Nitrosyl Iron(II) Complex of *meso*-Tetrakis(*α,α,α,α-o*-pivalamidophenyl)porphyrin with a Covalently Linked 2-Methylimidazolylalkyl Group

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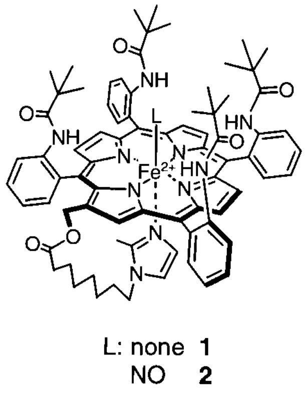
meso-Tetrakis(*α,α,α,α-o*-pivalamidophenyl)porphinatoiron(II) with an intramolecularly bound 2-methylimidazole forms a six-coordinate nitrosyl complex in toluene at 298 K, which is revealed by ESR and IR spectroscopy; the NO-binding affinity ($P_{1/2}$) is 1.8 × 10^{-8} Torr and the association rate constant (k_{on}) is 8.9 × 10^{8} $M^{-1}s^{-1}$.

The unusual binding properties of nitric oxide (NO) with hemoproteins have created great interest in the coordination chemistry of nitrosyl iron(II) and iron(III) complexes of the synthetic porphyrins.[1–6] Because NO shows a negative-trans effect, which is quite different from other gaseous ligands such as carbon monoxide (CO),[4b,c] it binds more tightly to the four-coordinate heme in comparison to the five-coordinate complex with a nitrogenous base. Correspondingly, the proximal base bonding to the Fe(II)porphyrin is weakened upon addition of NO; this often leads to a base elimination. In particular, for the T-state model of hemoglobin, which contains sterically hindered 2-methylimidazole, a delicate balance of the proximal strain controls the release of the axial base ligand.[7,8] Exposure of NO (1 atm) to Fe(II)protoporphyrin IX(2-methylimidazole) [Fe(II)PP(2-MeIm)] in aqueous solution results in complete conversion to Fe(II)PP(NO) involving the dissociation of 2-MeIm.[7] On the contrary, tetraphenylporphinatoiron(II) [Fe(II)TPP] formed the six-coordinate nitrosyl complex in the presence of an excess amount of 1,2-dimethylimidazole ([1,2-Me_2Im] = 1 M).[8] These observations rouse our interest in the binding properties of NO to the synthetic hemes bearing a covalently bound proximal base.[9] No attempt has, however, been made to study their nitrosyl compounds so far. We report herein for the first time the formation of the six-coordinate nitrosyl complex of tetrakis(*α,α,α,α-o*-pivalamidophenyl)porphinatoiron(II) with a covalently linked 2-methylimidazolylalkyl arm (**1**) at 298 K, which is revealed by ESR and IR spectroscopy. The equilibrium and kinetic constants for the NO-binding to **1** are also given.



L: none **1**
NO **2**

The ferric porphyrin prepared according to our previously reported procedure was converted to its ferrous state by reduction in a heterogeneous two-phase system (toluene/aqueous dithionate) under an argon atmosphere.[10] The UV–vis absorption spectrum of the orange solution showed a typical five-*N*-coordinate high-spin Fe(II) complex (λ_{max}: 440, 541, 559, and 608 (sh) nm, Figure 1), indicating that the 2-methylimidazole moiety binds to the central ferrous ion. NO (5 ppm in N_2) was then bubbled through the solution until the spectrum reached equilibrium.[11] The final UV–vis absorption with λ_{max} at 415, 479 (sh), 542, and 610 nm was constant in the range of 10 μM – 3 mM at 10–70 °C. This spectral pattern slightly resembles that of the five-coordinate nitrosyl Fe(II)TPP (Figure 1),[1a,3a,b] but the λ_{max} of the Soret band appearing at 415 nm is significantly red-shifted relative to that of the nitrosyl tetrakis(*α,α,α,α-o*-pivalamidophenyl)porphinatoiron(II) [Fe(II)TpivPP(NO)] (λ_{max}: 407 nm).[3b] Upon addition of 100% CO gas through this solution, the spectrum changed to that of the well-known carbonyl complex (λ_{max}: 425 and 538 nm).

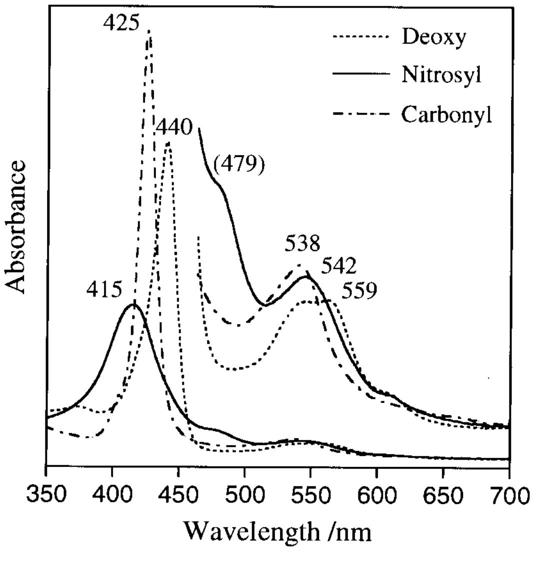


Figure 1. Visible absorption spectral changes of **1** in toluene at 298 K

We then employed ESR and IR spectroscopies to elucidate the coordination structure of this complex. (i) The ESR spectrum of the toluene solution of **1** under an NO atmosphere (1% NO) at 298 K exhibited the typical six-coordinate nitrosyl hemes (Figure 2a); the *g* value (g_{iso}: 2.049) appeared very close to that of nitrosyl Fe(II)PP dimethylester with 2-MeIm (g_{iso}: 2.050).[5a] Moreover, the spectrum at 77 K demonstrated a randomly oriented line shape with a rhombic symmetry, in which the central g_2 absorption was highly resolved into a triplet of triplets from the hyperfine interaction of an unpaired electron of NO with two axial N nuclei (Figure 2b). The obtained g values (g_1: 2.072, $g_{\text{II-1}}$: 2.034, g_2: 2.002, g_3: 1.976) were also in good agreement with those of the six-coordinate nitrosyl Fe(II)TPP(1-MeIm) at 77 K (Table 1).[5a,b] (ii) In the IR spectra, the coordinated NO showed a ν(N–O) at 1635 cm^{-1}, which is lower-shifted with respect to the corresponding values of the five-coordinate nitrosyl Fe(II)TPPs.[5b,c,6] This is obviously ascribed to the trans ligand effect of the axially coordinated imidazole; the enhancement of back-donation into the NO π^* orbital.[12] The similar ν(N–O) value was observed in the Fe(II)TPP(1-MeIm)(NO).[5b] These all findings provide direct evidence that **1** can form the six-coordinate nitrosyl heme with an intramolecularly bound 2-methylimidazolylalkyl arm.

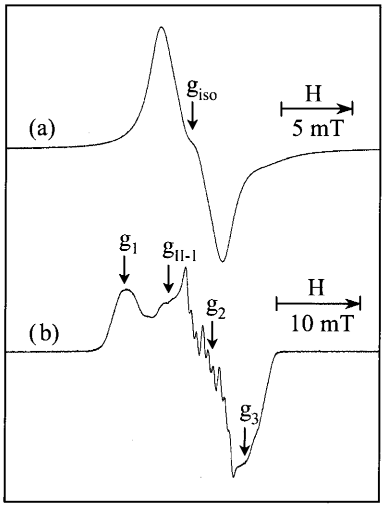


Figure 2. ESR spectra of **2** in toluene at (a) 298 K and (b) 77 K; [NO] = 1%.

For determination of the NO-binidng affinity (partial pressure at half NO-binding to **1**, $P_{1/2}$), we used the ligand-exchange method of Romberg and Kassner.[13] The $P_{1/2}$ of **1** was 1.8×10^{-8} Torr at 298 K, which means that **1** has a six fold larger NO-binding affinity to Fe(II)TPP(1,2-Me_2Im) ($P_{1/2}$: 1.1×10^{-7} Torr)[8] (Table 1). We predicted that the relatively high NO-binding affinity of **1** compared to that of Fe(II)TPP(1,2-Me_2Im) is mainly caused by the non-solvation effect by the four pivalamido substituents on the porphyrin ring plane.[14]

Laser flash photolysis provided the association rate constants (k_{on}) of NO. The transient absorption spectra of the NO-photodissociated product of **2** displayed a negative absorbance at 410 nm, which is due to the disappearance of the nitrosyl compound, and a positive absorbance at 443 nm, which is attributed to the deligated five-*N*-coordinate form. The spectral pattern was completely superimposed on the static spectra of **2** minus **1**. This agreement also supports the formation of the six-coordinate nitrosyl complex. The time dependence of the absorption decay at 445 nm after the laser flash photolysis showed second-order kinetics, and the k_{on} was determined to be $8.9 \times 10^8\ \text{M}^{-1}\text{s}^{-1}$. This value was appreciably lower than those of the four-coordinate Fe(II)TpivPP (k_{on}: $6.7 \times 10^9\ \text{M}^{-1}\text{s}^{-1}$) and Fe(II)TPP ($k_{on}$: $5.2 \times 10^9\ \text{M}^{-1}\text{s}^{-1}$),[1a] which is consistent with the earlier study on the Fe(II)PP complexes.[7]

Table 1. NO-Binding parameters of **1** at 298 K

	Solvent	$10^8\ P_{1/2}$ / Torr	$10^{-8}\ k_{on}$ / $\text{M}^{-1}\text{s}^{-1}$	$10^4\ k_{off}$ / s^{-1}
1	toluene	1.8	8.9	2.3[a]
Fe(II)TPP(1,2-Me_2Im)[b]	toluene	11	—	—
Fe(II)PP(1-MeIm)[c]	water	57	1.8	2.9

[a] The dissociation rate of NO was determined by k_{on}/K. [b] From Ref. 8. [c] From Ref. 7.

To the best of our knowledge, this is the first example of a six-coordinate nitrosyl Fe(II)TPP derivative with an intramolecularly bound 2-methylimidazole. We concluded that covalently attaching the 2-methylimidazolyl group directly to the porphyrin periphery provides an incredibly large equilibrium constant for the imidazole bonding and prevents the base-off reaction even when NO is bound to the trans side.

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