SHORT PAPER

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Synthesis, characterisation and spectral studies of some molecular adducts of organotin(IV) chlorides with free base *meso*-tetraarylporphyrins[†]

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Some molecular complexes of diethyltin(IV) dichloride and methyltin(IV) trichloride with *para*-substituted *meso*-tetraphenylporphyrins of the general formula $[(Et_2SnCl_2)_2H_2T(4\text{-}X)PP]$ and $[(MeSnCl_3)_2H_2T(4\text{-}X)PP]$; {X= OCH_3, CH_3, H, and Cl} have been synthesised and characterised by means of ^1H NMR, UV-Vis, and elemental microanalysis methods.

Keywords: porphyrins, diethyltin(IV) dichloride, methyltin(IV) trichloride, organotin(IV) halide adducts.

Organotin(IV) halides are very important because of their antitumour properties.[1] Interactions of organotin(IV) halides with biological systems are also of high interest.[2–4] These studies led us to investigate the interactions of organotin(IV) halides with a number of free base *meso*-tetraarylporphyrins. Our earlier work dealt with solution studies of adduct formation of organotin(IV) halides with free base porphyrins. We investigated the thermodynamic parameters for coexistence of 1:1 and 2:1 adducts of Me_2SnCl_2 with $H_2T(4\text{-}X)PP$, with a $K_2 > K_1$, in solution while elemental analysis showed a composition 2:1 of acid to base, $[(Me_2SnCl_2)_2H_2T(4\text{-}X)PP]$, in the solid state.[5] There are some reports of stable complexes ML_2 of dialkyltin(IV) dihalide with monodentate ligands which have been isolated in the solid state, but solution studies have given evidence only for complexes of 1:1 stoichiometry.[6] We studied the thermodynamic parameters for adduct formations of R_2SnCl_2 (R= Et, Bu) with $H_2T(4\text{-}X)PP$ (X = OMe, Me, Cl, H),[7] and also interactions of $MeSnBr_3$ with H_2T(4-X and 3-X)PP {4-X = OMe, Me, Cl, H and 3-X = Me, Cl},[8] in solution. Our earlier studies on the interactions of *meso*-tetraarylporphyrins with organotin(IV) halides showed the following sequences for stability of adducts with respect to the free base porphyrins and organotin(IV) halides, respectively: $H_2T(4\text{-}CH_3O)PP > H_2T(4\text{-}CH_3)PP > H_2TPP > H_2T(4\text{-}Cl)PP > H_2T(4\text{-}NO_2)PP$ and $MeSnBr_3 > Me_2SnCl_2 > Et_2SnCl_2 > Bu_2SnCl_2$

This trend indicates a decrease of adduct stabilities with decreasing basicity of the free base porphyrins and increasing the bulkiness and the number of alkyl- groups on the tin atom. Here we report the synthesis and characterisation of diethyltin(IV) dichloride and methyltin(IV) trichloride complexes with $H_2T(4\text{-}X)PPs$, in which the $H_2T(4\text{-}X)PPs$ are H_2TPP (*meso*-tetraphenylporphyrin), $H_2T(4\text{-}Cl)PP$ (*meso-tetrakis*-(4-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). We believe that $H_2T(4\text{-}X)PPs$ act as bidentate bridging ligands toward organotin(IV) chlorides. Formation of a Sitting–Atop type[9] pre-complex has been suggested by previous investigations on the kinetics of metalation of free base porphyrins in solution,[10,11] but the instability of this pre-complex makes determination of its structure impossible. We think that our stable adducts give good evidence about the structure of this Sitting–Atop type pre-complex and this aids kinetic study of metalation of 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 determined relative to $CHCl_3$ line (7.26ppm). Me_4Sn (Fluka) was used as received. Diethyl ether was distilled over $LiAlH_4$ then used for preparation of Grignard reagent.

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: Organotin(IV) chlorides were prepared by the reaction between R_4Sn and anhydrous $SnCl_4$ and purified by sublimation.[12] Et_4Sn was prepared by reaction of anhydrous $SnCl_4$ with EtMgBr in dry diethylether and purified by vacuum distillation.[13] 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,[14] and purified by chromatography on neutral alumina.

General procedure for the synthesis of meso-tetraarylporphyrins:[14] *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 for 1 hour. On cooling, the porphyrin precipitated directly from the reaction mixture and was isolated by filtration.

Adduct formation: an excess of organotin(IV) chloride was added to a purple solution of free base porphyrin in chloroform, the colour changed to green, *n*-hexane was added to the green solution slowly, green powdery products were obtained, elemental analyses are in Table 1. These products also can be obtained by dissolving the $H_2T(4\text{-}X)PP$ and the excess of organotin(IV) chlorides in $CHCl_3$ or CH_2Cl_2 followed by evaporation of the solvent at room temperature. Unreacted substances remained on the wall of the beaker (reaction flask) and the green shiny product precipitated on the bottom of the reaction flask.

Results

UV–Vis analysis: On interaction of $H_2T(4\text{-}X)PP$ with organotin(IV) chlorides the original peaks of the free base tetraarylporphyrins vanished and two new peaks appeared (Fig. 1 and Table 2). For example, on addition of $MeSnCl_3$ to $H_2T(4\text{-}CH_3O)PP$ the original peaks at 421, 518, 555, 594, 649nm of the free base vanished and new peaks appeared at 454 and 690nm. The clear isosbestic point at 428 nm indicates the presence of an equilibrium in solution, Fig. 1.

^1H NMR analysis: ^1H NMR spectra of adducts show clear differences relative to reactants. Upon complexation of free base porphyrins, the N-H, H_o, $H_{m,p}$, and Me- or -OMe protons of the *para*-substituents move down field, while H_β has an up field shift (Table 3). On the other hand, the ethyl- and methyl

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Elemental analysis of $[(MeSnCl_3)_2H_2T(4\text{-}X)PP]$ and $[(Et_2SnCl_2)_2H_2T(4\text{-}X)PP]$ adducts

	Found			Calculated		
	% C	% H	% N	% C	% H	%N
$(MeSnCl_3)_2H_2T(4\text{-}Cl)PP$	44.16	2.25	4.15	44.74	2.56	4.54
$(MeSnCl_3)_2H_2TPP$	49.75	3.09	4.88	50.37	3.28	5.11
$(MeSnCl_3)_2H_2T(4\text{-}CH_3)PP$	51.62	4.12	4.63	52.10	3.82	4.86
$(MeSnCl_3)_2H_2T(4\text{-}CH_3O)PP$	48.53	4.04	4.20	49.35	3.62	4.61
$(Et_2SnCl_2)_2H_2T(4\text{-}Cl)PP$	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

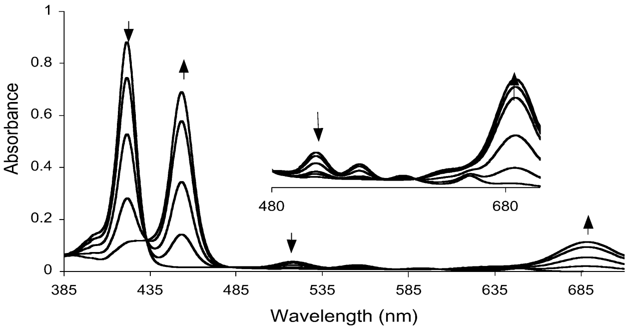
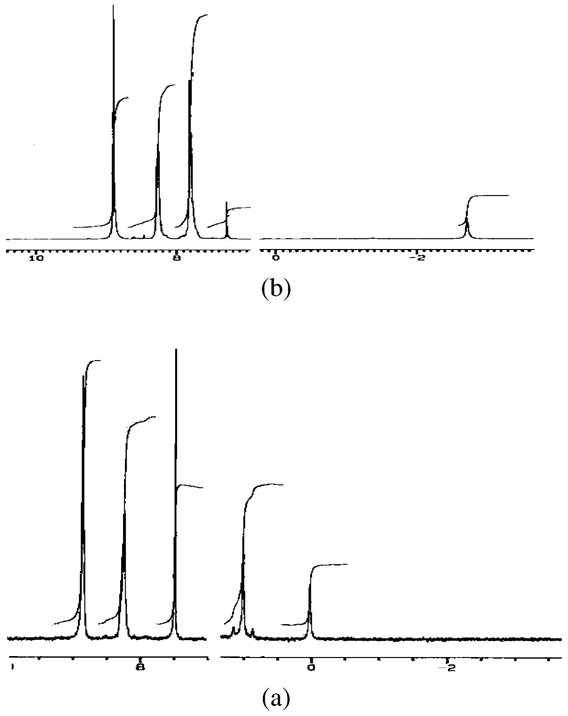


Fig.1 Titration spectra, for titration of $H_2T(4\text{-}CH_3O)PP$ with $MeSnCl_3$ in chloroform. Bands at 454 and 690nm are related to adduct, isosbestic point at 428 nm.



(b)

(a)

Fig.2 ^1H NMR spectra of: (a) H_2TPP; (b) $[(MeSnCl_3)_2H_2TPP]$ at –30°C, in $CDCl_3$. Chemical shifts are relative to $CHCl_3$(7.26ppm), peaks appeared at 7.46ppm(a) and 7.26ppm(b) belong to $CHCl_3$ impurity.

protons of organotin(IV) chloride show about 0.1–0.15ppm up field shift with complex formation, Fig.2.

Discussion

Table 2 UV-vis peaks λ ($CHCl_3$/nm) of the $H_2T(4\text{-}X)PP$ and their adducts with Lewis acids

$H_2T(4\text{-}Cl)PP$	418	514	550	590	646
$(MeSnCl_3)_2H_2T(4\text{-}Cl)PP$	452	–	–	–	670
$(Et_2SnCl_2)_2H_2T(4\text{-}Cl)PP$	448	–	–	–	664
H_2TPP	417	514	549	589	646
$(MeSnCl_3)_2H_2TPP$	448	–	–	–	666
$(Et_2SnCl_2)_2H_2TPP$	444	–	–	–	660
$H_2T(4\text{-}CH_3)PP$	419	516	553	591	649
$(MeSnCl_3)_2H_2T(4\text{-}CH_3)PP$	450	–	–	–	676
$(Et_2SnCl_2)_2H_2T(4\text{-}CH_3)PP$	447	–	–	–	670
$H_2T(4\text{-}CH_3O)PP$	421	518	555	594	649
$(MeSnCl_3)_2H_2T(4\text{-}CH_3O)PP$	454	–	–	–	690
$(Et_2SnCl_2)_2H_2T(4\text{-}CH_3)PP$	453	–	–	–	688

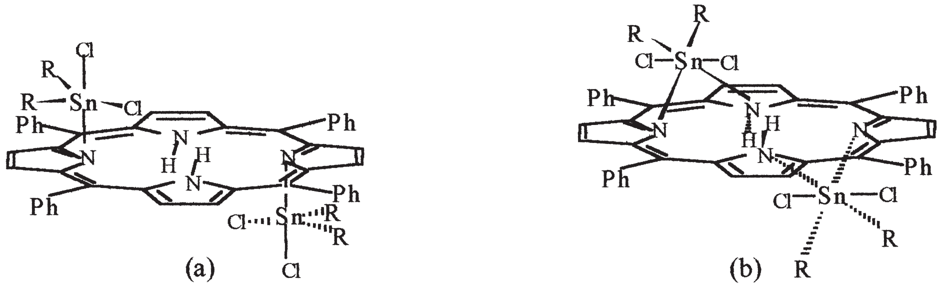
By studying the ^1H NMR spectra of solid products some interesting results have been obtained. Low-temperature ^1H NMR (–30°C) of these products were studied in $CDCl_3$. For example upon complexation of H_2TPP with $MeSnCl_3$, the original resources N-H (–2.71ppm), H_β (8.87ppm), H_o (8.26ppm), and $H_{m,p}$ (7.81ppm) of H_2TPP were shifted to –0.20, 8.59, 8.59, and 7.99ppm, respectively. Therefore we have three bands in the low-temperature ^1H NMR spectra of the porphyrin moiety of the adduct, Table 3, the bands related to H_β and H_o overlapped and gave a signal at 8.59ppm. Comparison of the chemical shifts of free base protons before and after complexation gives some useful information. The internal N–H proton signal moves down field about 2.71ppm and the H_β protons signal moves up field about 0.28 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 also move downfield about 0.33 and 0.18ppm, respectively. These changes can be ascribed to decrease of the aromatic ring current because of the coordination of porphyrin to the organotin(IV) chloride led to deformation of the porphyrin structure from planarity. However, for the organotin protons a shift about 0.1–0.2 ppm up field was observed due to the electron acceptance of the tin atom.

According to the ^1H NMR pattern of this product, it seems that the adduct has a symmetric structure, so that the coordination of porphyrin to organotin(IV) chloride could not differ between each class of free base proton (N–H, H_β, H_o, and $H_{m,p}$) upon adduct formation and these protons remained equivalent after complexation. On the other hand, we see only a definite shift for each class of protons in the adduct relative to the corresponding free base porphyrin protons.

The elemental analysis data shows that these adducts have the stoichiometry 2:1 of acid to base, $[(MeSnCl_3)_2(H_2T(4\text{-}X)PP)]$ and $[(Et_2SnCl_2)_2(H_2T(4\text{-}X)PP)]$. It is in a good agreement with our previous results on thermodynamic studies of these adducts.[7,8] For this mole ratio we propose the structures shown in Fig.3. In Fig. 3(a), because of attachment of the tin atoms to two of the pyrrolenine nitrogens, splitting of the ^1H NMR signal of the Hβs to produce a doublet band is expected. On the other hand, in Fig.3(b) the Hβs have an identical environment, therefore we predict a singlet band for them. Experimentally, in the low-temperature ^1H NMR spectra of the adducts a singlet appeared for the Hβs, thus confirming the Fig.3(b) structure for these adducts. On the basis of these results we suggest that free base porphyrin acts as a bidentate bridging ligand between two molecules of the Lewis acid. It is

Table 3 ^{1}H NMR chemical shift (δ/ppm) of the $H_2T(4\text{-}X)PP$ and their adducts with Lewis acids relative to $CHCl_3$

	δN-H	δ $H_{m,p}$	δ H_o	δ H_β	δ OCH_3,CH_3
H_2TPP	−2.71	7.81	8.26	8.87	
$(MeSnCl_3)_2H_2TPP$	−0.2	7.99–8.02	8.59–8.62	8.59–8.62	
$(Et_2SnCl_2)_2H_2TPP$	0.00	8.01–8.04	8.56–8.61	8.56–8.61	
$H_2T(4\text{-}Cl)PP$	−2.86	7.75	8.14	8.85	
$(MeSnCl_3)_2H_2T(4\text{-}Cl)PP$	0.13	8.01–8.05	8.52–8.59	8.52–8.59	
$(Et_2SnCl_2)_2H_2T(4\text{-}Cl)PP$	0.06	8.09–8.12	8.46–8.55	8.46–8.55	
$H_2T(4\text{-}CH_3)PP$	−2.77	7.56	8.11	8.86	2.71
$(MeSnCl_3)_2H_2T(4\text{-}CH_3)PP$	0.16	7.80–7.85	8.47–8.54	8.47–8.54	2.85
$(Et_2SnCl_2)_2H_2T(4\text{-}CH_3)PP$	0.15	7.81–7.85	8.49–8.59	8.49–8.59	2.80
$H_2T(4\text{-}CH_3O)PP$	−2.82	7.23	8.07	8.79	3.95
$(MeSnCl_3)_2H_2T(4\text{-}CH_3O)PP$	0.22	7.55–7.58	8.53–8.55	8.53–8.55	4.16
$(Et_2SnCl_2)_2H_2T(4\text{-}CH_3O)PP$	0.20	7.49–7.56	8.46–8.53	8.46–8.53	4.15



(a) (b)

Fig.3 Proposed structures of $[(Et_2SnCl_2)_2H_2TPP]$ adduct. (a) H_2TPP as a monodentate bridging ligand giving a 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 consistent with structure (b).

probable that two neighbor nitrogen atoms of the porphyrin bind to one of the organotin(IV) chloride molecules which is positioned above the porphyrin plane and the other two nitrogen atoms bind to the second organotin(IV) chloride molecule from below of this plane. Therefore we have a structure close to that suggested by Smith *et al.*[15] for XHg-TPP-HgX, X = Cl^- and CH_3COO^-.

Our results confirm the pre-equilibrium demonstrated by previous studies on the kinetics of incorporation of some divalent metal ions into the free base porphyrins. Hambright and Robinson[10] had studied the kinetics of catalysed and uncatalysed incorporation of Zn(II) into free base porphyrins (H_2P) in DMF. They suggested that metal ions and porphyrins formed an intermediate with composition [M-H_2P; M = Zn(II), Cd(II), Cu(II)][11,16] in which coordination of H_2P with the metal ion deforms the porphyrin plane in such a manner that a second metal ion can more readily be able to bind this bent porphyrin structure on the opposite side. Then formation of the M-H_2P-Zn system followed by dropping the Zn(II) ion into the porphyrin cavity.[10,11] But in our work, the bulky organotin(IV) chloride could not drop into the porphyrin cavity under these conditions. We think that our results can give good information about the structure of these pre-complexes and make help in a better understanding of the kinetics of incorporation of metal ions into the free base porphyrins cavity.

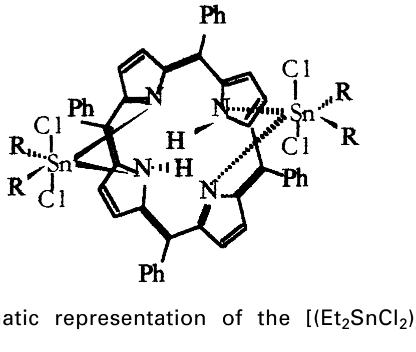


Fig.4 Schematic representation of the $[(Et_2SnCl_2)_2H_2TPP]$ adduct.

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