

## Six-co-ordinate High-spin Iron(III) Porphyrin Complexes with NADH Model Compounds

Shunichi Fukuzumi, Yuji Kondo, and Toshio Tanaka\*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

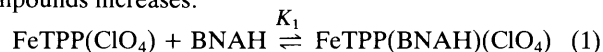
New types of six-co-ordinate high-spin iron(III) porphyrin complexes with NADH model compounds as ligands are formed in  $\text{CH}_2\text{Cl}_2$  containing perchlorato(meso-tetraphenylporphyrinato)iron(III) and NADH model compounds; the spectroscopic, electrochemical, and magnetic properties are reported.

A variety of nitrogenous bases having moderate-to-high ligand field strengths have been known to form six-co-ordinate low-spin complexes with iron(III) porphyrins for a long time.<sup>1</sup> Recently, six-co-ordinate high-spin iron(III) porphyrin complexes<sup>2</sup> have attracted considerable attention in relation with those observed in naturally occurring systems such as met-hemoglobin and met-myoglobin,<sup>3</sup> although most synthetic high-spin iron(III) porphyrin complexes are known to be five-co-ordinate.<sup>1</sup> In order to obtain six-co-ordinate high-spin iron(III) porphyrin complexes, the axial ligands should be chosen such that the ligand field strength is weak but strong enough to form stable complexes. Such ligands have hitherto been limited to abiological ones with weak ligand fields such as sulphoxides, dimethylformamide, triphenylphosphine oxide, pyridine *N*-oxide, and water.<sup>2</sup>

In this communication, we report that model compounds of reduced nicotinamide adenine dinucleotide (NADH), which is an important coenzyme in various biological redox reactions,<sup>4</sup> are the right choice of axial ligands to form stable six-co-ordinate high-spin iron(III) porphyrin complexes.

The visible spectrum of perchlorato(meso-tetraphenylporphyrinato)iron(III)  $\text{FeTPP}(\text{ClO}_4)$  in  $\text{CH}_2\text{Cl}_2$  was significantly affected by the addition of an NADH model compound, 1-benzyl-1,4-dihydronicotinamide (BNAH). The absorption maxima  $\lambda_{\text{max}}$  of  $\text{FeTPP}(\text{ClO}_4)$  observed at 399, 528, and 664 nm were shifted to 417, 511, and 690 nm, and then, to 417, 576, and 630(sh) nm, as the BNAH concentration increased. A similar stepwise spectral change has been reported for the formation of  $\text{FeTPP}(\text{L})(\text{SbF}_6)$  and  $[\text{FeTPP}(\text{L})_2]^+$  (L = imidazole and 4-methylimidazole) by the reaction of  $\text{FeTPP}(\text{SbF}_6)$  with L.<sup>5</sup> Thus, the change in  $\lambda_{\text{max}}$  of  $\text{FeTPP}(\text{ClO}_4)$  by the addition of BNAH may be ascribed to

the reactions shown in equations (1) and (2). Analogous spectral changes were observed upon the addition of other NADH model compounds, 1-(X-benzyl)-1,4-dihydronicotinamide (X-BNAH: X = 4-MeO, 4-Me, 4-Cl, 2,4-Cl<sub>2</sub>) and *N*-methylacridan ( $\text{AcH}_2$ ), to  $\text{CH}_2\text{Cl}_2$  solutions of  $\text{FeTPP}(\text{ClO}_4)$ . The formation constants  $K_1$  and  $K_2$  were different enough from each other ( $K_1 \gg K_2$ ) so that they could be determined separately from the change of absorbance at 417 and 576 nm, respectively, as shown in Table 1, which indicates that both the  $K_1$  and  $K_2$  values (the error limits are  $< \pm 10\%$ ) increase as the donor ability of NADH model compounds increases.



The formation of the iron(III) porphyrin complex with two BNAH ligands,  $[\text{FeTPP}(\text{BNAH})_2]^+$  [equation (2)], was confirmed also by the cyclic voltammograms of  $\text{FeTPP}(\text{ClO}_4)$  ( $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ ) in  $\text{CH}_2\text{Cl}_2$  containing excess amounts of BNAH and  $\text{NBu}_4\text{ClO}_4$  at 293 K. For the determination of the number of BNAH involved in the redox process of  $\text{FeTPP}(\text{ClO}_4)$ , half-wave potentials  $E_{1/2}$  were measured and plotted against the logarithm of the BNAH concentration  $\log[\text{BNAH}]$ . The  $E_{1/2}$  value for the  $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$  couple was shifted cathodically by 115 mV/ $\log[\text{BNAH}]$  on increasing the  $\log[\text{BNAH}]$  value. Such a dependence of  $E_{1/2}$  on the BNAH concentration agrees well with the theoretical value of 116 mV when the number of electrons transferred is one and the number of ligands bound to the oxidized and reduced species is two and zero, respectively.<sup>6</sup>

The spin-states of iron(III) porphyrin complexes can readily be distinguished from the  $^1\text{H}$  n.m.r. signal of the pyrrole ring, which appears in the  $\delta$  70–80 and  $\delta$  –15 regions for high-spin<sup>2,7</sup> and low-spin<sup>8</sup> species, respectively. The pyrrole proton signals of  $\text{FeTPP}(\text{ClO}_4)$  which has an admixed  $S$  3/2, 5/2 spin-state<sup>9</sup> appeared at  $\delta$  10 in  $\text{CD}_2\text{Cl}_2$ . Addition of one- and two-equivalent amounts of BNAH to a  $\text{CD}_2\text{Cl}_2$  solution of  $\text{FeTPP}(\text{ClO}_4)$  ( $2.03 \times 10^{-2} \text{ mol dm}^{-3}$ ) to form mainly

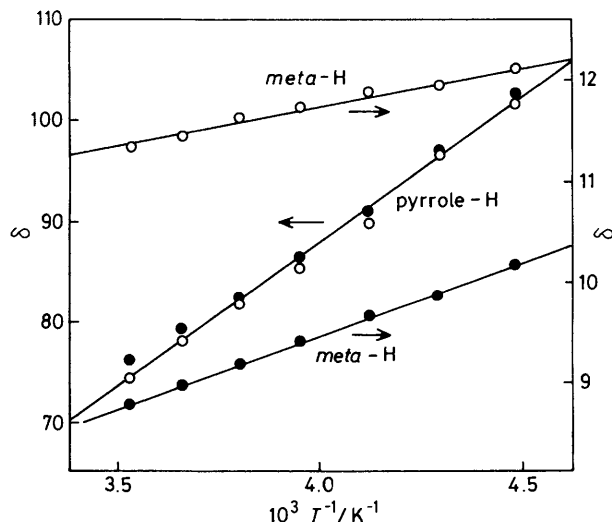


Figure 1. Curie plots for the pyrrole and *meta* phenyl protons of  $\text{FeTPP}(\text{BNAH})(\text{ClO}_4)$  (○) and  $[\text{FeTPP}(\text{BNAH})_2]^+$  (●) formed from  $\text{FeTPP}(\text{ClO}_4)$  ( $2.03 \times 10^{-2} \text{ mol dm}^{-3}$ ) in  $\text{CD}_2\text{Cl}_2$  containing one- and two-equivalent amounts of BNAH, respectively.

Table 1. Stepwise formation constants  $K_1$  and  $K_2$  for the complexes formed between  $\text{FeTPP}(\text{ClO}_4)$  and NADH model compounds in  $\text{CH}_2\text{Cl}_2$  at 298 K.

Ligand	$K_1$ $\text{mol}^{-1} \text{ dm}^3$	$K_2$ $\text{mol}^{-1} \text{ dm}^3$
4-MeOBNAH	$1.6 \times 10^4$	$7.6 \times 10^2$
4-MeBNAH	$9.3 \times 10^3$	$7.0 \times 10^2$
BNAH	$7.9 \times 10^3$	$6.7 \times 10^2$
4-CIBNAH	$1.5 \times 10^4$ <sup>a</sup>	$1.6 \times 10^2$ <sup>a</sup>
2,4-Cl <sub>2</sub> BNAH	$5.4 \times 10^3$	$3.6 \times 10^2$
AcH <sub>2</sub>	$4.9 \times 10^3$	$2.3 \times 10^2$
	$2.1 \times 10^3$	$2.4 \times 10^2$

<sup>a</sup> In the presence of  $0.10 \text{ mol dm}^{-3} \text{ NBu}_4\text{ClO}_4$ .

FeTPP(BNAH)(ClO<sub>4</sub>) and [FeTPP(BNAH)<sub>2</sub>]<sup>+</sup>, respectively, resulted in a significant downfield shift of the pyrrole proton signal in the δ 70–80 (high-spin) region. Approximate Curie-law behaviour is observed for the pyrrole proton and the *meta* phenyl proton resonances of FeTPP(BNAH)(ClO<sub>4</sub>) and [FeTPP(BNAH)<sub>2</sub>]<sup>+</sup>, as shown in Figure 1, which indicates that no spin admixture may be involved between *S* 3/2 and 5/2. Thus, these two BNAH complexes could be simple high-spin paramagnetic molecules with *S* 5/2. The *meta* phenyl proton resonance of FeTPP(ClO<sub>4</sub>) in the presence of one-equivalent amount of BNAH is different from that in the presence of two-equivalent amounts of BNAH, and a single averaged resonance was observed at the inbetween region where the ratio of BNAH to FeTPP(ClO<sub>4</sub>) was changed between one and two, indicating that the ligand exchange between FeTPP(BNAH)(ClO<sub>4</sub>) and [FeTPP(BNAH)<sub>2</sub>]<sup>+</sup> is fast on the n.m.r. time scale.

The formation of high-spin complexes FeTPP(BNAH)(ClO<sub>4</sub>) and [FeTPP(BNAH)<sub>2</sub>]<sup>+</sup> was supported also from the solution magnetic susceptibilities using the Evans n.m.r. method;<sup>10</sup> the effective magnetic moments  $\mu_{\text{eff}}$  in CD<sub>2</sub>Cl<sub>2</sub> were found to be 5.9  $\mu_{\text{B}}$  at 233 K and 5.6  $\mu_{\text{B}}$  at 296 K for FeTPP(BNAH)(ClO<sub>4</sub>) and 6.0  $\mu_{\text{B}}$  at 233 K for [FeTPP(BNAH)<sub>2</sub>]<sup>+</sup>, both of which agree well with the calculated value of 5.92  $\mu_{\text{B}}$  for a pure *S* 5/2 state. The high-spin state of [FeTPP(BNAH)<sub>2</sub>]<sup>+</sup> was further confirmed by the e.s.r. spectrum at 77 K which showed the characteristic signals at  $g_{\perp}$  5.7 and  $g_{\parallel}$  2.0, as expected for high-spin iron(III) species.<sup>11</sup>

This work was supported by the Takeda Science Foundation.

Received, 4th April 1985; Com. 455

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