride by either ethoxide or hydroxide in the case of adducts $SnCl_4\cdot ML$, this is certainly not always the case with chemical shift data. When the donor ligand is either Ni(salen) or Cu(salen), replacement of chloride by ethoxide and hydroxide causes a progressive and decisive lowering of the chemical shift. However, this effect is either less apparent or non-evident with other donor ligands [see, for example, adducts containing Ni(salpn) as donor group]. Careful analysis of the chemical shift data in Table 4 indicates that the replacement of chloride in adducts $SnBu^nCl_3\cdot ML$ by hydroxide more consistently causes a marked lowering of chemical shift. In these instances it must be borne in mind that for an adduct $SnBu^nCl_3\cdot ML$ the *mer* isomer will have a lower chemical shift value than that for the *fac* isomer;[1] this is clearly apparent for the chemical shift values for *mer* and *fac* isomers of both $SnBu^nCl_3\cdot Ni(salphen)$ and $SnBu^nCl_3\cdot Ni(salmphen)$. For both of these complexes it should be noted that while the *fac* isomers have the same quadrupole splitting values as those of their monohydroxo analogues (as a result of the latter having similar *fac* geometry), they have substantially greater chemical shift values than their monohydroxo analogues. Thus, bearing in mind that in all but one instance comparisons in Table 4 can only be made between *mer*-$SnBu^nCl_3\cdot ML$ and *fac* monohydroxo analogues, it is quite clear that, in most instances, replacement of chloride by hydroxide effectively gives rise to a decrease in chemical shift. The one clear exception to this trend is where the chemical shift of *mer*-$SnBu^nCl_3\cdot Ni(salpn)$ is the same as that of its *mer* monohydroxo analogue.

The lowering of the chemical shift accompanying the replacement of chloride by hydroxide cannot be rationalized satisfactorily simply on the basis of the electronegativities of the ligands. For example, the chemical shifts of $SnCl_6^{2-}$ and $SnCl_4F_2^{2-}$ are 0.52 and 0.29 mm s^{-1} respectively and thus, bearing in mind the good linear relationship between chemical shift and electronegativity which exists for the hexahalogenostannate(IV) series,[18] the predicted lowering of chemical shift accompanying replacement of one chloride of $SnCl_6^{2-}$ by fluoride is 0.12 mm s^{-1}. Alternatively, $SnCl_4\cdot NMe_3$ and $SnF_4\cdot NEt_3$ have chemical shifts of 0.59 and -0.22 mm s^{-1} respectively[19] from which it can be estimated that the average chemical shift change accompanying the replacement of chloride by fluoride is 0.2 mm s^{-1}. Reference to Tables 3 and 4 reveals examples of chemical shift changes accompanying the replacement of chloride by hydroxide which are significantly greater than 0.2 mm s^{-1}, despite the fact that the electronegativity of OH (3.51 on the Pauling scale) is appreciably less than that of fluoride.[20] The unexpectedly large chemical shift changes can be accounted for if it is assumed that tin–hydroxide bonds favour more s character than do tin–chloride bonds, and this would also be consistent with the hydroxo groups tending to be *trans* to the organo groups in the monoorganotin adducts (as discussed earlier).

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