Transition-metal Schiff-base Complexes as Ligands in Tin Chemistry. Part 3.[1] An X-Ray Crystallographic and Tin-119 Mössbauer Spectroscopic Study of Adduct Formation Between Tin(IV) Lewis Acids and Nickel 3-Methoxysalicylaldimine Complexes†

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1:1 Addition complexes of [$Ni^{II}L$]·H_2O [H_2L = *N,N'*-bis(3-methoxysalicylidene)ethylenediamine (3MeO-H_2salen), *N,N'*-bis(3-methoxysalicylidene)propane-1,2-diamine (3MeO-H_2salpn) or *N,N'*-bis(3-methoxysalicylidene)-*o*-phenylenediamine (3O-H_2salphen)] with SnR_2Cl_2 (R = Me or Ph), $SnBu^nCl_3$, or $SnCl_4$ have been found to be generally monoaqua adducts of the tin Lewis acids with the water engaged in hydrogen bonding with the methoxy and phenolic oxygen atoms of the Schiff-base ligand. Both water and methoxy oxygen atoms are involved in donor-bond formation to tin in the polymeric structures $2SnMe_2Cl_2$·[Ni(3MeO-salen)]·H_2O and $SnMe_2Cl_2$·[Ni(3MeO-salphen)]·H_2O, each of which has two very different tin environments. The two octahedral tin sites in the structure of $SnMe_2Cl_2$·2[Ni(3MeO-salphen)·H_2O] appear to result from two isomeric forms of the adduct co-existing in a lattice as a result of hydrogen-bonding interactions. Crystal-structure determinations revealed that the monoaqua adducts of dimethyltin dichloride which exist in the structures $SnMe_2Cl_2$·[Ni(3MeO-salen)]·H_2O and $SnMe_2Cl_2$·[Ni(3MeO-salpn)]·H_2O differ in that, in the former tin is in a trigonal-bipyramidal environment, whereas in the latter it is in an octahedral environment as a result of an intermolecular Sn ··· Cl contact of 3.615 Å.

We, and other groups, have shown that tin(IV) Lewis acids form 1:1 adducts with transition-metal Schiff-base complexes,[1-5] and the structures of two such adducts have been reported.[6,7] One of our specific interests in complexes of this type relates to the manner in which the dioxygen-carrying properties of cobalt salicylaldimine complexes are altered when they assume the role of donor ligands, particularly to tin.[7] This interest focused our attention on the donor properties of [M(3MeO-salen)] [M = divalent metal; 3MeO-H_2salen = *N,N'*-bis(3-methoxysalicylidene)ethylenediamine], since the cobalt analogue, unlike most cobalt salicylaldimines, forms a superoxo rather than a μ-peroxo complex with dioxygen.[8] A number of interesting influences of the methoxy substituents on the ligating properties of [M(3MeO-salen)], and closely related salicylaldimine complexes, will be demonstrated in this and other papers of the present series. The present paper reports on the nature of the adducts formed between tin(IV) Lewis acids and the nickel complexes [Ni(3MeO-salen)]·H_2O, Ni(3MeO-salpen)·H_2O [3MeO-H_2salpn = *N,N'*-bis(3-methoxysalicylidenepropane-1,2-diamine], and [Ni(3MeO-salphen)]·H_2O [3MeO-H_2-salphen = *N,N'*-bis(3-methoxysalicylidene)-*o*-phenylenediamine.

Experimental

Infrared spectra were recorded on a Perkin Elmer 983G spectrometer. Details of the Mössbauer spectrometer and spectrum curve-fitting procedure have been published.[5]

Adducts of Dimethyl- and Diphenyl-tin Dichloride.—The 1:1 adducts were prepared by stirring the Lewis acid (0.01 mol) and the metal Schiff-base complex (0.01 mol) in either acetonitrile (for the preparation of $SnMe_2Cl_2$·[Ni(3MeO-salen)]·H_2O or chloroform (for the preparation of other 1:1 adducts) for 4 h, after which time the adducts were filtered off. Doubling the quantity of the Lewis acid yielded the 2:1 adducts in Table 1 when reactions were conducted in chloroform, and the 1:2 adduct $SnMe_2Cl_2$·2[Ni(3MeO-salphen)·H_2O] when the reaction was conducted in acetonitrile. The 2:1 and 1:2 adducts were filtered off after reaction for 4 h.

Both the 1:2 and 2:1 adducts of $SnMe_2Cl_2$ with [Ni(3MeO-salphen)]·H_2O gave ^{119}Sn Mössbauer spectra exhibiting two doublets. Adducts of similar stoichiometry, prepared under reflux conditions, gave identical Mössbauer and infrared spectra to those of their analogues prepared at room temperature. Furthermore, Mössbauer and infrared spectra recorded for the adducts after they had been washed in a variety of solvents in which they were partially soluble were identical to those obtained for the same adducts prior to washing.

Adducts of n-*Butyltin Trichloride.*—Reactions were carried out as described for the dialkyltin dichloride adducts. An acid:base ratio of 1:1 in either acetonitrile or chloroform yielded the 1:1 adduct $SnBu^nCl_3$·[Ni(3MeO-salen)]·H_2O. In chloroform with an acid:base ratio of 1:1 the 1:1 adduct $SnBu^nCl_3$·[Ni(3MeO-salphen)]·H_2O was obtained while a similar reaction employing an acid:base ratio of 2:1 yielded a second modification of the adduct. An acid:base ratio of either 1:1 or 2:1 in acetonitrile yielded the 1:2 adduct $SnBu^nCl_3$·2-[Ni(3MeO-salphen)·H_2O].

Adducts of Tin Tetrachloride and Monohydroxotin Trichloride.—Reactions were carried out as described for the dialkyltin dichloride adducts. The 1:1 adducts of Table 1 were prepared in acetonitrile with an acid:base ratio of 1:1, but $SnCl_4$·[Ni-(3MeO-salphen)]·H_2O could also be prepared in chloroform. After the initial addition of $SnCl_4$ in these reactions, further

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical data (%) for the adducts *

Adduct	C	H	N	Cl
$\mathrm{SnMe_2Cl_2\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$	37.65 (38.45)	4.35 (4.15)	4.10 (4.50)	11.85 (11.35)
$\mathrm{2SnMe_2Cl_2\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$	31.35 (31.30)	3.85 (3.80)	4.00 (3.30)	16.90 (16.80)
$\mathrm{SnMe_2Cl_2\cdot[Ni(3MeO\text{-}salphen)]\cdot H_2O}$	43.20 (42.95)	3.75 (3.90)	4.40 (4.20)	10.65 (10.65)
$\mathrm{SnMe_2Cl_2\cdot 2[Ni(3MeO\text{-}salphen)\cdot H_2O]}$	48.95 (49.25)	4.50 (4.10)	4.65 (5.00)	7.15 (6.35)
$\mathrm{SnMe_2Cl_2\cdot[Ni(3MeO\text{-}salpn)]\cdot H_2O}$	39.80 (39.45)	4.45 (4.40)	4.25 (4.40)	10.85 (11.10)
$\mathrm{SnPhCl_2\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$	48.40 (48.10)	4.15 (4.00)	3.85 (3.75)	8.95 (9.50)
$\mathrm{SnBu^nCl_3\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$	37.80 (38.45)	4.25 (4.20)	4.00 (4.10)	15.55 (15.50)
α-$\mathrm{SnBu^nCl_3\cdot[Ni(3MeO\text{-}salphen)]\cdot H_2O}$	43.00 (42.55)	4.25 (3.95)	4.20 (3.80)	14.35 (14.55)
β-$\mathrm{SnBu^nCl_3\cdot[Ni(3MeO\text{-}salphen)]\cdot H_2O}$	42.27 (42.57)	4.10 (3.95)	4.00 (3.80)	13.75 (14.55)
$\mathrm{SnBu^nCl_3\cdot 2[Ni(3MeO\text{-}salphen)\cdot H_2O]}$	48.20 (48.65)	4.35 (4.15)	4.95 (4.75)	9.85 (9.00)
$\mathrm{SnCl_4\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$	33.05 (32.45)	3.20 (3.00)	4.20 (4.20)	20.60 (21.35)
$\mathrm{2SnCl_4\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$	23.30 (23.35)	2.40 (2.15)	2.95 (3.00)	30.70 (30.70)
$\mathrm{SnCl_4\cdot Sn(OH)Cl_3\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$	26.55 (25.80)	3.05 (2.35)	4.20 (4.50)	27.20 (26.70)
$\mathrm{SnCl_4\cdot[Ni(3MeO\text{-}salphen)]\cdot H_2O}$	36.85 (37.10)	3.00 (2.80)	3.95 (3.95)	20.80 (19.95)
$\mathrm{2SnCl_4\cdot[Ni(3MeO\text{-}salphen)]\cdot H_2O}$	26.90 (27.15)	2.35 (2.05)	2.55 (2.90)	28.60 (29.25)
$\mathrm{SnCl_4\cdot 2[Ni(3MeO\text{-}salphen)\cdot H_2O]}$	44.90 (45.45)	3.00 (3.45)	4.75 (4.80)	12.50 (12.20)
$\mathrm{SnCl_4\cdot[Ni(3MeO\text{-}salpn)]\cdot H_2O}$	33.70 (33.55)	3.75 (3.25)	3.90 (4.10)	20.30 (20.90)
$\mathrm{2Sn(OH)Cl_3\cdot[Ni(3MeO\text{-}salpn)]\cdot H_2O}$	24.70 (25.25)	3.20 (2.65)	3.90 (3.10)	24.15 (23.60)

* Theoretical data are in parentheses.

precautions against hydrolysis were unnecessary. Reactions with an acid:base ratio of 2:1 yielded the adducts $\mathrm{2SnCl_4\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$ (in either acetonitrile or chloroform), $\mathrm{2SnCl_4\cdot[Ni(3MeO\text{-}salpn)]\cdot H_2O}$ (in acetonitrile), $\mathrm{2SnCl_4\cdot[Ni(3MeO\text{-}salphen)]\cdot H_2O}$ (in chloroform) and $\mathrm{SnCl_4\cdot 2[Ni(3MeO\text{-}salphen)\cdot H_2O]}$ (in acetonitrile). The last two adducts were air stable, but exposure of the first two to air led to the formation of $\mathrm{SnCl_4\cdot Sn(OH)Cl_3\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$ and $\mathrm{2Sn(OH)Cl_3\cdot[Ni(3MeO\text{-}salpn)]\cdot H_2O}$. The latter formulation is preferred over $\mathrm{SnCl_4\cdot Sn(OH)_2Cl_2\cdot[Ni(3MeO\text{-}salpn)]\cdot H_2O}$ since we have shown that hydrolysis of tin tetrachloride adducts does not readily proceed beyond hydrolysis of one Sn–Cl bond.[1]

With the exceptions of $\mathrm{SnCl_4\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$, $\mathrm{SnCl_4\cdot Sn(OH)Cl_3\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$ and $\mathrm{2Sn(OH)Cl_3\cdot[Ni(3MeO\text{-}salpn)]\cdot H_2O}$ with magnetic moments of 2.5, 2.6 and 2.6 respectively, all other adducts of the present study were diamagnetic.

X-Ray Crystallography.—Crystals of $\mathrm{[Ni(3MeO\text{-}salen)]\cdot H_2O}$ were obtained from chloroform, while crystals of $\mathrm{SnMe_2Cl_2\cdot[Ni(3MeO\text{-}salpn)]\cdot H_2O}$ and $\mathrm{SnPh_2Cl_2\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$ were obtained from acetonitrile. Best-quality crystals of $\mathrm{SnMe_2Cl_2\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$ were obtained from the attempted crystallization of $\mathrm{2SnMe_2Cl_2\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$. Crystallographic details are in Table 2. The structure of $\mathrm{SnPh_2Cl_2\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O}$ failed to refine satisfactorily (monoclinic space group $P2_1/n$, $a = 8.545(3)$, $b = 25.455(5)$, $c = 14.511(3)$ Å, $\beta = 101.294(5)°$, $U = 3095.10$ Å^3, $Z = 4$). The other three structures were solved by direct methods, SHELX 86,[9] and refined by full-matrix least squares, SHELX 76.[10] Data were corrected for Lorentz polarization and extinction effects, but not initially for absorption. Hydrogen atoms were included in calculated positions for final refinement cycles. In the case of $\mathrm{[Ni(3MeO\text{-}salen)]\cdot H_2O}$, nickel, carbon and oxygen atoms of the methoxy groups and carbon atoms of the ethylene bridge were refined anisotropically. In the case of $\mathrm{SnMe_2Cl_2\cdot[Ni(3MeO\text{-}salen)]\cdot H_2O\cdot CHCl_3}$, metal and chlorine atoms were refined anisotropically. In the case of $\mathrm{SnMe_2Cl_2\cdot[Ni(3MeO\text{-}salpn)]\cdot H_2O}$, metal atoms, all oxygen and nitrogen atoms, and carbon atoms of methyl groups were refined anisotropically. Since the degree of refinement achieved for each structure was not particularly good, structural refinements were again carried out after data had been corrected for absorption, DIFABS.[11] This did not, in any case, lead to more satisfactory refinement. Data in Table 1 refer to refinement without absorption corrections. The atomic scattering factors for all atoms and the anomalous dispersion correction factors for non-hydrogen atoms were taken from refs. 12–14. Calculations were carried out on a VAX 8700 computer. Final atomic coordinates are in Tables 3–5. The programs PLUTO[15] and ORTEP[16] were used to produce the drawings in Figs. 2–5.

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

Discussion

The complexes $\mathrm{[Ni(3MeO\text{-}salen)]\cdot H_2O}$, $\mathrm{[Ni(3MeO\text{-}salpn)]\cdot H_2O}$ and $\mathrm{[Ni(3MeO\text{-}salphen)]\cdot H_2O}$ behave as their anhydrous analogues without methoxy substituents[4] in that they readily

Table 2 Crystallographic data[a]

Complex	[Ni(3MeO-salen)]·H_2O	**A**	**B**
Formula	$C_{18}H_{20}N_2NiO_5$	$C_{21}H_{27}Cl_5N_2NiO_5Sn$	$C_{21}H_{28}Cl_2N_2NiO_5Sn$
Space group	*Pbcn* (orthorhombic)	$P\bar{1}$ (triclinic)	$P\bar{1}$ (triclinic)
a/Å	12.025(3)	9.986(2)	10.360(7)
b/Å	15.200(4)	9.972(2)	10.129(4)
c/Å	19.555(5)	15.246(3)	13.143(8)
α/°	90.0	88.03(3)	80.81(2)
β/°	90.0	75.33(7)	88.59(2)
γ/°	90.0	87.90(6)	65.90(2)
U/Å^3	3574.26	1467.28	1241.65
Z	8	2	2
D_c/g cm^3	1.498	1.680	1.703
F(000)	1680.0	740.0	640.0
Crystal dimensions/mm	0.21 × 0.22 × 0.30	0.21 × 0.19 × 0.29	0.19 × 0.21 × 0.25
μ(Mo-Kα)/cm^{-1}	10.52	18.53	18.82
Data collected	$+h, +k, +l$	$\pm h, \pm k, +l$	$\pm h, \pm k, +l$
Unique reflections	3046	2195	3786
Reflections with $I > n\sigma(I)$[b]	954	2032	2545
R[c]	0.071	0.050	0.083
R'[d]	0.078	0.057	0.085
$10^2\,g$	0.43	0.277	0.0525
No. of parameters fitted	140	178	204
Maximum shift/e.s.d.	0.001	0.001	0.001
Maximum and minimum residual density/e Å^{-3}	0.35, −0.18	0.34, −0.31	0.95, −0.72
Goodness of fit[e]	1.16	1.13	2.23

[a] Measurements were performed at approximately 22 °C on a Hilger and Watts Y290 diffractometer for [Ni(3MeO-salen)]·H_2O, and on an Enraf–Nonius CAD4F diffractometer for both **A** and **B**, with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) in all cases. The scan method in all cases was ω–θ to θ_{max} 24° for both [Ni(3MeO-salen)]·H_2O and **A**, and 30° for **B**. [b] $n = 3$ for [Ni(3MeO-salen)]·H_2O and **A**, and 2 for **B**. [c] $[\Sigma||F_o| - |F_c||]/\Sigma|F_o|$. [d] $\Sigma w(|F_o - F_c|)^2]/\Sigma w(|F_o|)^2]^{\frac{1}{2}}$; $w = 1/[(\sigma F_o)^2 - gF_o^2]$. [e] $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_p)]^{\frac{1}{2}}$, where N_o and N_p are the numbers of observations and parameters.

Table 3 Fractional atomic coordinates for [Ni(3MeO-salen)]·H_2O

Atom	x	y	z
Ni	0.199 63(10)	−0.045 47(15)	0.550 08(13)
O(3)	0.030 0(6)	−0.295 1(11)	0.547 1(11)
O(4)	0.253 3(7)	−0.301 3(10)	0.746 1(8)
C(8)	0.277 1(10)	−0.131 9(17)	0.486 8(13)
C(9)	0.204 8(11)	−0.161 6(16)	0.469 2(14)
C(17)	−0.022 8(10)	−0.365 2(17)	0.564 0(19)
C(18)	0.267 0(11)	−0.391 3(15)	0.804 1(13)
O(1)	0.124 3(5)	−0.138 7(8)	0.543 1(7)
O(2)	0.232 1(5)	−0.147 9(8)	0.630 4(7)
O(5)	0.107 9(8)	−0.214 8(13)	0.727 9(10)
N(1)	0.165 8(7)	0.056 9(12)	0.471 6(8)
N(2)	0.277 4(6)	0.044 7(11)	0.554 4(9)
C(1)	0.289 6(8)	−0.139 7(12)	0.677 2(9)
C(2)	0.303 7(10)	−0.221 9(14)	0.738 9(11)
C(3)	0.361 4(9)	−0.218 6(15)	0.791 7(12)
C(4)	0.408 4(10)	−0.131 6(15)	0.780 7(12)
C(5)	0.397 1(10)	−0.052 7(18)	0.724 4(12)
C(6)	0.335 2(8)	−0.053 1(14)	0.667 6(10)
C(7)	0.328 3(9)	0.034 6(15)	0.605 7(11)
C(10)	0.111 6(8)	−0.047 6(15)	0.425 0(10)
C(11)	0.064 9(7)	−0.041 3(13)	0.427 0(9)
C(12)	0.007 2(8)	−0.040 2(15)	0.368 9(12)
C(13)	−0.035 8(10)	−0.120 6(17)	0.371 0(14)
C(14)	−0.031 8(9)	−0.209 2(15)	0.427 0(11)
C(15)	0.022 4(9)	−0.211 4(14)	0.486 4(11)
C(16)	0.072 4(7)	−0.129 2(13)	0.486 5(9)

Table 4 Fractional atomic coordinates for complex **A**

Atom	x	y	z
Sn	0.531 58(9)	0.293 40(9)	0.320 26(6)
Ni	0.136 51(16)	0.888 76(15)	0.486 00(10)
Cl(1)	0.350 1(4)	0.473 6(4)	0.870 4(3)
Cl(2)	0.360 7(4)	0.142 5(4)	0.807 9(3)
Cl(3)	0.786 5(6)	−0.405 5(6))	0.864 8(4)
Cl(4)	1.035 8(6)	−0.338 8(7)	0.908 6(4)
Cl(5)	0.815 9(8)	−0.138 8(6)	0.910 3(5)
O(1)	0.263 2(8)	0.994 0(7)	0.406 0(5)
O(2)	0.094 7(8)	0.825 2(8)	0.383 3(5)
O(3)	0.416 5(9)	1.129 2(8)	0.271 4(6)
O(4)	0.060 3(10)	0.777 3(10)	0.225 0(7)
O(5)	0.684 1(8)	0.112 0(8)	0.770 7(5)
N(1)	0.180 7(11)	0.949 6(10)	0.586 6(7)
N(2)	0.008 9(11)	0.781 8(10)	0.565 8(7)
C(1)	0.346 2(11)	1.081 7(10)	0.427 4(7)
C(2)	0.429 6(13)	1.159 3(12)	0.354 2(8)
C(3)	0.518 3(14)	1.254 6(13)	0.370 0(9)
C(4)	0.522 6(16)	1.273 4(15)	0.461 2(10)
C(5)	0.446 0(14)	1.202 7(13)	0.529 8(10)
C(6)	0.351 1(12)	1.108 3(12)	0.514 7(8)
C(7)	0.270 3(13)	1.036 4(13)	0.590 5(10)
C(8)	0.108 1(18)	0.878 5(17)	0.672 0(11)
C(9)	−0.005 2(17)	0.814 5(16)	0.659 8(11)
C(10)	−0.069 8(16)	0.692 9(15)	0.544 8(11)
C(11)	−0.076 4(13)	0.662 2(12)	0.456 6(8)
C(12)	−0.170 7(15)	0.563 9(14)	0.444 7(10)
C(13)	−0.186 5(17)	0.541 8(16)	0.358 5(11)
C(14)	−0.110 9(15)	0.613 4(14)	0.285 5(11)
C(15)	−0.019 7(13)	0.704 6(12)	0.296 4(9)
C(16)	0.001 9(12)	0.732 0(12)	0.380 4(8)
C(17)	0.509 0(15)	1.192 0(15)	0.193 8(10)
C(18)	0.031 3(16)	0.772 2(16)	0.136 4(10)
C(19)	0.577 0(15)	0.268 5(14)	0.946 3(9)
C(20)	0.627 5(15)	0.397 1(14)	0.698 0(9)
C(21)	0.859 0(19)	−0.304 8(18)	0.931 9(14)

form 1:1 adducts with $SnCl_4$, $SnBu^nCl_3$ and SnR_2Cl_2 (R = Me or Ph), but differ in being also able to form adducts of other stoichiometries. For example, [Ni(3MeO-salphen)]·H_2O forms 1:2 adducts with all of the tin Lewis acids except $SnPh_2Cl_2$. The three nickel complexes form 2:1 adducts with $SnCl_4$, while [Ni(3MeO-salen)]·H_2O is also capable of forming a 2:1 adduct with $SnMe_2Cl_2$.

The parent nickel Schiff-base complexes crystallize from solution as monohydrates, in which respect they resemble many other metal complexes having the same salicylaldimine ligands. The crystal structures of [Fe(3MeO-salen)(pim)(H_2O)]BPh_4

Table 5 Fractional atomic coordinates for complex **B**

Atom	*x*	*y*	*z*
Sn	0.450 50(11)	0.236 32(9)	0.410 51(7)
Ni	0.184 0(2)	0.403 6(2)	0.055 9(1)
Cl(1)	0.676 3(4)	0.039 7(4)	0.487 7(3)
Cl(2)	0.555 7(4)	0.401 5(4)	0.353 1(3)
O(1)	0.223 4(11)	0.530 0(10)	0.121 7(7)
O(2)	0.115 2(10)	0.354 1(9)	0.182 1(7)
O(3)	0.240 6(11)	0.703 4(10)	0.240 4(8)
O(4)	0.028 1(11)	0.323 6(10)	0.367 1(8)
O(5)	0.238 3(9)	0.434 3(9)	0.339 7(7)
N(1)	0.260 6(14)	0.453 8(15)	−0.069 3(9)
N(2)	0.136 5(16)	0.286 3(15)	−0.014 4(11)
C(18)	0.270 4(18)	0.778 3(16)	0.311 3(14)
C(19)	0.020 6(17)	0.307 9(17)	0.468 6(13)
C(20)	0.359 4(17)	0.283 3(15)	0.549 9(10)
C(21)	0.439 1(16)	0.130 7(15)	0.289 6(10)
C(1)	0.276 0(14)	0.623 4(15)	0.082 8(11)
C(2)	0.287 1(14)	0.717 6(15)	0.144 1(11)
C(3)	0.340 6(16)	0.823 3(18)	0.107 6(12)
C(4)	0.384 7(18)	0.825 4(21)	0.006 9(14)
C(5)	0.377 4(18)	0.737 3(19)	−0.050 4(15)
C(6)	0.323 0(16)	0.633 2(17)	−0.020 5(12)
C(7)	0.316 6(19)	0.544 6(20)	−0.085 2(15)
C(8)	0.259 0(25)	0.363 2(26)	−0.149 9(17)
C(9)	0.170 8(29)	0.308 7(31)	−0.129 2(19)
C(10)	0.162 2(24)	0.202 4(26)	−0.193 9(18)
C(11)	0.074 7(20)	0.209 5(22)	0.025 1(15)
C(12)	0.033 4(17)	0.186 5(17)	0.124 3(12)
C(13)	−0.036 4(20)	0.092 4(22)	0.154 0(16)
C(14)	−0.081 3(19)	0.078 6(21)	0.250 5(14)
C(15)	−0.064 0(17)	0.153 3(19)	0.323 5(14)
C(16)	0.004 3(16)	0.244 7(17)	0.299 7(12)
C(17)	0.054 4(15)	0.265 4(16)	0.197 5(11)

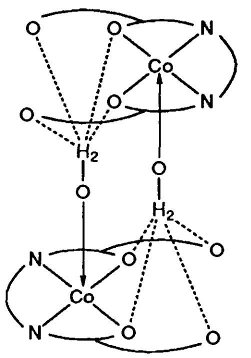

Fig. 1 Schematic representation of the structure of [Co(3MeO-salen)]·H_2O.[18] Dotted lines signify hydrogen-bonding interactions

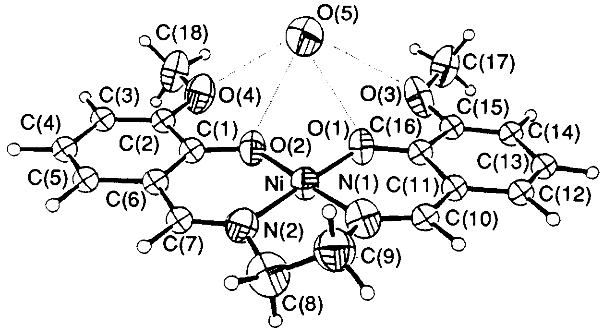

Fig. 2 The asymmetric unit of [Ni(3MeO-salen)]·H_2O. Dotted lines represent hydrogen-bonding interactions

Table 6 Selected bond lengths (Å) and angles (°) for [Ni(3MeO-salen)]·H_2O

Ni–O(1)	1.854(10)	Ni–O(2)	1.847(10)
Ni–N(1)	1.837(14)	Ni–N(2)	1.869(12)
O(1)–C(16)	1.337(16)	O(2)–C(1)	1.335(16)
O(3)–C(15)	1.373(10)	O(3)–C(17)	1.357(22)
O(4)–C(2)	1.376(19)	O(4)–C(18)	1.422(19)
N(1)–C(9)	1.472(23)	N(1)–C(10)	1.281(18)
N(2)–C(7)	1.271(19)	N(2)–C(8)	1.468(22)
C(1)–C(2)	1.390(20)	C(1)–C(6)	1.379(20)
C(2)–C(3)	1.386(23)	C(3)–C(4)	1.403(23)
C(4)–C(5)	1.297(24)	C(5)–C(6)	1.487(23)
C(6)–C(7)	1.419(22)	C(8)–C(9)	1.48(3)
C(10)–C(11)	1.406(21)	C(11)–C(12)	1.433(21)
C(11)–C(16)	1.399(20)	C(12)–C(13)	1.282(23)
C(13)–C(14)	1.366(25)	C(14)–C(15)	1.394(21)
C(15)–C(16)	1.390(21)		
O(2)–Ni–O(1)	84.7(5)	N(1)–Ni–O(1)	94.7(6)
N(1)–Ni–O(2)	178.8(5)	N(2)–Ni–O(1)	177.8(5)
N(2)–Ni–O(2)	94.8(5)	N(2)–Ni–N(1)	85.8(6)
C(16)–O(1)–Ni	126(1)	C(1)–O(2)–Ni	126.4(9)
C(17)–O(3)–C(15)	120(1)	C(18)–O(4)–C(2)	116(1)
C(9)–N(1)–Ni	114(1)	C(10)–N(1)–Ni	127(1)
C(10)–N(1)–C(9)	119(2)	C(7)–N(2)–Ni	127(1)
C(8)–N(2)–Ni	113(1)	C(8)–N(2)–C(7)	120(1)
C(2)–C(1)–O(2)	118(1)	C(6)–C(1)–O(2)	123(1)
C(5)–C(7)–N(2)	123(2)	C(9)–C(8)–N(2)	108(1)
C(8)–C(9)–N(1)	106(2)	C(11)–C(10)–N(1)	126(2)
C(11)–C(16)–O(1)	124(1)	C(15)–C(16)–O(1)	118(1)

Table 7 A comparison of hydrogen-bonding interactions involving water and salicylaldimine oxygen atoms[a]

Distance/Å	**I**	**II**	**III**	**IV**	**V**
$H_2O \cdots O(1)$[b]	2.973	2.845	2.869	2.85	2.858
$H_2O \cdots O(2)$	2.956	2.857	2.857	2.85	2.887
$H_2O \cdots O(3)$	3.288	2.796	2.852	2.97	3.108
$H_2O \cdots O(4)$	3.039	2.835	2.824	2.97	3.129

[a] **I** refers to [Ni(3MeO-salen)]·H_2O, **II** to $SnMe_2Cl_2$·[Ni(3MeO-salen)]·H_2O, **III** to $SnMe_2Cl_2$·[Ni(3MeO-salpn)]·H_2O, **IV** to [Co(3-MeO-salen)]·H_2O,[18] and **V** to [Fe(3MeO-salen)(pim)]BPh_4·H_2O.[17] [b] For **I**–**III** the atom labelling corresponds to that in Figs. 2–4. For **IV** and **V** O(1) and O(2) refer to phenolic oxygens while O(3) and O(4) refer to methoxy oxygens.

(pim = 5-phenylimidazole)[17] and [Co(3MeO-salen)(H_2O)][18] reveal a common structural role for water, behaving as a donor ligand to a metal while participating in hydrogen bonding with ligand oxygens of a neighbouring molecule (see, for example, the schematic representation of the cobalt salicylaldimine structure in Fig. 1).

In the case of [Ni(3MeO-salen)]·H_2O, water similarly engages in hydrogen-bonding interactions with the Schiff-base oxygen atoms (see the asymmetric unit of Fig. 2 and molecular parameters in Table 6) but does not form a donor bond with nickel. In view of the diamagnetic nature of the other two nickel salicylaldimine complexes of this study, and the position of water-related bands in their infrared spectra (to be discussed later), it is reasonably certain that they are isostructural with [Ni(3MeO-salen)]·H_2O.

Table 7 compares distances from the water oxygen to the Schiff-base oxygen atoms in the iron and cobalt salicylaldimine structures with those for [Ni(3MeO-salen)]·H_2O, from which two points are noteworthy. First, in all three structures hydrogen-bonding interactions are stronger with the phenolic than with the methoxy oxygens. Secondly, and most significantly, hydrogen-bonding interactions are weaker in the nickel structure than in the iron and cobalt structures, in which the water is engaged in donor-bond formation.

The crystal structures of $SnMe_2Cl_2$·[Ni(3MeO-salen)]·H_2O·$CHCl_3$ **A** and $SnMe_2Cl_2$·[Ni(3MeO-salpn)]·H_2O **B** (see Figs. 3 and 4 for the asymmetric units, and Tables 8 and 9 for

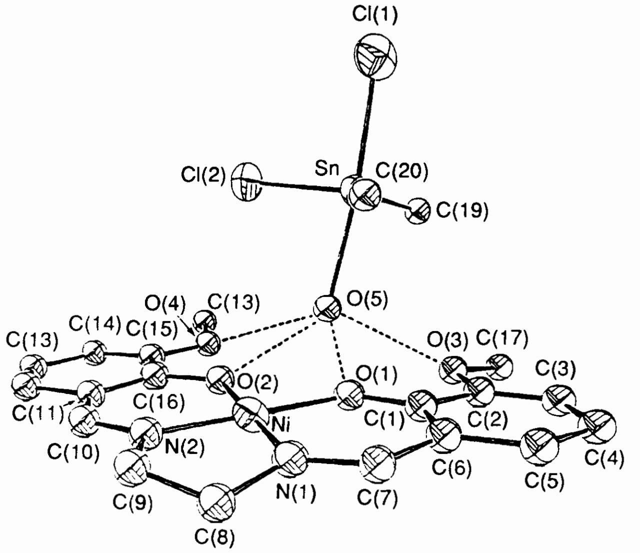

Fig. 3 The asymmetric unit of $SnMe_2Cl_2$·[Ni(3MeO-salen)]·H_2O **A** with hydrogen atoms omitted for clarity. Dotted lines represent hydrogen-bonding interactions

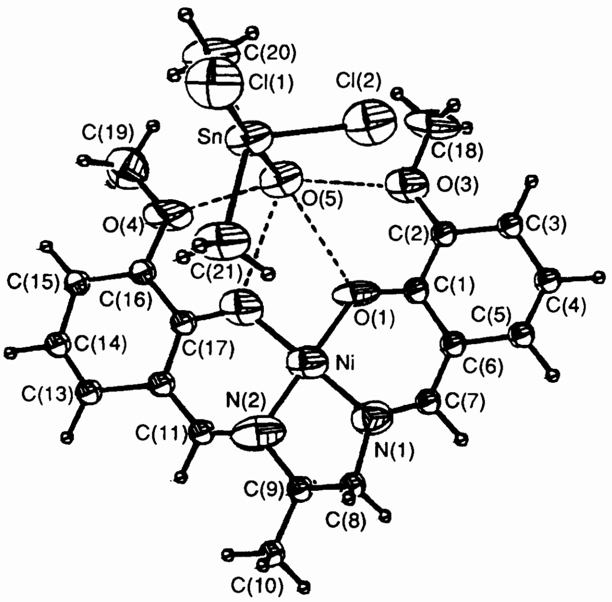

Fig. 4 The asymmetric unit of $SnMe_2Cl_2$·[Ni(3MeO-salpn)]·H_2O **B**. Dotted lines represent hydrogen-bonding interactions

Table 8 Selected bond lengths (Å) and angles (°) for complex **A**

Sn–Cl(1)	2.501(4)	Sn–Cl(2)	2.363(3)
Sn–O(5)	2.339(8)	Sn–C(19)	2.087(14)
Sn–C(20)	2.120(13)	Ni–O(1)	1.848(8)
Ni–O(2)	1.856(8)	Ni–N(1)	1.828(10)
Ni–N(2)	1.862(10)	O(1)–C(1)	1.330(12)
O(2)–C(16)	1.346(14)	O(3)–C(2)	1.346(14)
O(3)–C(17)	1.443(15)	O(4)–C(15)	1.377(15)
O(4)–C(18)	1.453(17)	N(1)–C(7)	1.281(15)
N(1)–C(8)	1.490(18)	N(2)–C(9)	1.451(18)
N(2)–C(10)	1.305(17)	C(1)–C(2)	1.434(16)
C(1)–C(6)	1.378(15)	C(2)–C(3)	1.390(17)
C(3)–C(4)	1.421(20)	C(4)–C(5)	1.326(19)
C(5)–C(6)	1.425(17)	C(6)–C(7)	1.420(17)
C(8)–C(9)	1.374(21)	C(10)–C(11)	1.407(19)
C(11)–C(12)	1.431(18)	C(11)–C(16)	1.404(17)
C(12)–C(13)	1.387(20)	C(13)–C(14)	1.371(20)
C(14)–C(15)	1.354(19)	C(15)–C(16)	1.388(17)
Cl(2)–Sn–Cl(1)	90.6(1)	O(5)–Sn–Cl(1)	174.4(2)
O(5)–Sn–Cl(2)	83.8(2)	C(19)–Sn–Cl(1)	94.8(4)
C(19)–Sn–Cl(2)	110.4(4)	C(19)–Sn–O(5)	87.8(4)
C(20)–Sn–Cl(1)	93.8(4)	C(20)–Sn–Cl(2)	114.9(4)
C(20)–Sn–O(5)	87.9(4)	C(20)–Sn–C(19)	133.7(6)
O(2)–Ni–O(1)	85.5(3)	N(1)–Ni–O(1)	94.2(4)
N(1)–Ni–O(2)	179.0(4)	N(2)–Ni–O(1)	179.5(3)
N(2)–Ni–O(2)	94.0(4)	N(2)–Ni–N(1)	86.3(5)
C(1)–O(1)–Ni	126.6(7)	C(16)–O(2)–Ni	127.0(7)
C(17)–O(3)–C(2)	118(1)	C(18)–O(4)–C(15)	119(1)
C(7)–N(1)–Ni	128.1(9)	C(8)–N(1)–Ni	113.2(9)
C(8)–N(1)–C(7)	118(1)	C(9)–N(2)–Ni	112.2(9)
C(10)–N(2)–Ni	127(1)	C(10)–N(2)–C(9)	121(1)
C(2)–C(1)–O(1)	117(1)	C(6)–C(1)–O(1)	125(1)
C(7)–C(6)–C(1)	121(1)	C(7)–C(6)–C(5)	118(1)
C(6)–C(7)–N(1)	125(1)	C(9)–C(8)–N(1)	110(1)
C(8)–C(9)–N(2)	112(1)	C(11)–C(10)–N(2)	126(1)
C(12)–C(11)–C(10)	119(1)	C(16)–C(11)–C(10)	121(1)
C(11)–C(16)–O(2)	124(1)	C(15)–C(16)–O(2)	118(1)

molecular parameters) reveal that in each adduct tin forms a donor bond to water without disrupting hydrogen-bonding interactions. As a result, water acquires the dual bonding role displayed in the iron and cobalt salicylaldimine structures.[17,18] However, the hydrogen bonding in the tin adducts is stronger, and results in more uniform involvement of the Schiff-base oxygen atoms (see Table 7). It is also apparent from a comparison of hydrogen-bonding data for [Ni(3MeO-salen)]·H_2O with those for its dimethyltin dichloride adduct (see Table 7) that, as a result of water becoming involved in donor-bond formation to tin, hydrogen-bonding interactions increase; this is consistent with earlier comments relating to data in Table 7. Furthermore, a comparison of hydrogen-bonding data for the adducts **A** and **B** reveals that the stronger the donor bond to tin the stronger become the hydrogen-bonding interactions.

The formation of a donor bond by water, coupled with a strengthening of hydrogen-bonding interactions, results in a decisive lowering in frequency of the water-related vibrations above 3000 cm^{-1} in the infrared spectra of the complexes. For example, the band at 3515 cm^{-1} in the spectrum of [Ni(3MeO-salen)]·H_2O compares with a band at 3320 cm^{-1} in the spectrum of its cobalt analogue, and with bands at 3335 and 3340 cm^{-1} for its dimethyl- and diphenyl-tin dichloride adducts respectively (crystallographic data for the latter did not refine satisfactorily, but did reveal that it is isostructural with its dimethyltin analogue). Likewise, water-related vibrations occurring at 3500 and 3450 cm^{-1} in the spectrum of [Ni(3MeO-salpn)]·H_2O are replaced by a band at 3360 cm^{-1} in the spectrum of its dimethyltin dichloride adduct.

The increase in hydrogen-bonding interactions resulting from donor-bond formation to tin has no significant effect on bond distances within [Ni(3MeO-salen)] (see Tables 6 and 8), but does have the expected effect of increasing the overall planarity of the metal salicylaldimine moiety.[19] For example [Ni(3MeO-salen)]·H_2O has a stepped conformation with dihedral angles of 5.412 and 7.646°, whereas $SnMe_2Cl_2$·[Ni(3MeO-salen)]·H_2O, which also has a stepped configuration, has dihedral angles of 1.712 and 2.015°. Crystallographic data are not available for [Ni(3MeO-salpn)]·H_2O, but its dimethyltin dichloride adduct has an umbrella conformation with small dihedral angles of 2.426 and 4.264°.

Adduct **A** appears to be the first example of a 1:1 neutral adduct of dimethyltin dichloride with tin having five-co-ordinate geometry. The geometry about tin in other 1:1 adducts is best described as six-co-ordinate as a result of short intermolecular contacts.[20] In adduct **A** the shortest intermolecular Sn ··· Cl contact, involving a chlorine atom of chloroform, is 4.186 Å, which exceeds the sum of the van der Waals radii of tin and chlorine. The geometry about tin in adduct **A** conforms well to trigonal bipyramidal, and in common with 1:1 adducts of diphenyltin dichloride, containing five-co-

Table 9 Selected bond lengths (Å) and angles (°) for complex **B**

Sn–Cl(1)	2.477(4)	Sn–Cl(2)	2.367(4)
Sn–O(5)	2.372(8)	Sn–C(20)	2.07(1)
Sn–C(21)	2.08(1)	Ni–O(1)	1.83(1)
Ni–O(2)	1.865(9)	Ni–N(1)	1.90(1)
Ni–N(2)	1.83(1)	O(1)–C(1)	1.31(2)
O(2)–C(17)	1.28(2)	O(3)–C(2)	1.35(2)
O(3)–C(18)	1.40(2)	O(4)–C(16)	1.37(2)
O(4)–C(19)	1.42(2)	N(1)–C(7)	1.26(2)
N(1)–C(8)	1.51(2)	N(2)–C(9)	1.54(3)
N(2)–C(11)	1.24(2)	C(1)–C(2)	1.38(2)
C(1)–C(6)	1.43(2)	C(2)–C(3)	1.41(2)
C(3)–C(4)	1.39(2)	C(4)–C(5)	1.28(2)
C(5)–C(6)	1.39(2)	C(6)–C(7)	1.35(2)
C(8)–C(9)	1.25(3)	C(9)–C(10)	1.50(3)
C(11)–C(12)	1.38(2)	C(12)–C(13)	1.42(2)
C(12)–C(17)	1.42(2)	C(13)–C(14)	1.35(2)
C(14)–C(15)	1.37(2)	C(15)–C(16)	1.37(2)
C(16)–C(17)	1.44(2)		
Cl(2)–Sn–Cl(1)	93.3(1)	O(5)–Sn–Cl(1)	176.8(2)
O(5)–Sn–Cl(2)	84.1(2)	C(20)–Sn–Cl(1)	95.5(4)
C(20)–Sn–Cl(2)	108.4(4)	C(20)–Sn–O(5)	83.4(5)
C(21)–Sn–Cl(1)	95.0(4)	C(21)–Sn–Cl(2)	109.1(4)
C(21)–Sn–O(5)	87.8(5)	C(21)–Sn–C(20)	140.3(6)
O(2)–Ni–O(1)	84.7(4)	N(1)–Ni–O(1)	93.5(5)
N(1)–Ni–O(2)	177.6(5)	N(2)–Ni–O(1)	176.7(5)
N(2)–Ni–O(2)	96.5(6)	N(2)–Ni–N(1)	85.4(7)
C(1)–O(1)–Ni	127.9(9)	C(17)–O(2)–Ni	124.2(9)
C(18)–O(3)–C(2)	118(1)	C(19)–O(4)–C(16)	117(1)
C(7)–N(1)–Ni	126(1)	C(8)–N(1)–Ni	112(1)
C(8)–N(1)–C(7)	121(2)	C(9)–N(2)–Ni	111(1)
C(11)–N(2)–Ni	123(1)	C(11)–N(2)–C(9)	126(2)
C(2)–C(1)–O(1)	119(1)	C(6)–C(1)–O(1)	123(1)
C(7)–C(6)–C(1)	122(2)	C(7)–C(6)–C(5)	122(2)
C(6)–C(7)–N(1)	127(2)	C(9)–C(8)–N(1)	110(2)
C(8)–C(9)–N(2)	116(2)	C(10)–C(9)–N(2)	117(2)
C(10)–C(9)–C(8)	119(2)	C(12)–C(11)–N(2)	131(2)
C(13)–C(12)–C(11)	122(2)	C(17)–C(12)–C(11)	119(2)
C(12)–C(17)–O(2)	126(1)	C(16)–C(17)–O(2)	116(1)

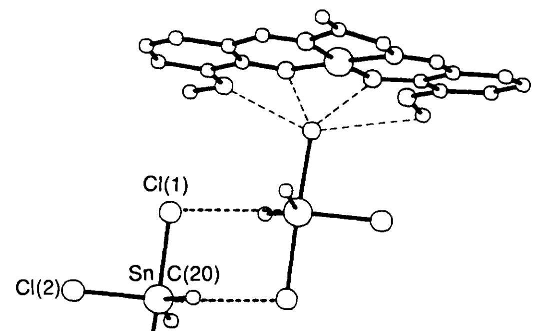

Fig. 5 Dimerization of $SnMe_2Cl_2$·[Ni(CMeO-salpn)]·H_2O **B**. Dotted lines represent hydrogen-bonding interactions, dashed lines intermolecular Sn ··· Cl bonds (3.615 Å)

ordinated tin,$^{21-25}$ the axial Sn–Cl bond length [2.501(4) Å] is considerably longer than the equatorial Sn–Cl bond length [2.363(3) Å]. The C–Sn–C bond angle of 133.7(6)° is well within the range of C–Sn–C bond angles which have been reported for diphenyltin dichloride adducts, but smaller than the corresponding angle of 140° for the five-co-ordinated tin anion^{26} $[SnMe_2Cl_3]^-$.

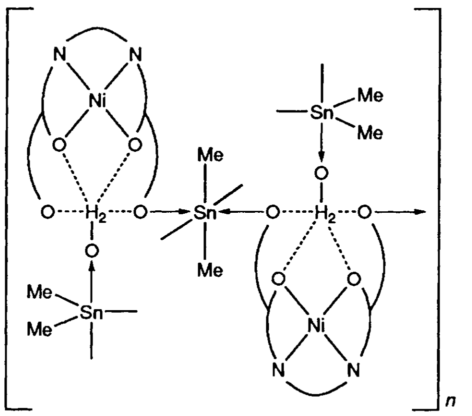

Fig. 6 Schematic representation of the structure of $2SnMe_2Cl_2$·[Ni(3MeO-salen)]·H_2O. Dotted lines represent hydrogen-bonding interactions

In the case of adduct **B**, there is an intermolecular Sn ··· Cl bond of 3.615 Å (see Fig. 5). This is well within the sum of the van der Waals radii of tin and chlorine and its influence is most clearly seen in the C–Sn–C bond angle of 140.3(6)°, which compares with a related bond angle of 133.7(6)° in the monomeric adduct. These angles compare with C–Sn–C bond angles of 154.4 and 153.2° which are associated with much stronger intermolecular Sn ··· Cl contacts of 3.311 and 3.05 Å respectively for the two crystallographically independent monoaqua adducts of dimethyltin dichloride in $[2(SnMe_2Cl_2 \cdot H_2O) \cdot 18\text{-crown-}6]_n$ (18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane).^{27} A final structural point worth noting in respect to the three monoaqua adducts is that the $Sn-OH_2$ donor bonds are all considerably longer than the corresponding donor-bond lengths of 2.235(4) Å in $SnMe_2Cl_2 \cdot 2H_2O$–purine (1:4).^{28}

The adduct $SnMe_2Cl_2$·[Ni(3MeO-salen)]·H_2O reacts with a further molecule of dimethyltin dichloride to form $2SnMe_2Cl_2$·[Ni(3MeO-salen)]·H_2O. The ^{119}Sn Mössbauer spectrum consists of two doublets, corresponding to quadrupole splittings of 3.29 (close to that observed for the 1:1 adduct) and 4.87 mm s^{-1}. The latter quadrupole splitting unquestionably results from a *trans*-methyl octahedral tin environment. There are two significant features associated with the infrared spectrum of the 2:1 adduct. First, the water-associated band at 3360 cm^{-1}, although at a somewhat higher frequency than that for the 1:1 adduct, is still considerably lower than that for the free nickel salicylaldimine hydrate. Secondly, the phenolic ν(C–O) stretching frequency at 1560 cm^{-1} compares with a value of 1546 cm^{-1} for the 1:1 adduct. These data suggest a similar, though somewhat weaker, interaction with water, and a greater interaction with the phenolic oxygen in the 2:1 than in the 1:1 adduct. The spectroscopic data, coupled with steric considerations, suggest the polymeric structure of Fig. 6 for the 2:1 adduct. The involvement of the methoxy oxygens in donor-bond formation in this structure may well result in hydrogen-bonding interactions being largely confined to the phenolic oxygens, thus accounting for the ν(C–O) stretching-frequency data.

The ^{119}Sn Mössbauer spectrum of $SnMe_2Cl_2$·[Ni(3MeO-salphen)]·H_2O is remarkably similar to that of $2SnMe_2Cl_2$·[Ni(3MeO-salen)]·H_2O (see Table 10). Its infrared spectrum shows a water-related band at 3410 cm^{-1}, but there is a pronounced shoulder on this band at approximately 3470 cm^{-1}, which is the position of the band in the spectrum of the free nickel salicylaldimine hydrate. These data suggest the structural possibilities of Fig. 7. The tin bonded to water may remain five-co-ordinated (n = 1) as in **A**, or it may become six-co-ordinated by forming an intermolecular contact, either with an axial chlorine (Cl_{ax}) of a neighbouring molecular unit (n = 2) as in

Table 10 Mössbauer spectroscopic and selected infrared data[a] for the adducts

	ν(OH)	ν(C–O)	Δ	δ
Adduct	cm^{-1}		$mm\ s^{-1}$	
$SnMe_2Cl_2$·[Ni(3MeO-salen)]·H_2O	3335 (3515)	1546 (1540)	3.12	1.35
$2SnMe_2Cl_2$·[Ni(3MeO-salen)]·H_2O	3360	1560	4.87 3.29	1.63 1.41
$SnMe_2Cl_2$·[Ni(3MeO-salphen)]·H_2O	3410 (3470)	1539 (1535)	4.63 3.29	1.59 1.42
$SnMe_2Cl_2$·2[Ni(3MeO-salphen)·H_2O]	3405	1540	4.77 3.63	1.65 1.42
$SnMe_2Cl_2$·[Ni(3MeO-salpn)]·H_2O	3360 (3500)	1549 (1546)	3.48	1.44
$SnPh_2Cl_2$·[Ni(3MeO-salen)]·H_2O	3340	1550	2.83	1.22
$SnBu^nCl_3$·[Ni(3MeO-salen)]·H_2O	3360	1546	1.81	1.10
α-$SnBu^nCl_3$·[Ni(3MeO-salphen)]·H_2O	3360	1542	1.75	1.16
β-$SnBu^nCl_3$·[Ni(3MeO-salphen)]·H_2O	3360	1540	2.08	1.11
$SnBu^nCl_3$·2[Ni(3MeO-salphen)·H_2O]	3360	1546	1.75	1.22
$SnCl_4$·[Ni(3MeO-salen)]·H_2O	3340	1552	0.61	0.27
$2SnCl_4$·[Ni(3MeO-salen)]·H_2O	3350	1565	0.65	0.49
$SnCl_4$·Sn(OH)Cl_3·[Ni(3MeO-salen)]·H_2O	3480	1550	0.57	0.31
$SnCl_4$·[Ni(3MeO-salphen)]·H_2O	3350	1543	0.50	0.39
$2SnCl_4$·[Ni(3MeO-salphen)]·H_2O	3340	1553	0.50	0.34
$SnCl_4$·2[Ni(3MeO-salphen)·H_2O]	3360	1548	0.67	0.32
$SnCl_4$·[Ni(3MeO-salpn)]·H_2O	3380	1548	0.0	0.54
2Sn(OH)Cl_3·[Ni(3MeO-salpn)]·H_2O	3460	1552	0.55	0.19

[a] Data in parentheses are for the free nickel Schiff-base complex.

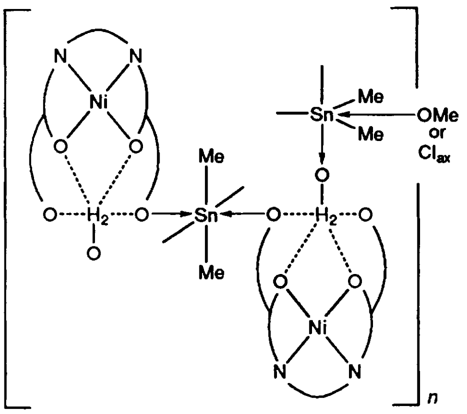

Fig. 7 Schematic representation of the structure of $SnMe_2Cl_2$·[Ni(3MeO-salphen)]·H_2O (see text for the value of *n*). Dotted lines signify hydrogen-bonding interactions

B, or with a methoxy oxygen of a neighbouring molecular unit (*n* = 2 or greater).

Since water-associated vibrations, above 3000 cm^{-1}, in the infrared spectra of the diamagnetic 1:1 adducts of *n*-butyltin trichloride and tin tetrachloride are at much lower frequencies than corresponding bands in the spectra of the parent nickel salicylaldimine hydrates, it is almost certain that, like **A** and **B**, they are aqua adducts of the tin Lewis acids. However, in view of the pronounced tendency for tin in both *n*-butyltin trichloride and tin tetrachloride to achieve six-co-ordination on adduct formation, it most likely does so in each of the present adducts, either by forming Sn–Cl or a Sn–OMe intermolecular bond. Perhaps it is the availability of these options for intermolecular bond formation which has resulted in the isolation of two modifications of $SnBu^nCl_3$·[Ni(3MeO-salphen)]·H_2O.

The origin of the anomalous paramagnetism (μ_{eff} = 2.5) of $SnCl_4$·[Ni(3MeO-salen)]·H_2O cannot, in the light of existing data, be explained. Attempts to grow crystals of the adduct resulted in the growth of crystals of $SnCl_2$(3MeO-salen). It was confirmed spectroscopically however that the latter complex

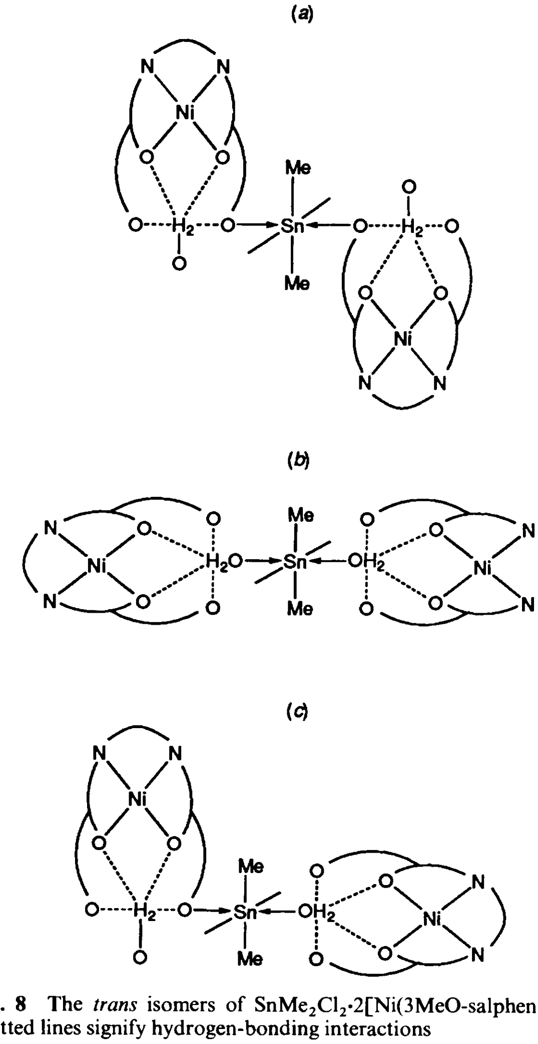

Fig. 8 The *trans* isomers of $SnMe_2Cl_2$·2[Ni(3MeO-salphen)·H_2O]. Dotted lines signify hydrogen-bonding interactions

and inevitably $NiCl_2$ (which would account for the paramagnetism) were not present in the uncrystallized material.

The ^{119}Sn Mössbauer spectrum of $SnMe_2Cl_2$·2[Ni(3MeO-salphen)·H_2O] consisting of two doublets (Δ = 4.77 and 3.63 mm s^{-1}) is most readily accounted for on the assumption that two of the linkage isomers depicted schematically in Fig. 8 have been formed in the reaction (*cis* forms of the adducts are excluded in view of the large quadrupole splittings). However, there is a strong suggestion (see Experimental section) that the reaction product is a single complex, in which case it must have some form of polymeric structure.

Polymeric structures resulting from intermolecular contacts to tin must necessarily (in view of the 1:2 stoichiometry of the adduct) contain tin with a co-ordination number greater than six. Such structures are, for this reason, unlikely, both in the light of the known structural chemistry of diorganotin(IV) and steric considerations. In view of the pronounced tendency for the Schiff-base oxygens to engage in hydrogen-bonding interactions (as shown in this paper and by other crystallographic data)[29] it is much more likely that the two tin sites result from some form of associated structure resulting from hydrogen bonding. For example, any two isomers of Fig. 8 could co-exist in a lattice as a result of a water molecule altering the hydrogen-bonding role shown to one in which it forms hydrogen bonds to Schiff-base oxygens of different molecular units.

The 1:2 adducts of $SnBu^nCl_3$ and $SnCl_4$ with [Ni(3MeO-salphen)]·H_2O appear to be structurally less complex than their dimethyltin analogue since none of their ^{119}Sn Mössbauer spectra show evidence for more than one tin environment. However, it must be borne in mind that for monoalkyltin(IV), and more particularly inorganic tin(IV) systems, Mössbauer parameters are considerably less sensitive to the tin environment than they are for diorganotin(IV) systems.

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