Letter

Novel 1:2 molecular complexation of free base *meso*-tetraphenylporphyrins with σ-acceptor trialkylsilyl chlorides

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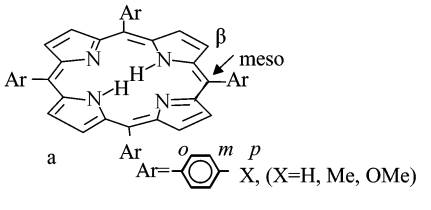
Interaction of various molar ratios of *meso*-tetraphenylporphyrins with two different trialkylsilyl chlorides in chloroform only afforded l:2 molecular complexes at room temperature. Spectral properties closely corresponded to those of diprotonated *meso*-tetraphenylporphyrin, strongly suggesting similar pseudo tetrahedrally distorted porphyrin core structures with σ-bonding from two pyrrolenine nitrogen donors to the silicon centers and two hydrogen bonds between two pyrrole NH· · · and · · ·ClSi groups from above and below the mean plane of the porphyrins with nearly trigonal bipyramidal coordination geometries for silicon centers, with alkyl groups located at the equatorial sites.

Despite the long interest that has been shown in molecular interactions between free base porphyrins and various neutral organic π-acceptors,[1] no attention has been given to the potentially important interactions of porphyrins with σ-acceptor molecules. This article provides the first direct spectroscopic evidence for specific 1:2 molecular complexation of free base *meso*-tetraphenylporphyrin (H_2tpp) and two *para*-substituted *meso*-tetraphenylporphyrins (H_2t(4-Me)pp, H_2t(4-OMe)pp) (Fig. 1a) with σ-acceptor trimethylsilyl chloride (A_I) and *tert*-butyldimethylsilyl chloride (A_{II}) molecules.

The ^{1}H NMR spectra of a $CDCl_3$ (passed through a short column of neutral alumina, grade I, and K_2CO_3) solution of the H_2tpp-A_I reaction system are represented in Fig. 2. The spectrum of the H_2tpp$(A_I)_2$ molecular complex (Fig. 2c) is quite different from those of the free base H_2tpp (Fig. 2a) and A_I with a single line at 0.43 ppm (not shown). The spectrum due to the 1:1 H_2tpp-A_I reaction mixture (Fig. 2b) clearly shows superimposition of both H_2tpp and H_2tpp$(A_I)_2$ spectra at their normal chemical shift values, with no indication of the presence of a 1:1 adduct. In fact, ^{1}H NMR spectra for the titration of 0.2, 0.5, 1.3 and 1.6 equivalents of A_I into a $CDCl_3$ solution of H_2tpp (0.006 M) displayed only resonances of the free H_2tpp and the corresponding 1:2 molecular complex. It should be noted that all of the proton integrations for the molecular complex closely matched with the 1:2 molar ratio of H_2tpp and A_I. However, the integration for the pyrrolic NH is critically concentration dependent.[1c] An excess of A_I beyond the 1:2 molar ratio caused no detectable changes in the spectrum of the H_2tpp$(A_I)_2$ complex (Fig. 2d). Similarly, the interaction of H_2tpp with A_{II} in chloroform solution led only to the production of the related 1:2 molecular adduct. However, the larger steric requirements for A_{II} as compared with the less hindered A_I caused the complexation time to be increased from less than an hour for A_I to several days for the more bulky σ-acceptor A_{II}, at room temperature. These



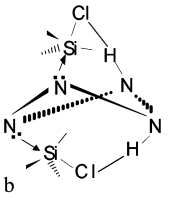


Fig. 1 (a) Schematic representation of the porphyrins. (b) Scheme for the proposed idealized structure and the bonding for por$(A_I)_2$ or por$(A_{II})_2$ complexes. For clarity, in the middle only the pseudo tetrahedrally distorted pyrrole nitrogens of a porphyrin core are shown. The acceptor molecules, bonded from above and below the mean porphyrin plane, are partially drawn.

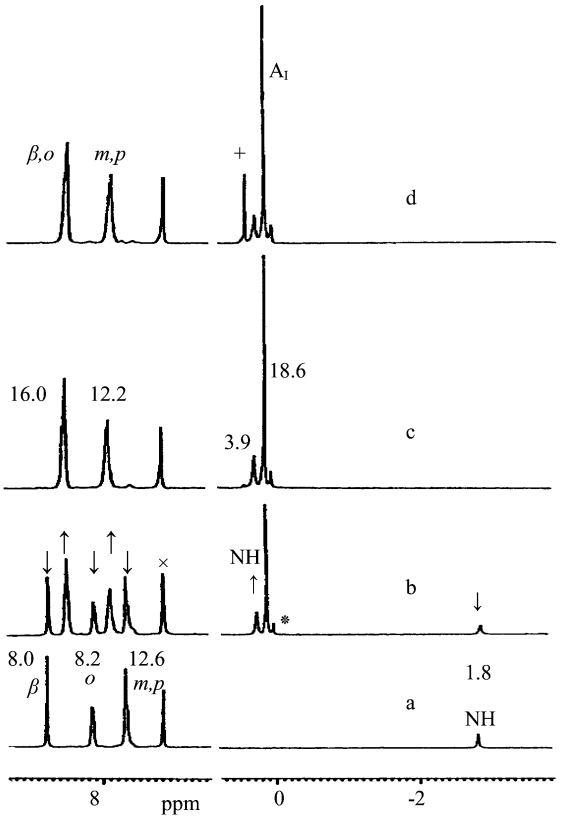


Fig. 2 ^{1}H NMR spectra (250 MHz) for titration of (a) H_2tpp (0.006 M) with (b) 1.0, (c) 2.0, (d) 2.5 equivalents of A_I in $CDCl_3$ at 25 °C. Integrations of the lines or multiplets are given on their sides. The line at 7.26 ppm (×) is related to $CHCl_3$ impurity in the solvent. On the right are displayed chemical shifts for NH proton lines. On the left the chemical shifts of aromatic proton lines are shown. The sharp line at 0.15 ppm is due to the coordinated A_Is. The line at 0.43 ppm (+) corresponds to the excess of A_I. Asterisk denotes the impurity in A_I.

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Table 1 ^{1}H NMR resonances of *meso*-tetraphenylporphyrins and their 1:2 complexes with A_I and A_{II}[a]

Compounds	NH	H_β	H_o	H_m	H_p[b]	Me[c]	Me[c]	Me
A_I	—	—	—	—	—	0.43	—	—
A_{II}	—	—	—	—	—	—	0.36	0.97
H_2tpp	−2.76	8.85	8.21, 8.24	7.75, 7.77	7.75, 7.77	—	—	—
A_I complex	0.28	8.57, 8.62	8.57, 8.62	7.94, 8.03	7.94, 8.03	0.15	—	—
$\Delta\delta$	3.04	−0.28	0.36	0.19	0.19	−0.28	—	—
A_{II} complex	0.32	8.59, 8.63	8.59, 8.63	7.93, 8.06	7.93, 8.06	—	0.10	0.92
$\Delta\delta$	3.08	−0.26	0.38	0.18	0.18	—	−0.26	−0.05
H_2t(4-Me)pp	−2.77	8.85	8.08, 8.10	7.53, 7.56	2.70	—	—	—
A_I complex	0.34	8.46, 8.53	8.46, 8.53	7.78, 7.82	2.76	0.15	—	—
$\Delta\delta$	3.11	−0.39	0.38	0.25	0.06	−0.28	—	—
A_{II} complex	0.34	8.42, 8.53	8.42, 8.53	7.79, 7.82	2.77	—	0.11	0.92
$\Delta\delta$	3.11	−0.43	0.34	0.26	0.07	—	−0.25	−0.05
H_2t(4-OMe)pp	−2.75	8.86	8.11, 8.14	7.27, 7.31	4.10	—	—	—
A_I complex	0.54	8.46, 8.53	8.46, 8.53	7.51, 7.54	4.16	0.17	—	—
$\Delta\delta$	3.29	−0.40	0.35	0.24	0.06	−0.26	—	—
A_{II} complex	0.54	8.46, 8.53	8.46, 8.53	7.50, 7.54	4.15	—	0.11	0.92
$\Delta\delta$	3.29	−0.40	0.35	0.23	0.05	—	−0.25	−0.05

[a] Chemical shifts in ppm from impurity of $CHCl_3$ (7.26 ppm) in $CDCl_3$ solvent. [b] *para*-H, -Me or -OMe. [c] Me directly attached to the silicon center.

1:2 adducts are stable in solution ($CHCl_3$) for days, however, even slow evaporation of the solvent, at room temperature, resulted in a degraded solid residue.

In the free base porphyrins the internal NH protons are upfield (−2.75 to −2.77 ppm), and β protons appear at 8.85 to 8.86 ppm (Table 1).[2,3] The *meso*-phenyl protons are composed of a doublet for the *ortho*-hydrogens (8.08 to 8.24 ppm), and another doublet (7.27 to 7.56 ppm) for the *meta*-protons. For H_2tpp the *meta*- and *para*- hydrogens overlap and give a doublet (7.75, 7.77 ppm) (Fig. 2a).[2,3]

Complexation of these porphyrins (por) with A_I and A_{II}, analogous to the diprotonation of H_2tpp[4] and complexation of porphyrins with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ)[1c] and tetracyanoethylene (TCNE),[1d] affords a downfield motion of NH signals ($\Delta\delta$ = 3.04 to 3.29 ppm) and an upfield shift of β-protons ($\Delta\delta$ = −0.26 to −0.43 ppm) (Table 1). Also, in a similar fashion, all the phenyl ring protons show a downfield shift, *ortho*-phenyl and β-pyrrole hydrogens overlap and give a broad line at 8.42 to 8.63 ppm. The 8 *meta*-phenyl protons of the *para*-substituted *meso*-tetraphenylporphyrin complexes, and the 12 *meta*- as well as *para*- hydrogens of the H_2tpp complexes give a signal in the 7.50 to 8.11 ppm region (Fig. 2c).

The three methyl groups of the coordinated A_I in different molecular complexes give a single ^{1}H NMR peak in the 0.15 to 0.17 ppm region with an upfield shift of −0.26 to −0.28 ppm relative to the free A_I. Complexation of A_{II} with the porphyrins also leads to an upfield shift of all its protons in the NMR spectra. The two methyl groups directly attached to the silicon centers give a single NMR peak at 0.10 to 0.11 ppm with −0.25 to −0.26 ppm upfield shifts. The *tert*-butyl protons produced a single NMR line (0.92 ppm) with a smaller upfield shift (−0.05 ppm), as might be expected.

^{29}Si NMR spectrum of H_2t(4-OMe)pp(A_{II})$_2$ in $CDCl_3$ showed a single line at 20.81 ppm, which displayed an upfield shift of −16.65 ppm relative to the corresponding signal of the free A_{II} at 36.46 ppm. This upfield shift suggests formation of pentacoordinate silicons,[5] through their coordination to the pyrrolenine nitrogen donor sites of the porphyrin. The observed ^{29}Si NMR single peak also implicates the equivalency of both silicon centers in the H_2t(4-OMe)pp(A_{II})$_2$ complex.

It is interesting to note that addition of an equivalent of A_I into a chloroform solution of the H_2tpp (A_{II})$_2$ complex, as monitored by ^{1}H NMR, led to the release of most of the bulky A_{II} and complexation of A_I with H_2tpp. In the same fashion when an equivalent amount of A_{II} was added into a H_2tpp(A_I)$_2$ chloroform solution, partial displacement of A_I occurred. These results indicate that the coordinated A_I and A_{II} are easily exchangeable, and remain intact through their complexation with the porphyrins. In line with the latter statement, interaction of trifluoroacetic acid with por($A_{I,II}$)$_2$ adducts in $CHCl_3$, gave unchanged $A_{I,II}$ species, and the protonated porphyrins.

Further evidence for 1:2 complexation of porphyrins with A_I and A_{II} was obtained from the UV-VIS spectra of $CHCl_3$ solutions of the porphyrins and their molecular complexes. The spectrum of the green $CHCl_3$ solution of the H_2tpp(A_I)$_2$ complex (Fig. 3a) with two new main absorption bands at 444 and 661 nm was completely different from the spectrum of H_2tpp (Fig. 3b). The spectrum of the 1:1 H_2tpp-A_I reaction system (Fig. 3c), clearly demonstrated superimposition of H_2tpp and H_2tpp(A_I)$_2$ spectra, with no indication for the occurrence of a 1:1 adduct. The employment of an excess of A_I beyond the required molar ratio for the complexation caused no observable changes in the spectrum of the H_2tpp(A_I)$_2$ complex. Similar results were obtained for the interaction of the various porphyrins with A_I and/or A_{II}. All the 1:2 molecular complexes produced a strong Soret band in the 444 to 452 nm region and another weaker band in the 654 to 689 nm region.

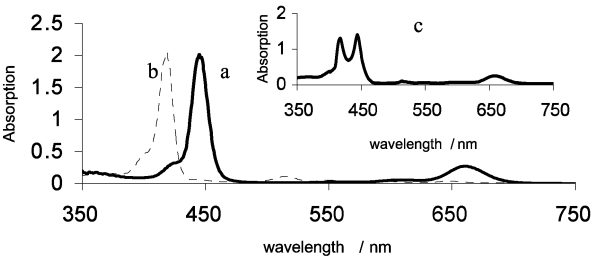

Fig. 3 UV-VIS spectra of (a) H_2tpp (A_I)$_2$ (8.8×10^{-5} M); (b) H_2tpp (8.8×10^{-5} M) in $CHCl_3$ at ~25 °C. Inset: (c) the 1:1 H_2tpp-A_I system (8.8×10^{-5} M). A_I has no absorption line in this region.

The very close correspondence among UV-VIS, ^{1}H NMR spectral data of the por$(A_I)_2$ and por$(A_{II})_2$ adducts, and those of the H_4tpp^{2+} acid dication[4,6] and the related por$(DDQ)_2$[1c] and por$(TCNE)_2$[1d] complexes leads to the presumption of a similar porphyrin core structure in all these species, with non-coplanar[7] 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 empty hybrid σ-orbitals of the two bonded silicon centers, presumably from above and below the mean plane of the porphyrin (Fig. 1b), analogous to electron donation to the protons in H_4tpp^{2+} acid dication.[7] In the proposed structure the pseudo tetrahedrally tilted pyrrole nitrogens would minimize the van der Waals repulsion between the two adjacent NH hydrogens.

Observation of a single ^{1}H NMR signal for methyl groups of the two coordinated A_Is in the molecular complexes suggests their equivalency.[8] Thus, it seems reasonable to assume a nearly trigonal bipyramidal coordination environment for the silicon centers with three methyl groups at the equatorial positions, and the more electronegative chlorine and porphyrin pyrrole nitrogen occupying the axial sites. ^{1}H NMR data for A_{II}s in the molecular complexes are also consistent with a trigonal bipyramidal geometry for the silicon centers, with all alkyl groups residing on the equatorial sites. These observations are in accord with the electronegativity arguments given for substitutional site preferences in d^0, D_{3h}, five-coordinate species.[9]

The unusually large downfield shifts observed for the NH signals upon complexation of the porphyrins with both A_I and A_{II} do not appear to be solely related to the porphyrin ring current effects.[10] Even a large out of plane deformation of the porphyrins leads only to about 5 percent change in the ring current.[11] Thus, it is possible that the rather stronger intramolecular hydrogen bonding in these molecular complexes *vs.* the relatively weaker intramolecular hydrogen bonding in the free base porphyrins, would have important contributions to these large changes. It appears plausible that the stronger (NH···ClSi) hydrogen bonding in the complexes lead to the weakening of the NH bonds, and further removal of the hydrogens from the porphyrin ring current, hence causing a pronounced downfield shift in their proton signals. It is noteworthy that the observed symmetrical ^{1}H NMR spectra (*i.e.* Fig. 2c) of the adducts appear to be in apparent contrast to the presence of unsymmetrical pyrrole rings in the proposed structure (Fig. 1b). However, this may be explained by the occurrence of a rapid dynamic equilibrium of the form:

$$\text{por}(A_{I,II})_2 \rightleftarrows \text{por} + 2A_{I,II}$$

in these systems. The same process would also explain why all the three methyl groups in por$(A_I)_2$ complexes have an identical environment.

A remarkable feature of the complexation of porphyrins with these σ-acceptors, analogous to the protonation of H_2tpp,[6,7] is that no 1:1 adducts were observed. We suggest that the initial 1:1 adduct formation step, which may lead to (1) a substantial tilting of the pyrrole rings of the flexible porphyrin core,[7] and (2) an extensive perturbation of intramolecular H-bonding within the core, is a relatively slow process, and requires a high energy barrier. This step presumably provides suitable orientations for both the lone electron pair of the pyrrolenine nitrogen and the pyrrole NH bond, on the open face of the porphyrin, for a facile interaction with another acceptor molecule. Consequently, the 1:1 adduct is expected to have a very short lifetime and almost instantly react with an incoming acceptor, forming the final 1:2 molecular complex, or to immediately dissociate into its components.

In conclusion, our results show for the first time that free base porphyrin systems can quantitatively associate with σ-acceptor trialkylsilyl chlorides and form exclusively 1:2 molecular adducts. These findings suggest unbounded possibilities for designing a variety of 1:2 molecular complexes composed of suitable free base porphyrins and acceptors, in accordance with the proposed binding model.[1c,d] Currently, we are extending our studies to explore various aspects of this peculiar complexation in terms of the steric and electronic nature of the species involved.

Experimental

Synthesis and purification of all *meso*-tetraphenylporphyrins were carried out following literature method.[12] Chloroform employed for complexation of porphyrins with trialkylsilylchlorides was passed through a column of neutral alumina, grade I, and K_2CO_3 to remove traces of moisture and H^+. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX spectrometer. The ^{29}Si NMR spectrum was obtained on a Bruker Avance DRX 500 MHz. UV-VIS absorption spectra were recorded with a Multispect-1501 Shimadzu.

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8 ^{13}C NMR spectra of por$(A_I)_2$ molecular complexes gave a single line for the coordinated A_I methyl groups at 2.32–2.33 ppm, which showed an upfield shift of 1.32–1.33 ppm with respect to the free A_I ^{13}C signal (3.64 ppm). These results indicate that the two A_Is in por$(A_I)_2$ are equivalent. ^{13}C NMR spectra of por$(A_{II})_2$ species also demonstrated the equivalency of the corresponding carbons of both coordinated A_{II} groups.

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