THE FREE BASE OF TETRAPHENYLPORPHINE SERVES AS A HOST FOR ALKALI METAL SALTS

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Abstract: The unionized form of tetraphenylporphine complexes alkali metal salts in acetone with association constants ranging from 6.0 to 60 M^{-1}.

In 1967, Pederson reported the properties of a series of synthetic multidentate macrocyclic compounds now commonly referred to as crown ethers.[1] These neutral species, as well as subsequently reported congeners, bind a variety of charged compounds including metal and ammonium salts. Although porphyrins are also able to complex metal ions, this process generally proceeds via the concomitant loss of the two inner pyrrolenine NH protons. However, we report herein that a simple *unionized* porphyrin can also serve as a complexing agent for alkali metal salts.

Upon treatment of tetraphenylporphine[2] with two equivalents of $NaB(C_6H_5)_4$, the inner pyrrolenine NH protons of the porphyrin experience a downfield chemical shift of 0.267 ppm.[3] This alteration in chemical shift is reversed upon addition of 18-crown-6, thereby demonstrating that it is the metal ion which is responsible for the observed NMR behavior. Analogous results were obtained with lithium, sodium, and potassium iodides. This dramatic response in chemical shift implies that the alkali metal ions are not only bound to the porphyrin, but are in close proximity to the pyrrolenine nitrogen atoms.

^{23}Na NMR linewidth measurements are also consistent with the notion that alkali metal ions interact with tetraphenylporphine. Upon addition of trifluoroacetic acid (final concentration: 5%) to a 2:1 mole ratio of $NaB(C_6H_5)_4$:porphyrin, a 10% decrease (from 22.44 Hz to 20.05 Hz) in the linewidth of the ^{23}Na NMR signal was observed, suggesting that the complex had been disrupted.[4] Since the porphyrin is protonated under these conditions, it is not surprising that the sodium cation is no longer associated with the porphyrin moiety. In the absence of the porphyrin, trifluoroacetic acid induces a 20% increase (from 13.28 Hz to 15.83 Hz) in the linewidth of the ^{23}Na NMR signal.[5] This increase may be indicative of ion pairing with trifluoroacetate. Consequently, ion pairing effects may contribute, along with protonation of the porphyrin, to the disruption of the metal:porphyrin complex. Whether disruption of the complex is a consequence of protonation and/or ion pairing, these results demonstrate that the metal ion is associated with the porphyrin moiety.

The alkali metal salts also induce an observable increase in the extinction coefficient of the porphyrin Soret band in the UV-vis spectrum (absorbance measurements performed at 414 nm). Consequently, association constants were obtained via UV-vis spectrophotometry. The Scatchard plots for the formation of the $NaB(C_6H_5)_4$, NaI, and KI complexes of tetraphenylporphine proved to be nonlinear and concave, which is consistent with the notion that an unionized porphyrin can bind more than one alkali metal ion. The association constants (table 1) were extracted from Scatchard plots,[6] assuming a two step binding process (which has been previously reported for a porphyrin-containing supramolecular complex[7]). Interestingly, for all three alkali salts, the equilibrium constants associated with the second step (K_2) are smaller than those obtained for the formation of the 1:1 complexes (K_1).

Negative cooperativity for this two step binding process is not unexpected, since the first bound alkali cation should decrease the electron density associated with the metal binding site of the porphyrin (confirmed by the downfield chemical shifts observed in the ^{1}H NMR spectra - *vide supra*) and thereby decrease the affinity of the porphyrin for the second alkali cation.

Salt	K_1 (M^{-1})	K_2 (M^{-1})
NaI	27.5 ± 4.5	6.0 ± 0.7
KI	25.9 ± 2.1	10.3 ± 1.9
NaB(C$_6$H$_5$)$_4$	58.5 ± 7.9	10.8 ± 1.1

LiI, like its sodium and potassium counterparts, interacts with the unionized tetraphenylporphyrin to produce a metal-porphyrin complex. However, LiI in large excess generates a previously described *ionized* dilithium metalloporphyrin.[8-9] The fact that this behavior is not observed with equivalent concentrations of sodium and potassium salts is intriguing and may be a consequence of the lithium ion's comparatively high charge-to-mass ratio.[10] This "proton-like" characteristic may enable lithium to efficiently replace the NH protons contained within the porphyrin macrocycle.

On the basis of the above experiments, we propose that the 2:1 alkali metal ion:porphyrin complexes possess the structure depicted in **1**. It seems likely that the cations would be positioned on opposite faces of the porphyrin, which would partially alleviate deleterious electrostatic interactions between the two metal ions. In addition, since the pyrrole moieties in the corresponding free base and diprotonated forms of tetraphenylporphine are known to be tilted out from the best mean plane of the nitrogens,[11] it is reasonable to conclude that an analogous conformation exists for the bimetallic complex **1** (ie. each alkali metal ion is interacting with just two of the four nitrogens).

1
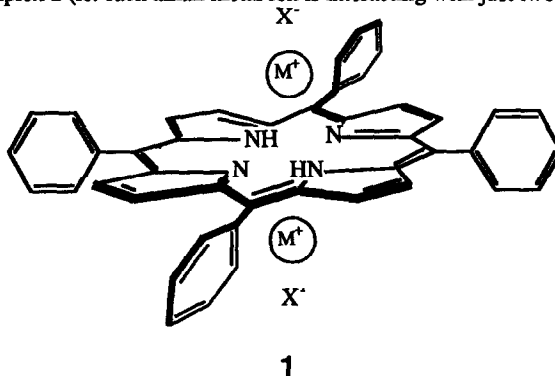
The 2:1 complex **1** bears some resemblance to the sitting-atop complexes of Fleischer and Wang.[12] These investigators proposed that transition metal ions associate with the unionized dimethyl ester of protoporphyrin in a 1:1 stoichiometry. This so-called "sitting-atop" phenomenon has subsequently generated a great deal of controversy.[13] Much of the discussion has centered on the striking resemblance of the visible spectra of 1:1 transition metal:porphyrin sitting-atop complexes to that of the corresponding diprotonated porphyrin. Consequently it has been suggested that what has actually been observed is simply the diprotonated porphyrin. However, in contrast to the controversy that has surrounded the transition metal-based sitting-atop complexes, it is not possible to

confuse the alkali metal ion:porphyrin complexes described in this paper with a diprotonated porphyrin. The four-banded visible spectrum observed for the free base porphyrin is retained in the presence of excess sodium or potassium salt.[14] In contrast, diprotonated porphyrins exhibit a two-banded spectrum. This is attributed to a D_{4h} symmetry associated with the diprotonated form and a D_{2h} symmetry affiliated with the free base form.[15] Since the 2:1 alkali metal:porphyrin complexes described herein exhibit a four-banded spectrum, this suggests that when alkali metal ions interact with the metal binding site, the complex retains a D_{2h} symmetry.

In summary, we have found that the free base form of tetraphenylporphine serves as a host for alkali metal salts. Such behavior appears to confirm Fleischer and Wang's original proposal that metal ions are capable of forming weak complexes with free base porphyrins.

Acknowledgments

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(3) ^{1}H NMR spectra were recorded on a Varian Gemini-300 and the chemical shifts are reported with respect to external tetramethylsilane. Due to the limited solubility of tetraphenylporphine in acetone, we found it necessary to employ a mixed benzene/acetone solvent system for the NMR studies. 8.1 x 10^{-6} moles of the porphyrin were dissolved in 1.8 mL of benzene-d_6 and 1.62 x 10^{-5} moles of the appropriate salt were dissolved in 0.2 mL acetone-d_6. The solutions were mixed and centrifuged to remove any remaining undissolved porphyrin and salt. The chemical shifts of the pyrrolenine nitrogen protons were referenced with respect to tetramethylsilane. 18-crown-6 (1.8 x 10^{-5} moles) was added to the solution containing NaB(C_6H_5)$_4$ and the NMR spectrum was recorded. ^{23}Na NMR spectra were recorded on a Varian VXR-400 at 105.8 MHz. 26K of data was collected for each spectrum and zero filled to 64 K, giving a digital resolution of 0.46 Hz. The observed signals were not subjected to line broadening or weighted functions. ^{23}Na NMR linewidths were obtained by measuring the width at half peak height.

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(5)   We note that the resultant ^{23}Na NMR linewidth observed for the trifluoroacetic acid-treated NaB(C_6H_5)$_4$ solution (15.83 Hz) is smaller than that of trifluoroacetic acid-treated NaB(C_6H_5)$_4$-porphyrin mixture (20.05 Hz). This may reflect a possible increase in solution viscosity associated with the latter.

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(9) The ionized dilithiometalloporphyrin exhibits a two banded UV-vis spectrum in the 500 - 700 nm region [574 nm (ε = 5750 M^{-1} cm^{-1}); 614 nm (ε = 4780 M^{-1} cm^{-1})]. In contrast, the alkali metal complexes of the free base porphyrin, as well as the free base porphyrin itself, display a four-banded spectrum in this region. See reference 14.

(10) The enthalpy of solution for lithium salts is generally much more negative than that for sodium and potassium salts. Indeed, the evolution of heat is obvious upon dissolving LiI in acetone. This evolved heat could serve as a driving force for the formation of the ionized dilithium metalloporphyrin. Consequently, we prepared all of our acetone-salt mixtures well in advance to eliminate this possibility.

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(14) The four- and two-banded terminology refers to the number of absorbance bands in the 500-700 nm region. Free base tetraphenylporphine displays a four-banded spectrum [512 nm (ε = 4732 M^{-1} cm^{-1}); 546 nm (ε = 3549 M^{-1} cm^{-1}); 586 nm (ε = 2958 M^{-1} cm^{-1}); 646 nm (ε = 2760 M^{-1} cm^{-1})]; Soret band: 414 nm (ε = 52,269 M^{-1} cm^{-1}). In the presence of 1 M NaB(C$_6$H$_5$)$_4$, the porphyrin (1.42 x 10^{-6} M) also exhibits a four-banded spectrum [512 nm (ε = 4338 M^{-1} cm^{-1}); 546 nm (ε = 2761 M^{-1} cm^{-1}); 586 nm (ε = 2366 M^{-1} cm^{-1}); 646 nm (ε = 2169 M^{-1} cm^{-1})]; Soret band = 414 nm (ε = 57,590 M^{-1} cm^{-1}). In contrast, tetraphenylporphine, in the presence of 5% trifluoroacetic acid in acetone, displays a two-banded spectrum [602 nm (ε = 1120 M^{-1}cm^{-1}); 656 (ε = 5500 M^{-1} cm^{-1}).

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