

Carboxylate and carboxylic acid recognition by tin(IV) porphyrins

Joanne C. Hawley,^a Nick Bampos,^a Raymond J. Abraham^b and Jeremy K. M. Sanders^{*a†}

^a Cambridge Centre for Molecular Recognition, University Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 1EW

^b Department of Chemistry, University of Liverpool, Liverpool, UK L69 3BX

The scope of carboxylate binding by tin(IV) porphyrins and the solution geometries of the resulting complexes have been explored using ¹H NMR spectroscopy; ring current induced shifts and competition experiments indicate the operation of an attractive anthracene–porphyrin interaction; outer sphere carboxylic acid complexes of dihydroxy tin(IV) porphyrins have been characterised, apparently for the first time.

As part of a larger project^{1,2} aimed at supramolecular catalysis we have been exploring the ligand recognition properties of tin(IV) porphyrins. We report here on the scope of carboxylate recognition and the solution state geometry of the resulting complexes, demonstrate that anthracene–porphyrin interactions can overcome the usual geometrical preference, and present what we believe is the first direct evidence for hydrogen-bonded carboxylic acid outer sphere complexes.

It has long been known^{3,4} that the hard metal centre endows a strongly oxophilic character on tin(IV) porphyrins:‡ carboxylate complexes of acids with $pK_a \leq ca. 5$ can be prepared rapidly and effectively quantitatively by mixing a large excess of the free carboxylic acid with dihydroxy tin(IV) porphyrins in non-polar solvents. However, by employing low concentrations of acids, following the reactions by ¹H NMR spectroscopy, and exploiting the fact that the ring currents associated with porphyrins lead to large upfield shifts for axially bound ligands, we have uncovered several previously unreported phenomena:

(i) The rate and extent of complex formation increases with acid strength: using 5 mM porphyrin and 5 mM propionic acid, complexation is complete in 30 min at room temperature, while carboxylate complex formation with dichloroacetic acid is complete within a few seconds.§ Fig. 1 shows the complexation

shifts observed in several dicarboxylate complexes of Sn^{IV}(tpp).¶ The carboxylate complexes are in slow exchange on the NMR chemical shift timescale with any excess carboxylic acid that is present.

(ii) With weaker acids or in the presence of <2 equiv. of stronger acids the monohydroxymonocarboxylate complex is readily observed as the major complex.

(iii) Stronger acids generally displace the carboxylates of weaker acids. However, in such competition experiments, anthracene-9-carboxylic acid ($pK_a \approx 3.6$) behaves as if it were intermediate in strength between monochloroacetic acid ($pK_a \approx 2.9$) and dichloroacetic acid ($pK_a \approx 1.5$). This unusual result is discussed below.

(iv) 'Free' carboxylic acid resonances are broadened and shifted upfield unexpectedly: immediately after addition of 1 equiv. of propionic acid to a CDCl₃ solution of Sn^{IV}(tpp)(OH)₂, the methylene resonance of the added acid was upfield shifted by 1.02 ppm, but as carboxylate complex formation took place over a period of minutes the residual 'free' carboxylic acid signals shifted back towards their normal positions. This observation is consistent with the formation, in fast exchange on the chemical shift timescale, of a weak outer sphere complex between the Sn–OH and carboxylic acid. Such a complex is the first intermediate in the likely mechanism of formation of the final covalent complex (Fig. 2).|| As the reaction proceeds the concentrations of Sn–OH sites and free carboxylic acids decrease, so the fraction of outer-sphere bound acid molecules also decreases. At low temperatures the formation of the covalent carboxylate complex of adamantane-1-carboxylic acid is slowed sufficiently that it does not interfere with observation of essentially complete formation of the hydrogen-bonded complex (Fig. 3). From analysis of the concentration dependence of shifts we estimate the apparent association constant for this hydrogen-bonded species to be *ca.* 10⁴ dm³ mol⁻¹, while analysis of the ring current-induced shift of H_A indicates a distance of *ca.* 5 Å from the carboxylate oxygen to the Sn centre. To our knowledge, such complexes have never been directly observed previously, although their existence has been

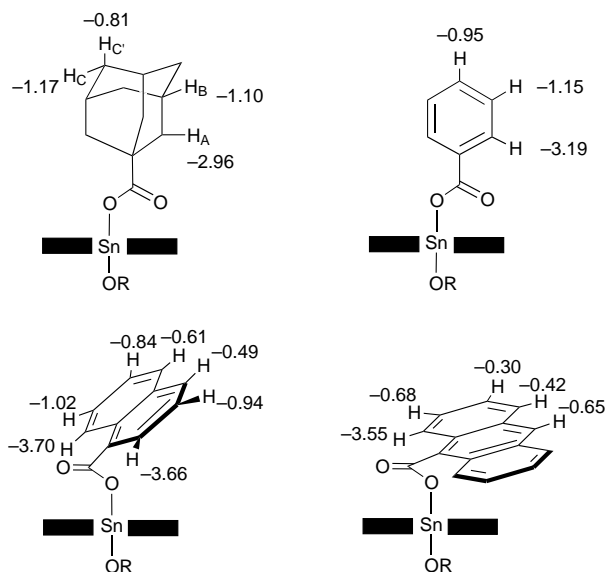


Fig. 1 Porphyrin-induced shifts ($\Delta\delta$ /ppm) for some Sn^{IV}(tpp) dicarboxylate complexes. In each case $\Delta\delta = \delta(\text{complex}) - \delta(\text{free acid})$.

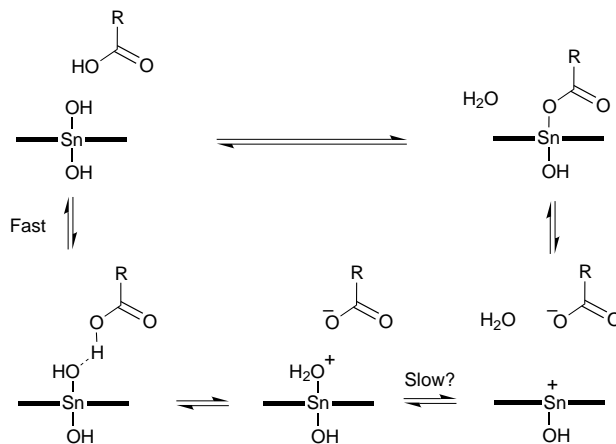


Fig. 2 Presumed mechanism of formation for tin–carboxylate complexes

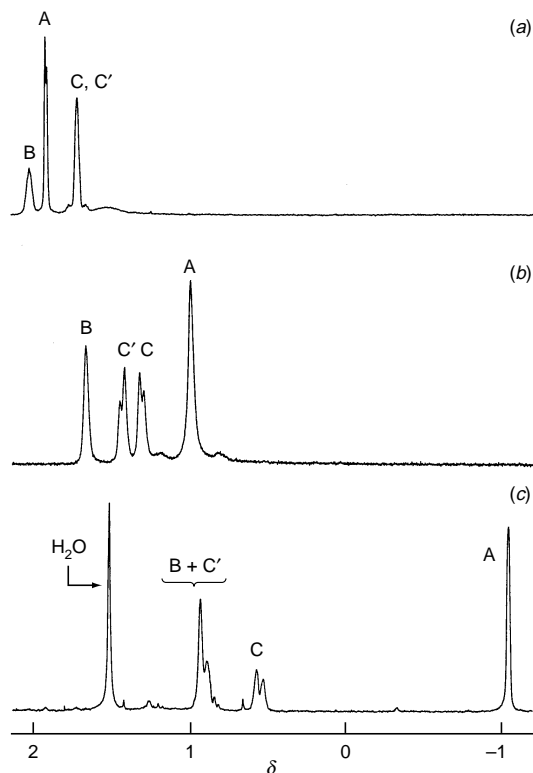


Fig. 3 Partial ^1H NMR spectra of adamantane acid (a) free, (b) hydrogen-bonded to $\text{Sn}^{\text{IV}}(\text{tpp})(\text{OH})_2$ and (c) as dicarboxylate complex. Traces (a) and (c) were obtained at 250 MHz, 20 $^\circ\text{C}$, and trace (b) at 400 MHz, -53 $^\circ\text{C}$.

postulated in connection with tin(IV) porphyrin electrochemistry.⁵

Since the porphyrin ring current is quite well characterised geometrically and has been applied to a range of metalloporphyrin complexes,⁶ we elected to apply the same approach to the tin(IV) systems. In the first instance, the known X-ray⁷ structure for the dibenzoate complex was used to parametrise the ring current for our observed solution state NMR shifts in the same complex. With the ring current thus calibrated, the observed $\Delta\delta$ were fitted to give best-fit geometries. While it is not possible to obtain great precision it is clear that simple aromatic carboxylates are bound with their aryl rings effectively perpendicular to the porphyrin plane, with the dihedral angle $\text{Sn}-\text{O}-\text{C}-\text{C}$ of *ca.* 180 $^\circ$ and with an $\text{Sn}-\text{O}$ bond length of *ca.* 2.1 Å.

However, the shifts observed in the anthracene complex do not match this geometry: they are consistent only with an arrangement where the $\text{Sn}-\text{O}-\text{C}-\text{C}$ angle is reduced to *ca.* 100 $^\circ$, bringing the anthracene ring almost coplanar with the porphyrin as shown in Fig. 1. We attribute this geometry to an attractive

$\pi-\pi$ or donor-acceptor interaction with the porphyrin ring; this additional interaction also explains the unexpectedly strong binding described above. Naphthoic-1-carboxylic acid, perhaps unsurprisingly, displays a shift (and therefore spatial) behaviour that is intermediate between its anthracene and benzoic homologues (Fig. 1), but we cannot distinguish rapid exchange between 'vertical' and 'horizontal' conformations from a static conformation that is intermediate in geometry.

The exclusive oxophilicity of tin(IV) porphyrins complements perfectly the strong preference of zinc and ruthenium(II) porphyrins for nitrogen ligands. Pyridines do indeed bind to zinc or ruthenium(II) porphyrins in the same solution as carboxylic acids bind to Sn^{IV} porphyrins without mutual interference, so it is possible to construct mixed metal dimers and trimers with completely independent ligand specificities at each site.⁹ This greatly expands the repertoire of recognition and catalytic processes that are now available. At a simpler level, $\text{Sn}^{\text{IV}}(\text{tpp})(\text{OH})_2$ may prove useful as a diamagnetic NMR shift reagent for carboxylates.

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Notes and References

† E-mail: jkms@cam.ac.uk

‡ Tin(II) porphyrins bind soft ligands such as S and Se, but their sensitivity to air and moisture renders them unsuitable for routine molecular recognition studies.⁸

§ Detailed analysis of NMR shifts and couplings, and of X-ray structures, reveals that the $\text{Sn}-\text{O}$ bond length increases slightly but systematically as the $\text{p}K_{\text{a}}$ of the carboxylic acid decreases. Details will be discussed in a full paper, but the trends are broadly in line with those expected.^{4,7}

¶ H_2tpp = 5,10,15,20-tetraphenylporphyrin.

|| It is possible that the hydrogen bonding pattern is actually $\text{Sn}-\text{O}-\text{H}\cdots\text{O}=\text{C}$ rather than as shown. The $\text{p}K_{\text{a}}$ dependent behaviour described above is also consistent with the suggested mechanism.

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