

Thermodynamic and Multinuclear Magnetic Resonance Study of Dimethyltin(IV) Complexes with Tridentate Ligands in Aqueous Solution †

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The complex formation of $[\text{SnMe}_2]^{2+}$ ion with iminodiacetate, oxydiacetate and thiodiacetate ligands has been investigated by potentiometric, calorimetric and multinuclear magnetic resonance measurements in aqueous solution at 25 °C and $I = 0.1 \text{ mol dm}^{-3}$ (KNO_3). Both the thermodynamic values and NMR parameters revealed the flexibility of the organometallic ion, as regards both the Me–Sn–Me angle and its ability to adopt unusual asymmetric stereochemistries. A new stereochemistry was found for the five-coordinated iminodiacetate complex, the formation of which exhibits three-site kinetics.

Structural results obtained both in the solid state¹ (X-ray and NMR) and in organic solvents² (NMR) show that the Me–Sn–Me angle in six-co-ordinated dimethyltin(IV) compounds can be much less than 180°. The variation of the Me–Sn–Me angle and the *cis-trans* preference of the alkyl groups in such compounds has been attributed to steric³ (the 'bite' of the chelating ligand and the steric interactions in the co-ordination sphere) and/or electronic effects⁴ (s-character redistribution due to complexation). Based on ligand–ligand repulsion calculations, Tse⁵ has shown that the repulsion model predicts, for many SnR_2L_2 (L = bidentate ligand, R = alkyl) compounds, a *cis* structure, but electronic effects can outweigh the steric requirements. As expressed by Bent's rule,⁴ the strong σ -donor methyl groups prefer a *trans* conformation for better overlap with tin sp hybrids. However, the structural flexibility of the two methyl groups of the dimethyltin(IV) ion has not been studied in polar solvents, like water, where other interactions should be taken into account to explain this very interesting feature. It is likely that in such solvents the two methyl groups would have a tendency to stay closer to each other than in non-polar solvents, thereby minimizing the hydrophobic surface exposed to the solvent molecules.

Recently, we characterized the thermodynamic behaviour of the dimethyltin(IV) ion in aqueous solution by means of potentiometry and calorimetry.^{6,7} The data obtained for hydrolysis⁶ and complexation with carboxylic acids⁷ indicate that dimethyltin(IV) behaves like a 'hard' ion, which supports previous findings.⁸

In order to understand better the role played by the electronic, steric and solvation (co-ordination ability of the solvent and solvophobic nature of the methyl groups) forces in the variation of the Me–Sn–Me angle, it is important comparatively to investigate on thermodynamic grounds species with different stereochemistries. We have carried out potentiometric titrations to determine ΔG° values and calorimetric measurements, under the same experimental conditions, *i.e.* 25 °C and $I = 0.1 \text{ mol dm}^{-3}$ (KNO_3), in order to obtain useful information on the contributions of both enthalpy and entropy changes to the stability and structural features of different organometallic complexes formed in solution by dimethyltin(IV) and dicarboxylate tridentate ligands such as

iminodiacetate (ida^{2-}), oxydiacetate (oda^{2-}) and thiodiacetate (tda^{2-}). These ligands present a central heteroatom with different donor abilities and different geometries upon complexation. Both iminodiacetate and oxydiacetate can adopt either a meridional⁹ or a facial co-ordination,¹⁰ while thiodiacetate has strong facial preferences.¹¹

We have also performed NMR measurements in aqueous solution in order to highlight structural details. While NMR spectroscopy has been widely used for non-aqueous¹ and solid-state² studies of dimethyltin(IV), very little NMR data concerning aqueous solutions are available. Owing to the peculiarity of the water molecule, any attempt to extrapolate data obtained in other solvents to those pertaining to water solution appears unjustified and any comparison between such different media should be done with great care. As a consequence, we have to choose a specific reference for ¹¹⁹Sn NMR spectroscopy in water solution. The most obvious system is the aqua ion $[\text{SnMe}_2(\text{H}_2\text{O})_4]^{2+}$ which forms in strong acidic solution (pH < 1.5). For comparison, we report the parameters concerning the most important hydroxo species $[\text{SnMe}_2(\text{OH})_2]$. The structures of both dimethyltin species in water solution were previously determined as octahedral and tetrahedral respectively.¹²

Experimental

Chemicals.—Iminodiacetic acid (Sigma), oxydiacetic acid (Fluka) and thiodiacetic acid (Sigma) were used without further purification. Their purity, checked by alkalimetric titrations, was always >99.5%.

Dimethyltin ($[\text{SnMe}_2]^{2+}$) nitrate was obtained using dimethyltin oxide (ICN Biomedical) as the starting material. The oxide was purified to remove chloride ions and converted into the nitrate as previously described.⁶ The purity of the dimethyltin(IV) nitrate solution was checked potentiometrically by using the computer program SUPERQUAD (see Calculations). The coincidence between the stoichiometrically calculated and observed excess of nitric acid, added to dimethyltin oxide to make up the dimethyltin nitrate solution, indicates that the purity was >99.5%. Stock solutions of HNO_3 and KOH were prepared by diluting concentrated ampoules (Merck). Twice distilled water and Grade A glassware were used throughout.

† Non-SI unit employed: cal = 4.184 J.

Table 1 Stability constants for dimethyltin(IV) hydroxo complexes^a and protonation constants of the ligands^b at 25 °C and *I* = 0.1 mol dm⁻³ (KNO₃)

Reaction	log β
[SnMe ₂] ²⁺ + H ₂ O ⇌ [SnMe ₂ (OH)] ⁺ + H ⁺	-3.124
2[SnMe ₂] ²⁺ + 2H ₂ O ⇌ [(SnMe ₂) ₂ (OH) ₂] ²⁺ + 2H ⁺	-5.05
2[SnMe ₂] ²⁺ + 3H ₂ O ⇌ [(SnMe ₂) ₂ (OH) ₃] ⁺ + 3H ⁺	-9.74
[SnMe ₂] ²⁺ + 2H ₂ O ⇌ [SnMe ₂ (OH) ₂] ⁺ + 2H ⁺	-8.428
[SnMe ₂] ²⁺ + 3H ₂ O ⇌ [SnMe ₂ (OH) ₃] ⁻ + 3H ⁺	-19.450
[ida] ²⁻ + H ⁺ ⇌ [Hida] ⁻	9.30
[Hida] ⁻ + H ⁺ ⇌ H ₂ ida	2.60
H ₂ ida + H ⁺ ⇌ [H ₃ ida] ⁺	1.65
[oda] ²⁻ + H ⁺ ⇌ [Hoda] ⁻	3.90
[Hoda] ⁻ + H ⁺ ⇌ H ₂ oda	2.83
[tda] ²⁻ + H ⁺ ⇌ [Htda] ⁻	4.12
[Htda] ⁻ + H ⁺ ⇌ H ₂ tda	3.14

^a Ref. 6. ^b Ref. 19.

Electromotive Force Measurements.—The potentiometric measurements were carried out by means of two sets of fully automated apparatus. These made use of Metrohm equipment (burette, E665; meter, E654; glass electrodes, EA109; calomel electrodes, EA404) and were controlled by an IBM computer, using a program written in our laboratory. All experiments were carried out at 25.0 ± 0.1 °C using thermostatted cells (25 cm³). All solutions were magnetically stirred and kept in an atmosphere of CO₂- and O₂-free nitrogen, previously bubbled through 0.1 mol dm⁻³ KNO₃. The values of *E*^o and the electrode system slope were determined by titrating HNO₃ (20–25 cm³) with CO₂-free KOH. Each experiment was run in the two different sets of potentiometric apparatus to avoid systematic errors and to check for reproducibility. In addition, the readings of parallel experiments were taken at different time intervals to exclude the presence of kinetic problems. Checks on the pH stability of each solution to be titrated showed no detectable drift in electromotive force over a period of 90 min. Other details were as previously described.¹³

Calorimetric Measurements.—The calorimetric measurements were performed at 25.000 ± 0.001 °C using a Tronac 450 isoperibolic calorimeter equipped with a titration Dewar (25 cm³). In all cases, the titration data, corrected for all non-chemical energy terms, determined in separate experiments, were refined simultaneously to obtain the final Δ*H*^o.

Calculations.—The calculations concerning the electrode system as well as the slope were performed by the computer program ACBA,¹⁴ which refines the parameters of acid–base titrations by using a non-linear least-squares method minimizing the function $U = \sum (v_{i,\text{exptl.}} - v_{i,\text{calc.}})^2$, where *v* is the volume of titrant added. All other potentiometric data were handled by the program SUPERQUAD.¹⁵ The above program minimizes the error-square sum based on measured electrode potentials. For the analysis of residuals the procedure recommended by Vacca *et al.*¹⁶ was followed.

The enthalpies of formation were computed by means of the least-squares program DOEC,¹⁷ which minimizes the function $U = \sum (Q_{i,\text{calc.}} - Q_{i,\text{exptl.}})^2$, where *Q* is the heat of reaction related to Δ*H*^o by the equation $-Q = \sum \delta n_i \Delta H^o$, where δ*n*_{*i*} is the change in the number of moles of the *i*th species.

The distribution diagrams were obtained by means of the computer program DISDI.¹⁸

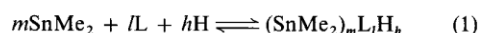
NMR Spectra.—Proton NMR spectra were run at 250 MHz in D₂O on a Bruker AC-250 spectrometer and at 80 MHz on a Bruker WP-80 spectrometer. Hydrogen-1 decoupled insensitive nuclei enhanced by polarization transfer (INEPT) ¹³C and ¹¹⁹Sn NMR spectra, as well as broad-band ¹³C spectra, were run in water–D₂O (80:20) solutions, respectively at 62.9 and

93.3 MHz on a Bruker AC-250 spectrometer, by using a multinuclear probe. 2,2-Dimethyl-2-silapentanesulfonic acid was used as a reference for ¹H and ¹³C spectra, while ¹¹⁹Sn spectra were referenced (externally) to the dimethyltin aqua ion (absolute frequency Ξ = 93.243 238 8 MHz), the only species present in strongly acidic water solution. The reference commonly used, SnMe₄, is insoluble in water and it would be inappropriate to reference our spectra to a frequency obtained in a different solvent. Following the usual convention, positive values mean chemical shifts downfield with respect to the reference.

Simulations were carried out by the program DOEC,¹⁷ in order to choose the optimum conditions for analytical concentrations, allowing us to run the NMR spectra of solutions such that the complex to be characterized was at least 85% of the total [SnMe₂]²⁺. It was impossible to obtain such a condition for the tda complex, owing to its low formation constant and the low solubility already mentioned; therefore no NMR data are reported for it.

Results

Thermodynamic Results.—The reaction of the tridentate ligands with the organometallic cation is represented in equation (1), where L is the dianionic form of the ligand with



charges omitted for simplicity. The corresponding stability constants β_{*m*h} are defined by equation (2). The protonation

$$\beta_{mh} = [(\text{SnMe}_2)_m\text{L}_l\text{H}_h] / [\text{SnMe}_2]^m [\text{L}]^l [\text{H}]^h \quad (2)$$

constants and the thermodynamic parameters obtained at 25 °C and *I* = 0.1 mol dm⁻³ (KNO₃) for ida,¹⁹ oda¹⁹ and tda¹⁹ as well as for dimethyltin(IV) hydrolysis⁶ have already been reported and are shown in Table 1.

Owing to the presence of the same number of potential donor atoms, the same species list was considered for all three systems, namely [SnMe₂(L)H]⁺, [SnMe₂(L)], [SnMe₂(L)H₋₁]⁻, [SnMe₂(L)₂H₂]⁺, [SnMe₂(L)₂H]⁻, [SnMe₂(L)₂]²⁻, [(SnMe₂)₂(L)₂H₂]²⁺, [(SnMe₂)₂(L)₂H]⁺ and [(SnMe₂)₂(L)₂].

ida. For this system all the species added to the base model {*i.e.* [SnMe₂(ida)] and [SnMe₂(ida)H₋₁]⁻} were always rejected by the program as negative or excessive. Owing to the low degree of formation, the changes in Δ*H*^o and Δ*S*^o parameters pertinent to the [SnMe₂(ida)H₋₁]⁻ species are not reliable. Thus, in order to avoid attribution of its thermal effect to other species, we performed the calorimetric experiments assuming the absence of [SnMe₂(ida)H₋₁]⁻.

oda. The same base model as for ida was considered. The only additional species not rejected by SUPERQUAD was [(SnMe₂)₂(oda)₂H]⁺. However, owing to the low degree of formation (less than 5%), this species was not included in the final model. As regards the determination of the thermodynamic parameters of [SnMe₂(oda)H₋₁]⁻, owing to the low degree of formation we used the same approach as for the analogous species of ida.

tda. For this system precipitation phenomena prevented investigation above pH 4.0. It was possible to investigate up to pH 6 only for solutions with ligand to metal ratios greater than 2:1. The base model is represented by the species [SnMe₂(tda)H]⁺, [SnMe₂(tda)] and [SnMe₂(tda)H₋₁]⁻; all the other species listed above were rejected by SUPERQUAD. The [SnMe₂(tda)H₋₁]⁻ species, was treated as for the analogous ida and oda species.

Differently from the other two systems investigated, in the case of tda the protonated species [SnMe₂(tda)H]⁺ is obtained in significant amounts. This may be ascribed to the lower strength of this ligand, which may more easily behave as

Table 2 Stability constants for dimethyltin(IV) complexes of ida, oda and tda at 25 °C and $I = 0.1 \text{ mol dm}^{-3}$ (KNO_3) with standard deviations in parentheses

<i>m</i>	<i>l</i>	<i>h</i>	$\log \beta_{mlh}$		
			ida	oda	tda
1	1	1	—	—	6.30(1)
1	1	0	9.414(6)	5.184(6)	3.103(6)
1	1	-1	2.41(2)	-1.36(2)	-1.22(3)

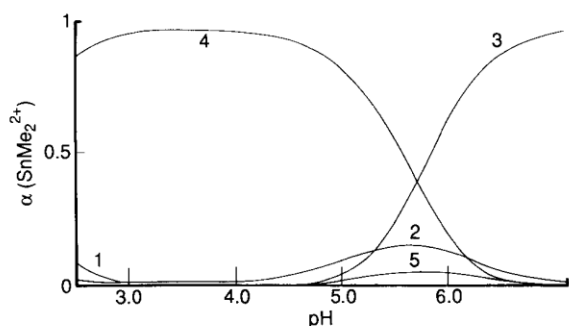


Fig. 1 Species distribution diagram for the dimethyltin(IV)-oxydiacetate system. $[\text{SnMe}_2^{2+}] = 4.0$, $[\text{oda}^{2-}] = 8.0 \text{ mmol dm}^{-3}$. Species: 1, free cation; 2, $[\text{SnMe}_2(\text{OH})]^+$; 3, $[\text{SnMe}_2(\text{OH})_2]$; 4, $[\text{SnMe}_2(\text{oda})]$; 5, $[\text{SnMe}_2(\text{oda})\text{H}_{-1}]^-$

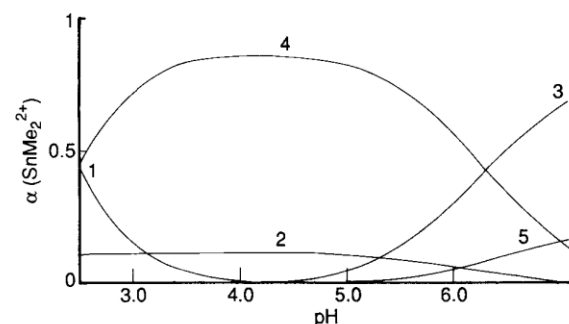


Fig. 2 Species distribution diagram for the dimethyltin(IV)-iminodiacetate system. $[\text{SnMe}_2^{2+}] = 4.0$, $[\text{ida}^{2-}] = 8.0 \text{ mmol dm}^{-3}$. Species: 1-3 as in Fig. 1; 4, $[\text{SnMe}_2(\text{ida})]$; 5, $[\text{SnMe}_2(\text{ida})\text{H}_{-1}]^-$

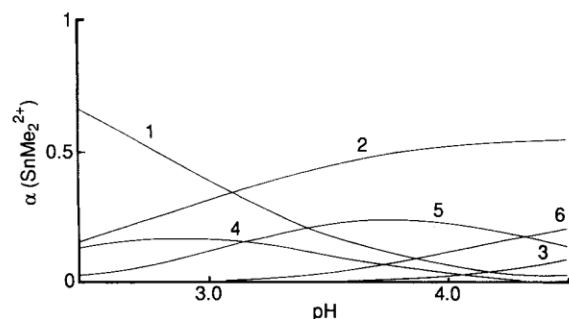


Fig. 3 Species distribution diagram for the dimethyltin(IV)-thiodiacetate system. $[\text{SnMe}_2^{2+}] = 4.0$, $[\text{tda}^{2-}] = 8.0 \text{ mmol dm}^{-3}$. Species: 1-3 as in Fig. 1; 4, $[\text{SnMe}_2(\text{tda})\text{H}]^+$; 5, $[\text{SnMe}_2(\text{tda})]$; 6, $[\text{SnMe}_2(\text{tda})\text{H}_{-1}]^-$

bidentate, and thus the protonated and the unprotonated species can form in comparable amounts.

Table 2 shows stability constants pertaining to the three

systems. The corresponding species distributions *vs.* pH are illustrated in Figs. 1-3.

No comparison is possible with other, previously determined, stability constants, since, to the best of our knowledge, such data are reported here for the first time. The stability order of the $[\text{SnMe}_2\text{L}]$ species shows the same trend as found for the analogous complexes of $[\text{UO}_2]^{2+}$ ion²⁰ (Table 3), a typical 'hard' cation. Table 4 shows the thermodynamic parameters of the complexes of $[\text{SnMe}_2]^{2+}$.

The formation of all the investigated complexes is entropy favoured, while the enthalpy contribution is favourable only for $[\text{SnMe}_2(\text{ida})]$. The positive ΔS° values, greater than those for $[\text{SnMe}_2(\text{O}_2\text{CMe})]^+$ (Table 3), suggest that both the carboxylic oxygen atoms of the potentially tridentate ligands are bound to the cation. The exothermic enthalpy change accompanying the formation of $[\text{SnMe}_2(\text{ida})]$ and the endothermic contributions associated with the oxydiacetate and thiodiacetate show a trend similar to that found for the analogous complexes of a hard ion like $[\text{UO}_2]^{2+}$ (Table 3), indicating the involvement of the heteroatoms in the co-ordination sphere of the organometallic ion.

NMR Results.—The results of our multinuclear NMR investigation are summarized in Table 5. The ^{119}Sn chemical shifts of the investigated species show large differences between each other. Such differences reflect corresponding variations in the co-ordination number of tin. Thus, as a first conclusion, we can assert that, despite the strong co-ordination ability of water molecules, co-ordination numbers lower than six are possible in aqueous solution. Nevertheless, other factors that may affect the ^{119}Sn chemical shifts should be considered, *e.g.* the nature of the donor atoms, and it should not be excluded that geometric factors also play a role in determining the δ values. Bearing in mind that Raman data¹² indicate that in the $[\text{SnMe}_2(\text{H}_2\text{O})_4]^{2+}$ the tin atom is six-co-ordinated, the differences in the δ value of the $[\text{SnMe}_2(\text{oda})]$ complex, which shows the largest upfield shift, may be explained by the higher electron-donating ability of the charged oxygen atoms of the oda ligand with respect to that of the neutral water molecules and not by a change in the co-ordination number. The four-co-ordinated $[\text{SnMe}_2(\text{OH})_2]$ shows the largest downfield shift. The difference in chemical shift between this hydroxo species and the oda complex (almost 336 ppm) is close to twice the usually estimated difference²¹ (about 150 ppm) for the variation in one donor atom. Analogously the intermediate value of the $[\text{SnMe}_2(\text{ida})]$ complex (Table 5) suggests five-co-ordination of tin in this species.

On the basis of these data, and of the hypothesized co-ordination numbers of the considered species, it is possible to quantify the corresponding upfield shift induced by the co-ordinated ^{119}Sn nucleus for each kind of donor atom in these complexes, namely neutral oxygen, charged oxygen and neutral nitrogen, by the following procedure. First, the difference between the tetraqua ion and the oda complex, divided by two, gives us the difference between a charged and a neutral oxygen atom (23 ppm). Then, half the difference between the dihydroxo species and the oda species gives the value due to a neutral oxygen atom (168 ppm), and consequently we now also know the value for a charged oxygen atom (191 ppm). By subtracting the difference between the ida and oda complex from the value for neutral oxygen we obtain the difference between a neutral nitrogen and a neutral oxygen atom (36 ppm), and thus the value for the nitrogen atom will be 204 ppm. As the only available test of the internal consistency of such a calculation, we may compare the values for the dihydroxo species with that for the ida complex. The difference between these values (204 ppm) corresponds exactly to the value for a neutral nitrogen atom, calculated independently. Even if there are too little data to draw a definitive conclusion, it is nevertheless promising to verify such an exact consistency for the four determined chemical shifts. Furthermore, the observed agreement suggests

Table 3 Thermodynamic data for $[\text{UO}_2]^{2+}$ complexes^a and for dimethyltin(IV) acetate and malonate (mal^{2-})^b complexes

Reaction	$-\Delta G^\circ/\text{kcal mol}^{-1}$	$\Delta H^\circ/\text{kcal mol}^{-1}$	$\Delta S^\circ/\text{cal K}^{-1} \text{mol}^{-1}$
$[\text{UO}_2]^{2+} + \text{ida}^{2-} \rightleftharpoons [\text{UO}_2(\text{ida})]$	11.98	-0.53	38.5
$[\text{UO}_2]^{2+} + \text{oda}^{2-} \rightleftharpoons [\text{UO}_2(\text{oda})]$	6.97	4.03	36.9
$[\text{UO}_2]^{2+} + \text{tda}^{2-} \rightleftharpoons [\text{UO}_2(\text{tda})]$	4.05	3.54	25.3
$[\text{SnMe}_2]^{2+} + \text{MeCO}_2^- \rightleftharpoons [\text{SnMe}_2(\text{O}_2\text{CMe})]^+$	3.85	-1.00	9.5
$[\text{SnMe}_2]^{2+} + \text{mal}^{2-} \rightleftharpoons [\text{SnMe}_2(\text{mal})]$	6.19	5.60	39.5

^a Ref. 20. ^b Ref. 7.**Table 4** Thermodynamic parameters for dimethyltin(IV)-ida, -oda and -tda complexes at 25 °C and $I = 0.1 \text{ mol dm}^{-3}$ (KNO_3) with standard deviations in parentheses

Reaction	$-\Delta G^\circ/\text{kcal mol}^{-1}$	$\Delta H^\circ/\text{kcal mol}^{-1}$	$-\Delta S^\circ/\text{cal K}^{-1} \text{mol}^{-1}$
$[\text{SnMe}_2]^{2+} + \text{ida}^{2-} \rightleftharpoons [\text{SnMe}_2(\text{ida})]$	12.831(8)	-2.09(3)	36.1(1)
$[\text{SnMe}_2]^{2+} + \text{oda}^{2-} \rightleftharpoons [\text{SnMe}_2(\text{oda})]$	7.066(8)	0.9(1)	26.7(3)
$[\text{SnMe}_2]^{2+} + \text{tda}^{2-} + \text{H}^+ \rightleftharpoons [\text{SnMe}_2(\text{tda})\text{H}]^+$	8.60(1)	1.6(2)	34.2(6)
$[\text{SnMe}_2]^{2+} + \text{tda}^{2-} \rightleftharpoons [\text{SnMe}_2(\text{tda})]$	4.229(8)	5.1(2)	31.6(6)

Table 5 NMR data for the investigated species *

Species	$\delta(^{119}\text{Sn})$	$\delta(^{13}\text{C})$	$^1J/\text{Hz}$	$\delta(^1\text{H})$	$^2J/\text{Hz}$
$[\text{SnMe}_2(\text{H}_2\text{O})_4]^{4+}$	0.0	12.8 (CH_3)	1058		108.0
$[\text{SnMe}_2(\text{OH})_2]$	289.9				83.6
$[\text{SnMe}_2(\text{ida})]$	86.4	10.2 (CH_3) 51.8 (CH_2) 52.7 (CH_2) 174.0 (CO) 178.9 (CO)		0.913 (CH_3) 3.941 (CH_2)	100.2
$[\text{SnMe}_2(\text{oda})(\text{H}_2\text{O})]$	-45.8	14.3 (CH_3) 69.9 (CH_2)			111.8

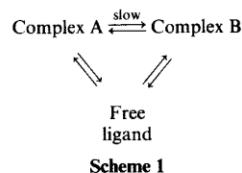
* Experimental details in the text.

that it is not necessary, for these complexes, to invoke any specific influence of geometrical factors on the ^{119}Sn chemical shift to be able to rationalize them.

Analogously to the behaviour of the chemical shifts, while on qualitative grounds the increase in J value with the Me-Sn-Me angle is certainly general, the quantitative relationship between these two values is dependent on the specific solvent used. Thus, it would be useless to try to correlate our data with those obtained in non-aqueous solution. As shown in Table 5, only the $^2J_{\text{SnH}}$ values are available for the investigated species, owing to insufficient complex solubility, which prevents the observation of the ^{119}Sn satellites in the ^{13}C NMR spectra. The proton-tin coupling constants range from the low value for the dihydroxo species (83.6 Hz), expected for tetrahedral coordination (109°), to the high value for both the tetraaquaion and the oda complex (108.0 and 111.8 Hz, respectively), due to a *trans* disposition of the methyl groups into a distorted-octahedral complex. As regards the ida complex, an intermediate value of 100.2 Hz is observed, which suggests a skew disposition of the methyl groups, with an angle of about 135°.

The ^{13}C NMR data show the non-equivalence of both the methylene and the carbonyl groups in the ida complex (Table 5). Considering the known lability of dimethyltin(IV) complexes, the presence of this non-equivalence in the NMR spectra is quite surprising and needs additional comment.

Spectra were recorded at different $\text{SnMe}_2:\text{ida}$ ratios. In all cases we observed two peaks, each of similar intensity. Therefore, it is not possible to ascribe one of the two peaks to the free ligand. Furthermore, from the ^{119}Sn NMR spectrum, which shows one peak only, the possibility of the formation of two different complexes (functional species) must be ruled out. Thus, in order to explain the experimental data a three-site kinetics has been hypothesized, according to Scheme 1.



In complexes A and B, entirely equivalent to each other, the two acetate moieties of ida are not equivalent and exchange their position from A to B. If the direct interconversion between A and B is slow the main process will be the two-stage interconversion through the free ligand. The effect of an intermediate rate of the processes involving the free ligand in the ^1H NMR spectra is different to that in the ^{13}C spectra. Owing to their small chemical shift difference the signals due to the two different protons coalesce. In contrast in the ^{13}C NMR spectrum we might expect two sub-spectra, one averaging between the free ligand and complex A and the other averaging between the free ligand and complex B. Owing to the chemical identity of A and B, the two sub-spectra are superimposable and we observe the experimental spectrum. Interconversions among different conformations in five-co-ordinated tin(IV) complexes have been observed,²² in which also a dissociation-inversion mechanism has been ascertained.

Small differences in the methyl carbon chemical shifts are also observed among the investigated species, which perfectly parallel the ^{119}Sn chemical shift data.

Discussion

If the comparison between the thermodynamic parameters of the complexes of $[\text{SnMe}_2]^{2+}$ and $[\text{UO}_2]^{2+}$ indicates tridentate

bonding of the investigated ligands, the differences of ΔH° and ΔS° values among the complexes of the dimethyltin(IV) ion deserve further consideration. In particular, we have to rationalize the differences in ΔS° between the iminodiacetate and the oxydiacetate complexes (negligible in the case of the analogous $[\text{UO}_2]^{2+}$ complexes), and in ΔH° between the oxydiacetate and thiodiacetate complexes [larger than that found for the analogous complexes of $[\text{UO}_2]^{2+}$ ion and opposite, the enthalpy for $[\text{SnMe}_2(\text{tda})$ formation being more endothermic than that for $[\text{SnMe}_2(\text{oda})]$].

We recall, at this point, that in the complex formation of dimethyltin(IV) species we have to take into account, besides the factors which usually influence the thermodynamic parameters of complex formation (desolvation of the ligand and of the metal ion, formation of new bonds, etc.), another contribution that can affect the enthalpy and entropy values, that is the variation of the Me–Sn–Me angle on going from the aqua ion to the complex species. In particular, we have shown that in the malonate complex this variation is characterized by a favourable entropy and an unfavourable enthalpy contribution (Table 3).⁷

Thus, the entropy difference between the ida and oda complex (about 9 cal K⁻¹ mol⁻¹) might be due to different desolvation processes associated with different dispositions of methyl groups. In particular, a *trans* arrangement should involve a less-favourable entropy contribution with respect to a *cis** one which should be favoured by a larger desolvation process. In the absence of such a rearrangement, the ΔS° differences should be ascribable to different direct interactions of the organometallic ion with water molecules, modulated by the different 'strengths' of the ligands.

To explain the differences in ΔS° values we can hypothesize that in the ida complexes the stronger equatorial field will result in a Me–Sn–Me angle less than 180° with consequent desolvation of the central organometallic ion. This hypothesis is consistent with the NMR results which show a 'skew trigonal bipyramidal' structure, with a further asymmetry in the plane. A difference in length between the two bonds of the carboxylate oxygens of ida is indicated by the ¹³C NMR spectrum (see Table 5), similarly to that ascertained in the solid state for six-co-ordinated species.^{23–25} In the oda complex the lower entropy term is explained by the presence of a water molecule needed to complete the octahedral geometry of the dimethyltin(IV) ion, again in agreement with the NMR results. This explanation of the entropy change is further supported by the ΔH° value associated with formation of $[\text{SnMe}_2(\text{oda})(\text{H}_2\text{O})]$.

If we compare the ΔG° values for the tda unprotonated complexes of both the uranyl and $[\text{SnMe}_2]^{2+}$ ion with the corresponding values for the oda complexes, the same differences are observed. However, looking at the individual enthalpy and entropy contributions, one can see that, for the uranyl complex of oda the ΔH° value is higher (more disfavoured), for the SnMe_2 complex of oda the value is lower (less disfavoured) and the contrary is observed for the ΔS° values. This may be explained by a greater desolvation in the case of the tda complex of $[\text{SnMe}_2]^{2+}$, leading to a five-co-ordinated species, though in this case one would expect a slightly higher ΔS° value. Recalling the tda ligand co-ordination preference we can suggest an alternative explanation. To achieve its preferred *facial* type co-ordination the sulfur atom must co-ordinate at an apical position; to do this, a methyl group has to leave its apical position to approach the equatorial plane. In this way the Me–Sn–Me angle should decrease substantially, maybe reaching the tetrahedral value. On the

other hand, it is known⁴ that to maximize tin 5s density in a Sn–C bond the strong σ -donor methyl groups prefer the *trans* geometry. Thus, the positive enthalpy term {very close to that found for the formation of the hypothesized tetrahedral $[\text{SnMe}_2(\text{mal})]$ complex (Table 3)} might be mainly ascribable to the Me–Sn–Me angle rearrangement which will leave the methyl groups in an unfavourable electronic situation. The weak sulfur co-ordination to the central ion is not able to counterbalance this unfavourable enthalpy variation. The entropy contribution, intermediate between those for the ida and oda complexes, does not permit a clear distinction between five- or six-co-ordination. On the other hand, as already recalled, the thioether sulfur atom is not a 'good' donor atom for tin and is not likely to induce extensive desolvation processes. The achievement of the preferred co-ordination geometry may explain the more favourable entropy contribution (about 4 cal K⁻¹ mol⁻¹) with respect to the oda complex. Thus, in this case steric factors seem to predominate with respect to the electronic ones in the final conformation of the methyl groups, but the thermodynamic values are mainly ascribable to electronic effects.

Conclusion

In conclusion, we should like to underline some points of general interest which arise from our investigation. First the results obtained in aqueous solution seem to confirm most of the conclusions reached by other researchers, both in non-aqueous solution and in the solid state, primarily the magnitude of the effect of the co-ordination number on the ¹¹⁹Sn chemical shifts, as well as the conformational flexibility of $[\text{SnMe}_2]^{2+}$ in its complexes. Such flexibility consists, not only in the variability of the Me–Sn–Me angle, but also in its ability to give rise to unusual asymmetric stereochemistries. In the case of the $[\text{SnMe}_2(\text{ida})]$ complex, in particular, our results are consistent with a structure to our knowledge never before observed, though both the 'skew' disposition of the methyl groups and the different bond lengths of equivalent donor groups have been found in other stereochemistries.^{23–25}

A first step towards the quantitative (or semiquantitative) estimate of the influence of different kinds of donor atoms on the ¹¹⁹Sn chemical shifts has been made, though more data are necessary in order to make definite conclusions.

Lastly, we would once more remark on the usefulness of an integrated thermodynamic–spectroscopic approach to investigations in aqueous solutions.

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* The term '*cis*' may be misleading when referred to stereochemistries different from square planar or octahedral, and when the considered geometries are too asymmetric. In these cases, a '*cis*' conformation of the methyl groups might only mean an angle of 90°. However, this is not the case here because it is known² that the smallest Me–Sn–Me angle is approximately tetrahedral.

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