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The Thermodynamic Studies of the Molecular Interactions of Diethyl- and Dibutyltin(IV) Dichloride with Free Base *meso*-Tetraarylporphyrins

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The thermodynamic parameters for the interactions of Et_2SnCl_2 and Bu_2SnCl_2 with *para*-substituted *meso*-tetraphenylporphyrins ($H_2T(4\text{-}X)PP$; X = OCH_3, CH_3, H, Cl) were determined. The overall formation constants K ($mol^{-2}\ dm^6$), where ($K = K_1 \times K_2$), were calculated by using UV–vis spectrophotometry titration, and a data refinement was carried out with a computer program, SQUAD. The adducts had a 2 : 1 composition of R_2SnCl_2 to porphyrin. The overall formation constants decreased with decreasing electron releasing of porphyrins and increasing steric hindrance on an organotin compound, as follow: $H_2T(4\text{-}CH_3O)PP > H_2T(4\text{-}CH_3)PP > H_2TPP > H_2T(4\text{-}Cl)PP$ and $Et_2SnCl_2 > Bu_2SnCl_2$.

The thermodynamics of organotin(IV) halides adducts with various uni- and bidentate ligands have been the subject of many studies.[1–4] Recently, more attention has concentrated on the antitumour properties of organotin(IV) halides, and a large number of studies have been made concerning the interactions of these compounds with biological systems.[5–9] The molecular interactions of tetraarylporphyrins with π-acceptor molecules, such as nitroaromatic systems,[10–12] tetracyanoethylene,[13] and 2,3-dichloro-5,6-dicyanobenzoquinone, have been studied.[14]

In the present work we investigated the thermodynamic parameters for the interaction of diethyl- and dibutyltin(IV) dichloride with H_2TPP (*meso*-tetraphenylporphyrin), $H_2T(4\text{-}Cl)PP$ (*meso*-tetrakis(*p*-chlorophenyl)porphyrin), $H_2T(4\text{-}CH_3)PP$ (*meso*-tetrakis(4-methylphenyl)porphyrin), and $H_2T(4\text{-}CH_3O)PP$ (*meso*-tetrakis(4-methoxyphenyl)porphyrin) in chloroform as a solvent.

Experimental

Reagents: Benzaldehyde and *para*-substituted benzaldehydes (Merck and Fluka) were used as received. Pyrrole (Fluka) was distilled before use. Propionic acid and chloroform (Merck) were employed for the synthesis and purification of porphyrins were used as received. Chloroform solvent for UV–vis measurements was distilled over K_2CO_3 before use. Diethylether was distilled over $LiAlH_4$, and then used for preparing Grignard reagent.

Instrumental: UV–vis measurements were preformed using a Jasco V-530 UV–vis spectrometer equipped with a LAUDA ecoline RE 104 thermostat.

Preparations: Diethyltin(IV) dichloride was prepared by a reaction between Et_4Sn and anhydrous $SnCl_4$ and purified by sublimation.[15] Et_4Sn was prepared according to the Kocheskov method by a reaction of anhydrous $SnCl_4$ with Grignard reagent (EtMgBr) in dry diethylether and purified by vacuum distillation.[16] Dibutyltin(IV) dichloride was purchased from Fluka and used without further purification. H_2TPP, $H_2T(4\text{-}Cl)PP$, $H_2T(4\text{-}CH_3)PP$, $H_2T(4\text{-}CH_3O)PP$ were prepared and purified by the usual methods.[17]

General Method: UV–vis measurements were carried out by a titration method at 5, 10, 15, 20, and 25 °C. In a typical measurement, 2.5 mL solution of H_2TPP (1×10^{-5} mol dm^{-3}) in chloroform was titrated by Et_2SnCl_2 (0.0166 mol dm^{-3}). UV–vis spectra were recorded over the range of 396–710 nm about 15 min after each addition. In this range of spectra, about 30–45 wavelengths that have suitable variations of absorbance were selected, and the formation constants and the other thermodynamic parameters of adduct formations were calculated. The overall formation constants K ($mol^{-2}\ dm^6$) were calculated by the SQUAD program.[18,19]

SQUAD is a program with a capability to refine the stability constants of a general complex, $M_mM_lH_kL_nL_q$, where $m, l, n, q > 0$ and k is positive for protons and negative (hydroxide ions) or zero, employing a non-linear least-squares approach. The data fed to SQUAD are the absorption spectra, chemical composition (total concentrations of M, M′, L, L′, and pH) and a chemical model to describe the system. The residual sum (U) is calculated from the following equation:

$$U = \Sigma_1{}^{I}\Sigma_I{}^{NW}\,(A_{i,k}{}^{calc} - A_{i,k}{}^{obs})^2,$$

where the $A_{i,k}$ is the absorbance value of the ith solution at the kth wavelength. A total of I solutions and a grand total of NW wavelength are given.

Results and discussion

Upon the addition of excess folds of R_2SnCl_2 (R = Et, Bu) to a solution of free base porphyrin in chloroform, its purple color changes to green. This change in color is due to the interactions of R_2SnCl_2 with porphyrin. By the addition of *n*-hexane to these green solutions, slowly, green powdery products were obtained; attempts to further purify and recrystallize these crude products were unsuccessful. This product can also be obtained by dissolving $H_2T(4\text{-}X)PP$ and excess folds of R_2SnCl_2 in $CHCl_3$ or CH_2Cl_2, followed by evaporation of the solvent at room temperature. An elemental analysis of these

Table 1. Elemental Microanalysis of $[(R_2SnCl_2)_2H_2T(4\text{-}X)PP]$ Adducts

Adduct	Found			Calculated		
	C/%	H/%	N/%	C/%	H/%	N/%
$(Et_2SnCl_2)_2H_2T(4\text{-}Cl)PP$	49.18	3.70	4.29	49.96	3.68	4.48
$(Et_2SnCl_2)_2H_2TPP$	55.46	4.44	4.79	56.17	4.50	5.04
$(Et_2SnCl_2)_2H_2T(4\text{-}CH_3)PP$	56.86	4.73	4.55	57.59	4.97	4.80
$(Et_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP$	55.51	4.98	4.56	54.60	4.71	4.55
$(Bu_2SnCl_2)_2H_2T(4\text{-}Cl)PP$	51.88	3.70	4.29	52.91	4.56	4.12
$(Bu_2SnCl_2)_2H_2TPP$	55.79	4.96	4.63	58.97	5.41	4.59
$(Bu_2SnCl_2)_2H_2T(4\text{-}CH_3)PP$	58.75	5.45	4.63	60.15	5.80	4.39
$(Bu_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP$	55.65	5.49	3.83	57.28	5.52	4.18

products (Table 1) as well as a spectrophotometry titration curve (Fig. 1) show good agreement with adducts of a 2:1 composition of R_2SnCl_2 to $H_2T(4\text{-}X)PP$. The interactions of R_2SnCl_2 with $H_2T(4\text{-}X)PPs$ are reversible and very sensitive to temperature (see Fig. 2). Upon increasing the temperature, the green color changes to brown, and then eventually returns to the primary color of free base porphyrin solution. Adduct formation is not observed in ligating solvents, such as CH_3CN and DMSO; the addition of these solvents to chloroform leads to dissociation of the adducts. Interactions of diethyl- and dibutyltin(IV) dichloride with porphyrins were studied by means of UV–vis spectrophotometry.

Thermodynamic Studies: Upon the interaction of free base tetraarylporphyrins with R_2SnCl_2 Lewis acids the original

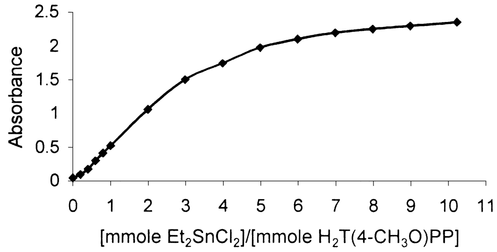


Fig. 1. Spectrophotometric titration curve for titration of $H_2T(4\text{-}CH_3O)PP$ (5×10^{-6} mol dm^{-3}) with Et_2SnCl_2 (2.5×10^{-3} mol dm^{-3}) at 5 °C, because of non-rigid structure of H_2TpAP and dissociation of adduct, mole ratio obtained for adduct in solution is grater than two (≈ 2.6). On the other hand, for completion of reaction a little excess of Et_2SnCl_2 is needed.

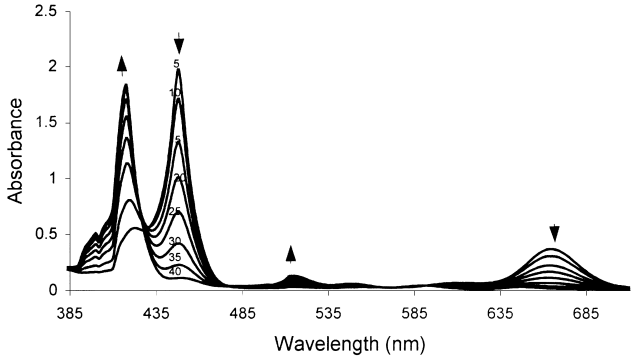
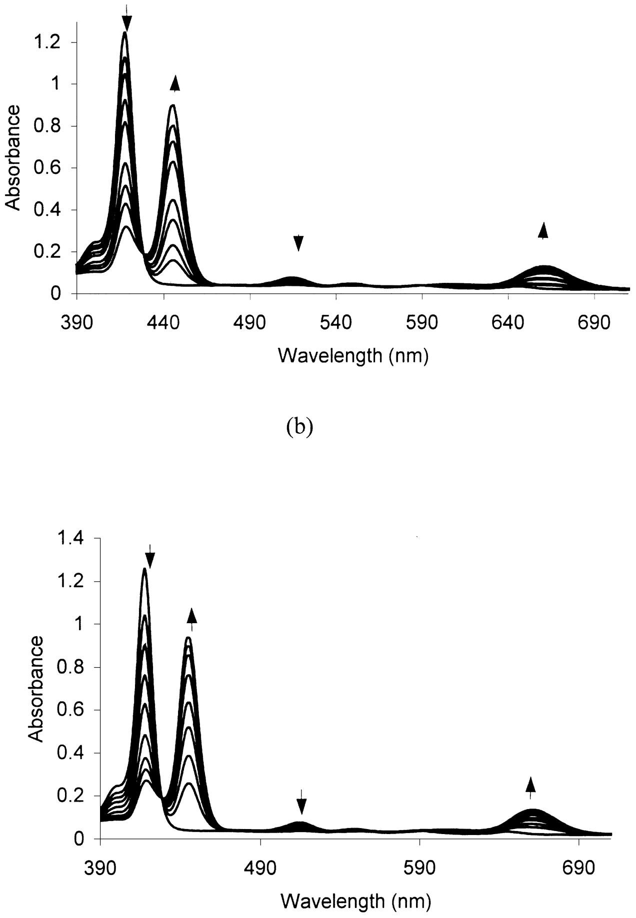


Fig. 2. Thermal dissociation spectra of $(Et_2SnCl_2)_2H_2TPP$ adduct: By addition of Et_2SnCl_2 (0.0166 mol dm^{-3}, 0.5 mL) to the solution of H_2TPP (5×10^{-6} mol dm^{-3}, 2.5 mL) in chloroform in a UV–vis cell at 5 °C, the $(Et_2SnCl_2)_2H_2TPP$ adducts was formed. Then composition of the cell has remained constant and the temperature was raised to 40 °C stepwisely. This spectrum is similar to the previous work on acidic dissociation of ClHg-TPP-HgCl complex,[24] in which ClHg-TPP-HgCl returned to H_2TPP and $HgCl_2$.



(b)

(a)

Fig. 3. Typical spectrophotometric titration curve for titration of H_2TPP (3×10^{-6} mol dm^{-3}): (a) with Bu_2SnCl_2 (0.0025 mol dm^{-3}; isosbestic point at 426 nm); (b) with Et_2SnCl_2 (0.0025 mol dm^{-3}; isosbestic point at 428 nm) in chloroform. Bands appeared at 444 and 660 nm are related to the adducts.

peaks of tetraarylporphyrins slowly vanished and two new peaks appeared (Figs. 3a and 3b). For example, upon the addition of Et_2SnCl_2 to H_2TPP, the original peaks λ (417, 514, 549, 589, and 646 nm) vanished and the new peaks appeared at λ (444 and 660 nm). The clear isosbestic points in Figs. 2 and 3 represent corresponding adduct formations in solutions. Tables 2 and 3 give the original peaks of free base porphyrins and two new peaks produced by the addition of Et_2SnCl_2 or Bu_2SnCl_2 to a solution of porphyrin in chloroform, respectively.

The thermodynamic parameters are useful tools for studying these interactions and understanding the relative stability of the adducts. The overall formation constants, K ($mol^{-2}\ dm^6$), were determined at several temperatures by analyzing the concentration and the temperature dependence of UV–vis absorptions by the SQUAD program. These absorptions were analyzed by proposing the following mole ratios of the acid to base as models of the interaction between the R_2SnCl_2 (R = Et, Bu) and the typical porphyrin: (1) the formation of a 1:1 adduct, (2) the formation of a 2:1 adduct, (3) the simultaneous formation of 1:1 and 2:1 adducts. In fitting the model to the experimental data, 15 points were measured by summing the squares of the deviations of the experimental points from the point calculated by the model. For the proposed models the formation of a 2:1 adduct of acid to base in the case of both diethyl- and dibutyltin(IV) dichloride has the best fitting and the produced error sum of squares was 10^{-2}–10^{-3}. Van't Hoff plots of these overall formation constants, K ($mol^{-2}.dm^6$), lead to other thermodynamic parameters, $\Delta H°$ and $\Delta S°$ (Tables 6, 7).

The data in Tables 4 and 5 show that the overall formation constant, K ($mol^{-2}\ dm^6$) of the adducts undergo a regular increase from $H_2T(4\text{-}Cl)PP$, H_2TPP, $H_2T(4\text{-}CH_3)PP$, to $H_2T(4\text{-}CH_3O)PP$, respectively. For example, at 5 °C we have the following order of the overall formation constants, K ($mol^{-2}\ dm^6$): Et_2SnCl_2–$H_2T(4\text{-}Cl)PP$ < Et_2SnCl_2–H_2TPP < Et_2SnCl_2–$H_2T(4\text{-}CH_3)PP$ < Et_2SnCl_2–$H_2T(4\text{-}CH_3O)PP$, 1.8×10^5

Table 2. UV–Vis Peaks λ($CHCl_3$, nm) of the Free Base Tetraarylporphyrins and Tetraarylporphyrins of the Adducts with Et_2SnCl_2

$H_2T(4\text{-}Cl)PP$	418 (5.65)[a]	514	550	590	646
$(Et_2SnCl_2)_2H_2T(4\text{-}Cl)PP$	448 (5.54)	—	—	—	664
H_2TPP	417 (5.69)	514	549	589	646
$(Et_2SnCl_2)_2H_2TPP$	444 (5.61)	—	—	—	660
$H_2T(4\text{-}CH_3)PP$	419 (5.71)	516	553	591	649
$(Et_2SnCl_2)_2H_2T(4\text{-}CH_3)PP$	447 (5.63)	—	—	—	670
$H_2T(4\text{-}CH_3O)PP$	421 (5.72)	518	555	594	649
$(Et_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP$	453 (5.64)	—	—	—	688

a) log (ε/mol $dm^{-3}\ cm^{-1}$).

Table 3. UV–Vis Peaks λ($CHCl_3$, nm) of the Free Base Tetraarylporphyrins and Tetraarylporphyrins of the Adducts with Bu_2SnCl_2

$H_2T(4\text{-}Cl)PP$	418 (5.65)[a]	514	550	590	646
$(Bu_2SnCl_2)_2H_2T(4\text{-}Cl)PP$	448 (5.51)	—	—	—	664
H_2TPP	417 (5.69)	514	549	589	646
$(Bu_2SnCl_2)_2H_2TPP$	444 (5.57)	—	—	—	660
$H_2T(4\text{-}CH_3)PP$	419 (5.71)	516	553	591	649
$(Bu_2SnCl_2)_2H_2T(4\text{-}CH_3)PP$	447 (5.62)	—	—	—	670
$H_2T(4\text{-}CH_3O)PP$	421 (5.72)	518	555	594	649
$(Bu_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP$	453 (5.63)	—	—	—	688

a) log (ε/mol $dm^{-3}\ cm^{-1}$).

Table 4. The Overall Formation Constants K ($mol^{-2}\ dm^6$) for Et_2SnCl_2 Adducts with Tetraarylporphyrins in $CHCl_3$ Solvent[a]

Temp/°C	5	10	15	20	25
$(Et_2SnCl_2)_2H_2T(4\text{-}Cl)PP$	1.8×10^5	5.7×10^4	2.3×10^4	1.1×10^4	—
	$(\pm1\times10^4)$	$(\pm1\times10^3)$	$(\pm1\times10^3)$	$(\pm1\times10^3)$	—
$(Et_2SnCl_2)_2H_2TPP$	2.4×10^6	7.4×10^5	3.4×10^5	1.2×10^5	—
	$(\pm1\times10^5)$	$(\pm1\times10^4)$	$(\pm2\times10^4)$	$(\pm1\times10^4)$	—
$(Et_2SnCl_2)_2H_2T(4\text{-}CH_3)PP$	9.1×10^6	3.2×10^6	1.1×10^6	2.8×10^5	1.3×10^5
	$(\pm1\times10^5)$	$(\pm1\times10^5)$	$(\pm1\times10^5)$	$(\pm1\times10^5)$	$(\pm1\times10^5)$
$(Et_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP$	1.2×10^8	2.2×10^7	1.1×10^7	2.4×10^6	8.5×10^5
	$(\pm1\times10^7)$	$(\pm1\times10^6)$	$(\pm1\times10^6)$	$(\pm1\times10^5)$	$(\pm1\times10^4)$

a) Numbers in the parentheses are standard deviations.

Table 5. The Overall Formation Constants K ($\mathrm{mol}^{-2}\ \mathrm{dm}^6$) for Bu_2SnCl_2 Adducts with Tetraarylporphyrins in $CHCl_3$ Solvent[a)]

Temp/°C	5	10	15	20	25
$(Bu_2SnCl_2)_2H_2T(4\text{-}Cl)PP$	5.0×10^4	2.1×10^4	6.6×10^3	3.5×10^3	1.3×10^3
	$(\pm1\times10^3)$	$(\pm1\times10^4)$	$(\pm1\times10^2)$	$(\pm1\times10^2)$	$(\pm1\times10^2)$
$(Bu_2SnCl_2)_2H_2TPP$	4.9×10^5	2.2×10^5	7.6×10^4	2.4×10^4	1.1×10^4
	$(\pm1\times10^4)$	$(\pm1\times10^4)$	$(\pm1\times10^3)$	$(\pm1\times10^3)$	$(\pm1\times10^3)$
$(Bu_2SnCl_2)_2H_2T(4\text{-}CH_3)PP$	7.7×10^6	2.5×10^6	9.8×10^5	2.1×10^5	1.4×10^5
	$(\pm1\times10^5)$	$(\pm1\times10^5)$	$(\pm1\times10^4)$	$(\pm1\times10^4)$	$(\pm1\times10^4)$
$(Bu_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP$	7.1×10^7	1.4×10^7	5.7×10^6	1.6×10^6	6.3×10^5
	$(\pm1\times10^6)$	$(\pm1\times10^6)$	$(\pm1\times10^5)$	$(\pm1\times10^5)$	$(\pm1\times10^4)$

a) Numbers in the parentheses are standard deviations.

Table 6. Thermodynamic Parameters[a)] for Interactions of Et_2SnCl_2 with Tetraarylporphyrins in Chloroform

	ΔH°	ΔS°	$\Delta G^{\circ\ \mathrm{b)}}$
$(Et_2SnCl_2)_2H_2T(4\text{-}Cl)PP$	-125 ± 14	-348 ± 50	-26 ± 14
$(Et_2SnCl_2)_2H_2TPP$	-134 ± 5	-360 ± 19	-32 ± 5
$(Et_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP$	-145 ± 4	-393 ± 16	-35 ± 4
$(Et_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP$	-164 ± 12	-436 ± 41	-40 ± 12

a) ΔH° ($\mathrm{kJ\ mol^{-1}}$) and ΔS° ($\mathrm{J\ K^{-1}\ mol^{-1}}$).

b) ΔG° at 10 °C ($\mathrm{kJ\ mol^{-1}}$)

Table 7. Thermodynamic Parameters[a)] for Interactions of Bu_2SnCl_2 with Tetraarylporphyrins in Chloroform

	ΔH°	ΔS°	$\Delta G^{\circ\ \mathrm{b)}}$
$(Bu_2SnCl_2)_2H_2T(4\text{-}Cl)PP$	-120 ± 5	-344 ± 19	-23 ± 5
$(Bu_2SnCl_2)_2H_2TPP$	-132 ± 6	-364 ± 23	-29 ± 6
$(Bu_2SnCl_2)_2H_2T(4\text{-}CH_{3p})PP$	-140 ± 11	-373 ± 39	-35 ± 11
$(Bu_2SnCl_2)_2\ H_2T(4\text{-}CH_3O)PP$	-156 ± 5	-412 ± 19	-39 ± 5

a) ΔH° ($\mathrm{kJ\ mol^{-1}}$) and ΔS° ($\mathrm{J\ K^{-1}\ mol^{-1}}$).

b) ΔG° at 10 °C ($\mathrm{kJ\ mol^{-1}}$).

$< 2.4\times10^6 < 9.1\times10^6 < 1.2\times10^8$; Bu_2SnCl_2–$H_2T(4\text{-}Cl)PP$ < Bu_2SnCl_2–H_2TPP < Bu_2SnCl_2–$H_2T(4\text{-}CH_3)PP$ < Bu_2SnCl_2–$H_2T(4\text{-}CH_3O)PP$, $5.0\times10^4 < 4.9\times10^5 < 7.7\times10^6 < 7.1\times10^7$.

Tables 6 and 7 show the thermodynamic parameters obtained for the interactions of Et_2SnCl_2 and Bu_2SnCl_2 with $H_2T(4\text{-}CH_3O)PP$, $H_2T(4\text{-}CH_3)PP$, H_2TPP, and $H_2T(4\text{-}Cl)PP$ in chloroform.

Our work shows that the kind of substituent (X) on the phenyl rings of the $H_2T(4\text{-}X)PP$ significantly influences the interactions of the corresponding porphyrin with the dialkyltin(IV) dichloride via its electron-releasing property. Both the free energy and the enthalpy of adduct formations become considerably more negative through the series $H_2T(4\text{-}Cl)PP$, H_2TPP, $H_2T(4\text{-}CH_3)PP$, to $H_2T(4\text{-}CH_3O)PP$ which indicates the stronger interaction along this sequence.

Our results are in agreement with a preequilibrium step demonstrated by previous studies on the kinetics of the incorporation of some divalent metal ions into the free base porphyrins. Tanaka et al.[20] investigated the reaction of transition metal ions with H_2TPP in DMF. They suggested pre-complexes ($M\text{-}H_2TPP$, M = Cu(II), Zn(II)) with the formation constant K, 1.6×10^4 for Cu(II) and 7.2×10^2 for Zn(II). Similar results were obtained by Hambright and Robinson[21] on the kinetics of the catalyzed and the uncatalyzed incorporation of Zn(II) into free base porphyrins(H_2P) in DMF. They suggested that metal ions and porphyrins form an intermediate with composition [$M\text{-}H_2P$; M = Zn(II), Cd(II), Cu(II)][20,21] in which the coordination of H_2P with a metal ion causes the porphyrin plane to deform, in such a manner that a second metal ion is readily able to be incorporated into this bent porphyrin structure on the opposite side. Thus, formation of the $M\text{-}H_2P\text{-}Zn$ is followed by dropping the Zn(II) ion into the porphyrin cavity.[21,22] However, we considered stable adducts, because our bulky Lewis acids, R_2SnCl_2, couldn't be dropped into the porphyrin cavity under these conditions. We think that primarily 1:1 adduct formation, [$(R_2SnCl_2)H_2T(4\text{-}X)PP$], induces a distortion of the porphyrin plane; this deformation would enhance the coordinating ability of the nitrogen lone pairs by directing them away from the central porphyrin cavity. Therefore, the distorted porphyrin more readily accepts a second R_2SnCl_2 molecule at the opposite side and eventually favors the formation of a 2:1 adduct [$(R_2SnCl_2)_2H_2T(4\text{-}X)PP$].[23] Presumably, a 1:1 adduct has a smaller stability relative to the corresponding successive 2:1 adduct; thus, we couldn't determine the formation constants, K_1 ($\mathrm{mol^{-1}\ dm^3}$) and K_2 ($\mathrm{mol^{-1}\ dm^3}$) separately. The adducts have negative values of ΔH°, ΔS°, and ΔG°. Generally, the negative values of $\Delta S°$ refer to the association between the donor and the acceptor molecules, let alone the solvation contribution in $\Delta S°$ (see Tables 6 and 7). The most negative values of $\Delta H°$, and $\Delta G°$ for the $(R_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP$ system indicate stronger interactions in this system relative to the other members of the corresponding series. These results show that the interactions of *para*-substituted tetraphenylporphyrins toward R_2SnCl_2 (R = Et, Bu) vary in the order: $H_2T(4\text{-}CH_3O)PP > H_2T(4\text{-}CH_3)PP > H_2TPP > H_2T(4\text{-}Cl)PP$.

This trend is in accord with the electron-releasing properties of the free base porophyrins. On the other hand, a comparison of the formation constants and other thermodynamic parameters show that replacing the ethyl- by a more bulky butyl- group on an organotin compound causes a weakening of the interactions. The butyl- group can affect the interaction in two ways: 1) A more bulky butyl- group makes adduct formation unfavorable because of its greater steric hindrance than an ethyl- group.[2] 2) Butyl-groups, through, have better electron-releasing properties to reduce the acid strength of an organotin Lewis acid and to decrease its interactions with porphyrins.

However, this is in accord whit the Lewis acidity of dialkyltin(IV) dichlorides:[8]

$$Et_2SnCl_2 > Bu_2SnCl_2.$$

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