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Reactions of Nitrogen Oxides with the Five-Coordinate Fe^{III}(porphyrin) Nitrito Intermediate Fe(Por)(ONO) in Sublimed Solids

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Abstract: Detailed experimental studies are described for reactions of several nitrogen oxides with iron porphyrin models for heme/N_xO_y systems. It is shown by FTIR and optical spectroscopy and by isotope labeling experiments that reaction of small increments of NO_2 with sublimed thin layers of the iron(II) complex Fe(Por) (Por = *meso*-tetraphenylporphyrinato dianion, TPP, or *meso*-tetra-*p*-tolylporphyrinato dianion, TTP) leads to formation of the 5-coordinate nitrito complexes Fe(Por)(η^1-ONO) (**1**), which are fairly stable but very slowly decompose under vacuum giving mostly the corresponding nitrosyl complexes Fe(Por)(NO). Further reaction of **1** with new NO_2 increments leads to formation of the nitrato complex Fe(Por)(η^2-O_2NO) (**2**). The interaction of NO with **1** at low temperature involves ligand addition to give the nitrito−nitrosyl complexes Fe(Por)(η^1-ONO)(NO) (**3**); however, these isomerize to the nitro−nitrosyl analogs Fe(Por)(η^1-NO_2)(NO) (**4**) upon warming. Experiments with labeled nitrogen oxides argue for an intramolecular isomerization ("flipping") mechanism rather than one involving dissociation and rebinding of NO_2. The Fe(III) centers in the 6-coordinate species **3** and **4** are low spin in contrast to **1**, which appears to be high-spin, although DFT computations of the porphinato models Fe(P)(nitrite) suggest that the doublet nitro species and the quartet and sextet nitrito complexes are all relatively close in energy. The nitro−nitrosyl complex **4** is stable under an NO atmosphere but decomposes under intense pumping to give a mixture of the ferrous nitrosyl complex Fe(Por)(NO) and the ferric nitrito complex Fe(Por)(η^1-ONO) indicating the competitive dissociation of NO and NO_2. Hence, loss of NO from **4** is accompanied with nitro → nitrito isomerization consistent with **1** being the more stable of the 5-coordinate NO_2 complexes of iron porphyrins.

Introduction

Nitric oxide (nitrogen monoxide) has several well-established roles in mammalian biology closely tied to its interactions with metalloproteins, especially heme proteins.[1] In this context, there is a continuing interest in other physiological pathways involving NO and other N_xO_y species, including nitrogen dioxide (NO_2), nitrite ion (NO_2^-), and nitrate (NO_3^-). NO_2 is a strong oxidant and nitrating species that initiates destructive pathways in living systems,[2] and several disease states have been suggested to be connected with its exogenous and endogenous formation.[3,4] Possible endogenous NO_2 sources are NO autoxidation in lipid membranes[5] and nitrite ion oxidation by peroxidase enzymes;[6] in addition the NO reactions with superoxide ion lead to peroxynitrite ion ($ONOO^-$),[7] the decay of which affords nitrate ion and NO_2 in competitive processes.[8] Reaction of NO with nitrate as mediated by a heme center also produces nitrogen dioxide.[9] With regard to NO_2^-, nitrite ion is ubiquitous in mammalian tissues and fluids and is the largest reservoir of accessible NO equivalents in the cardiovascular system.[10] Recent studies indicate that NO_2^- may be a vasodilator or, more likely,

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forms the known vasodilator NO via nitrite reductase activity of deoxyhemoglobin or deoxymyoglobin.[10d,e]

The role of nitrate ion (NO_3^-) in the biology of metabolically linked nitrogen oxides (NO, NO_2^-, NO_3^-, etc.) remains to be fully elucidated. It is generally considered a relatively unreactive final oxidation product in mammalian systems that is excreted in the urine,[11] although infantile methemoglobinemia (blue baby syndrome) has been attributed to excessive ingested nitrate that is reduced by intestinal bacteria.[12] In addition, physiological nitrate is known to concentrate in the saliva where it is reduced by bacterial nitrate reductase enzymes to nitrite, ingestion of which has been proposed to serve a positive effect in normal healthy humans.[13] Mammalian nitrate reductases are essentially unknown, although it has recently been shown that nitrate can be activated by NO and heme models to yield other highly reactive N_xO_y species.[9] Such processes are potentially relevant to the chemical biology of the nitrogen oxides as well as to schemes for using such species as mediators in catalytic partial oxidation of various substrates.[14] Clearly, there is continuing incentive to elucidate the fundamental chemistry of these N_xO_y related to their interactions with heme models.[15]

As an ambidentate ligand, there are several modes by which nitrite ion may bind to metal centers,[16] including N(nitro) and O(nitrito) coordination as well as η^2-O_2N linkage isomer coordination.[17] Before 2004, however, the only well-characterized NO_2^- complexes of a synthetic ferrous or ferric porphyrins[18] or of a heme protein[19] were N-coordinated nitro complexes. An exception would be the anion of [K(222)][Fe(TpivPP)(NO_2)(NO)] prepared by the reaction of Fe(TpivPP) with Kryptofix-222-solubilized KNO_2 followed by the reaction with NO. The product had two crystalline forms. In one, the Fe(TpivPP)(NO_2)(NO)$^-$ anion had the nitro nitrosyl structure, and in the other, one of the two independent anions in the asymmetric unit displayed disorder that was concluded to result from the presence of both nitro and nitrito isomers in the same crystal; this linkage isomerism was manifested by differing spectroscopic properties of these crystals.[20]

More recently, there have been several demonstrated nitrito complexes of heme models.[21-23] For example, a metastable compound prepared[21] by photolysis of Fe(TPP)(NO_2)(NO) in a low-temperature KBr pellet was concluded to be the nitrito−nitrosyl complex Fe(TPP)(ONO)(NO) on the basis of the observation of N-isotope sensitive bands in difference IR spectra characteristic for the ν(N═O) and ν(N−O) stretching modes of the Fe−O−N═O moiety and extensive DFT calculations. In 2006, the first example of a structurally characterized nitrito complex of a heme protein was prepared by the soaking preformed crystals of aquo horse heart metmyoglobin (ferric form with the proximal coordination site occupied by a histidine residue) in sodium nitrite solution. The crystal structure clearly shows the NO_2^- ligand to be coordinated as the O-bound nitrito isomer.[23]

Moreover, in a preliminary communication,[22] we reported that the reaction of incremental NO_2 with the iron(II) complex Fe(Por) (Por = *meso*-tetraphenylporphyrinato dianion, TPP, or *meso*-tetra-*p*-tolylporphyrinato dianion, TTP) gives the "elusive" 5-coordinate iron(III) nitrito complexes Fe(Por)(η^1-ONO) (**1**) (eq 1).

$$\mathrm{Fe(Por)} + \mathrm{NO_2} \rightarrow \mathrm{Fe^{III}(Por)(\eta^1\text{-}ONO)} \tag{1}$$

In this article, we describe full details of the interaction of NO with this species. The nitrito−nitrosyl complexes Fe(Por)(NO)(ONO) have been obtained by low-temperature interaction of NO with **1,** and the mechanism of the nitrito → nitro isomerization upon warming has been investigated by using mixed isotope substituted species. The reaction of additional NO_2 increments with **1**, leading eventually to formation of nitrato complexes, is also described in detail. These investigations are supported by DFT calculations that show that nitro and nitrito structures have similar energies and provide insight into the mechanism of the ligand exchange reaction upon supplying labeled NO_2 to **1**.

Experimental Section

The ferrous porphyrinates Fe(Por) are very sensitive to oxygen and are readily oxidized to Fe(III) derivatives. For this reason the more stable hexacoordinate ferrous complexes Fe(Por)$(B)_2$ with nitrogen bases (B is Py or Pip) were synthesized[24] and used as the Fe(Por) precursors. The low-temperature sublimates were prepared[25] by placing a Fe(Por)$(B)_2$ sample in a Knudsen cell and heating to about 470 K under high vacuum ($P = 3 \times 10^{-5}$ Torr). Evacuation for 3 h resulted in the complete elimination of the axial ligands, as monitored by measurement of the pressure at the cryostat outlet. Liquid nitrogen (LN_2) was then poured into the cryostat, and the Knudsen cell was heated to 520 K, whereupon Fe(Por) sublimed onto the 77 K surface of the KBr or CaF_2 substrate. In the latter case, CaF_2 plates were also used as the optical windows of the cryostat. The metallo−arylporphyrinato layers obtained in this manner are spongelike and have high microporosity, similar to

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Table 1. IR and UV−Visible Spectra of the Nitrito and Nitrato Complexes Fe(Por)(ONO) and Fe(Por)(O_2NO).

	IR freq in cm^{-1} [a]				
compds	ax ligand stretching bands			spin-sensitive bands[c]	UV–vis, λ_{max} in nm
Fe(TTP)(ONO)	1528 (1496) m, ν(N=O)	901 (878) w, ν(N−O)	751 (747) w, δ(ONO)	1495 m, 1340 m 428 w	509, 574 sh, 621 sh, 693
Fe(TPP)(ONO)	1526 (1499) m, ν(N=O)	904 (885) w, ν(N−O)	750 (747) w,[b] δ(ONO)	1339 m, 436 w	508, 577 sh, 659, 689
Fe(TTP)(O_2NO)	1529 (1495) m, ν(N=O)	1271 (1251) s, $\nu_a(NO_2)$	966 (957) w, $\nu_s(NO_2)$	1495 m, 1340 m, 428 w	515, 578 sh, 618 sh, 698
Fe(TPP)(O_2NO)	1527 (1493) m, ν(N=O)	1271 (1253) s, $\nu_a(NO_2)$	966 (956) w, $\nu_s(NO_2)$	1340 m, 436 w	513, 579 sh, 658, 691

[a] In parentheses data for ^{15}N-labeled compounds are given. [b] Masked by intense porphyrin bands and is seen only in difference spectra. [c] In intermediate spin-state Fe(Por) these bands are disposed at 1346 and 464 cm^{-1} (Por = TPP) and 1505, 1346, and 454 cm^{-1} (Por = TTP).

bulk samples of these compounds.[26] Potential reactants easily diffuse across these layers, and adducts thus formed can be studied spectroscopically without solvent interference.

Sublimation was typically carried out over periods of 0.3−2.0 h to build up layers of thickness sufficient for UV−visible and IR spectral studies. The Fe(Por) sublimed layer was then heated to room temperature under dynamic vacuum, after which small increments of NO_2 ($^{15}NO_2$, $N^{18}O_2$) gas were introduced for a short time period (∼30 s) followed by a period of evacuating the apparatus. During this procedure the red Fe(Por) film immediately turns brown indicating the formation of Fe(Por)(ONO). After formation of this complex was confirmed by FTIR measurements,[27] the layered film was exposed to new, small increments of NO_2 (or the ^{15}N- or ^{18}O-labeled analogs) which were introduced into cryostat and then were removed by evacuating the system after 3−5 min. Reactions of the layers containing **1** with NO were carried out by first cooling the substrate to LN_2 temperature and then introducing into the cryostat a known quantity of NO measured by a mercury manometer. The layer was slowly warmed, and IR or UV−visible spectra were measured at different substrate temperatures determined by a thermocouple.

NO (^{15}NO) gas was purified by passage through KOH pellets and a cold trap (dry ice/acetone) to remove higher nitrogen oxides and trace quantities of water. The purity was checked by IR measurements of the layer obtained by slow deposition of NO on the cooled substrate of the optical cryostat (80 K). The IR spectra did not show the presence of any N_2O, N_2O_3, or H_2O. NO_2 ($^{15}NO_2$), obtained by oxidizing purified NO (^{15}NO) with excess pure dioxygen, was purified by fractional distillation until a pure white solid was obtained. It was noted that storage of NO_2 in the glass bulb slowly led to formation of trace quantities of NO.[28] This was not a problem when dry O_2 was added to the NO_2 storage bulb. This O_2 was removed by a multiple freeze−pump−thaw procedure just before introducing NO_2 into the cryostat. ^{15}NO with 98.5% enrichment was purchased from the Institute of Isotopes, Tbilisi, Republic of Georgia. $N^{18}O_2$ with 50% enrichment was purchased from “Icon” and was additionally enriched by maintaining with excess of $^{18}O_2$ (Stanford Isotope Laboratory, 95% enrichment) in a glass bulb. According to the mass spectra, the $N^{18}O_2$ used in the experiments was about 75% enriched by ^{18}O isotope.

FTIR spectra were measured by “Nexus” and UV−visible spectra by “Helios γ” spectrophotometers of Thermo Nicolet Corp.

DFT calculations of the Fe(P)(ONO) and the Fe(P)(NO_2) (P = the porphinato dianion) were performed with the Spartan’04 program package (Wavefunction, Inc., Irvine, CA) at the B3LYP level using the LACVP* without symmetry constraints. The optimized structures represent the equilibrium geometries of the molecules in gas phase. The calculations were performed on a Western Scientific dual Xeon 2.66 GHz CPU workstation. Analogous calculations were also carried out using the Gaussian 03 suite of programs (Gaussian, Inc.; Pittsburgh, PA) at the B3LYP level with the LANL2DZ basis set, but no significant differences were seen.

Results and Discussion

Interaction of Small NO_2 Increments with Fe(Por). In a recent communication,[22] we described the cryostat reaction of small increments of NO_2 gas with sublimed layers of Fe(TTP) at room temperature. These results will be briefly summarized here. Introduction of NO_2 led to the appearance of three new IR bands at 1528, 901, and 751 cm^{-1} and immediate change of the film color from red to brown. These bands displayed their isotope counterparts at 1495, 878, and 747 cm^{-1} when $^{15}NO_2$ was used and were assigned to ν(N=O), ν(N−O), and δ(ONO) of O-coordinated nitrito ligand in the 5-coordinate iron porphyrin complex Fe(TTP)(η^1-ONO) (Supporting information Figure S1). For the analogous NO_2 reaction with Fe(TPP), small deviations from these values were seen for the first two bands (Table 1), but the third was masked by an intense TPP band and could be registered only in the difference spectra. Hence the reaction of NO_2 with Fe(II) porphyrins leads to formation of the O-bound nitrito complex Fe(Por)(η^1-ONO) (**1**) as represented in eq 1 and not the N-bound nitro adduct Fe(Por)(η^1-NO_2).

The nitrito complexes were fairly stable at ambient temperature but under vacuum decomposed within a few days to give (principally) the nitrosyl analogs Fe^{II}(Por)(NO). Heating to 340 K under vacuum shortens the time required for conversion of **1** to Fe(TTP)(NO) to several hours. Some μ-oxo-dimer $[Fe(TTP)]_2O$ (manifested by characteristic IR bands at 875 and 893 cm^{-1})[27b] and very minor quantities of the nitrato complex **2** were formed during this procedure.

DFT calculations for the model complexes Fe(P)(ONO) and Fe(P)(NO_2) (P^{2-} = porphinato dianion) at the B3LYP level using the LACVP* basis set using no symmetry constraints gave the nitrito isomer as the lowest energy structure but with the intermediate quartet spin state ^{4}[Fe(P)(ONO)]. The calculated energy difference between this and the low-spin nitro isomer ^{2}[Fe(P)(NO_2)] is insignificant (<1 kJ mol^{-1}) while the high-spin nitrito complex ^{6}[Fe(P)(ONO)] is somewhat higher energy (6.3 kJ mol^{-1}). The suggestion that ^{4}[Fe^{III}(P)(ONO)] is the lowest energy species was unexpected given an indication on the basis of spin-sensitive ring vibrations (see below) that **1** is high-spin, i.e., a sextet. While provocative to think that intermediate-spin or mixed S = 3/2, 5/2 ferric porphyrinato complexes may be playing a role,[29] Ghosh[30] has reported that DFT computation of the analogous chloro complex Fe(P)Cl gave

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(27) The IR spin-sensitive band[27b] in the range of 1350 cm^{-1} is a good indicator for monitoring the reaction. The band at 1346 cm^{-1} of intermediate-spin Fe(TPP)[27c] shifts to 1340 cm^{-1} upon formation of **1** and is absent when the reaction proceeds completely. On the other hand the $\nu_a(NO_2)$ band of nitrato complex at 1271 cm^{-1} serves as criteria that the nitrato complex is not yet formed. (b) Oshio, H.; Ama, T.; Watanabe, T.; Kincaid, J.; Nakamoto, K. *Spectrochim. Acta* **1984**, *40A*, 863−870. (c) Collman, J. P.; Hoard, J. L.; Kim, N.; Lang, G.; Reed, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 2676−2681.

(28) This effect is more noticeable at low pressures of NO_2. Freezing the purified NO_2 with the liquid nitrogen on the wall of the glass storage bulb serves as a rapid procedure for checking purity, since, in the presence of NO, this solid takes on the bluish color from the trace N_2O_3.

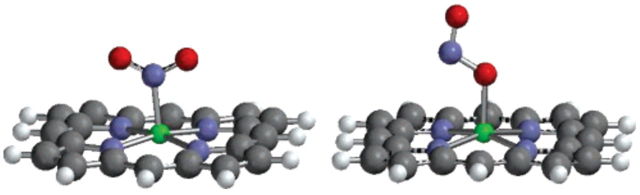

Figure 1. Computed structures using DFT at the B3LYP level using the LACVP* basis set of the lowest energy nitro and nitrito isomers (^{2}[Fe(P)-(NO_2)] and ^{4}[Fe(P)(ONO)], respectively) of the NO_2 adduct to a iron(II) porphinato complex Fe(P).

a quartet but ab initio computation gave a sextet lowest energy state. Thus, there is computational ambiguity[30] whether **1** is a quartet, a sextet, or a mixed state.

Optimized structures for ^{2}[Fe^{III}(P)(NO_2)] and ^{4}[Fe(P)(ONO)] are shown in Figure 1, and calculations for all spin states are summarized in the Supporting Information. The optimized nitro isomer has a distorted square-pyramidal geometry that correlates with the rhombic EPR spectrum recorded for a transient picket fence porphyrinato complex proposed to be Fe(TPivPP)(NO_2).[31a] The porphine plane of ^{2}[Fe^{III}(P)(NO_2)] is slightly ruffled with a 7.2° angle between the planes defined by the oppositely located sets of two pyrrole nitrogens and the *meso*-C atom between them, and the Fe atom is 0.20 Å out of the plane defined by the porphyrin nitrogens. Similar results were obtained for another DFT/B3LYP computation[32] of Fe(P)(NO_2); however, in that work only nitro isomers were considered and the calculations were done under C_{2v} symmetry constraint. The optimized structure of ^{4}[Fe(P)(ONO)] shows a less distorted porphine (the angles between planes defined above are 0.7 and 1.5°), with the Fe out of the porphine plane by 0.26 Å.

These computations suggest that the nitrito and nitro linkage isomers Fe(Por)(ONO) and Fe(Por)(NO_2) should have similar energies, although our experimental studies show only the former as the initial product of NO_2 reaction with Fe(TPP) or Fe(TTP) in layered solids. One rationalization would be that the more distorted nitrito complex ^{2}[Fe^{III}(P)(NO_2)] may be destabilized by the *meso* substituents of TPP and TTP or by interactions in the polarizable condensed phase.

For the picket fence porphyrinato complexes,[18] structural[31b] and computational[32] analyses of the 6-coordinate complex Fe-(TPivPP)(NO_2)(py) suggest weak hydrogen bonding between O-atoms of nitro group and picket fence NH groups. Such H-bonding may be expected to be present for 5-coordinate nitro-complex Fe(TpivPP)(NO_2) as well and to favor N-coordinated isomer in that case.

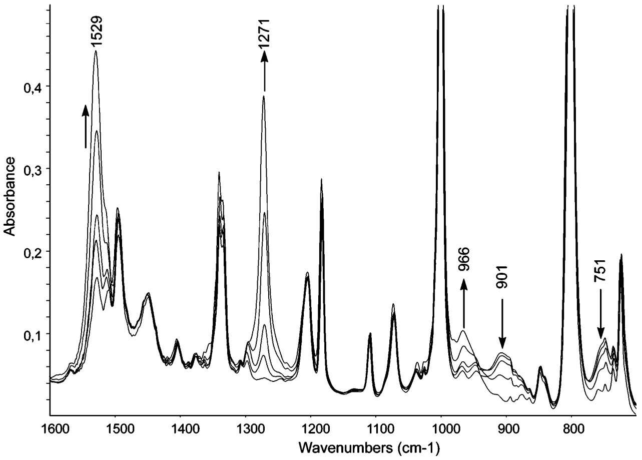

Figure 2. FTIR spectral changes for Fe(TTP)(ONO) in sublimed layers as the result of stepwise addition of new NO_2 increments ($P_{NO_2} \approx 0.5$ Torr, 2−3 min exposure at 293 K) and evacuation after each introduction.

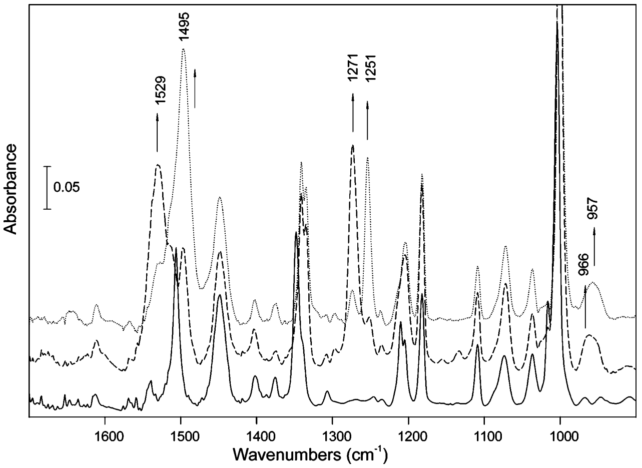

Figure 3. FTIR spectra of thin layers of Fe(TTP) (solid line), Fe(TTP)-(η^2-O_2NO) (dashed line), and Fe(TTP)(η^2-$O_2{}^{15}NO$) (dotted line).

Further Reaction of Fe(TTP)(ONO) with NO_2. FTIR spectral changes observed upon addition of new NO_2 increments to layers containing **1** are represented in the Figure 2. It is seen that this procedure was accompanied by gradual disappearance of the bands at 901 and 751 cm^{-1} while new bands at 1271 and 966 cm^{-1} grew in intensity. Additionally, the band in the vicinity of 1530 cm^{-1} gained very significantly in intensity. In experiments with the labeled ${}^{15}NO_2$, these bands appeared at 1251, 957, and 1495 cm^{-1}, respectively shifted to lower frequencies (Figure 3), confirming that they are characteristic of the coordinated nitrate. The X-ray crystal structure of Fe-(TPP)(O_2NO) has been determined,[33] and this compound shows an asymmetrically bidentate nitrato ligand with the high-spin Fe(III) displaced 0.6 Å from the porphyrin plane. Such a η^2-nitrato ligand would be expected to show three IR-active stretching modes, a ν(N=O) stretch for the uncoordinated oxygen plus symmetric and asymmetric modes $\nu_s(NO_2)$ and ν_a-(NO_2) for the coordinated NO_2 fragment.[34] The two higher frequency bands (ν(N=O) and $\nu_a(NO_2)$) had been identified previously;[35a] the present work also identifies the lower frequency $\nu_s(NO_2)$. These data are summarized in Table 1. The recently synthesized ruthenium complex Ru(TTP)(NO)(NO_3) displays similar bands at 1269, 950, and 1515 cm^{-1} for the nitrate ligand.[36]

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(29) Weiss, R.; Gold, A.; Terner, J. *Chem. Rev.* **2006**, *106*, 2550−2579 and references therein.

(30) Ghosh, A. *J. Biol. Inorg. Chem.* **2006**, *11*, 712−724 and references therein.

(31) (a) Munro, O. Q.; Scheidt, W. R. *Inorg. Chem.* **1998**, *37*, 2308−2316. (b) Cheng, L.; Powell, D. R.; Khan, M. A.; Richter-Addo, G. B. *Chem. Commun.* **2000**, 2301−2302.

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(35) (a) Kurtikyan, T. S.; Stepanyan, T. G.; Akopyan, M. E. *Russ. J. Coord. Chem.* **1999**, *25*, 721−725. (b) Kurtikyan, T. S.; Stepanyan, T. H.; Martirosyan, G. G.; Kazaryan, R. K.; Madakyan, V. N. *Russ. J. Coord. Chem.* **2000**, *26*, 345−348. (c) Kurtikyan, T. S.; Stepanyan, T. G.; Gasparyan, A. V.; Zhamkochyan, G. H. *Russ. Chem. Bull.* **1998**, *47*, 695−698.

(36) Kang, Y.; Zyryanov, G. V.; Rudkevich, D. M. *Chem. Commun.* **2003**, 2470−2471.

Thus, as demonstrated earlier,[35a] the final product of the NO_2 reaction with Fe(TPP)(ONO) is the η^2-nitrato species Fe(TPP)(η^2-O_2NO) (eq 2). While similar reactivity is seen with manganese(II) analogs Mn(TPP),[35b] this behavior contrasts with cobalt(II) complex Co(TPP), which gave only the nitro complex Co(TPP)(NO_2) under analogous experimental conditions.[35c]

$$\mathrm{Fe(TPP)(ONO)} + \mathrm{NO_2} \rightarrow \mathrm{Fe(TPP)}(\eta^2\text{-}\mathrm{O_2NO}) + \mathrm{NO} \qquad (2)$$

Comparison of the IR spectra of Fe(TPP)(η^1-ONO) and Fe(TPP)(η^2-O_2NO) (Table 1) shows that the ν(N=O) bands occur at nearly the same frequency for the two complexes, although the band for the latter is more intense. A similar coincidence of the high-frequency stretching modes is seen for the ruthenium nitrito and nitrato complexes Ru(TPP)(NO)(ONO)[37] and Ru(TTP)(NO)(NO_3),[36] for which the values of 1515 and 1516 cm^{-1} were respectively reported.

Certain porphyrin vibrational modes of Fe(TPP) complexes, for example, bands at ~1350 cm^{-1} ($\nu(C_a-C_m)$ mixed with $\nu(C_m$−phenyl)) and at ~450 cm^{-1} (δ(Pyr rotation))[38] are sensitive to the spin and oxidation state of the metal center.[27b] For the intermediate-spin state Fe(TPP),[27c] these bands lie at 1346 and 464 cm^{-1}. Upon coordination with NO_2, they shift to 1341 and 434 cm^{-1} consistent with a change to high-spin for the new complex (Table 1). For Fe(TTP), the analogous bands appear initially at 1346 and 455 cm^{-1} and correspondingly shift upon both nitrito and nitrato complex formation to 1340 and 428 cm^{-1}. In this case, there is an additional band disposed at 1505 cm^{-1} that undergoes a shift to 1495 cm^{-1} upon the formation of **1** and **2** that may also be indicative for an intermediate-spin → high-spin transition. Complete band assignments for the TTP derivatives on the basis of normal coordinate calculations have not been made, although it is reasonable to suggest that this band should belong to a complex mode consisting of $\nu(C_\beta-C_\beta) + \nu_a(C_a-C_m) + \nu_s(C_a + C_m)$ that also appears in the IR spectrum of Fe(TPP)Cl.[38]

DFT calculations (B3LYP/LACVP*) for the porphinato complex Fe(P)(NO_3) gave the quartet state as the lowest energy species, but the sextet was very close ($\Delta E = +0.3$ kJ mol^{-1}) while the doublet was much higher energy ($\Delta E = +27.2$ kJ mol^{-1}). The optimized quartet structure was effectively monodentate (Fe−O values of 1.97, 3.15, and 4.03 Å) while the sextet was symmetrically bidentate (Fe−O values of 2.17, 2.17, and 3.80 Å) (Supporting Information Table S3). The latter is consistent with the published structure of Fe(TPP)(η^2-O_2NO), which is bidentate although unsymmetrical with bond lengths of 2.019(4) and 2.323(8) Å.[33] Nonetheless, the similar energies of the monodentate and bidentate bonding modes is notable in the context that the both have been reported for crystal structures of Fe(Por)(NO_3) complexes, depending on the nature of the porphyrin ligand.[18]

Figure 4 illustrates changes in the UV−visible spectra upon reaction of Fe(TTP) in sublimed layers with NO_2 increments at 293 K to give first **1** and then **2**. The optical spectra were recorded after it was shown from the FTIR spectral changes that the specified transformation had occurred in that sample.

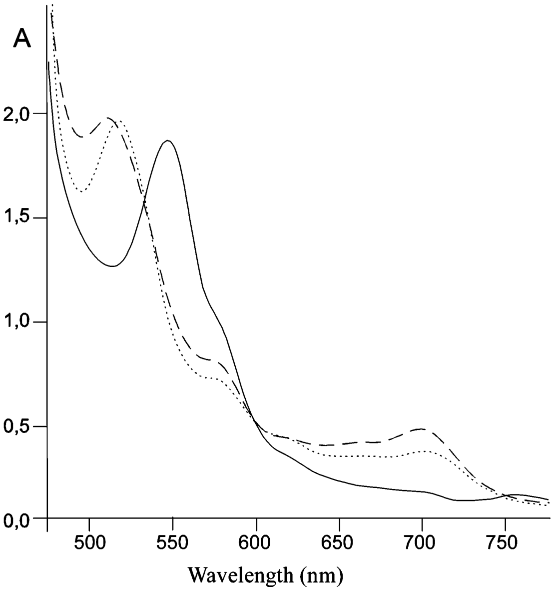
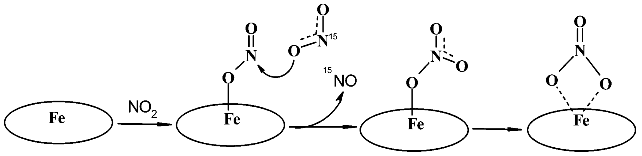


Figure 4. Optical spectra of Fe(TTP) in a sublimed layer on a CaF_2 plate (solid line) and of the products formed after sequential addition of NO_2 increments. The spectra were recorded after the FTIR spectra of the same sample demonstrated first the formation of nitrito Fe(TTP)(ONO) (dashed line) and then of nitrato Fe(TTP)(η^2-O_2NO) complexes (dotted line).

Scheme 1. Prospective Mechanism for Formation of **2** by the Oxo Transfer from Free NO_2 to **1**



Both products displayed spectra characteristic of conversion from the initial ferrous state to the ferric state, but the optical spectra of **1** and **2** are quite similar (Table 1).

It is clear from the FTIR data that the reaction of NO_2 with ferrous porphyrinato complexes proceeds via two distinct stages. During the first stage, seen for short reaction times with a very low P_{NO_2}, simple NO_2 coordination to give the 5-coordinate nitrito complex **1** occurs. Subsequent reaction at higher P_{NO_2} leads to the slower formation of the nitrato species **2**, presumably with the concomitant formation of NO as illustrated in eq 2. The prospective formation of NO draws support from the observation that when, at the conclusion of this procedure, the gaseous contents were frozen onto the cryostat wall with LN_2, a bluish solid was observed. This is a good qualitative indication of the presence of N_2O_3 formed by reaction of NO with excess NO_2. Although NO is known to react with **2** to give the adduct Fe(Por)(NO)(NO_3), the latter is relatively unstable[39] and is not formed in spectrally registered quantities under the conditions of this experiment.

One can envision two different scenarios for the second stage of this transformation. One would be oxygen atom transfer from the incoming NO_2 to the N of the nitrito ligand (Scheme 1). An alternative pathway would involve bond formation between the N of the incoming NO_2 and the coordinated O of the nitrito ligand followed by NO release from that ligand (Scheme 2). Both would give the monodentate nitrato complex as an

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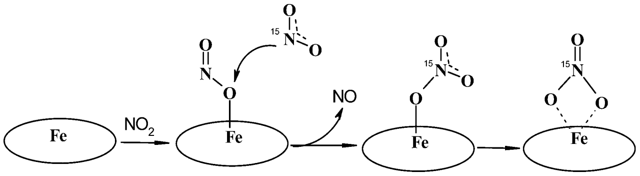
(37) Kurtikyan, T. S.; Martirosyan, G. G.; Lorkovic, I. M.; Ford, P. C. *J. Am. Chem. Soc.* **2002**, *124*, 10124−10129.

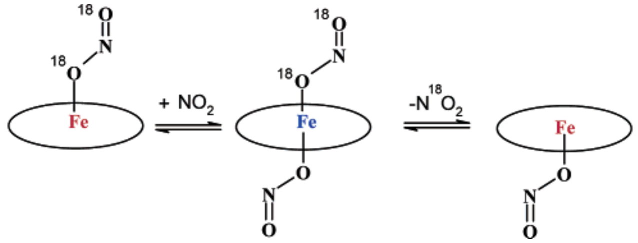
(38) Paulat, F.; Praneeth, V. K. K.; Nather, C.; Lenhert, N. *Inorg. Chem.* **2006**, *45*, 2835−2856.

(39) Kurtikyan, T. S.; Martirosyan, G. G.; Hakobyan, M. E., Ford, P. C. *Chem. Commun.* **2003**, 1706−1707.

Scheme 2. Prospective Mechanism for Formation of **2** by the NO_2 Attack at the Coordinated O Atom of Fe(Por)(ONO)



Scheme 3. Possible Mechanism for Exchange of $Fe(Por)(^{18}ON^{18}O)$ with Added NO_2



intermediate. In principle, these two mechanisms could be differentiated by isotope labeling experiments. For the first, the reaction of unlabeled **1** with $^{15}NO_2$ would give unlabeled **2**. For the second, the nitrogen of the nitrate ligand found in the product would have originated with the gaseous $^{15}NO_2$ giving the labeled product $Fe(Por)(\eta^2\text{-}O_2{}^{15}NO)$.

However, such analysis was complicated by the discovery that concomitant to the second stage of the reaction exchange between the added and coordinated nitrogen dioxide also occurs. For example, when a sample of $Fe(TTP)(^{18}ON^{18}O)$ prepared from Fe(TTP) and $N^{18}O_2$ was exposed to a small increment of unlabeled NO_2, there was a shift in the δ(ONO) consistent with such exchange (Supporting Information Figure S2). This process can be envisioned to occur by reaction of the free NO_2 at the open coordination site of **1** to give a transient dinitrito intermediate $Fe(Por)(ONO)_2$ or one of its isomers (Scheme 3). Such a pathway is analogous to the exchange of free and coordinated NO demonstrated for Fe(Por)(NO) complexes using isotopic labeling methods.[40] For example, Fe(TPPyP) (TPPyP = pyridyltriphenylporphyrinato dianion) in sublimed layers reacts with NO to form the 5-coordinate Fe(TPPyP)(NO) and the 6-coordinate *trans*-Fe(TPPyP)(L)(NO). In this case L is a pyridyl from an adjacent Fe(TPPyP).[41] Notably, isotopic exchange with labeled NO occurred only with Fe(TPPyP)(NO), and these data were interpreted in terms of reaction of the latter with NO to give a *trans*-dinitrosyl intermediate. Analogous *trans*-$Fe(Por)(NO)_2$ species have been observed in low-temperature solutions and characterized spectroscopically and theoretically.[42]

The intermediate species that would be formed by the reaction of NO_2 with the model compound $^4[Fe(P)(ONO)]$ (in a gas phase analog to Scheme 3 for the porphinato analogs) was examined by DFT calculations. The lowest energy linkage isomer of this (nominally) Fe(IV) complex was found to be the triplet spin state dinitro complex $^3[Fe(P)(NO_2)_2]$ (Supporting Information Table S4), although the triplet dinitrito analog $^3[Fe(P)(ONO)_2]$ is less than 5 kJ mol^{-1} higher energy and several mixed nitrito nitro spin states are within 10 kJ mol^{-1} of the lowest energy structure. If one takes into account the calculated energies of $^4[Fe(P)(ONO)]$, NO_2 (−205.072 18 au), and $^3[Fe(P)(NO_2)_2]$, formation of the dinitro complex is estimated to be favorable (−17 kJ mol^{-1}), although the negative ΔS of this process would make the equilibrium constant small. Nonetheless, these data suggest that the reaction pathway shown in Scheme 3 is an energetically reasonable mechanism for the NO_2 exchange processes.

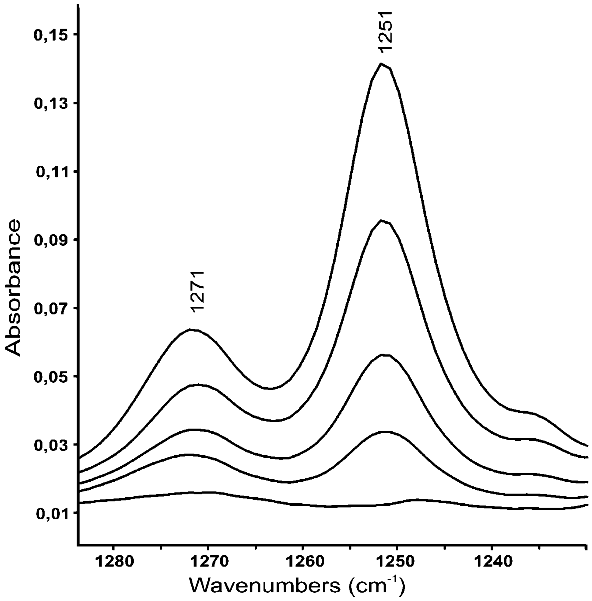


Figure 5. FTIR spectra of $Fe(TTP)(\eta^1\text{-}ONO)$ (lowest curve) after sequential exposure under increments of $^{15}NO_2$ gas (0.3 Torr, 3 min at 293 K) and evacuation after each introduction. The bands at 1271 and 1251 cm^{-1} belong to $\nu_a(NO_2)$ and $\nu_a(^{15}NO_2)$ of $Fe(TTP)(\eta^2\text{-}O_2NO)$ and $Fe(TTP)(\eta^2\text{-}O_2{}^{15}NO)$ correspondingly.

Another point to take into account when examining isotope labeling experiments to test possible mechanisms for the NO_2 oxidation of **1** is that free NO once formed will undergo rapid isotopic exchange with the free NO_2 present.[43]

Figure 5 illustrates the FTIR spectral changes at frequencies corresponding to the $\nu_a(NO_2)$ band of the coordinated nitrate when small increments of $^{15}NO_2$ were added to unlabeled $Fe(TTP)(\eta^1\text{-}ONO)$ and allowed to react for a short period. After each $^{15}NO_2$ addition, the system was evacuated to remove any nitric oxide and other gases. This spectral range is free from any bands of the nitrito complex and, thus, is convenient for such analysis. Interaction of small amounts of $^{15}NO_2$ with Fe(Por)(ONO) leads principally to formation of $Fe(Por)(O_2{}^{15}NO)$; however, all spectra show that some $Fe(Por)(O_2NO)$ is also formed during this process. On first impression, these results would appear to favor Scheme 2, since that mechanism predicts that the nitrato nitrogen would originate with the free nitrogen dioxide. The formation of some unlabeled product might be explained by the simultaneous operation of both mechanisms. However, the aforementioned isotope exchange between free

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(40) O'Shea, S. K.; Wang, W.; Wade, R. S.; Castro, C. E. *J. Org. Chem.* **1996**, *61*, 6388−6395.

(41) Kurtikyan, T. S.; Ogden, J. S.; Kazaryan, R. K.; Madakyan, V. N. *J. Porphyrins Phthalocyanines* **2003**, *7*, 623−629.

(42) (a) Lorkovic, I. M.; Ford, P. C. *J. Am. Chem. Soc.* **2000**, *122*, 6516−6517. (b) Patterson, J. C.; Lorkovic, I. M.; Ford, P. C. *Inorg. Chem.* **2003**, *42*, 4902−4908. (c) See also the following: Conradie, J.; Wondimagegn, T.; Ghosh, A. *J. Am. Chem. Soc.* **2003**, *125*, 4968−4969.

(43) Such isotope-scrambling takes place in the amorphous layer of Ni(TPP) even at very low temperatures[9] and should proceed readily under the conditions of the present experiments; it is presumably facilitated by formation of dinitrogen trioxide species isomers.[43b] (b) Fateley, W. G.; Bent, H. A.; Crawford, B. *J. Chem. Phys.* **1959**, *31*, 204−217.

Table 2. IR and UV−Visible Data for 6-Coordinate Nitrito−Nitrosyl and Nitro−Nitrosyl Complexes of Iron(III) Porphyrins in Amorphous Thin Layers

	IR freq, cm^{-1} [a]		
compds	ax ligand stretching bands	spin-sensitive bands	UV−vis, λ_{max}, nm
Fe(TPP)(ONO)(NO)	1887 (1850) s, ν(N≡O); 1496 (1471) m, ν(N=O); 938 (920) m, ν(N−O)	1351 m, 462 w	548, 584
Fe(TTP)(ONO)(NO)	1886 (1850) s, ν(N≡O); 1497 (1464) m, ν(N=O); 935 (917) m, ν(N−O), 594 (585) vw, ν{Fe−N(N≡O)}	1507 m, 1350 m, 452 w	546, 580, 618 sh
Fe(TPP)(NO_2)(NO)	1863 (1824) s, ν(N≡O); 1455 (1425) m, $\nu_a(NO_2)$; 1295 (1274) vs, $\nu_s(NO_2)$	1350 m, 461 w	547, 582
Fe(TTP)(NO_2)(NO)	1860 (1824) s, ν(N≡O); 1456 (1424) m, $\nu_a(NO_2)$; 1293 (1274) vs, $\nu_s(NO_2)$; 553 (545) vw, ν{Fe−N(N≡O)}	1507 m, 1349 m, 451 w	547, 579, 617 sh

[a] In parentheses data for ^{15}N-labeled compounds are given.

nitrogen dioxide and **1** is significant when but minor quantities of **2** are yet formed, so it appears that this exchange is faster than the reaction leading to formation of **2** and there is considerable scrambling of the isotopic labeling. Nonetheless, formation of unlabeled **2** at very early stages of the reaction suggests that the Scheme 1 is clearly in operation, at least in competition with Scheme 2.

Rudkevich et al.[36] reported that reaction of Ru(TTP)(CO) with 2 equiv of NO_2 in CH_2Cl_2 gives the nitrato−nitrosyl complex Ru(TTP)(NO_3)(NO). As a possible mechanism they proposed N_2O_4 disproportionation to nitrosonium nitrate $NO^+NO_3^-$ followed by NO^+ displacement of the carbonyl and then NO_3^- coordination at the *trans* axial site. Such a pathway is unlikely in the present case owing to the low P_{NO_2} and the absence of a solvent to support ionic intermediates. On the other hand, a mechanism such as described here for Fe(Por) can be envisioned for the ruthenium analogs. For example, NO_2 coordination to Ru(TTP)(CO) would give Ru(TTP)(CO)(NO_2), and the resulting Ru center should be quite labile to CO dissociation to give Ru(TTP)(NO_2) (linkage isomer unspecified). If the latter is present as the nitrito isomer, then reaction with a second NO_2 would give Ru(TTP)(NO_3) plus NO, which could combine to give Ru(TTP)(NO)(NO_3).

Reaction of NO with 1. Introduction of NO into the cryostat containing sublimed layers of Fe(Por)(ONO) at room temperature leads to rapid formation of the known nitro−nitrosyl complexes Fe(Por)(NO_2)(NO).[44] However, as we reported in the preliminary communication,[22] another pattern is observed when this was done at LN_2 temperature. At 80 K there was no apparent reaction but slow warming of the layer to 140 K led to the appearance of new FTIR bands at 1886, 1496, and 934 cm^{-1} at the expense of the Fe(TTP)(ONO) bands at 1528, 901, and 751 cm^{-1} (Supporting Information Figure S3). The former bands have their isotope counterparts at 1850, ∼1464, and 917 cm^{-1} when ^{15}NO interacts with layers containing Fe(TTP)($O^{15}NO$) (Figure S4). Concomitantly, the color of the layer changes from brown to red-purple. These observations and spectral comparison to the metastable species obtained upon photolysis of a low-temperature KBr pellet containing Fe(TPP)(NO)(NO_2)[21] led to the conclusion that the low-temperature addition of NO to Fe(Por)(ONO) gives the nitrito−nitrosyl complex Fe(Por)(ONO)(NO) (eq 3). Infrared frequencies of nitrito−nitrosyl complexes are in good agreement with those calculated and reported in literature[21b] with frequencies of coordinated nitrito group at about 1500 cm^{-1} [ν(N=O)] and 930 cm^{-1} [ν(N−O)].

$$\text{Fe(Por)(ONO)} + \text{NO} \rightleftharpoons \text{Fe(Por)(ONO)(NO)} \qquad (3)$$

Upon further warming of the layered Fe(TPP)(ONO)(NO) sample from 130 to 220 K, the FTIR spectral changes displayed in Figure 6 are observed. New bands at 1860, ∼1452, and 1294 cm^{-1} appear and grow at the expense of Fe(TTP)(ONO)(NO) bands at 1886, 1496, and 934 cm^{-1}. The former bands have their ^{15}N-isotope counterparts at 1825, 1426, and 1274 cm^{-1} when layered Fe(TPP)($O^{15}NO$)(^{15}NO) is warmed (Supporting information Figure S5). The resulting spectrum is that of the nitro−nitrosyl complex Fe(TTP)(NO_2)(NO), a type of structure reported by Yoshimura and characterized spectroscopically and structurally for several iron porphyrins.[18,44] Hence warming Fe(Por)(ONO)(NO) results in the nitrito → nitro isomerization of coordinated NO_2 (eq 4). This process proceeds both in the presence of excess NO as well as when NO was evacuated at 130 K before warming the Fe(Por)(ONO)(NO) layer. The spin-sensitive bands remain unchanged during this process consistent with a low-spin nature of both 6-coordinate complexes.

$$\text{Fe(TPP)(ONO)(NO)} \rightarrow \text{Fe(TTP)(NO}_2\text{)(NO)} \qquad (4)$$

This linkage isomerization was also probed using optical spectroscopy; however, the difference between the UV−visible spectrum of the nitrito−nitrosyl complex and that of the nitro−nitrosyl analog is too small (Figure 7) to be used to differentiate between these two forms (Table 2). This may explain why the oft-postulated nitrito−nitrosyl isomer had not been characterized previously by optical spectroscopy.[9,45]

It is worth noting that interaction of NO with sublimed layers of **1** at 170 K leads to the formation of **3** and **4** in comparable quantities.

The isomerization of Fe(TPP)(ONO)(NO) back to Fe(TPP)(NO_2)(NO) has been described by Lee et al.,[21] who examined the photolysis of the latter in solid KBr matrices. One photoproduct is Fe(Por)(ONO)(NO), and this undergoes a slow return to the initial nitro complex. DFT computations by those workers (for the porphinato analogs) demonstrated the lowest energy nitrito nitrosyl complexes to be ∼20 kJ mol^{-1} higher energy than the six-coordinate nitro−nitrosyl complexes. Similar studies of the optimized structures of these isomers in one of our laboratories using the 6-31g basis set led to the same conclusion.[46]

Mixed Isotope Experiments: **Mechanism of Nitrito−Nitro Isomerization.** Potential mechanisms for this linkage isomerization are represented by Scheme 4a,b. The former would

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[44] Yoshimura, T. *Inorg. Chim. Acta* **1984**, *83*, 17−21. (b) Ellison, M. K.; Schulz, C. E.; Scheidt, W. R. *Inorg. Chem.* **1999**, *38*, 100−108.

[45] Lim, M. D.; Lorkovic, I. M.; Wedeking, K.; Zanella, A. W.; Works, C. F.; Massick, S. M.; Ford, P. C. *J. Am. Chem. Soc.* **2002**, *124*, 9737−9743.

[46] Patterson, J. C. Ph.D. Dissertation, University of California, Santa Barbara, CA, 2004.

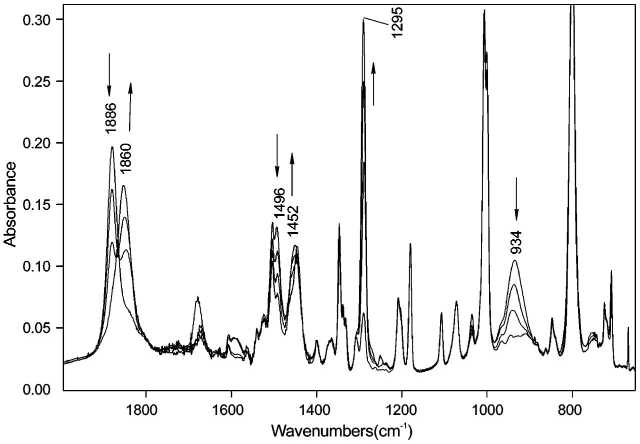


Figure 6. FTIR spectral changes demonstrating nitrito−nitro isomerization upon warming of thin layers containing Fe(TTP)(ONO)(NO) from 140 to 220 K.

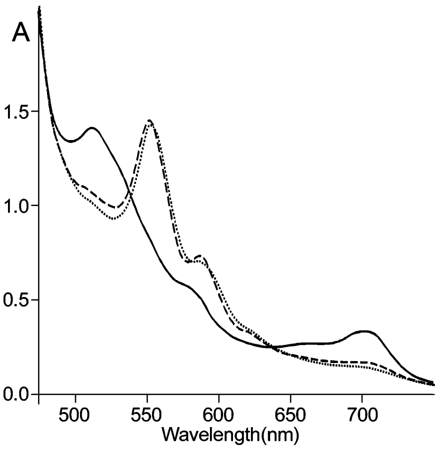
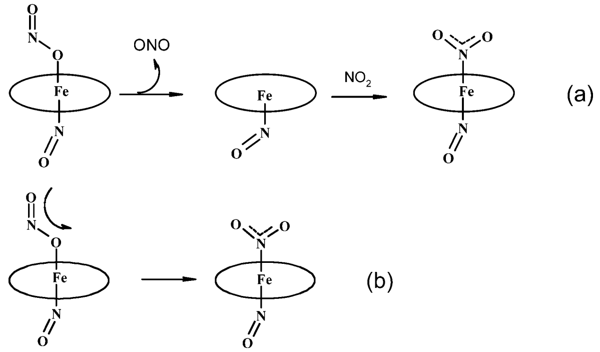


Figure 7. UV−visible spectra of Fe(TTP)(ONO) (solid line) after low-temperature interaction (130 K) with NO and formation of nitrosyl−nitrito complex (NO)Fe(TTP)(ONO) (dashed line) and its isomerization to nitrosyl−nitro complex upon warming (NO)Fe(TTP)(NO_2) (dotted line).

Scheme 4. Possible Mechanisms of Nitrito−Nitro Isomerization upon Transition from **3** to **4**



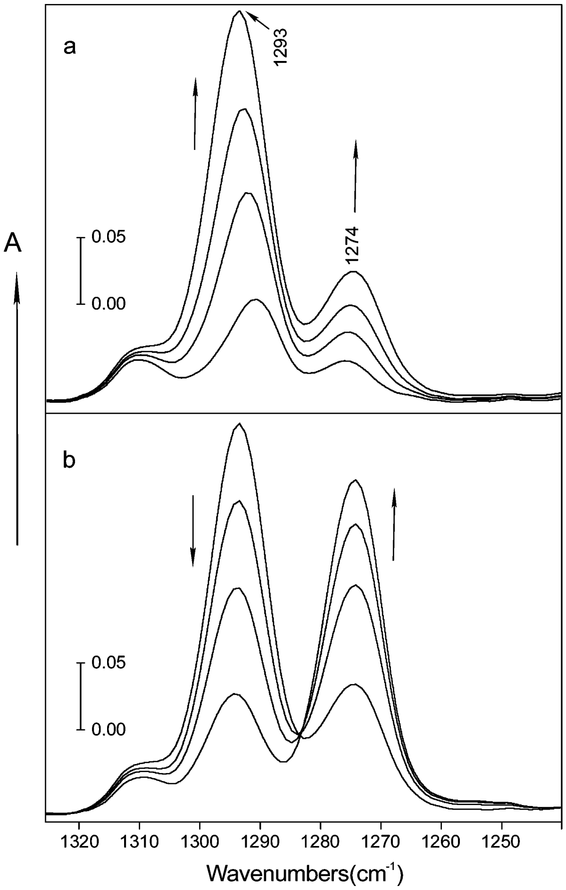


Figure 8. (a) FTIR spectra demonstrating isomerization of **3** to **4** upon warming the layer containing Fe(TTP)(ONO)(^{15}NO) under 2.5 Torr ^{15}NO from 160 to 200 K. (b) After further warming to 260 K.

involve NO_2 dissociation from **3** to give the nitrosyl complex Fe(Por)(NO) plus free NO_2 followed by intermolecular reaction at the NO_2 nitrogen atom to form **4**. An alternative would be an intramolecular concerted migration (“flipping”) of nitrogen dioxide from the O- to the N-coordinated isomer (Scheme 4b). It should be possible to differentiate such pathways by isotopic labeling experiments. In the presence of excess ^{15}NO, any NO_2 released in a dissociative mechanism (Scheme 4a) would undergo rapid isotopic exchange (e.g., $^{15}NO + NO_2 \rightleftharpoons NO + {}^{15}NO_2$) via the formation of N_2O_3.[9] In that case, the linkage isomerization of the selectively labeled compound Fe(Por)(ONO)(^{15}NO) would give largely the doubly labeled product Fe(Por)($^{15}NO_2$)(^{15}NO). In contrast, the intramolecular mechanism (Scheme 4b) would give primarily the half-labeled product Fe(Por)(NO_2)(^{15}NO).

The methodology described here can be used to prepare nitrito−nitrosyl complexes with specifically labeled nitrogen oxides. For example, Fe(Por)(ONO)(^{15}NO) was obtained by the low-temperature reaction of ^{15}NO with Fe(Por)(ONO) layers, while Fe(Por)(O^{15}NO)(NO) was obtained by interaction of NO with Fe(Por)(O^{15}NO) (Figures S6a and S6b, respectively). The frequencies of the individual bands characteristic of the stretching modes for the coordinated nitrogen oxides in these mixed labeled species are the same as those found for the respective vibrational modes in the corresponding isotopically uniform samples.[47] This observation indicates that kinematic coupling between the axial ligands is weak.

Figure 8a displays FTIR spectral changes seen when the layered material containing Fe(TTP)(ONO)(^{15}NO) in the presence of excess ^{15}NO (pressure) was warmed to temperatures where nitrito → nitro isomerization starts to occur. The frequency range shown is that where the intense $\nu_s(NO_2)$ stretch

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[47] Stretching modes of nitrogen oxide groups in Fe(TTP)(ONO)(^{15}NO) are disposed at 1851, 1496, and 934 cm^{-1} while those of Fe(TTP)(O^{15}NO)(NO) are at 1888, 1469, and 920 cm^{-1}. Compare with the data of Table 2 for isotopically uniform species. The same pattern was observed for the corresponding nitro−nitrosyl complexes.

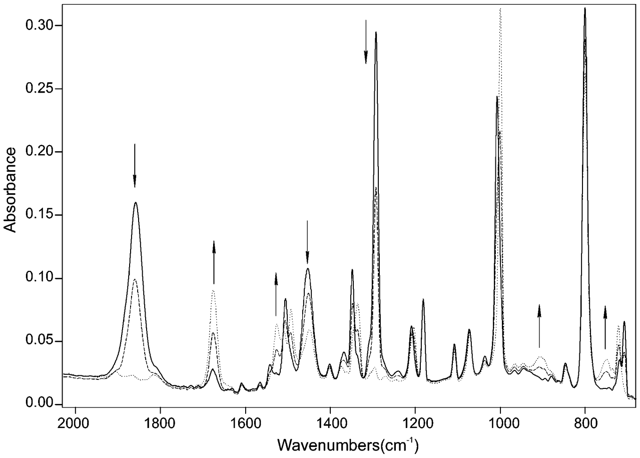


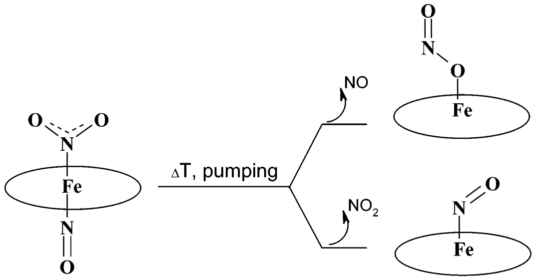
Figure 9. FTIR spectral changes demonstrating decomposition of nitro−nitrosyl complex Fe(TPP)(NO_2)(NO) upon warming its thin layers under intense evacuation: 220 K (solid line); 250 K (dashed line); 280 K (dotted line).

of the coordinated nitro group of **4** is disposed. These data show that the 1294 cm^{-1} band corresponding to the isotopic species Fe(TTP)(NO_2)(^{15}NO) grows faster and eventually is much stronger than the lower frequency band at 1274 cm^{-1}. The latter corresponds to the ν_s($^{15}NO_2$) of Fe(TTP)($^{15}NO_2$)(^{15}NO) but may also be intensified by overlap with a similar vibration of $^{15}N_2O_3$, a small amount of which may be formed as evidenced by the appearance of a weak band at 1560 cm^{-1} belonging to the ν_a($^{15}NO_2$) of this species.[48] These data clearly show isomerization of Fe(TTP)(ONO)(^{15}NO) results mostly in formation of Fe(TTP)(NO_2)(^{15}NO), and we interpret this result as indicating that the intramolecular isomerization ("flipping") pathway is the predominant one operating under these conditions. However, the observation of a lesser amount of Fe(TTP)($^{15}NO_2$)(^{15}NO) as well as of some $^{15}N_2O_3$ implies that NO_2 dissociation is also occurring during the course this study, although this may reflect, at least partially, secondary reactions of the product (see below).

When the sample primarily consisting largely of Fe(TTP)(NO_2)(^{15}NO) (the final curve in Figure 8a) was further heated to 260 K under excess ^{15}NO, the spectral changes (Figure 8b) show that Fe(TTP)(^{15}NO)(NO_2) decreases while the fully labeled Fe(TTP)(^{15}NO)($^{15}NO_2$) increases. Therefore, the nitro nitrosyl complex **4** is labile to NO_2 exchange, and such lability may be responsible for at least some of the exchange seen in Figure 8a.

Decomposition of Fe(TTP)(NO$_2$)(NO) at Higher *T*. When layered **4** was warmed from 220 to 280 K under high vacuum with active pumping, the FTIR spectral changes demonstrated in Figure 9 were observed. Bands characteristic of **4** at 1860, ~1452, and 1295 cm^{-1} completely disappeared and bands at 1680, 1528, 901, and 751 cm^{-1} gained in intensity. The band at 1680 cm^{-1} certainly belongs to the nitrosyl complex Fe(TTP)(NO), while three others are assigned to stretching modes of nitrito ligand in Fe(TTP)(ONO) (see above). The nitrato complex manifested by a band at 1271 cm^{-1} is formed in negligibly small quantities. Thus, the nitro−nitrosyl **4** is labile toward dissociation both of NO and of NO_2, competitively, under these conditions (Scheme 5). Loss of NO would give the 5-coordinate nitro complex Fe(TTP)(NO_2), which isomerizes to more stable nitrito form **1**, while loss of NO_2 would give the stable nitrosyl complex Fe(TTP)(NO). Notably, Lim et al.[45] showed in solution experiments that Fe(TPP)(NO)(NO_2) dissociates NO to form Fe(TPP)(NO_2) and proposed that this is followed by linkage isomerization to Fe(TPP)(ONO).

Scheme 5. Decomposition of **4** upon Warming from 220 to 280 K under Intense High-Vacuum Pumping



In a different experiment, excess NO was removed from the layered **4** at 220 K, and then the material was allowed to warm to room temperature without further pumping. Under these conditions, the main products were Fe(Por)NO and Fe(Por)(NO_3). This result now can be easily understood taking into account the oxidation of nitrito ligand by free NO_2 (eq 2). Although this reaction is relatively slow, failure to actively remove the dissociated NO_2 results in subsequent oxidation of **1** to **2** (eq 2). Here it is worth reexamining an earlier experiment,[45] in which concentrated solution of Fe(TPP)(NO_2)(NO) was rapidly evacuated so that the solvent and all volatile NO_x species were removed. The solid residue was redissolved in benzene where it displayed in NMR a resonance of 76.55 ppm, which was suggested to be the β-pyrrole of Fe(TPP)(NO_2). Over the course of 1 h, this peak disappeared and gave way to a new one at 78.46 ppm thought to be Fe(TPP)(O_2NO). It now appears likely that the initial signal observed was that of Fe(TPP)(ONO).

Why Does Fe(Por)(NO$_2$)(NO) Need Excess NO for Stability? On the basis of present and previous studies, one may postulate an answer for this question. Since NO and NO_2 competitively dissociate from **4** to give Fe(Por)(ONO) and Fe(Por)(NO), respectively, the NO_2 released reacts with the nitrito complex **1** to give the nitrato complex **2**. In the absence of excess NO, the accumulation of **1** and NO_2 favors this reaction. However, the presence of excess NO adds new parameters. One is the role of N_2O_3, which is formed by the reaction of NO with NO_2 under such conditions and is known from solution studies to oxidize Fe(Por)(NO) back to **4**.[45] In addition excess NO reacts with Fe(Por)(NO_3) via a sequence of steps described earlier[9] and illustrated in Scheme 6 to re-form **4**. Thus, under such conditions, the nitro−nitrosyl complex **4** appears to be the thermodynamic sink.

Summary. The interaction of NO_2 gas with the Fe(II) porphyrinato complex Fe(Por) proceeds via two distinct stages. The first is the formation of the 5-coordinate Fe(III) nitrito intermediate Fe(Por)(η^1-ONO) (**1**); the second is the reaction of **1** with new NO_2 increments to form, eventually, the Fe(III) nitrato complex Fe(Por)(η^2-O_2NO) (**2**). The mechanism of the second stage of reaction was probed by using differently labeled

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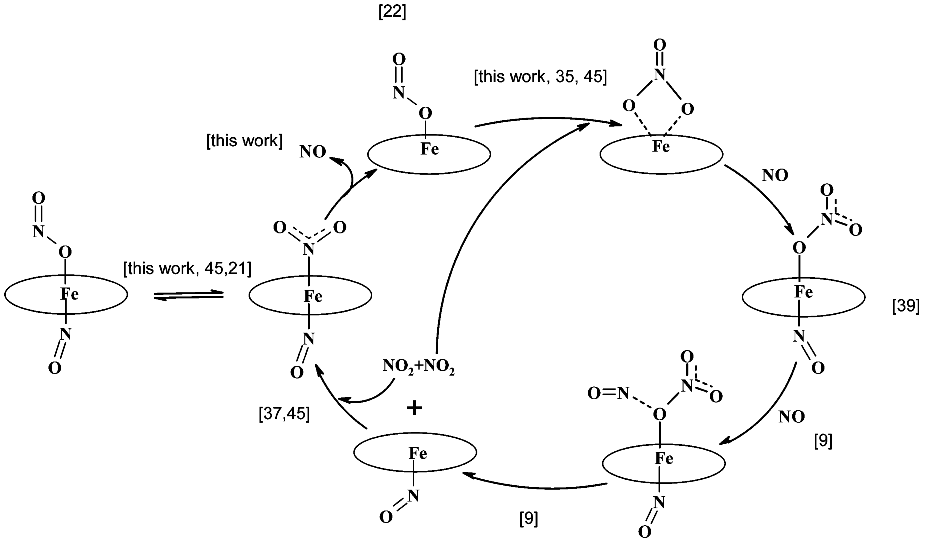
[48] The frequencies of two other vibrations (nitrosyl stretching and ν_s(NO_2)) of **4** and dinitrogen trioxide (N_2O_3) are close to each other and are not diagnostic for the low-temperature experiments where both these species are present.

Scheme 6. Dynamic Processes Taking Place in the Systems Containing **4** under Excess NO[a]



[a] In parentheses, the references cited describe corresponding processes or compounds.

NO_2 in the first and second stages of reaction. However isotope exchange reactions that also occur in the layer prevented an unambiguous conclusion regarding this mechanism. Interaction of the nitrito intermediate **1** with NO at low *T* resulted in formation of the nitrito−nitrosyl complex **3** that had been previously detected[21] by the differential FTIR spectra as the result of photolysis of low-*T* KBr pellets containing the nitro−nitrosyl complex **4**. Complex **3** isomerizes to the more stable nitro−nitrosyl form **4** upon warming. Both **3** and **4** are low-spin in contrast to the high- or intermediate-spin parent complex **1**. By using isotope labeled compounds, it was shown that the **3** to **4** isomerization proceeds predominantly via intramolecular "flipping" of the NO_2 ligand rather than by dissociation followed by reassociation with the formation of new Fe−N(NO_2) bond. Warming of **4** under conditions of continuous high-vacuum pumping results in formation of the low-spin nitrosyl complex Fe(Por)(NO) and high-spin **1**, demonstrating competitive dissociation of NO and NO_2 from the initial nitro−nitrosyl complex **4**. These and earlier results also provide an explanation why excess NO is needed to stabilize the nitro−nitrosyl complex **4**. The upshot of these studies is that systems illustrate the multiple interconversions of the various nitrogen oxide species mediated by the heme model compounds and presumably by heme proteins.

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Supporting Information Available: Complete citation of ref 14b, Figure S1, demonstrating FTIR spectra of FeTPP and FeTPP(ONO), Figure S2, showing FTIR spectral changes describing isotope exchange reaction Fe(TTP)(^{18}ON^{18}O) → Fe(TTP)(ONO), Figure S3, showing FTIR spectral changes in Fe(TTP)(ONO) sublimed layer in course of low-temperature interaction with NO, Figure S4, demonstrating FTIR spectra of Fe(TTP)(NO)(ONO) and Fe(TTP)(^{15}NO)(O^{15}NO), Figure S5, showing FTIR spectra of Fe(TTP)(NO_2)(NO) and Fe(TTP)($^{15}NO_2$)(^{15}NO) obtained by warming the corresponding nitrito−nitrosyl species, Figure S6a, showing FTIR spectral changes demonstrating formation of Fe(TTP)(ONO)(^{15}NO) upon low-temperature interaction of ^{15}NO gas with Fe(TTP)(ONO), Figure S6b, showing formation of Fe(TTP)(O^{15}NO)(NO) upon interaction of NO gas with Fe(TTP)(O^{15}NO), and Tables S1−4, providing additional information regarding DFT computational results. This material is available free of charge via the Internet at http://pubs.acs.org.

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