Co-ordination Properties of Dialkyltin(IV) in Aqueous Solution. Thermodynamics of Complex Formation with Carboxylic Acids *

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The complex formation of $[SnMe_2]^{2+}$ ion with acetate, malonate, and succinate ligands has been investigated by means of potentiometric measurements at 25 °C and I = 0.1 mol dm^{-3} (KNO_3). Values of ΔH° and ΔS° have been obtained by means of calorimetric titrations. On the basis of these values, bonding details have been inferred for the major species. The thermodynamic data are also discussed in view of the *cis-trans* disposition of the alkyl groups.

Recently, we reported thermodynamic data pertinent to the hydrolytic species formed by dimethyltin(IV) and diethyltin(IV) ions, in aqueous solution.[1] It was necessary to obtain the hydrolysis data before studying the complexation equilibria of the above organotins since, for instance, $[SnR_2]^{2+}$ (R = Me or Et) appear to be among the most extensively hydrolysed divalent ions which have so far been studied.[2] This reflects the strong polarization of the water molecules in the first co-ordination sphere of this cation. Despite the importance of understanding the fate of these organometallic species, the solution chemistry and structure of organotin complexes have only partially been investigated. Very few stability constants of organotin ion complexes in aqueous solution have been reported.[3,4] In this paper the discussion will be restricted to complexes of $SnMe_2{}^{2+}$. It was decided to undertake a detailed thermodynamic study of the complexation equilibria of this ion with carboxylic acids in order to obtain some reliable information on the nature and the extent of the interaction between the organotin ion and these ligands. Diorganotin dicarboxylates are widely used in industry as homogeneous catalysts for polyurethane and room-temperature vulcanization silicone polymerization and for transesterification reactions.[5] Notwithstanding these important applications, the structure, in solution, of even simple diorganotin carboxylates remains a matter of speculation.[6,7] For the reasons above, besides the potentiometric measurements carried out to obtain ΔG° values, we have also performed calorimetric measurements, under the same experimental conditions, *i.e.* 25 °C and I = 0.1 mol dm^{-3} (KNO_3), in order to obtain useful information on both the contributions of enthalpy and entropy changes to the stability and the structural features of different organometallic complexes formed in solution by $[SnMe_2]^{2+}$ and carboxylate ligands such as acetate ($MeCO_2^-$), malonate (mal^{2-}), and succinate ($succ^{2-}$).

Experimental

Chemicals.—Dimethyltin(IV) nitrate was obtained using dimethyltin oxide (ICN Biomedical Inc.) as a starting material. The procedure used to obtain chloride-free dimethyltin(IV) oxide has been described elsewhere.[1] The purity of the final dimethyltin(IV) nitrate solution was checked potentiometrically by using the computer program SUPERQUAD (see Calculations) for the data treatment. The virtual coincidence between the stoicheiometrically calculated and the observed excess of nitric acid, added to dimethyltin oxide to make up the dimethyltin nitrate solution, indicated that the purity was higher than 99.5%.

Acetic acid solutions were prepared by diluting concentrated ampoules Titrisol (Merck). The concentration of the solution was checked by means of potentiometric titration. Anhydrous sodium acetate (C. Erba, R.P.E., A.C.S.) was employed as received. Malonic and succinic acids (C. Erba R.P.E.) were recrystallized from a diethyl ether–light petroleum (b.p. 50—70 °C) mixture. When the melting point indicated the absence of impurities, the purity was checked potentiometrically by (*i*) titration with CO_2-free KOH and (*ii*) determination of the pK values. In all cases a purity >99.7% was found; pK_1 and pK_2 agreed with literature values[8] to within 0.02 and 0.01 logarithmic units. All standard solutions were prepared using twice distilled water. The ionic strength was adjusted to 0.1 mol dm^{-3} by adding KNO_3. Grade A glassware was used throughout.

E.M.F. Measurements.—The potentiometric measurements were carried out by means of two fully automated computer-controlled meters (Metrohm E 654) using glass electrodes (Metrohm EA 109) and single saturated calomel electrodes (Metrohm EA 404). In both systems the titrant was delivered by digital dispensers (Metrohm 665) equipped with 5-cm^3 barrels. All experiments were carried out at 25.0 ± 0.1 °C using thermostatted cells (25 cm^3). All solutions were magnetically stirred and kept in an atmosphere of CO_2- and O_2-free nitrogen, previously bubbled through 0.1 mol dm^{-3} KNO_3 solutions. Values of the E° and slope of the electrode system were determined by titrating HNO_3 (20—25 cm^3) with CO_2-free KOH. Experimental details for the potentiometric titrations are reported in Table 1. Each experiment was run in the two different potentiometric apparatuses to avoid systematic errors and to check for reproducibility. In addition, the readings of parallel experiments were taken at different time intervals to ascertain that there was no kinetic problems. Checks on the pH stability of each solution to be titrated showed no detectable drift in e.m.f. over a period of 90 min. Other details were as previously described.[9]

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 cm^3). For the malonate and succinate systems, 25 cm^3 of solution, with the concentrations shown in Table 2, were

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* *Non-S.I. unit employed:* cal = 4.184 J.

Table 1. Experimental conditions of potentiometric measurements at 25 °C and I = 0.1 mol dm^{-3} (KNO$_3$)

$c^0{}_M$/mmol dm^{-3} [SnMe$_2$]$^{2+}$	$c^0{}_L$/mmol dm^{-3} Acetate	Malonate	Succinate	Titrant (mol dm^{-3}) KOH	pH range	No. of points
3.502			11.970	0.100 20	2.7—5.3	46
3.502			11.970	0.098 93	2.7—5.0	46
4.031			7.617	0.099 58	2.3—4.7	44
4.031			7.647	0.099 68	2.3—4.6	42
3.011			9.270	0.099 72	2.8—5.3	45
3.011			9.270	0.099 80	2.8—5.3	36
3.006			6.507	0.099 68	2.8—4.7	35
5.170			6.680	0.100 70	2.6—4.4	30
5.001			6.018	0.100 10	2.5—4.2	54
5.001			6.018	0.100 24	2.5—4.2	56
2.002	8.999			0.100 07	2.9—6.4	61
2.002	8.999			0.098 93	2.9—6.4	62
4.016	13.982			0.100 07	2.7—6.6	72
4.016	13.982			0.098 93	2.7—6.6	61
7.008	14.949			0.099 26	2.6—6.6	51
7.008	14.949			0.098 56	2.6—6.4	50
6.992	21.028			0.099 26	2.6—6.4	48
6.992	21.028			0.099 56	2.6—6.4	46
3.001		9.010		0.099 72	2.4—6.0	45
3.005		6.118		0.099 60	3.0—6.3	33
3.005		6.118		0.099 90	3.0—6.2	34
4.055		10.556		0.099 72	2.6—6.3	56
4.000		16.126		0.100 26	2.6—6.5	43
4.000		16.126		0.100 16	2.3—6.0	45
7.987		8.005		0.100 24	2.3—6.5	55
7.987		8.005		0.100 10	2.3—6.5	60
7.999		8.015		0.102 4	2.3—5.7	61
7.999		8.015		0.100 10	2.3—6.6	67

Table 2. Experimental conditions of calcrimetric measurements at 25 °C and I = 0.1 mol dm^{-3} (KNO$_3$)

$c^0{}_M$/mmol dm^{-3}	$c^0{}_L$/mmol dm^{-3} Acetate	Malonate	Succinate	Titrant (mol dm^{-3}) HNO$_3$	Na(O$_2$CMe)	pH range	No. of points
3.002			9.033	0.5998		4.4—2.2	27
3.003			9.017	0.5998		4.6—2.2	28
2.018			7.002	0.5998		4.6—2.2	42
3.002		8.987		0.5998		6.8—2.4	105
3.007		9.086		1.0056		6.9—2.3	56
3.487		8.849		1.0056		6.5—2.3	47
2.992		6.040		1.0056		6.5—2.5	57
9.00	8.98				0.3006		33
7.984	0.00				0.3006		43
8.94	8.98				0.3006		38

titrated with standard HNO$_3$. Totals of 97 and 230 points were recorded for the succinate and malonate systems, respectively. This procedure could not be utilized for the acetate system, since the changes in mmol from the (n − 1)th to the nth point of a titration were small. In this case, in order to optimize the experimental conditions, *i.e.* to obtain sizable changes in mmol between successive points of a titration, which would minimize the error in the ΔH° evaluated by the DOEC program (see Calculations), 25 cm^3 of solution of the concentrations shown in Table 2 were titrated with fully deprotonated acetic acid. A total of 114 points were collected.

In all cases the titration data, corrected for all non-chemical energy terms, determined in separate experiments, were refined simultaneously to obtain the final ΔH° values.

Calculations.—The calculations concerning the electrode system as well as the slope were performed by the computer program ACBA,[10] which refines the parameters of an acid–base titration by using a non-linear least-squares method minimizing the function $U = (v_{i,\text{exptl.}} - v_{i,\text{calc.}})^2$, where v is the volume of titrant added. All other potentiometric data were handled by the programs MINIQUAD 76A[11] and SUPERQUAD.[12] These two programs, which minimize two different functions, namely the error-square sum in the analytical concentrations (MINIQUAD) and the error-square sum based on measured electrode potentials (SUPERQUAD), were a good strategic choice for model selection. The residuals were analysed according to the procedure recommended by Vacca *et al.*[13] The enthalpies of formation were computed by means of the least-squares program DOEC,[14] which minimizes the function $U = \Sigma(Q_{i,\text{calc.}} - Q_{i,\text{exptl.}})^2$, where Q is the heat of reaction related to ΔH° by the equation $-Q = \Sigma\delta n_i \Delta H^{\circ}{}_i$, where δn_i is the change in the number of moles of the ith species. The distribution diagrams were obtained by means of the computer program DISDI.[15]

Table 3. Overall formation constants at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)[a]

			log β_{pqr}[b]		
p	q	r	$MeCO_2$	mal	succ
1	1	1		6.95(1)[c]	8.25(1)
1	1	0	2.815(7)	4.543(2)	4.54(1)
1	1	−1	−1.320(4)	−0.744(5)	−0.30(2)
1	2	0	4.62(3)	6.14(3)	
1	2	1			11.28(3)

[a] The hydrolysis constants for $[SnMe_2]^{2+}$ have been determined previously:[1] log $\beta_{1-1} = -3.124$, log $\beta_{2-2} = -5.05$, log $\beta_{2-3} = -9.74$, log $\beta_{1-2} = -8.428$, log $\beta_{1-3} = -19.450$; log β_{pr} refers to the reaction $p\text{SnMe}_2{}^{2+} + r\text{H}_2\text{O} \rightleftharpoons (\text{SnMe}_2)_p(\text{OH})_r{}^{(2p-r)+} + r\text{H}^+$. [b] β_{pqr} refers to the reaction $p\text{SnMe}_2 + q\text{L} + r\text{H} \rightleftharpoons (\text{SnMe}_2)_p\text{L}_q\text{H}_r$. [c] σ In parentheses.

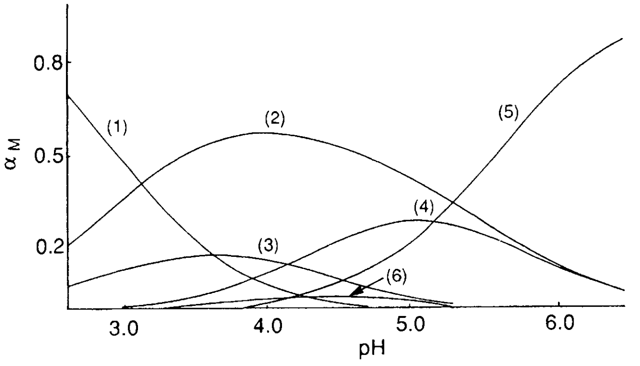

Figure 1. Species distribution diagram for the dimethyltin(IV)–acetate system. $[SnMe_2{}^{2+}] = 4 \times 10^{-3}$, $[MeCO_2{}^-] = 16 \times 10^{-3}$. Species: (1) free central ion; (2) $[SnMe_2(OH)]^+$; (3) $[SnMe_2(O_2CMe)]^+$; (4) $[SnMe_2(O_2CMe)H_{-1}]$; (5) $[SnMe_2(OH)_2]$; and (6) $[SnMe_2(O_2CMe)_2]$

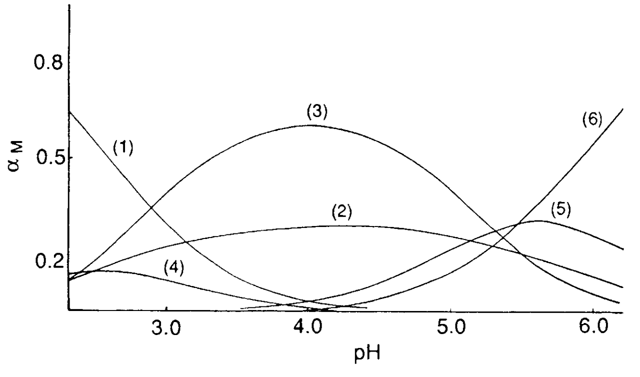

Figure 2. Species distribution diagram for the dimethyltin(IV)–malonate system. $[SnMe_2{}^{2+}] = 5 \times 10^{-3}$, $[mal^{2-}] = 12.5 \times 10^{-3}$. Species: (1) free central ion; (2) $[SnMe_2(OH)]^+$; (3) $[SnMe_2(mal)]$; (4) $[SnMe_2(mal)H]^+$; (5) $[SnMe_2(mal)H_{-1}]^-$; and (6) $[SnMe_2(OH)_2]$

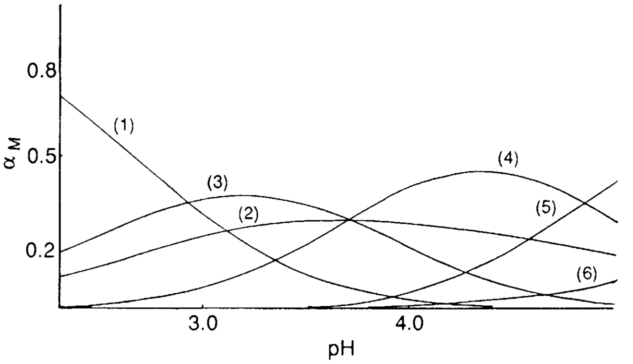

Figure 3. Species distribution diagram for the dimethyltin(IV)–succinate system. $[SnMe_2{}^{2+}] = 5 \times 10^{-3}$, $[succ^{2-}] = 12.5 \times 10^{-3}$. Species: (1) free central ion; (2) $[SnMe_2(OH)]^+$; (3) $[SnMe_2(succ)H]^+$; (4) $[SnMe_2(succ)]$; (5) $[SnMe_2(succ)H_{-1}]$; and (6) $[SnMe_2(OH)_2]$

Results and Discussion

The stability constants obtained in the present investigation are reported in Table 3.

Acetate.—Various species such as $[(SnMe_2)_2(O_2CMe)_2]^{2+}$, $[(SnMe_2)_2(O_2CMe)H_{-1}]^{2+}$, $[SnMe_2(O_2CMe)_2]$, $[SnMe_2(O_2CMe)_3]^-$, $[(SnMe_2)_2(O_2CMe)_2H_{-2}]$ were added to the base model represented by $[SnMe_2(O_2CMe)]^+$ and $[SnMe_2(O_2CMe)H_{-1}]$ and tried in different combinations. Regardless of the combination, though, these species were always rejected by the program, with the exception of $[SnMe_2(O_2CMe)_2]$. The introduction of the latter into the base model caused an improvement in the statistical parameters ($\chi^2 = 3.24$ and 7.34 with and without this species, respectively). However, this species is present in small percentages and its introduction does not significantly alter the values of the other species. No evidence was found for $[SnMe_2(O_2CMe)_3]^-$, the existence of which had been demonstrated in $CHCl_3$ solution by means of n.m.r. investigations.[16]

Malonate.—For this system the species $[SnMe_2(mal)_2H]^-$, $[SnMe_2(mal)_2H_2]$, $[(SnMe_2)_2(mal)_2]$, $[(SnMe_2)_2(mal)_2H_{-1}]^-$, $[(SnMe_2)_2(mal)_2H_{-2}]^{2-}$, $[(SnMe_2)_2(mal)]^{2+}$, $[SnMe_2(mal)_2]^{2-}$ were considered with $[SnMe_2(mal)H]^+$, $[SnMe_2(mal)]$, and $[SnMe_2(mal)H_{-1}]^-$ as the base model and the other species added in different combinations. Both MINIQUAD and SUPERQUAD (see Calculations) gave essentially the same set of constants, *i.e.* the set shown in Table 3; MINIQUAD sometimes rejected $[SnMe_2(mal)_2]^{2-}$, on examination of the individual curves one by one. This species never exceeds 7% of the total organotin. However, fitting the data with SUPERQUAD without taking this species into account caused a large increase of χ^2 (25.2 *vs.* 6.33). Moreover, analysis of the residuals of the calorimetric curves gave no systematic errors (with this species included in the model), thus providing further evidence for its existence.

Succinate.—The same species list and base model as for the malonate system was considered for succinate. Precipitation prevented investigation above pH 5.3 (see Table 1) and this accounts, in our opinion, for the impossibility of obtaining a satisfactory value for $[SnMe_2(succ)_2]^{2-}$, which was rejected by SUPERQUAD, because of an 'excessive' standard deviation. Introduction of the species $[SnMe_2(succ)_2H]^-$ into the base model improved the statistical parameters of both MINIQUAD and SUPERQUAD; namely, χ^2 and σ varied from 13.3 and 2.27 to 6.80 and 1.78, respectively. Doubts arise about the existence of dimeric species such as $[(SnMe_2)_2(succ)_2]$ and $[(SnMe_2)_2(succ)_2H_{-1}]^-$; these species, though not rejected by either program, produced no significant improvement in the statistical parameters of both programs. Analysis of the residuals, according to Vacca *et al.*,[13] did not support their existence. For these reasons they were not included in the 'best' model reported in Table 3.

Figures 1—3 show the species distribution *versus* pH for all three systems. The formation of $[SnMe_2(O_2CMe)]^+$ (Table 4) is both enthalpy and entropy favoured, while the bis(acetate) complex is stabilized by an entropy contribution, only. As far as inner complexes are concerned, the formation of a complex

Table 4. Thermodynamic parameters for dimethyltin(IV)–acetate, –malonate, and –succinate simple complexes at 25 °C and I = 0.1 mol dm^{-3} (KNO_3)

Equilibrium	$-\Delta G^{\ominus}$/ kcal mol^{-1}	$\Delta H^{\ominus}$/ kcal mol^{-1}	$\Delta S^{\ominus}$/ cal K^{-1} mol^{-1}
$[SnMe_2]^{2+} + MeCO_2^- \rightleftharpoons [SnMe_2(O_2CMe)]^+$	3.85(1)	−1.00(6)	9.5(2)
$[SnMe_2(O_2CMe)]^+ + MeCO_2^- \rightleftharpoons [SnMe_2(O_2CMe)_2]$	2.45(4)	7.50(3)	34(1)
$[SnMe_2]^{2+} + MeCO_2^- \rightleftharpoons [SnMe_2(O_2CMe)H_{-1}] + H^+$	−1.80(1)	8.10(9)	21.2(4)
$[SnMe_2]^{2+} + mal^{2-} \rightleftharpoons [SnMe_2(mal)]$	6.19(1)	5.60(4)	39.5(1)
$[SnMe_2(mal)] + mal^{2-} \rightleftharpoons [SnMe_2(mal)_2]^{2-}$	2.18(4)	−2.50(7)	0.0(2)
$[SnMe_2]^{2+} + H^+ + mal^{2-} \rightleftharpoons [SnMe_2(mal)H]^+$	9.48(1)	5.50(2)	50.1(8)
$[SnMe_2]^{2+} + mal^{2-} \rightleftharpoons [SnMe_2(mal)H_{-1}]^- + H^+$	−1.01(7)	10.2(1)	30.9(3)
$[SnMe_2]^{2+} + succ^{2-} \rightleftharpoons [SnMe_2(succ)]$	6.19(1)	7.0(3)	44(1)
$[SnMe_2]^{2+} + H^+ + succ^{2-} \rightleftharpoons [SnMe_2(succ)H]^+$	11.25(1)	2.4(2)	45.8(7)
$[SnMe_2]^{2+} + succ^{2-} \rightleftharpoons [SnMe_2(succ)H_{-1}]^- + H^+$	−0.41(3)	8.7(3)	28(1)

[a] σ In parentheses. [b] The thermodynamic parameters of proton–acetate complex formation were found to be $-\Delta G^{\ominus}$ = 6.22(1), $-\Delta H^{\ominus}$ = 0.19(1) kcal mol^{-1}, and $\Delta S^{\ominus}$ = 20.2(4) cal K^{-1} mol^{-1}. [c] The thermodynamic parameters for proton–malonate and –succinate complexes have been previously determined.[8]

Table 5. Thermodynamic parameters for $[UO_2]^{2+}$ carboxylate complexes

Reaction	$-\Delta G^{\ominus}$/ kcal mol^{-1}	$\Delta H^{\ominus}$/ kcal mol^{-1}	$\Delta S^{\ominus}$/ cal K^{-1} mol^{-1}	Ref.
$[UO_2]^{2+} + MeCO_2^- \rightleftharpoons [UO_2(O_2CMe)]^+$	3.35	2.83	20.7	*a*
$[UO_2(O_2CMe)]^+ + MeCO_2^- \rightleftharpoons [UO_2(O_2CMe)_2]$	2.62	1.45	13.1	*a*
$[UO_2(O_2CMe)_2] + MeCO_2^- \rightleftharpoons [UO_2(O_2CMe)_3]^-$	2.92	−0.28	8.8	*a*
$[UO_2^{2+}] + mal^{2-} \rightleftharpoons [UO_2(mal)]$	7.40	2.12	32	*b*
$[UO_2(mal)] + mal^{2-} \rightleftharpoons [UO_2(mal)_2]^{2-}$	3.12	0.68	21	*b*
$[UO_2^{2+}] + succ^{2-} \rightleftharpoons [UO_2(succ)]$	5.26	5.14	35	*c*

[a] R. Portanova, P. Di Bernardo, A. Cassol, E. Tondello, and L. Magon, *Inorg. Chim. Acta*, 1974, **8**, 233. [b] P. Di Bernardo, V. Di Napoli, A. Cassol, and L. Magon, *J. Inorg. Nucl. Chem.*, 1977, **37**, 1659. [c] A. Bismondo, A. Cassol, P. Di Bernardo, L. Magon, and G. Tomat, *Inorg. Nucl. Chem. Lett.*, 1981, **17**, 79.

normally implies the substitution of hydration water molecules by the donor atoms of a ligand.[17,18] The overall process is enthalpically favoured only if the energetics of formation of the newly formed metal–donor atom bonds (exothermic contribution) is larger than that of the breaking of metal–solvent bonds (endothermic contribution). Besides, if the ligand is a charged one a significantly positive $\Delta S^{\ominus}$ value is to be expected together with an even more endothermic $\Delta H^{\ominus}$ value, owing to the desolvation of both the ligand and the metal ion, resulting from the neutralization of their charges. The negative $\Delta H^{\ominus}$ (−1.0 kcal mol^{-1}) and the relatively low $\Delta S^{\ominus}$ value (9.5 cal K^{-1} mol^{-1}) indicate that the complexation of the acetate group does not result in a high degree of desolvation. As usual for 'hard acid–hard base' interactions, larger $\Delta S^{\ominus}$ (more positive) and positive $\Delta H^{\ominus}$ contributions would be expected. Indeed this is so for a typical hard acid–hard base interaction such as the first step of complexation of $MeCO_2^-$ to $[UO_2]^{2+}$ {leading to $[UO_2(O_2CMe)]^+$} (see Table 5). Similar behaviour was found for the formation of $[SnMe_2(OH)]^+$.[1] In this latter case the large desolvation of the $[SnMe_2]^{2+}$ cation, which contains four water molecules in the first co-ordination sphere,[19] was also attributed to a structural rearrangement of the two methyl groups from a *trans* to a *cis* conformation.[1] Since the *cis* conformation is not energetically favoured,[20] we have to conclude that a *trans–cis* conformation change is not occurring in the first complexation step of $SnMe_2^{2+}$ with $MeCO_2^-$; probably the 'weaker' $MeCO_2^-$ (if compared to OH^-) is not able to induce such a conformation change. The complexation of a second $MeCO_2^-$ group is not only more endothermic than the first step but also much more endothermic than usually found for similar interactions (see second step for $[UO_2]^{2+}$–$MeCO_2^-$ complexation in Table 5). This can only be interpreted by assuming that the unfavourable *trans–cis* rearrangement[20] is occurring at this stage.

The formation of $[SnMe_2(mal)]$ and $[SnMe_2(succ)]$ is enthalpically unfavoured and entropically favoured (Table 4), as expected for dicarboxylic acid ligands (see Table 5). Comparison of the thermodynamic parameters pertaining to the mono complex formation of succinate and malonate with those of the bis(acetate) complex indicates that both dicarboxylic acid ligands are acting in a bidentate manner. The $\Delta S^{\ominus}$ values for $[SnMe_2(mal)]$ and $[SnMe_2(succ)]$ resemble more closely the entropic change for the bis(acetate) complex than that of $[SnMe_2(O_2CMe)]^+$. This suggests that the desolvation process associated with the formation of the two $[SnMe_2L]$ species (L = dicarboxylic acid ligand) resembles that for the overall formation of $[SnMe_2(O_2CMe)_2]$. Despite the differences observed for the enthalpic and entropic changes, all three complexes show similar $\Delta G^{\ominus}$ values. This is surprising since malonate complexes are usually more stable[17] than either succinate or bis(acetate) complexes, as also indicated in Table 5. An explanation for this might be that the thermodynamic parameters reflect not only bond formation and breaking but in the case of organotin ions also the conformation change of the alkyl groups upon co-ordination of the two carboxylic oxygens. In our opinion, the $\Delta G^{\ominus}$ of the monomalonate species (unusually low for a six-membered ring when compared to the value for the analogous succinate species) reflects an unfavourable structural rearrangement of the alkyl groups.

Table 4 shows that the formation of $[SnMe_2(mal)_2]^{2-}$ is enthalpically favoured. The ion $[SnMe_2]^{2+}$ achieves six-co-ordination in this step; this process is not accompanied by a large desolvation ($\Delta S^{\ominus}$ = 0.0 cal K^{-1} mol^{-1}), which mostly takes place in the first step of complexation. This behaviour is significantly different from that shown by $[UO_2]^{2+}$ in the formation of the bis(malonate) species (Table 5). One might hypothesize that the exothermic contribution accompanying the formation of $[SnMe_2(mal)_2]^{2-}$ is a consequence of the attainment of the energetically favoured

Table 6. Derived thermodynamic values for the $[SnMe_2]^{2+}$ complexes of malonate and succinate ligands together with protonation constants[8] for the same ligands at 25 °C and $I = 0.1$ mol dm^{-3} (KNO_3)

Equilibrium	ΔG°/ kcal mol^{-1}	ΔH°/ kcal mol^{-1}	ΔS°/ cal K^{-1} mol^{-1}
$[SnMe_2]^{2+} + H_2mal \rightleftharpoons [SnMe_2(mal)H]^+ + H^+$	1.2	5.4	14
$[SnMe_2]^{2+} + H_2succ \rightleftharpoons [SnMe_2(succ)H]^+ + H^+$	1.2	3.5	8
$[SnMe_2]^{2+} + Hmal^- \rightleftharpoons [SnMe_2(mal)H]^+$	−2.32	4.8	24
$[SnMe_2]^{2+} + Hsucc^- \rightleftharpoons [SnMe_2(succ)H]^+$	−4.23	2.6	23
$H^+ + mal^{2-} \rightleftharpoons Hmal^-$	−7.16	0.7	26
$H^+ + succ^{2-} \rightleftharpoons Hsucc^-$	−7.02	−0.2	23
$H^+ + Hmal^- \rightleftharpoons H_2mal$	−3.6	−0.5	10
$H^+ + Hsucc^- \rightleftharpoons H_2succ$	−5.5	−0.9	15
$2H^+ + mal^{2-} \rightleftharpoons H_2mal$	−10.7	0.1	36
$2H^+ + succ^{2-} \rightleftharpoons H_2succ$	−12.5	−1.1	38

trans conformation of the alkyl groups due to the in-plane co-ordination of two additional oxygen atoms of the second carboxylate group.

The succinate protonated species seems to be more stable than the analogous malonate species ($\Delta G^\circ = -11.25$ and -9.48 kcal mol^{-1} for succinate and malonate, respectively). However if the equilibria are rewritten as in Table 6 it becomes evident that discussing the data in terms of ΔG° is either ambiguous or misleading. If we look at the first two rows in Table 6 the two species seem to have the same stability, whereas they show different stability if the equilibria are rewritten as in the third and fourth rows. This contradiction appears only when ΔG° values are considered and not when all the thermodynamic parameters are taken into account. Thus both equilibria in Table 6 lead to the same interpretation. The more endothermic value (5.4 *vs.* 3.5 kcal mol^{-1} for malonate and succinate, respectively) of the malonate species (first two rows in Table 6) is due to the greater nucleophilicity of the malonate anion, which causes a larger desolvation of the metal ion, as also indicated by the entropy values.

Looking at the equilibria $[SnMe_2]^{2+} + HL^- \rightleftharpoons [SnMe_2(L)H]^+$ (third and fourth entries of Table 6) the ΔH° value for succinate is lower (less unfavourable) than that for the analogous species of malonate. On the contrary the ΔS° values are quite similar (24 and 23 cal K^{-1} mol^{-1} for malonate and succinate, respectively) conversely to the situation pertaining to $[SnMe_2]^{2+} + H_2L \rightleftharpoons [SnMe_2(L)H]^+ + H^+$. This is not surprising, since we are considering here an initial state (HL) different to that considered in the first two entries and whose interaction with the $[SnMe_2]^{2+}$ ion involves, for Hmal, the breaking of a hydrogen bond bridging the two carboxylic oxygens.[8] As shown by the fifth and sixth entries of Table 6, the protonation of a system with no hydrogen bond[8] (Hsucc) is some 0.4 kcal mol^{-1} more enthalpically favoured and 5 cal K^{-1} mol^{-1} more entropically favoured than that of a system (Hmal) with such a bond. This similarity of the ΔS° values for the third and fourth entries 'hides' the different contributions due to the presence in Hmal of a hydrogen bond.

As Table 4 shows, the formation of the deprotonated species is favoured more for succinate than for malonate. This is almost entirely due to the larger enthalpic contribution of the succinate species; ΔG° values indicate a slightly more favourable contribution for the malonate species. The thermodynamic data for the two deprotonated species suggest that the greater nucleophilicity of the malonate ligand, with respect to succinate, renders the formation of the hydroxo species more difficult. However, considering the similarity of ΔH° values for acetate and succinate, it cannot be excluded that only one carboxylic oxygen of succinate is co-ordinated to the dimethyltin ion.

Conclusion

A complete thermodynamic approach, *i.e.* the determination of ΔH° and ΔS° in addition to ΔG° values, proved useful in describing the bonding details of some carboxylic ligands to both 'hard' and 'soft' type metals.[17,18,21] The utilization, extended to an organometallic ion here for the first time, of enthalpy and entropy values to provide structural information on the species existing in solution has allowed the identification of the donor atoms, even in the presence of other on-going processes, such as the rearrangement of the alkyl groups. The contribution of this latter process to ΔG°, ΔH°, and ΔS° values for complex formation is hypothesized here for the first time. A more well founded interpretation of the thermodynamic data would require a parallel spectroscopic approach aimed at the determination of the disposition of the alkyl groups (*i*) before and after the complexation and (*ii*) as a function of the ligands examined. N.m.r. studies have been carried out by other researchers[20] in order to correlate the angle of the alkyl residues of organotin cations in various complexes with magnetic parameters. While good correlations have been found, unfortunately these data only concern the solid state or non-aqueous solvents.[22–26] Despite the various attempts to obtain valid n.m.r. spectra, the degree of formation of the complex species reported here has not enabled us to obtain 'reliable' n.m.r. data under the conditions employed for the potentiometric and calorimetric study. On the other hand, too great a divergence from the conditions employed for the potentiometric and calorimetric study would result in a species distribution change, and therefore in erroneous assignments of the n.m.r. data. Investigations of systems that would not limit the use of n.m.r. spectroscopy should permit a clear-cut correlation of the thermodynamic data with the structural characteristics of the dimethyltin cation in aqueous solution.

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