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Effect of Molecular Complexation of the Porphyrin Ligand on the Axial Ligation of FeTPPCl

C. T. BREWER and G. A. BREWER

Department of Chemistry, The Catholic University of America, Washington, D.C. 20064, U.S.A.

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Abstract

The formation of a molecular complex between tetraphenylporphyrin or a metallotetraphenylporphyrin and electron acceptors in toluene and in dimethylsulfoxide is evidenced by a red shift and loss of intensity in the Soret region. Complexation between a donor or acceptor and the porphyrin periphery in a metalloporphyrin is expected to effect reactions at the metal center. The effect of molecular complexation on the axial ligation of 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine iron(III) chloride (FeTPPCl) was investigated by a determination of the equilibrium constant and thermodynamic data for the reaction between FeTPPCl and 1-methylimidazole (MeIm) in dimethylsulfoxide in the presence of an electron donor and an electron acceptor. ΔH values in the presence of the donor 1,10-phenanthroline and the acceptor **II** are −58.3 and −32.8 kJ mol^{-1}, respectively, compared to −47.8 in the absence of either a donor or an acceptor. ΔS values for the reaction in the presence of a donor, in the presence of an acceptor, and in the absence of either are −0.12, −0.036 and −0.082 kJ $(\mathrm{Kmol})^{-1}$, respectively. The enthalpies indicate that an electron donor favors the low spin bisadduct of FeTPPCl and MeIm while an acceptor favors the high spin non-ligated form. The entropy effects are in opposition to the enthalpy effects.

Introduction

The ligand **I**, shown in Fig. 1, was specifically designed for binding to a metalloporphyrin through the deprotonated imidazole ring to form an imidazolate bridged porphyrin–M_1–imidazolate–M_2–ligand species. For the case M_1 = Fe(III) and M_2 = Cu(II), the product was proposed as a model of the active site of cytochrome *c* oxidase [1]. In this earlier work, the bisadduct of FeTPPCl with **I** formed in dimethylsulfoxide with an equilibrium constant at 25 °C of $\beta_2 = 4.4 \times 10^7$ M^{-2} which is more than three orders of magnitude greater than with MeIm in the same solvent ($\beta_2 = 1.2 \times 10^4$ M^{-2}). A large difference in the entropy of reaction was found to be primarily responsible although the reason for the more positive entropy change observed with **I** as opposed to MeIm was unclear. It is now apparent that association between the aromatic system of **I** and the porphyrin ring may be largely responsible for the strongly favorable entropy changes observed in the reaction of FeTPPCl with **I**.

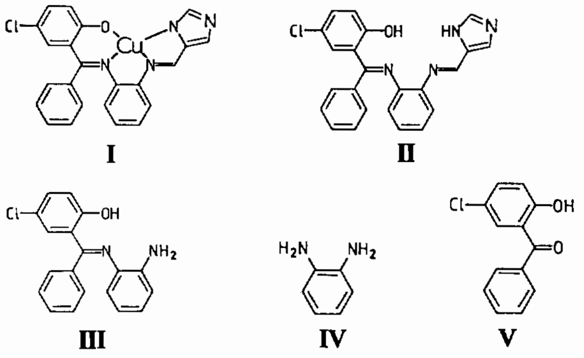

Fig. 1. Molecules used in this work.

The ability to form pi complexes with electron donors and acceptors is a well established property of porphyrins and metalloporphyrins manifested by their tendencies to form aggregates with themselves and with other aromatic molecules [2–9]. NMR studies of the interaction of various aromatic molecules with the porphyrin ring suggest a parallel orientation of the two aromatic systems allowing overlap of pi electron density between the porphyrin and the donor or acceptor molecule [10, 11]. These systems provide the opportunity to determine what effect, if any, pi–pi interactions at the porphyrin periphery have on axial ligation of the metal center. The effect of molecular complexation on metal centered reactions is relevant to the study of enzyme function in natural systems where they have been invoked to explain such phenomena as cooperativity of O_2 binding in hemoglobin [12, 13].

This work reports spectral evidence for molecular complexation between 5,10,15,20-tetraphenyl-21*H*,23*H*-porphine (H_2TPP) and its Zn(II) and Fe(III) derivatives and a series of electron acceptors and results of an investigation of the effects of molecular complexation on the axial ligation of FeTPPCl. Thermodynamic parameters for the axial ligation

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of the iron(III) porphyrin in the presence of a donor and an acceptor were determined and compared to the data in the absence of a molecular adduct forming molecule. The data indicate that the low spin bisadduct of FeTPPCl with 1-methylimidazole is stabilized relative to high spin $FeTPP^+$ in the presence of an electron donor and destabilized relative to $FeTPP^+$ in the presence of an electron acceptor. The entropy change of the reaction is also affected by the presence of a donor or acceptor molecule, but in the opposite direction.

Experimental

1-Methylimidazole was obtained from Aldrich, vacuum distilled, and stored over molecular sieves prior to use. H_2TPP and its iron(III) complex (FeTPPCl) were obtained from Aldrich and stored in the dark at −5 °C until needed. Zinc was inserted into H_2TPP following the method of Adler *et al.* [14]. It was chromatographed on alumina with $CHCl_3$ as eluant, the solution was evaporated, and the ZnTPP was dried at 100 °C and then stored in the dark at −5 °C. Spectrophotometric grade dimethylsulfoxide (DMSO) was used as received from Aldrich. Toluene was obtained from Fisher and distilled from sodium before use. Compounds **I**, **II**, and **III** were prepared according to literature procedures [15]. All other reagents were obtained from Aldrich and used as received.

UV–Vis spectra were obtained with a Perkin-Elmer lamda 4 or model 576 spectrophotometer both equipped with a temperature controller. Equilibrium constants were determined from the variation of the FeTPPCl absorbance at 529 nm as a function of MeIm concentration. The ratio of FeTPPCl to 1,10-phenanthroline or **II** was approximately 1:13. Data were worked up by the method of Drago as described elsewhere [16]. Enthalpies and entropies of reaction were determined from the variation of the logarithm of the equilibrium constant with temperature over the range 20.0–35.0 °C.

Results and Discussion

In addition to the spectral changes expected upon axial ligation of FeTPPCl by **I**, the Soret band red shifts from 426 to 458 nm at high concentrations of **I** and decreases to about one sixth of its original intensity. The effect of **I** on the spectrum of FeTPPCl was studied further in toluene since axial ligation of the iron porphyrin is not observed in that solvent [1]. In toluene, the Soret changes are reproduced, but spectral changes due to bisligation are not observed as shown in Fig. 2a. Two separate interactions must give rise to the two sets of spectral changes. This was verified by noting the effect of adding the copper free ligand **II**, which does not bind to the metalloporphyrins, to H_2TPP, ZnTPP, and FeTPPCl in toluene. The Soret bands of all three red shift and decrease in intensity, resulting in new extinction coefficients which are in the order of those for the visible bands. The visible bands are unchanged in position. This is illustrated for the case of H_2TPP in Fig. 2b. In the case of ZnTPP, the addition of **I** causes the same changes in the Soret region, as well as spectral changes associated with formation of the axial adduct (Fig. 2c). The strong effect on the Soret absorption which is observed both in the presence and absence of axial ligation is attributed to an interaction at the porphyrin periphery between the pi system of the

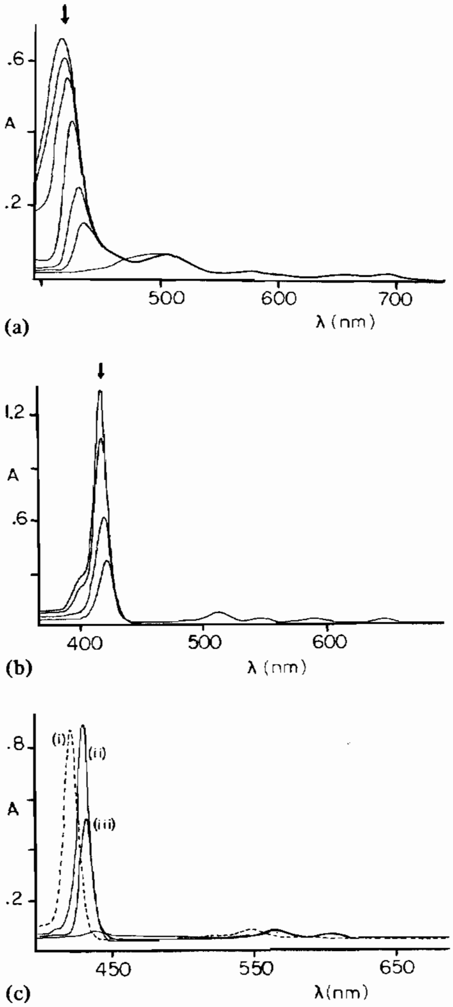

Fig. 2. (a) Spectral changes observed upon addition of **I** to FeTPPCl in toluene. (b) Spectral changes observed upon addition of **II** to H_2TPP in toluene. (c) Spectral changes observed upon addition of **I** to ZnTPP in toluene: (i) ZnTPP; (ii) ZnTPP + **I** to give Zn(TPP)(**I**); (iii) ZnTPP + excess **I**.

ligand and the porphyrin pi system. No new absorption which could be attributed to a charge transfer transition is observed in the region between 400 and 900 nm. Strong absorption by the addends in the ultraviolet region prevented observation of the spectrum below 400 nm. The spectral changes are temperature reversible and reversible upon dilution. The lack of clean isosbestic points may arise from the formation of a series of complexes with varying numbers of interacting ligands depending upon ligand concentration.

The interaction between **I** or **II** and the porphyrins was examined further by observing the effect of adding **III**, **IV** and **V** to H_2TPP in toluene. Since **II**, **III**, **IV** and **V** represent basic structural units comprising **I**, their effects on the spectra of the porphyrin species should provide some evidence for the specific interaction giving rise to the spectral changes described. The results obtained with **III** are essentially the same as those described for **I** and **II** while addition of **IV** (phenylenediamine) had no effect. Addition of **V** (5-chloro-2-hydroxybenzophenone) produces a spectrum almost identical to that produced by oxidation of H_2TPP by iodine. The Soret band at 417 nm in toluene is replaced by a new Soret band at 446 nm. The visible region between about 480 and 650 nm is featureless with a strong broad band appearing between 600 and 700 nm. The same spectral changes can be brought about by the addition of 3-chlorobenzophenone. Oxidation of the porphyrin ring by **V** is an extreme case of a charge transfer interaction in which the porphyrin is the donor and **V** the acceptor. Based on this evidence and other reports of pi–pi complexation between porphyrins or metalloporphyrins and aromatic molecules, the observed spectral changes when **I**, **II** and **III** (which do not oxidize the porphyrin) are added to H_2TPP can be attributed to an interaction between the porphyrin ring as an electron donor and the chlorohydroxybenzophenone fragment (**V**) of the ligands as an electron acceptor. Chlorohydroxybenzophenone (**V**) does not oxidize either the zinc or iron porphyrin although the red shift and decrease in the Soret band for both metalloporphyrins upon addition of the above ligands indicates that the same interaction between porphyrin and ligand occurs in these systems.

Studies of pi bonding in ferric porphyrins have indicated the importance of Fe—Por π^* charge transfer in the high spin form and of Por—Fe π charge transfer in the low spin form [17, 18]. The high spin form might then be expected to be stabilized by molecular complexation to an electron acceptor and the low spin form by molecular complexation to an electron donor. In light of these considerations, the formation of a molecular complex between an iron(III) porphyrin and a donor or acceptor would be expected to influence its axial ligation reactions since the non-ligated iron(III) porphyrin undergoes a change from high spin to low spin upon formation of the bisadduct. In support of this prediction, both the pi acceptor trinitrobenzene and the donor 1,10-phenanthroline have been shown to affect the position of equilibrium between an iron porphyrin chloride and its bisimidazole or bismethylimidazole adduct [19, 20].

In order to determine the effect of a donor or acceptor molecule on the axial ligation of an iron(III) porphyrin and, in particular, to clarify the role that molecular complexation has in the axial ligation of FeTPPCl by **I**, a comparison of the enthalpy and entropy of axial ligation in the presence and absence of the donor or acceptor was undertaken using 1,10-phenanthroline as the donor and **II** as the acceptor. Due to the similarity between **I** and **II**, the results should give some indication of the extent to which molecular complexation contributes to the unusually positive entropy value determined for the axial ligation of FeTPPCl by **I** compared to the same reaction with MeIm [1]. Since the earlier work was carried out in DMSO, that solvent was also chosen for this study.

Titration of fixed concentrations of FeTPPCl and acceptor or donor (~13 mol excess over the iron porphyrin) with varying aliquots of MeIm produces spectral changes between 500 and 700 nm that are qualitatively identical to those obtained in the absence of a molecular adduct former. The visible band at 529 nm red shifts and decreases in intensity and a new visible maximum grows in at 547 nm in the presence of **II** and at 549 nm in the presence of 1,10-phenanthroline. Isosbestic points occur at 544 and 622 nm for the reaction in the presence of 1,10-phenanthroline and at 545 and 654 nm in the presence of **II**.

The reaction between FeTPPCl and an axial base in DMSO is shown in eqn. (1).

$$\mathrm{FeTPP(DMSO)_2^+ + 2MeIm \overset{\beta_2}{\rightleftharpoons} FeTPP(MeIm)_2^+} \quad (1)$$

Table I compares equilibrium constants at 25 °C, enthalpies of reaction, and entropies of reaction for the bisligation of FeTPPCl with MeIm in the presence and in the absence of 1,10-phenanthroline and **II**. Figure 3 shows the van't Hoff plots from which ΔH and ΔS for the reactions were determined. A more negative enthalpy change for the reaction in the presence of phenanthroline implies that the low spin bisadduct is stabilized relative to $FeTPP^+$ by the formation of a molecular complex with an electron donor as predicted. Preferential formation of molecular complexes with the low spin bisadduct would decrease the entropy of the system as phenanthroline and metalloporphyrin molecules become more highly complexed on

TABLE I. Thermodynamic Data for the Reaction $FeTPPCl + 2MeIm \rightleftharpoons FeTPP(MeIm)_2^+Cl^-$

Addend	β_2 (25 °C) (M^{-2})	ΔH (kJ mol^{-1})	ΔS (kJ $(Kmol)^{-1}$)
None	1.2×10^4	−47.8	−0.082
1,10-Phenanthroline	1.0×10^4	−58.3	−0.12
II	7.2×10^3	−32.8	−0.036

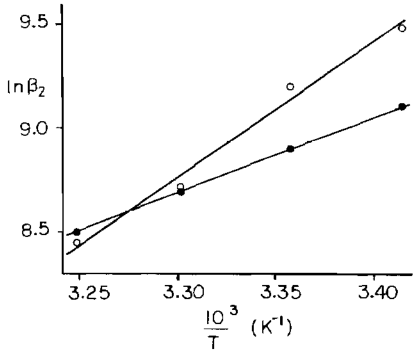

Fig. 3. Van't Hoff plots for the reaction of FeTPPCl with 1-methylimidazole in the presence of 1,10-phenanthroline (open circles) and of II (closed circles).

proceeding from high spin reactant to low spin product. A more positive enthalpy change for the reaction in the presence of **II** implies that the low spin bisadduct is destabilized relative to $FeTPP^+$ by the formation of a molecular adduct with an electron acceptor. A more positive ΔS could occur as a result of partial dissociation of the molecular complexes formed between $FeTPP^+$ and **II** upon axial ligation.

The binding of **I** to FeTPPCl in DMSO occurs with an enthalpy of reaction, −47.5 kJ mol^{-1}, which is comparable to that observed for the binding of MeIm in DMSO, −47.8 kJ mol^{-1} [3]. However, the entropy of reaction, −0.013 kJ $(Kmol)^{-1}$, is significantly more positive than that for the binding of MeIm, −0.082 kJ $(Kmol)^{-1}$. From the results presented here, it is reasonable to assume that these differences in entropy arise, at least in part, from an interaction of **I** at the periphery of the metalloporphyrin, which, as in the case of the ligand **II**, occurs to a greater extent in the high spin reactant than in the low spin adduct.

It should also be noted that for both the donor and the acceptor, the observed equilibrium constants at 25 °C were lower than that measured in the absence of either, which points out the ineffectiveness of the equilibrium constant alone to distinguish the relative stabilities of reactant and product.

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References

1 C. T. Brewer and G. A. Brewer, *Inorg. Chem., 26,* 3420 (1987).
2 M. Gouterman and P. E. Stevenson, *J. Chem. Phys., 37,* 2266 (1962).
3 D. Mauzerall, *Biochemistry, 4,* 1801 (1965).
4 H. A. O. Hill, A. J. Macfarlane and R. J. P. Williams, *J. Chem. Soc. A,* 1704 (1969).
5 G. N. La Mar, J. D. Satterly and R. V. Snyder, *J. Am. Chem. Soc., 96,* 7137 (1974).
6 H. Yokoi and M. Iwaizumi, *Bull. Chem. Soc. Jpn., 53,* 1489 (1980).
7 J. A. Shelnutt, *J. Phys. Chem., 88,* 6121 (1984), and refs. therein.
8 T. K. Chandrashekar and V. Krishnan, *Inorg. Chem., 20,* 2782 (1980).
9 T. K. Chandrashekar and V. Krishnan, *Can. J. Chem., 62,* 475 (1983).
10 C. D. Barry, H. A. O. Hill, B. E. Mann, P. J. Sadler and R. J. P. Williams, *J. Am. Chem. Soc., 95,* 4545 (1973).
11 G. P. Fulton and G. N. La Mar, *J. Am. Chem. Soc., 98,* 2119 (1975).
12 M. F. Perutz, *Nature (London), 228,* 726 (1970).
13 R. T. Ogata and H. McConnell, *Proc. Natl. Acad. Sci. U.S.A., 69,* 335 (1972).
14 A. D. Adler, F. R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem., 32,* 2443 (1970).
15 R. Atkins, G. Brewer, G. KoKot, G. M. Mockler and E. Sinn, *Inorg. Chem., 24,* 127 (1985).
16 C. T. Brewer and G. A. Brewer, *Inorg. Biochem., 26,* 247 (1986).
17 G. N. La Mar and F. A. Walker, *J. Am. Chem. Soc., 95,* 1782 (1973).
18 G. N. La Mar, G. R. Eaton, R. H. Holm and F. A. Walker, *J. Am. Chem. Soc., 95,* 63 (1976).
19 G. N. La Mar, J. D. Satterlee and R. V. Snyder, *J. Am. Chem. Soc., 96,* 7137 (1974).
20 E. H. Abbott and P. A. Rafson, *J. Am. Chem. Soc., 96,* 7378 (1974).