

## Metalloporphyrin *Cis* Effects and the Coordination Properties of Benzporphyrin Complexes. Ligand Binding to Octamethyltetrabenzporphyrinzinc(II)

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### Introduction

Metalloporphyrins fulfill a variety of roles in biological systems including oxygen transport and storage (hemoglobin and myoglobin), electron transport (cytochrome c) and hydroxylation reactions (cytochrome P450) [1]. The protein defines and modulates these processes but for each the metal-porphyrin bond must accommodate a remarkable diversity of ligation and redox changes. Metalloporphyrin properties have been interpreted both in terms of extensive orbital mixing [2] as well as by means of simpler electrostatic (ligand field) models [3]. An appreciation of the nature of the metal-porphyrin bond is clearly a prerequisite to a better understanding of the heme proteins.

Benzporphyrin derivatives should be especially suited to investigations of metalloporphyrin bonding and *cis* effects. Mössbauer data [4] suggest that the octamethyltetrabenzporphyrin dianion, OMBP, is a weak  $\sigma$  donor but a strong  $\pi$ -bonding ligand. If the limiting delocalization model obtains for  $M(\text{OMBP})$  complexes, ligation reactions should be particularly sensitive to the nature of the metal,  $M$ , and its ability to transmit  $\sigma$  and/or  $\pi$  electronic effects. In order to evaluate this proposal it is necessary to first consider a system where these effects are separated. Enhanced ligand affinity is consistent with decreased  $\text{Por} \rightarrow M$  donation [5]. For  $\text{Zn}^{2+}$  there are no empty d orbitals available for  $\pi$ -bonding and ligand binding to  $\text{Zn}(\text{OMBP})$  (Fig. 1) should only reflect the  $\sigma$ -donor properties of OMBP. Although the unusual optical [6] and redox [7] properties of benzporphyrins have recently been investigated, this is the first report describing the coordination

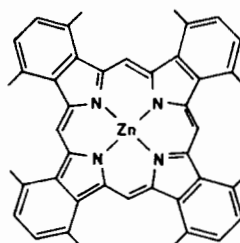


Fig. 1. The structure of octamethyltetrabenzporphyrinzinc(II),  $\text{Zn}(\text{OMBP})$ .

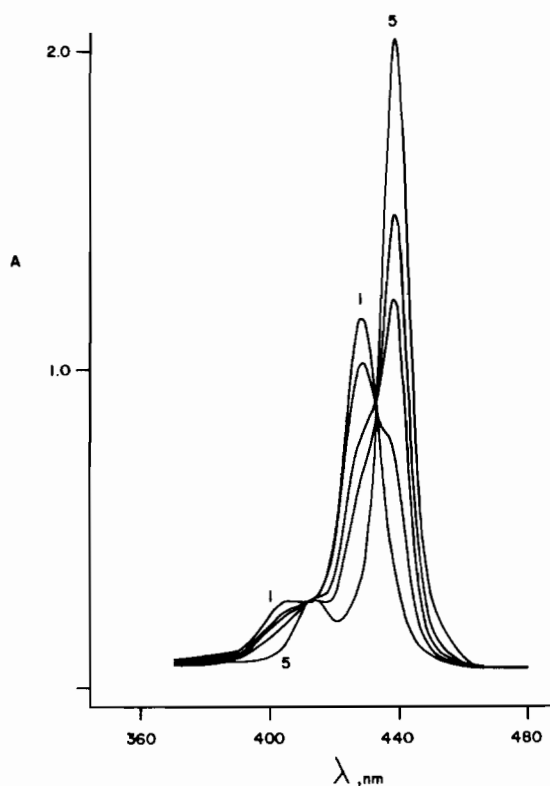


Fig. 2. The addition of 1-MeIm to a  $10^{-7} M$  toluene solution of  $\text{Zn}(\text{OMBP})$ . [1-MeIm] for successive spectra 1:5: 0,  $2.16 \times 10^{-8}$ ,  $7.02 \times 10^{-7}$ ,  $1.24 \times 10^{-6}$ ,  $6.12 \times 10^{-5}$ .

chemistry of a four-coordinate [8] benzporphyrin complex.

### Experimental

Samples of  $\text{Zn}(\text{OMBP})$  were prepared by a modification of the literature [9] procedure and recrystallized by the slow cooling of a saturated 20% pyridine/ether solution. Toluene (Fisher spectroscopy grade)

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was distilled under nitrogen from calcium hydride. Amines (pyridine, py; piperidine, pip; 1-methylimidazole, 1-MeIm) were refluxed over, and distilled from, potassium hydroxide under anaerobic conditions.

Binding measurements were conducted by the syringe addition of the ligand in toluene to dilute ( $\sim 10^{-7}$  M) solutions of Zn(OMBP) contained in a 10 cm pathlength spectroscopic cell. No aggregation was observed at the low zinc concentration employed.

## Results and Discussion

The position of the Soret band of Zn(OMBP) is strongly solvent dependent (429 nm-toluene, 435 nm- $\text{CH}_2\text{Cl}_2$ ) and is red-shifted upon ligation (Fig. 2). The magnitude of these shifts is related to the nature of the donor atom (10 nm for N-donors, 3 nm for O-donors; for Zn(OMBP) in toluene). Similar effects have been noted for tetraphenylporphyrinzinc(II), Zn(TPP), as have changes in the extinction coefficients of the  $\alpha$  and  $\beta$  bands [10]. However, the 584 and 633 nm bands of Zn(OMBP) are relatively insensitive to ligand and solvent effects. Although iron and cobalt derivatives of OMBP display hyper-spectral [2] characteristics Zn(OMBP) does not – consistent with the absence of  $\pi$  effects in this  $d^{10}$  system.

The successive addition of amines to toluene solutions of Zn(OMBP) gave excellent isosbestic points (Fig. 2). For the reaction



the equilibrium expression may be written as:

$$\log \frac{A_0 - A}{A - A_\infty} = \log K + \log [L]$$

where  $A_0$  and  $A_\infty$  are the absorbances of Zn(OMBP) and Zn(OMBP)L respectively. Plots of  $\log[(A_0 - A)/(A - A_\infty)]$  against  $\log [L]$  were linear with slopes of  $1 \pm 0.05$ . No higher coordination numbers were observed; solutions of Zn(OMBP) in neat amine gave  $\epsilon$  values identical to those observed in the titration experiments. Five coordination has been noted in all ligand binding studies [10, 11] of zinc porphyrins. This has been attributed [12] to structural restrictions on the accommodation of a six-coordinate zinc atom in the porphyrin plane. The present results are also consistent with this explanation but contrast the atypical behaviour of Mn- and Co-OMBP systems (see later). The magnitude of the equilibrium constants for the ligation of Zn-(OMBP) are unique (Table I), being 10–100 times greater than those reported for similar reactions of Zn(TPP) [10, 11]. These data are indicative of an extremely electron-

TABLE I. Equilibrium Constants<sup>a</sup> for the Reaction  $\text{Zn(Por)} + \text{L} \rightleftharpoons \text{Zn(Por)L}$ .

Porphyrin	Ligand	$\log K^d, M^{-1}$	References
OMBP <sup>b</sup>	py <sup>e</sup>	5.63	This work
OMBP <sup>b</sup>	pip <sup>f</sup>	6.00	This work
OMBP <sup>b</sup>	1-MeIm <sup>g</sup>	6.20	This work
TPP <sup>c</sup>	py	3.78	10, 11
TPP <sup>c</sup>	pip	5.05	10, 11

<sup>a</sup>Temperature 298 K. <sup>b</sup>Toluene solution. <sup>c</sup>Benzene solution. <sup>d</sup>Estimated error  $\log K \pm 0.05$  for this work. These error limits also encompass the range of values reported for ligand binding to Zn(TPP). <sup>e</sup> $\epsilon = 1.2 \times 10^5 M^{-1} \text{ cm}^{-1}$ . <sup>f</sup> $\epsilon = 1.8 \times 10^5 M^{-1} \text{ cm}^{-1}$ . <sup>g</sup> $\epsilon = 2.0 \times 10^5 M^{-1} \text{ cm}^{-1}$ .  $\lambda_{\text{max}} = 439 \text{ nm}$  for e–g.

deficient metal center and provide the first quantitative support for the suggestion that OMBP is an extremely weak  $\sigma$  donor. Indeed, since the next lowest K values are for derivatives of TPP, itself a weak Lewis base [5, 13] OMBP is possibly the weakest  $\sigma$  donor porphyrin yet investigated. Several features of OMBP chemistry are consistent with this proposal.

For example, aggregation of Zn(OMBP) is unusually facile [14], three aggregates being formed at 300 K in the concentration range  $10^{-6}$ – $10^{-3}$  M and between 320 and 225 K for a  $10^{-5}$  M solution. The red shifts associated with the first two aggregates are due to coordination of this very electro-positive metal to the porphyrin  $\pi$  cloud and via a unique Zn–N (pyrrole) intermolecular bond. Also consistent with the greatly reduced donor ability of OMBP is the enhanced affinity for Co(OMBP) for axial ligands, both five- and six-coordinate derivatives being readily formed [15]. Typically, the destabilization of the  $d_{z^2}$  orbital (upon the addition of a ligand to Co(II)PL) inhibits six-coordination. It is significant that for Co(OMBP) this simple ligand field approach fails, presumably overwhelmed by the diminished porphyrin  $\rightarrow$  metal donation.

As has been found for other metalloporphyrins there is no general relationship between K for equation (1) and the basicity of the ligand ( $\text{p}K_a$  for py, 1-MeIm and pip: 5.27, 7.06 and 11.12 respectively [5]). Such correlations have been observed for structurally similar ligands [11]. This would appear to favor the limiting electrostatic model [3], at least for zinc porphyrins. However, it should also be noted that the magnitude of the red shift depends on both the charge and polarization of the axial ligand and not on the strength of the Zn–L bond [10]. The ligand field model was partly based on the insensitivity of the ligation equilibria to different porphyrin complexes of the same metal. No such insensitivity is observed here. These data underline

the complexity of the relationship between the metal-axial ligand bond and the porphyrin  $\pi$  system even for a  $d^{10}$  metal.

For metals with partly filled d orbitals  $\pi$  effects appear to become increasingly important. This is especially true for OMBP complexes. Although strong metal-porphyrin  $\pi$ -bonding has been proposed on the basis of spectroscopic data, the coordination chemistry of manganese(II) porphyrins has been simply explained in terms of a ligand field model - a high spin metal forcing exclusive five-coordination [16]. In contrast to this typical behavior, Mn(OMBP) forms unprecedented high- and low-spin six-coordinate species when amines are added to dimethylacetamide solutions of this metalloporphyrin [17]. These data indicate extensive and complex delocalization effects which appear to be a consequence of the strong  $\pi$ -donor/weak  $\pi$ -acceptor [4] properties of OMBP. This will form the basis of future, full discussions of the cobalt and manganese systems.

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#### References

- 1 'Inorganic Biochemistry', G. Eichhorn, ed., Elsevier, Amsterdam, 1973.
- 2 J. W. Buchler, W. Kokisch and P. D. Smith, *Structure and Bonding*, **34**, 79 (1978).
- 3 G. McLendon and M. Bailey, *Inorg. Chem.*, **18**, 2120 (1979).
- 4 B. R. James, J. R. Sams, T. B. Tsin and K. J. Reimer, *J. Chem. Soc. Chem. Comm.*, 746 (1978); D. H. Dolphin, J. R. Sams, T. B. Tsin and K. L. Wong, *J. Am. Chem. Soc.*, **98**, 6970 (1976).
- 5 B. R. James, in 'The Porphyrins', D. Dolphin, ed., Vol. V, Academic Press, New York, N.Y., 1978.
- 6 L. Edwards, M. Gouterman and C. B. Rose, *J. Am. Chem. Soc.*, **98**, 7638 (1976).
- 7 A. Vogler, H. Kunkely and B. Rethwisch, *Inorg. Chim. Acta*, **46**, 101 (1980); T. E. Phillips, R. P. Scaringe, B. M. Hoffman and J. A. Ibers, *J. Am. Chem. Soc.*, **102**, 3435 (1980).
- 8 B. R. James, K. J. Reimer and T. C. T. Wong, *J. Am. Chem. Soc.*, **99**, 4815 (1977). Carbonylation reactions of Fe(OMBP)L<sub>2</sub> have been studied.
- 9 D. Dolphin, J. R. Sams and T. B. Tsin, *Inorg. Synth.*, **20**, 155 (1980).
- 10 M. Nappa and J. S. Valentine, *J. Am. Chem. Soc.*, **100**, 5075 (1978).
- 11 O. W. Kolling, *Inorg. Chem.*, **18**, 1175 (1979); G. C. Vogel and J. R. Stahlbush, *Inorg. Chem.*, **16**, 950 (1977); G. C. Vogel and B. A. Beckmann, *Inorg. Chem.*, **15**, 483 (1976); C. C. Vogel and L. A. Searby, *Inorg. Chem.*, **12**, 936 (1973); S. J. Cole, G. C. Curthoys, E. A. Magnusson and J. N. Phillips, *Inorg. Chem.*, **11**, 1024 (1972); C. H. Kirksey, P. Hambright and C. B. Storm, *Inorg. Chem.*, **8**, 2141 (1969).
- 12 W. R. Scheidt, M. E. Kastner and K. Hatano, *Inorg. Chem.*, **17**, 706 (1978).
- 13 J. E. Falk, 'Porphyrins and Metalloporphyrins', Elsevier, Amsterdam, 1964, p. 28.
- 14 K. J. Reimer, M. Reimer and M. J. Stillman, *Can. J. Chem.*, in press.
- 15 K. J. Reimer, B. R. James and D. W. Smith, *62nd CIC Conference, Vancouver*, B.C., June 3-6, 1979, paper IN-44.
- 16 R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.*, **79**, 139 (1979).
- 17 K. J. Reimer, H. R. Harmer and C. Sibley, *63rd CIC Conference, Ottawa*, Ontario, June 8-11, 1980, paper IN-67.