The 1:1 and 2:1 complexes of diethyl ether with tin tetrachloride and their stability, studied by ^{119}Sn NMR spectroscopy†

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A variable-temperature ^{119}Sn NMR study of mixtures of tin tetrachloride and diethyl ether dissolved in dry dichloromethane has evidenced the existence of two complexes. The first (B, δ −600), predominates at a 5 : 1 Et_2O-to-$SnCl_4$ molar ratio; it corresponds to the compound $(Et_2O)_2{\cdot}SnCl_4$ (2 : 1 complex.) The other, A, more labile and exchanging with free tin chloride in solution, predominates at a 2 : 1 molar ratio of reactants. The signal for (A + $SnCl_4$) splits into separate resonances, for $SnCl_4$ (δ −163) and for A (δ −579), at temperatures below 205 K. Complex A was identified as Et_2O–$SnCl_4$ (1 : 1 complex). The concentrations of the components at various temperatures were determined by the integration of spectra and by chemical shift interpolation, and the two equilibrium constants, K_a and K_b, were calculated. The formation of a complex with one ether molecule had $\Delta H°$ −6.1 ± 1.6 kcal mol^{-1} and $\Delta S°$ −20.2 ± 5.3 cal mol^{-1} K^{-1}, whereas for the second step, $\Delta H°$ and $\Delta S°$ were −8.5 ± 0.6 kcal mol^{-1} and −26.6 ± 1.6 cal mol^{-1} K^{-1}, respectively. Thus, the enthalpy of complex formation in both steps is not much lower than for the reaction of Et_2O with BF_3. The lability of the complexes of $SnCl_4$ is caused by the unfavorable entropy of reaction.

Introduction

In previous papers, we have discussed the deficiencies of the methods most often used for quantitative evaluation of Lewis acid strength of molecules or sites on solid surfaces.[1a,2] We proposed instead a method based on the determination of the energy barriers for dissociation of complexes between the Lewis acids and aliphatic ethers, particularly diethyl ether, determined by dynamic ^{13}C NMR spectroscopy and we tested it on boron trifluoride as the Lewis acid.[1a] A study of the relative basicity of ethers in complexes with boron trifluoride has also been published.[3]

In the continuation of our research program in this area, we turned our attention to tin tetrachloride as a Lewis acid.[4] Reports on the interaction of this metal halide with Lewis bases had been published before. Thus, the order of strength was reported as $AlCl_3 > SnCl_4 > GaCl_3 \cdots > BF_3$ towards benzamide as base,[5] $BF_3 \geqslant SnCl_4 > GaCl_3$ towards pyridine as base,[6] and $SnCl_4 > AlCl_3 > GaCl_3$ towards substituted anilines as bases.[7] UV spectroscopy was the method of investigation in those studies. From IR studies with acetophenone as base and ^{1}H NMR chemical shift measurements with dimethylformamide as base, the order $AlCl_3 > SnCl_4 > BF_3$ was deduced,[8] whereas xanthone as base and IR as method gave $BF_3 > SnCl_4$.[9] That "strength" or "coordinating power" of different Lewis acids can vary widely as a function of the Lewis base has been known for a long time.[10] Nonetheless, valid comparisons can be achieved for well-determined series of related compounds.[1a,3] We observed that an important role of the Lewis sites in solid acid catalysts is to generate Brønsted acid sites by reaction with water,[11] Therefore molecules with basic oxygen should be the most appropriate as probe bases, and we used ethers in our investigations.[1a,3] We note also that a straight-chain ether can easily access Lewis acid sites of solids with narrow pores, like the zeolites. We report now the results of our study of tin tetrachloride and diethyl ether.

Experimental

Materials

Anhydrous, reagent grade diethyl ether and a 1 M solution of $SnCl_4$ in dichloromethane were used as purchased. They were opened and handled under nitrogen. Dichloromethane was refluxed for 45 min over calcium hydride (3.05 g for 100 mL of CH_2Cl_2) under nitrogen and distilled from the same pot, after which it was stored and opened only under nitrogen.[1a,3] The purity of diethyl ether and dichloromethane was verified from the ^{1}H and ^{13}C NMR spectra. Batch solutions (1, 2, 3 and 5 M) of diethyl ether in dichloromethane were prepared for mixing with the $SnCl_4$ solution.

NMR experiments

The NMR samples were prepared in 8 mm heavy-walled tubes (5.5 mm id) pre-dried overnight in an oven at 120 °C. The precise volumes of the $SnCl_4$ and ether solutions were mixed so as to give the intended molar ratios of reactants, then solvent was added to achieve the desired concentration. The quantity of each material introduced in a sample was determined by weighing on an analytical balance (0.1 mg uncertainty). After mixing, the solutions used for equilibrium constant determination had a 0.38–0.43 M concentration of $SnCl_4$. The content of the tubes was then frozen in liquid nitrogen and the tubes were sealed in a flame. For analysis, a tube was placed coaxially inside a 10 mm NMR tube, containing acetone-d$_6$ as lock solvent.[1a] The ^{119}Sn spectra were run at 111.937 MHz, with a pulse length ($p1$) of 7.5 µs (90 deg pulse) and a relaxation delay of 330 ms. Because of the negative NOE of ^{119}Sn, a pulse sequence with inverse gated decoupling was used.[12] A number of 76188 points were collected in the time domain, over a window of 146 kHz. Between 1000 scans at the lowest temperature and 200 000 scans or more at room temperature were acquired per spectrum. The temperature controller of the NMR instrument was calibrated with a methanol sample and the actual probe temperature was rechecked after each experiment. The chemical shifts of Sn are

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† See ref. 1(*a*).
‡ See ref. 1(*b*).

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measured from the signal of tetramethyltin dissolved in acetone-d_6 (1%) in the outer tube, assigned δ 0.0, rather than from neat tetramethyltin.[12,13] Fourth-order polynomial baseline correction was performed before each integration. Repeated integration of spectra gave an excellent reproducibility.

The frequency domain defined by $1/p1$ is at the center lobe of a $(\sin x)/x$ function and for a 7.5 µs pulse 30–35 kHz in its center can be considered to be of maximum (constant) intensity. Therefore, no integration of an entire spectrum obtained below the coalescence point of the signals for $SnCl_4$ and **2** was attempted. Only the ratio of **1** and **2** ($\Delta\delta$ 20 ppm) was determined for such spectra. In the spectra integrated for the determination of the equilibrium constants, the distance between the peaks of **1** and ($SnCl_4$ + **2**) was 250–320 ppm. Also, placement of the point of irradiation midway between the two peaks to be integrated was considered to minimize the error in integration, even if the intensity of irradiation was not constant over the entire interval.

Results and discussion

For strong Lewis acids, the complexation equilibrium is fully displaced toward the complex. Quantitative evaluation of the strength of the interaction can be achieved by determining the rate of exchange between the complexed ether and the excess of free ether present in solution, by dynamic NMR spectroscopy at several temperatures. The method is valid if the slow step is a unimolecular decomposition of the complex (S_N1), rather than a bimolecular reaction with the ether (S_N2).[14] This determination has been made for boron trifluoride,[1a] and also boron trichloride and antimony pentachloride.[15] Because the complex formation has a very low energy barrier, the activation parameters for the process are measures of the strength of bonding between the Lewis acid and the ether molecule.[1a]

A weaker Lewis acid reacts incompletely with the base and the concentrations of free and complexed acid (or base) can be measured. The strength of interaction is then established by the determination of the equilibrium constant at several temperatures and the calculation of the enthalpy and entropy of complex formation. This was the case for tin tetrachloride.

Tin(IV) normally forms complexes in which tin is hexacoordinated.[4,16] Certain amines (strong Lewis bases) form, however, 1:1 complexes in addition to the more usual 2:1 complexes.[4] Complexes of ethers, of composition $(R_2O)_2{\cdot}SnCl_4$, were prepared as solids a long time ago.[17] At least some of them were later assessed to be very stable.[18] The geometry of the complexes is octahedral. The IR spectra of the complexes with tetrahydrofuran and with diethyl ether, $(Et_2O)_2{\cdot}SnCl_4$ (**1**), indicated that the two ether ligands are positioned *trans* to each other.[4] This conclusion was confirmed for **1** by X-ray diffraction.[19] The disposition of the ether ligands is expected to be *cis* in complexes with bidentate ligands, like dimethoxyethane or 1,4-dioxane,[20] but a polymeric structure of these complexes in the crystals cannot be excluded outright.[20]

As dichloromethane had been found before to be a good solvent for the studies of Lewis acid–Lewis base interactions,[1a,3] we investigated the interaction of diethyl ether with tin tetrachloride in dichloromethane solution, by ^{119}Sn NMR. The ^1H and ^{13}C NMR spectra of the mixtures provided additional evidence for our conclusions.

The chemical shift of tin in $SnCl_4$ was reported to change very little from the pure compound (δ −150[21a] or −147.8[21b]) to the carbon disulfide solution (δ −150).[22] In dichloromethane, however, we found the tin resonance of this compound at −157.3 ppm. The formation of a very weak complex of tin tetrachloride with the chlorine atoms of the solvent is possible, but because we used an external standard, a difference in magnetic susceptibility might account for the difference as well. The chemical shift does not change significantly with concentration or with temperature between ambient and 187 K.

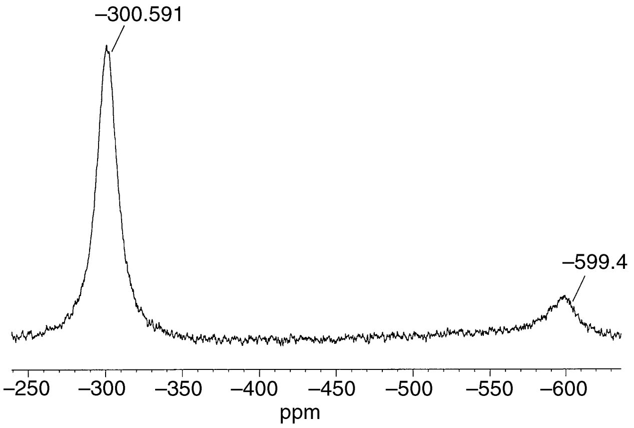


Fig. 1 ^{119}Sn NMR spectrum of a 2:1 mixture of diethyl ether and $SnCl_4$ in dichloromethane (0.25 M $SnCl_4$) at 294 K.

The spectrum of $SnCl_4$ in diethyl ether solution at room temperature has also been reported in the literature. The chemical shift measured, −606 ppm,[23] can be assigned to complex **1**. When we examined, however, a 2:1 (molar) Et_2O-to-$SnCl_4$ mixture in dichloromethane (0.25 M $SnCl_4$), two broad signals were recorded, at δ −300.6 (A) and −599.4 (B). The latter corresponds to the much sharper −606 ppm resonance observed in ether solution, but the former indicates the presence of another tin(IV) compound as the predominant species in solution (intensity ratio 5.5:1) (Fig. 1). An increase in the Et_2O-to-$SnCl_4$ molar ratio to 3:1, with the same concentration of $SnCl_4$ (0.25 M), reduced the intensity ratio of the signals to 1.5:1. Complex B (**1**) was predominant in solution (A:B integral area 0.8:1) only at the Et_2O-to-$SnCl_4$ molar ratio of 5 to 1. An increase in temperature broadened both signals, but they did not coalesce up to 40 °C (313 K).

The low-frequency peak did not change its position when the ratio of ether to tin tetrachloride was varied between 0.6:1 and 5:1, whereas the other signal shifted toward lower frequencies (to −379 ppm for the 3:1 mixture and −421 ppm for the 5:1 mixture). Also, a reduction in the temperature of the 2:1 Et_2O-to-$SnCl_4$ sample from 295 to 270 K sharpened the low-frequency signal, but did not reduce the line width of the high-frequency signal. The latter moved, however, to −338 ppm and its intensity relative to the low-frequency peak decreased to 1.9:1 (for the 2:1 mixture). Further cooling broadened again the high-frequency peak. This behavior indicated that the high-frequency peak corresponds to an exchanging mixture of two tin species, which then exchange with **1** at a slower rate.

The reaction of tin tetrachloride with diethyl ether is different from the reaction with the bidentate reagent dimethoxyethane (DME). We observed a single ^{119}Sn resonance in a complex, both for 1:1 (δ −550.0) and 0.5:1 (δ −548.7) DME-to-tin tetrachloride ratios, at a 0.66 M concentration of $SnCl_4$. We assign this resonance to the chelated hexacoordinated complex with DME. The sample with an excess of tin tetrachloride exhibited the signal for the latter at −164.2 ppm. Interestingly, the peak of the complex was sharper (600 Hz) in the 1:1 mixture (complex only) than in the 0.5:1 mixture, which contained both complex and $SnCl_4$ (2000 Hz), suggesting an exchange in the presence of excess Lewis acid [eqn. (1)].

For the mixtures with diethyl ether, the high-frequency peak split on deep cooling into a signal at δ −163 ($SnCl_4$) and another one at about δ −579 (complex A), but crystallization, presumably of complex **1**, complicated the investigation of samples containing two or more moles of ether per mole of tin tetrachloride. The mixtures with ratios of Et_2O to $SnCl_4$ of 1.6:1 to 0.6:1 could be cooled below the coalescence temperature until the line width for complex B did not change any more and its chemical shift was −579.8 ppm. The effect of

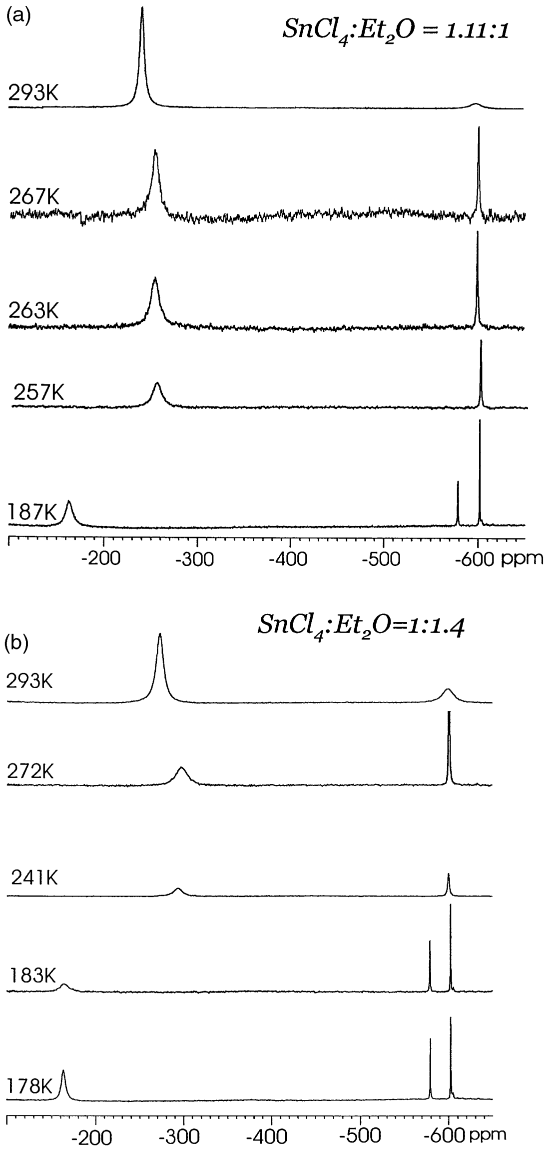
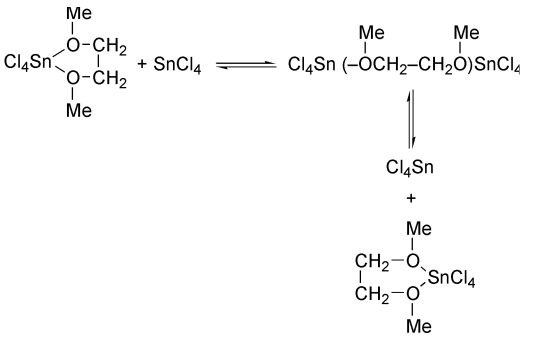


Fig. 2 Temperature dependence of the ^{119}Sn NMR spectrum of mixtures of diethyl ether and $SnCl_4$ in dichloromethane. (a) $Et_2O:SnCl_4 = 1:1.11$ (0.42 M $SnCl_4$). (b) $Et_2O:SnCl_4 = 1.4:1$ (0.43 M $SnCl_4$).



(1)

cooling on the spectra of mixtures with ratios of ether to tin tetrachloride of 1 : 1.11 and 1.4 : 1 is shown in Fig. 2.

Two structures were considered for A. The first was a 1 : 1 Et_2O-to-$SnCl_4$ complex (**2**). The second, was the *cis* stereoisomer (**3**) of the stable[4] *trans*-$(Et_2O)_2 \cdot SnCl_4$ (**1**). *Cis* hexacoordinated complexes of tin tetrachloride have been reported as the major isomer for water as the second ligand[16d] and as minor isomers (5–7%) for acetone and tributylphosphine as second ligands.[24] The *cis* : *trans* ratio was found to depend on solvent polarity.[25] The chemical shift of A was reasonable for **3**. Nonetheless, structure **2** was chosen, for the following reasons:

(a) The widely different rates of exchange with free tin tetrachloride (and ether) seemed unlikely for the stereoisomers **1** and **3**.

(b) The two stereoisomers should also coexist in ether solution and exhibit separate peaks, because the exchange of **1** cannot be faster in that medium than in dichloromethane solution. Instead, only the −606 ppm signal was recorded.[23]

(c) For two solutions with the same concentration of tin tetrachloride, the molar ratio of the stereoisomeric complexes should be independent of the concentration of ether, whereas the molar ratios of complexes of different stoichiometry vary with the concentration of ether, but not necessarily in a simple manner. The molar ratios of the two complexes can be determined from the integration of spectra at temperatures where the exchange is slow for both complexes. For a concentration of 0.4 M $SnCl_4$, the integration of the spectra shown in Fig. 2 of solutions with ether-to-tin tetrachloride molar ratios of 1 : 1.11 [(a), spectrum at 187 K] and 1.4 : 1 [(b) spectrum at 183 K] gave A:B ratios of 1 : 1.84 and 1 : 1.43, respectively. At higher temperatures, the concentration of complex A can be determined by integration and interpolation of chemical shifts, as discussed below. The variability of the molar ratio of complexes with the ratio of reactants is confirmed.

The reaction of tin tetrachloride with diethyl ether is, therefore, described by eqns. (2) and (3). The same equations should

$$Et_2O + SnCl_4 \rightleftharpoons Et_2O\text{–}SnCl_4 \qquad (2)$$

$$Et_2O\text{–}SnCl_4 + Et_2O \rightleftharpoons (Et_2O)_2SnCl_4 \qquad (3)$$

describe the dissociation of complex **1** upon dissolution in benzene, evidenced by cryoscopic measurements.[26] If the *cis* isomer of **1** exists in the mixture, it should be present in a very small concentration. The existence of both 1 : 1 and 1 : 2 complexes in mixtures of tin tetrachloride and dibutyl ether was indicated by the variation of viscosity of their mixtures with composition and temperature.[27] In complex **2**, tin is pentacoordinated. An alternative with hexacoordinated tin is conceivable in a 2 : 2 complex, but the experimental results could not be fitted with an equilibrium of that kind.

The changes seen in the spectrum upon cooling are caused by the displacement of the equilibria in both eqn. (2) (reflected primarily in the chemical shift of the high-frequency peak) and eqn. (3) (reflected mainly in the relative areas of peaks) to the right. The ether exchange according to eqn. (2) is much faster than the exchange according to eqn. (3).

The proton and carbon spectra showed only one set of ethyl group resonances at room temperature. Upon cooling, splitting into the signals of **1** and the exchanging signals of **2** and free ether, occurred in each spectrum. The precise coalescence temperatures were not sought, but they were around 250–260 K. Because the signals of the exchanging components are much closer to each other in the carbon and the proton spectra than in the tin spectra, the coalescence temperatures are lower and the spectra of complex **2** could not be obtained. An estimation of the chemical shifts for **2** was made based on the calculated composition of the mixtures and on the chemical shifts of diethyl ether in dichloromethane, recorded separately. The results are listed, together with the other spectral data, in Table 1. It is seen that the complex formation shifts of diethyl ether are smaller for the reactions with tin tetrachloride [eqns. (2) and (3)] than for the reaction with boron trifluoride.[1a,3]

A published ^{1}H NMR spectrum of a 0.03 molal (*ca.* 0.04 M) $SnCl_4$ and four equivalents of dimethyl ether in dichloromethane at 183 K exhibited several signals, which were interpreted as representing a mixture of *cis* and *trans* $(Me_2O)_2 \cdot SnCl_4$ bonded to and coupled with ^{117}Sn and ^{119}Sn and free ether.[28] It is peculiar, however, that the corresponding singlets for the ether coordinated with the major isotopes ^{116}Sn, ^{118}Sn, and ^{120}Sn, which represent 71.25% of natural tin, as compared with

Table 1 Chemical shifts of complexes of tin tetrachloride with diethyl ether in dichloromethane solutions[a]

Compound	$\delta(^{119}Sn)$[b,c]	$\delta(^{13}C)$[d,e]	$\delta(^{1}H)$[f,g]
1	−599.8 ± 0.3[h]	64.4 (CH_2); 12.5 (CH_3)	4.64 CH_2; 1.59 CH_3 *J* 7.0 Hz
2	−579.8[i]	(65–67) (CH_2); (11.5–11.9) (CH_3)	(4.34) CH_2; (1.51) CH_3 *J* 7.0 Hz

[a] In ppm, from the standard indicated. [b] From external (coaxial) tetramethyltin (1%) in acetone-d_6. [c] $\delta(SnCl_4)$: −157.3 (in CH_2Cl_2), −163.6 ± 0.6 (in CH_2Cl_2 containing complexes **1** and **2**, or the DME·$SnCl_4$ complex). [d] From the dichloromethane solvent, taken as 53.74 ppm (calibrated separately with TMS). [e] Free ether: 65.74 and 15.12 ppm. [f] From the dichloromethane solvent taken as 5.55 ppm (calibrated with TMS). [g] Free ether: 3.625 and 1.35 ppm, *J* 6.9 Hz. [h] At room temperature; the variation shown is caused by the change in the ether-to-tin tetrachloride ratio. [i] At 200 to 178 K.

Table 2 Values of the equilibrium constants for eqns. (2) and (3), (*C*/M)

Experiment no.	$Et_2O:SnCl_4$	*T*/K	*C*(**1**)	*C*(**2**)	$C(Et_2O)$ free	$C(SnCl_4)$ free	K_a/l mol^{-1}	K_b/l mol^{-1}
1.1	1 : 1.11[a]	294	0.0347	0.0770	0.2112	0.3063	1.19	2.14
1.2		267	0.0908	0.0754	0.1007	0.2519	2.97	12.0
1.3		263	0.0937	0.0749	0.0954	0.2494	3.14	13.1
1.4		256	0.1096	0.0703	0.0682	0.2381	4.32	22.9
1.5		230	0.1395	0.0555	0.0231	0.2230	10.8	109
2.1	1.4 : 1[b]	294	0.0971	0.0928	0.2790	0.2439	1.36	3.75
2.2		272	0.1705	0.0854	0.1395	0.1778	3.44	14.3
2.3		241	0.2350	0.0661	0.0298	0.1326	16.7	119
3.1	1.6 : 1[c]	294	0.1112	0.0883	0.3045	0.1849	1.57	4.13
3.2		270	0.2005	0.0780	0.1364	0.1061	5.39	18.8
3.3		246	0.2541	0.0633	0.0437	0.0671	21.6	91.7

[a] $C_o(SnCl_4)$ = 0.42 M. [b] $C_o(SnCl_4)$ = 0.43 M. [c] $C_o(SnCl_4)$ = 0.38 M.

16.26% for ^{117}Sn and ^{119}Sn together, were not identified in the spectrum. Moreover, based on our results, there is a good probability that at the low concentration employed in that study[28] the 2 : 1 complex was dissociated in part to the 1 : 1 complex and dimethyl ether. Indeed, the authors mentioned briefly that the signal of the presumed *cis* complex exchanged faster (peaks coalesce at lower temperature) with the free ether than the *trans* complex and stated that the interpretation of those results was not obvious.[28]

In the present study, the concentrations of **1** were determined in all the solutions by integration and the concentrations of **2** by the interpolation of chemical shifts between the values measured for tin tetrachloride and **2** at the lowest temperatures. The chemical shift of **1** showed little temperature dependence. For various samples it was between −599.5 and −600.2 ppm at room temperature and −602.1 and −602.5 ppm at 178–187 K, but the broad signal at room temperature indicated that the mixture had come close to the coalescence temperature. The signal for **2** could be measured only between 200 and 178 K, where it was temperature-invariant, −579.8 ppm. For the chemical shift interpolation it was assumed that the change in δ(**2**) with the temperature is negligible over the entire interval. From the level of accuracy of the reactant weights and of the NMR measurements, it can be assessed that the error of the concentrations calculated from them was ±1%. Because the concentration of free ether was obtained by difference, however, its level of error was higher for the spectra where the difference was very small. Those experiments were not used for equilibrium constant calculations, so the errors in the concentration of ether are ±2%. The equilibrium constants for eqn. (2) (K_a) and eqn. (3) (K_b) were determined for three mixtures containing about 0.4 M tin tetrachloride with ratios of ether to tin tetrachloride between 1 : 1.11 and 1.6 : 1, at three to five temperatures. The results are given in Table 2. Repeated measurements on the same mixtures indicated a 10% uncertainty of the values for the equilibrium constants. In fact, even a 20% error would not alter our conclusions. From the temperature variation of the equilibrium constants (Fig. 3), the enthalpies and entropies of reaction for the two steps ($\Delta H_a°$, $\Delta H_b°$, $\Delta S_a°$ and $\Delta S_b°$) were calculated. The results are given in Table 3.

Examination of parts (a) and (b) of Fig. 3 shows that the dispersion of results is greater in the former. Although the uncertainties in the slopes of individual lines are smaller than the differences between lines, average values were calculated for all four parameters and are given in Table 3. The slight but systematic change observed in the slope of the lines with the ratio of reactants, deserves, however, some comment. Some changes in the properties of the solvent, as part of the dichloromethane is replaced by ether, might be responsible for this result. Additionally, the existence of still another equilibrium, for example as in eqn. (4) or in the similar reaction in which

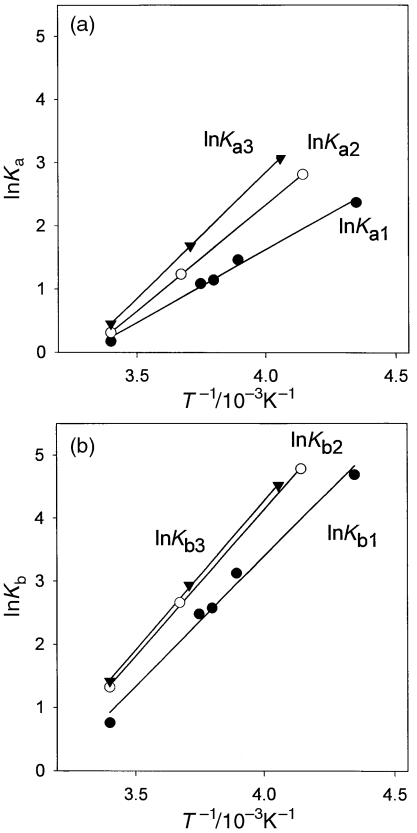


Fig. 3 Temperature dependence of the equilibrium constants deduced from ^{119}Sn NMR spectra for eqn. (2) (a) and eqn. (3) (b). ● $Et_2O:SnCl_4$ = 1 : 1.11 (K_{a1}, K_{b1}); ○ $Et_2O:SnCl_4$ = 1.4 : 1 (K_{a2}, K_{b2}); ▼ $Et_2O:SnCl_4$ = 1.61 (K_{a3}, K_{b3}).

Table 3 Reaction enthalpy and entropy values for eqns. (2) (a) and (3) (b)

Series	$\Delta H_a°$/kcal mol^{-1}	$\Delta S_a°$/cal mol^{-1} K^{-1}	$\Delta H_b°$//kcal mol^{-1}	$\Delta S_a{}^b$/cal mol^{-1} K^{-1}
1	−4.4	−14.5	−7.8	−24.8
2	−6.4	−21.1	−8.8	−27.3
3	−7.5	−24.9	−8.9	−27.7
Average[a]	−6.1 ± 1.6	−20.2 ± 5.3	−8.5 ± 0.6	−26.6 ± 1.6

[a] Standard deviations given.

$$2\ Et_2O\text{–}SnCl_4 \rightleftharpoons Et_2O\text{–}SnCl_3{}^+ + SnCl_5{}^- \qquad (4)$$

$SnCl_6{}^{2-}$ is the anion, might intervene to an extent too small to give measurable peaks in the NMR spectra, but large enough to produce the deviation of the calculated equilibrium constants. The corresponding reaction, prevalent in aqueous solutions,[16d] was also evidenced for the complex of aluminium chloride with diethyl ether.[29]

The values of the thermodynamic parameters for the equilibria of eqns. (2) and (3) lead to the conclusion that in terms of enthalpy there is no dramatic difference between the stability of the ether complexes of tin tetrachloride, **1** and **2**, and the boron trifluoride–ether complex. For the latter, an activation enthalpy for decomposition of 9.7 kcal mol^{-1} was determined in dichloromethane solution.[1a] It is the complexation entropy which sets apart the two Lewis acids: the boron trifluoride (strong Lewis acid) complex does not dissociate measurably in solution, whereas the complexes of tin tetrachloride are formed only to a small extent at the stoichiometric ratio (2 : 1) in solution. This constitutes a limitation for the evaluation of Lewis acid strengths from the heat of complexation of probe bases determined by calorimetry,[30] as noted before in a different context.[7]

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