# Adducts of Tin(IV) Tetrahalides with Neutral Lewis Bases. III. Dynamic Study by NMR*

S. J. RUZICKA, C. M. P. FAVEZ and A. E. MERBACH

Institut de chimie minérale et analytique, Université de Lausanne, CH-1005 Lausanne, Switzerland

Received November 8, 1976

Solutions of octahedral adducts $SnX_4 \cdot 2L$ (X = Cl, Br) in inert solvents in general undergo two exchange processes observable by ^1H NMR. The fastest corresponds to neutral ligand exchange on the cis isomer, and the slowest is believed to be the same exchange on the trans *adduct.*

$$i\text{-}SnX_4 \cdot 2L + {}^*L \rightleftharpoons i\text{-}SnX_4 \cdot L \cdot {}^*L + L$$
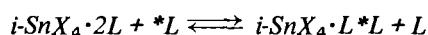
(i = cis, trans)

For the slower process, a cis–trans isomerization could not be excluded. Both exchange reactions obey a D mechanism and are first order in adduct with the following activation parameters ΔH^* (kcal mol^{-1}) and ΔS^* (cal K^{-1} mol^{-1}): 12.3, +21 (cis– Me_2CO); 15.3, +24 and 17.8, +15 (cis- and trans-Me_2S); 15, +9 and 19, +9 (cis- and trans-TMPA). The ΔG^*'s for the cis and trans adducts differ by 4 to 5 kcal mol^{-1} at 250 K and increase in the same order as the stability constant sequence:

$$Me_2CO < Me_2O \lessdot Me_2S < Me_2Se \lessdot TMPA \lessdot HMPA$$

Reaction rates of the tetrabromide are greater than those of the tetrachloride adducts due to a change in the effective charge on the metal and to steric hindrance.

Introduction

A series of $SnX_4 \cdot 2L$ (X = Cl, Br) adducts were synthesized and their cis or trans geometry determined by infrared and Raman spectroscopy [1]. The existence of a cis–trans equilibrium in solution for the majority of these adducts has been demonstrated, and the isomerization constants measured by NMR spectroscopy [2]. We decided to study their dynamic behaviour in the presence of an excess of ligand, L, in order to understand their isomerization mechanism and more generally the substitutions on tin(IV). Proton NMR, a well established method [3]

for the study of fast inter- and intramolecular exchange reactions was used.

Substitution reactions of octahedral adducts of tin(IV) halides have rarely been studied. A kinetic investigation of the $SnCl_4$–$CH_2(OMe)_2$–dioxalane system in dichloromethane is known [4]. The solvolysis of *trans*-$SnCl_4 \cdot 2py$ in triethylphosphate shows a complicated mechanism, and the reaction of this adduct with acetyl chloride in the same solvent results in replacement of py by Cl⁻, this latter reaction occurring more rapidly than the solvolysis [5]. The following straightforward nucleophilic substitution mechanism [6] will be considered for the $SnCl_4 \cdot 2L$ adducts.

For a *dissociative* ligand exchange, it is usually assumed that the most probable structure for the pentacoordinate intermediate is a tetragonal pyramid or a trigonal bipyramid. As shown in Figure 1, the formation of a tetragonal pyramid always leads to retention of the initial structure while the trigonal bipyramid intermediate may lead to an isomerization reaction. Starting with the *trans* isomer, only bi-
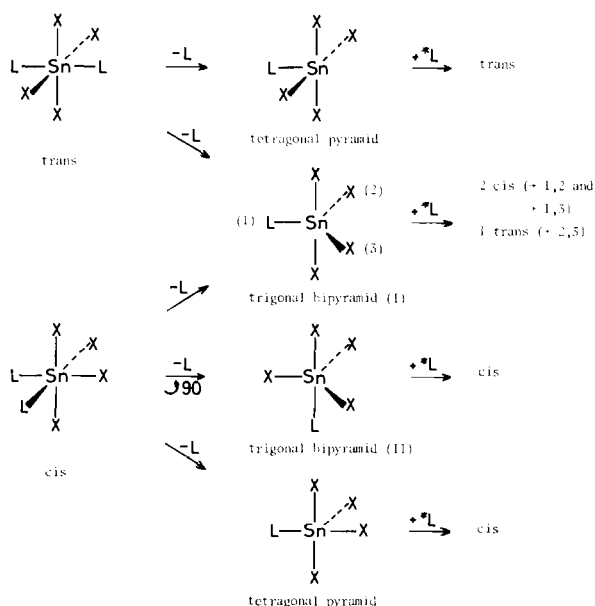

Fig. 1. Stereochemical changes for dissociative ligand L exchange reactions in *cis-* and *trans-*$SnX_4 \cdot 2L$ adducts [6].

TABLE I. Exchange Probability Matrices.

a) Exchange on cis-SnX$_4$·2L (L = Me$_2$O, Me$_2$S)

	1	2	3	4	5	6
1	−1	0	0	0	0	1
2	0	−1	0	0	0	1
3	0	0	−1	0	0	1
4	0	0	0	−1	0	1
5	0	0	0	0	−1	1
6	p_1/p_6	p_2/p_6	p_3/p_6	p_4/p_6	p_5/p_6	$-(1-p_6)/p_6$

where $\quad p_1 = p_5 = cis$ population due to $^3J(^1H-^{119}Sn)$
$\qquad\quad p_2 = p_4 = cis$ population due to $^3J(^1H-^{117}Sn)$
$\qquad\quad p_3 \qquad = cis$ population arising from I = 0 tin isotopes
$\qquad\quad p_6 \qquad =$ free ligand population

with $\sum\limits_{i=1}^{6} p_i = 1$

b) Exchange on cis-SnX$_4$·2Me$_2$Se

	1	2	3	4	5	6	7	8	9	10
1	−1	0	0	0	0	0	0	0	1	0
2	0	−1	0	0	0	0	0	0	1	0
3	0	0	−1	0	0	0	0	1	0	0
4	0	0	0	−1	0	0	0	0	1	0
5	0	0	0	0	−1	0	0	0	0	1
6	0	0	0	0	0	−1	0	0	1	0
7	0	0	0	0	0	0	−1	0	1	0
8	0	0	p_3/p_8	0	0	0	0	$-p_3/p_8$	0	0
9	p_1/p_9	p_2/p_9	0	p_4/p_9	0	p_6/p_9	p_7/p_9	0	$-c/p_9$	0
10	0	0	0	0	p_5/p_{10}	0	0	0	0	$-p_5/p_{10}$

where $\quad p_1 = p_7 = cis$ population due to $^3J(^1H-^{119}Sn)$
$\qquad\quad p_2 = p_6 = cis$ population due to $^3J(^1 H-^{117}Sn)$
$\qquad\quad p_3 = p_5 = cis$ population due to $^2J(^1H-^{77}Se)$
$\qquad\quad p_4 \qquad = cis$ population "uncoupled"
$\qquad\quad p_8 = p_{10} =$ free ligand population due to $^2J(^1H-^{77}Se)$
$\qquad\quad p_9 \qquad =$ free ligand population "uncoupled"
with $c = 2p_1 + 2p_2 + p_4$
The complexed species simultaneously coupled to tin ^{119}Sn, or ^{117}Sn, and to ^{77}Se were neglected: their total concentration equals to 1.2% of the coupled species.

c) Exchange on cis-SnX$_4$·2R$_3$PO (R = MeO, or Me$_2$N)

	1	2	3	4
1	−1	0	1	0
2	0	−1	0	1
3	p_1/p_3	0	$-p_1/p_3$	0
4	0	p_2/p_4	0	$-p_2/p_4$

where $\quad p_1 = p_2 = cis$ population due to $^3J(^1H-^{31}P)$
$\qquad\quad p_3 = p_4 =$ free ligand population due to $^3J(^1H-^{31}P)$

d) Exchange on $trans$-SnX$_4$·2L
For the $trans$ adducts, the above matrices are used in the following way: each cis population is replaced by the corresponding $trans$ one, and the free ligand population by the (cis + free) one.

pyramid (I) seems a probable intermediate since formation of pyramid (II) would require an important rearrangement. However, *cis* isomer may lead to either bipyramid (I) or (II) as an intermediate. The ligand addition reaction is assumed to take place in the trigonal plane and the statistical ratios of isomer formation are indicated in Figure 1.

For an *associative* ligand exchange, a heptacoordinate intermediate is formed. The ligand addition may then occur at the position adjacent to the leaving ligand (*cis* attack) or at the opposite position (*trans* attack). A *cis* attack always results in retention of the initial configuration. A *trans* attack leads to a complete conversion of the *trans* isomer into *cis* while the *cis* isomer is partially converted into *trans*.

Experimental

Work in inert atmosphere, the purification of chemicals and the preparation of solutions have been reported previously [1]. ^{1}H NMR measurements on a Bruker WP-60 spectrometer have been described [2]. ^{119}Sn{^{1}H}-NMR spectra were recorded at 22.34 MHz on the same instrument.

Determination of Rate Constants

The two following methods have been used:

Slow exchange approximation

The residence time of a nucleus in a chemical environment j is inversely proportional to the signal width. The full width at half height, W_j, for any signal is given by $W_j = W^{measd} - W_{TMS}^{measd}$, where W^{measd} and W_{TMS}^{measd} are the full widths at half height measured on the spectrum; this takes into account the instrumental broadening. For a system with n sites, the residence time τ_j^r for a given nucleus in site j is given by $1/\tau_j^r = \pi(W_j - W_j^0)$, where W_j^0 is the full width at half height in the absence of exchange. The validity of the latter equation has been verified [7].

Line shape analysis

In the case of intermediate and rapid exchange, the spectra were simulated on a CDC CYBER 7326 computer and plotted for comparison with the experimental spectra. For a limited number of sites, the DNMR3 [8] program was used. For more complex spectra the EXCHNG [9] program was used. This program is based on the Kubo–Sack stochastic theory, using Block's modified equations. The populations, chemical shifts and relaxation times for the different sites are introduced as well as the exchange probability matrix which represents the fraction of nuclei exchanging between the different sites. This matrix is defined for each type of exchange, and obeys precise rules [10]. The matrices used are shown in Table I and were extended with zero elements when non exchanging species were present. The chemical shifts and coupling constants have been

tabulated previously [2]. Their temperature dependence has also been taken into account.

Abbreviations

Trimethylphosphate = TMPA, hexamethylphosphoramide = HMPA.

Results

In solutions containing free and coordinated ligand exchange reactions take place. At low temperature the NMR spectra show in general three main signals. As an example, Figure 3 shows the signals for *trans*-(δ = 2.73 ppm), *cis*-SnCl$_4$·2Me$_2$S (δ = 2.67 ppm) and their satellites due to coupling with ^{119}Sn and ^{117}Sn isotopes at 191 K. The free ligand signal is observed at higher field (δ = 2.12 ppm). Upon increasing the temperature, one first observes the collapse of the *cis* and free ligand signals. At higher temperature (Figure 4), the *trans* ligand signal collapses with the single *cis*-free ligand signal. This allows us the study of both kinetic processes independently.

The first collapse corresponds to a ligand exchange between the *cis* complexed ligand site and the bulk ligand site. The second collapse, from a kinetic point of view, may be due to either a ligand exchange reaction on the *trans* adduct, or to a *cis–trans* isomerisation reaction, or even to both reactions. Proton NMR spectroscopy does not allow to distinguish between those two reactions or both of them combined. As a working hypothesis, we shall assume that only the *trans* ligand exchange reaction takes place. This allows us to write $\tau_{t\text{-}SnX_4 \cdot 2L} = \frac{1}{2}\tau_{t\text{-}SnX_4 \cdot 2L}^r$. In the case of a *cis–trans* isomerisation reaction, the mean life-time of the *trans* adduct would be equal to the residence time of the ligand in the *trans* adduct.

Similar ligand exchange reactions between the free and complexed ligand sites have been studied in MX$_5$·L adducts (M = Nb, Ta) [11]. For tin tetrahalide adducts this reaction may be expressed as
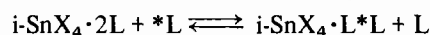
$$i\text{-}SnX_4 \cdot 2L + {}^*L \rightleftharpoons i\text{-}SnX_4 \cdot L^*L + L$$

(i = *cis* or *trans*)

In the case of a first-order reaction, *i.e.* zero-order in ligand and first order for complex, the mean lifetimes τ_{Ci} of the complex and τ_F of the free ligand are defined by

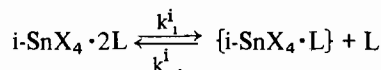$$1/\tau_{Ci} = -d[i\text{-}SnX_4 \cdot 2L]/[i\text{-}SnX_4 \cdot 2L]\,dt = k_i^i$$

and

$$1/\tau_F = -d[L]/[L]\,dt = k_1^i[i\text{-}SnX_4 \cdot 2L]/[L],$$
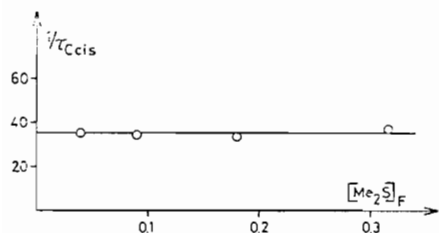
where $\tau_{Ci}^r = 2\tau_{Ci}$ and $\tau_F^r = \tau_F$
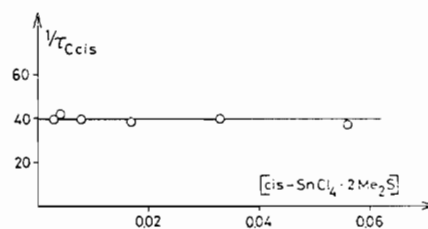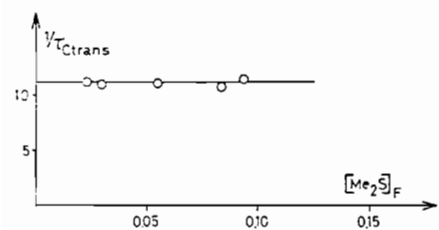
These equations apply for a dissociative mechanism D as

$$i\text{-}SnX_4 \cdot 2L \underset{k_{-1}^i}{\overset{k_1^i}{\rightleftharpoons}} \{i\text{-}SnX_4 \cdot L\} + L$$
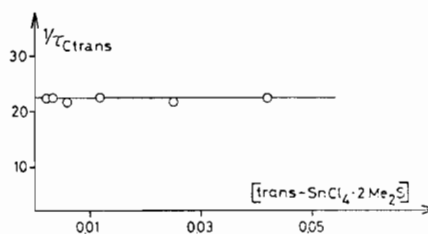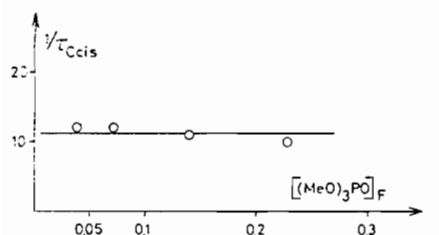
Fig. 2. Mean lifetime $1/\tau_{Ci}$ of i-SnCl$_4 \cdot$2L determined by the slow exchange approximation (a–e), by DNMR3 (f) and EXCHNG (g), as a function of free ligand and adduct concentration.

$$\{\text{i-SnX}_4 \cdot \text{L}\} + \text{*L} \underset{k_1^i}{\overset{k_{-1}^i}{\rightleftharpoons}} \text{i-SnX}_4 \cdot \text{L*L}$$
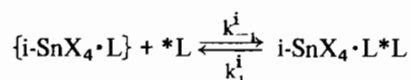
In the same way, one may define the kinetic equations for a second-order rate law, applying for an associative mechanism [11].

The rate laws for the ligand exchange reactions have been determined for three systems (Figure 2). First order behaviour with respect to the adduct and zero order behaviour with respect to free ligand are observed for cis- and trans-SnCl$_4 \cdot$2Me$_2$S. For cis-SnCl$_4 \cdot$2Me$_2$CO and the two isomers of SnCl$_4 \cdot$

TABLE II. Rate Constant k_1^i (s^{-1}) for the Ligand Exchange Reaction i-SnCl$_4$·2L + *L $\rightleftharpoons$ i-SnCl$_4$·L*L + L, as a Function of Temperature T (K). Enthalpy ΔH^* (kcal mol^{-1}) and Entropy ΔS^* (cal K^{-1} mol^{-1}) of Activation. [SnCl$_4$·2Me$_2$CO] = 0.03 m, [Me$_2$CO] = 0.06 m in CH$_2$Cl$_2$; [SnCl$_4$·2Me$_2$S] = 0.10 m, [Me$_2$S] = 0.06 m in CH$_2$Cl$_2$; [SnCl$_4$·2TMPA] = 0.05 m, [TMPA] = 0.10 m in CHCl$_3$. W^0(i-SnCl$_4$·2L) $\simeq$ 0.3 Hz and W^0(L) = 0.1 Hz.

SnCl$_4$·2Me$_2$CO^a		SnCl$_4$·2Me$_2$S^b				SnCl$_4$·2TMPA			
T	k_1^c	T	k_1^c	T	k_1^t	T	k_1^c	T	k_1^t
170.0	19	191.0	2.2	257.7	6.0	228.7	3.0^c	296.7	4.2^c
173.0	44	196.5	7.8	261.5	10.8	236.2	9.4	296.7	5.0
175.5	66	198.7	15.2	266.7	21.4	236.2	10.9	298.2	7.4
176.0	90	201.6	21	270.8	38			298.2	7.4
179.0	128	205.6	47	275.5	72	239.7	19^b	305.2	10.1
180.0	170	210.0	113	279.8	120	251.7	88	305.2	10.7
184.0	360	214.6	257	285.1	210	263.2	240		
188.0	740	219.2	560	301.9	1120			311.7	24^b
		225.2	1120					323.2	88
		232.0	3870						
ΔH^* = 12.25 ± 0.97		ΔH^* = 15.31 ± 0.61		ΔH^* = 17.81 ± 0.76		ΔH^* = 14.8 ± 2.0		ΔH^* = 19.2 ± 3.7	
ΔS^* = 20.68 ± 5.44		ΔS^* = 24.33 ± 2.91		ΔS^* = 14.58 ± 2.79		ΔS^* = 9.0 ± 8.3		ΔS^* = 9.2 ± 12.1	
c^d = 0.9938		c = 0.9976		c = 0.9982		c = 0.990		c = 0.964	

^{a}Determined by DNMR3. ^{b}Determined by EXCHNG. ^{c}Determined by the slow exchange approximation. ^{d}Linear correlation coefficient obtained from least squares fitting.
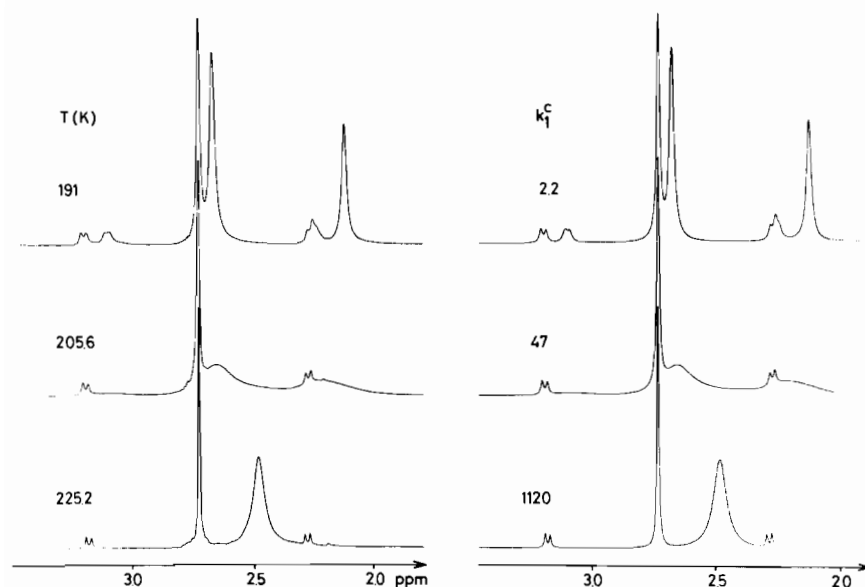

Fig. 3. Observed, at T (K), and calculated, k_1^c (s^{-1}), ^{1}H-NMR spectra for the ligand exchange reaction in *cis*-SnCl$_4$·2Me$_2$S (experimental conditions in Table I).

2TMPA, the ligand exchange has also been shown to be of zero order in free ligand.

The rates of reaction as a function of temperature have been obtained from line shape analysis in the same three systems (Table II). The observed and calculated spectra for the exchange on *cis*- and *trans*-SnCl$_4$·2Me$_2$S are shown in Figures 3 and 4 respectively. We may note that all entropies of activation are positive.

For all SnX$_4$·2L adducts (X = Cl, Br; L = Me$_2$CO, Me$_2$O, Me$_2$S, Me$_2$Se, TMPA, HMPA), the kinetic behaviour as a function of the temperature is the same. The rate constants were obtained by line shape analysis. The temperatures at which rate constants were measured were selected in order to be able to compare the reactivity of the adducts as a function of the nature of the ligand L, and the halogen X. The numerical data are reported in Table III, and the line
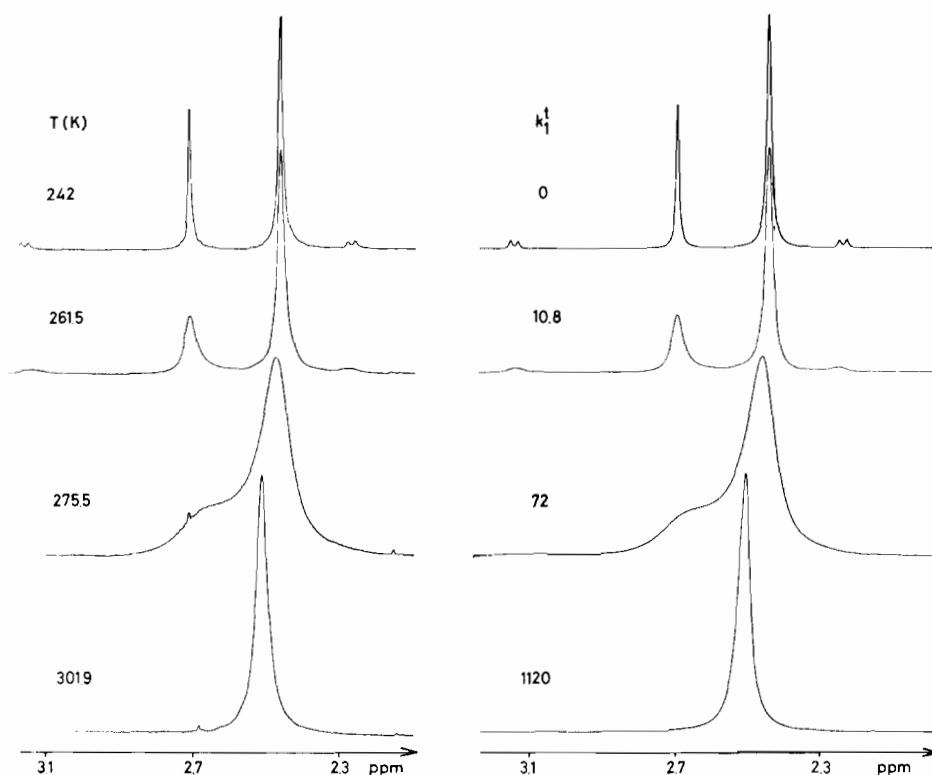
Fig. 4. Observed, at T (K), and calculated, k_1^t (s^{-1}), ^{1}H-NMR spectra for the ligand exchange reaction in *trans*-SnCl$_4$·2Me$_2$S (experimental conditions in Table I).

TABLE III. Rate Constant k_1^i (s^{-1}) and Free Energy ΔG^{*i} (kcal mol^{-1}) for the Ligand Exchange Reaction i-SnX$_4$·2L + *L $\rightleftharpoons$ i-SnX$_4$·L*L + L (X = Cl, Br) in CH$_2$Cl$_2$. [i-SnX$_4$·2L] ≃½[L] = 0.03–0.10 m.

	Me$_2$CO	Me$_2$O	Me$_2$S		Me$_2$Se	TMPA[a]		HMPA[a]
cis-SnCl$_4$·2L								
k_1^c	8040[b]	2500	29	0.3[b]	7	0.02[b]	2.6	4.4
ΔG^{*c}	8.07	8.54	10.33	10.87	10.90	13.26	12.98	16.87
T	203.0	203.0	203.0	182.0	203.0	203.0	232.0	304.4
cis-SnBr$_4$·2L								
k_1^c	—	—	400		10.8		780	140
ΔG^{*c}	—	—	8.28		9.58		10.35	14.79
T	—	—	182.0		182.0		232.0	304.4
trans-SnCl$_4$·2L								
k_1^t	—	720	28	5.5[b]	24	0.1[b]	7.2	<1
ΔG^{*t}	—	12.11	13.84	14.05	13.92	16.83	16.30	>20.3
T	—	268.6	268.6	257.0	268.6	268.6	299.5	346.9
trans-SnBr$_4$·2L								
k_1^t	—	—	60[c]		32		120	20
ΔG^{*t}	—	—	12.83		13.15		14.63	18.28
T	—	—	257.0		257.0		299.5	346.9

[a]In CHCl$_3$.   [b]Calculated from activation parameters in Table I.   [c]Determined from the Me$_2$S linewidth in *trans*-SnBr$_4$·2Me$_2$S. At this temperature, the *cis*-free ligand signal shows a broadening too large for a two sites exchange. This may be due to a partial dissociation of the adduct SnBr$_4$·2Me$_2$S. The Me$_2$O analog is strongly dissociated [1, 2] while the Me$_2$Se one shows no measurable dissociation.
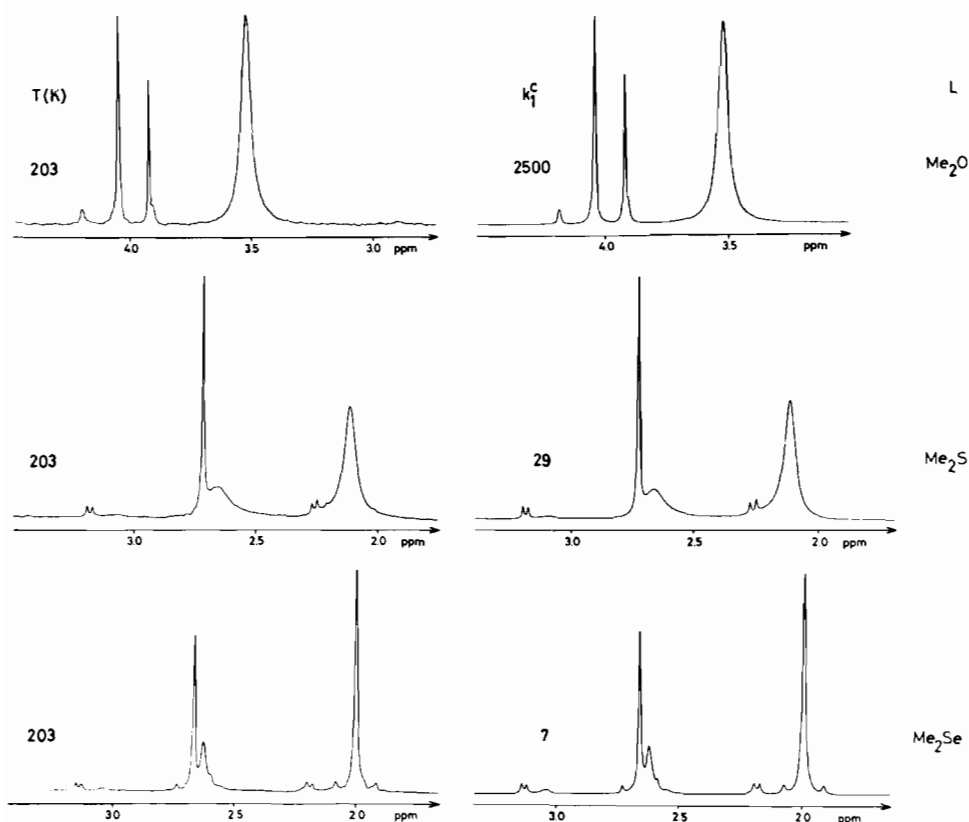
Fig. 5. Observed, at 203 K, and calculated, k_1^c (s^{-1}), ^{1}H-NMR spectra for the ligand exchange reaction in *cis*-SnCl$_4\cdot$2L for L = Me$_2$O, Me$_2$S and Me$_2$Se (* = ^{13}CH$_2$Cl$_2$; experimental conditions as in Table II).

shape analysis for the *cis*- and *trans* chalcogen ligand exchange on SnCl$_4$ adducts are shown in Figures 5 and 6.

Discussion

Exchange Reaction in Cis-SnCl$_4\cdot$2L Adducts

At low temperature, *cis*-SnCl$_4\cdot$2L adducts undergo a first order ligand exchange with positive ΔS^* which implies a D mechanism.* In this temperature range, the *trans* adduct exchange rate is very slow and not detectable by its NMR line broadening. We may thus exclude an isomerisation reaction which would lead to the coalescence of both *cis* and *trans* signals. The dissociative pathway shown in Figure 1 thus does not pass through the formation of bipyramid (I). To keep the retention of the *cis* configuration, the intermediate structure must be the tetragonal pyramid or the trigonal bipyramid (II). This latter structure seems to be unlikely, as both trigonal bipyramid stabilities must be equivalent. Since bipyramid (I) is not formed, it is most probable that

---

*We adopt the classification of substitution mechanisms introduced by Gray and Langford [12].

bipyramid (II) will not be formed either. The ligand exchange reaction on the *cis* adduct may be written as follows:
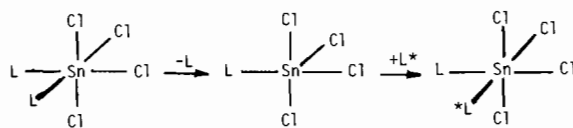
Exchange Reaction on Trans-SnCl$_4\cdot$2L Adducts

For the *trans* adducts which follow a first order reaction with positive ΔS^*, we also propose, as for the *cis* adducts, a D mechanism. As shown in Fig. 1, the dissociation may be followed by two types of reactions. When a tetragonal pyramid is formed as an intermediate, the *trans* configuration is retained. When the intermediate is a trigonal bipyramid an isomerization reaction may occur. Our results show only that the transition state is reached by a dissociative activation step, but give no information on the structure of the intermediate. We tried to resolve this question by recording the ^{119}Sn{^{1}H}-NMR spectrum for this reaction; if the isomerization reaction takes place, the NMR spectra should show a coalescence of the *cis* and *trans* signals; if the *trans* structure is retained during the ligand exchange reaction, the
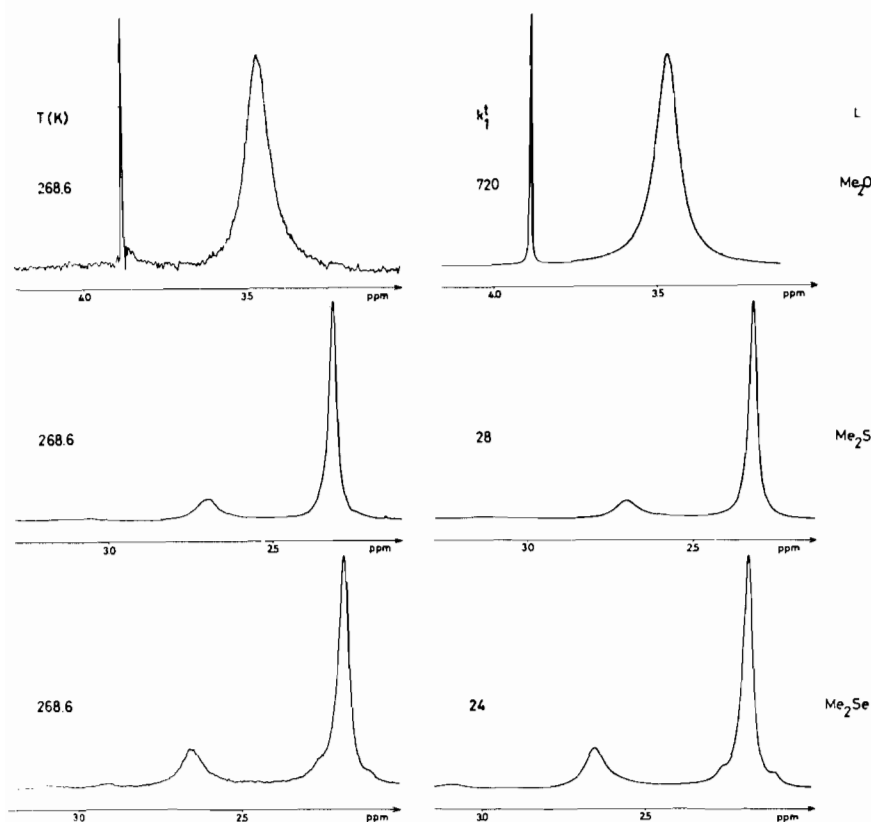
Fig. 6. Observed, at 268.6 K, and calculated, k_1^t (s^{-1}), ^{1}H-NMR spectra for the ligand exchange reaction in *trans*-SnCl$_4$·2L for L = Me$_2$O, Me$_2$S and Me$_2$Se (* = $^{13}CH_2Cl_2$; experimental conditions as in Table II).

signal for the *cis* and *trans* species must remain unchanged. However, various factors did not allow conclusive results: the low solubility of SnCl$_4$· 2Me$_2$S, the low natural abundance and sensitivity of ^{119}Sn, and the broadening of the tin signals due to coupling to the quadrupolar chlorine nuclei (I = 3/2).

Ligand Dependence of the Activation Free Energy

The comparison of the kinetic parameters for the ligand exchange reaction in *cis*- and *trans*-SnX$_4$·2L (X = Cl, Br) shows that the free energies of activation ΔG^* (Table III) increase in the following order:

$$Me_2CO < Me_2O \ll Me_2S < Me_2Se \ll TMPA \ll HMPA$$

This sequence is identical to the stability constant sequence determined for these adducts [2]. For a D mechanism, we expect a linear free energy relationship as reported previously for NbCl$_5$·L adducts (L = RCN, Me$_2$O, R$_3$PO [11, 13]. In our case, the stability constant data are not sufficiently well established to try to demonstrate such a relationship. However, we can see that the variation in the ΔG^*'s parallels the variation of the free energy of formation for the SnX$_4$·2L adducts. For example, the differences in the free energy of activation $\Delta(\Delta G^*)$ between the *cis*-SnCl$_4$ adducts of Me$_2$O and Me$_2$S amount to 1.8

kcal mol^{-1}, and between the Me$_2$S and TMPA* analog to 2.9 kcal mol^{-1}. This explains why the relative stability constants of these pairs of adducts were too large to be measured and could only be estimated by the NMR competitive equilibrium method [2]. This can be contrasted with the Me$_2$S and Me$_2$Se pair which has a small $\Delta(\Delta G^*)$ value of 0.57 kcal mol^{-1}; the relative stability constant could be obtained and corresponds to 0.31 kcal mol^{-1} for the difference in free energy of formation of one Sn—L bond in these adducts.

Reactivity of the Cis and Trans Isomers

It is obvious, from the coalescence figure of the NMR spectra, that the ligand L exchange reaction is always much faster in *cis*-SnX$_4$·2L adducts than in the *trans* ones. The differences in free energies of activation for both isomers of SnCl$_4$·2L (L = Me$_2$S and TMPA), calculated at 250 K from the activation parameters in Table II, amount to 4–5 kcal mol^{-1}. However, the free energy of formation of the *cis* and *trans* adducts are nearly equal (isomerization

---

*Determined in CHCl$_3$; it has been shown previously for similar systems that the ΔG^*'s for the ligand exchange are nearly identical in CH$_2$Cl$_2$ and CHCl$_3$ [11].

constants determinations give for ΔG_{iso}: 0.1 kcal mol^{-1} for Me$_2$S (CH$_2$Cl$_2$) and 0.2 kcal mol^{-1} for TMPA (CHCl$_3$) at 250 K). The difference in the ΔG^* values therefore comes mainly from the difference in the transition state energies for the *cis* and the *trans* ligand exchange. We may argue that this reactivity difference arises from a stronger metal–halogen than metal–ligand bond. This assumption is substantiated first by the observation that a large excess of ligand does not lead to a halogen displacement, and secondly by the fact that the force constants for the Sn–Cl bonds are larger by 30–50% than the Sn–L force constants [14]. The *trans* influence would therefore be greater for a chloride or bromide anion than for a neutral Lewis base like Me$_2$S or TMPA. Thus we expect that the halide ion will weaken and labilize the opposite Sn–L bond as in the *cis* adducts, while this labilizing effect of the Lewis base on the opposite Sn–L bond will be much weaker, as in the *trans* adducts. This strong *trans* influence of the halide ion observed in the SnX$_4$·2L adducts is the reverse of the *trans* influence observed in the square MX$_2$·L$_2$ (M = Pt, Pd) adducts.

Nature of the Reaction Center

In dissociative D ligand exchange reactions of octahedral adducts MX$_5$·Me$_2$O (M = Nb, Ta) the rate constants increase from the pentachloride to the pentabromide. The differences in activation free energies $\Delta(\Delta G^*)$ amount to 2 kcal mol^{-1} [11]. The same rate increase is observed for the adducts SnX$_4$· 2L (L = Me$_2$S, TMPA, HMPA), the effect being greater in the *cis* adduct where $\Delta(\Delta G^*)$ = 2–3 kcal mol^{-1}, than in the *trans* adduct where $\Delta(\Delta G^*)$ = 1–2 kcal mol^{-1} (Table III). The effective charge on the reaction center is reduced on going from a metal chloride to a metal bromide, since chloride holds back its electrons more tightly than bromide. This explains why the dissociation of a ligand L becomes easier from SnCl$_4$ to SnBr$_4$ adducts. Steric effects may also play a role: bromine atoms, being larger than chlorine atoms, favor the dissociation of the leaving ligand.

Conclusion

Octahedral adducts of tin(IV) tetrachloride and tetrabromide show, in general, a *cis–trans* equilibrium in solution. The *cis* adduct is the more labile and reacts *via* a D mechanism in a ligand exchange reaction. This mechanism is observed whatever the nature of the exchanging Lewis base: strong or

weak (HMPA or Me$_2$CO), hard or soft (Me$_2$O or Me$_2$Se). The reaction is believed to occur through a square pyramid intermediate with retention of configuration, so that no isomerization takes place during this exchange process. A second reaction, slower and also dissociative, occurs on the *trans* isomer. This reaction is interpreted as pure ligand exchange on the *trans* isomer, however a *cis–trans* isomerization cannot be excluded and the two alternatives are not mutually exclusive. The octahedral adducts SnX$_4$·2L show no dissociative/associative crossover for the ligand-substitution mechanism as observed for MX$_5$·L (M = Nb, Ta) [13]. The lower oxidation number and the filled 5d orbitals of tin in these adducts may explain this change in behaviour.

References

1 S. J. Ruzicka and A. E. Merbach, *Inorg. Chim. Acta, 20,* 221 (1976).
2 S. J. Ruzicka and A. E. Merbach, *Inorg. Chim. Acta,* in press.
3 L. M. Jackman and F. A. Cotton, "Dynamic Nuclear Magnetic Resonance", Academic Press, New York (1975).
4 I. S. Morozova, G. M. Tarasova, V. V. Ivanov, E. V. Bryukhova and N. S. Eniokolopyan, *Dokl. Akad. Nauk. SSSR, 199,* 654 (1971).
5 R. C. Paul, V. P. Kapila and J. C. Bhatia, *J. Inorg. Nuclear Chem., 35,* 833 (1973).
6 F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions", Wiley, New York (1967).
7 A. Allerhand, H. S. Gutowsky, J. Jonas and R. A. Meinzer, *J. Am. Chem. Soc., 88,* 3185 (1966).
8 *Quantum Chemistry Program Exchange,* Indiana University, program No. 140.
9 EXCHNG is a modification, by J. Wenger, of Prof. J.-J. Delpuech's program ECHGNC.
10 C. S. Johnson, Jr., and C. G. Moreland, *J. Chem. Educ., 50,* 477 (1973).
11 A. E. Merbach and J.-C. Bünzli, *Helv. Chim. Acta, 55,* 1903 (1972); R. Good and A. E. Merbach, *Inorg. Chem., 14,* 1030 (1975).
12 C. H. Langford and H. B. Gray, "Ligand Substitution Processes", Benjamin, New York (1965).
13 C. Favez and A. E. Merbach, to be submitted to Helv. Chim. Acta.
14 N. Ohkaku and K. Nakamoto, *Inorg. Chem., 12,* 2440 (1973).