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Axial Ligation of Nitrogenous Bases to Five-coordinate Chloro-*meso*-tetraphenylporphyrinatochromium(III)

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Abstract

The axial ligations of nitrogenous bases to the five-coordinate chloro-*meso*-tetraphenylporphyrinatochromium(III) [Cr(III)(TPP)(Cl)] were studied in a non-coordinating solvent, dichloromethane (CH_2Cl_2), by spectrophotometric methods. A correlation exists between log K for the axial ligation:

$$Cr(TPP)(Cl) + L \overset{K}{\rightleftharpoons} Cr(TPP)(Cl)(L)$$

and pK_a for the N-donor ligand. This correlation suggests that ligand to metal σ bonding contributes to the complex formation, rather than does metal to ligand π back-donation.

Introduction

Various biological roles of the natural hemoproteins are intimately related to properties of the axial ligation in the heme moiety. In a previous paper [1] we reported that the addition of neutral or anionic ligands to *meso*-tetraphenylporphyrinatocadmium (CdTPP) caused red shifts in the visible absorption spectrum. The magnitude of the red shift was dependent on the density of the negative charge transferred from the ligand to the porphyrin ring via metal, but not on the strength of the Cd–ligand bond. Further, we observed that the electronic absorption spectrum of chloro-*meso*-tetraphenylporphyrinatochromium(III) [Cr(III)(TPP)(Cl)] undergoes blue or red shift upon addition of axial ligands, such as superoxide ion, O_2^- and OH^- [2]. In order to understand the various functions of the heme proteins it is important to know how the axial ligation affects the electronic structure and reactivity of a metalloporphyrin.

Recently, Basolo *et al.* [3] and O'Brien *et al.* [4] have shown the formation of a variety of complexes Cr(porphyrin) (A) (B), where A and B represent anionic and neutral ligands respectively in toluene. However, since Cr(III)(TPP)(Cl) is sparingly soluble in toluene, Basolo *et al.* could not obtain any absolute values for the affinity of a ligand to the five-coordinate Cr(III)(TPP)(Cl) [3]. Therefore, we re-examined the axial ligation of nitrogenous bases to the five-coordinate Cr(III)(TPP)(Cl) in dichloromethane (CH_2Cl_2), which does not ligate with metalloporphyrins.

In this paper we report on the relative affinities of neutral ligands such as nitrogenous bases to Cr(III)(TPP)Cl.

Experimental

Materials

meso-Tetraphenylporphyrin (TPP)*, prepared by the method of Alder *et al.* [5], was purified by refluxing with 2,3-dichloro-5,6-dicyanobenzoquinone in dichloromethane (CH_2Cl_2) to remove *meso*-tetraphenylchlorine [6]. Cr(III)(TPP)(Cl) was prepared by the reported methods [3a, 7].

1-methylimidazole (1-MeIm) was distilled from KOH under reduced pressure and stored over freshly activated 4A molecular sieves. Pyridine (Py) and 3,4-lutidin (3,4-Lut) were dried over KOH, purified by standard methods and distilled prior to use. 4-Cyanopyridine (4-CNPy) was recrystallized from benzene. *sec*-Butylamine (*sec*-ButNH_2) was used without further purification. Dimethyl sulfoxide (DMSO) was distilled under reduced pressure from CaH_2 and stored over freshly activated 4A molecular sieves under dry argon. Dichloromethane was distilled, and passed through a neutral alumina column to remove stabilizer.

All other reagents were reagent grade and were used without further purification, unless otherwise noted.

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*Abbreviations used in this paper are as follows: TPP, *meso*-tetraphenylporphyrin; DMSO, dimethyl sulfoxide; CH_2Cl_2, dichloromethane; MeIm, methylimidazole; Im, imidazole; Py, pyridine; Lut, lutidine; CNPy, cyanopyridine; *sec*-ButNH_2, *sec*-butylamine; THF, tetrahydrofuran; THTP, tetrahydrothiophene; sh, shoulder; Pip, piperidine; OAc^-, acetate; A, anionic ligand; B, neutral ligand; L, nitrogenous ligand; D, donor ligand.

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TABLE I. Absorption Spectral Parameter of Cr(III) Porphyrin Complexes.

Compound	λ_{max} (nm) (log ϵ)						
Cr(TPP)(Cl)	398 (4.59)	450 (5.37)	528 (3.66)	565 (4.01)	604 (3.94)		
Cr(TPP)(Cl)(DMSO)	397 (4.39)	449 (5.40)	528 (3.59)	568 (3.99)	607 (4.02)		
Cr(TPP)(Cl)(Py)	370 (4.39)	412 (4.59)	459 (5.20)	530 (3.66)	573 (3.97)	613 (4.06)	
Cr(TPP)Cl)(THF)[a]	398 (4.60)	450 (5.38)	528 (3.62)	565 (3.99)	604 (3.95)		
Cr(TPP)(Cl)(THTP)[a]	398 (4.43)	412 (4.39)	450 (5.00)	464 (4.87)	530 (3.62)	573 (3.90)	608 (3.92)
Cr(TPP)(Cl)(4-CNPy)	404 (4.52)	440 sh[a]	455 (4.89)	462 sh[a]	530 (3.63)	575 (3.93)	615 (4.00)
Cr(TPP)(Cl)(3,4-Lut)	367 (4.45)	408 (4.66)	459 (5.29)	532 (3.66)	574 (3.95)	614 (4.06)	
Cr(TPP)(Cl)(1-MeIm)	404 (4.63)	456 (5.36)	532 (3.62)	574 (3.93)	615 (4.06)		
Cr(TPP)(Cl)(*sec*-ButNH$_2$)	400 (4.03)	453 (5.40)	530 (3.62)	571 (3.96)	612 (4.08)		

[a] Abbreviations: THF, tetrahydrofuran; THTP, tetrahydrothiophene; sh, shoulder.

Methods

Aliquots of ~10^{-2} M ligands solutions were successively added to 2 ml of CH$_2$Cl$_2$ solution of Cr(III)(TPP)(Cl) (10^{-6}–10^{-5} M) in a capped quartz cell with a light path of 10 mm, as mentioned previously [8].

Spectral and Equilibrium Constant Measurements

Ultraviolet(UV)/visible absorption spectra were measured at 25.0 °C using a Union Giken SM-401 spectrometer. The equilibrium constants (K_{eq}) were estimated by use of the method of Basolo *et al.* [3].

Results and Discussion

Since Cr(III)(TPP)(Cl) is sparingly soluble in dry distilled toluene, it seems impossible to obtain the absolute values for the affinity of sixth ligands to the five-coordinate Cr(III)(TPP)(Cl). But Cr(III)(TPP)(Cl) is adequately soluble in CH$_2$Cl$_2$, which does not coordinate to the metalloporphyrins. By using CH$_2$Cl$_2$ instead of toluene, it is possible to get the absolute values for the affinity of sixth ligands to the five-coordinate Cr(III)(TPP)(Cl).

The absorption spectrum of Cr(III)(TPP)(Cl) in CH$_2$Cl$_2$ is shown in Fig. 1. The addition of coordinating solvents (*e.g.*, DMSO, Py) resulted in an immediate change in the visible spectrum (Table I). It is apparent from Table I that the spectral change upon addition of the weak-field ligands such as DMSO, THF and THTP was slight, whereas upon addition of the strong-field ligands (such as nitrogenous bases) the spectrum shifted remarkably to red. These red shifts are observed upon addition of the axial ligand to many metalloporphyrins [1]. The absorption spectra of the Cr(III)(TPP)(Cl) with axial ligands listed in Table I did not change over a period of at least 24 h in the dark at room temperature.

Spectrophotometric titrations of Cr(III)(TPP)(Cl) with nitrogenous ligands, L, were performed in CH$_2$Cl$_2$ at 25 °C. A typical example is shown in Fig. 2. A plot of log[Cr(TPP)(Cl)(L)]/[Cr(TPP)(Cl)]$_{total}$ *vs.* log (L) gave a straight line with the slope of approximately 1. The observed equilibrium constants are given in Table II.

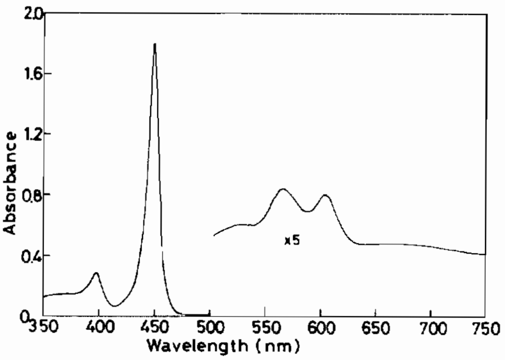

Fig. 1. Visible absorption spectrum of Cr(III)(TPP)(Cl) in CH$_2$Cl$_2$ at room temperature. Concentration of Cr(III)(TPP)(Cl) is 2.86 × 10^{-6} M.

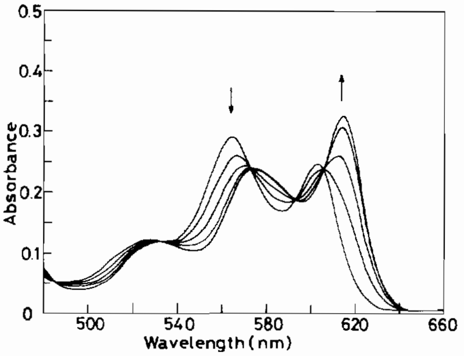

Fig. 2. Titration of Cr(III)(TPP)(Cl) with 1-MeIm in CH$_2$Cl$_2$ at room temperature. 0.5 μl of 1-MeIm (9.51 × 10^{-3} M) solution was successively added to 2 ml of Cr(III)(TPP)(Cl) (2.85 × 10^{-5} M) solution by microsyringe.

These results indicate that one mol of Cr(III)(TPP)(Cl) reacts with one mol of ligand to form the Cr(III)(TPP)(Cl)(L), as shown in eqn. (1). For all of

TABLE II. Equilibrium Constants for the Reaction Cr(TPP)(Cl) + L = Cr(TPP)(Cl)(L).

L	pK_a of L	K (M^{-1})	log K
4-CNPy	1.86[a]	1.19×10^5	5.07
Py	5.27[b]	1.87×10^5	5.27
3,4-Lut	6.46[b]	3.17×10^5	5.50
1-MeIm	7.25[b]	2.28×10^5	5.36
sec-ButNH$_2$	10.56[c]	6.55×10^5	5.82

[a] Ref. 9. [b] Ref. 10. [c] Ref. 11.

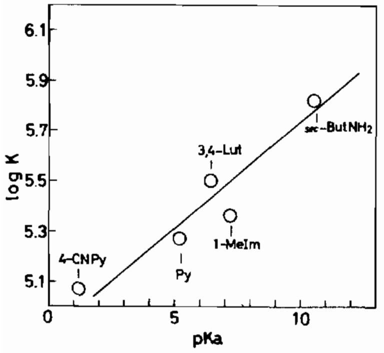

Fig. 3. Correlation between pK_a for the conjugate acids (LH^+) and log K for the reaction Cr(TPP)(Cl) + L = Cr(TPP)(Cl)(L) in CH_2Cl_2 at 25 °C.

$$\mathrm{Cr(TPP)(Cl)} + \mathrm{L} \overset{K}{\rightleftharpoons} \mathrm{Cr(TPP)(Cl)(L)} \qquad (1)$$

the nitrogenous ligands studied, the spectra data could be explained as assuming only a 1:1 complex. Since further spectral changes were not observed upon addition of excess pyridine (~10 M) over the metalloporphyrin, chloride may not be displaced in these reactions.

A plot of log K (eqn. (1)) *vs.* pK_a of N-donor ligand, L, is shown in Fig. 3, which shows the approximately linear relationship between log K for the reaction (1) and pK_a for the ligand. The values of log K are somewhat larger than those reported in the substitution reactions of axial ligands in Cr(III)(TPP)(Cl)(D) (D: O- or S-donor) [3a]. The linearity of the plot for the π-acceptor substituted pyridine ligands and the non-π-bonding *sec*-butylamine was observed.

These results suggest that metal to ligand π-bonding is unimportant for the ligation to the five-coordinate Cr(III)(TPP)(Cl), as suggested by Basolo *et al.* [3a] for the substitution of the six-coordinate Cr(III)(TPP)(Cl)(D). The increase in log K with pK_a presumably indicates that ligand to metal σ bonding is predominant. Inverse correlations such as formed with iron(II) porphyrins with substituted pyridines have been explained in terms of appreciable metal–ligand back-donation [12].

In conclusion, we obtained the absolute values for the axial ligation of nitrogenous bases to the five-coordinate Cr(III)(TPP)(Cl).

References

1 T. Ozawa and A. Hanaki, *Chem. Pharm. Bull., 31,* 2110 (1983).
2 T. Ozawa and A. Hanaki, *Chem. Pharm. Bull., 32,* 4226 (1984).
3 (a) D. A. Summerville, R. D. Jones, B. M. Hoffman and F. Basolo, *J. Am. Chem. Soc., 99,* 8195 (1977); (b) F. Basolo, R. D. Jones and D. A. Summerville, *Acta Chem. Scand., Ser. A:, 32,* 771 (1978).
4 P. O'Brien and D. A. Sweigart, *Inorg. Chem., 21,* 2094 (1982).
5 A. D. Alder, F. R. Longo, R. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem., 32,* 476 (1967).
6 G. H. Barnett, M. F. Hadson and K. M. Smith, *Tetrahedron Lett.,* 2887 (1973).
7 A. D. Alder, F. R. Longo, F. Kampas and J. Kim, *J. Inorg. Nucl. Chem., 32,* 2443 (1970).
8 (a) T. Ozawa and A. Hanaki, *Inorg. Chim. Acta, 80,* 33 (1983); (b) T. Ozawa and A. Hanaki, *Chem. Pharm. Bull., 31,* 2142 (1983).
9 K. Schofield, in 'Hetero-Aromatic Nitrogen Compounds', Plenum Press, New York, 1967, p. 146.
10 A. Albert, *Phys. Methods Heterocycl. Chem.,* 1 (1963).
11 P. A. S. Smith, in 'The Chemistry of Open-Chain Organic Nitrogen Compounds, Vol. I', Benjamin, New York, 1965, p. 19.
12 J. E. Folk, J. N. Philips and E. A. Magunussen, *Nature (London), 212,* 1531 (1966).