Synthesis, characterisation and spectroscopic studies of sitting-atop adducts of dimethyl- and diethyl-tin(IV) dichlorides with *meso*-tetraalkylporphyrins

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The formation of the sitting-atop (SAT) adducts of *meso*-tetra(*n*-propyl)porphyrin and *meso*-tetra(*tert*-butyl)porphyrin with dimethyl- and diethyl-tin(IV) dichlorides has been investigated. These adducts have the general formula $[(R_2SnCl_2)_2H_2T(n\text{-propyl})P]$ and $[(R_2SnCl_2)_2H_2T(tert\text{-butyl})P]$; [R = Me and Et] and have been characterised by means of ^1H NMR, UV-Vis and elemental analysis methods.

Keywords: alkylporphyrin, dimethyl- and diethyl-tin(IV) dichlorides, organotin(IV) halide adducts, sitting-atop complexes

Porphyrins and metalloporphyrins are versatile synthetic base materials for research projects in many disciplines of chemistry and physics, like electronics, opto-electronics, electrochemistry, catalysis and photophysics, because of the possibility of tailoring their physical and chemical properties at the molecular level.[1] Understanding the metallation of porphyrins has also long been important in biochemistry because of their central role in photosynthesis, biological redox processes, and oxygen transport.[2–10] A particularly attractive idea in the kinetics and mechanism of metallation of free-base porphyrins is that of sitting-atop (SAT) complexes. In these SAT complexes metal ions are located out of the porphyrin plane and so the planar form is distorted. In 1960, Fleischer and Wang proposed that the metallation of a free-base porphyrin proceeded through a pre-equilibrium SAT complex in which there was partial bonding of the metal to two of the nitrogen atoms. The metal was out of the (distorted) porphyrin plane, and the two protons remain on nitrogen.[11,12]

Since then, several SAT complexes of porphyrins as intermediates have been isolated such as those of ions of platinum(II),[13] copper(II),[14] and rhodium(I)[15] and their structures determined by XAFS spectroscopy. Funahashi and coworkers have also recently obtained the SAT complexes of some porphyrins with several 3D-block cations in acetonitrile.[16–19]

We report here the isolation of the SAT adducts of *meso*-tetrakis(*n*-propyl)porphyrin ($H_2T(n\text{-propyl})P$) and *meso*-tetrakis (*tert*-butyl)porphyrin ($H_2T(tert\text{-butyl})P$) with dimethyltin dichloride and diethyltin dichloride as stable compounds, which we believe to be the first SAT complexes of tin, or indeed of any main group metal, to be described. This provides a new context in which the mechanism of the formation of free base porphyrins can be studied.

Experimental

Butyraldehyde and trimethylacetaldehyde (pivaldehyde) (Merck), Me_4Sn, Et_4Sn and $SnCl_4$ (Fluka) were used as received. All other chemicals used were of analytical grade and were purchased from Merck. Silica gel 60 (Merck) was used for column chromatography.

UV-Vis measurements were carried out on a SINCO S-2100 UV-Vis spectrophotometer equipped with a Tech DTRC-620 DESK TOP REF.CIR thermostat. The ^1H NMR spectra were recorded on a Bruker 300 MHz spectrometer in $CDCl_3$.

Dimethyltin(IV) dichloride and diethyltin(IV) dichloride were prepared by the reaction between Me_4Sn and Et_4Sn respectively with anhydrous $SnCl_4$ and purified by sublimation.[20] *Meso*-tetrakis (*n*-propyl)porphyrin and *meso*-tetrakis(*tert*-butyl)porphyrin were synthesised using modified Lindsey conditions.[21]

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Adduct formation

An excess of the Lewis acid, organotin(IV) dichloride, was added to a purple solution of the free base porphyrin in chloroform. *N*–Hexane was slowly added to the resulting solution and green powdery products were obtained. These adducts can also be obtained by dissolving the respective $H_2T(Alkyl)P$ and an excess of organotin(IV) halides 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 a green shiny product precipitated on the bottom of the reaction flask. The products were washed with *N*–hexane to remove the unreacted organotin(IV) dichloride. The progress of the reaction was monitored by the UV-Vis spectra. The porphyrins were completely converted into the SAT complexes and the mixtures did not show an absorption band (Soret band) related to the free base *meso*-tetraalkylporphyrins. The results of elemental analyses and the related melting points are compiled in Table 1.

Results and discussion

UV-Vis analysis

On addition of R_2SnCl_2 to a solution of the free base porphyrin in chloroform its purple colour changes to green. This change is due to the adduct formation between R_2SnCl_2 and the porphyrin. The original spectrum of the tetraalkylporphyrin (Soret band and Q bands) changes giving a number of isosbestic points. For example, by addition of Me_2SnCl_2 to $H_2T(n\text{-Propyl})P$, Fig. 1, the original peaks of the free base (417, 520, 555, 600 and 659 nm) diminished and two new peaks appeared at (432.5 and 640.3 nm) with a well defined isosbestic point around 425 nm.

Table 2 gives the original peaks of the free-base porphyrins and the new peaks produced by addition of R_2SnCl_2 to a solution of porphyrins in chloroform.

By addition of Me_2SnCl_2 (6.25×10^{-4} M) to 2.5 mL of the solution of $H_2T(n\text{-Propyl})P$ (2.5×10^{-6} M) in chloroform in a UV-Vis cell at 5 °C, the $(Me_2SnCl_2)_2H_2T(n\text{-Propyl})P$ adduct was formed. Then the composition of the cell was held constant and the temperature was raised to 50 °C in steps showing an isosbestic point around 425 nm as the adduct dissociated.

It seems that the spectroscopic changes mainly relate to the first step of the adduct formation which leads to a deformation of the porphyrin plane, the later step having only exert a minor effect on the

Table 1 Elemental analysis of diorganotin(IV) dihalide-porphyrin adducts

	Found			Calculated			
	% C	% H	% N	% C	% H	% N	m.p.
$(Me_2SnCl_2)_2H_2T$ (*n*-propyl) P	47.34	5.52	6.02	47.10	5.49	6.10	284 °C
$(Me_2SnCl_2)_2H_2T$ (*tert*-butyl)P	49.17	5.89	5.79	49.32	6.00	5.75	□350 °C
$(Et_2SnCl_2)_2H_2T$ (*n*-propyl) P	49.18	6.11	5.65	49.32	6.00	5.75	291 °C
$(Et_2SnCl_2)_2H_2T$ (*tert*-butyl)P	51.23	6.52	5.50	51.30	6.46	5.44	□350 °C

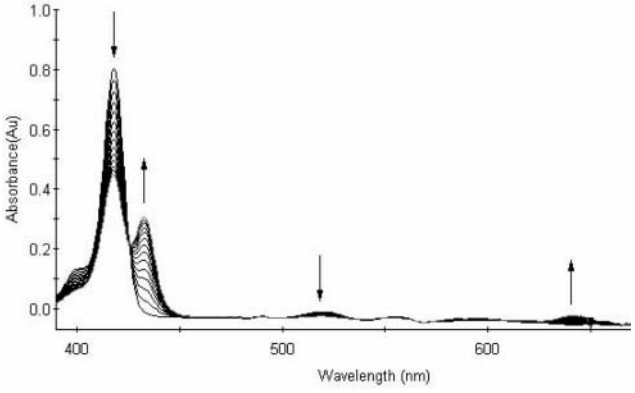


Fig. 1 Titrametric absorption spectra of H_2T(*n*-Propyl)P with Me_2SnCl_2 in chloroform. Bands appearing at 432.5 and 640.3 nm are related to the adduct, with an isosbestic point at around 425 nm.

Table 2 UV-Vis peaks λ ($CHCl_3$/nm) of the free bases $H_2T(X)P$ and their adducts with Me_2SnCl_2 and Et_2SnCl_2

Compound	Wavelength/nm				
H_2T(*n*-Propyl)P	417	520	555	600	659
$(Me_2SnCl_2)_2$ H_2T(*n*-Propyl)P	432.5	640.3			
$(Et_2SnCl_2)_2$ H_2T(*n*-Propyl)P	433.6	643			
H_2T(*tert*-Butyl)P	446	552	596	628	691
$(Me_2SnCl_2)_2$ H_2T(*tert*-Butyl)P	453	690.5			
$(Et_2SnCl_2)_2$ H_2T(*tert*-Butyl)P	453.6	695.5			

λ_{max} of the adduct. We think that the primary 1:1 adduct formation, of $(Me_2SnCl_2)H_2T$(alkyl)P, induces a distortion of the porphyrin plane; this deformation would enhance the coordination 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 favours the formation of a 2:1 adduct $(Me_2SnCl_2)_2H_2T$(alkyl)P. Since the distortion of the porphyrin plane occurred during the 1:1 adduct formation, the attachment of the second Lewis acid is not accompanied by a significant displacement in the position of these bands (about 2–4 nm shift to longer wavelength for the Soret band). This statement can be better understood by comparison of electronic absorption spectra of a planar free-base porphyrin such as *meso*-tetrakis(*n*-propyl)porphyrin; UV-Vis ($CHCl_3$): Soret band (417 nm) and Q bands (520, 555, 600, 659 nm) with a severely ruffled (distorted) one like free-base *meso*-tetrakis(*tert*-butyl)porphyrin: Soret band (446 nm) and Q bands (552, 596, 628, 691 nm). This example shows that the observed bathochromic shift resulted mainly from distortion of the porphyrin structure. The observed red shifts for the sitting-atop complexation of *meso*-tetraalkylporphyrins with R_2SnCl_2 are similar to diprotonation of the porphyrins or molecular complexation with various acceptors.[22–25] These similarities suggest analogous porphyrin core structures in all of the species (SAT complex, diprotonated porphyrin and molecular complex). It is noticeable that these adducts dissociate on increasing the temperature, Fig. 2. This spectrum is similar to that in previous work on the acidic dissociation of the ClHg-TPP-HgCl complex,[26] in which ClHg-TPP-HgCl returned to H_2TPP and $HgCl_2$.

^1H NMR analysis

The ^1H NMR spectra of the porphyrin moiety of the adducts show clear differences compared with the corresponding free-base porphyrin. Upon complexation of free-base porphyrins with organotin halides the signal corresponding to N–H moved downfield, while H_β has an up field shift (Table 3, Fig. 3). The ^1H NMR spectra of these adducts

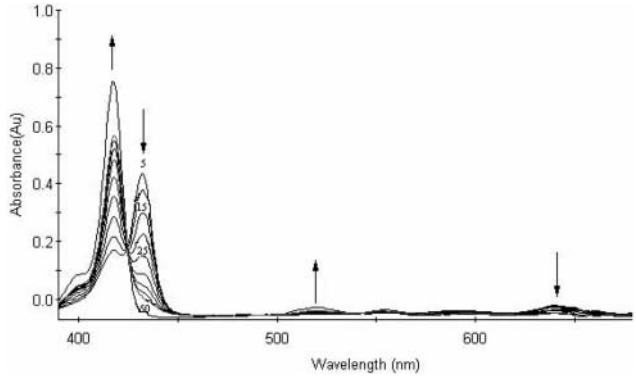
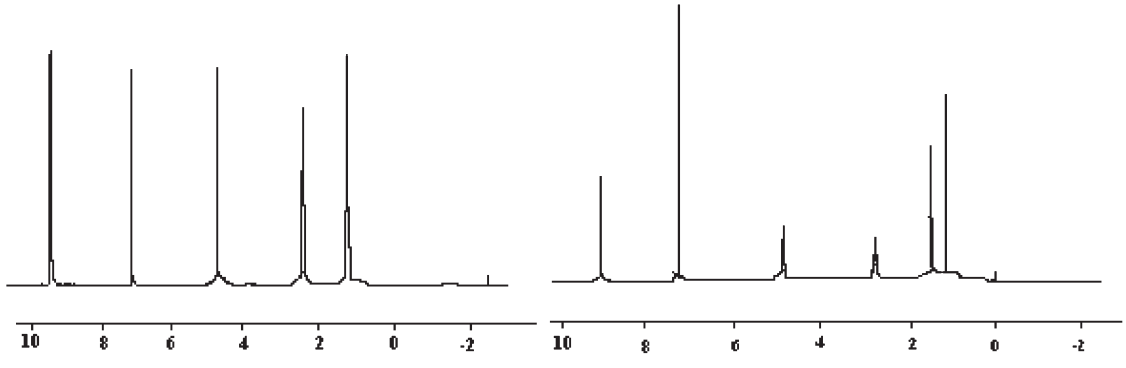


Fig. 2 Temperature dependence spectra of: $(Me_2SnCl_2)_2H_2T$(n-Propyl)P adduct.

Table 3 ^1H NMR chemical shifts {δ(ppm)} of the meso-tetraakylporphyrins and their adducts relative to $CHCl_3$ 7.26ppm)

Compounds	δN–H	δH_β	δCH_2[a]	δCH_2	δCH_3
H_2T(*n*-propyl)P	–2.52	9.48	4.95	2.64	1.42
$(Me_2SnCl_2)_2$ H_2T(*n*-Propyl)P	0.00	9.1	4.79	2.61	1.41
$(Et_2SnCl_2)_2$ H_2T(*n*-Propyl)P	0.00	9.03	4.75	2.60	1.40
H_2T(*tert*-Butyl)P	1.52	9.08			2.01
$(Me_2SnCl_2)_2$ H_2T(*tert*-Butyl)	1.65	8.09			1.57
$(Et_2SnCl_2)_2$ H_2T(*tert*-Butyl)P	1.67	8.1	1.60		

[a] Near the porphyrin ring



(a) (b)

Fig. 3 ^1H NMR spectra of : (a) H_2T(*n*-Propyl)P; (b)$(Me_2SnCl_2)_2H_2T$(*n*-Propyl)P at 25 °C in $CDCl_3$. Chemical shifts are relative to $CHCl_3$ (7.26 ppm).

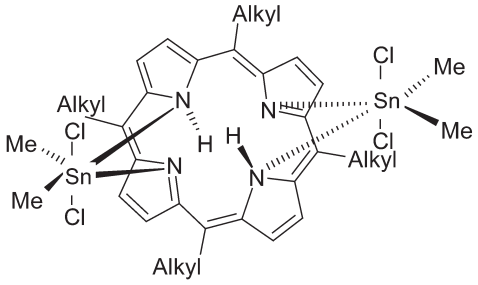


Fig. 4 The schematic illustration of bonding interaction for $[(Me_2SnCl_2)_2H_2T(Alkyl)P]$ adducts.

were studied in $CDCl_3$ at 25 °C. On complexation of $H_2T(n\text{-Propyl})P$ with Me_2SnCl_2, the original signals of N–H (–2.52 ppm) and H_β (9.48 ppm) of the free base $H_2T(n\text{-Propyl})P$ were shifted to 0.00 and 9.1 ppm respectively. The internal N–H proton's signal moves downfield about 2.52 ppm and H_β protons signal move upfield about 0.38 ppm. Both changes are discontinuous and are in the directions to be expected if the aromatic ring current decreases with complexation.

The CH_2 and CH_3 protons related to the *meso*-substituents of the free base porphyrin also move upfield. These changes can be ascribed to coordination of the porphyrin to the organotin(IV) halide which leads to a deformation of the porphyrin structure from planarity so decreasing the aromatic ring current. According to the ^1H NMR pattern, it seems that the adduct has a symmetric structure, so that coordination of the porphyrin to the organotin(IV) halide could not differentiate between each class of the free base protons (N–H and H_β) 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 very close correspondence among UV-VIS and ^1H NMR spectroscopic data of our adducts and those of the H_4TPP^{2+} acid dication,[27–29] $[H_2TPP(DDQ)_2]$,[22] $[H_2TPP(TCNE)_2]$[23] and $[H_2TPP(R_3SiCl)_2]$[24] (R= alkyl) leads to the presumption of a similar porphyrin core structure in all these species, with non-coplanar pyrrole rings tilted alternately up and down. Such a conformation makes the lone electron pairs of the two pyrrolenine nitrogens more accessible for donation to the empty π-orbital's of the two bonded tin centres, presumably from above and below the mean plane of the porphyrin. In the proposed structure, the lone pairs of two pyrrolenine nitrogens act as electron donors to one molecule of R_2SnCl_2 and so two hydrogen atoms of pyrrole (N–H) still remain on the macrocycle, Fig. 4. The elemental analysis data show that these adducts have the stoichiometry 2:1 of acceptor to donor, $[(Me_2SnCl_2)_2(H_2T(n\text{-Propyl})P)]$, $[(Et_2SnCl_2)_2(H_2T(n\text{-Propyl})P)]$, $[(Me_2SnCl_2)_2(H_2T(tert\text{-Butyl})P)]$, $[(Et_2SnCl_2)_2(H_2T(tert\text{-Butyl})P)]$. 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 probable that two neighbour 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 this plane. Therefore we have a structure close to that suggested by Hudson and Smith for XHg–TPP–HgX, X = Cland CH_3COO– (Fig. 4).[26]

Conclusions

We conclude that our results are best interpreted in terms of a SAT structure where the presence of the protons on the pyrrole nitrogen atoms prevent the bulky organotin(IV) halide from occupying the centre of the porphyrin plane so that it resides above the ring plane. We think that these results should aid in the understanding of SAT structures and the kinetics and mechanism of the metallation of free base porphyrins.

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