Transition Metal Schiff-base Complexes as Ligands in Tin Chemistry. Part 1. A Tin-119 Mössbauer Spectroscopic Investigation of the Adducts SnX_4·ML, $SnMe_2(NCS)_2$·ML, and $SnRCl_3$·ML (X = Halide; M = Cu^{II} or Ni^{II}; L = Quadridentate Schiff-base Ligand; R = Phenyl or n-Butyl)

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Mössbauer quadrupole splitting data for adducts SnX_4·ML, $SnRCl_3$·ML, and $SnMe_2(NCS)_2$·ML [R = Ph or Bu^n, X = Cl, Br, or I; M = Cu^{II} or Ni^{II}; L = *NN'*-ethylenebis(salicylideneiminate), *NN'-o*-phenylenebis(salicylideneiminate), or derivatives of these] are discussed in terms of the point-charge model, and calculated quadrupole splitting data are presented for 27 of the adducts $SnRCl_3$·ML. For each adduct $SnRCl_3$·ML the *mer* and *fac* calculated values differ substantially and one is generally in excellent agreement with the experimental value; on this basis geometry is assigned. Examples of *mer* and *fac* isomers occur with the former being favoured by the more strongly donating metal Schiff-base complexes. In the case of two complexes it proved possible to isolate both the *mer* and *fac* isomers.

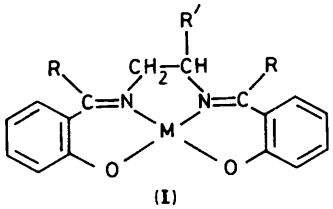
The observation that transition-metal Schiff-base complexes, [ML] (L = quadridentate Schiff base), can function as neutral donor ligands[1] has led to several investigations of their reactions with tin Lewis acids and to the isolation of adducts SnX_2·ML (X = Cl or Br)[2] and $SnR_{4-n}X_n$·ML (*n* = 4, X = Cl or Br;[2] *n* = 2 or 3, X = Cl, R = organo group[3,4]). Crystallographic studies have established the neutral donor role of the Schiff-base complexes in the octahedral organotin(IV) adducts $SnMe_2Cl_2$·Ni(salen)[5] and $SnBu^n(OMe)Cl_2$·CoCl(salen)[6] [salen = *NN'*-ethylenebis(salicylideneiminate)]. In the case of $SnMe_2Cl_2$·Ni(salen) and $SnPh_2Cl_2$·Ni(salen) the *trans* organo-group geometry at tin was clearly evident from tin-119 Mössbauer quadrupole splitting data,[3] but in view of the limited Mössbauer data initially available it was not possible to assign geometry to the adducts $SnRCl_3$·Ni(salen) (R = Ph or Bu^n). With a more extended range of data for adducts $SnRCl_3$·ML, in conjunction with those for adducts SnX_4·ML at our disposal we have come to the conclusion that in many instances structures can be confidently assigned to the mono-organotin(IV) adducts; some of our conclusions have appeared in preliminary communications.[7,8] This paper presents a detailed discussion of Mössbauer data for adducts $SnRCl_3$·ML, $SnMe_2(NCS)_2$·ML, and SnX_4·ML (R = Ph or Bu^n; M = Cu or Ni; L = salen, salpn, α,α'-Me_2-salen, salphen, salmphen, or saldmphen; X = Cl, Br, or I). The problem of assigning geometry from Mössbauer data to the adducts $SnRCl_3$·ML and more generally to adducts $SnRCl_3$·2L', where L' is a unidentate donor group, is considered in detail.

Experimental

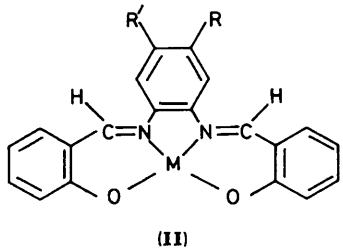
Starting Materials and Instrumentation.—Tin(IV) chloride (Aldrich), n-butyltin trichloride (Fluka), and phenyltin-trichloride (prepared by a literature method[9]) were distilled at reduced pressure prior to use. Tin(IV) bromide (Aldrich) was sublimed at reduced pressure and tin(IV) iodide (prepared by the reaction of tin with iodine) was recrystallised from chloroform. The compound $SnMe_2(NCS)_2$ was prepared and purified as described in the literature.[10] The Schiff-base ligands and their metal complexes were prepared by literature methods.[11]

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 (supplied by the Radiochemical Centre, Amersham). The spectrometer was regularly calibrated from the positions of the four inner lines of natural iron. The spectra were computer fitted using a least-squares procedure.[12]

Preparation of the Adducts.—Tin(IV) halide adducts were prepared in dry chloroform under a dry nitrogen atmosphere. Typically, tin(IV) halide (0.01 mol) in approximately 20 cm^3 solvent was added dropwise to a solution (*ca.* 100 cm^3) or



(I)



(II)

	Structure	Ligand name (abbreviation)
(I)	R = R' = H	*NN'*-ethylenebis(salicylideneiminate) (salen)
(I)	R = H, R' = Me	*NN'*-propylenebis(salicylideneiminate) (salpn)
(I)	R = Me, R' = H	*NN'*-ethylenebis(α-methylsalicylideneiminate) (α,α'-Me_2-salen)
(II)	R = R' = H	*NN'-o*-phenylenebis(salicylideneiminate) (salphen)
(II)	R = Me, R' = H	*NN'-o*-(4-methylphenylene)bis(salicylideneiminate) (salmphen)
(II)	R = Me, R' = Me	*NN'-o*-(4,5-dimethylphenylene)bis(salicylideneiminate) (saldmphen)

Table 1. Analytical data (%) for the adducts (X = Cl, Br, or I)

Adduct	Found				Calc.			
	C	N	H	X	C	N	H	X
$SnCl_4$·Ni(salen)	33.00	4.65	2.40	24.00	32.80	4.80	2.40	24.25
$SnBr_4$·Ni(salen)	26.05	3.70	1.85	41.65	25.15	3.75	1.85	41.90
SnI_4·Ni(salen)	19.85	2.80	1.55	53.35	20.20	2.85	1.45	53.35
$SnCl_4$·Cu(salen)	32.30	4.60	2.45	24.10	32.55	4.75	2.35	24.05
$SnCl_4$·Ni(salpn)	34.51	4.80	2.30	23.20	34.05	4.65	2.65	23.65
SnI_4·Ni(salpn)	20.55	2.80	1.95	51.95	21.15	2.90	1.65	52.60
$SnCl_4$·Cu(salpn)	33.10	4.45	2.30	23.80	33.75	4.65	2.65	23.50
$SnCl_4$·Ni(α,α′-Me_2-salen)	34.95	4.35	2.75	22.70	35.25	4.55	2.95	23.15
$SnCl_4$·Cu(α,α′-Me_2-salen)	34.50	4.40	2.80	22.40	34.95	4.55	2.90	22.95
$SnCl_4$·Ni(salphen)	36.90	4.55	2.20	21.65	37.90	4.40	2.20	22.40
SnI_4·Ni(salphen)	23.55	2.65	1.70	49.95	24.00	2.80	1.40	50.80
$SnCl_4$·Cu(salphen)	36.95	4.40	2.15	21.75	37.60	4.40	2.20	22.20
$SnCl_4$·Ni(salmphen)	38.60	4.30	2.60	21.85	38.95	4.35	2.45	21.90
$SnCl_4$·Cu(salmphen)	38.40	4.25	2.25	21.55	38.65	4.30	2.45	21.75
$SnCl_4$·Cu(saldmphen)	39.45	3.80	1.65	21.00	39.65	4.20	2.70	21.30
$SnBu^nCl_3$·Ni(salen)	39.40	4.35	3.70	17.35	39.50	4.60	3.80	17.50
$SnPhCl_3$·Ni(salen)	42.30	4.40	3.10	16.95	42.15	4.45	3.05	16.95
$SnBu^nCl_3$·Cu(salen)	38.80	4.65	3.80	17.05	39.20	4.55	3.75	17.40
$SnPhCl_3$·Cu(salen)	41.80	4.60	2.95	16.80	41.75	4.45	3.00	16.85
$SnBu^nCl_3$·Ni(salpn)	40.45	4.55	4.10	17.20	40.60	4.50	4.05	17.15
$SnPhCl_3$·Ni(salpn)	42.95	4.25	3.15	16.55	43.10	4.35	3.30	16.60
$SnBu^nCl_3$·Cu(salpn)	40.60	4.45	4.10	16.90	40.30	4.50	4.00	17.00
$SnPhCl_3$·Cu(salpn)	42.35	4.35	3.20	16.30	42.75	4.35	3.25	16.45
$SnBu^nCl_3$·Ni(α,α′-Me_2-salen)	41.50	4.40	4.15	16.75	41.60	4.40	4.25	16.75
$SnPhCl_3$·Ni(α,α′-Me_2-salen)	44.00	4.25	3.60	16.10	44.00	4.30	3.50	16.25
$SnBu^nCl_3$·Cu(α,α′-Me_2-salen)	41.15	4.25	4.20	16.65	41.30	4.40	4.20	16.65
$SnPhCl_3$·Cu(α,α′-Me_2-salen)	43.50	4.15	3.50	16.35	43.65	4.25	3.50	16.10
mer-$SnBu^nCl_3$·Ni(salphen)	44.35	4.35	3.50	16.10	43.95	4.30	3.50	16.20
fac-$SnBu^nCl_3$·Ni(salphen)	43.85	4.25	3.35	15.95	43.95	4.30	3.50	16.20
$SnPhCl_3$·Ni(salphen)	46.45	4.30	2.90	15.90	46.20	4.15	2.80	15.75
$SnBu^nCl_3$·Cu(salphen)	43.20	4.40	3.40	16.25	43.65	4.25	3.50	16.10
$SnPhCl_3$·Cu(salphen)	45.70	4.30	2.70	15.50	45.90	4.10	2.80	15.65
mer-$SnBu^nCl_3$·Ni(salmphen)	44.70	4.30	3.90	16.20	44.85	4.20	3.75	15.90
fac-$SnBu^nCl_3$·Ni(salmphen)	44.80	4.05	3.80	16.20	44.85	4.20	3.75	15.90
$SnPhCl_3$·Ni(salmphen)	46.45	4.20	3.10	15.50	47.05	4.05	3.05	15.45
$SnBu^nCl_3$·Cu(salmphen)	44.25	4.10	3.75	15.90	44.50	4.15	3.70	15.75
$SnPhCl_3$·Cu(salmphen)	46.50	3.80	2.85	15.25	46.75	4.05	3.00	15.35
$SnBu^nCl_3$·Ni(saldmphen)	45.65	4.20	3.95	15.50	45.70	4.10	3.95	15.60
$SnPhCl_3$·Ni(saldmphen)	47.70	3.95	3.15	15.20	47.80	4.00	3.25	15.15
$SnBu^nCl_3$·Cu(saldmphen)	45.45	4.10	3.90	15.55	45.40	4.05	3.95	15.45
$SnPhCl_3$·Cu(saldmphen)	47.35	3.95	3.30	15.05	47.50	3.95	3.25	15.05
$SnMe_2(NCS)_2$·Ni(salen)	41.65	8.95	3.05		40.70	9.50	3.40	
$SnMe_2(NCS)_2$·Cu(salen)	40.00	9.10	3.10		40.40	9.40	3.35	
$SnMe_2(NCS)_2$·Cu(salpn)	40.65	8.95	3.65		41.45	9.25	3.60	
$SnMe_2(NCS)_2$·Ni(salphen)	45.45	8.70	3.15		45.20	8.80	3.15	
$SnMe_2(NCS)_2$·Cu(salphen)	45.50	8.25	3.10		44.85	8.70	3.10	
$SnMe_2(NCS)_2$·Ni(salmphen)	45.40	8.65	3.40		46.10	8.60	3.35	
$SnMe_2(NCS)_2$·Cu(salmphen)	45.15	7.90	3.20		45.75	8.50	3.35	
$SnMe_2(NCS)_2$·Ni(saldmphen)	46.60	8.35	3.55		46.90	8.40	3.60	
$SnMe_2(NCS)_2$·Ni(saldmphen)	46.30	8.45	3.60		46.55	8.35	3.60	

suspension of the metal Schiff-base complex (0.01 mol). Following the addition, stirring was continued for several hours. The solid product was isolated by filtration under dry nitrogen and dried under vacuum. All manipulations of the moisture-sensitive adducts were carried out in a dry-box.

Adducts of the mono-organotin trichlorides were prepared in similar fashion but precautions against hydrolysis were unnecessary. These adducts can also be prepared in acetonitrile. The modifications of $SnBu^nCl_3$·Ni(salphen) and $SnBu^nCl_3$·Ni(salmphen) obtained from acetonitrile differ from those obtained from chloroform. The acetonitrile modifications readily convert into the chloroform modifications in chloroform, and *vice versa*. The chloroform modification of $SnBu^nCl_3$·Ni(salphen) was found to have converted into the other modification when stored in the solid state under ambient conditions for several months.

Apart from $SnMe_2Cl_2$·Ni(salen), other adducts of $SnMe_2Cl_2$ could not be obtained in a pure form, but those of $SnMe_2(NCS)_2$ were obtained using the preparative method described. All analytical data are in Table 1.

Results and Discussion

All of the adducts in Table 1 have low solubilities in chloroform, dichloromethane, and acetonitrile. Solubilities in hot methanol and acetone are considerably greater but the complexes are largely, if not totally, dissociated in these solvents; when concentrated warm solutions of the organotin(IV) adducts are

Table 2. Mössbauer spectroscopic and phenolic C–O stretching frequency data for tin(IV) halide adducts

	Complex	δ^a/mm s^{-1}	Δ^a/mm s^{-1}	$\tilde{\nu}$(C–O)^b/cm^{-1}
(1)	$SnCl_4$·Ni(salen)	0.45	0.60	1 565 (1 540)
(2)	$SnBr_4$·Ni(salen)	0.80	0.66	1 560
(3)	SnI_4·Ni(salen)	1.22	0.82	1 548
(4)	$SnCl_4$·Cu(salen)	0.38	0.49	1 560 (1 530, 1 540)
(5)	$SnCl_4$·Ni(salpn)	0.37	0.51	1 564 (1 540)
(6)	SnI_4·Ni(salpn)	1.16	0.86	1 550
(7)	$SnCl_4$·Cu(salpn)	0.37	0.40	1 557 (1 532)
(8)	$SnCl_4$·Ni(α,α′-Me_2-salen)	0.37	0.49	1 553 (1 530)
(9)	$SnCl_4$·Cu(α,α′-Me_2-salen)	0.34	0.54	1 557 (1 532)
(10)	$SnCl_4$·Ni(salphen)	0.43	0.45	1 552 (1 525)
(11)	SnI_4·Ni(salphen)	1.39	0.65	1 550
(12)	$SnCl_4$·Cu(salphen)	0.43	0.39	1 554 (1 525)
(13)	$SnCl_4$·Ni(salmphen)	0.41	0.45	1 553 (1 520)
(14)	$SnCl_4$·Cu(salmphen)	0.39	0.45	1 550 (1 531)
(15)	$SnCl_4$·Cu(saldmphen)	0.40	0.42	1 549 (1 527)

^{a} Data ±0.03 mm s^{-1}. ^{b} Data in parentheses refer to the free metal Schiff-base complexes.

Table 3. Mössbauer spectroscopic and phenolic (C–O) stretching frequency data for mono-organotin(IV) adducts

	Complex	δ^a/mm s^{-1}	Δ(obs.)^a/mm s^{-1}	Δ_{mer}(calc.)^b/mm s^{-1}	Δ_{fac}(calc.)^b/mm s^{-1}	$\tilde{\nu}$(C–O)/cm^{-1}
(16)	$SnBu^nCl_3$·Ni(salen)	1.05	1.53	1.64	2.46	1 555
(17)	$SnMeCl_3$·Ni(salen)	0.90	1.63	1.64	2.46	
(18)	$SnPhCl_3$·Ni(salen)	0.86	1.38	1.42	2.27	1 560
(19)	$SnBu^nCl_3$·Cu(salen)	0.99	1.67	1.67	2.35	1 550
(20)	$SnPhCl_3$·Cu(salen)	0.84	1.45	1.47	2.16	1 556
(21)	$SnBu^nCl_3$·Ni(salpn)	0.99	1.50	1.66	2.37	1 554
(22)	$SnPhCl_3$·Ni(salpn)	0.86	1.42	1.48	2.18	1 554
(23)	$SnBu^nCl_3$·Cu(salpn)	1.00	1.69	1.70	2.26	1 551
(24)	$SnPhCl_3$·Cu(salpn)	0.79	1.43	1.51	2.07	1 553
(25)	$SnBu^nCl_3$·Ni(α,α′-Me_2-salen)	0.96	1.49	1.67	2.35	1 554
(26)	$SnPhCl_3$·Ni(α,α′-Me_2-salen)	0.98	1.91	1.49	2.16	1 551
(27)	$SnBu^nCl_3$·Cu(α,α′-Me_2-salen)	0.99	1.66	1.66	2.40	1 553
(28)	$SnPhCl_3$·Cu(α,α′-Me_2-salen)	0.80	1.40	1.48	2.21	1 550
(29)	*mer*-$SnBu^nCl_3$·Ni(salphen)	1.05	1.48	1.68	2.31	1 548
(30)	*fac*-$SnBu^nCl_3$·Ni(salphen)	1.21	2.13	1.68	2.31	1 548
(31)	$SnPhCl_3$·Ni(salphen)	1.06	2.01	1.50	2.12	1 545
(32)	$SnBu^nCl_3$·Cu(salphen)	1.14	2.07	1.70	2.25	1 545
(33)	$SnPhCl_3$·Cu(salphen)	0.98	2.03	1.51	2.06	1 545
(34)	*mer*-$SnBu^nCl_3$·Ni(salmphen)	1.08	1.53	1.68	2.31	1 549
(35)	*fac*-$SnBu^nCl_3$·Ni(salmphen)	1.15	2.18	1.68	2.31	1 549
(36)	$SnPhCl_3$·Ni(salmphen)	0.99	2.04	1.50	2.12	1 550
(37)	$SnBu^nCl_3$·Cu(salmphen)	1.04	1.70	1.68	2.31	1 549
(38)	$SnPhCl_3$·Cu(salmphen)	0.95	1.96	1.50	2.12	1 547
(39)	$SnBu^nCl_3$·Ni(saldmphen)	0.98	1.48	1.69	2.28	1 548
(40)	$SnPhCl_3$·Ni(saldmphen)	0.84	1.34	1.50	2.09	1 547
(41)	$SnBu^nCl_3$·Cu(saldmphen)	0.99	1.58	1.69	2.28	1 545
(42)	$SnPhCl_3$·Cu(saldmphen)	0.89	1.55	1.50	2.09	1 546

^{a} ±0.03 mm s^{-1}. ^{b} Δ_{mer}(calc.) and Δ_{fac}(calc.) refer to calculated data for the isomers of Figure (*a*) and (*c*) respectively. P.q.s. values for Ph and Bu^n are from D. Cunningham, M. Little, and K. McLoughlin, *J. Organomet. Chem.*, 1979, **165**, 287. P.q.s. values for the donor groups, [ML], were estimated from the quadrupole splitting values for the tin(IV) chloride adducts of Table 2. Experimental linewidths fall within the range 0.85—1.05 mm s^{-1}.

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

	Complex	δ*/mm s^{-1}	Δ*/mm s^{-1}	$\tilde{\nu}$(CO)/cm^{-1}
(43)	$SnMe_2Cl_2$·Ni(salen)	1.50	4.06	
(44)	$SnMe_2(NCS)_2$·Ni(salen)	1.30	4.04	1 543
(45)	$SnMe_2(NCS)_2$·Cu(salen)	1.29	4.11	1 550
(46)	$SnMe_2(NCS)_2$·Cu(salpn)	1.34	4.13	1 549
(47)	$SnMe_2(NCS)_2$·Ni(salphen)	1.39	4.22	1 538
(48)	$SnMe_2(NCS)_2$·Cu(salphen)	1.42	4.39	1 547
(49)	$SnMe_2(NCS)_2$·Ni(salmphen)	1.40	4.15	1 532
(50)	$SnMe_2(NCS)_2$·Cu(salmphen)	1.35	4.33	1 545
(51)	$SnMe_2(NCS)_2$·Ni(saldmphen)	1.38	4.30	1 540
(52)	$SnMe_2(NCS)_2$·Cu(saldmphen)	1.34	4.33	1 548

* ±0.03 mm s^{-1}.

cooled the free metal salicylideneiminates crystallise from solution. As a result of the low solubilities and dissociation in solution structural studies are necessarily confined to the solid state.

The copper and nickel Schiff-base complexes possess a common structural feature in that ligand constraints impose approximately square-planar geometry about the bivalent metal with the oxygen atoms locked in a *cis* configuration. This constraining influence of the ligands, coupled with the disposition of the available oxygen donor orbitals,[13] assures that, while the salicylideneiminate complexes can act as *cis* chelating donor ligands (as has been shown crystallographically[5,6,14]), they are extremely unlikely to adopt a bridging role. This restricts the structural possibilities for the adducts.

As a result of adduct formation the i.r.-active phenolic C–O stretch of metal salicylideneiminates has invariably been observed to shift to a higher frequency; the shift is generally considered as diagnostic of adduct formation.[1,13] The extensive data for C–O stretching in Tables 2—4 indicate that the magnitude of the shift is to an extent dictated by the strength of the donor–acceptor interaction. For example, in the case of those adducts in Table 2 containing a common donor the order of increasing C–O stretching frequency is always iodide < bromide < chloride. On the other hand, the data do not always reflect the order of acceptor strengths of the organotin(IV) Lewis acids (see Tables 3 and 4). All of the tin(IV) chloride adducts exhibit a broad intense band in the 300—350 cm^{-1} region of their i.r. spectra, which is almost certainly associated with the tin–halogen stretching frequencies. In most cases the well defined shoulders on this band provide clear evidence for the presence of four stretching frequencies thus confirming the expected *cis* octahedral tin geometry. The organotin trihalide adducts all display a broad band in their i.r. spectra with a maximum very close to 300 cm^{-1}. The shoulders on this band provide good evidence in each case for the presence of three tin–chlorine stretching frequencies which is consistent with either *mer* or *fac* octahedral tin geometry; from the point of view of structural elucidation it is unfortunate that the isomers give rise to the same number of i.r.-active tin–chlorine stretching vibrations.

The tin-119 Mössbauer spectra of five of the tin(IV) halide adducts [compounds (**1**), (**2**), (**3**), (**6**), and (**11**)] in Table 2 consist of partially resolved doublets, and for the series SnX_4·Ni(salen) [compounds (**1**)—(**3**)] the resolution of the doublet increases in the order Cl < Br < I. The spectra of other tin(IV) chloride adducts in the Table consist of broadened single lines which clearly result from unresolved doublets. In all cases the spectra were satisfactorily computer fitted to doublets and the resulting quadrupole splitting data (Δ) are tabulated (Table 2). Two important conclusions can be drawn from these data. First, since the values for the isostructural tin(IV) chloride adducts fall within a very confined range (0.4—0.6 mm s^{-1}) it would appear that the nature of the tin–donor bonds is quite insensitive to the nature of either the transition metal or the Schiff-base ligand. Secondly, since quadrupole splitting values for adducts with the same donor complex increase in the order Cl < Br < I (this trend also exists for other adducts SnX_4·ML not included in the present study[15]) it must be concluded that partial quadrupole splitting (p.q.s.) values for the donor groups are positive. This has generally been found for oxygen and nitrogen donor ligands,[16—18] and implies that the Schiff-base complexes are weaker donor ligands than chloride.

In view of the narrow range of quadrupole splitting values exhibited by the tin(IV) chloride adducts the data for the mono-organotin(IV) trichloride adducts (Table 3) show a surprisingly wide spread. The variations in the values are more than could reasonably be attributed to deviations from ideal octahedral geometry. Furthermore, the possibility of tin adopting five-co-ordination in some complexes, as a result of ligands donating in a unidentate fashion, is remote since this does not happen in the case of the adducts $SnMe_2(NCS)_2$·ML, where donor–acceptor interactions will undoubtedly be weaker (these complexes are discussed at a later point). A reasonable explanation for the spread in the data is that both *mer* and *fac* isomers of the adducts are being isolated; this explanation is strongly supported by point-charge calculations. The three possible isomers for adducts $SnRX_3$·2L′, in conjunction with the values of the V_{zz} components of their associated electric field gradients, are shown in the Figure. It is clear from the V_{zz} values that the only possible successful application of point-charge calculations will be in distinguishing between the *mer* isomer of Figure (*a*) and either of the other two isomers, and the ability to do so confidently will depend on the p.q.s. value of L′. Thus, even where excellent agreement exists between the observed quadrupole splitting and that calculated for the *mer* isomer of Figure (*a*) (as an example) it would be unsound to make a structural assignment if this calculated value differed from the other values by less than *ca.* 0.4 mm s^{-1},[16] *i.e.* if 3 p.q.s. (L′) is less than *ca.* 0.4 mm s^{-1}. Unfortunately, p.q.s. values for very many donor groups are considerably less than this. Observed and calculated quadrupole splitting data are included in Table 5 for adducts for which crystallographic or other structural data are available, and for which p.q.s. values of the donor groups are greater than the minimum value defined above. The data clearly indicate that considerable weight ought to be placed on the predictions (insofar as they can be made) of point-charge calculations for mono-organotin trihalide adducts when p.q.s. values are suitably large (as defined) and, of course, where an acceptable level of agreement exists between experimental and calculated data. These conditions are clearly met in the case of adducts $SnRCl_3$·ML in Table 3.

In view of the constrained planar geometry of the Schiff-base metal complexes only the *mer* and *fac* structures of Figure (*a*) and (*c*) respectively are considered likely for the adducts

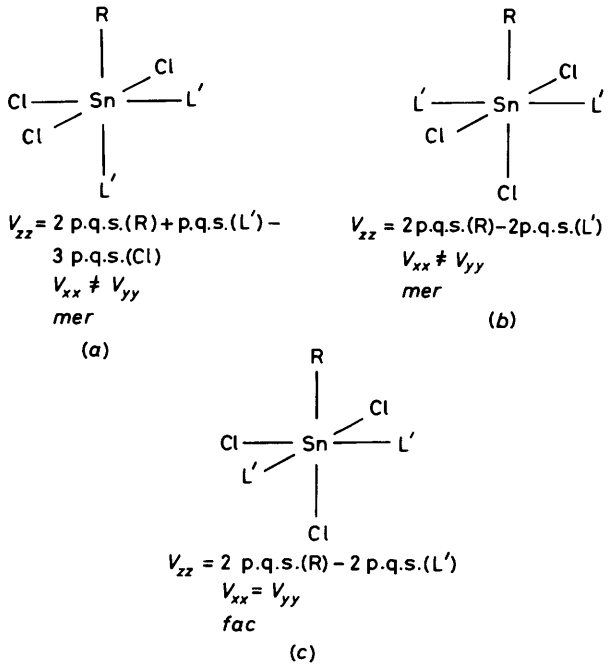


Figure. Three possible isomers for adducts $SnRX_3$·2L′ (L′ = unidentate donor group) with values of V_{zz} components of associated electric field gradients

Table 5. Calculated and observed Mössbauer quadrupole splitting data (mm s^{-1}) for mono-organotin(IV) adducts for which *X*-ray crystallographic or other structural data are available[a]

Complex	Δ(obs.)	Δ(*a*)	Δ(*b*)	Δ(*c*)
$SnMeCl_3$·2hmpt	2.35[b]	1.71[c]	*2.30*[d]	2.22
$SnMeBr_3$·2hmpt	2.34[b]	1.71	*2.30*[d]	2.22
$SnBu^nCl_2(OMe)$·CoCl(salen)[e]	2.27	1.65		*2.30*[f]
$SnMeCl_3$·2thf	2.37[b]	1.63[g]	2.75	*2.51*[h]
$SnMeBr_3$·2thf	2.42[b]	1.63	2.75	*2.51*[h]
$SnMeCl_3$·dioxane	2.43[b]	1.62[i]	2.90	*2.60*[h]
$SnBu^nCl_3$·$2PPh_3O$	2.34[j]	1.67[i]	2.38	*2.36*[j]
$SnPhCl_3$·$2PPh_3O$	2.01[j]	1.46[i]	2.17	*2.15*[j]
		Δ_{cis}(calc.)	Δ_{trans}(calc.)	
$[NEt_4][SnBu^nCl_4$·$PBu^n_3]$	2.42[k]	1.66[l]	*2.39*[m]	
$[NEt_4][SnPhCl_4$·$PBu^n_3]$	2.10[k]	1.47	*2.18*[m]	

[a] Italicised calculated data indicate the known or previously suggested structures. Δ(*a*), Δ(*b*), and Δ(*c*) refer to calculated data for the isomers of Figure (*a*), (*b*), and (*c*) respectively. P.q.s. values for phenyl and n-butyl are from the references in footnote *b* of Table 3. [b] Data from ref. 26. [c] P.q.s. value for hmpt from S. S. Bashkirov, I. Y. Kuramshin, A. S. Khramox, and A. N. Pudovik, *Russ. Chem. Rev.*, 1981, **50**, 749. [d] Structural assignment from crystallographic data (ref. 21). [e] Data from ref. 15. [f] Structural assignment from crystallographic data (ref. 6). [g] P.q.s. value for thf (tetrahydrofuran) from D. Cunningham, J. Finnegan, J. D. Donaldson, and M. J. Frazer, *J. Chem. Soc., Dalton Trans.*, 1977, 162. [h] Structural assignment from n.q.r. data (V. S. Petrosyan, N. S. Yashina, O. A. Reutov, E. V. Bryuchova, and G. K. Semin, *J. Organomet. Chem.*, 1973, **52**, 321). [i] P.q.s. value from P. A. Yeats, J. R. Sams, and F. Aubke, *Inorg. Chem.*, 1970, **9**, 740. [j] Quadrupole splitting data and structural assignment from dipole moment data (F. P. Mullins, *Can. J. Chem.*, 1971, **49**, 2719.). [k] Data from ref. in footnote *b* of Table 3. [l] P.q.s. value of phosphine from D. Cunningham, M. J. Frazer, and J. D. Donaldson, *J. Chem. Soc. A*, 1971, 2049; *J. Chem. Soc., Dalton Trans.*, 1972, 1647. [m] Structural assignment based on ^{31}P and ^{119}Sn n.m.r. data (V. S. Petrosyan, The Fifth International Conference on the Organometallic and Coordination Chemistry of Germanium, Tin and Lead, Padua, 1986).

$SnRCl_3$·ML. In fact, there is clear evidence from the data in Table 3 that both isomeric forms occur. In view of the common structural features shared by the complexes [ML] they will probably give rise to very similar bite angles at tin and exert essentially similar steric influences in the immediate tin environment. Thus, the relative stabilities of the *mer* and *fac* isomers is more likely, in these instances, to be controlled by electronic rather than steric effects. In fact, there are clear indications that electron density on the donor oxygen atoms exerts a subtle, but nonetheless crucial, influence on the geometry about tin.

The donor complexes [ML] break down broadly into two categories, namely those in which an ethylene-type bridge links the Schiff-base nitrogen atoms [in complexes (**16**)—(**28**)], and those which, instead, contain a phenylene-type bridge [in complexes (**29**)—(**42**)]. In view of the increased electron delocalisation which will result from the introduction of a phenylene bridge,[13] it would intuitively be predicted that complexes [M(α,α′-Me_2-salen)] and [M(salphen)] represent the strongest and weakest donors respectively of the present study; it has, in fact, recently been shown[19] from equilibrium measurements that complexes [M(salen)] donate more strongly to sodium ions in solution than do [M(salphen)] (M = Ni or Co). Introduction of methyl groups into the phenylene bridge should, if anything, have the effect of enhancing the donor strength of the complexes. With the probable exception of $SnPhCl_3$·Ni(α,α′-Me_2-salen) (**26**) all other adducts with an ethylene-type nitrogen-bridging group [adducts (**16**)–(**28**)] clearly exist as *mer* isomers. The observed Δ value for $SnPhCl_3$·Ni(α,α′-Me_2-salen) is significantly greater than the values observed for other phenyltin adducts of this group and is in much better agreement with the *fac* than the *mer* calculated value. Adducts (**30**)—(**33**), containing a phenylene bridging group, exist as *fac* isomers, and this also is the geometry adopted by adducts (**35**), (**36**), and (**38**), which have a methyl group incorporated into the phenylene group. However, the introduction of the methyl group appears to have the effect of re-establishing *mer* geometry in $SnBu^nCl_3$·Cu(salmphen) (**37**). On the other hand, the introduction of a second methyl group in the phenylene bridge [in complexes (**39**)—(**42**)] has the effect of re-establishing *mer* geometry for all adducts.

Clearly, in the case of the adducts of this study an extremely fine balance exists between the stabilities of the *mer* and *fac* isomers. The balance is apparently controlled by what probably amounts to small changes in the basicities of the donor complexes, with the *mer* isomer being favoured by the stronger Lewis bases (a similar dependence of isomer stability on base strength has been observed for other series of adducts of mono-organotin trihalides[15]). Since the balance is so finely controlled it is not surprising when there are apparent structural anomalies [as in the case of (**26**) and (**37**)]; other factors, such as lattice energies, cannot be ignored. Furthermore, it may not necessarily be correct to order the basicities of the Schiff-base complexes entirely on the basis of the substituents on the Schiff-base ligand, since it is known that the electron density on the donor oxygen atoms of a Schiff-base complex is also dictated both by the degree and nature of distortion of the complex from overall planarity.[13]

The mono-organotin trihalide adducts so far discussed were all prepared in chloroform, but in the majority of cases they could equally well be prepared in acetonitrile. However, the modifications of $SnBu^nCl_3$·Ni(salphen) and $SnBu^nCl_3$·Ni(salmphen) obtained from chloroform [(**30**) and (**35**) respectively] have substantially different *X*-ray powder diffraction patterns to those of their respective modifications (**29**) and (**34**) from acetonitrile. Mössbauer parameters for the modifications also differ substantially, and there is extremely convincing evidence from the quadrupole splitting data in Table 3 that, in fact, the *mer* and *fac* isomers are obtained from acetonitrile and chloroform respectively. The adducts are thus the first mono-organotin complexes for which it has proved possible to isolate separate geometric isomers in the solid state; several adducts of n-butyltin trichloride with *N*-substituted pyridine-2-carbaldimine donor ligands are known to exist as equilibrium isomeric mixtures in solution.[20] The *mer* and *fac* isomers of both $SnBu^nCl_3$·Ni(salphen) and $SnBu^nCl_3$·Ni(salmphen) are easily interconvertible. For example, the *mer* isomers are rapidly converted into the *fac* isomers when stirred in chloroform, and likewise the *fac* isomers are converted into the *mer* isomers in acetonitrile. Furthermore, it was found that the *fac* isomer of $SnBu^nCl_3$·Ni(salphen) had largely changed to the *mer* isomer when stored for several months in the solid state under ambient conditions.

A noteworthy feature of the chemical shift data (δ) in Table 3 is that the *mer* isomers of $SnBu^nCl_3$·Ni(salphen) and $SnBu^nCl_3$·Ni(salmphen) have lower chemical shifts than their *fac* analogues; in the case of the isomers of $SnBu^nCl_3$·Ni(salphen) the shifts differ substantially. The trend is maintained for other adducts of $SnBu^nCl_3$ where chemical shift values for *mer* isomers fall within the range 0.96—1.05 mm s^{-1}, whereas those for the *fac* isomers fall within the range 1.14—1.21 mm s^{-1}. [In this respect it is interesting that the chemical shift value for $SnBu^nCl_3$·Cu(salmphen) (**37**) (1.04 mm s^{-1}) is consistent with its 'anomalous' *mer* structure, suggested by the quadrupole splitting data.] The lower chemical shift values for the *mer* isomers can be related to the fact that an electronegative oxygen

will more effectively withdraw *s*-electron density from tin when *trans* to the n-butyl group than when in a *cis* position.[21-23] The tendency for the *mer* isomers to have the lower chemical shift values is apparent in the case of the phenyltin adducts also, where the *mer* and *fac* isomers have values in the ranges 0.79—0.89 and 0.95—1.06 mm s^{-1} respectively.

Since the quadrupole splitting values for all of the dimethyltin adducts in Table 4 are greater than 4.0 mm s^{-1} they undoubtedly possess octahedral tin geometry with *trans* (or approximately so) methyl groups, as has been confirmed crystallographically in the case of $SnMe_2Cl_2$·Ni(salen).[5] With the structures of the adducts thus established they could, in principle, be chosen as estimator compounds for deriving p.q.s. values for the donor complexes. However, by this procedure a p.q.s. value of 0.05 mm s^{-1} is obtained for $\frac{1}{2}$[Ni(salen)],[24] which is significantly different to the value of 0.3 mm s^{-1} derived from $SnCl_4$·Ni(salen) as estimator compound. The smaller value obviously gives rise to very similar calculated quadrupole splitting data for the *mer* and *fac* isomers of both $SnBu^nCl_3$·Ni(salen) and $SnPhCl_3$·Ni-(salen) and, in fact, these data are in poor agreement with the experimental data.[24] It is quite generally the case that the dimethyltin adducts in Table 4, as estimator compounds, give rise to very much smaller p.q.s. values for the donor groups than those derived using the tin(IV) halide adducts as estimator compounds. The dimethyltin adducts were considered unsuitable estimator compounds since the p.q.s. values they yield result in very similar calculated quadrupole splitting values for the *mer* and *fac* isomers of the adducts in Table 3, which is contrary to observation. By contrast, by using p.q.s. values obtained from tin(IV) halide data the excellent agreement between the observed and calculated data of Tables 3 and 5 is achieved. Dialkyltin adducts may be unsuitable estimator compounds for two reasons. First, the values are estimated on the assumption that the C–Sn–C bond angle is 180°, which is rarely the case; in the case of $SnMe_2Cl_2$·Ni(salen) the angle is reduced to 161°. This can lead to a serious error in the p.q.s. value towards the negative end of the p.q.s. scale, since the quadrupole splitting is particularly sensitive to the C–Sn–C bond angle, decreasing as the angle decreases.[16] Secondly, as a result of the large concentration of *s*-electron density along the *trans* C–Sn–C direction, the nature of the tin–donor bond may be significantly different to that in a mono-organotin or tin(IV) halide adduct. However, the extent to which changing bond character from one adduct to another is reflected in the p.q.s. value of a donor ligand may not in many cases be significant. This appears to be the case for the donor ligand hmpt, $P(NMe_2)_3O$. The crystal structures of $SnCl_4$·2hmpt, $SnMeCl_3$·2hmpt, and $SnMe_2Cl_2$·2hmpt have been determined and the C–Sn–C bond angle in the latter is exactly 180° (since tin sits on an inversion centre[21,25]). Thus, the Δ value of 4.45 mm s^{-1} for the dimethyltin adduct[26] results in a p.q.s. value of 0.165 mm s^{-1} for hmpt, which agrees very well with the value of 0.18 mm s^{-1} derived from the quadrupole splitting of the tin(IV) halide adduct and, as can be seen from Table 5, the mono-organotin(IV) trihalide adducts must yield similar values.

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