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Six-Coordinate Nitrato Complexes of Iron(III) Porphyrins

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The interaction of tetrahydrofuran (THF) with thin films of the nitrato complexes $Fe^{III}(Por)(\eta^2\text{-}O_2NO)$ [Por = *meso*-tetraphenylporphyrinato (TPP) and *meso*-tetratolylporphyrinato (TTP) dianion] at low temperature leads to the formation of the six-coordinate nitrato complex $Fe(Por)(THF)(NO_3)$, which was characterized by IR and UV–visible spectroscopies. Formation of the THF adduct was accompanied by nitrate linkage isomerization from bidentate to monodentate coordination. The iron(III) center remains in a high spin state in contrast with the previously observed low-spin nitratonitrosyl complex $Fe(TPP)(NO)(\eta^1\text{-}ONO_2)$. Upon warming, THF dissociates to restore the initial five-coordinate bidentate nitrato complex.

The biological roles of the nitrogen oxides (NO_x) often involve interactions with heme proteins; thus, there is considerable interest in model studies of these reactions.[1] For the ligands NO and NO_2, a number of five- and six-coordinate iron(II) and iron(III) porphyrinato complexes have been characterized;[2] however, examples of six-coordinate nitrato (NO_3) complexes are limited. Among these are *trans*-$Fe(Por)(H_2O)(\eta^1\text{-}ONO_2)$, described in a review,[2] the unstable nitrosyl species $Fe(Por)(NO)(\eta^1\text{-}ONO_2)$ spectrally characterized at low temperature,[3] and the η^1-nitrate adduct of chloroperoxidase (with cysteine in the proximal coordination site), for which the crystal structure has been determined.[4] In addition, a nitratoferriheme complex is a likely transient in the decay of the peroxynitritoiron(III) intermediate formed by the reaction of NO with oxyhemoglobin or oxymyoglobin.[5] Thus, it is of interest to establish whether nitratoferriheme models could be prepared with other Lewis base proximal ligands. Reported here are spectroscopic studies demonstrating the formation of metastable six-coordinate complexes upon the low-temperature reaction of tetrahydrofuran (THF) with the five-coordinate precursors $Fe^{III}(Por)(NO_3)$ in sublimed layered solids. We also describe experiments with NH_3, demonstrating that the nitrate ion can be reversibly displaced by such Lewis bases in the layered solids.

The nitrato complex $Fe(TPP)(\eta^2\text{-}O_2NO)$ (**I**) was prepared by the reaction of excess NO_2 gas with thin amorphous $Fe^{II}(TPP)$ layers (TPP = *meso*-tetraphenylporphyrin dianion) formed by sublimation onto a CaF_2 or KBr surface as previously described.[6] When a low-temperature sample of **I** under vacuum was exposed to THF vapors, the IR spectral changes shown in Figure 1 were observed. The bands at 1527, 1273, and 967 cm^{-1} assigned to the η^2- coordinated nitrato ligand disappeared, and new bands emerged at 1491, 1280, and ~1000 cm^{-1}. Band assignments were substantiated by isotopic labeling, with the latter bands having isotopic analogues at 1457, 1258, and 986 cm^{-1} for the THF reaction with $Fe(TPP)(\eta^2\text{-}O_2{}^{15}NO)$ (Figure 2). Analogous results were seen for Por = TTP (Table 1and Figure S1 in the Supporting Information; TTP = *meso*-tetra-*p*-tolylporphyrin dianion).

Recent low-temperature structural studies reveal symmetric bidentate coordination mode of the nitrato ligand in $Fe(TPP)(\eta^2\text{-}O_2NO)$.[7a] Because of unrecognized nitrate ion disorder, slightly asymmetric bidentate coordination was suggested earlier.[7b] The iron(III) center is in the high-spin electronic state with a large out-of-plane displacement (~0.6 Å) from the porphyrin ring. The three IR-active stretching modes

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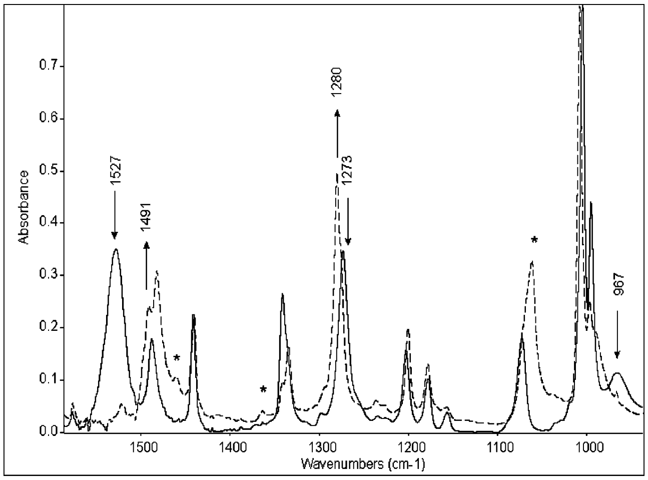

Figure 1. Solid line: FTIR spectrum of Fe(TPP)(η^2-O_2NO) in the sublimed solid at 180 K. Dashed line: Spectrum after introduction of THF into the cryostat at 120 K, slow warming to 180 K, followed by intense pumping to remove excess THF. Asterisks denote bands due to coordinated THF.

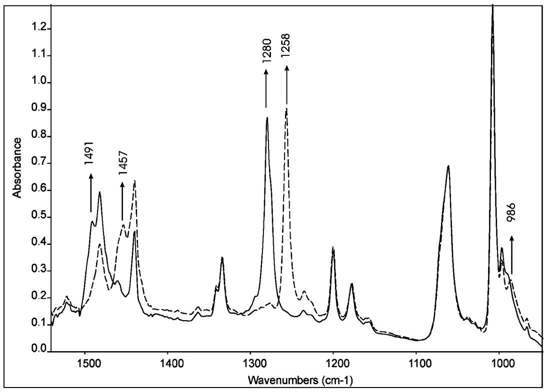

Figure 2. FTIR spectra at 180 K of Fe(TPP)(THF)(η^1-ONO_2) (solid line) and Fe(TPP)(THF)(η^1-$O^{15}NO_2$) (dashed line) formed by low-temperature (155 K) interactions of THF with layered Fe(TPP)(η^2-O_2NO) and Fe(TPP)(η^1-$O_2{}^{15}NO$), respectively.

expected for this structure would be a high-frequency ν(N=O) for the uncoordinated oxygen and two (symmetric and asymmetric) modes for the coordinated NO_2 fragment, as seen in Table 1. The addition of THF shifted the higher frequency bands at 1527 and 1273 cm^{-1} by -36 and $+7$ cm^{-1}, respectively, with noticeable changes of the intensity ratio; the higher frequency band diminished, and the lower frequency band increased. The same pattern was observed for the ^{15}N-enriched sample (Figure 2). In addition, a weak, isotopically sensitive band appeared at ~1000 cm^{-1} that overlaps with an intense porphyrin band but is clearly seen for the ^{15}N-labeled compound. These changes can be reasonably interpreted in terms of nitrate isomerization from bidentate to monodentate coordination (Scheme 1).

The high-frequency band at 1491 cm^{-1} is now assigned to $\nu_a(NO_2)$ and that near 1280 cm^{-1} to $\nu_s(NO_2)$. The smaller separation of the high-frequency bands is characteristic of monodentate nitrate coordination.[8] The weak band at ~1000 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 NO with Fe(TPP)(η^2-O_2NO) in layered solids to give Fe(TPP)(NO)(η^1-ONO_2).[3] This interpretation also gains support from experiments with the octaethylporphyrinato complex Fe(OEP)(η^1-ONO_2), which had been shown to have monodentate coordination.[9] When this was prepared by the reaction of NO_2 with Fe(OEP) in sublimed layers, the Fourier transform infrared (FTIR) spectrum revealed nitrate bands at 1515 and 1276 cm^{-1} [$\nu_a(NO_2)$, and $\nu_s(NO_2)$, respectively], with the latter much more intense than the former (Figure S2 in the Supporting Information).

The same reaction with THF occurs also with Fe(OEP). In this case, however, because of initial monodentate nature of the coordinated nitrato ligand, FTIR spectral changes are not so drastic compared with *meso*-aryl-substituted derivatives. The high-frequency $\nu_a(NO_2)$ band at 1515 cm^{-1} shifts to 1489 cm^{-1} while the $\nu_s(NO_2)$ band undergoes a minor high-frequency shift and slightly gains in intensity (Figure S3 in the Supporting Information). The decomposition temperature and reversibility of the THF binding in this case are very close to those for *meso*-aryl-substituted species.

Figure 3 illustrates the changes in the electronic absorption spectra (Q-band region) as Fe(TPP) reacts with NO_2 to give (eventually) **I**, which was then was exposed to THF vapors at 155 K to give Fe(TPP)(THF)(η^1-ONO_2). In each case, the IR spectrum of the layered solid was recorded to confirm the identity of the species under consideration. At $T > 180$ K, the complex began to dissociate THF, regenerating the original spectrum.

The porphyrin vibrations provide additional insight into the electronic structure of the new complexes.[10] A band in the vicinity of 1350 cm^{-1} representing the porphyrin core mode corresponding to $\nu(C_a-C_m)$ mixed with some $\nu(C_m-\text{phenyl})$ 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 complex **I**, these bands lie at 1341 and 436 cm^{-1}. However, for Fe(TPP)(THF)(η^1-ONO_2) and its TTP analogue, these bands remain at the ranges characteristic of the high-spin complexes (Table 1). In contrast, the nitrosylnitrato complex Fe(TPP)(NO)(η^1-ONO_2) was found to be low-spin (Figure S4 in the Supporting Information) because of the very strong Fe−NO interaction.[3]

Missing from the FTIR spectra of the η^1-nitrato complexes described here is a band at 1385 cm^{-1} that has been reported for IR spectra recorded in KBr pellets for several metalloporphyrinatonitrato complexes, including Fe(OEP)(η^1-ONO_2).[11] This band was also absent in the spectrum of the thin layers of Fe(OEP)(η^1-ONO_2) solids prepared using the cryostat technique (Figure S2 in the Supporting Informa-

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Table 1. FTIR and UV−Visible Data for Fe(Por)(η^2-O_2NO) and Fe(Por)(THF)(η^1-ONO_2)[a]

compound	ν(N=O), cm^{-1}	ν(N−O), cm^{-1}	$\nu_a(NO_2)$, cm^{-1}	$\nu_s(NO_2)$, cm^{-1}	spin-sensitive bands, cm^{-1}	Q region, λ_{max} (nm)
Fe(TPP)(η^2-O_2NO)	1527 (1489)		1273 (1253)	967 (958)	1341; 436	512; 579 (sh); 654; 691
Fe(TPP)(THF)(η^1-ONO_2)		∼997[b] (986)	1491 (1457)	1280 (1258)	1334; 434	496; 529; 573 (sh); 650; 693
Fe(TTP)(η^2 -O_2NO)	1529 (1494)		1273 (1254)	966 (957)	1341/1334; 428	515; 573 (sh); 698
Fe(TTP)(THF)(η^1-ONO_2)		∼995[b] (984)	1486 (1454)	1277 (1258)	1334; 427	498; 534; 575 (sh); 612; 701
Fe(TPP)(NO)(η^1-ONO_2)[c]		978 (963)	1505 (1470)	1266 (1248)	1351; 464	508; 547; 582

[a] Data in parentheses are for ^{15}N-labeled compounds. [b] Masked by the intense porphyrin band. [c] Reference 3a.

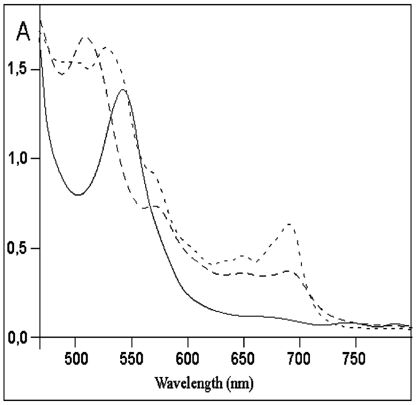
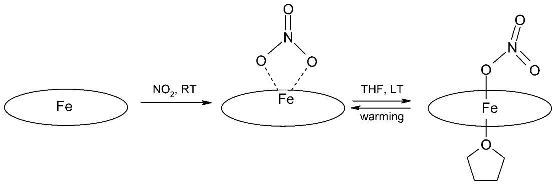


Figure 3. Visible spectra of the Fe(TPP) sublimed layer (solid line), after interaction with NO_2 to form the nitrato complex Fe(TPP)(η^2-O_2NO) (dashed line), and after further reaction with THF by warming of the layer from 120 to 155 K (dotted line) (all on a CaF_2 substrate).

Scheme 1



tion). It has been found that grinding solid Mn(TPP)(η^1-ONO_2) with KBr leads to anion exchange to give Mn(TPP)Br and KNO_3 with concomitant growth of the 1385 cm^{-1} band at the expense of those at 1473 and 1286 cm^{-1},[12] and a similar exchange of weakly bound anionic ligands during KBr pellet preparation has been reported.[13] For KBr pellets with Fe(OEP)(NO_3), the effect is dependent on the grinding time as well (Figure S5 in the Supporting Information). Thus, we conclude that the 1385 cm^{-1} band commonly seen in such systems is likely due to free NO_3^- formed by solid-phase ion exchange with the KBr medium.

The lability of the nitrate ligand is emphasized by the reaction of Fe(TPP)(η^2-O_2NO) sublimed layers with ammonia. Exposure of **I** to excess NH_3 at 180 K led to the disappearance of the nitrate bands at 1527, 1273, and 967 cm^{-1} and the appearance of a strong absorbance at 1370 cm^{-1} (Figure S6 in the Supporting Information). The latter can be attributed to the intense ν_3(E) vibration of free NO_3^- in the matrix. This band has its isotopic counterpart at 1335 cm^{-1} in the experiments where NH_3 interacts with layered solid containing Fe(TPP)(η^2-$O_2{}^{15}NO$). Vigorous pumping on the system led to regeneration of **I**, so the likely scenario is the reversible process described by eq 1. The absence of a similar isotopically sensitive band in the spectra of products formed by the reaction of **I** with THF (Figures 1 and 2) indicates that analogous nitrate displacement does not occur with this weaker base.

$$\mathrm{Fe(TPP)}(\eta^2\text{-}\mathrm{O_2NO}) + 2\mathrm{NH_3} \rightleftharpoons \mathrm{Fe(TPP)(NH_3)_2}^+ + \mathrm{NO_3}^- \qquad (1)$$

In summary, the low-temperature interaction of THF with thin layers of Fe(Por)(η^2-O_2NO) results in the formation of six-coordinate nitrato complexes of iron porphyrins displaying IR bands in the vicinity of 1500, 1280, and 1000 cm^{-1}. Trans ligation is accompanied by the bidentate-to-monodentate linkage isomerization of the nitrato ligand, but the complex remains in the high spin state. This behavior contrasts with the analogous reaction with NO that gives a low-spin product. The known six-coordinate nitrato complexes of iron porphyrins all display monodentate nitrate coordination perhaps as the result of nonbonded repulsions between the oxygen atoms of bidentate nitrate and the nitrogen atoms of the porphyrin core. Given that the five-coordinate Fe(Por)(NO_3) complexes display both modes of coordination, e.g., Fe(OEP)(η^1-ONO_2)[9] and Fe(TPP)(η^2-O_2NO),[7] the energy difference between the η^1 and η^2 isomers must be small, as is also shown by density functional theory calculations.[3b] The complexes spectrally characterized in the present study and formulated as Fe(Por)(THF)(η^1-ONO_2) are stable only at temperatures lower than 180 K. At higher temperatures, they dissociate the weakly bound THF ligand, and at room temperature, the initial nitrato complexes Fe(Por)(η^2-O_2NO) are completely restored.

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Supporting Information Available: Reference 6b describing experimental details, Figure S1a,b demonstrating FTIR and UV−visible spectra of Fe(TTP)(η^2-O_2NO) and Fe(TTP)(THF)(η^1-ONO_2), respectively, Figure S2 representing FTIR spectra of Fe(OEP) and Fe(OEP)(η^1-ONO_2), Figure S3 demonstrating FTIR spectra of Fe(OEP)(η^1-ONO_2) and Fe(OEP)(THF)(η^1-ONO_2), Figure S4 demonstrating low-frequency FTIR spectra of FeTPP(η^2-O_2NO), Fe(TPP)(NO)(η^1-ONO_2), and Fe(TPP)(THF)(η^1-ONO_2), Figure S5 representing FTIR spectra of Fe(OEP)(η^1-ONO_2) in a thin layer and as KBr pellets with different extents of grinding, and Figure S6 representing FTIR spectral changes observed in the sublimed layer of Fe(TPP)(η^2-O_2NO) upon low-temperature interaction with NH_3. This material is available free of charge via the Internet at http://pubs.acs.org.

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