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Interaction of Nitrogen Bases with Iron–Porphyrin Nitrito Complexes Fe(Por)(ONO) in Sublimed Solids

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The reactions of the nitrogen Lewis bases (B) 1-methylimidazole (1-MeIm), pyridine (Py), and NH_3 as gases with sublimed layers containing the 5-coordinate nitrito iron(III)–porphyrinato complexes Fe(Por)(η^1-ONO) (**1**) are described (Por = *meso*-tetraphenyl-porphyrinato or *meso*-tetra-*p*-tolyl-porphyrinato dianions). In situ FTIR and optical spectra are used to characterize the formation of the 6-coordinate nitro complexes formed by the reaction of **1** with B = 1-MeIm, Py, or NH_3. These represent the first examples of 6-coordinate amino–nitro complexes with sterically unprotected iron–porphyrins. The interaction of ammonia with Fe(Por)(ONO) at 140 K initially led to the nitrito species Fe(Por)(NH_3)(η^1-ONO), and this species isomerized to the nitro complexes Fe(Por)(NH_3)(η^1-NO_2) upon warming to 180 K. When the latter were warmed to room temperature under intense pumping, the initial nitrito complexes Fe(Por)(η^1-ONO) were restored. Assignments of vibrational frequencies for the coordinated nitro group in 6-coordinate iron–porphyrin complexes are given and confirmed using ^{15}N-labeled nitrogen dioxide to identify characteristic infrared bands. For M(Por)(B)(NO_2) complexes (M = Fe or Co), an inverse correlation between the net charge transfer from the axial ligand B to the nitro group and the value of $\Delta\nu = \nu_a(NO_2) - \nu_s(NO_2)$ is proposed. These observations are discussed in the context of growing interest in potential physiological roles of nitrite ion reactions with ferro– and ferri–heme proteins.

Introduction

The long-standing interest in the reactions of the nitrite ion with heme protein models relevant to the action of assimilatory and dissimilatory nitrite reductase (NiR) enzymes[1] has been strengthened by the recognition that nitrite may play important roles in human physiology and therapeutics.[2] This in turn has attracted renewed experimental and theoretical attention to the interactions and reactions of nitrite with heme proteins[3] and with iron−porphyrin heme model systems.[4]

The ambidentate nitrite ion can coordinate to metals either at the oxygen to give nitrito complexes (M−ONO) or at the nitrogen to give nitro complexes (M−NO_2). Iron porphyrins are known to form 5- and 6-coordinate nitro complexes,[4] and recent studies show that the nitrito mode of coordination

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is obtained for 5-coordinate species formed by the interaction of small NO_2 increments with thin layers of iron(II)−porphyrinato complexes Fe(Por).[5] The crystal structures for NO_2^- complexes of several ferri−heme NiR proteins demonstrate nitro coordination.[1a,b,f] However, the recently reported structure of the 6-coordinate complex prepared by soaking preformed horse heart metmyoglobin crystals in aqueous $NaNO_2$ is the oxygen-bound nitrito isomer, perhaps stabilized by hydrogen bonding between a nitrito oxygen and the distal His64 residue.[6]

Nitrite complexes of iron(III)−porphyrins are difficult to obtain because of the reactive nature of coordinated nitrite and reactions between coordinated and free nitrite, leading, inter alia, to the formation of nitrosyl complexes.[7] This instability has been addressed by using picket fence porphyrinato (TpivPP) complexes, in which the coordinated nitrite would be located in the pocket formed by four pivalamido residues.[4b] Such a complex with a protected ligand binding site is the bis(nitrite) species [K(18-C-6)-(H_2O)][Fe(TpivPP)(NO_2)$_2$], which was synthesized and structurally characterized by Scheidt and co-workers.[8] This is a precursor for the synthesis of mixed-ligand nitrite ion complexes with N− and S− donor ligands[9,10] by displacing the nitrite group disposed on the open side of porphyrin and leaving an N-coordinated nitro ligand in the protected site. Structural[11] and computational[3d] analyses of the 6-coordinate pyridine−nitro complex Fe(TPiv)(py)(NO_2) suggest weak hydrogen bonding between oxygen atoms of the nitro group and the picket fence NH groups.

As it was mentioned above, the interaction of incremental NO_2 gas with iron(II)−porphyrins in sublimed solids leads to the formation of 5-coordinate iron(III)−nitrito complexes Fe(Por)(η^1-ONO) (**1**).[5] Can these species serve as a synthetic entry for obtaining 6-coordinate mixed-ligand complexes with trans nitrogen donors, and, if so, what type of coordination (nitro or nitrito) will be realized? This study has been undertaken to address these questions.

Experimental Section

Low-temperature sublimates of the ferrous porphyrinates Fe-(Por)[12] were prepared as described previously[5] by heating the hexacoordinate Fe(Por)(B)$_2$ complexes (B is pyridine (Py) or piperidine)[13] in a Knudsen cell at ∼470 K under a high vacuum ($P = 3 \times 10^{-5}$ Torr) to eliminate the axial ligands. The Knudsen cell was then heated to 520 K, whereupon Fe(Por) sublimed onto the 77 K surface of the KBr or CaF_2 substrate (cooled by liquid nitrogen, LN_2) to give sponge-like metallo-arylporphyrinato layers with high microporosity.[14]

Once Fe(Por) layers of thickness sufficient for UV−vis and IR spectral studies were formed (0.3−2.0 h), they were heated to room temperature under a dynamic vacuum. Small increments of NO_2 ($^{15}NO_2$) gas were then introduced for ∼ 30 s, after which the apparatus was evacuated. During this procedure, the red Fe(Por) film turns brown, indicating the formation of Fe(Por)(ONO), and this was confirmed by FTIR measurements.[5] Measured quantities of the nitrogen bases were then introduced into cryostat, and FTIR or optical spectra of the layers were measured over the course of time. Alternatively, the layered film of Fe(Por)(ONO) was cooled by LN_2, and small portions of pyridine, 1-Me-imidazole, or ammonia were introduced into the cryostat. The film was slowly warmed, and IR or UV−vis spectra (using CaF_2 windows) were measured at different substrate temperatures determined by a thermocouple.

The NO_2 ($^{15}NO_2$) was obtained by oxidizing pure NO (^{15}NO)[15] with excess pure dioxygen, and this was further purified by fractional distillation until a pure white solid was obtained. ^{15}NO with 98.5% enrichment was purchased from the Institute of Isotopes, Republic of Georgia.

The FTIR and UV−vis spectra were respectively recorded using Nexus and Helios γ spectrophotometers of the Thermo Nicolet Corporation.

Results and Discussion

The iron(III)−nitrito complexes Fe(Por)(ONO) were obtained by the interaction of NO_2 gas with sublimed layers of Fe^{II}(Por) (Por = *meso*-tetraphenylporphyrinato dianion, TPP, or *meso*-tetra-*p*-tolylporphyrinato dianion, TTP) as described elsewhere.[5a] Reactants easily diffuse across these layers, and this procedure allows spectroscopic studies of the adducts without solvent interference. Exposure of the Fe-(Por)(ONO) to low pressures (∼0.1 Torr) of Py or 1-MeIm (1-methylimidazole) at room temperature leads to the quick changes in the FTIR spectra that indicate reaction with these nitrogen bases B. For B = NH_3, much higher pressures (20 Torr) and the presence of ammonia in the gas phase were needed to prepare the 6-coordinate complexes. The FTIR spectra showed that the bands at 1527, 903, and 750 cm^{-1} characteristic of Fe(TTP)(ONO) diminished in intensity upon the addition of B, whereas the new bands grew in the vicinity of 1400, 1300, and 800 cm^{-1}. This is illustrated in Figure 1 for the reaction of Fe(TTP)(ONO) with 1-MeIm.

These bands lie in the spectral ranges where the $\nu_a(NO_2)$, $\nu_s(NO_2)$, and $\delta(NO_2)$ frequencies of coordinated nitro groups

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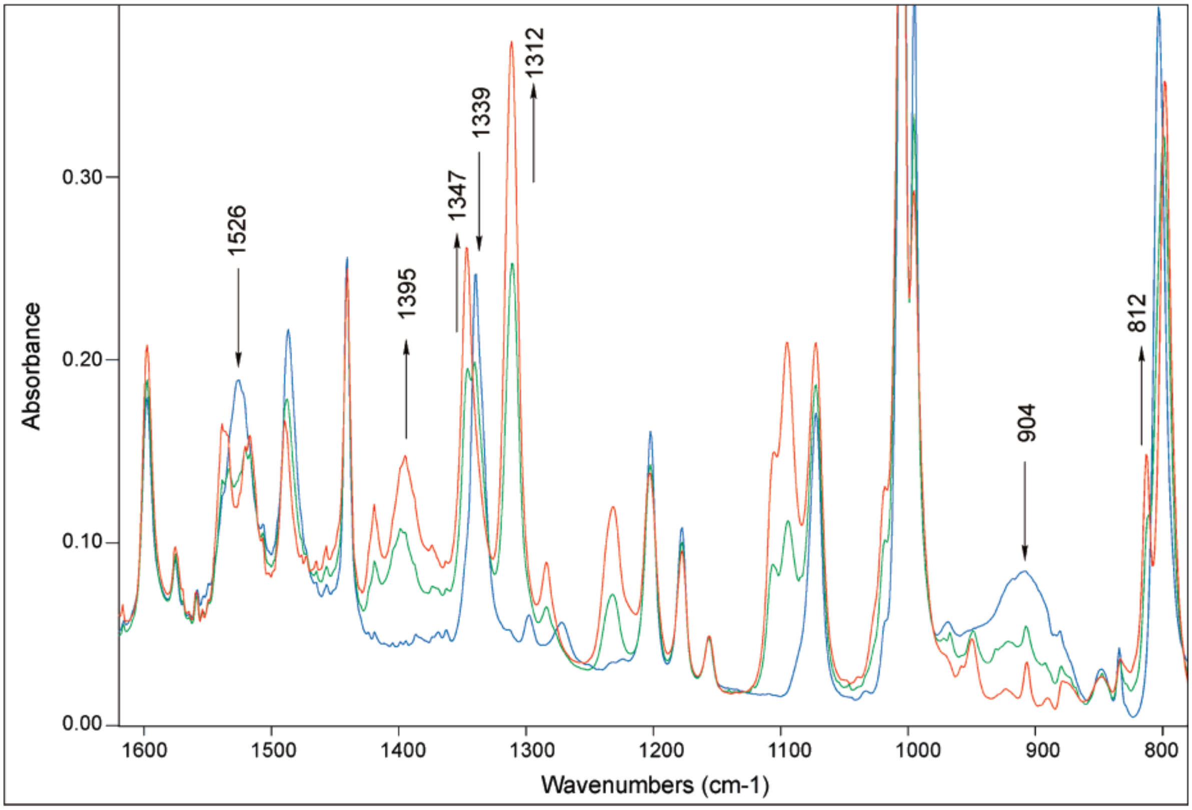

Figure 1. FTIR spectral changes observed in sublimed layers of Fe(TPP)(ONO) (blue) after supplying into cryostat ∼0,1 Torr 1-MeIm and subsequent measurements after 2 (green) and 5 (red) min.

are usually disposed.[16] In support of that conclusion, the relevant bands displayed the expected isotopic shifts when $^{15}NO_2$ gas was used to prepare the Fe(Por)(O^{15}NO) precursor, and this was reacted with the nitrogen bases to prepare the products (Figure 2 and Table 1). The band positions, relative intensities, and isotopic shifts are analogous to those observed for amino−nitro complexes of Co(TPP)[17] (Table 1). From these data, it can be concluded that interaction of nitrogen bases with Fe(Por)(ONO) leads to the formation of 6-coordinate amino−nitro complexes Fe(Por)(B)(NO_2); that is, the addition of the trans ligand B also leads to isomerization of the oxygen-coordinated nitrito ligand to the nitrogen-bound nitro form.

In an earlier study, it was shown that NO reacts with Fe(Por)(ONO) at very low temperatures to form, first, the nitrosyl−nitrito complex Fe(Por)(NO)(ONO), which isomerizes to the nitrosyl nitro form Fe(Por)(NO)(NO_2) upon mild warming.[5] Thus, it was of interest to evaluate whether such 6-coordinate nitrito species might be also obtained for nitrogen Lewis bases such as ammonia. With this in mind, the ligands B were introduced to the cryostat containing the nitrito complexes Fe(Por)(ONO) in porous layers at LN_2 temperature. FTIR spectra were recorded to characterize the species first formed and then repeatedly recorded during the slow-warming process.

Figure 3 illustrates this experiment for B = NH_3. The disappearance of IR bands characteristic of Fe(Por)(ONO) began at ∼130 K and was almost completely finished at 150 K. New bands grew in at ∼1470 (1435), 976 (954), and 827 (822) cm^{-1} at the expense of those at 1527 (1495), 903 (880), and 751 (747) cm^{-1} of Fe(TTP)(ONO) (the data in parentheses are those for the Fe(TTP)(O^{15}NO)). At these temperatures, it is noteworthy that there is no spectral indication for the formation of the 6-coordinate nitro complexes, Fe(Por)(NH_3)(NO_2). While it is possible that IR spectral changes would be due to the specific interaction of Fe(Por)(ONO) with the excess NH_3 in the sublimed layers, this would not explain the significant differences observed in the electronic spectra (Figure 4) or the changes in the spin state of the iron (below). Instead, the IR and electronic spectral changes are consistent with the formation of the 6-coordinate nitrito complexes, Fe(Por)(NH_3)(ONO).

The analogous 6-coordinate nitrito complexes Fe(Por)(NO)(ONO) with a trans NO ligand have been prepared by the reaction of NO with Fe(Por)(ONO) layers at low temperature[5] and by irradiation of the nitrosyl−nitro complex Fe(Por)(NO)(NO_2),[3a,b] in a low-temperature KBr pellet. FTIR spectral characteristics for several such complexes and for other 6-coordinate metalloporphyrin complexes of the nitrito ligand are given in Table 1. It is seen from these examples that, upon the addition of the sixth ligand, the frequency difference between the NO stretching bands of the nitrito

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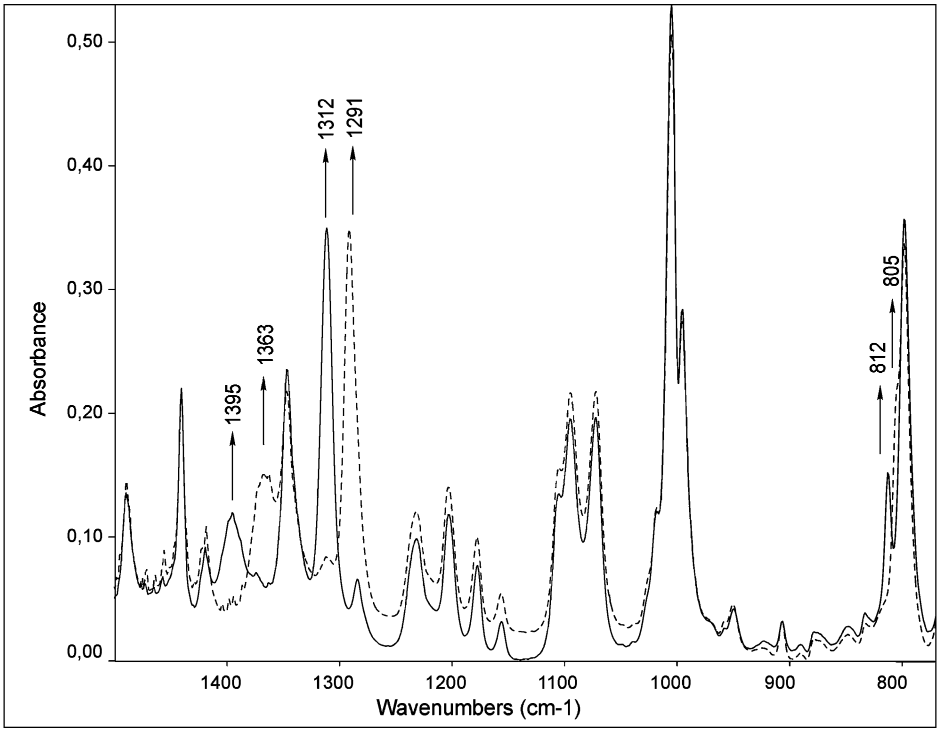

Figure 2. FTIR spectra of Fe(TPP)(NO$_2$)(1Me-Im) (solid line) and Fe(TPP)(^{15}NO$_2$)(1-MeIm) (dashed line) obtained by the interaction of 1-MeIm vapors (∼0,1 Torr) with thin layers containing Fe(TPP)(ONO) and Fe(TPP)(O^{15}NO).

Table 1. IR Frequencies of Coordinated Nitro or Nitrito Groups in 6-coordinate Complexes of Some Metalloporphyrins^{a,b}

compounds*	ν_a(NO$_2$), ν(N═O) (cm^{-1})	ν_s(NO$_2$), ν(N−O) (cm^{-1})	δ(ONO), δ(NO$_2$) (cm^{-1})	$\Delta\nu^c$	ref
Fe(TTP)(NH$_3$)(ONO)	1470 (1438)	969 (952)	∼827 (822)		this work
Fe(TPP)(NH$_3$)(ONO)	1475 (1445)	971 (952)	∼828 (821)		this work
Fe(TTP)(NO)(ONO)	1497 (1464)	935 (917)			5b
Fe(TPP)(NO)(ONO)	1496(1471)m	938 (920)m			5b
Mn(TTP)(NO)(ONO)	1480 (1455)	971 (950)	822 (818)		17d
Mn(TPP)(NO)(NO$_2$)	1421 (1392)	1304 (1286)		117(106)	17e
Fe(TTP)(NH$_3$)(NO$_2$)	1401(1367)	1312(1291)	810(∼804)	89 (76)	this work
Fe(TPP)(NH$_3$)(NO$_2$)	1399 (1373)	1312 (1291)	812 (∼805)	87 (82)	this work
Fe(TTP)(Py)(NO$_2$)	1405 (1373)	1306 (1287)	810 (∼804)	99 (86)	this work
Fe(TPP)(Py)(NO$_2$)	1406 (1379)	1307 (1287)	810 (∼804)	99 (92)	this work
Fe(TTP)(1-MeIm)(NO$_2$)	1396 (1363)	1312 (1291)	813 (∼805)	84 (72)	this work
Fe(TPP)(1-MeIm)(NO$_2$)	1395 (1371)	1312 (1290)	812 (∼805)	83 (81)	this work
Fe(TTP)(NO)(NO$_2$)	1455 (1423)	1295 (1275)	∼805 (800)	160 (148)	5b
Co(TPP)(NH$_3$)(NO$_2$)	1431 (1400)	1309 (1289)	814 (805)	122 (111)	17a
Co(TPP)(Py)(NO$_2$)	∼1439 (1404)	1310 (1288)	816 (806)	129 (116)	17a
Co(TPP)(1-MeIm)(NO$_2$)	1420 (1394)	1313 (1292)	816 (809)	107 (102)	this work
Co(TPP)(NO$_2$)	1468 (∼1440)	1282 (1264)	∼805 (796)	186 (176)	17b

[a] Frequencies in parentheses are the values recorded for the ^{15}N nitro and nitrito complexes. [b] Six-coordinate complexes having the nitrito ligand and (NO)Mn(NO$_2$) are stable only at low temperatures. [c] $\Delta\nu = \nu_a(NO_2) - \nu_s(NO_2)$.

ligand becomes smaller with a lower ν(N═O) and a higher ν(N−O). The same pattern was observed upon the reaction of NH$_3$ with Fe(Por)(ONO) in the temperature interval 130−140 K. We conclude, therefore, that the spectral changes observed in Figure 3 are further evidence for the formation of the ammonia−nitrito complex Fe(Por)(NH$_3$)(ONO). However, at these low temperatures it was not possible to eliminate all of the free NH$_3$, and the excess ammonia is present in the porous layers.[18] It is possible that this provides extra stabilization of the nitrito isomer via hydrogen bonding similar to the interaction reported for the crystal structure of the nitrito complex of horse heart myoglobin.[6]

Further warming of the Fe(Por)(NH$_3$)(ONO) adduct led to the FTIR spectral changes demonstrated in the Figure 5 for the Fe(TTP) derivative. The ν(N═O) and ν(N−O) bands of Fe(TTP)(NH$_3$)(ONO) decreased while bands at 1395, 1312 and 812 cm^{-1} grew in intensity consistent with isomerization to the ammine−nitro complex Fe(TTP)(NH$_3$)(NO$_2$). At room temperature, the latter is stable only in the presence of excess NH$_3$ (>20 Torr). When instead this system was warmed to room temperature under an intense high vacuum pumping, the Fe(TTP)(NH$_3$)(NO$_2$) underwent complete transformation

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(18) The broad band in the vicinity of 1060 cm^{-1} overlapped with porphyrin bands (Figure 3) belongs to the intense ν_2(A$_1$) vibration of solid NH$_3$.[16] This band together with other ammonia bands at 3200−3300 and 1630 cm^{-1}(not shown) disappear after NH$_3$ evaporation upon layer warming (Figure 5).

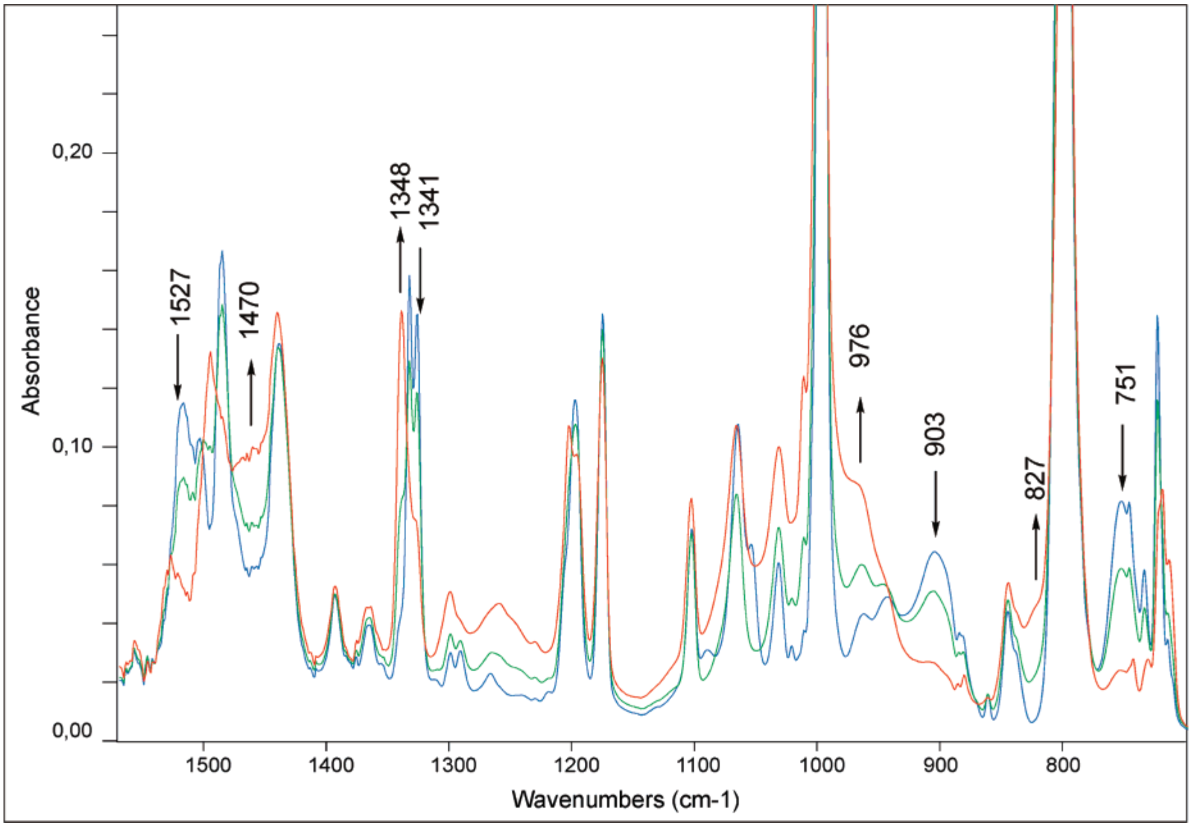

Figure 3. FTIR spectral changes observed for a sublimed layer of Fe(TTP)(ONO) (blue) after introducing 1 Torr equivalent of NH_3 into the cryostat at 77 K and while warming from 130 (green) to 150 K (red).

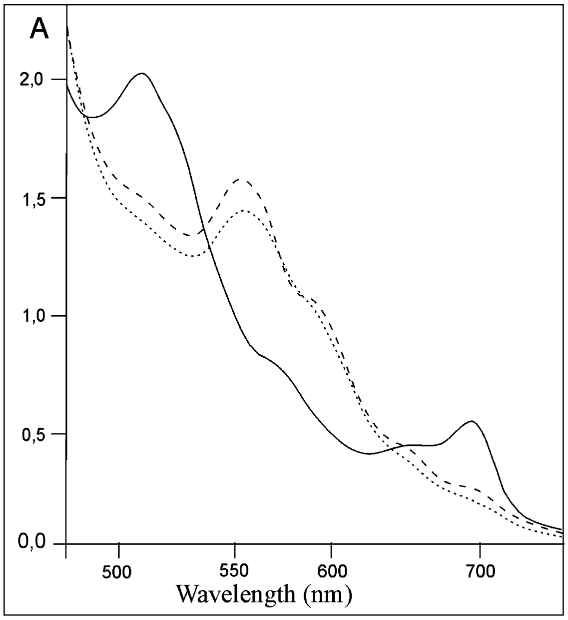

Figure 4. Optical spectra of Fe(TTP)(ONO) (solid line), Fe(TTP)(NH_3)(ONO) (dashed line), and Fe(TTP)(NH_3)(NO_2) (dotted line).

to the initial nitrito complex Fe(TTP)(ONO) (Figure 6). Hence, loss of the trans ammine results in reverse linkage isomerization (Scheme 1).

An analogous pattern was previously observed for the nitrosyl−nitro complex Fe(Por)(NO)(NO_2); intense pumping at room-temperature gave the pentacoordinate nitrito isomer, Fe(Por)(ONO).[5] However, in that case some nitrosyl complex Fe(Por)(NO) was also formed, thus there was competitive dissociation of NO and NO_2. These observations clearly demonstrate that under analogous experimental conditions the nitrito coordination mode is preferred for the 5-coordinate complexes while the nitro isomer is realized for the 6-coordinate species in the absence of specific interactions such as the hydrogen bonding noted in the structure of met-Mb(ONO).[6] This phenomenon may be significant with regard to the action of nitrite reductase enzymes.

Similar attempts to obtain amino−nitrito iron−porphyrin complexes with B = Py or MeIm were unsuccessful; only the analogous nitro complexes were spectrally detected. This may be due to the much slower diffusion of these bulkier (and higher melting point) ligands into the porous layers of Fe(Por)(ONO) at the low temperatures where the metastable ammine−nitrito complexes were observable. Higher temperatures (~170 K for B = Py; ~200 K for B = 1-MeIm) were required to form complexes of these ligands, and in both cases the reaction led to the formation of the amino−nitro complexes. It is in this temperature range that the ammonia−nitrito complexes, observed at lower temperature, undergo linkage isomerization to the nitro analogs. An alternative explanation for the observation of the ammine−nitrito isomer would be that this species receives additional stabilization at lower temperature through interaction with the excess NH_3 in the sublimed layer, as speculated above.

Additional information about the electronic structure of the amino−nitro complexes Fe(Por)(B)(NO_2) can be drawn from Figures 1 and 3. Certain porphyrin vibrational modes of Fe(TPP) complexes, for example bands at ~1350 cm^{-1}

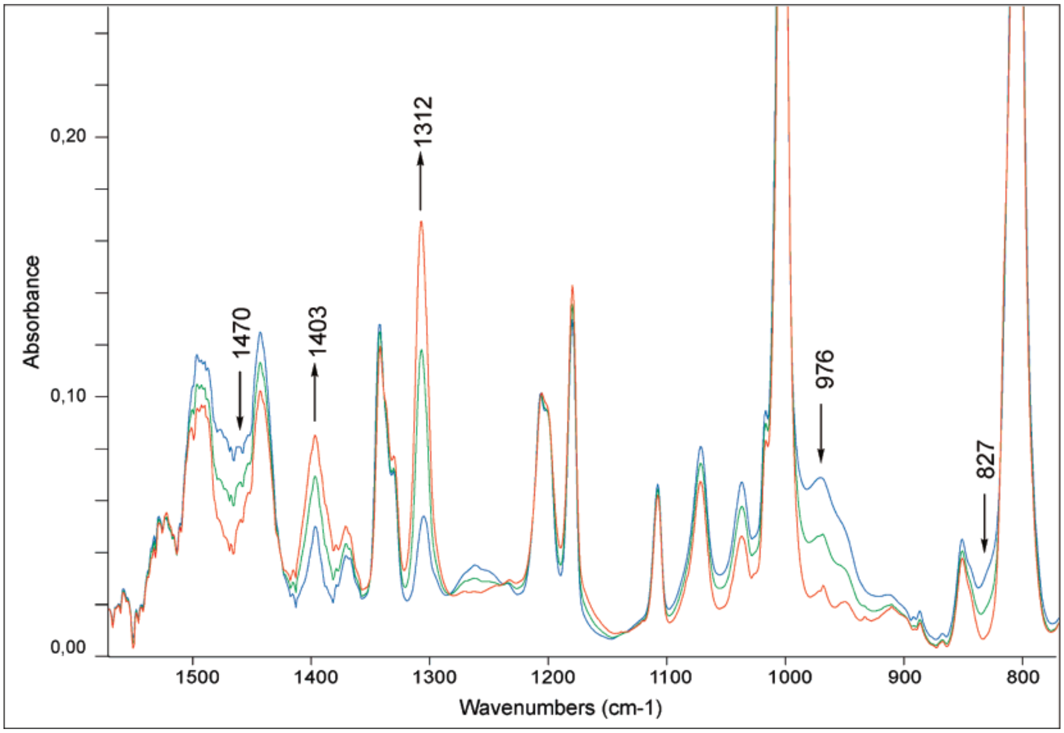

Figure 5. FTIR spectral changes observed in a sublimed layer of Fe(TTP)(ONO) in the presence of 1 Torr equivalent of NH_3 upon warming from 150 (blue) to 170 (green) and 200 K (red) and removal of excess NH_3.

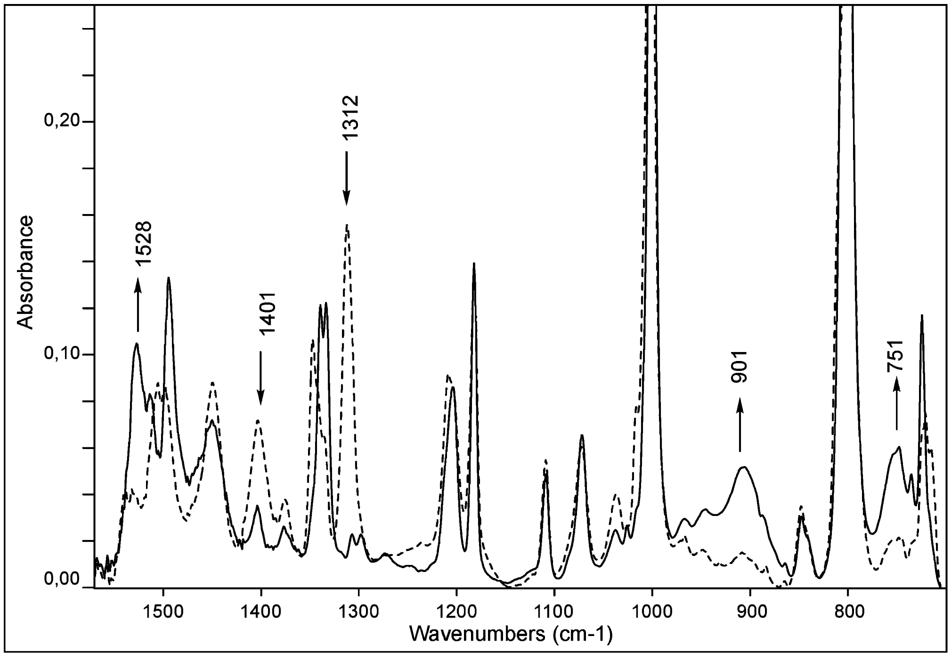

Figure 6. FTIR spectra of the ammine−nitro complex $Fe(TTP)(NH_3)(NO_2)$ (dashed line) after warming from 240 to 293 K upon intense pumping.

($\nu(C_a-C_m)$ mixed with $\nu(C_m-\text{phenyl})$) and at ~450 cm^{-1} (δ(Pyr. rotation))[19] have been demonstrated to be sensitive to the spin and oxidation state of the metal center.[20] For the intermediate-spin state Fe(TPP),[21] 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 Fe(TTP), the analogous bands appear initially at 1346 and 455 cm^{-1} and correspondingly shift upon nitrito complex formation to 1340 and 428 cm^{-1}. In this case, there is an additional spin-sensitive band disposed at 1505 cm^{-1}. Upon the formation of the amino−nitro complexes, the spin-sensitive bands shift to higher frequency, consistent with a change to the low-spin electronic configurations.[20] It is noteworthy that for the ammine−nitrito intermediate Fe(Por)-(NH_3)(ONO) observed only at very low temperatures, the

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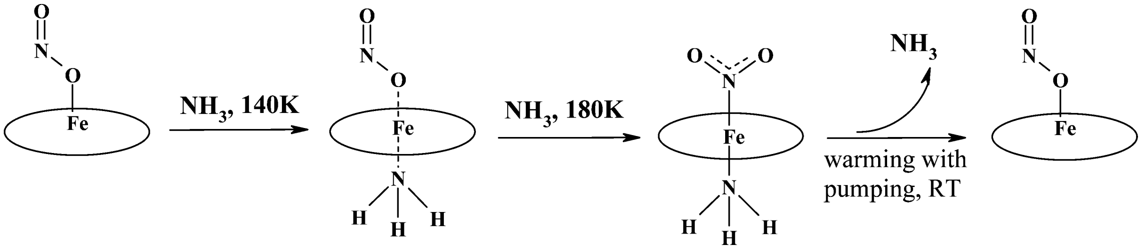
Scheme 1. The Reaction of Fe(Por)(ONO) with NH_3



spin-sensitive bands also indicate a low-spin state for the iron center (Figure 3).

The various $Fe(Por)(B)(NO_2)$ complexes reveal different thermal stabilities depending on the nature of the nitrogen base ligand. For B = ammonia, these complexes were stable in the porous layers at room temperature but only when excess NH_3 was present. In contrast, the pyridine complex decomposed slowly within a few days if left under a vacuum at room temperature, whereas the 1-MeIm complex was fairly stable in a vacuum and under an ambient atmosphere. Furthermore, $Fe(Por)(1\text{-MeIm})(NO_2)$ is relatively stable even in dry solutions (toluene, chloroform, and dichloromethane were tested), where it survived several hours before decomposing.

The present results give evidence that nitrogen-bound nitro complexes, rather than the oxygen-bound nitrito analogs, are the more stable 6-coordinate ferri−heme models when trans N donor bases are coordinated. Nitro complexes have also been reported for the sterically protected picket fence derivatives[9] and for three other structurally characterized heme proteins.[1a,b,e] In contrast, the nitrite ion complex of horse heart metmyoglobin demonstrates an oxygen-coordinated nitrito ligand, although in this case, there is also evidence of hydrogen bonding between the distal His64 residue and a nitrito oxygen. These differences indicate that subtle changes in the ligand binding pocket of heme proteins can determine the mode of NO_2^- coordination to iron(III). In this context, a density functional computational study (at the UBP86/DN** level) of the nitro and nitrito complexes of Fe(P′)(imidazole) (P′ = a truncated heme d_1) concluded that although nitrogen coordination (nitro) is energetically favored over oxygen coordination (nitrito) by 4.5 kcal/mol in the ferric form, a strong hydrogen bond would provide the stabilization required to put the two isomers on equivalent terms.

The FTIR data summarized in Table 1 for the amino−nitro complexes of iron(III) (this work) and for the cobalt(III) analogs[17a,22] provide the basis for assigning vibrational frequencies for the coordinated nitro group, and these assignments are sustained by data for $^{15}NO_2$-labeled isotopomers. Table 1 also suggests an interesting correlation between the nature of the ligand trans to the nitro group and the difference between the frequencies of symmetric and asymmetric stretches, $\Delta\nu = \nu_a(NO_2) - \nu_s(NO_2)$. Within each series $Fe(Por)(B)(NO_2)$ (Por = TTP or TPP), $\Delta\nu$ follows the order for the respective trans ligand: 1-MeIm < NH_3 < Py ≪ NO, whereas the cobalt(III) series $Co(Por)(B)(NO_2)$ follows an analogous order: 1-MeIm < NH_3 < Py ≪ empty coordination site (no ligand). Electronic communication between the axial ligands B and NO_2 occurs largely through the metal d_{z^2} and the d_{xz} and d_{yz} orbitals. In this context, we propose that $\Delta\nu$ is reflective of the net charge transfer to or from the nitro group with the smaller $\Delta\nu$ representing more charge transfer.[23] In all three series, the order 1-MeIm < NH_3 < Py holds true for $\Delta\nu$. This does not correlate with the Brønsted base strengths of these ligands, where 1-MeIm is intermediate between Py and NH_3;[24] however, the observed order may be rationalized by taking into account the modest π-donor character of 1-MeIm, whereas NH_3 is a σ donor only and Py is a π acceptor.[25] In the cobalt(III) series, the empty coordination site clearly leads to a much larger value of $\Delta\nu$ as would be expected from the premise that this reflects the relative electron-donor strength (in this case, none) of the trans ligand. If so, however, the position of NO in the iron(III) series (largest $\Delta\nu$) is especially interesting, because it suggests that there is very little net electron transfer from NO to the nitro ligand in the complex $Fe(Por)(NO)(NO_2)$. Such a conclusion draws some confirmation in DFT calculations (both B3LYP/3-21 g and B3LYP/6-31 g) for $Fe(P)(NO)(NO_2)$ (P = porphinato dianion) that found the coordinated NO to have a slightly negative charge, hence having a net electron withdrawing effect.[26]

A higher value of $\Delta\nu$ corresponds to a larger ONO angle.[22,23b] The $\Delta\nu$ values are systematically higher for the cobalt(III) complexes $Co(TPP)(B)(NO_2)$ than for the iron(III) analogs, suggesting less charge transfer in the former case. This is also consistent with the ONO angles, which are in the 120−124° range[22] for the cobalt(III) complexes, compared to the more acute angles (116−120°) seen for similar nitrito complexes of iron(III)−porphyrins.[9]

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(23) (a) In the nitrite anion NO_2^- that represents the limiting case with complete electron transfer, the $\nu_a(NO_2)$ and $\nu_s(NO_2)$ are close to each other,[16] with $\nu_a(NO_2)$ even lower than $\nu_s(NO_2)$. (b) In the NO_2 molecule, the ONO angle is equal to 134°, whereas in the nitrite anion it is 115°, and intermediate values were obtained for the structurally characterized nitro complexes of the cobalt− and iron−porphyrins. The calculated value of the ONO angle for the $Co(TPP)(NO_2)$ complex is 124.4°.[22]

(24) (a) The pK_a's of the conjugate acids for Py, 1-MeIm, and NH_3 are equal to 5.25, 6.95, and 9.25, respectively.[24b] (b) *Handbook of Chemistry and Physics*, 77th ed.; Lide, D. A., Ed.; CRC Press: Boca Raton, FL, 1996, pp. 45−55.

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Summary

The present studies show that the 5-coordinate iron(III)−nitrito intermediates Fe(Por)(ONO) can serve as an entry for preparing mixed-ligand complexes with trans nitrogen base ligands in sublimed solids. The stable conformation of the nitrite ion ligand in these 6-coordinate species is the nitrogen-bound nitro isomer Fe(Por)(B)(NO_2) rather than the oxygen-coordinated nitrito coordination realized in the 5-coordinate species. The metastable ammine−nitrito complex Fe(Por)(NH_3)(ONO) could be prepared and characterized at low temperatures, although it is not clear whether hydrogen bonding of coordinated nitrito ligand with the excess ammonia present under these experimental conditions might provide extra stabilization. However, upon warming, this oxygen-bound nitrito complex isomerizes to the nitrogen-bound nitro form. The use of $^{15}NO_2$ isotopomers has provided the opportunity for the unequivocal assignment of vibrational modes for the coordinated nitro group in these 6-coordinate species. Furthermore, there appears to be an inverse correlation between values of $\Delta\nu = \nu_a(NO_2) - \nu_s(NO_2)$ and the net charge transfer from the sixth ligand B to the nitro group via the d_σ and d_π orbitals of the metal center.

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