Synthesis of Sitting-Atop Type Adducts of Diphenyl and Dimethyltin(IV) Dihalides with *meso*-Tetraarylporphyrins

Abedien Zabardasti [†]*, Mozaffar Asadi [††] and Ali Kakanejadifard [†]

[†]Chemistry Department, College of Sciences, Lorestan University, Khoramabad, I.R. IRAN.
E-mail: zabardasti.a@lu.ac.ir; Tel-fax: +986612200185
[††]Chemistry Department, College of Sciences, Shiraz University, Shiraz, I.R. IRAN.
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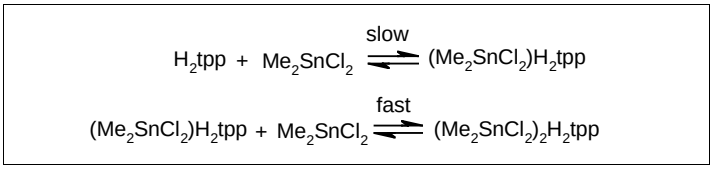

Some molecular adducts of dimethyltin(IV) dichloride, diphenyltin(IV) dichloride and diphenyltin(IV) dibromide with *para*-substituted *meso*-tetraphenylporphyrin have been prepared. This adducts with general formula [$(Me_2SnCl_2)_2H_2T(4\text{-}X)PP$], [$(Ph_2SnCl_2)_2H_2T(4\text{-}X)PP$], and [$(Ph_2SnBr_2)_2H_2T(4\text{-}X)PP$]; {X= CH_3O, CH_3, H, and Cl} have been synthesized and characterized by means of ^1H NMR, UV-Vis, and elemental microanalysis methods.

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Introduction.

Interactions of organotin(IV) halides with biological systems are of interest [1-3]. These encouraging studies prompted us to explore the interactions of organotin(IV) halides with a number of free base *meso*-tetraarylporphyrins. In earlier work we studied the adduct formation of organotin(IV) halides with free base porphyrins in solution. The thermodynamic parameters for adducts of R_2SnCl_2 (R= Me, Et, Bu) with $H_2T(4\text{-}X)PP$ (X= CH_3O, CH_3, Cl, H) and $MeSnBr_3$ with $H_2T(4\text{-}X)PP$ {X= CH_3O, CH_3, Cl, H} and $H_2T(3\text{-}X)PP$ {X= Me, Cl} were investigated [4-6]. The following sequences for stability of adducts with respect to the free base porphyrins and organotin(IV) halides were found: $MeSnBr_3 > Me_2SnCl_2 > Et_2SnCl_2 > Bu_2SnCl_2$ and $H_2T(4\text{-}CH_3O)PP > H_2T(4\text{-}CH_3)PP > H_2TPP > H_2T(4\text{-}Cl)PP > H_2T(4\text{-}NO_2)PP$.

The first trends indicate a direct dependence between basicity of the free base porphyrins and adduct stability. On the other hand, adduct stability decreased with increasing bulkiness and number of alkyl- groups on the tin atom. Here we are reporting the synthesis and spectral properties of dimethyltin(IV) dichloride, diphenyltin(IV) dichloride and diphenyltin(IV) dibromide adducts with free base porphyrins, $H_2T(4\text{-}X)PP$s. The $H_2T(4\text{-}X)PP$s are *meso*-tetraphenylporphyrin(H_2TPP), *meso*-tetrakis(4-chlorophenyl)porphyrin($H_2T(4\text{-}Cl)$ PP), *meso*-tetrakis(4-methylphenyl)porphyrin($H_2T(4\text{-}CH_3)PP$) and *meso*-tetrakis(4-methoxyphenyl)porphyrin ($H_2T(4\text{-}CH_3O)PP$). We believe that $H_2T(4\text{-}X)PP$s act as bidentate bridging ligands toward organotin(IV) halides. A structural resemblance to so called Sitting-Atop type (SAT) complex [7-12], is expected for these adducts. It seems, that our stable adducts are unique and can give remarkable information about structure of the SAT complex and helps the kinetics study of metallation of the free base porphyrins.

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*) employed for the synthesis and the purification of porphyrins were used as received. Chloroform solvent for UV-Vis measurements was distilled over K_2CO_3 before use. $CDCl_3$ was used as the NMR solvent and the chemical shifts were determined relative to $CHCl_3$ line (7.26 ppm). Me_4Sn (*Fluka*) and Ph_4Sn (*Merck*) were used as received.

Instrumental.

UV-Vis measurements were done by Jasco V-530 UV-Vis spectrometer equipped with a LAUDA ecoline RE 104 thermostat. The proton NMR spectra were run on a Brucker Avance DPX 250 MHz spectrometer.

Preparations.

Dimethyltin(IV) dichloride was prepared by the reaction of Me_4Sn and anhydrous $SnCl_4$ and purified by sublimation [13]. Diphenyltin(IV) dichloride was prepared by comproportionation reaction of Ph_4Sn with anhydrous $SnCl_4$ and purified by recrystallization from petroleum ether boiling point 50-70 °C [14]. Diphenyltin(IV) dibromide was prepared by reaction of Ph_2SnO with hydrobromic acid and purified by recrystallization from petroleum ether boiling point 50-70 °C. Ph_2SnO were obtained by hydrolysis of Ph_2SnCl_2 in alkali solution. Free base porphyrins H_2TPP, $H_2T(4\text{-}Cl)PP$, $H_2T(4\text{-}CH_3)PP$, $H_2T(4\text{-}CH_3O)PP$ were prepared by reported methods [15], and purified by column chromatography on neutral alumina.

General Procedure for the Synthesis of *meso*-Tetraaryl-porphyrins [15].

meso-Tetrakis-(4-methoxyphenyl)porphyrin.

4-methoxybenzaldehyde (10 mmoles) was mixed with propionic acid (35 ml) and nitrobenzene (15 ml). Pyrrole (10 mmoles) was added and the mixture was kept at 120°C during 1 hour. On cooling, the porphyrin precipitated directly from the reaction mixture and was isolated by filtration.

Adduct Formations.

Excess of Lewis acids organotin(IV) halide were added to a purple solution of free base porphyrin in chloroform, *n*-hexane was added to the resulted green solution, slowly, and green powdery products were obtained, elemental analyses are compiled in Table I. These products can also be obtained by dissolving the respective $H_2T(4\text{-}X)PP$ and an excess of organotin(IV) halides in $CHCl_3$ or CH_2Cl_2 and evaporation of the solvent at room temperature, unreacted substances were settled on the wall of the beaker (reaction flask) and green shiny product were precipitated.

On the other hand, phenyl- and methyl protons of organotin(IV) chloride show a small (about 0.10-0.30 ppm)up field shift with complex formation.

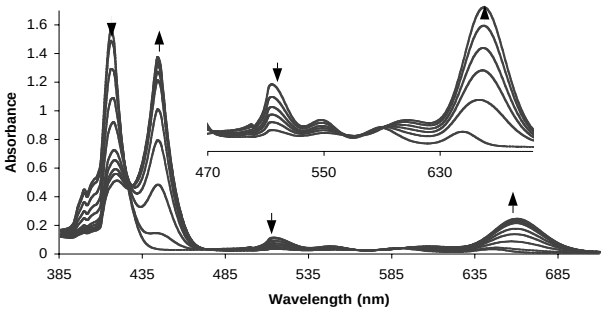

Figure 1. Titration spectra, for titration of $H_2T(4\text{-Cl})PP$ with Ph_2SnCl_2 in chloroform. Bands appeared at 448 and 664 nm are related to adduct, isosbestic point at 428 nm.

Table I

Elemental Analysis of Diorganotin(IV) dihalide-porphyrin Adduct

	Found			Calculated		
	%C	%H	%N	%C	%H	%N
$(Me_2SnCl_2)_2H_2TPP,0.5CHCl_3$	52.15	3.89	4.98	52.30	3.85	5.03
$(Me_2SnCl_2)_{1.9}H_2T(4\text{-Cl})PP$	49.07	3.22	4.79	49.03	3.20	4.77
$(Me_2SnCl_2)_{1.7}H_2T(4\text{-}CH_3)PP$	59.10	4.72	5.30	59.11	4.65	5.36
$(Me_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP,0.5CHCl_3$	51.13	4.46	4.50	51.10	4.13	4.54
$(Ph_2SnCl_2)_2H_2TPP,\ 0.23CHCl_3$	61.57	3.91	3.98	61.62	3.81	4.21
$(Ph_2SnCl_2)_2H_2T(4\text{-Cl})PP,0.45CHCl_3$	55.10	3.37	3.18	55.02	3.14	3.75
$(Ph_2SnCl_2)_2H_2T(4\text{-}CH_3)PP,0.6CHCl_3$	60.85	4.01	3.82	60.97	4.13	3.92
$(Ph_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP,0.6CHCl_3$	58.30	3.76	3.35	58.35	3.95	3.75
$(Ph_2SnBr_2)_2H_2TPP$	55.60	3.80	4.20	55.19	3.38	3.78
$(Ph_2SnBr_2)_2H_2T(4\text{-Cl})PP$	50.60	3.20	3.60	50.49	2.84	3.46
$(Ph_2SnBr_2)_2H_2T(4\text{-}CH_3)PP,0.8CHCl_3$	53.50	3.90	3.30	53.58	3.63	3.43
$(Ph_2SnBr_2)_2H_2T(4\text{-}CH_3O)PP,CHCl_3$	50.70	3.70	3.00	50.98	3.46	3.25

Results and Discussion.

UV-Vis analysis.

Interaction of $H_2T(4\text{-}X)PP$ with organotin(IV) halides caused the original peaks of free base porphyrins to disappear and two new peaks to appeare (Figure 1 and Table II). For instance by addition of Ph_2SnCl_2 to $H_2T(4\text{-Cl})PP$ the original peaks (418, 514, 550, 590, 646 nm) of the free base vanished and new peaks appeared at (448 and 664 nm) which distinctly differ from the original peaks of the free base $H_2T(4\text{-Cl})PP$. The isosbestic point at 428 nm indicates the presence of an equilibrium in solution, Figures 1, 2.

^{1}H NMR Analysis.

^{1}H NMR spectra of the porphyrin moiety of the adducts show clear differences with respect to corresponding free base porphyrin. Upon complexation of free base porphyrins with organotin halids the signals correspond to N-H, H_o, $H_{m,p}$, and CH_3- or -CH_3O protons of *para*-substituents porphyrin moved down field, while H_β has an up field shift (Table III, Figure 3).

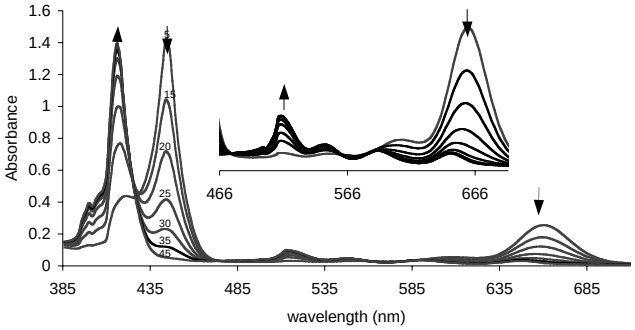

Figure 2. Temperature dependence of absorption profile of the $[(Ph_2SnCl_2)_2H_2T(4\text{-Cl})PP]$ adduct in chloroform. By addition of Ph_2SnCl_2 (0.0125 *M*, 0.5 ml) to the solution of $H_2T(4\text{-Cl})PP$ (5×10^{-6} *M*, 2.5 ml) in chloroform in an UV-Vis cell at 5 °C, the $(Ph_2SnCl_2)_2H_2T(4\text{-Cl})PP$ adduct was formed. Then composition of the cell has kept constant and the temperature was raised to 45 °C stepwisely.

The ^{1}H NMR spectra of adducts show some interesting results. The ^{1}H NMR of these adducts were studied in $CDCl_3$ at

Table II

UV-Vis peaks λ ($CHCl_3$/nm) of the $H_2T(4\text{-}X)PP$ and their Adducts

$H_2T(4\text{-}Cl)PP$	418	514	550	590	646	$H_2T(4\text{-}CH_3)PP$	419	516	552	591	647
$(Me_2SnCl_2)_{1.9}H_2T(4\text{-}Cl)PP$	447		-		664	$(Me_2SnCl_2)_{1.7}H_2T(4\text{-}CH_3)PP$	448	-	-	-	672
$(Ph_2SnCl_2)_2H_2T(4\text{-}Cl)PP$	448	-	-	-	664	$(Ph_2SnCl_2)_2H_2T(4\text{-}CH_3)PP$	448	-	-	-	670
$(Ph_2SnBr_2)_2H_2T(4\text{-}Cl)PP$	452	-	-	-	668	$(Ph_2SnBr_2)_2H_2T(4\text{-}CH_3)PP$	450	-	-	-	676
H_2TPP	417	514	549	589	646	$H_2T(4\text{-}CH_3O)PP$	421	518	555	594	649
$(Me_2SnCl_2)_2H_2TPP$	445	-	-	-	660	$(Me_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP$	453	-	-	-	690
$(Ph_2SnCl_2)_2H_2TPP$	444	-	-	-	660	$(Ph_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP$	453	-	-	-	688
$(Ph_2SnBr_2)_2H_2TPP$	448	-	-	-	662	$(Ph_2SnBr_2)_2H_2T(4\text{-}CH_3O)PP$	456	-	-	-	694

Table III

^1H NMR Chemical Shift (δ/ppm) of the $H_2T(4\text{-}X)PP$ and their Adducts Relative to $CHCl_3$

	δN-H	$\delta H_{m,p}$	δH_o	δH_β	δCH_3
H_2TPP	-2.71	7.81	8.26	8.87	
$(Me_2SnCl_2)_2H_2TPP$	0.00	7.95-8.02	8.57-8.62	8.57-8.62	
$(Ph_2SnCl_2)_2H_2TPP$	0.00	8.05-8.07	8.64	8.64	
$(Ph_2SnBr_2)_2H_2TPP$	-0.45	7.92-8.00	8.54-8.57	8.54-8.57	
$H_2T(4\text{-}Cl)PP$	-2.86	7.75	8.14	8.85	
$(Me_2SnCl_2)_{1.9}H_2T(4\text{-}Cl)PP$	0.00	8.00-8.05	8.54-8.59	8.54-8.59	
$(Ph_2SnCl_2)_2H_2T(4\text{-}Cl)PP$	0.00	8.04-8.07	8.53-8.62	8.53-8.62	
$(Ph_2SnBr_2)_2H_2T(4\text{-}Cl)PP$	0.00	8.18-8.21	8.37	8.52	
$H_2T(4\text{-}CH_3)PP$	-2.77	7.56	8.11	8.86	2.71
$(Me_2SnCl_2)_{1.7}H_2T(4\text{-}CH_3)PP$	0.00	7.94-8.02	8.50-8.54	8.50-8.54	2.89
$(Ph_2SnCl_2)_2H_2T(4\text{-}CH_3)PP$	0.00	7.83-7.86	8.49-8.59	8.49-8.59	2.80
$(Ph_2SnBr_2)_2H_2T(4\text{-}CH_3)PP$	-0.30	7.83-7.86	8.51-8.56	8.51-8.56	2.79
$H_2T(4\text{-}CH_3O)PP$	-2.82	7.23	8.07	8.79	3.95
$(Me_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP$	0.00	7.50-7.58	8.48-8.55	8.48-8.55	4.11
$(Ph_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP$	0.00	7.41-7.56	8.37-8.42	8.37-8.42	4.04
$(Ph_2SnBr_2)_2H_2T(4\text{-}CH_3O)PP$	0.00	7.94	8.24-8.27	8.48-8.53	4.08

-30 ºC. For instance by complexation of $H_2T(4\text{-}Cl)PP$ with Ph_2SnCl_2, the original signals of N-H (-2.86 ppm), H_β (8.85ppm), H_o (8.14ppm), and $H_{m,p}$ (7.75ppm) of the free base $H_2T(4\text{-}Cl)PP$ were shifted to 0.00, 8.53-8.62, 8.53-8.62, and 8.04-8.07 ppm, respectively. Therefore, the ^1H NMR spectra of porphyrin moiety of the adduct have three signals at -30 ºC, Table III, signals related to H_β and H_o overlapped and gave a signal at (8.53-8.62 ppm). From the comparison of the chemical shifts of porphyrin's protons before and after complexation some useful information has been deduced. The internal N-H protons signal moves downfield about 2.86ppm and H_β protons signal move upfield about 0.32 ppm. Both changes are discontinuous and are in the directions to be expected if the aromatic ring current decreases with complexation. The two aromatic proton doublets related to the H_o and $H_{m,p}$ of the phenyl rings of the free base porphyrin also move downfield about 0.40 and 0.29 ppm, respectively. These changes can be described by coordination of porphyrin to the organotin(IV) halide which leads to a

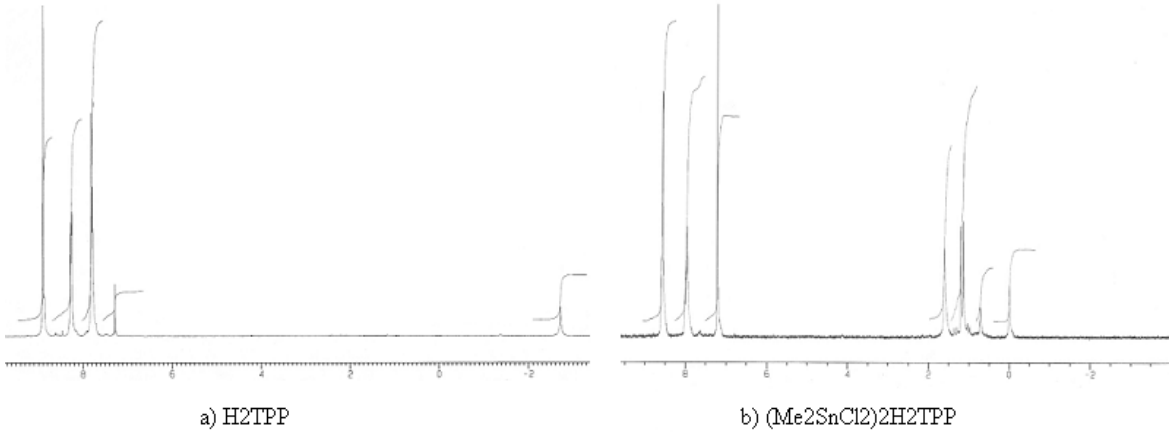

Figure 3. ^1H NMR spectra of: (a) H_2TPP; (b) [$(Me_2SnCl_2)_2H_2TPP$] at -30ºC, in $CDCl_3$. Chemical shifts are relative to $CHCl_3$(7.26 ppm), peaks appeared at 7.46 ppm (a) and 7.26 ppm (b) belong to $CHCl_3$ impurity.

deformation of porphyrin structure from planarity and so decreasing of the aromatic ring current.

According to ^{1}H NMR pattern, it seems that adduct has a symmetric structure, so that coordination of porphyrin to organotin(IV) halide couldn't differentiate between each class of the free base protons (N-H, H_β, H_o, and $H_{m,p}$) with adduct formation and these protons remained equivalent after complexation. On the other hand, we only see a definite shift for each class of protons in the adduct with respect to the corresponding free base porphyrin protons.

The elemental analysis data show that these adducts have the stoichiometry 2:1 of acceptor to donor, $[(Me_2SnCl_2)_2(H_2T(4\text{-}X)PP)]$, $[(Ph_2SnCl_2)_2(H_2T(4\text{-}X)PP)]$, and $[(Ph_2SnBr_2)_2(H_2T(4\text{-}X)PP)]$. It is in a good agreement with our previous results on thermodynamic studies of these adducts [5,6]. For this mole ratio we sketched the proposed structures in Figure 4. In Figure 4 (a), because of the attachment of tin atoms to two of the pyrrolenine nitrogen atoms, splitting of ^{1}H NMR signal of H_βs to produce a doublet for beta hydrogens is expected. On the other hand, in Figure 4(b) H_βs have identical environment, therefore we predict a singlet for them. Experimentally, in the low-temperature ^{1}H NMR spectra of the adducts a singlet appeared for H_βs. This confirms the structure shown in Figure 4(b) for these adducts. On the basis of these results we suggest that free base porphyrin as a bidentate bridging ligand forms a bridge between two molecules of the Lewis acid. It is probable that two neighboring nitrogen atoms of the porphyrin bind to one of the organotin(IV) chloride molecules which are positioned above of the porphyrin plane and the other two nitrogen atoms bind to the second organotin(IV) chloride molecule from below this plane.

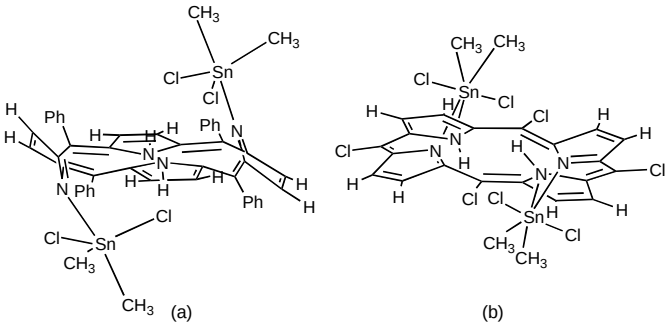

Figure 4. Proposed structures of $[(R_2SnCl_2)_2H_2TPP]$ adduct. (a) H_2TPP as a monodentate bridging ligand made adducts with five-coordinated trigonal bipyramidal structure for tin atoms; (b) H_2TPP as a bidentate bridging ligand make adducts with six-coordinated octahedral structure around the tin atoms. Our ^{1}H NMR data are in consistent with structure (b).

The close resemblance between ^{1}H NMR and especially the electronic spectra of $H_2T(4\text{-}X)PP$ in these adducts with those reported for the corresponding porphyrin diacid, $H_4T(4\text{-}X)PP^{2+}$ is an interesting feature of these studies [16,17]. These observations suggest a similar distortion in the free base porphyrin structure after both organotin adduct and diacid formation.

Our results suggest the presence of the SAT intermediate, which have been kinetically deduced in the course of the mechanistic studies of metallation of the free base porphyrins [7-12,18]. A SAT complex is a complex of a free base porphyrin with a metal ion, where the latter coordinates to both of the unprotonated pyrrole nitrogen atoms. The protons on two of the pyrrole nitrogen atoms prohibit the metal ion from residing in the centre of the porphyrin plane therefore it lies above the ring plane [8,9]. Here dealing with stable adducts, because of our bulky and stable Lewis acids, organotin(IV) halides couldn't drop into the porphyrin cavity. We think, that our results can give good information about details of the SAT structure and make help in better understanding the kinetic of metallation of the free base porphyrins.

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