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Six-Coordinate Nitrate Complexes of Iron Porphyrins with *trans* S-Donor Ligands

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ABSTRACT: The reaction of dimethyl sulfide (DMS) and tetrahydrothiophene (THT) with thin, amorphous layers of the nitrate complexes $\text{Fe}(\text{Por})(\eta^2\text{-O}_2\text{NO})$, Por = meso-tetraphenylporphyrinato or meso-tetra-(*p*-tolyl)porphyrinato dianion, at low temperature leads to formation of the corresponding six-coordinate complexes $\text{Fe}(\text{Por})(\text{L})(\eta^1\text{-ONO}_2)$ (L = DMS, THT) as characterized by infrared and optical spectroscopy. Adduct formation was accompanied by bidentate to monodentate isomerization of the nitrate ligand with the Fe(III) center remaining in a high-spin electronic state. These adducts are thermally unstable; warming to room temperature restores the $\text{Fe}(\text{Por})(\eta^2\text{-O}_2\text{NO})$ species.

The biological roles of nitrogen oxides (NO_x) are strongly associated with their interactions with heme proteins,^{1,2} and this feature has prompted continuing interest in the reactions of various NO_x with ferro- and ferri-porphyrin complexes. While there are numerous examples of 6-coordinate nitrosyl (NO) and nitrite (NO_2^-)³ iron-porphyrin complexes with proximal ligands, analogous complexes of nitrate (NO_3^-) are relatively rare. A nitratoferriheme complex has been shown to be a transient in the reaction of NO with oxymyoglobin.⁴ Similar products might be expected upon reactions of other heme dioxygen complexes with NO. Nonetheless, there are few examples of η^1 -nitrate iron porphyrin complexes with a proximal ligand. For examples, *trans*- $\text{Fe}(\text{Por})(\text{H}_2\text{O})(\eta^1\text{-ONO}_2)$ (Por = not identified), was described in a review,³ and the unstable complexes $\text{Fe}(\text{TPP})(\text{NO})(\eta^1\text{-ONO}_2)$ (TPP = meso-tetraphenylporphyrinato dianion) and $\text{Fe}(\text{Por})(\text{THF})(\eta^1\text{-ONO}_2)$ (THF = tetrahydrofuran and Por = TPP or meso-tetra-(*p*-tolyl)porphyrinato dianion TPP) have been spectrally characterized at low temperatures.^{5,6} Another is $\text{Fe}(\text{Por})(\text{NH}_3)(\eta^1\text{-ONO}_2)$ formed from the NO reaction of $\text{Fe}(\text{Por})(\text{NH}_3)(\text{O}_2)$ ⁷ (Por = TPP or TTP) as a model for heme mediated NO dioxygenation (NOD). More recently the six-coordinate nitrate complex $\text{Fe}^{\text{III}}(\text{P}^{\text{Im}})(\text{ONO}_2)$ (P^{Im} = a porphyrin moiety with a

covalently tethered proximal imidazole ligand) was reported to be formed by isomerization of the peroxyxynitrite analog $\text{Fe}^{\text{III}}(\text{P}^{\text{Im}})(\text{OONO})$, itself the product of NO addition to the dioxygen complex $\text{Fe}^{\text{III}}(\text{P}^{\text{Im}})(\text{O}_2)$ in -80°C THF solution.⁸

Although numerous heme proteins have a S-coordinated cysteine or methionine proximal ligand, the only known nitrate complex of such proteins is the η^1 -nitrate adduct of chloroperoxidase (with a cysteine thiolate proximal ligand) for which a crystal structure was reported.⁹ To our knowledge, there are no published examples of nitrate coordination to a heme protein or model with a thioether proximal ligand. Described here are spectroscopic studies demonstrating the formation of metastable six-coordinate complexes upon the low-temperature reaction of dimethyl sulfide (DMS) or tetrahydrothiophene (THT) with the precursors $\text{Fe}^{\text{III}}(\text{Por})(\eta^2\text{-O}_2\text{NO})$ (Por = TPP or TTP).

Sublimation of $\text{Fe}^{\text{II}}(\text{Por})$ precursors onto the surface of the low-temperature (77 K) substrate (KBr or CaF_2) in an optical cryostat leads to the formation of amorphous, spongelike layers with high microporosity.¹⁰ Volatile reactants diffuse across these layers, and adducts thus formed can be interrogated spectroscopically without solvent interference. The temperature can be varied in order to evaluate the reactivities and stabilities of these adducts under various conditions.

In the present case, the $\text{Fe}^{\text{II}}(\text{Por})$ layers were prepared on the 77 K substrate and then were heated to room temperature (RT) under dynamic vacuum. Small increments of NO_2 gas were then introduced for several minutes followed by pumping to evacuate the cryostat. This procedure led initially to the formation of the O-nitrito species $\text{Fe}(\text{Por})(\eta^1\text{-ONO})$.¹¹ Reaction with additional NO_2 at RT resulted in oxidation of the nitrito complex to the η^2 -nitrate complex $\text{Fe}(\text{Por})(\eta^2\text{-O}_2\text{NO})$ (**1**).^{12,6} FTIR and UV-visible spectra were recorded after each introduction of NO_2 to confirm the formation of these products. Subse-

quently, the cryostat was evacuated to remove excess NO_2 and other volatiles, and then the substrate and deposited layers were cooled to 140 K. At this point, the volatile thio-ethers DMS or THT were introduced and FTIR or electronic absorption spectra were recorded. The layers were slowly warmed and the FTIR and UV-visible spectra were periodically recorded on a Nexus (Thermo Nicolet) and “Specord M-40” (Carl Zeiss, Jena) or Helios γ (Thermo Electron Corporation) spectrometers, respectively.

Figure 1 represents the FTIR spectral changes observed for layers of **1** that have been exposed to THT. Upon slow warming from 150 to 170 K, there were noticeable changes in the FTIR spectrum. The bands at 1527, 1273, and 966 cm^{-1} assigned to the η^2 -nitrate complex **1** disappeared, and new bands emerged at 1489, 1278, and ~ 990 cm^{-1} implying the formation of a new species (THT)Fe(TPP) (**2**). That all these bands can be assigned to the nitrate ligand was substantiated by isotopic labeling. When the η^2 -nitrate complex Fe(TPP)($\eta^2\text{-O}_2^{15}\text{NO}$) was prepared by starting with $^{15}\text{NO}_2$, the latter bands displayed isotopic analogues at 1457, 1256, and 978 cm^{-1} for the product (Figure 2).

Upon comparison of the FTIR spectra of **1** and **2**, it is seen that the high-frequency $\nu(\text{N}=\text{O})$ band noticeably shifts to lower frequency, while the low frequency $\nu_s(\text{NO}_2)$ band underwent a minor shift to higher frequency and gained in intensity (Fig. 1). The ^{15}N -labeled species show analogous shifts (Fig. 2, Table 1). These shifts are similar to those observed upon the reaction of **1** with

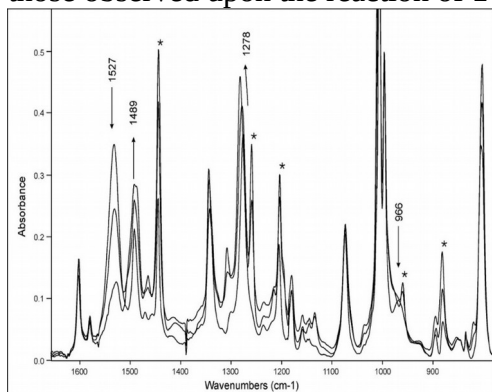


Figure 1. FTIR spectral changes observed in sublimed layers of **1** upon warming from 150 to 170 K in the presence of THT. Spectra were recorded at 150 K. Asterisks indicate bands of excess THT. THF to give (THF)Fe(TPP)($\eta^1\text{-O}_2\text{NO}$),⁶ thus, can be attributed to reaction of **1** with THT to give

the six-coordinate nitrate complex (THT)Fe(TPP)($\eta^1\text{-ONO}_2$) (**2**, Scheme 1). This reaction also leads to corresponding shifts in the electronic absorption spectrum (see below).

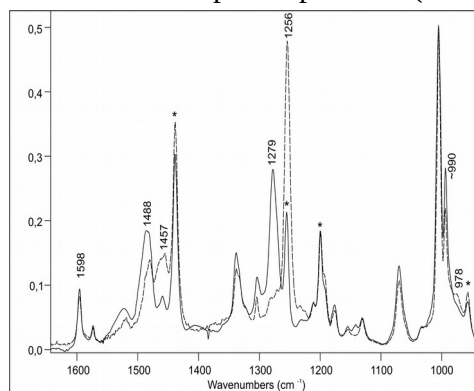


Figure 2. FTIR spectra at 150 K of layered samples of **2** (solid line) and (THT)Fe(TPP)($\eta^1\text{-O}^{15}\text{NO}_2$).

Table 1 also summarizes the IR bands (Figure 3) attributed to the product formed when low temperature layers of **1** (and its ^{15}N -nitrate analog) react with DMS. The IR spectral changes indicate that this reaction leads to analogous S-coordination of the thioether to the proximal site of the ferri-heme model and the shift from bidentate to monodentate coordination of the nitrate ion.

In addition, Table 1 summarizes the IR absorption bands for products for the reactions of Fe(TTP)($\eta^2\text{-O}_2\text{NO}$) (**3**) and its ^{15}N -nitrate analog with THT and DMS. The similarities of the spectral shifts for these products to those for the TPP complexes, argues that the respective products are also the hexacoordinate complexes with monodentate nitrate coordination and a proximally coordinated thio-ether, namely (THT)Fe(TTP)($\eta^1\text{-ONO}_2$) and (DMS)Fe(TTP)($\eta^1\text{-ONO}_2$).

Symmetric bidentate coordination of nitrate in Fe(TPP)($\eta^2\text{-O}_2\text{NO}$) was previously demonstrated in low-temperature structural studies.¹³ The iron(III) center is high-spin with a large out-of-plane displacement (0.6 Å) from the porphyrin ring. The three IR-active stretching modes sensitive to labeling with ^{15}N -nitrate would be a high-frequency N=O stretch ($\nu(\text{N}=\text{O})$) for the uncoordinated oxygen and the asymmetric and symmetric stretching modes for the coordinated NO_2 fragments ($\nu_a(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$) (Table 1). The addition of THT or DMS changed this pattern dramatically. The $\nu_a(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$ bands shift by several

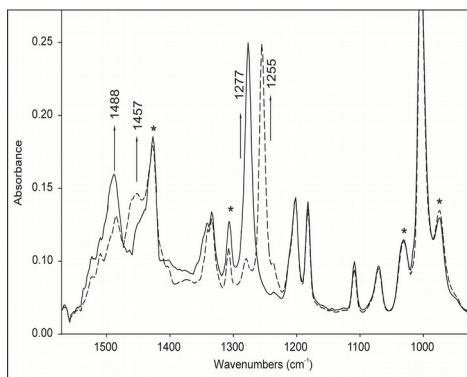


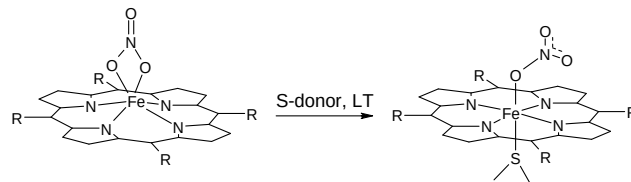
Figure 3. FTIR spectra of layered (DMS)Fe(TTP)(η^1 -ONO₂) (solid line) and (DMS)Fe(TTP)(η^1 -O¹⁵NO₂) (dashed line) complexes at 150 K. Some excess DMS was pumped out at 150 K.

hundred wavenumbers to higher frequencies with the intensity of the former decreasing and that of the latter increasing. The same pattern was observed for the ¹⁵N-enriched samples (Figures 2 & 3). In addition, a weak, isotopically sensitive band at ~ 990 cm⁻¹ in the spectrum of **1** that overlaps an intense porphyrin band, which is more clearly seen at 978 cm⁻¹ for the ¹⁵N-nitrato complex (THT)Fe(TPP)(η^1 -O¹⁵NO₂) (Figure 2). This band, assigned as the N-O stretch of the coordinated O of the monodentate nitrate, was obscured in the reaction with DMS owing to the interference with other bands (Fig. 3).

These changes can be reasonably interpreted in terms of nitrate isomerization from bidentate to monodentate coordination (Scheme 1). The band at 1488 cm⁻¹ is now assigned to $\nu_a(\text{NO}_2)$ and that near 1280 cm⁻¹ to $\nu_s(\text{NO}_2)$. The smaller separation of these high-frequency bands is characteristic of monodentate nitrate coordination.¹⁴ The weak band at about 990 cm⁻¹ can be assigned to the N-O bond for the oxygen atom bound to iron(III). Similar changes for the nitrate stretching modes were observed upon the low-temperature interaction of THF with Fe(Por)(η^2 -O₂NO) in layered solids to give (THF)Fe(Por)(η^1 -ONO₂).⁶ This interpretation gains further support the octaethylporphyrinato complex Fe(OEP)(η^1 -ONO₂), which has been shown to have monodentate coordination.¹⁵ The FTIR spectrum of this complex displays nitrate bands at 1515 and 1276 cm⁻¹ [$\nu_a(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$, respectively], with the latter the much more intense.⁶ Additional support is provided by the spectra of recently obtained nitrato complexes of Mn-porphyrin, in which the nitrato ligand is initially coordinated in a mon-

odentate fashion and the formation of six-coordinate species is accompanied by the lowering of the $\nu_a(\text{NO}_2)$ and enhancing of the $\nu_s(\text{NO}_2)$ frequencies.¹⁶

Scheme 1.



Changes in the electronic absorption spectra for the reactions of **1** and of **3** with THT or DMS (Figure 4) confirm the formation of thioether adducts in the low temperature layers (Table 1). The characteristic metalloporphyrin Q-bands of the bidentate nitrato complexes undergo bathochromic shifts upon formation of the six-coordinate complexes with the thioether ligands.

Table 1. IR and UV-visible data of 6-coordinate nitrato complexes with thioethers (L)Fe(Por)(η^1 -ONO₂) (L = DMS, THT; Por – TPP, TTP).^a

Compounds	$\nu(\text{N}=\text{O})$, cm ⁻¹	$\nu(\text{N}-\text{O})$, cm ⁻¹	$\nu_a(\text{NO}_2)$, cm ⁻¹	$\nu_s(\text{NO}_2)$, cm ⁻¹	Spin-sensitive bands, cm ⁻¹	UV-vis, Q-bands, λ_{max} , nm	Reference
Fe(TPP)(η^2 -O ₂ NO) (1)	1527 (1493)	^b	1273 (1253)	966 (956)	1341, 436	513, 579 sh, 658, 692	12
(DMS)Fe(TPP)(η^1 -ONO ₂)	-	^c	1488 (1456)	1277 (1256)	1340, 435	503, 543, 652 sh, 699	this work
(THT)Fe(TPP)(η^1 -ONO ₂) (2)	-	~990 (978)	1489 (1457)	1278 (~1255)	1339, 435	503, 543, 605 sh, 708	this work
Fe(TTP)(η^2 -O ₂ NO) (3)	1528 (1495)	-	1271 (1251)	966 (957)	1340, 428	515, 578 sh, 653 sh, 698	6
(DMS)Fe(TTP)(η^1 -ONO ₂)	-	^c	1488 (1456)	1278 (1256)	1341, 431	503, 538, 652 sh, 708	this work
(THT)Fe(TTP)(η^1 -ONO ₂)	-	~990 (978)	1494 (1460)	1278 (1256)	1339, 429	503, 538, 693	this work
(NO)Fe(TPP)(η^1 -ONO ₂)	-	968 (960)	1507 (1471)	1265 (1246)	1350, 455	547, 582	5

^aFor comparison the data of 5-coordinate bidentate Fe(Por)(η^2 -O₂NO) complexes are also given. The bands in parenthesis are for ¹⁵N-labeled nitrato complexes. ^b This vibrational mode is not present.

^cMasked by DMS bands.

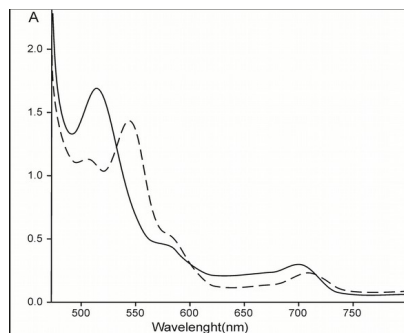


Figure 4. Optical spectra of thin layers of **3** (solid line) and (DMS)Fe(TTP)(η^1 -ONO₂) (dashed line) at 130 K recorded after the FTIR spectra demonstrated the formation first of **3** and then of the DMS complex (see text).

The porphyrin vibrations provide additional insight into the electronic structures of the new complexes.¹⁷ The porphyrin core mode in the vicinity of 1350 cm⁻¹ corresponding to $\nu(\text{C}_a-\text{C}_m)$ mixed with $\nu(\text{C}_m\text{-phenyl})$ lies at higher frequencies for low-spin complexes, which also demonstrate a low-energy porphyrin core deformation mode at 450 cm⁻¹. For the high-spin nitrato complexes **1** and **3**, these bands lie at 1341 and 436 cm⁻¹ and at 1340 and 428 cm⁻¹, respectively. For

(L)Fe(Por)(η^1 -ONO₂) (L = DMS or THT; Por = TPP or TTP) these bands remain at ranges characteristic of the high-spin complexes (Table 1). In contrast, for (NO)Fe(TPP)(η^1 -ONO₂), these bands shift to 1350 and 464 cm⁻¹, consistent with a low-spin electronic configuration owing to the very strong Fe-NO π -bonding interaction.⁵

The six-coordinate nitrato complexes formed with the *trans* (proximal) S-donor thioether ligands are less stable than those the analogous complexes formed with the O-donor tetrahydrofuran.⁶ Although the former are observable in the 150 K porous layers, they slowly lose the sixth ligand in the course of pumping at temperatures higher than 150 K. In comparison, the latter are stable under pumping at 180 K and only after a further increase in temperature begin to decompose. This trend is in line with the concept of hard and soft acids and bases,¹⁸ according to which the soft acids form stronger bonds with soft bases, whereas hard acids form stronger bonds with hard bases, all other factors being equal. Fe(III) ion is a hard acid and will tend to form more stable complexes with harder base THF.

In summary, the low temperature interaction of S-donor ligands (DMS, THT) with thin films of Fe(Por)(η^2 -O₂NO) (Por = TPP or TTP) leads to formation of new six-coordinate complexes that are formulated as (S-donor)Fe(Por)(η^1 -ONO₂) based on the FTIR and UV-Vis data. This reaction is accompanied by bidentate-to-monodentate isomerization of coordinated nitrate with the Fe(III) center remaining in the high-spin electronic state. These complexes are stable at low temperature but upon warming release the sixth ligand almost completely restoring the parent Fe(Por)(η^2 -O₂NO) complexes.

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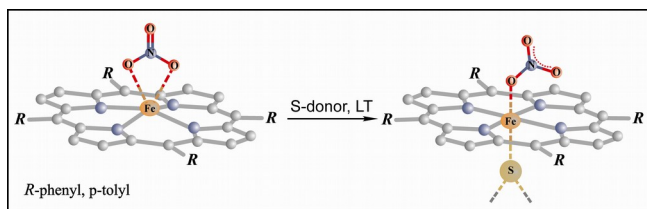
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The preparation and spectroscopic characterization (FTIR and UV-vis) of the hexacoordinate complex $\text{Fe}(\text{Por})(\text{L})(\eta^1\text{-ONO}_2)$ (Por = meso-tetraphenyl-porphyrinato dianion, TPP, or meso-tetra-(*p*-tolyl)-porphyrinato dianion, TTP, L = DMS, THT) at low temperature is described for the first time. Adduct formation was accompanied by bidentate to monodentate linkage isomerization of the nitrate ligand with the Fe(III) center remaining in a high-spin electronic state. These adducts are thermally unstable; warming to room temperature restores the initial $\text{Fe}(\text{Por})(\eta^2\text{-O}_2\text{NO})$ species.