Reactions of Nitric Oxide with Cobalt(II) Tetraphenylporphyrin: A Unique Bis Nitric Oxide Complex

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Summary (Nitric oxide) tetraphenylporphyrincobalt, [Co(TPP)(NO)], is found to add nitric oxide sequentially to form an $S = 1/2$ complex $[Co(TPP)(NO)_2]$ and a diamagnetic species tentatively formulated as $[Co(TPP)(NO)(N_2O_2)]$.

As part of a systematic examination of the occurrence and properties of diatomic molecule complexes of metalloporphyrins with diatomic molecules,[1–4] we have investigated the interaction of tetraphenylporphyrincobalt(II), Co^{II}(TPP), with nitric oxide. The diamagnetic mono nitric oxide complex, [Co(TPP)(NO)] (I), has been previously reported and fully characterized by *X*-ray structural study.[5] [Co(TPP)(NO)] has a bent Co–NO unit (ν_{NO} 1690 cm^{-1}) and is formulated as a $Co^{III}(NO)^-$ complex.

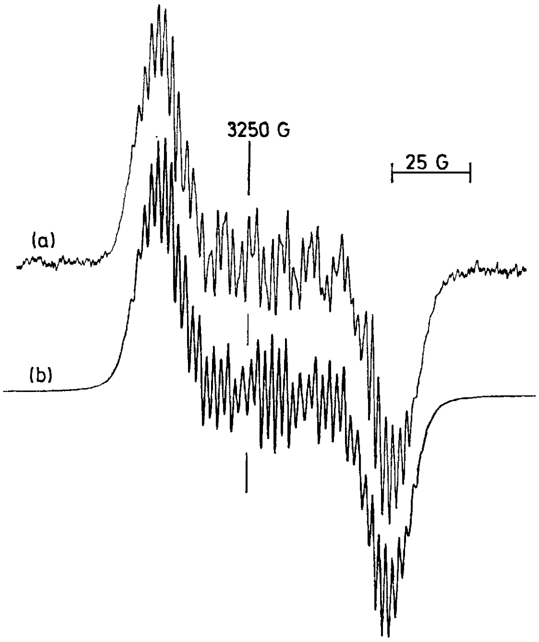

FIGURE 1. E.s.r. spectrum for $[Co(TPP)(NO)_2]$ in toluene at 300 K: (a) observed; (b) computer simulation.

A toluene solution of (I) exposed to nitric oxide (0·1—5 Torr) results in the observation of a new paramagnetic complex (II). The isotropic e.s.r. spectrum indicates formation of an $S = 1/2$ species (Figure 1). An isotropic *g* value of 2·007 is indicative of a complex with a ligand-based odd electron. Use of ^{15}NO and computer simulation have assisted in assigning the hyperfine coupling constants, $A(^{59}Co)$ 12·4, $A(^{14}N)$ porphyrin 2·4, and $A(^{14}N)NO$ 4·6 G. Hyperfine coupling from two equivalent nitric oxide units demonstrates that this species is $[Co(TPP)(NO)_2]$. A metastable solid sample of this material can be isolated which has a single NO stretching frequency at 1696 cm^{-1} characteristic of bent Co–NO units. The solid loses nitric oxide to reform (I). Solution e.s.r. and solid i.r. spectra are consistent with $[Co(TPP)(NO)_2]$ containing two equivalent bent nitric oxide groups. This can be contrasted with $[Fe(TPP)(NO)_2]$, which has two NO stretching frequencies (1880 cm^{-1} and 1680 cm^{-1}) characteristic of linear NO^+ and bent NO^- units which lead to the formulation of this complex as $[Fe(TPP)(NO^+)(NO^-)]$.[2] The single additional electron which enters the NO π system in $[Co(TPP)(NO)_2]$ must be responsible for the observed equivalency of the nitric oxide units.

In terms of a valence bonding model, (II) can be depicted as a resonance hybrid $Co^{III}(TPP)(NO)(NO^-) \leftrightarrow Co^{III}(TPP)(NO^-)(NO)$ and $Co^{III}(TPP)(NO^+)(NO^{2-}) \leftrightarrow Co^{III}(TPP)(NO^{2-})(NO^+)$. In molecular orbital terminology the odd electron is in an MO consisting of equal contributions from the two nitric oxide π^* orbitals. $[Co(TPP)(NO)_2]$ is formally related to the dioxygen complexes, such as the isoelectronic complex, $[Co^{III}(TPP)(CO)(O^-)]$, which we previously reported.[1] Both complexes can be formulated as fulfilling the 18-electron rule for the metal site by placing the highest energy electron (unpaired e$^-$) predominantly in the π^* ligand orbitals.

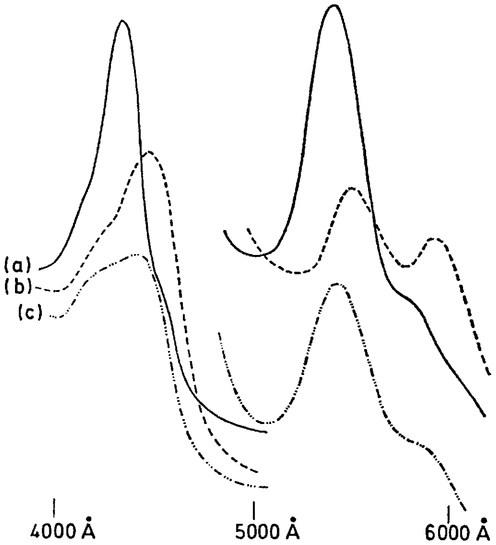

FIGURE 2. Electronic spectra for nitric oxide complexes of Co(TPP) in toluene glass media (77 K); (a) [Co(TPP)(NO)]; (b) $[Co(TPP)(NO)_2]$; (c) $[Co(TPP)(NO)_{(2+x)}]$.

As the equilibrium NO pressure above a toluene solution of (I) and (II) is increased beyond several Torr, the e.s.r. spectrum of (II) vanishes and a third new electronic spectrum appears. The nitric oxide complex of Co(TPP) at pressures greater than 20 Torr is diamagnetic. These spectroscopic and magnetic changes are inductive of a third nitric oxide complex, (III). Species (I), (II), and (III) are all readily interconverted with change in the equilibrium NO pressure. Electronic spectra for (I), (II), and (III) are shown in Figure 2. We believe that the diamagnetism of (III) results from addition of a third nitric oxide molecule to (II) with spin pairing. Nitric oxide could bind (II) at either the porphyrin or co-ordinated NO centres. Considering the electronic structure of (II), we currently favour formation of co-ordinated $N_2O_2^{2-}$. Although species (II), [(Co(TPP)-$(NO)_2$], appears to have two equivalent NO groups, it may react as if it contained co-ordinated NO^{2-} [*i.e.* Co(TPP)-$(NO^+)(NO^{2-})$]. There is a precedent for reactivity of this type in the interaction of donor molecules with nitric oxide. When a donor species interacts with NO to form a 1:1 complex, the NO group can be viewed as co-ordinated NO^{2-}. Species of this type are known to react with a second NO to give a co-ordinated N_2O_2[2] (*e.g.* $SO_3^{2-} + NO \rightarrow [O_3SNO]^{2-}$; $[O_3SNO]^{2-} + NO \rightarrow [O_3SN_2O_2]^{2-}$).[6] Further characterization and reactivity studies of (III) are important in that co-ordinated N_2O_2 has been implicated in metal-catalysed reductions of NO by CO to form N_2O and CO_2.[7]

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