Supporting Information

Hexacoordinate Oxy-Globin Models Fe(Por)(NH_3)(O_2) React with NO to form the Nitrato Analogs Fe(Por)(NH_3)(η^1-ONO_2), even at 100 K

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References

Experimental: Procedures for preparing and studying sublimed layers of heme models.

Materials: Since Fe(II) porhyrinates are very sensitive to oxygen and readily transform to Fe(III) derivatives, the more stable Fe(Por)$(B)_2$ complexes (Por = TPP and TTP, B = pyridine or piperidine), synthesized according to the literature procedure,[1] were used as the precursor compounds. NO was purified by passage through KOH pellets and a cold trap (dry ice/ acetone) to remove higher nitrogen oxides and trace quantities of water. ^{15}NO with 98.5 % enrichment was purchased from the Institute of Isotopes, Tbilisi, Republic of Georgia, and was purified by the same procedures. $^{18}O_2$ with 95% enrichment was purchased from Cambridge Isotope Laboratories.

Spectra: The FTIR spectra have been recorded using “Nexus” spectrophotometer of the Thermo Nicolet Corporation and UV-visible spectra have beem measured on a “Specord M-40” (Carl Zess, Jena) spectrophotometer.

Preparation of sublimed layers: The low temperature sublimate was prepared by placing a Fe(TPP)$(B)_2$ sample in a Knudsen cell and heating to ~470 K under high vacuum ($P = 3{\cdot}10^{-5}$ Torr).[2] Evacuation for 3 h resulted in the complete elimination of the coordinated axial ligands B. Then liquid nitrogen was poured into the cryostat, and the Knudsen cell was heated to 520 K, at which temperature sublimation of Fe(Por) onto the cold KBr and CaF_2 substrate occurred. In the latter case the CaF_2 was also used as the optical windows of cryostat. In order to build up layers of thickness convenient for UV-Visible and IR spectral studies, sublimation was typically carried out over periods of 0.1 – 2.0 h.

Reactivity studies: The dioxygen complexes Fe(Por)(O_2) were prepared by supplying a few tenth mm of O_2 ($^{18}O_2$) into the vacuum cryostat containing cold layers (~80 K, LN_2) of Fe^{II}(Por). These layers were then annealed by raising the temperature to 110 K. The temperature was lowered to ~80 K and the excess O_2 removed by pumping out . NH_3 (~1 mm_{Hg}) was then supplied to the cryostat, and the layers were slowly warmed to 140 K . This procedure led to formation of the 6-coordinate ammonia-dioxygen complexes Fe(Por)$(NH_3)(O_2)$. The cryostat was then again pumped out for ~0.5 h at ~150 K to remove any uncoordinated NH_3 adsorbed in the layers. The layers were then cooled back to LN_2 temperature and NO (~0.1 mm_{Hg}) was supplied to the cryostat. The products formed in the solid layers of the heme models were then studied by recording the FTIR and/or visible spectra during the course of slow warming.

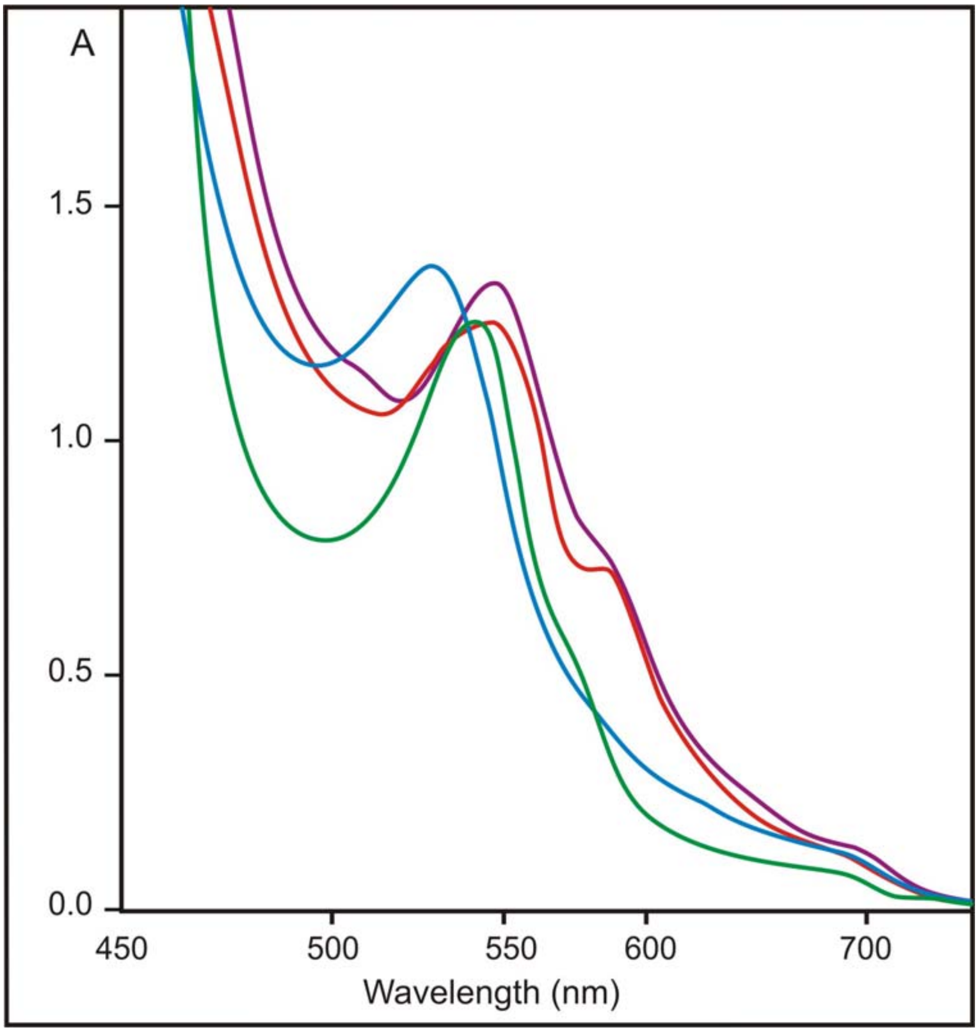
The ammonia-nitrato complexes Fe(Por)$(NH_3)(\eta^1\text{-}ONO_2)$ were prepared as follows. The bidentate nitrato complexes Fe(Por)$(\eta^2\text{-}O_2NO)$ were prepared in the cryostat as layered solids on a substrate by the room temperature interaction of low pressure NO_2 gas with porous layers of Fe(II)(Por) as described previously.[3] After pumping out the excess NO_2, the layered solid was cooled to LN_2 temperature. Then small quantitities of NH_3 (0.1 mm_{Hb}) were supplied into the cryostat and IR spectra were recorded upon slow warming. This procedure is accompanied by the shifts of stretching bands of coordinated nitrate evidencing formation of $Fe(Por)(NH_3)(\eta^1\text{-}ONO_2)$.

Comments on the potential rate of reaction in the 100 K layered solids:

The reaction rate to form $Fe(Por)(NH_3)(ONO_2)$ from NO and $Fe(Por)(NH_3)(O_2)$ is limited by diffusion of the NO into the $Fe(Por)(NH_3)(O_2)$ solid. However, there is no build up of any intermediates, so these must decay with a relatively short lifetime (regardless of mechanism). One can use the Eyring equation to evaluate the rate constant k for unimolecular decay, and hence the lifetime ($\tau = i/k$)

$$k = (k_b\mathrm{T}/h)\, e^{-\Delta G^*/RT}, \text{ where } k_b\mathrm{T}/h = 2.1 \times 10^{12}\ \mathrm{s}^{-1} \text{ at } 100\ \mathrm{K}.$$

If one assumes for such a process in the layered solids that entropy changes are minor, then a $\Delta H^\ddagger$ of 6 kcal/mole would give a lifetime of about 5 s while a $\Delta H^\ddagger$ of 7 kcal/mole would extend this to ~760 s. Our techniques allow measurements within 15 s, so our failure to see any intermediates indicate that the barriers for decay of the putative peroxynitrito intermediate must be quite low, namely less than ~7 kcal/mole.



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References:

1. (a) Epstein, L. M.; Straub, D. K.; Maricondi, C. *Inorg. Chem.* **1967**, *6*, 1720-1722. (b) Bhatti, W.; Bhatti, M.; Imbler, P.; Lee, A.; Lorenzen, B. *J. Pharm. Sci.* **1972,** *61,* 307-309.
2. Nakamoto, K.; Watanabe, T.; Ama, T.; Urban, M. W. *J. Am. Chem. Soc.* **1982**, *104,* 3744-3745.
3. Kurtikyan, T. S.; Stepanyan, T. G.; Akopyan M. E. *Russ. J. Coord. Chem.*, **1999**, *25*, 721-725.