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Six-Coordinate Nitro Complexes of Iron(III) Porphyrins with *trans* S-Donor Ligands. Oxo-Transfer Reactivity in the Solid State

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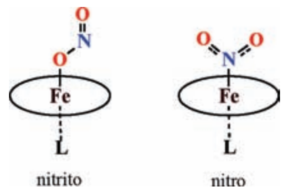
Spectroscopic studies demonstrate that the 5-coordinate O-nitrito complexes Fe(Por)(η^1-ONO) (Por - *meso*-tetraphenyl- or *meso*-tetra-p-tolyl-porphyrinato dianions) react with the thioethers (R_2S) dimethylsulfide and tetrahydrothiophene to give the 6-coordinate N-nitrito complexes Fe(Por)(R_2S)(NO_2). These reactions were conducted in low-temperature porous layered solids formed in a cryostat; however, with excess R_2S in the atmosphere, the same species are moderately stable at room temperature. Six-coordinate O-nitrito isomers were not observed with the R_2S proximal ligands, even though DFT calculations for the Fe(P)(DMS)(η^1-ONO) and Fe(P)(DMS)(NO_2) models (P=porphinato dianion, DMS=dimethyl sulfide) show the latter to be only modestly lower energy (~8 kJ/mol) than the former. Leaving this system at room temperature in the presence of excess R_2S leads eventually to the appearance in the FTIR spectra of the ν(NO) band characteristic of the ferrous nitrosyl Fe(Por)(NO). Concomitantly, the mass spectrum of the gas phase demonstrated the molecular peaks of the sulfoxides R_2SO, indicating oxygen atom transfer reactivity for the ferric porphryinato complexes of nitrite.

Introduction

The nitrite ion NO_2^- is present throughout the mammalian organism[1] and has been reported to help regulate vasodilation during hypoxic events and modulate ischemia-reperfusion tissue injury.[2] Much of the growing interest in the physiological chemistry of nitrite has focused on its interactions and reactions with ferro- and ferri-heme proteins.[3] Nitrite is ambidentate and can bind to the metal through an oxygen as a "nitrito" ligand or through the nitrogen as a "nitro" ligand, and both forms have been observed not only for iron-porphyrin models[4] but also for heme proteins.[5] Furthermore, the difference in binding energy for nitrito- and nitro-isomers may be sufficiently small that hydrogen-bonding interactions may change the mode of coordination.[6] In this context, fundamental questions remain regarding how systemic parameters, such as the nature of the proximal ligand L, influence the coordination of the nitrite as well as its reactivity.



In this context, we have investigated the coordination of nitrite (and other NO_x species) with the iron centers of heme model compounds by preparing microporous layers of Fe(Por) (Por = *meso*-tetraphenyl- or *meso*-tetra-p-tolyl-porphyrinato dianions) on solid substrates in a cryostat.[7] Volatile reactants are added in specific sequences, and the reaction chemistry of these systems is probed spectroscopically at tunable and carefully controlled temperatures in a solvent-free environment. These studies have shown that nitrite linkage isomerism is very sensitive to the nature of L.

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(1) Feelisch, M.; Rassaf, T.; Mnaimneh, S.; Singh, N.; Bryan, N. S.; Jourd'Heuil, D.; Kelm, M. *FASEB J.* **2002**, *16*, 1775–85.

(2) (a) Lundberg, J. O.; Weitzberg, E.; Gladwin, M. T. *Nat. Rev. Drug Discov.* **2008**, *7*, 156. (b) Feelisch, M.; Fernandez, B. O.; Bryan, N. S.; Garcia-Saura, M. F.; Bauer, S.; Whitlock, D. R.; Ford, P. C.; Janero, D. R.; Rodriguez, J.; Ashrafian, H. *J. Biol. Chem.* **2008**, *283*, 33927–33934.

(3) (a) Gladwin, M. T.; Grubina, R.; Doyle, M. P. *Acc. Chem. Res.* **2009**, *42*, 157–167. (b) Heinecke, J.; Ford, P. C. *Coord. Chem. Rev.* in press.

(4) (a) Willie, G. R. A.; Scheidt, W. R. *Chem. Rev.* **2002**, *102*, 1067–1089. (b) Nasri, H.; Ellison, M. K.; Krebs, C.; Huynh, B. H.; Scheidt, W. R. *J. Am. Chem. Soc.* **2000**, *122*, 10795. (c) Nasri, H.; Haller, K. J.; Wang, Y.; Huynh, B. H.; Scheidt, W. R. *Inorg. Chem.* **1992**, *31*, 4459–4467.

(5) Copeland, D. M.; Soares, A. S.; West, A. H.; Richter-Addo, G. B. *J. Inorg. Biochem.* **2006**, *100*, 1413–1425.

(6) Silaghi-Dumitrescu, R. *Inorg. Chem.* **2004**, *43*, 3715–3718.

The reaction of NO_2 with Fe(Por) gives the 5-coordinate nitrito complexes Fe(Por)(η^1-ONO) (**1**),[7a] which react further with volatile Lewis bases to form the 6-coordinate species for which the N-bound nitro form Fe(Por)(L)(η^1-NO_2) is generally favored.[7b] However, when the reaction of **1** with L was carried out at very low temperatures (<140 K), it was possible to spectrally characterize the metastable nitrito isomers Fe(Por)(L)(η^1-ONO) where L = NO,[7a,c] NH_3,[7b] or tetrahydrofuran.[7d] With the first two, warming led to the nitrito → nitro isomerization, whereas with THF, both isomers were present over a narrow low temperature interval, but THF dissociated upon further warming to restore the nitrito complex **1**.[7d]

Numerous heme proteins have proximal S-donor ligands, either a cysteine thiolate or a methionine residue.[8] In the present study, the effect of the proximal thioethers dimethylsulfide (DMS) and tetrahydrothiophene (THT) on heme nitrite coordination and reactivity is addressed. In the course of these studies, we also observed apparent oxygen atom transfer (OAT) at ambient temperature from the nitrite complexes of the ferric porphyrins to the R_2S to give the corresponding sulfoxides R_2SO.

Heme nitrite complexes with proximal S-donor ligands have been characterized only for sterically protected porphyrins.[4] An example is the ferrous "picket fence" porphyrinato complex $[Fe^{II}(TpivPP)(PMS)(NO_2)]^-$ (TpivPP = *meso*-tetrakis(*o*-pivalamido-phenyl)porphyrinato dianion, PMS is the thioether pentamethylene sulphide.[4a] In this case, the NO_2^- is in the pocket formed by the four pivalamide groups and is N-coordinated (nitro). Notably, the O-atoms of the nitrite ion ligand are positioned at distances from NH-groups of the pivalamide chains appropriate for H-bonding interactions that might stabilize one isomer or another. In this context, it was of interest to evaluate what structures would be realized without such a stabilizing factor.

Experimental Section

Low temperature sublimates of the ferrous porphyrinates Fe(Por) were prepared as described previously[7a] by heating the hexacoordinate $Fe(Por)(B)_2$ complexes (B is pyridine (Py) or piperidine) in a Knudsen cell at ~470 K under high vacuum ($P = 3 \times 10^{-5}$ Torr) to eliminate the labile 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 to give sponge-like metallo-arylporphyrinato layers with high microporosity.[7e]

Once Fe(Por) layers of thickness sufficient for UV−visible and IR spectral studies were formed (0.3−2.0 h), they were heated to room temperature under 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 turned brown indicating the formation of Fe(Por)(ONO) and this was confirmed by FTIR measurements.[7a] The layered film of Fe(Por)(ONO) was cooled by liquid nitrogen and small portions of DMS or THT were introduced into the cryostat. The film was slowly warmed and IR or UV−visible spectra (using CaF_2 windows) were measured at different substrate temperatures determined by a thermocouple. After the reaction was completed the cryostat was shortly pumped out to remove the excess of supplied ligands for obtaining FTIR spectra relatively free from the bands of adsorbed S-donors.

In the experiments pursuing the study of oxo-transfer reactivity of **I** measured quantities of the sulfur bases were introduced into cryostat at room temperature and FTIR spectra of the layers were measured over the course of time. The layer was maintained under S-donors vapors overnight after which the gaseous content of the cryostat was analyzed by FTIR spectroscopy and mass spectrometry. For the first purpose the gaseous content of the cryostat was deposited through the injector to the cold (77 K) KBr substrate of another cryostat. The deposited layer thus formed was heated in course of pumping until the temperatures at which the excess R_2S was completely eliminated from the deposit. The FTIR spectra of remaining products were then measured. The mass spectrometric measurements were performed using a residual gas analyzer. At this point also the main part of the excess R_2S was pumped out from the cryostat at lowered temperatures then the remaining mixture was introduced into the chamber of the gas analyzer through the variable leak valve.

The NO_2 ($^{15}NO_2$) was obtained by oxidizing with excess dioxygen NO (^{15}NO) that was purified according to procedure described elsewhere.[7g] This was then 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. DMS (Aldrich, 99%) and THT (99+%) were stored overnight over sodium in a gastight flask to remove trace quantities of thiols and water and were vacuum distilled before using.

The FTIR spectra and UV−visible spectra were respectively recorded using "Nexus" and "Helios γ" spectrophotometers of the Thermo Nicolet Corporation and mass spectra were recorded by residual gas analyzer "RGA-200" of Stanford Research Systems. The spectral slit width during FTIR measurements was 2 cm^{-1}.

Unrestricted density functional theory (DFT) optimization calculations were performed with the Spartan'04 (Wave function, Inc.) or Jaguar 6.0 (Schrodinger, Inc.) at the B3LYP level using the LACVP* basis set without symmetry constraints. The optimized structures represent the equilibrium geometries of the molecules in gas phase. The calculations were performed on a Dell Precision 490 dual core Xeon 3.0 GHz CPU workstation or a custom built core 2 duo 3.0 Ghz Pentium CPU workstation.

Results and Discussion

To study the reactions with the thioethers, the 5-coordinate nitrito complexes Fe(Por)(η^1-ONO) (**1**) were prepared on the KBr or CaF_2 substrates in the vacuum cryostat as described above and the temperature was lowered to < 140 K. Small amounts of a thioether, either dimethyl sulfide or tetrahydrothiophen, were then introduced into the cryostat as gas whereupon they condensed onto the substrate covered with the microporous layers of **1**. For temperatures < 140 K for DMS and < 160 K for THT there were no changes in the intensities of FTIR bands characteristic of the coordinated nitrito moiety of **1**, and the only new spectral features were those attributed to the S-donors adsorbed on the layers.

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(7) (a) Kurtikyan, T. S.; Ford, P. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 492–496. (b) Kurtikyan, T. S.; Hovhannisyan, A. A.; Gulyan, G. M.; Ford, P. C. *Inorg. Chem.* **2007**, *46*, 7024–7031. (c) Kurtikyan, T. S.; Hovhannisyan, A. A.; Hakobyan, M. E.; Patterson, J. C.; Iretskii, A.; Ford, P. C. *J. Am. Chem. Soc.* **2007**, *129*, 3576–3585. (d) Kurtikyan, T. S.; Hovhannisyan, A. A.; Iretskii, A. V.; Ford, P. C. *Aust. J. Chem.* **2009**, *62*, 1226–1230. (e) Kurtikyan, T. S.; Ford, P. C. *Coord. Chem. Rev.* **2008**, *252*, 1486–1496. (f) Kurtikyan, T. S.; Gasparyan, A. V.; Martirosyan, G. G.; Zhamkochyan, G. A. *J. Appl. Spectrosc.* **1995**, *65*, 62–66. (g) Martirosyan, G. G.; Azizyan, A. S.; Kurtikyan, T. S.; Ford, P. C. *Inorg. Chem.* **2006**, *45*, 4079–4087. (h) Kurtikyan, T. S.; Martirosyan, G. G.; Lorkovic', I. M.; Ford, P. C. *J. Am. Chem. Soc.* **2002**, *124*, 10124–10129.

(8) Turano, P.; Lu, Y. In *Handbook on Metalloproteins* Bertini, I., Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 2001; Chapter 9, pp 269−356.

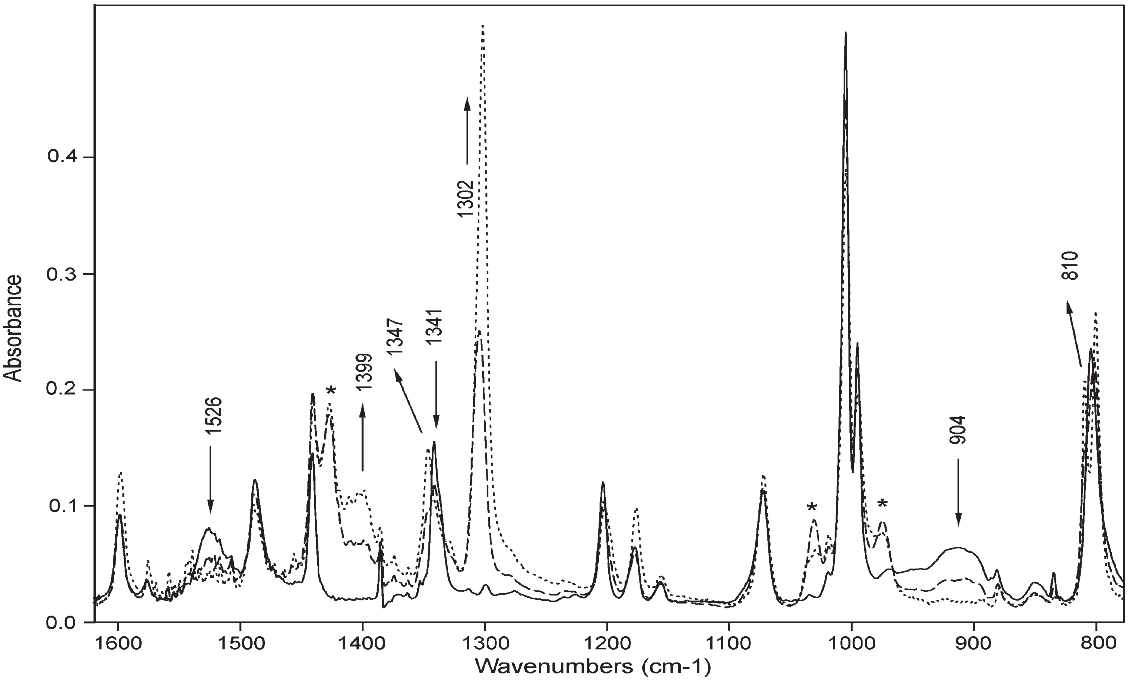

Figure 1. FTIR spectral changes observed in the layered Fe(TPP)(η^1-ONO) (solid line) after supplying into cryostat 0.4 Torr equivalent DMS and warming from 140 to 170 K (dashed and dotted lines). The bands of excess DMS are denoted by asterisks.

Table 1. Infrared Spectral Data (in cm^{-1}) for Coordinated Nitrite and for Spin Sensitive Bands of the Fe(Por)(R_2S)(NO_2) Adducts and the Starting Pentacoordinate Nitrito Complexes (Data Listed in Parentheses Represent the Bands Observed for the Reaction Products of Fe(Por)(η^1-$O^{15}NO$) plus R_2S)

compounds	$\nu_a(NO_2)$ or ν(N=O)	$\nu_s(NO_2)$ or ν(N−O)	δ(ONO) or $\delta(NO_2)$	spin-sensitive bands
Fe(TTP)(ONO)[a]	1528 (1496);	901 (878);	751 (747);	1340, 428
Fe(TPP)(ONO)[a]	1527 (1495);	900 (877);	~750 (~746)*	1340, 436
Fe(TTP)(DMS)(NO_2)	1401 (1374);	1300 (1281);	809 (~803);	1348, 456
Fe(TPP)(DMS)(NO_2)	1399 (1373);	1302 (1283);	810 (~803);	1347, 465
Fe(TTP)(THT)(NO_2)	1405 (1376);	1302 (1283);	808 (~802);	1349, 457
Fe(TPP)(THT)(NO_2)	1407 (1377);	1303 (1284);	807 (~802);	1347, 465

[a] Reported previously in ref [7a]. [b] Overlapped with the intense porphyrin band and seen in difference spectra.

However, when *T* was further raised from 140 to 170 K for DMS and 160 to 190 K for THT, several key spectral changes were evident. Specifically, the ν(N=O) and ν(N−O) stretching bands for the nitrito moiety at 1525 cm^{-1} and 906 cm^{-1} disappeared, while new bands at 1399, 1302, and 810 cm^{-1} grew in intensity (Figure 1, Table 1). All these bands have lower frequency isotopic counterparts that were apparent when DMS or THT was allowed to react with layers of the isotopically labeled Fe(Por)(η^1-$O^{15}NO$) (Figure 2, Table 1).

The electronic absorption spectra also underwent noticeable changes upon interaction of Fe(Por)(η^1-ONO) with R_2S (Figure 3), indicating the formation of new compounds.

The infrared spectral changes upon reaction of R_2S with **1** are analogous to those seen when 6-coordinate nitro complexes are formed upon interaction of the ligands NH_3, pyridine, 1-methylimidazole (1-MeIm), and THF with **1**. Nitro and nitrito isomers can be differentiated from the high-frequency stretching modes that are much closer to each other for the former than for nitrito species.[9] The asymmetric and symmetric stretching modes $\nu_a(NO_2)$ and $\nu_s(NO_2)$ for the hexacoordinate nitro-complexes are located in the vicinity of 1400 and 1300 cm^{-1}, while $\delta(NO_2)$ is at ~810 cm^{-1}. In this context, the bands at 1399, 1302, and 810 cm^{-1} seen for the DMS adduct of Fe(TPP)(ONO) and at 1373, 1283, and ~803 cm^{-1} for that of Fe(TPP)($O^{15}NO$) can be attributed to formation of the nitro isomers as indicated in Scheme 1.

The spectral changes observed upon low-temperature interaction of R_2S with the Fe(Por)(η^1-ONO) differ significantly from those obtained when NO,[7a] NH_3[7b], or THF[7d] were used as the ligands. For the first two ligands, disappearance of the nitrito bands at low temperature was accompanied by the growth of the bands slightly shifted from the ν(N=O) and ν(N−O) bands of **1**, the former being shifted to lower frequency, the latter shifted to higher frequency. These data were reasonably interpreted as resulting from the low-temperature formation of the metastable 6-coordinate nitrito-complexes, namely, Fe(Por)(NO)(η^1-ONO) and Fe(Por)(NH_3)(η^1-ONO). Upon warming these each isomerized to the nitro isomers Fe(Por)(NO)(NO_2) and Fe(Por)(NH_3)(NO_2) that were stable even at room temperature when excess NO(g) and NH_3(g) were present, respectively. However, in the case of the S-donor ligands, it was not possible to detect the 6-coordinate nitrito species that would be the anticipated intermediate upon reaction of R_2S with **1**. Instead, only 6-coordinate nitro complexes were observed, even at the lowest temperatures where a reaction of **1** with R_2S was apparent. Hence, the barrier for nitrito to nitro linkage

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(9) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed.; Wiley & Sons: New York, 1978; pp 244−247.

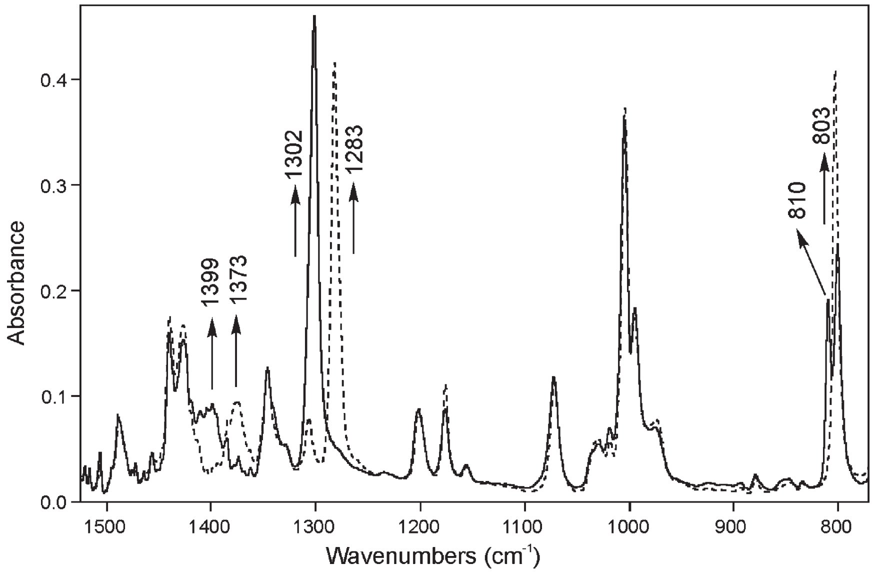


Figure 2. FTIR spectra of samples obtained after low-temperature DMS interaction with sublimed layers containing Fe(TPP)(η^1-ONO) (solid line) and Fe(TPP)(η^1-O^{15}NO) (dashed line).

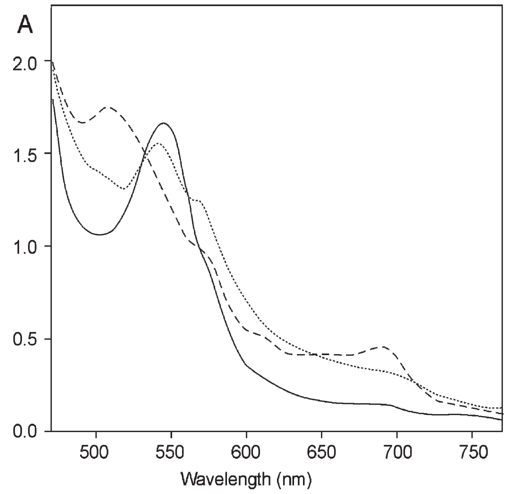
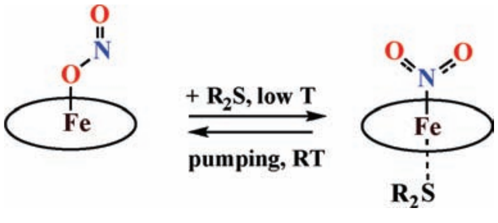


Figure 3. UV−visible spectra of Fe(TPP) (solid line), Fe(TPP)(η^1-ONO) (dashed line), and after interaction with DMS (dotted line). The spectra were taken after FTIR measurements of the same samples confirming the indentity of each species.

Scheme 1



isomerization of the nitrite ligand must be sufficiently low that this pathway is facile at the lowest temperatures where R_2S is sufficiently mobile to penetrate into the porous layers of **1** and form the 6-coordinate complexes.

In the presence of excess DMS (P > 40 Torr), the Fe(Por)(DMS)(NO_2) nitro complexes formed in this manner are stable at room temperature. For the less volatile THT ligand it was impossible to have enough THT pressure to conserve the 6-coordinate Fe(Por)(THT)(NO_2) complexes. In the presence of 12 Torr THT at ambient conditions, they decompose within a few hours. However, the reaction between **1** and R_2S is also fully reversible since pumping at elevated temperatures led to complete restoration of the original spectral properties of **1**.

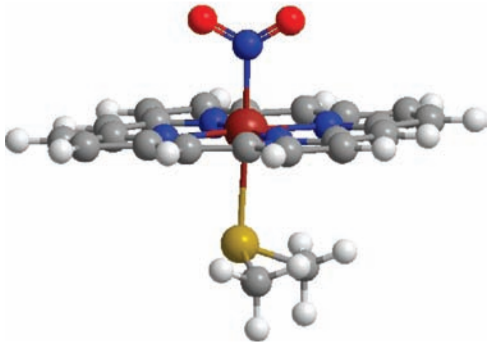


Figure 4. Structure of computed (B3LYP/LACVP*) porphinato complex Fe(P)(DMS)(NO_2).

Certain ring vibration modes of Fe(TPP) complexes, for example, bands at ~1350 cm^{-1} (ν(C_a−C_m) mixed with ν(C_m−phenyl)) and at ~450 cm^{-1} (δ(Pyr. rotation)) have been shown to be sensitive indicators of the metal center spin state.[10] For the intermediate spin state Fe(TPP),[11] these bands lie at 1346 and 464 cm^{-1}. Upon reaction with NO_2 to give Fe(TPP)(η^1-ONO), they shift to 1341 and 434 cm^{-1} consistent with a high-spin state. (For Fe(TTP), the analogous bands appear at 1346 and 455 cm^{-1} and correspondingly shift upon reaction with NO_2 to 1340 and 428 cm^{-1}). In previous studies, it was shown that the 6-coordinate nitro complexes Fe(TPP)(L)(NO_2) formed by the porous layer reactions of Fe(TPP)(η^1-ONO) with NO or a nitrogen base such as NH_3 or Py consistently display these porphyrin bands

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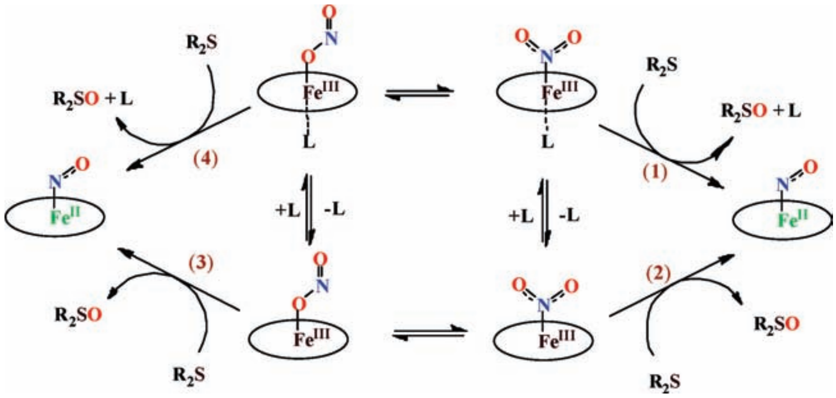
[10] (a) Oshio, H.; Ama, T.; Watanabe, T.; Kincaid, J.; Nakamoto, K. *Spectrochim. Acta* **1984**, *40A*, 863–870. (b) Paulat, F.; Praneeth, V. K. K.; Nather, C.; Lehnert, N. *Inorg. Chem.* **2006**, *45*, 2835–2856.

[11] Collman, J. P.; Hoard, J. L.; Kim, N.; Lang, G.; Reed, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 2676–2681.

Scheme 2. Possible pathways for oxygen atom transfer from nitrite to R_2S mediated by Fe^{III}(Por)



at ~1350 and 460 cm^{-1}, indicating a Fe(III) center in the low-spin electronic state.[7a−c] The IR spectra of the $Fe(Por)(R_2S)(NO_2)$ products formed from the reaction of Fe(Por)(η^1-ONO) with DMS and THT show new bands in the vicinity of 1350 and 460 cm^{-1} (see Table 1) indicating a low spin state for these Fe(III) complexes.

DFT calculations for the porphinato analogs are consistent with these experimental observations. The (gas phase) structures of isomeric $Fe^{III}(P)(DMS)(NO_2)$ and Fe^{III}(P)(DMS)(ONO) (P = porphinato dianion) complexes at different spin states were computationally optimized at B3LYP level using the LACVP* basis set without symmetry constraints. The lowest energy species was $Fe^{III}(P)(DMS)(NO_2)$ in the doublet spin state (Figure 4), and this was about 8 kJ/mol lower in energy than the most stable nitrito isomer, which was also in the doublet spin state. The results of these computations are given in the Supporting Information (Table S1).

Notably, when the cryostat containing excess DMS in the gas phase (5 Torr) and sublimed layers of Fe(TPP)(η^1-ONO) and the R_2S adduct was maintained at room temperature, a new band at 1676 cm^{-1} appeared in the IR spectrum of the iron porphyrin layer over a period of several hours. (See Supporting Information Figure S-1). This band was attributed to the ν(NO) frequency of the 5-coordinate ferrous nitrosyl complexes Fe(TPP)(NO) which has been shown in earlier experiments to appear at 1677 cm^{-1} for this complex as a result of NO interaction with sublimed layer of Fe(TPP).[7h] In addition, bands attributed to the coordinated nitrite ion correspondingly decreased in intensity (Supporting Information Figure S1). To determine other possible products, the gaseous content of the cryostat after reacting overnight was transferred through the injector into another cryostat and deposited onto a KBr substrate cooled by liquid nitrogen. The FTIR spectra were recorded during a warming/pumping procedure. According to these measurements pumping at 180 K completely removed the excess DMS from the substrate, and the IR spectrum of remaining compound was identical to that of solid DMSO layer obtained by depositing directly on the substrate (Supporting Information Figure S2). The same results were obtained when the layered Fe(TTP) was used as an iron-porphyrin.

Mass spectral analysis of the gaseous content of this cryostat by a residual gas analyzer shows the *m*/*z* molecular peaks of DMSO at 78. When the analogous experiments were conducted using the isotopically substituted Fe(Por)(η^1-$^{18}ON^{18}O$) as the parent nitrito species, the mass spectrum of the isotopically labeled DMS^{18}O was registered. When THT was used instead of DMS, the behavior was fully analogous and the *m*/*z* molecular peaks of THT-oxide at 104 and of THT^{18}O at 106 were respectively observed for the reactions of THT with **1** and with ^{18}O labeled **1** (see Supporting Information Figure S3). These observations provide clear evidence that the iron porphyrins are somehow facilitating oxygen atom transfer (OAT) reactions from coordinated nitrite to the substrates DMS and THT.

In previous studies, it has been shown that solutions of Fe^{III}(Por) complexes with added nitrite salts mediate oxygen atom transfers to various substrates with concomitant formation of ferrous nitrosyls Fe^{II}(Por)(NO). This reaction was observed both in organic solvents[12] and in aqueous media at physiologically relevant pH values.[13] In the latter case, the use of DMS as substrate, the water-soluble ferric porphyin $Fe^{III}(TPPS)(H_2O)_2$, and sodium nitrite gave the corresponding products DMSO and Fe^{II}(TPPS)(NO).[13] The observation of this reaction in the much simpler system described here, containing only the layered iron-porphyrin nitrite complexes and gas phase substrate suggests the generality of such oxygen transfers for these heme model systems when nitrite is present. Similar oxygen atom transfer activity of thin layers was previously observed in our laboratory for the Co porphyrin nitro complex $Co(TPP)(NO_2)$.[14]

However, at this stage it is not possible to identify conclusively which ferric porphyrin species might be responsible for the promotion of R_2S oxidation. FTIR spectral analysis of the layers containing iron−porphyrin nitrite complexes at room temperature in the presence of excess R_2S indicate that both 5-coordinate Fe(Por)(η^1-ONO) and 6-coordinate $Fe(Por)(R_2S)(NO_2)$ are present. Furthermore, the computational studies have found only modest differences in energy between Fe(P)(η^1-ONO) and its linkage isomer $Fe(P)(NO_2)$[7c] (1 kJ, the high spin state of the former being insignificantly more stable according to the calculation) and between $Fe(P)(DMS)(NO_2)$ and Fe(P)(DMS)(η^1-ONO) (8 kJ, the doublet state of the former being the more stable as described above).[7c] While the calculations are for the gas phase porphinato complexes and therefore have to be considered qualitative, they clearly suggest that all four of these

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

(13) Khin, C.; Heinecke, J.; Ford, P. C. *J. Am. Chem .Soc.* **2008**, *130*, 13830–13831.

(14) Kurtikyan, T. S.; Mardyukov, A .N.; Goodwin, J. A. *Inorg. Chem.* **2003**, *42*, 8489–8593.

species need to be taken into account when considering possible mechanisms for the oxygen atom transfer as illustrated in Scheme 2. As we have seen, the nitrite ion linkage isomerization pathways seem to be reasonably facile, so we would not expect the potential transformations between these four species to be rate limiting in the slow OAT reactions.

Since the predominant species present in the ambient temperature solids with excess R_2S present are the pentacoordinate nitrito complex **1** and the hexacoordinate nitro complex $Fe(Por)(R_2S)(NO_2)$, OAT pathways 1 and 3 might seem to be the most reasonable. However, a problem with pathway 3 is that if the oxygen atom transferred in a concerted pathway was the uncoordinated O in the γ position, the isonitrosyl species $Fe^{II}(Por)(ON)$ would be an intermediate along the reaction coordinate. However, our DFT computations for the porphine analogs show the optimized structure of the isonitrosyl isomer to be 67 kJ higher in energy than the product nitrosyl species. Thus it seems more likely that **1** would isomerize to the energetically accessible 5-coordinate nitro isomer, followed by OAT from this species to the substrate, that is, pathway 2. A similar argument can be used to discount the importance of pathway 4 to the oxygen atom transfer mechanism. Lastly, with regard to possible OAT from the 6-coordinate nitro complex, concerted OAT and R_2S dissociation from the proximal position would be one possible pathway for this to occur (step 1), but given the relative slowness of these OAT reactions, the stepwise dissociation of R_2S to give $Fe(Por)(NO_2)$ followed by step 2 seems equally likely. Indeed, an earlier computational study by Conradie and Ghosh[15] has suggested that oxygen atom transfer to DMS via pathway 2 would give a lower energy activation barrier than the concerted reaction indicated by pathway 1. Better identifying which of these species and pathways are responsible for the oxygen atom transfer reactivity is the subject of ongoing investigation.

Summary

This study shows that low-temperature interaction of S-donor thioethers DMS and THT with 5-coordinate iron-porphyrin O-nitrito complexes $Fe(Por)(\eta^1\text{-}ONO)$ leads to formation of 6-coordinate N-nitrito species $Fe(Por)(R_2S)(NO_2)$. Hence, coordination of the proximal S-donor ligand leads to O-nitrito → N-nitrito isomerization of the nitrite ligand. In the presence of gas phase R_2S donors these six-coordinate complexes can be observed even at room temperature. In contrast to high spin 5-coordinate O-nitrito complexes, the 6-coordinate species are in the low spin state. DFT calculations for these 6-coordinate species give minimal energies for the low-spin doublet states for the N-nitrito and O-nitrito isomers with the N-nitrito isomer only 8 kJ/mol more stable than O-nitrito one. There are several indications of oxo-transfer reactivity of solid-state iron-porphyrin nitrite system in the presence of gas phase R_2S: appearance of the iron-nitrosyl band in the layered solid and formation of corresponding sulfoxides demonstrated by the FTIR and mass spectrometric measurements together with ^{18}O isotope labeling experiments.

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Supporting Information Available: Figure S1 demonstrating formation of nitrosyl iron-porphyrin upon standing O-nitrito complex $Fe(TPP)(\eta^1\text{-}ONO)$ in the atmosphere of DMS; Figure S2 representing both the FTIR spectra of the gaseous content of cryostat where the layer of $Fe(TPP)(\eta^1\text{-}ONO)$ has been under DMS vapors overnight and solid DMSO; Figure S3 representing mass spectra of THT, and gaseous content of cryostat where the layer of $Fe(TPP)(\eta^1\text{-}ONO)$ has been under vapors of THT overnight; DFT calculations including total energies for all spin states of the 6-coordinate ferric porphinato complexes $Fe(P)(DMS)(\eta^1\text{-}ONO)$ and $Fe(P)(DMS)(NO_2)$ (Table S1); selected bond distances computed for the doublet states of the 6-coordinate ferric porphinato complexes $Fe(P)(DMS)(\eta^1\text{-}ONO)$ and $Fe(P)(DMS)(NO_2)$ (Table S2); and final geometries for $Fe(P)(DMS)(\eta^1\text{-}ONO)$ and $Fe(P)(DMS)(NO_2)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] Conradie, J.; Ghosh, A. *Inorg. Chem.* **2006**, *45*, 4902–4909.