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Adducts of Tin(IV) Tetrahalides with Neutral Lewis Bases. II. Quantitative Study of the *Cis–Trans* Equilibria by NMR

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The cis–trans *equilibria of $SnX_4 \cdot 2L$ and $SnX_4 \cdot L{-}L$ adducts in solution were studied quantitatively by ^{19}F, ^{31}P and ^1H NMR spectroscopy (X = F, Cl, Br; L = Me_2O, Et_2O, Me_2S, Et_2S, Me_2Se, MeCN, Me_3CCN, Me_2CO, TMPA, $Me_2N(MeO)_2PO$, HMPA; $L{-}L$ = $(MeOCH_2{-})_2$). The relative stabilities for* cis- *and* trans-*$SnX_4 \cdot 2L$ adducts were estimated, and the following sequence obtained: HMPA > $Me_2N(MeO)_2PO$ > TMPA > Me_2Se > Me_2S > Me_2O. The existence of $SnCl_4 \cdot L_a \cdot L_b$ mixed species when tin tetrachloride is present with two different ligands has been shown, and their concentrations at equilibrium obey a statistical distribution. The* cis–trans *isomerization constant is relatively independent of temperature, but depends strongly on solvent polarity, the* trans *isomer being favoured in weakly polar media The trends in the isomerization constants as a function of substitution of the ligand and the halogen is discussed on the basis of tin(IV) orbital overlap.*

Introduction

In the previous paper in this series [1] we determined the structure of numerous 1:2 $SnX_4 \cdot 2L$ (X = Cl, Br) solid adducts by vibrational spectroscopy. We demonstrated that the majority of them undergo *cis–trans* equilibrium in solution. Several ^{19}F NMR studies have also shown the existence of *cis–trans* equilibria for $SnF_4 \cdot 2L$ adducts with ligands such as pyridine oxides and substituted quinolines [2], ethanol [3], or anionic ligands in mixed halide adducts [4]. In order to determine the parameters which affect these equilibria (*i.e.* solvent polarity, temperature, nature of the ligand L donor atom and of the halogen, steric hindrance), we have choosen Nuclear Magnetic Resonance as a technique for quantitative studies of these equilibria.

Experimental

Work in inert atmosphere and purification of chemicals have been reported previously [1]. $Me_2N(MeO)_2PO$ has been synthesized from $H(MeO)_2PO$ (prepared from PCl_3 and MeOH [5]) and Me_2NH [6]. Tin tetrafluoride (ROC/RIC 95%) was used without further purification.

Spectral Measurements

Chemical shifts downfield from the reference signal have been assigned positive signs. The following reference substances were used: tetramethylsilane (TMS) for ^1H NMR, fluorotrichloromethane ($CFCl_3$) for ^{19}F NMR and 62.5% phosphoric acid in a capillary in the NMR tube for ^{31}P NMR.

^1H NMR spectra were recorded on a Bruker WP-60 spectrometer. $^{31}P\{^1H\}$ NMR and ^{19}F NMR spectra were obtained on a Bruker HX-90 spectrometer operating in the pulsed Fourier transform mode, at 36.44 and 84.67 MHz, respectively. Temperature was stabilized with a Bruker BST-100/-700 unit, and measured with a Hewlett–Packard 2802A digital thermometer.

Abbreviations

TMPA = trimethylphosphate, HMPA = hexamethylphosphortriamide, DME = 1,2-dimethoxyethane.

Results

The ^1H NMR spectrum for a *cis–trans* isomerization, with an excess of ligand, should show resonances for *cis, trans* and non bonded ligand. Moreover, ligand protons may couple with tin 115, 117 and 119 isotopes (I = ½, natural isotopic abundance = 0.35, 7.67 and 8.68% respectively). Isomerization and ligand exchange reactions may be fast at room temperature so that the exchanging species cannot be distinguished from one another; the rate of these reactions can be decreased by lowering the temperature and the different species present can then be observed. All spectra were recorded in the limit of slow exchange. It is observed in these systems that increasing the

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TABLE I. Chemical Shifts δ (ppm), Differences of Chemical Shift $\Delta\delta = \delta(SnX_4 \cdot 2L) - \delta(L)$, Coupling Constants (Hz), Stoichiometry and Isomerization Constant (K_{iso}) for *Cis*- and *Trans*-$SnX_4 \cdot 2L^a$ in CH_2Cl_2. Internal Reference TMS, ^1H NMR 60 MHz.

	$SnCl_4 \cdot 2L$								$SnBr_4 \cdot 2L$					
	Me_2O	Me_2S	Me_2Se	DME^b	TMPA	HMPA	MeCN	Me_2CO	Me_2S	Me_2Se	DME^b	TMPA	$Me_2N(MeO)_2PO^c$	HMPA
trans-$SnX_4 \cdot 2L$														
δ	4.05	2.73	2.68		4.09	2.74			2.64	2.58		4.10	4.00	2.79
Δδ	0.72	0.61	0.67		0.29	0.14			0.50	0.57		0.33	0.20	0.18
$^3J(^1H-^{119}Sn)$	18.4	57.3	60.5		–	–			57.8	59.7		–	–	–
$^3J(^1H-^{117}Sn)$	17.0	54.9	57.5		–	–			55.0	57.3		–	–	–
$^3J(^1H-^{31}P)$					12.0	9.7						11.9	12.1	10.1
cis-$SnX_4 \cdot 2L$														
δ	3.92	2.67	2.64	3.98	4.04	2.72	2.64	2.81	2.56	2.53	3.90	4.05	3.93	2.74
Δδ	0.59	0.55	0.63	0.59	0.24	0.12	0.52	0.57	0.43	0.52	0.73	0.26	0.13	0.14
$^3J(^1H-^{119}Sn)$	18.4	52.8	52.0	20.6	–	–	–	–	52.4	50.4	22.2	–	–	–
$^3J(^1H-^{117}Sn)$	17.0	50.5	49.0		–	–	–	–	49.4	48.0		–	–	–
$^3J(^1H-^{31}P)$					11.9	10.1						11.8	12.3	9.9
Stoichiometry[d]	2.12:1	2.11:1	2.07:1	0.98:1	1.96:1	1.88:1	1.92:1	1.84:1	1.93:1	1.98:1	0.92:1	2.08:1	1.95:1	2.00:1
K_{iso}	0.64	0.79	1.37	0.	0.25	1.46	0.	0.	1.38	2.33	0.	0.15	0.35	1.04
T (K)	175	190	190	250	230	230	170	170	170	180	200	203	203	203

[a] $SnX_4 \cdot L-L$ for the bidentate DME. [b] Values reported for CH_3 groups; for CH_2: δ = 4.26, Δδ = 0.69, ^3J = 20.1 ($SnCl_4 \cdot DME$) and δ = 4.25, Δδ = 0.54, ^3J = 21.8 ($SnBr_4 \cdot DME$).
[c] All values reported for OMe groups. [d] [bonded ligand]/[SnX_4].

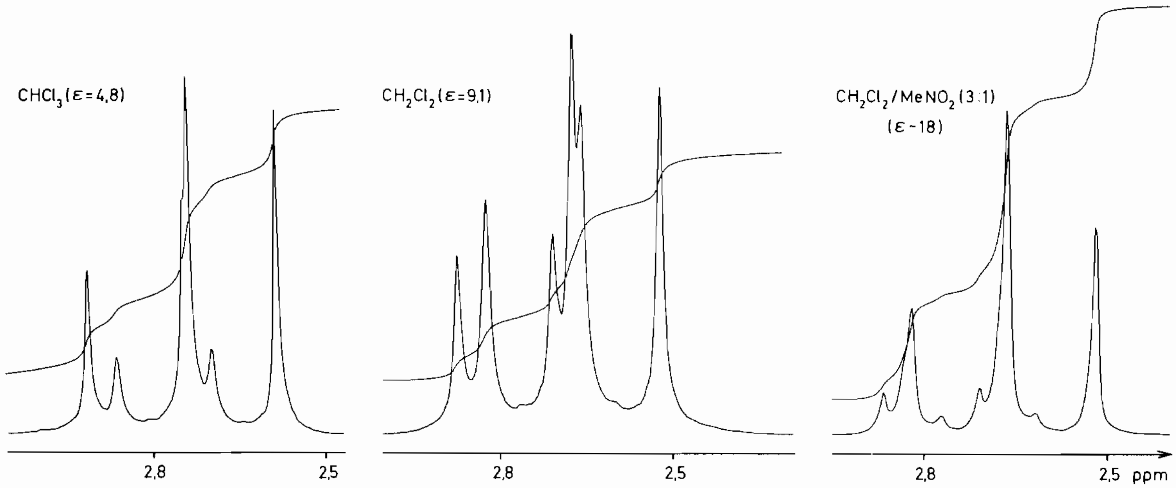

Figure 1. ^{1}H NMR spectra (60 MHz) at 275 K of $SnBr_4$/HMPA (1:4) in $CHCl_3$, CH_2Cl_2 and $CH_2Cl_2/MeNO_2$ (3:1). [$SnBr_4\cdot$2HMPA] = 0.1 *m*. Internal reference: TMS.

TABLE II. Solvent Dielectric Constant Effect on the Isomerization Constant (K_{iso}) for $SnBr_4\cdot$2HMPA, by ^{1}H NMR, and the Ratios of the *Trans/Cis* Raman Band Intensities at 298 K.

	$CHCl_3$	CH_2Cl_2	CH_2Cl_2/ $MeNO_2$ (3:1)
Dielectric Constant	4.8	9.1	18
^{1}H NMR K_{iso}	1.74	0.85	0.38
Raman $I(\nu_1^t)/I(\nu_1^c)$	2.8	1.8	1.4
$I(\nu_1^t)/I(\nu_2^c)$	5.9	2.8	1.8

temperature first leads to the coalescence of the *cis* and the non bonded ligand signals and then to the coalescence of the *trans* signal with the *cis*-free ligand collapsed peak. For all of our $SnX_4\cdot$2L and $SnX_4\cdot$L–L adducts (X = Cl, Br; L = MeCN, Me_2CO, Me_2O, Me_2S, Me_2Se, TMPA, $Me_2N(MeO)_2PO$, HMPA; L–L = $(MeOCH_2\text{–})_2$) we have calculated the stoichiometry, defined as the ratio of bonded ligand to metal halide, from the known concentrations of metal and ligand and from the integration of free and bonded ligand signals, including the signals due to ligand–tin coupling. The isomerization constant K_{iso}, defined as the ratio [*trans*-$SnX_4\cdot$2L]/[*cis*-$SnX_4\cdot$2L], is obtained by integration of the NMR resonances. Stoichiometries, isomerization constants and NMR data are reported in Table I.

Adducts with Phosphorylated Ligands

The ^{1}H NMR spectrum of $SnBr_4\cdot$2HMPA with an excess of HMPA shows three doublets at 275 K in CH_2Cl_2 (the doubling is due to coupling with ^{31}P). The doublet centered at 2.60 ppm is assigned to the free ligand. The two remaining doublets at low field can be assigned to the *cis* and *trans* isomers of the 1:2 adducts: their relative intensities are independent of the free ligand concentration and 1:2 overall stoichiometry is established for these species. This system was studied in $CHCl_3$, CH_2Cl_2 and $CH_2Cl_2/MeNO_2$ 3:1, and shows a strong variation in the intensities ratio for complexed ligand signals (Figure 1). Comparing these ratios with those obtained by vibrational spectroscopy (Table II), one can assign the low field signal (2.79 ppm) to the *trans* adduct, and the higher field signal (2.74 ppm) to the *cis* one. A weak new signal appears with increasing solvent polarity; it may be due to the formation of ionic species*. The isomerization constant varies from 0.85 (275 K) to 1.04 (203 K) and the following enthalpy and entropy of isomerization can be calculated: $\Delta H_{iso}(SnBr_4\cdot$2HMPA) = –0.3 ± 0.3 Kcal/mol and $\Delta S_{iso}(SnBr_4\cdot$2HMPA) = –1.4 ± 1.2 cal/°mol. When the temperature is increased to 300 K, one observes the coalescence of the signals of free and *cis* ligands, leaving the *trans* signal unaffected.

In the following ^{1}H NMR spectra of $SnX_4\cdot$2L adducts, the *cis* and *trans* signals were assigned, whenever possible, from the vibrational data of our previous paper. In all cases the *trans* signal appears at lower field than the *cis* one.

The spectrum of $SnCl_4\cdot$2HMPA also shows the *cis* and *trans* isomers. When the temperature is lowered to 190 K, one observes an appreciable broadening (~1 Hz) for bonded ligand signals only. By analogy to data obtained in sulfur donor ligand–platinum complexes [8], one may interprete this broadening to be due to an inversion reaction for the oxygen electronic pairs. The isomerization constant varies

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*Turin [7] established by NMR and conductivity measurements the following equilibrium in CH_3NO_2: $TiCl_4\cdot$2HMPA + HMPA ⇄ $[TiCl_3\cdot 3HMPA]^+ + Cl^-$.

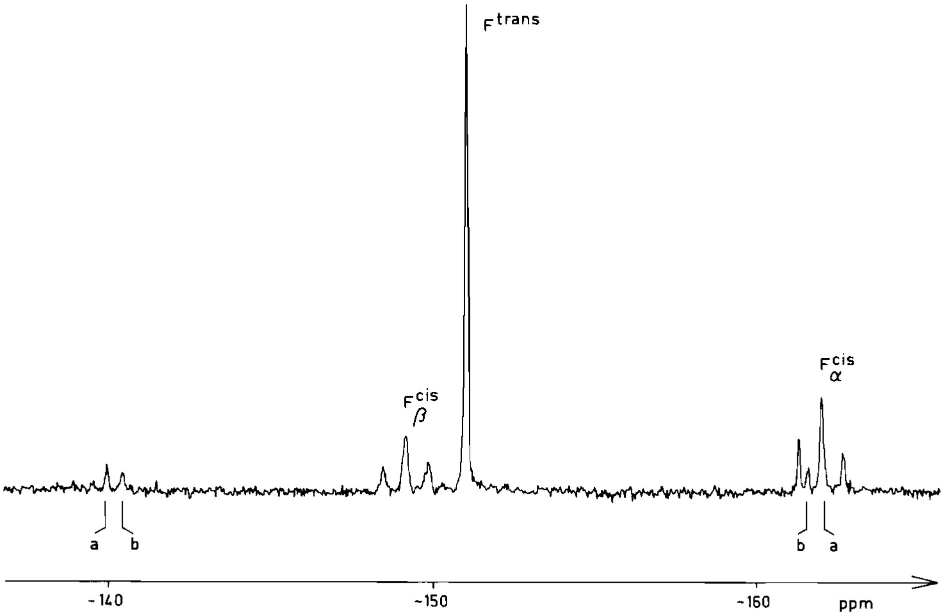

Figure 2. ^{19}F NMR spectrum (84.67 MHz) showing the *cis–trans* equilibrium of $SnF_4 \cdot 2TMPA$ at 173 K in CH_2Cl_2. $[SnF_4 \cdot 2TMPA] \lesssim 10^{-2}$ *m*, [TMPA] = 0.3 *m*. Internal reference: $CFCl_3$.
trans-$SnF_4 \cdot 2TMPA$: a) $^1J(^{19}F-^{119}Sn)$ = 1700 Hz, and b) $^1J(^{19}F-^{117}Sn)$ = 1620 Hz.
cis-$SnF_4 \cdot 2TMPA$: F_α *cis* to L, and F_β *trans* to L.

from 1.46 (230 K) to 1.33 (293 K) and the following thermodynamic parameters have been calculated: $\Delta H_{iso}(SnCl_4 \cdot 2HMPA) = -0.2 \pm 0.4$ Kcal/mol and $\Delta S_{iso}(SnCl_4 \cdot 2HMPA) = -0.1 \pm 3$ cal/°mol.

The isomerization constant has been determined at 230 K for $SnCl_4 \cdot 2TMPA$ in CH_2Cl_2 and $CHCl_3$ where the values of K_{iso} are 0.25 and 0.79 respectively. The ^1H NMR spectrum of $SnBr_4 \cdot 2TMPA$ shows at 203 K in CH_2Cl_2 nearly only the *cis* isomer (K_{iso} = 0.15); this explains why the *trans* isomer was not observed in the Raman spectra [1].

The ^{19}F NMR spectrum of $SnF_4 \cdot 2TMPA$ is shown in Figure 2. In the *trans* isomer, all fluorines are equivalent and a singlet should be observed, while for the *cis* one two different types of fluorines (F_α and F_β) are present, and two equal intensity triplets should be observed. Our spectrum shows a singlet at –151 ppm, assigned to the *trans* isomer and two triplets at –149 and –162 ppm assigned to the *cis* isomer. Coupling between the fluorines in the *trans* isomer and tin isotopes is also observed. The triplet at –149 ppm has been assigned to the F_β *cis* fluorines, on the basis of a weak splitting of this triplet arising from $^{19}F-^{31}P$ coupling. This type of coupling has been clearly demonstrated in octahedral $TaF_5 \cdot TMPA$ [9] where the ^3J coupling constant between the axial fluorine and the ligand phosphorus is 7 Hz, while no coupling of this type was observed for the equatorial fluorines.

The $^{31}P\{^1H\}$ NMR spectra have been run for $SnCl_4$/TMPA, $SnCl_4/Me_2N(MeO)_2PO$ and $SnCl_4$/TMPA/$Me_2N(MeO)_2PO$ in CH_2Cl_2 at 203 K. The data are reported in Table III. In the latter system, in addition to the *cis*- and *trans*-$SnCl_4 \cdot 2L$ signals, one observes new signals due to the *cis*- and *trans*-$SnCl_4 \cdot TMPA \cdot Me_2N(MeO)_2PO$ mixed adducts. The assignments, shown in Figure 3, are based on the known chemical shifts of *cis*- and *trans*-$SnCl_4 \cdot 2L$ species and on the fact that the signal intensity for *cis*- and *trans*-$SnCl_4 \cdot L_a \cdot L_b$ species must be equal for both L_a and L_b ligand resonances.

In order to determine the relative stability constants $K^L_{a,b}$ for these i-$SnCl_4 \cdot 2L$ adducts, the following equilibria and equilibrium constants have been considered (where L_a is $Me_2N(MeO)_2PO$ and L_b is TMPA):

$$trans\text{-}SnX_4 \cdot 2L_b + 2L_a \rightleftharpoons trans\text{-}SnX_4 \cdot 2L_a + 2L_b \qquad K^t_{a,b} \qquad (1)$$

$$cis\text{-}SnX_4 \cdot 2L_b + 2L_a \rightleftharpoons cis\text{-}SnX_4 \cdot 2L_a + 2L_b \qquad K^c_{a,b} \qquad (2)$$

$$trans\text{-}SnX_4 \cdot 2L_b + trans\text{-}SnX_4 \cdot 2L_a \rightleftharpoons 2trans\text{-}SnX_4 \cdot L_a \cdot L_b \qquad K^t_m \qquad (3)$$

$$cis\text{-}SnX_4 \cdot 2L_b + cis\text{-}SnX_4 \cdot 2L_a \rightleftharpoons 2cis\text{-}SnX_4 \cdot L_a \cdot L_b \qquad K^c_m \qquad (4)$$

$$cis\text{-}SnX_4 \cdot 2L_a \rightleftharpoons trans\text{-}SnX_4 \cdot 2L_a \qquad K^a_{iso} \qquad (5)$$

TABLE III. $^{31}P\{^1H\}$ NMR (36.44 MHz) Data for $SnCl_4\cdot 2TMPA$, $SnCl_4\cdot 2Me_2N(MeO)_2PO$ and the System $SnCl_4/TMPA/Me_2N(MeO)_2PO$: Chemical Shifts (ppm) $\delta(SnCl_4\cdot 2L)$ and $\delta'(SnCl_4\cdot L_a\cdot L_b)$, Differences in Chemical Shift $\Delta\delta = \delta(SnCl_4\cdot 2L) - \delta(L)$ and $\Delta\delta' = \delta(SnCl_4\cdot L_a\cdot L_b) - \delta(L)$, Coupling Constants (Hz), Stoichiometry and K_{iso}, in CH_2Cl_2, at 203 K. External reference: H_3PO_4 62.5%.

	$(MeO)_3PO$	$(MeO)_3PO$	$Me_2N(MeO)_2PO$	$Me_2N(MeO)_3PO$
$[M]_{total}$	0.1	0.075	0.075	0.075
$[L]_{total}$	0.4	0.435	0.187	0.3
Trans-adduct				
δ	−6.81	−6.93	5.34	5.24
δ'		−7.05	5.52	
$\Delta\delta$	−8.46	−8.58	−7.86	−7.96
$\Delta\delta'$		−8.70	−7.68	
$^2J(^{31}P–^{119}Sn)$	195			194
$^2J(^{31}P–^{117}Sn)$	186			188
Cis-adduct				
δ	−7.58	−7.68	4.79	4.72
δ'		−7.73	4.79	
$\Delta\delta$	−9.23	−9.33	−8.41	−8.48
$\Delta\delta'$		−9.38	−8.41	
$^2J(^{31}P–^{119}Sn)$	146			141
$^2J(^{31}P–^{117}Sn)$	139			135
Stoichiometry	1.9:1			2.2:1
K_{iso}	0.24			0.49

TABLE IV. Relative Intensities (%) for the $^{31}P\{^1H\}$ NMR Signals for *cis*- and *trans*-$SnCl_4\cdot 2L$ and $SnCl_4\cdot L_a\cdot L_b$ Species in the System $SnCl_4/TMPA/Me_2N(MeO)_2PO$ (concentrations, *cf.* Table III), at 203 K in CH_2Cl_2.

	Trans-adduct	*Cis*-adduct	Free Ligand
$SnCl_4\cdot 2(MeO)_3\underline{P}O$	2.6	21.4 { 10.8[a]	42.6
$SnCl_4\cdot (MeO)_3\underline{P}O\cdot Me_2N(MeO)_2PO$	3.1	10.6[a]	
$SnCl_4\cdot (MeO)_3PO\cdot Me_2N(MeO)_2\underline{P}O$	3.1	21.3 { 11.9[b]	1.3
$SnCl_4\cdot 2Me_2N(MeO)_2\underline{P}O$	4.6	9.4[b]	

[a] The integration for each signal alone was not possible; the relative intensity for the *cis*-$SnCl_4\cdot 2TMPA$ adduct was obtained from K_{iso}(TMPA) (see Table III), and the other was then deduced by difference. [b] The same procedure was followed from K_{iso}($Me_2N(MeO)_2PO$).

$$cis\text{-}SnX_4\cdot 2L_b \rightleftharpoons trans\text{-}SnX_4\cdot 2L_b \qquad K^{b}_{iso} \qquad (6)$$

$$cis\text{-}SnX_4\cdot L_a\cdot L_b \rightleftharpoons trans\text{-}SnX_4\cdot L_a\cdot L_b \qquad K^{m}_{iso} \qquad (7)$$

Most of the intensities for the ^{31}P NMR signals* could be integrated in the $SnCl_4/TMPA/Me_2N(MeO)_2PO$ system and are reported in Table IV. The following equilibrium constants were determined from the relative area measurements:

$$K^{t}_{a,b} = 1900 \text{ and } K^{c}_{a,b} = 935$$

$$K^{t}_{m} = 3.2 \quad \text{and } K^{c}_{m} = 5.0, \text{and } K^{m}_{iso} = 0.28.$$

The formation constants for the mixed adducts, K^{i}_{m}, are close to the value of 4.0 which would be obtained for a statistical distribution.

In the case of $SnX_4/L_a/L_b$ systems where the concentrations of the i-$SnX_4\cdot 2L$ species cannot be determined independently from those of mixed i-$SnX_4\cdot L_a\cdot L_b$ species, the relative stability constant can however be estimated. If I^{i}_{a} and I^{i}_{b} are the total relative intensities for the isomer i present as i-$SnX_4\cdot 2\underline{L}_a$ and i-$SnX_4\cdot \underline{L}_a\cdot L_b$, and i-$SnX_4\cdot 2\underline{L}_b$ and i-$SnX_4\cdot L_a\cdot \underline{L}_b$ respectively, one may write:

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*It has been shown [10] that the Nuclear Overhauser Effect (NOE) is relatively unimportant when protons are not directly bonded to ^{31}P.

TABLE V. Relative Intensities (%) for the ^1H NMR Signals for $SnX_4/L_a/L_b$ Systems and Estimated Relative Stability Constants $K^i_{a,b}$ for the Adducts i-$SnX_4 \cdot 2L$ in CH_2Cl_2 (~210 K).

	I^t_L	I^c_L	I_L	$K^t_{a,b}$	$K^c_{a,b}$
$SnCl_4$ $L_a = Me_2Se$[a]	20.5	16.7	8.6	8.5	4.7
$L_b = Me_2S$[a]	16.3	17.9	20.0		
$SnBr_4$ L_a = TMPA[b]	5.4	39.7	15.6	0.6	6.1
$L_b = Me_2Se$[c]	7.0	16.4	15.9		
$SnBr_4$ $L_a = Me_2Se$[d]	27.9	14.1	4.7	69	39
$L_b = Me_2S$[d]	17.4	11.7	24.2		

[a] I^t_L and $(I^c_L + I_L)$ determined at 245 K, I_L at 173 K; then $I^c_L = (I^c_L + I_L) - I_L$. [b] I^t, I^c and I_L determined at 181 K. [c] I_{Me_2Se} and $(I^t_{Me_2Se} + I^c_{Me_2Se})$ are obtained at 181 K; $I^t_{Me_2Se}$ determined at 226 K and $I^c_{Me_2Se}$ then obtained by difference. [d] I_L obtained at 184 K; at 205 K, $(I^c_L + I^L)$ is determined and I^c_L obtained by difference; at 298 K, $(I^t_L + I^c_L + I_L)$ is obtained and I^t_L deduced.

$$n_a(a^i + m/2) \propto I^i_a, \tag{8}$$

$$n_b(b^i + m/2) \propto I^i_b, \tag{9}$$

where $a^i = [\text{i-}SnX_4 \cdot 2L_a]$, $b^i = [\text{i-}SnX_4 \cdot 2L_b]$, $m = [\text{i-}SnX_4 \cdot L_a \cdot L_b]$ and n_a, n_b = multiplicity of the nucleus under observation in the ligands L_a and L_b, respectively.

The relative stability constants for equation (1) or (2) can be obtained, if $c^i = (a^i/b^i)^{1/2}$ is known:

$$K^i_{a,b} = (c^i)^2 \frac{[L_b]^2}{[L_a]^2} \tag{10}$$

Dividing equation (8) by equation (9), substituting m by its value obtained from equation (3) or (4), and solving for the positive root of c, we have:

$$c^i = \frac{1}{4}(K^i_m)^{1/2}\left(\frac{I^i_a n_b}{n_a I^i_b} - 1\right) + \\ + \left[\frac{1}{16} K^i_m \left(\frac{I^i_a n_b}{n_a I^i_b} - 1\right)^2 + \frac{I^i_a n_b}{n_a I^i_b}\right]^{1/2} \tag{11}$$

In our hypothesis, K^i_m cannot be determined, and we shall take as an approximation that it equals the statistical value of 4.0, as the observed values in $SnCl_4/TMPA/Me_2N(MeO)_2PO$ frame this value. Equation (11) then reduces as $c^i = I^i_a\ n_b/n_a\ I^i_b$, and substituting c^i in equation (10), one obtains:

$$K^i_{a,b} = \left(\frac{I^i_a \cdot I_b}{I^i_b \cdot I_a}\right) [2] \tag{12}$$

where I_a and I_b are the relative intensities of the free ligands L_a and L_b.

In the case where the difference in stabilities is so great that only one $SnX_4 \cdot 2L$ adduct is formed, one can just write a stability sequence. The ^1H NMR spectra for $SnCl_4$/HMPA/TMPA in a 1:2.2:6 ratio, and $SnBr_4$/HMPA/TMPA (1:2.2:5) only show the formation of the adduct with HMPA, leaving TMPA uncomplexed. One may then write the following stability sequence:

$$SnX_4 \cdot 2HMPA >> SnX_4 \cdot 2TMPA \quad (X = Cl, Br)$$

Adducts with Dialkylchalcogen Ligands

The ^1H NMR spectra for $SnCl_4$ and $SnBr_4$ adducts with *dimethylchalcogen* (Me_2O, Me_2S, Me_2Se) all show the resonances for *trans, cis* and free ligand in order of decreasing chemical shifts, except for $SnBr_4$ with Me_2O. In this latter system, it has been shown by vibrational spectroscopy [1] that only a small amount of adduct is formed at room temperature. At 180 K, the ^1H NMR spectrum shows a weak signal at 4.07 ppm which would correspond to 6% of complex formation if a 1:2 adduct is formed; a second intense signal is observed at 3.57 ppm, and corresponds to the coalescence of free ligand (δ_{Me_2O} = 3.33 ppm) with some other bonded ligand signals.

Various studies have been concerned with $J(^1H-^{119,117}Sn)$ coupling constants in $Me_{4-n}SnL_n$ complexes (L = X, SMe, SeMe, NMe_2) [11]. The dependence of ^2J coupling constants on the electronic distribution on the Sn–C–H bonds as well as the geminal angle between the Sn–C and C–H bonds have been demonstrated. The values for ^3J constants ranged from 37.7 to 51.7 Hz for L = SMe and SeMe. A few $^4J(^1HCCO^{119,117}Sn)$ coupling constants have been reported for tin(IV) octahedral complexes with values around 7 Hz [12, 13]. In $SnX_4 \cdot 2L$, the ^3J coupling constants are slightly greater in *trans* adducts than in *cis* ones. Their values for the dimethyloxide adduct are about 18 Hz, while they amount to about 50 Hz for the dimethylsulfide and selenide adducts.

The isomerization constants K_{iso} increase from Me_2O to Me_2S and Me_2Se. They weakly depend on temperature; for $SnCl_4 \cdot 2Me_2S$, the following values 0.79 (190 K), 0.74 (240 K) and 0.72 (260 K) allow the determination of the isomerization thermodynamic parameters: $\Delta H_{iso}(SnCl_4 \cdot 2Me_2S) = -0.13 \pm 0.4$ kcal/mol and $\Delta S_{iso}(SnCl_4 \cdot 2Me_2S) = -1.1 \pm 3$ cal/°mol.

The relative stability constants have been quantitatively estimated for $SnX_4/Me_2Se/Me_2S$ and $SnBr_4$/TMPA/Me_2Se using equation (12). Their values as well as the results for the ^1H NMR signal integrations are reported in Table V. Even if these integrations were obtained at different temperatures, our estimations can reasonably be accepted, as has been shown in $MX_5 \cdot L$ adducts [14] that the relative stability constants are quite temperature independent. For $SnX_4/Me_2S/Me_2O$ and $SnCl_4$/TMPA/Me_2Se, only an order of magnitude for the relative stabilities could be determined.

The ^1H NMR spectrum of $SnCl_4 \cdot 2Et_2S$ in CH_2Cl_2 shows at 183 K three quadruplets for methylene protons, while methyl protons have resonances too close for the different species to be distinguished. On the basis of our vibrational results [1], where a *cis*–*trans* equilibrium was demonstrated, one can assign the low field quadruplet at 3.40 ppm to the *trans* isomer, the 3.05 ppm one to the *cis* isomer and the 2.54 one to the free ligand. The stoichiometry and the isomerization constant could not be determined as the quadruplet signals are partially superimposed.

The ^1H NMR spectrum for $SnCl_4 \cdot 2Et_2O$ in CH_2Cl_2 at 213 K shows at 4.46 ppm a quadruplet assigned to the *trans* isomer, and at 3.72 ppm a second sharp quadruplet. At 175 K this latter signal broadens, indicating a slower exchange between free ligand with another form of bonded ligand. These results can be compared to the vibrational data at room temperature, where the *trans* isomer was found in presence of other complexed species.

The ^1H NMR spectra for both $SnX_4 \cdot (MeOCH_2)_2$ adducts (X = Cl, Br) confirm a 1:1 stoichiometry and only show the presence of one complexed species, assigned to the *cis* isomer on the basis of our vibrational results [1]. The *cis*-free ligand exchange is slow at the NMR time scale at 253 K for the chloride adduct, and at 203 K for the bromide one, indicating greater lability for the latter one. ^3J coupling constants between methyl or methylene protons with the tin isotopes correlate well with those obtained in the $SnCl_4 \cdot 2Me_2O$ adduct. The coordinating ability of the oxygen atoms in $(MeOCH_2)_2$ towards $SnBr_4$, while very little adduct formation was observed between Me_2O and $SnBr_4$, is evidently explained by the entropy contribution due to the chelate effect.

Adducts with Nitriles and Acetone

^1H NMR spectra at ~160 K for $SnCl_4 \cdot 2MeCN$ and $SnCl_4 \cdot 2Me_2CO$ show only one signal for bonded ligand, assigned to the *cis* isomer on the basis of our vibrational results [1]. A $^4J(^1H-^{119,117}Sn)$ coupling was not observed. This type of coupling has been reported in $SnCl_2(acac)_2$, with values of about 6 Hz [12], probably enhanced by π electron delocalization.

In the $SnCl_4 \cdot 2Me_3CCN$ spectrum at ~170 K, one only observes a broadened signal at 1.47 ppm due to the fast *cis*-free ligand exchange, indicating a greater lability for this adduct compared to $SnCl_4 \cdot 2MeCN$.

Discussion

Relative Stability of $SnX_4 \cdot 2L$ Adducts (X = Cl, Br)

The following stability sequence was obtained from the relative stability constants for the *cis*- and *trans*-$SnX_4 \cdot 2L$ adducts with dimethylchalcogen ligands: $Me_2Se > Me_2S \gg Me_2O$. This sequence is identical to the one for the Sn–L bond strength in *trans*-$SnX_4 \cdot 2L$ adducts determined by vibrational spectroscopy [1]. For *cis*- and *trans*-$SnX_4 \cdot 2L$ adducts with phosphorylated ligands, the following stability sequence was obtained: HMPA > $Me_2N(MeO)_2PO$ > TMPA. Again, this sequence parallels the one obtained for the Sn–L bond strength from vibrational spectroscopy [1]. Charge localization calculations on the phosphoryl oxygen of the PO group [15], predict the observed sequence of stability constants. Such a behaviour has been observed in $NbX_5 \cdot L$ and $TaX_5 \cdot L$ adducts [9]. The following overall stability sequence is obtained when combining the two series above, with the exception that *trans*-$SnBr_4 \cdot 2Me_2Se$ is more stable than *trans*-$SnBr_4 \cdot 2$TMPA

$$\text{HMPA} > Me_2N(MeO)_2PO > \text{TMPA} > Me_2Se > Me_2S \gg Me_2O.$$

The overall Sn–L bond strength sequence obtained from the known Sn–X force constants [1], using the inductive model, does not coincide with the stability sequence. In this model, it is assumed that the Sn–X bond becomes weaker as the Sn–L bond becomes stronger, which is a reasonable assumption only in a homologous series. Moreover, as the enthalpies of formation of the adducts are not known, one may realistically question whether or not the free energy parallels the enthalpy. On the basis of their vibrational results, using the inductive model, Ohkaku and Nakamoto [16] proposed the following sequence for the Sn–L bond strength in *trans*-$SnX_4 \cdot 2L$ adducts: $P(PPh_3)$ > S(THT) > N(pyr) > O(THF). Moreover, they partially confirmed this order of Sn–L force constants for the adducts formed with pyridine and THF, by a normal coordinate analysis.

Mössbauer spectroscopy has also been used for the study of $SnX_4 \cdot 2L$ adducts [17]. While it has been assumed that the isomeric shift is a sensitive probe of the strength of the Sn–L interaction, no sequences have been deduced from the experimental data.

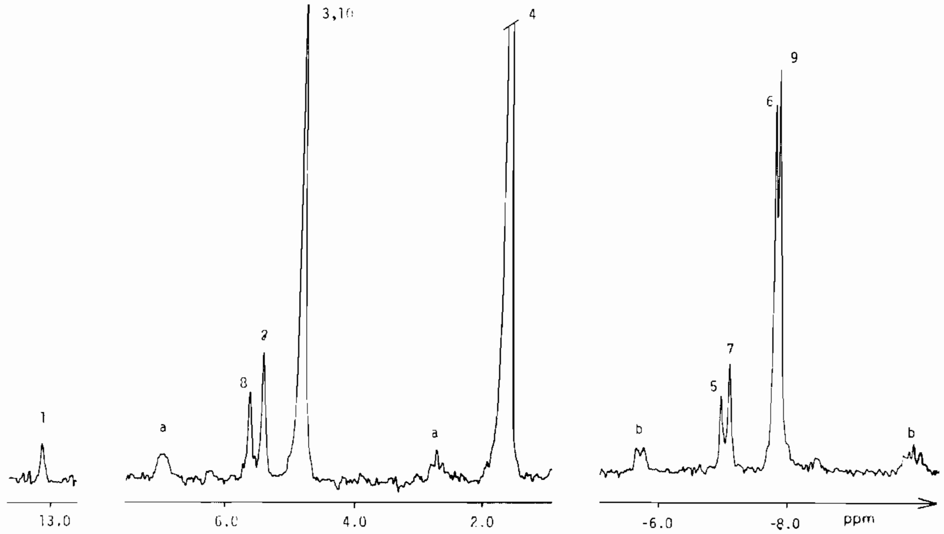

Figure 3. $^{31}P\{^1H\}$NMR spectrum (36.44 MHz) at 203 K in CH_2Cl_2 of $SnCl_4/Me_2N(MeO)_2PO/(MeO)_3PO$ (1:2.5:5.8). $[SnCl_4]$ = 0.075 *m*, external reference: H_3PO_4 62.5%. With the following assignments:
1 = $Me_2N(MeO)_2\underline{P}O$, 2 = *trans*-$SnCl_4 \cdot 2Me_2N(MeO)_2\underline{P}O$, 3 = *cis*-$SnCl_4 \cdot 2Me_2N(MeO)_2\underline{P}O$, 4 = $(MeO)_3\underline{P}O$, 5 = *trans*-$SnCl_4 \cdot 2$-$(MeO_3\underline{P}O$, 6 = *cis*-$SnCl_4 \cdot 2(MeO)_3\underline{P}O$, 7 = *trans*-$SnCl_4 \cdot (MeO)_3\underline{P}O \cdot Me_2N(MeO)_2PO$, 8 = *trans*-$SnCl_4 \cdot (MeO)_3PO \cdot Me_2N(MeO)_2$-$\underline{P}O$, 9 = *cis*-$SnCl_4 \cdot (MeO)_3\underline{P}O \cdot Me_2N(MeO)_2PO$, 10 = *cis*-$SnCl_4 \cdot (MeO)_3PO \cdot Me_2N(MeO)_2\underline{P}O$. Signals a (and b) arise from coupling of phosphorus 3,10 (and 6,9) with ^{119}Sn and ^{117}Sn isotopes.

TABLE VI. Isomerisation Constants $K_{iso} = [trans\text{-}SnX_4 \cdot 2L]/[cis\text{-}SnX_4 \cdot 2L]$ for $SnX_4 \cdot 2L$ Adducts in CH_2Cl_2.

	Me_2O	Me_2S	Me_2Se	TMPA	$Me_2N(MeO)_2PO$	HMPA
$SnF_4 \cdot 2L$	–	–	–	1.73	–	–
$SnCl_4 \cdot 2L$	0.64	0.79	1.37	0.24	0.49	1.46
$SnBr_4 \cdot 2L$	–	1.38	2.33	0.15	0.35	1.04
T(K)	~180	~180	~180	~215	~215	~215

Several UV and IR equilibrium studies have provided formation constants for 1:1 and 1:2 tin(IV) tetrahalide adducts with weak donor ligand such as nitriles, esters, ethers and amines [18].

Relative stabilities in $SnX_4 \cdot 2L$ adducts may be quantitatively discussed using the Hard and Soft Acid and Base concept. Sn^{4+} being classified as hard acid [19], Carty *et al.* then consider $SnCl_4$ as hard which agrees with their Mössbauer data [17]. Farona [20] also assumes a hard character for $SnCl_4$. He then compares Ohkaku's and Nakamoto's vibrational results [16] to the HSAB predictions reaching the conclusion that this theory fails for $SnCl_4 \cdot 2L$ adducts. We shall however consider $SnCl_4$ as a moderately soft acid. The acid softness in metal halides [14] increases when the acid center is bonded to a softer base, as predicted by Jϕrgensen's symbiotic effect [21]. Since bromide ions are softer than chloride ions, $SnBr_4$ should be softer than $SnCl_4$. Using these arguments, the following sequence for acid-base interaction should be observed for the ligand donor atom [19]: Se > S >> O, in agreement with the sequences we obtained for the stabilities and the Sn–L bond strength in $SnBr_4$ and $SnCl_4$ adducts. We could not determine the stabilities of the bromide relatively to the chloride adducts, by the competitive equilibria method, since all $SnCl_nBr_{4-n} \cdot 2L$ mixed adducts would be formed. However, we have shown that $SnBr_4$ interacts more weakly with hard bases such as Me_2O, Et_2O, MeCN and Me_2CO than $SnCl_4$ does.

Isomerization Constants

The isomerization constants for the $SnX_4 \cdot 2L$ adducts in CH_2Cl_2 are reported in Table VI. These are relatively temperature independent, as shown by the small (<0.3 Kcal/mol) enthalpies of isomerization in $SnBr_4 \cdot 2HMPA$, $SnCl_4 \cdot 2HMPA$ or $SnCl_4 \cdot$-$2Me_2S$. However, the isomerization constants vary strongly with solvent polarity, the *trans* isomer being favoured in a weakly polar solvent, as shown in the $SnBr_4 \cdot 2HMPA$ studies.

The arguments used in the literature to rationalize the occurence of one isomer or the other have only been applied to solid adducts, and we have shown [1] that both isomers could be synthesized for $SnCl_4 \cdot 2$-THT by changing the solvent polarity.

Arguments based on steric effects led Beattie [22] to propose that a *cis* adduct would be favoured if the ligands are larger than the halogens. However, Zahrobsky [23], using a stereochemical model based on nonbonded intramolecular interactions, has shown that irrespective of the relative solid angles of the monoatomic ligands in a MA_4B_2 complex, the *cis* isomer would always be favoured. This also holds in $SnX_4 \cdot 2L$ adducts, if the substituents in the ligand L do not spread out of the solid angle of the donor atom, which is the case in our ligands. Steric effects can thus not be taken into account to discuss the isomerization constants of our adducts. Other arguments are based on the nature of the Sn–X and Sn–L bonds. From all of these [22–24] we have retained those given by Smith and Wilkins [12], and Drago [25]. In $SnX_4 \cdot 2L$ octahedral adducts, the overlap of tin(IV) 5s, 5p and 5d orbitals depends on the positive charge on Sn(IV). When two low polarity Sn–L bonds are formed, the tin(IV) d orbitals are too high in energy to be appreciably involved in bonding. In this case, the tin atom then uses the sp_z hybrid orbitals, giving two strong Sn–L bonds *trans* to each other. When the six ligands have comparable electronegativities, a sp^3d^2 hybridization becomes possible, and the molecule adopts the configuration which minimizes the splitting between the $d_{x^2-y^2}$ and d_{z^2} orbitals, namely the *cis* one.

In $SnX_4 \cdot 2L$ adducts with *dimethylchalcogen* ligands, the isomerization constant increases from Me_2O to Me_2Se, and from $SnCl_4$ to $SnBr_4$ adducts. Upon adduct formation, the positive charge on Sn(IV) diminishes as the ligand donor atom electronegativity decreases and as the Sn–L bond becomes stronger. One predicts that the tin(IV) d orbitals will be destabilized in going from Me_2O to Me_2Se, making sp^3d^2 hybridization more difficult, which favours the *trans* isomer. In going from $SnCl_4$ to $SnBr_4$, the effective charge on tin(IV) decreases with the halogen electronegativity. The *trans* adduct is then favoured in bromide adducts compared to chloride ones.

In the series with *phosphorylated* ligands, the isomerization constant increases from TMPA to HMPA, but decreases from $SnCl_4$ to $SnBr_4$ adducts. We have shown previously that in SnX_4 adducts, the Sn–L bond is stronger for HMPA than for TMPA. In this case, the effective charge on tin(IV) decreases from TMPA to HMPA, favouring the *trans* isomer. We assumed that the effective charge on tin(IV) is higher in $SnCl_4$ than in $SnBr_4$. One should thus observe an increase in the isomerization constant going from $SnCl_4$ to $SnBr_4$ adducts. The increase in the isomerization constant for the chlorides over the bromides can only be explained if one assumes that the acid–base interaction with these ligands is stronger in $SnCl_4$ adducts than in $SnBr_4$ ones. The charge on tin(IV) would then be higher in $SnBr_4$ adducts, which favours the *cis* isomer.

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