Nitric Oxide Complexes of Iron(II) and Iron(III) Porphyrins

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Summary The reversible formation of a nitric oxide adduct with tetraphenylporphyriniron(III) chloride formulated as [Fe^{II}(TPP)Cl^-NO^+] is observed in toluene, but reductive nitrosylation to give Fe^{II}(TPP)·NO occurs in the presence of a hydroxylic solvent, in reactions analogous to hemeprotein interactions with nitric oxide.

INTEREST in the structure and bonding of diatomic molecules with metalloporphyrins and their relationship to corresponding hemeprotein complexes[1] prompt this report of nitric oxide complexes of Fe^{II}(TPP) and Fe^{III}(TPP)Cl.

We have examined the reaction of tetraphenylporphyriniron(III) chloride,[2] [Fe(TPP)Cl], with nitric oxide in an effort to understand why electronically related ferric hemeproteins can react with nitric oxide to yield different products.[3] Fe(TPP)Cl in toluene interacts with nitric oxide at low temperature reversibly to form a nitric oxide adduct. The electronic spectra of this complex in a frozen glass (77 K, ϵ_{max} = 5770, 5430, and 4350 Å) is very similar to that of the isoelectronic low-spin $MbFe^{II}CO$ (Mb = myoglobin)[4] and the NO complex of ferric peroxidase.[3] We formulate this complex as a low-spin Fe^{II} species, (Cl^-·Fe^{II}-(TPP)·NO^+], where virtually a full electron is transferred from nitric oxide to Fe^{III}.

Vaska and Nakai have recently isolated a material claimed to be Fe(TPP)Cl·NO with a magnetic moment of 4·5 B.M., and Fe–Cl stretching frequency (solid) and visible electronic spectra (solution) virtually unchanged from Fe(TPP)Cl.[5] These properties are inconsistent with our low temperature studies on Fe(TPP)Cl·NO as well as with the properties of related ferric peroxidase complexes. Under the temperature conditions of their electronic spectral experiments very little complex formation occurs in solution. Solid material was isolated by crystallization from CH_2Cl_2–EtOH solution, a procedure we find results in reductive nitrosylation as described below. The solid isolated in this manner is probably a mixture of unchanged Fe(TPP)Cl and Fe^{II}(TPP)·NO.

Addition of methanol and nitric oxide to a toluene solution of Fe^{III}(TPP)Cl results in reductive nitrosylation to form Fe^{II}(TPP)·NO.

$$Fe^{III}(TPP)Cl + NO \rightleftharpoons Fe^{III}(TPP)Cl{\cdot}NO$$

$$Fe^{III}(TPP)Cl{\cdot}NO + MeOH \rightarrow Fe^{II}(TPP) + MeONO + HCl$$

$$Fe^{II}(TPP) + NO \rightarrow Fe^{II}(TPP){\cdot}NO$$

Fe^{II}(TPP)·NO can form a variety of six-co-ordinate adducts by addition of donor molecules. The preparation of one such adduct, Fe^{II}(TPP)·NO· piperidine, has recently been reported to result from reaction of Fe^{II}(TPP)· (piperidine)$_2$ with nitric oxide.[6] This procedure is limited to this one Fe^{II} species, however, while synthesis of Fe(TPP)·NO by reductive nitrosylation affords a versatile five-co-ordinate molecule which can be further co-ordinated in the axial position.

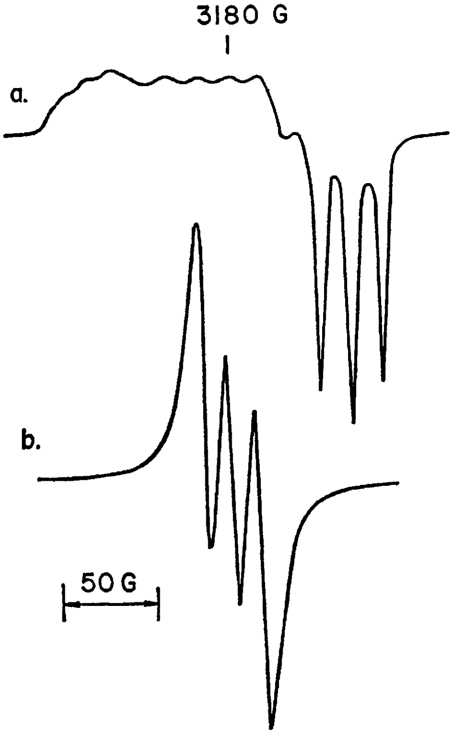

FIGURE. E.s.r. spectra for $\mathrm{Fe^{II}(TPP)NO}$ in toluene. (a) −140 °C ($g_1 = 2{\cdot}103$, $A_1 = 12{\cdot}6$ G; $g_2 = 2{\cdot}064$, $A_2 = 17{\cdot}2$ G; $g_3 = 2{\cdot}010$, $A_3 = 17{\cdot}3$ G). (b) Room temperature ($\langle g\rangle = 2{\cdot}051$, $\langle A\rangle = 16{\cdot}3$ G).

$\mathrm{Fe^{II}(TPP)\cdot NO}$ is a ground-state doublet species ($S = \frac{1}{2}$) and can be conveniently studied by e.s.r. spectroscopy (Figure). Three unique g values and ^{14}N hyperfine splittings are observed indicating non-axial symmetry and a bent Fe–NO unit. In the presence of a base such as piperidine or pyridine superhyperfine splitting from the second co-ordinated nitrogen is observed. These observations demonstrate that the magnetic and electronic properties of this model system parallel those of the corresponding ferrous hemeprotein complexes with nitric oxide.[7–10] Presence of a bent $\mathrm{Fe^{II}}$–NO unit in $\mathrm{Fe(TPP)\cdot NO}$ is evidence that electronic factors could result in the observed bent unit in $\mathrm{MbFe^{II}NO}$ irrespective of the heme pocket steric requirements and protein–nitric oxide contacts.

The reactivity with hydroxylic reagents provides chemical evidence that $\mathrm{Fe(TPP)Cl{\cdot}NO}$ can be formulated as an $\mathrm{Fe^{II}}$ complex of $\mathrm{NO^+}$. This reductive nitrosylation reaction is closely related to the reduction by nitric oxide of aqueous solutions of hemin chloride[8] and ferric myoglobin[9] and hemoglobin,[10] species in which the heme site is either bound to or readily accessible to a water molecule. We believe that reductive nitrosylation is a characteristic of an $\mathrm{Fe^{II}NO^+}$ species when an appropriate reagent is available for reaction with co-ordinated $\mathrm{NO^+}$. Failure of the ferric peroxidases to be reduced by nitric oxide provides a clear indication that the heme binding site is inaccessible to H_2O.

We acknowledge support of the National Science Foundation.

(*Received, 25th July* 1973; *Com.* 1079.)

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