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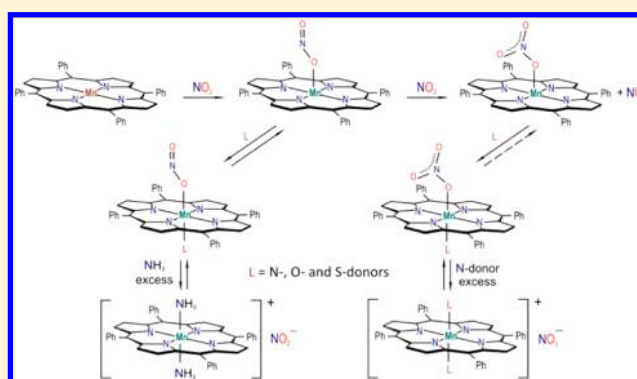
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## Six-Coordinate Nitrito and Nitrate Complexes of Manganese Porphyrin

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## Supporting Information

**ABSTRACT:** Reaction of small increments of NO<sub>2</sub> gas with sublimed amorphous layers of Mn<sup>II</sup>(TPP) (TPP = *meso*-tetraphenylporphyrinato dianion) in a vacuum cryostat leads to formation of the 5-coordinate monodentate nitrate complex Mn<sup>III</sup>(TPP)( $\eta^1$ -ONO<sub>2</sub>) (II). This transformation proceeds through the two distinct steps with initial formation of the five coordinate O-nitrito complex Mn<sup>III</sup>(TPP)( $\eta^1$ -ONO) (I) as demonstrated by the electronic absorption spectra and by FTIR spectra using differently labeled nitrogen dioxide. A plausible mechanism for the second stage of reaction is offered based on the spectral changes observed upon subsequent interaction of <sup>15</sup>NO<sub>2</sub> and NO<sub>2</sub> with the layered Mn(TPP). Low-temperature interaction of I and II with the vapors of various ligands L (L = O-, S-, and N-donors) leads to formation of the 6-coordinate O-nitrito Mn<sup>III</sup>(TPP)(L)( $\eta^1$ -ONO) and monodentate nitrate Mn<sup>III</sup>(TPP)(L)( $\eta^1$ -ONO<sub>2</sub>) complexes, respectively. Formation of the 6-coordinate O-nitrito complex is accompanied by the shifts of the  $\nu$ (N=O) band to lower frequency and of the  $\nu$ (N–O) band to higher frequency. The frequency difference between these bands  $\Delta\nu = \nu$ (N=O) –  $\nu$ (N–O) is a function of L and is smaller for the stronger bases. Reaction of excess NH<sub>3</sub> with I leads to formation of Mn(TPP)(NH<sub>3</sub>)( $\eta^1$ -ONO) and of the cation [Mn(TPP)(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> plus ionic nitrite. The nitrito complexes are relatively unstable, but several of the nitrate species can be observed in the solid state at room temperature. For example, the tetrahydrofuran complex Mn(TPP)(THF)( $\eta^1$ -ONO<sub>2</sub>) is stable in the presence of THF vapors (~5 mm), but it loses this ligand upon high vacuum pumping at RT. When L = dimethylsulfide (DMS), the nitrate complex is stable only to ~–30 °C. Reactions of II with the N-donor ligands NH<sub>3</sub>, pyridine, or 1-methylimidazole are more complex. With these ligands, the nitrate complexes Mn<sup>III</sup>(TPP)(L)( $\eta^1$ -ONO<sub>2</sub>) and the cationic complexes [Mn(TPP)(L)<sub>2</sub>]<sup>+</sup> coexist in the layer at room temperature, the latter formed as a result of NO<sub>3</sub><sup>–</sup> displacement when L is in excess.



## INTRODUCTION

Much of the physiological chemistry of the ubiquitous bioregulator nitric oxide (NO) and other nitrogen oxides is mediated by interactions of these species with metal centers, especially metalloporphyrins. For example, the protective effects of the nitrite anion (NO<sub>2</sub><sup>–</sup>) during incidents of hypoxic ischemia<sup>1</sup> has been attributed to its reduction by mammalian heme proteins to generate NO.<sup>2</sup> Nitrite can also be reduced by nitrite reductase (NiR) enzymes, many of which are heme proteins.<sup>2c</sup> In these contexts, we have proceeded to evaluate the interactions of various NO<sub>x</sub> species with sublimed layers of various metalloporphyrins in vacuum cryostats where the conditions (including T) can be precisely controlled to map relevant reactivities. Described here are such studies of the nitrito and nitrate complexes of *meso*-tetra-phenylporphyrin-manganese.

The ambidentate nitrite ion can coordinate to metals either at the oxygen to give O-nitrito (M-ONO) or at the nitrogen to

give N-nitrito (M-NO<sub>2</sub>, often called “nitro”) complexes. To our knowledge, a third potential coordination mode involving bidentate binding of both oxygens to the metal is unknown for metalloporphyrins and related metalloproteins. DFT calculations show that energy differences between O-nitrito and N-nitrito structures are small,<sup>3</sup> and there is evidence that the presence and nature of the ligand trans to the nitrite affects the relative stabilities of these linkage isomers. For example, the five-coordinate species Fe<sup>III</sup>(Por)(ONO) (Por = *meso*-tetraphenyl- or *meso*-tetra-*p*-tolyl-porphyrinato dianions, TPP<sup>2–</sup> or TTP<sup>2–</sup>) has O-nitrito coordination,<sup>4a</sup> but once the proximal ligand NH<sub>3</sub> is added, the N-nitrito isomer Fe(Por)(NH<sub>3</sub>)(NO<sub>2</sub>) is the more stable coordination complex.<sup>4b</sup>

For heme models and proteins, the most common is the N-nitrito coordination mode. The crystal structures for NO<sub>2</sub><sup>–</sup>

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complexes of several ferriheme NiR proteins demonstrate N-coordination.<sup>5</sup> However, there are several published structures of heme proteins with O-bound nitrito coordination.<sup>6</sup> Richter-Addo and co-workers have determined crystal structures of nitrite ion complexes for the ferric forms of myoglobin and hemoglobin (metMb and metHb, respectively) and found both to be O-nitrito species.<sup>6</sup> In this structure, the coordinated oxygen atom of nitrite forms a hydrogen bond with the NH group of histidine imidazole that stabilize O-nitrito coordination. Sustaining this suggestion, the H64 V mutant of metMb, which has the distal histidine replaced by a valine, binds  $\text{NO}_2^-$  as a N-nitrito complex.<sup>7</sup>

In analogy to the  $\text{Fe}(\text{Por})(\text{ONO})$  species, O-nitrito coordination is characteristic of the 5-coordinate  $\text{Mn}^{\text{III}}(\text{TPP})(\text{ONO})$  complex (I).<sup>8</sup> The crystal structure of the 6-coordinate manganese substituted met-myoglobin  $\text{Mn}(\text{III})\text{Mb}(\text{ONO})$  also reveals the O-bound nitrito coordination,<sup>9</sup> with the structural data also indicating hydrogen-bonding between distal His64 and coordinated oxygen atom of nitrite. However, to our knowledge, the 6-coordinate nitrite complexes of other Mn-porphyrin models have not been characterized. In this context, we describe here the use of sublimed porous layers of I as a synthetic precursor to the 6-coordinate complexes with various proximal ligands and use in situ spectroscopy to determine effect on the coordination mode of the nitrite ligand.

Nitrate complexes of metalloporphyrins are involved in key processes in nitrogen cycle and are likely transients formed as the result of heme mediated nitric oxide dioxygenation (NOD).<sup>10</sup> However, examples of 6-coordinate metalloporphyrin complexes of  $\text{NO}_3^-$  remain relatively rare. These include the trans aqua complex  $\text{Fe}(\text{Por})(\text{H}_2\text{O})(\eta^1\text{-ONO}_2)$  (Por not specified) described in a review,<sup>11</sup> the metastable nitrosyl and tetrahydrofuran species  $\text{Fe}(\text{Por})(\text{L})(\eta^1\text{-ONO}_2)$  (Por = TPP or TTP; L = NO, THF)<sup>12a,b</sup> obtained by the interaction of NO or THF with thin layers of the  $\text{Fe}(\text{Por})(\eta^2\text{-O}_2\text{NO})$  and the trans ammine species  $\text{Fe}(\text{Por})(\text{NH}_3)(\eta^1\text{-ONO}_2)$  obtained by reaction of NO with the dioxygen complex  $\text{Fe}(\text{Por})(\text{NH}_3)(\text{O}_2)$ .<sup>10d</sup> Recently, the 6-coordinate nitrate-complexes  $\text{Co}(\text{Por})(\text{L})(\eta^1\text{-ONO}_2)$  (Por = TPP or TTP, L =  $\text{NH}_3$  or pyridine (Py)) were demonstrated to result from NOD mediated by Coporphyrins.<sup>13</sup> These also proved to be thermally unstable and decomposed at temperatures above 210 K. However, to our knowledge there have been no reports of stable, 6-coordinate nitrate complexes of the manganese porphyrins.<sup>14</sup> We also describe here the formation and reactivities of such species.

## EXPERIMENTAL SECTION

The manganese(II) porphyrinates  $\text{Mn}(\text{Por})$  are very sensitive to oxygen and are readily oxidized. For this reason the more stable penta-coordinate complexes  $\text{Mn}(\text{TPP})(\text{B})$  with nitrogen bases (B is Py or piperidine) were used as the precursors to prepare sublimed layers. The complexes  $\text{Mn}(\text{TPP})(\text{B})$  were synthesized according to published methods.<sup>15</sup>

The low-temperature sublimate was prepared by placing a  $\text{Mn}^{\text{II}}(\text{TPP})(\text{B})$  sample in a Knudsen cell and heating to about 470 K under high vacuum ( $P = 3 \times 10^{-5}$  Torr). Evacuation for 2 h resulted in the elimination of the axial ligands B, as monitored by measurement of the pressure at the cryostat outlet. Liquid nitrogen was then poured into the cryostat, and the Knudsen cell was heated to 510 K, at which temperature sublimation of  $\text{Mn}(\text{TPP})$  onto the surface of the low-temperature (77 K) substrate (KBr or  $\text{CaF}_2$ ) occurred. In the latter case,  $\text{CaF}_2$  plates were also used as the optical windows of the cryostat. The metal tetra-arylporphyrin layers obtained in this manner are sponge-like and have high microporosity;<sup>16</sup> thus, 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 0.5–2.0 h to build up layers of thickness sufficient for UV–visible and IR spectral studies. The substrate with the  $\text{Mn}(\text{TPP})$  sublimed layers was then heated to room temperature under dynamic vacuum, after which small increments of  $\text{NO}_2$  gas were introduced for a short time period followed by a period of pumping out. This procedure led initially to formation of the O-nitrito species  $\text{Mn}(\text{TPP})(\eta^1\text{-ONO})$  (I) that is oxidized to the nitrate complex  $\text{Mn}(\text{TPP})(\eta^1\text{-ONO}_2)$  (II) after adding more  $\text{NO}_2$ .<sup>17</sup> FTIR and UV–visible spectra were measured after each  $\text{NO}_2$  introduction to ensure formation of I and II. After this was accomplished, a volatile ligand ( $\text{NH}_3$ , Py, 1-methylimidazole (1-Melm), THF or DMS) was fed to the cryostat containing cooled by  $\text{LN}_2$  layers of I or II and the FTIR or electronic absorption spectra were measured in the course of slow warming.

For solution experiments the thermally stable 6-coordinate complexes were scraped from the surface of the KBr substrate and put on the bottom of the flask fitted with an adapter, which allowed for syringe access and protected from air with a rubber septum. The small quantity of degassed  $\text{CCl}_4$  was transferred to this flask using a vacuum line and  $\text{LN}_2$ . The solution prepared in this way was sampled with a Hamilton gastight syringe and injected into the 0.6 mm IR cell through the septum. FTIR spectra were measured using the spectrum of  $\text{CCl}_4$  as a background.

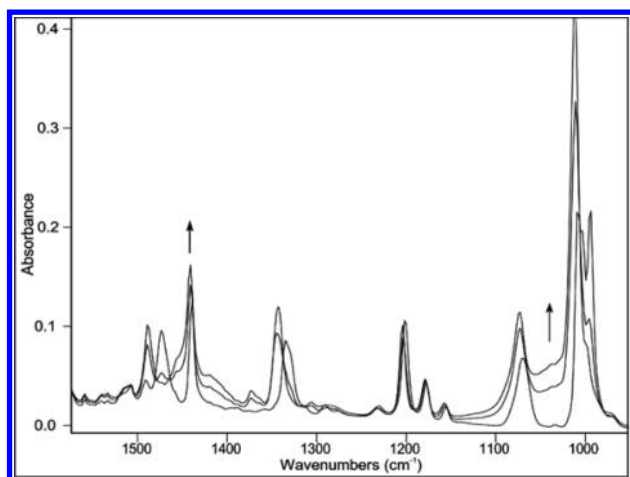
$\text{NO}_2$  ( $^{15}\text{NO}_2$ ), obtained by oxidation of NO ( $^{15}\text{NO}$ ) with excess of pure dioxygen, was dried over  $\text{P}_2\text{O}_5$  and then was purified by fractional distillation until a pure white solid was obtained. For isotopic experiments,  $^{15}\text{NO}$  with 98.5% enrichment was purchased from the Institute of Isotopes, Republic of Georgia.  $\text{N}^{18}\text{O}_2$  ( $^{15}\text{N}^{18}\text{O}_2$ ) was synthesized according to the following procedure. The 1:2 mixture of  $\text{N}_2$  ( $^{15}\text{N}_2$ ) and  $^{18}\text{O}_2$  gases (Cambridge Isotopic Laboratories) was introduced into an evacuated glass balloon provided with inserted electrodes. Upon continuous electric discharge the colorless gas mixture turned to reddish-brown indicating the formation of  $\text{N}^{18}\text{O}_2$  ( $^{15}\text{N}^{18}\text{O}_2$ ).

FTIR spectra were recorded using a “Nexus” spectrometer from Thermo Nicolet Corporation and UV–visible spectra on a Specord M-40 spectrophotometer.

## RESULTS AND DISCUSSION

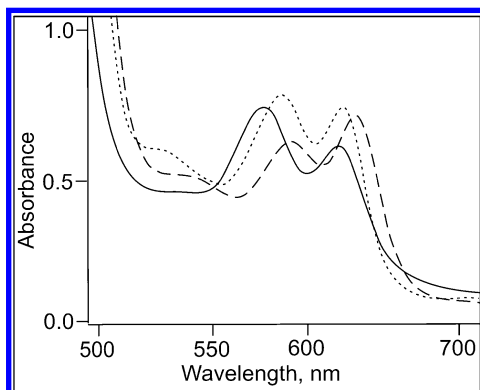
**Reaction of Nitrogen Dioxide Gas with Solid  $\text{Mn}^{\text{II}}(\text{TPP})$ .** Studies by Kurtikyan et al.<sup>17</sup> have shown that the reaction of  $\text{NO}_2$  with amorphous layers of  $\text{Mn}(\text{TPP})$  eventually leads to formation of the nitrate analog  $\text{Mn}(\text{TPP})(\eta^1\text{-ONO}_2)$  (II), which was characterized spectroscopically in these layers. II had previously been prepared and structurally characterized by Suslick and Watson<sup>8</sup> via the reaction of  $\text{Mn}(\text{TPP})(\text{Cl})$  with aqueous  $\text{Ag}(\text{NO}_3)$  in a biphasic  $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$  reaction mixture. The formation of insoluble  $\text{AgCl}$  effectively removed  $\text{Cl}^-$  from the reaction mixture, allowing the weaker binding  $\text{NO}_3^-$  to coordinate. The X-ray structure of the  $\text{Mn}(\text{TPP})(\text{NO}_3)_2 \cdot 2\text{C}_6\text{H}_6$  crystals showed monodentate coordination of nitrate.

It will be shown here that the reaction of  $\text{NO}_2$  gas with amorphous layers of  $\text{Mn}(\text{TPP})$  proceeds via two distinct stages. At low  $\text{NO}_2$  pressures and short contact time, new IR bands in the vicinity of 1445 and 1040  $\text{cm}^{-1}$  grow in intensity (Figure 1). In these spectral ranges the porphyrin itself has intense bands, and in amorphous layers the bands of the new species are not distinctly resolved. However, when the  $^{15}\text{NO}_2$ ,  $\text{N}^{18}\text{O}_2$ , and  $^{15}\text{N}^{18}\text{O}_2$  isotopomers are used, the high frequency band in the vicinity of 1450  $\text{cm}^{-1}$  shifts to 1420, 1410, and 1384  $\text{cm}^{-1}$ , respectively, and are clearly seen (see Supporting Information Figure S1 the spectrum of  $\text{Mn}(\text{TPP})(^{18}\text{O}^{15}\text{N}^{18}\text{O})$ ). The band at about 1040  $\text{cm}^{-1}$  also undergoes low-frequency shift, but overlap with an intense porphyrin band near 1000  $\text{cm}^{-1}$  prevents determining its frequency distinctly. These bands



**Figure 1.** Formation of Mn-porphyrin O-nitrito complex **I** upon reaction of small  $\text{NO}_2$  increments ( $\sim 0.1$  Torr) with amorphous layer of Mn(TPP).

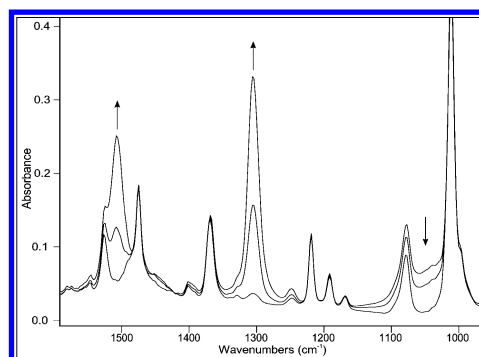
appear at frequencies corresponding to  $\nu(\text{N}=\text{O})$  and  $\nu(\text{O}-\text{N})$  of coordinated O-nitrito group,<sup>18</sup> as was seen in the IR spectrum of crystalline **I** at 1444 and 1029  $\text{cm}^{-1}$ ,<sup>8</sup> the X-ray structure of which reveals O-coordination.<sup>8</sup> Thus, we conclude that the first species formed in this reaction is the O-nitrito complex (**I**). Consistent with this assignment, the electronic absorption spectrum of this layered species (Figure 2, dashed line) is similar to that of **I** in benzene solution.



**Figure 2.** Electronic absorption spectra of layered Mn(TPP) (solid), **I** (dashed), and **II** (dotted line).

It should be noted that the formation of **I** is accompanied by the considerable other changes in the vibrational spectrum. Most of bands attributed to porphyrin ring vibrations<sup>19</sup> undergo shifts to higher frequency (See Supporting Information Figure S2), thus the shifting of these bands shows that none of the initial  $\text{Mn}^{\text{II}}(\text{TPP})$  remains in the layer at this stage of reaction. Especially useful for this purpose is the band corresponding to a porphyrin core deformational mode at 427  $\text{cm}^{-1}$  that shifts to 455  $\text{cm}^{-1}$  upon formation of **I**.

Supplying additional  $\text{NO}_2$  portions into the cryostat leads to the FTIR spectral changes represented in Figure 3. The nitrite band in the vicinity of 1040  $\text{cm}^{-1}$  disappears and new intense bands appear at 1470 and 1284  $\text{cm}^{-1}$ . These bands underwent expected shifts when labeled the nitrogen dioxides  $^{15}\text{NO}_2$ ,  $\text{N}^{18}\text{O}_2$ , and  $^{15}\text{N}^{18}\text{O}_2$  were used. (Supporting Information, Figure S3 for  $^{15}\text{N}$ -containing species). The data summarized in Table 1 and clearly indicate formation of the nitrate complex **II**.



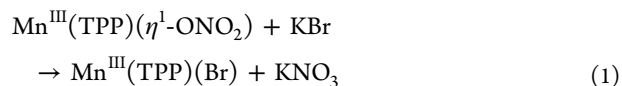
**Figure 3.** FTIR spectral changes resulting from stepwise addition of  $\text{NO}_2$  increments ( $P \approx 0.3$  Torr, 2–3 min exposure) to Mn(TPP)-(ONO) in sublimed layers and evacuation after each step.

**Table 1.** IR Frequencies in  $\text{cm}^{-1}$  of Differently Labeled Nitrate Group Coordinated in Monodentate Fashion in 5-Coordinate Complexes of Metalloporphyrins

adduct	$\nu_a(\text{NO}_2)$	$\nu_s(\text{NO}_2)$	$\nu(\text{O}-\text{N})$	Q bands	ref
Mn(TPP)( $\eta^1$ -ONO <sub>2</sub> )·2C <sub>6</sub> H <sub>6</sub> crystalline	1474	1286			8
Mn(TPP)( $\eta^1$ -ONO <sub>2</sub> ) amorphous	1470	1284	998	580, 615	17
Mn(TPP)( $\eta^1$ - <sup>15</sup> N <sup>18</sup> O <sub>2</sub> )	1433	1261	985		this work
Mn(TPP)( $\eta^1$ - <sup>18</sup> O <sup>15</sup> N <sup>18</sup> O <sub>2</sub> )	1448	1258	959		this work
Mn(TPP)( $\eta^1$ - <sup>18</sup> O <sup>15</sup> N <sup>18</sup> O <sub>2</sub> )	1412	1228	957		this work
Fe(OEP)( $\eta^1$ -ONO <sub>2</sub> )	1515	1276	980		12b

Notably, the electronic spectrum of this new species (Figure 2) is very close to that reported for **II** in benzene solution.<sup>8</sup>

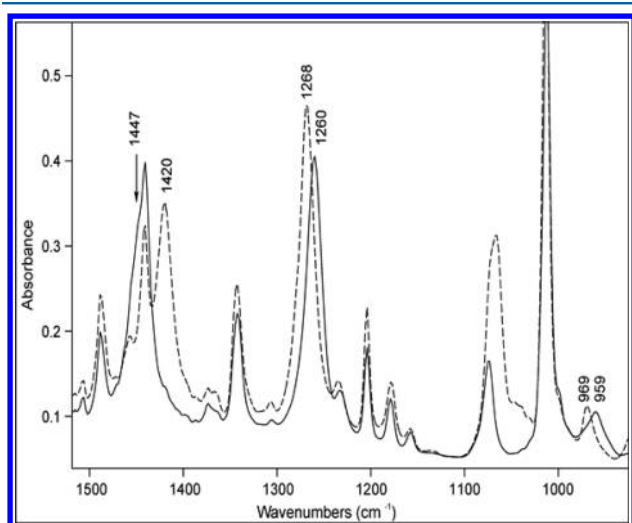
In these compounds, the nitrate ion is O-coordinated in monodentate fashion.<sup>8</sup> The three IR-active stretching modes expected for this structure would be a low-frequency  $\nu(\text{O}-\text{N})$  band for the coordinated oxygen and two (symmetric and asymmetric) modes for the uncoordinated  $\text{NO}_2$  fragment. Three bands at 1474, 1385, and 1286  $\text{cm}^{-1}$  were reported in the IR spectrum of crystalline **II** taken in KBr pellets.<sup>8</sup> The frequencies of the first and third bands are very close to those seen in the amorphous layers, the minor frequency differences easily explained by crystal packing effects. The band at 1385  $\text{cm}^{-1}$  is absent in our spectra. However, as demonstrated earlier for **II**<sup>8</sup> and also for Fe(OEP)( $\eta^1$ -ONO<sub>2</sub>),<sup>12b</sup> this discrepancy is due to ion exchange (eq 1) that occurs upon grinding nitrate complexes together with KBr. The band at 1385  $\text{cm}^{-1}$  can be attributed to the degenerate  $\nu_3(\text{E})$  vibration of the free nitrate anion.



By analogy with other nitrate complexes<sup>18</sup> the bands at 1470 and 1284  $\text{cm}^{-1}$  can be assigned to the  $\nu_a(\text{NO}_2)$  and  $\nu_s(\text{NO}_2)$  vibrations of the uncoordinated  $\text{NO}_2$  fragment. Hence the third band belonging to the  $\nu(\text{O}-\text{N})$  stretching for the coordinated oxygen usually disposed in the range of 1000  $\text{cm}^{-1}$ <sup>18</sup> is most likely masked by the intense porphyrin band in this range. This band is indeed apparent at 959  $\text{cm}^{-1}$  in the spectra of species containing the <sup>18</sup>O labeled nitrate group (Table 1, Figure 4, solid line). From Figure 4 it is also clear that this band has low



intensity and readily can be obscured in the unlabeled nitrate complex by the intense porphyrin band.



**Figure 4.** FTIR spectra of  $\text{Mn}(\text{TPP})(\eta^1\text{-}^{18}\text{ON}^{18}\text{O}_2)$  (solid line) and of  $\text{Mn}(\text{TPP})(\text{THF})(\eta^1\text{-}^{18}\text{ON}^{18}\text{O}_2)$  (dashed line).

The IR bands of porphyrin core are at the same positions for the  $\eta^1$ -nitrito and nitrate species but are shifted from those of  $\text{Mn}^{\text{II}}(\text{TPP})$ . The latter species has a high-spin  $d^5$  configuration and an ionic radius too large to form a planar porphyrinato complex.<sup>20</sup> While the  $\text{Mn}^{\text{III}}$  nitrito and nitrate complexes are also high-spin,<sup>8</sup> they have the  $d^4$  configuration and the vacancy in the  $d_{x^2-y^2}$  orbital allows the metal to sit closer to the plane of porphyrin. This changes the overlap of the manganese  $d_\pi$  orbitals with the porphyrin  $e_g(\pi^*)$  orbitals resulting in changes in the porphyrin ring vibrations.

From these data, it is clear that the formation of nitrate complex in the course of  $\text{NO}_2$  reaction with  $\text{Mn}^{\text{II}}(\text{TPP})$  proceeds via 2 stages. During the first, which is seen for short reaction times with a very low  $P_{\text{NO}_2}$ , simple  $\text{NO}_2$  coordination gives the 5-coordinate O-nitrito complex  $\text{Mn}^{\text{III}}(\text{TPP})(\eta^1\text{-ONO})$ . The formation of **I** upon reaction of low concentration  $\text{NO}_2$  gas with the solid  $\text{Mn}(\text{TPP})$  was also reported by Suslick and Watson.<sup>8</sup> Subsequent reaction at higher  $P_{\text{NO}_2}$  leads to the slower formation of the nitrate species **II**, presumably with the concomitant formation of  $\text{NO}$  (Scheme 1). The latter step draws support from the observation that when, at the conclusion of this procedure, the gaseous contents were frozen onto the cryostat wall with  $\text{LN}_2$ , a bluish solid was observed. This is a qualitative indication of the presence of  $\text{N}_2\text{O}_3$  formed by reaction of  $\text{NO}$  with excess  $\text{NO}_2$ .

The analogous  $\text{NO}_2$  reaction with  $\text{Fe}(\text{TPP})$  also results in formation of a nitrate complex<sup>21</sup> but in that case, nitrate

coordination is bidentate,  $\text{Fe}(\text{TPP})(\eta^2\text{-O}_2\text{NO})$ .<sup>11</sup> The characteristic differences between IR spectra of mono- and bidentate coordinated nitrate complexes of metalloporphyrins have been described previously.<sup>16c</sup>

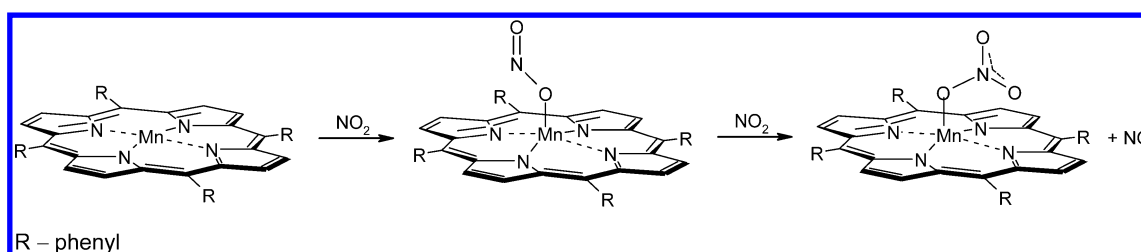
**Scenarios for the  $\text{NO}_2$  Oxidation of **I**.** For conversion of the O-nitrito complex to the O-nitrate analog, two scenarios can be suggested. The first would involve oxygen atom transfer from free  $\text{NO}_2$  to the nitrogen of the  $\text{Mn-O-N=O}$  moiety to give the nitrate analog (Scheme 2, a). The alternative mechanism would involve attack of  $\text{NO}_2$  at the coordinated O atom to give a new  $\text{Mn}(\eta^1\text{-ONO}_2)$  species with simultaneous displacement of  $\text{NO}$  from the originally coordinated nitrite ion (Scheme 2, b).

These possibilities can be probed by using isotope labeling experiments. If the first scenario were operating, the reaction of  $\text{NO}_2$  with the  $^{15}\text{N}$ -labeled O-nitrito complex  $\text{Mn}(\text{TPP})(\eta^1\text{-O}^{15}\text{NO})$  should give the labeled nitrate product  $\text{Mn}(\text{TPP})(\eta^1\text{-O}^{15}\text{NO}_2)$ , while the second scenario should give the unlabeled analog. The results of such a study are demonstrated in the Supporting Information, Figure S4, in which the sequential changes of the FTIR spectra upon addition of new  $\text{NO}_2$  increments to layered  $\text{Mn}(\text{TPP})(\eta^1\text{-O}^{15}\text{NO})$  are shown. It is seen from these spectra that this procedure is accompanied mostly by the appearance and growth of bands at 1284 and 1471  $\text{cm}^{-1}$  characteristic of  $\text{Mn}(\text{TPP})(\eta^1\text{-ONO}_2)$  (Table 1). Simultaneously, there was some growth in the band at 1261  $\text{cm}^{-1}$  characteristic of  $\text{Mn}(\text{TPP})(\eta^1\text{-O}^{15}\text{NO}_2)$ , but this was at least an order of magnitude less than that of the 1284  $\text{cm}^{-1}$  band.

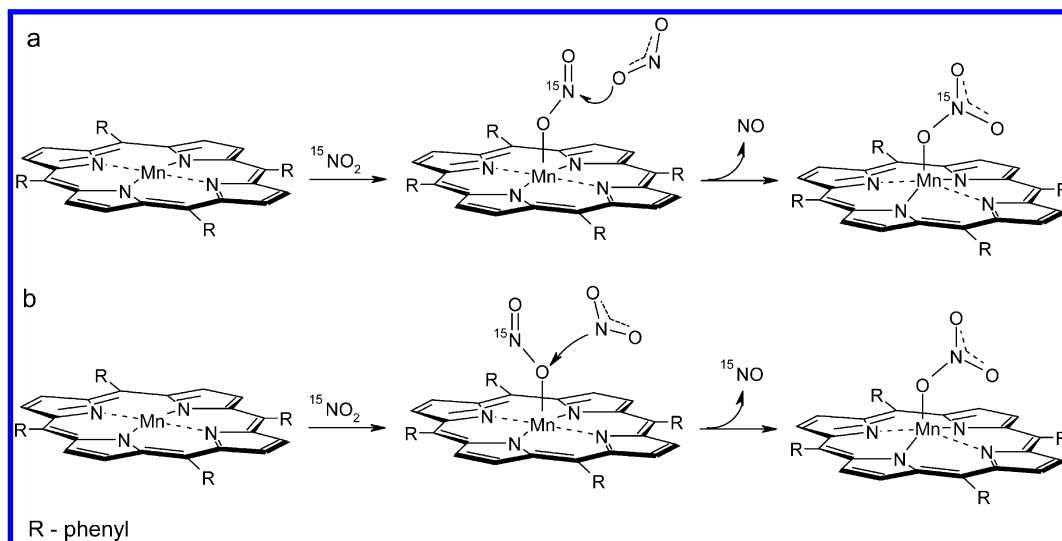
The experiments with sequential introduction of  $^{15}\text{NO}_2$  and  $\text{NO}_2$  increments to the  $\text{Mn}(\text{TPP})$  layer gave spectral changes indicating formation primarily of  $\text{Mn}(\text{TPP})(\eta^1\text{-ONO}_2)$  consistent with the second of these scenarios being dominant. However, if this is so, then why was some of labeled product formed upon sequential additions of  $^{15}\text{NO}_2$  and  $\text{NO}_2$  increments to the  $\text{Mn}(\text{TPP})$  layer (the first scenario described above). Although, this might indicate a lesser but active role for oxygen atom transfer to the O-coordinated nitrite, we believe the more likely explanation is related to the isotope scrambling reaction shown in eq 2. Once  $^{15}\text{NO}$  is released by the attack of  $\text{NO}_2$  on  $\text{Mn}(\text{TPP})(\eta^1\text{-O}^{15}\text{NO})$  this should undergo exchange with the free  $\text{NO}_2$  present. The resulting  $^{15}\text{NO}_2$  formed would then give the labeled product upon further reaction with the O-nitrito complex. This isotope-scrambling reaction has been shown to occur in analogous layers at very low temperatures<sup>16c</sup> and should readily proceed at room temperature conditions of the present experiment. Thus, we conclude that  $\text{NO}_2$  oxidation of the O-coordinated nitrite is proceeding by attack of  $\text{NO}_2$  at the coordinated oxygen of the  $\text{Mn-O}^{15}\text{NO}$  moiety.



**Scheme 1**



Scheme 2



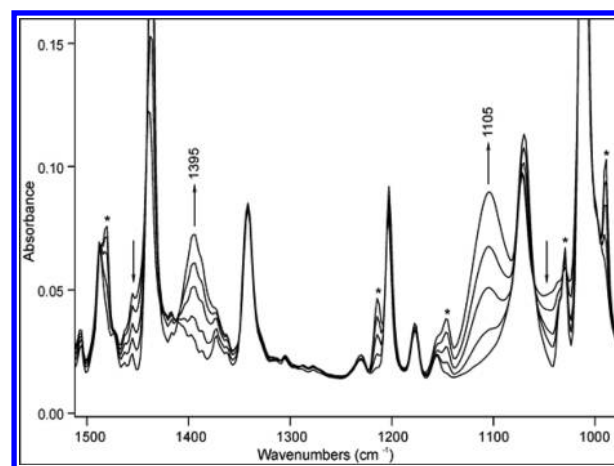
It is, however, noteworthy that above-mentioned isotope labeling experiments can not completely rule out a mechanism that involves homolytic disruption of the  $\text{Mn}^{\text{III}}\text{O}-^{15}\text{NO}$  bond of coordinated nitrito ligand to give a  $\text{Mn}^{\text{IV}}=\text{O}$  moiety that then reacts with free  $\text{NO}_2$  to give the  $\text{Mn}(\text{TPP})(\eta^1\text{-ONO}_2)$  end product. For example, this might be facilitated by  $\text{NO}_2$  attack at the  $^{15}\text{N}$  atom of the nitrito ligand to form  $\text{Mn}^{\text{IV}}=\text{O}$  plus dinitrogen trioxide. However, this would appear to be energetically much less likely than the concerted pathway described by the second scenario.

It is worth mentioning that an analogous reaction takes place in the case of iron porphyrins. Interaction of  $\text{NO}_2$  with  $\text{Fe}(\text{Por})$  leads initially to formation of nitrito complex and then to nitrate species.<sup>3c</sup> In contrast the Co-porphyrins reveal different reactivity; after formation of the 5-coordinate N-nitrito-complexes  $\text{Co}(\text{TPP})(\text{NO}_2)$  at low  $\text{NO}_2$  pressures, introduction of the new  $\text{NO}_2$  increments results in oxidation of porphyrin ring with formation of the  $\pi$ -cation radical.<sup>22</sup>

It will be shown below that the second stage of the reaction represented in Scheme 1 takes place also when nitrito complex is 6-coordinated. As a result, the 6-coordinate nitrate complex formed from the reaction of  $\text{Mn}(\text{TPP})(1\text{-MeIm})(\text{ONO})$  with  $\text{NO}_2$  is fairly stable in the solid state. This observation is of biological significance since in most Mn-substituted heme proteins, the metal is coordinated with the imidazole moiety of a proximal histidine.<sup>9</sup>

**Six-Coordinate O-Nitrito Complexes of Mn(TPP).** After preparation of the nitrito complex I by interaction of small increments of  $\text{NO}_2$  with a thin layer of  $\text{Mn}^{\text{II}}(\text{TPP})$  (Figure 1), the sample was cooled with  $\text{LN}_2$ , and then various ligands in the small quantities controlled with mercury manometer were introduced to the cryostat. The FTIR and UV-visible spectra were measured in the course of slow warming. At various temperatures, at which the ligands gain sufficient mobility to penetrate into the layers, the intensities of the  $\nu(\text{N}=\text{O})$  and  $\nu(\text{N}-\text{O})$  bands of coordinated O-nitrito group in I began to decrease, and new bands grew at frequencies disposed at lower than  $\nu(\text{N}=\text{O})$  and higher than  $\nu(\text{N}-\text{O})$  frequencies of I. As an example, such spectral changes for  $L = \text{Py}$  are represented in Figure 5.

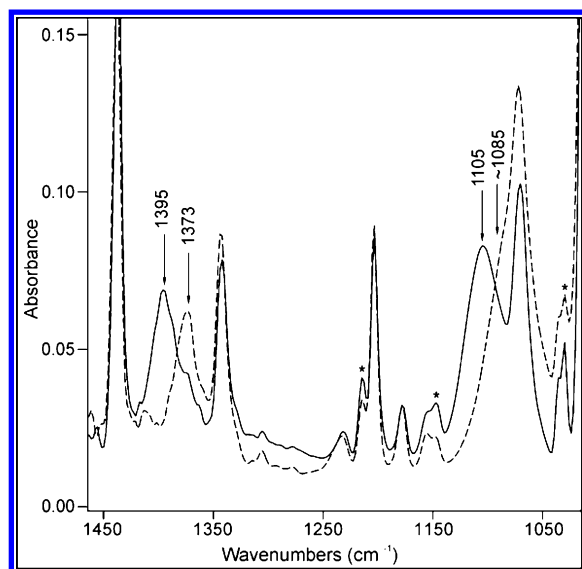
The low-frequency shift of  $\nu(\text{N}=\text{O})$  and high-frequency shift of  $\nu(\text{N}-\text{O})$  bands are more clearly seen in the  $^{15}\text{N}$ -labeled



**Figure 5.** FTIR spectral changes upon introducing 0.3 Torr equivalent of Py into the cryostat containing layered  $\text{Mn}(\text{TPP})(\eta^1\text{-ONO})$  and warming slowly from 170 to 210 K. The bands attributed to excess Py are denoted by asterisk.

species. As an example, the spectra of  $\text{Mn}(\text{TPP})(\eta^1\text{-O}^{15}\text{NO})$  before and after interaction with DMS are represented in Supporting Information, Figure S5. These bands reveal the expected isotopic shifts (Figure 6 for  $L = \text{Py}$ , Table 2), thus they can unambiguously be assigned to the species containing coordinated nitrite.

As noted above, the nitrite ion can coordinate to metals either at the oxygen ( $\text{M}-\text{ONO}$ ) or at the nitrogen ( $\text{M}-\text{NO}_2$ ). Infrared spectroscopy provides a diagnostic for differentiating between O-nitrito ( $\eta^1\text{-ONO}$ ) and N-nitrito ( $\eta^1\text{-NO}_2$ ) coordination.<sup>18</sup> The high frequency stretching modes are much more separated for the O-bound than for the N-bound species. Indeed, for the particular case of metalloporphyrins for the N-nitrito complexes  $\text{Fe}(\text{TPP})(L)(\text{NO}_2)$  ( $L = \text{N}$ ,  $\text{S}$ , and  $\text{O}$ -donor ligands) the asymmetric  $\nu_a(\text{NO}_2)$  and symmetric  $\nu_s(\text{NO}_2)$  modes of coordinated  $\text{NO}_2$  are located in the vicinity of 1400 and 1300  $\text{cm}^{-1}$ .<sup>4b,23</sup> The same bands of 6-coordinate N-nitrito complexes for  $\text{Co}(\text{TPP})$  are disposed in the vicinity of 1440 and 1300  $\text{cm}^{-1}$  for *trans*- $\text{N}$ -,  $\text{S}$ -, and  $\text{O}$ -donor ligands.<sup>24</sup> The distinctive feature of these bands is much the higher intensity of the lower frequency  $\nu_s(\text{NO}_2)$  band. Additionally, a fairly intense



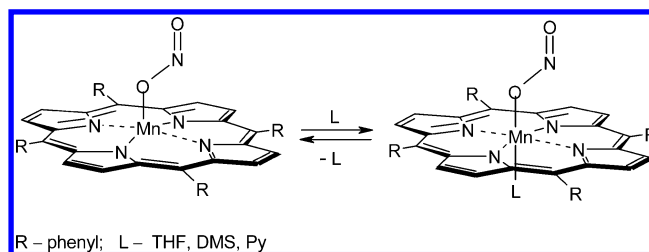
**Figure 6.** FTIR spectra of the product formed by the reaction of Py with Mn(TPP)(ONO) (solid line) and with Mn(TPP)(O<sup>15</sup>N) (dashed line) at 210 K. The bands attributed to excess Py are denoted by asterisk.

band for the deformational vibration  $\delta(\text{NO}_2)$  is disposed in the vicinity of  $820\text{ cm}^{-1}$ .

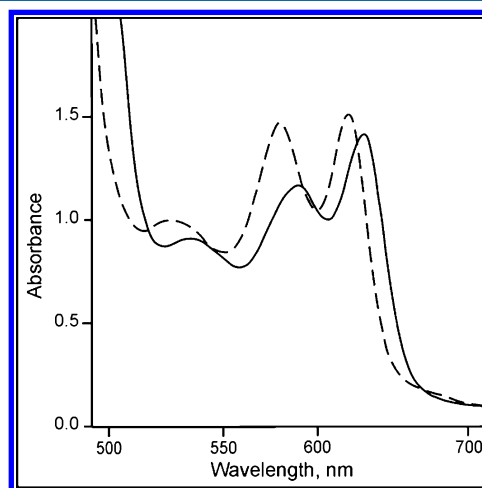
The limited examples of O-nitrito complexes of metal-porphyrins include the 5-coordinate nitrito complexes of iron- and manganese-porphyrins<sup>4,8</sup> and the 6-coordinate nitrito complexes of Fe-porphyrins with *trans*-NO,<sup>3b,4a</sup> -NH<sub>3</sub>,<sup>4b</sup> and -THF<sup>23</sup> ligands. The 5-coordinate Fe(Por)( $\eta^1$ -ONO) (Por = TPP and TTP) complexes displayed IR bands in the vicinity of 1520, 900, and  $750\text{ cm}^{-1}$  assigned to  $\nu(\text{N}=\text{O})$ ,  $\nu(\text{N}-\text{O})$ , and  $\delta(\text{ONO})$  of the O-coordinated nitrito ligand.<sup>4a</sup> These bands shift to about 1470, 970, and  $825\text{ cm}^{-1}$  upon formation of the 6-coordinate species Fe(Por)(NH<sub>3</sub>)( $\eta^1$ -ONO) upon reaction of gaseous NH<sub>3</sub> with layered Fe(Por)( $\eta^1$ -ONO) at low-temperature.<sup>4b</sup> Bands in the range of 1510 and  $930\text{ cm}^{-1}$  were reported for the metastable O-nitrito species Fe(TPP)(NO)( $\eta^1$ -ONO) obtained by photolysis of the N-nitrito complex Fe(TPP)(NO)(NO<sub>2</sub>) in a low-temperature KBr pellet,<sup>3b</sup> and also by low-temperature reaction of NO gas with sublimed layers of Fe(Por)( $\eta^1$ -ONO).<sup>3c</sup> Thus, transition from 5- to 6-coordination is accompanied by the low-frequency shift of  $\nu(\text{N}=\text{O})$  and high-frequency shift of  $\nu(\text{N}-\text{O})$  band. Additionally, in all these cases, the intensities of these bands are

close to each other in contrast to the N-nitrito analogs. Based on this spectral analysis, we conclude that the spectral changes observed for the reactions of I with various ligands can be interpreted in terms of forming the 6-coordinate O-nitrito Mn(TPP)(L)( $\eta^1$ -ONO) complexes as represented in Scheme 3.

**Scheme 3**



Optical spectra also display changes upon formation of these species. The Q-bands of I in the UV-visible spectrum undergo the blue shifts and change their relative intensities upon formation of the 6-coordinate complexes (Figure 7 for the Py derivative, Table 2).



**Figure 7.** UV-visible spectra of I (solid line) and Mn(TPP)(Py)(ONO) (dashed line) at 200 K.

It should be noted here that the above-mentioned 6-coordinate O-nitrito complexes of iron-porphyrins have been

**Table 2.** Frequencies of Stretching Vibrations ( $\text{cm}^{-1}$ ) for the Coordinated Nitrito Ligand in the 6-Coordinated Complexes of Mn- and Fe-Porphyrins with the Various Electron Donor Ligands<sup>a</sup>

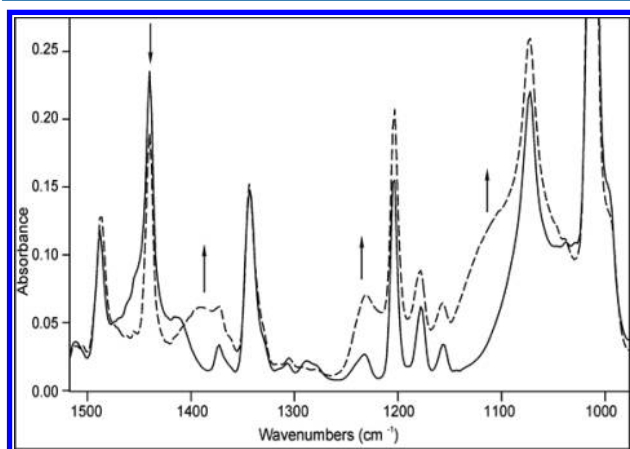
complex	$\nu(\text{N}=\text{O})$	$\nu(\text{N}-\text{O})$	$\Delta\nu = \nu(\text{N}=\text{O}) - \nu(\text{N}-\text{O})$	Q-bands (nm)	ref
Mn(TPP)( $\eta^1$ -ONO)	1445 (1421)	1040 (~1020)	405 (401)	587, 625	this work
Mn(TPP)(DMS)( $\eta^1$ -ONO)	1416 (1394)	~1072 (1052)	344 (342)	581, 622	this work
Mn(TPP)(THF)( $\eta^1$ -ONO)	1415 (1391)	1084 (1055)	331 (336)	577, 616	this work
Mn(TPP)(Py)( $\eta^1$ -ONO)	1398 (1375)	1105 (1084)	293 (291)	576, 616	this work
Mn(TPP)(NH <sub>3</sub> )( $\eta^1$ -ONO)	1384 (1357)	1115 (1094)	269 (263)		this work
Mn(TPP)(1-MeIm)( $\eta^1$ -ONO)	1382(1356)	1121 (~1100)	261 (256)	581, 619	this work
Fe(TPP)( $\eta^1$ -ONO)	1526 (1499)	904 (885)	622 (614)	508,577sh, 659, 689	4a
Fe(TPP)(THF)( $\eta^1$ -ONO)	1481 (1448)	963 (946)	518 (502)		23a
Fe(TPP)(NH <sub>3</sub> )( $\eta^1$ -ONO)	1475 (1445)	971 (952)	504 (493)	552, 595sh, 650sh, 695sh	4b
Fe(TPP)(NO)( $\eta^1$ -ONO)	1496 (1471)	938 (920)	558 (551)	548, 574	3c

<sup>a</sup>The data for <sup>15</sup>N-labeled nitrito group are given in the parentheses.

observed only at very low-temperatures. With *trans*-NH<sub>3</sub> and -NO ligands the O-nitrito complexes could be detected at temperatures lower than ~150 K. Further warming led to the isomerization of O-nitrito to N-nitrito coordination. With THF as a trans ligand, both O-nitrito and N-nitrito isomers were present in the narrow temperature interval 130–160 K. Further warming led to elimination THF ligand and restored the 5-coordinate O-nitrito complexes Fe(Por)( $\eta^1$ -ONO).<sup>23a</sup> In contrast, for the Mn-derivatives there is no spectral evidence indicating a change in the mode of nitrite coordination. Upon temperature increase the only reaction of the 6-coordinate species was dissociation of the proximal ligand to restore the parent O-nitrito complex I.

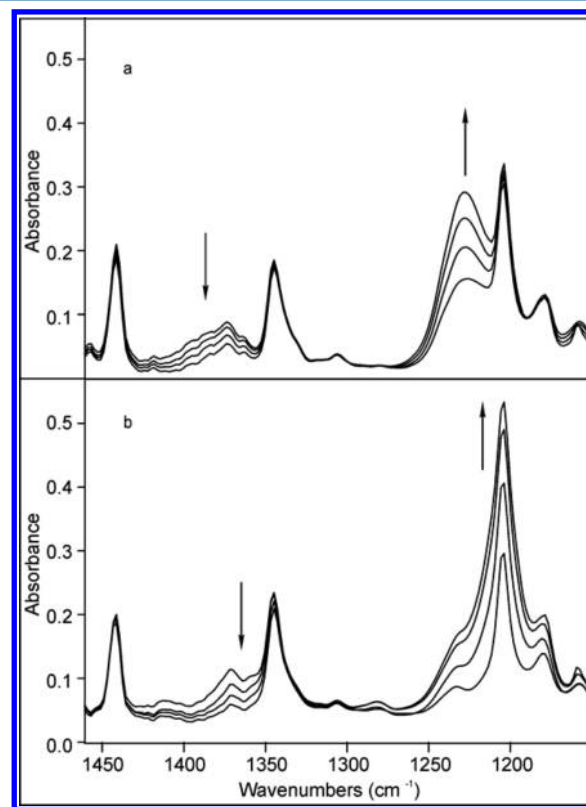
The FTIR data summarized in Table 2 provide the basis for assigning vibrational frequencies for coordinated O-nitrito group for the 6-coordinate nitrite complexes of Mn(TPP), and these assignments are sustained by the data for <sup>15</sup>NO<sub>2</sub> labeled isotopomers. Table 2 also suggests an interesting correlation between the nature of the ligand trans to the O-nitrito group and the difference between the frequencies of  $\nu(\text{N}=\text{O})$  and  $\nu(\text{N}-\text{O})$  vibrational modes  $\Delta\nu = \nu(\text{N}=\text{O}) - \nu(\text{N}-\text{O})$ , which follows the order: 1-MeIm < NH<sub>3</sub> < Py < THF < DMS. Electronic communication between the axial ligands, L and NO<sub>2</sub>, occurs largely through the metal d<sub>z<sup>2</sup></sub> and d<sub>xz</sub>, d<sub>yz</sub> orbitals. In this context, we propose that  $\Delta\nu$  is reflective of the net charge transfer to the nitrito group with the smaller  $\Delta\nu$  representing more charge transfer. The DMS and THF are weak  $\sigma$ -donor ligands and their influence on the frequencies of  $\nu(\text{N}=\text{O})$  and  $\nu(\text{N}-\text{O})$  stretching modes of I is noticeably less than for the stronger N-donor ligands. The latter  $\Delta\nu$  does not correlate with the Bronsted base strengths of these ligands with 1-MeIm intermediate between Py and NH<sub>3</sub>.<sup>25</sup> However, the observed order may be rationalized by taking into account the modest  $\pi$ -donor character of 1-MeIm, while NH<sub>3</sub> is a  $\sigma$ -donor only and Py is a  $\pi$ -acceptor.<sup>26</sup>

Introduction of NH<sub>3</sub> (~0.1 Torr equivalent) to the cryostat containing layered I at 120 K followed by slow warming to 170 K led to the FTIR spectral changes represented in Figure 8. The  $\nu(\text{N}=\text{O})$  band of I in the vicinity of 1445 cm<sup>-1</sup> disappears, and new bands in the spectral ranges of 1400, 1230, and 1120 cm<sup>-1</sup> appear. The bands at 1400 and 1120 cm<sup>-1</sup> grow with correlating intensities and have their isotopic counterparts seen for the reaction of NH<sub>3</sub> with Mn(TPP)-



**Figure 8.** FTIR spectra of I (solid line) after supplying the cryostat with ~0.1 Torr equiv NH<sub>3</sub> at 120 K and slow warming to 170 K (dashed line).

(O<sup>15</sup>NO) (see Table 2). By analogy with the other I + L systems they can be assigned to  $\nu(\text{N}=\text{O})$  and  $\nu(\text{O}-\text{N})$  of Mn(TPP)(NH<sub>3</sub>)(ONO). The band at 1228 cm<sup>-1</sup> is also isotope sensitive and greatly enhances in intensity at the expense of the former bands when the higher pressures of NH<sub>3</sub> are supplied in to cryostat as is demonstrated in Figure 9. This



**Figure 9.** FTIR spectral changes observed upon supplying 3 Torr equivalent NH<sub>3</sub> to the cryostat and warming from 120 to 170 K. (a) Mn(TPP)(ONO) + NH<sub>3</sub> and (b) Mn(TPP)(O<sup>15</sup>NO) + NH<sub>3</sub>.

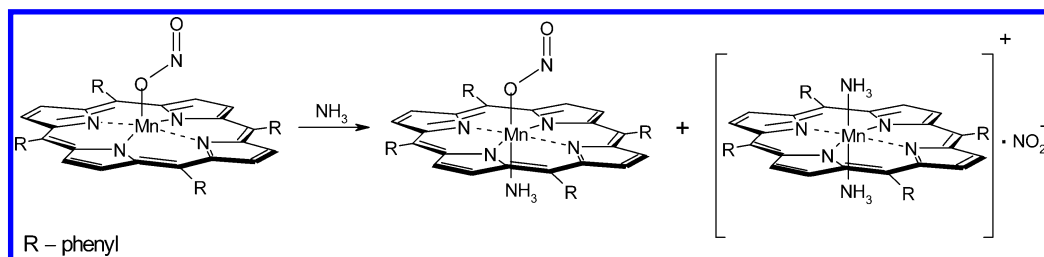
band is in the spectral range where the  $\nu_a(\text{NO}_2^-)$  stretching mode of free NO<sub>2</sub><sup>-</sup> is disposed.<sup>18</sup> Thus, it appears that nitrite is being displaced by the excess NH<sub>3</sub> with formation of the cationic diammine complex [Mn(TPP)(NH<sub>3</sub>)<sub>2</sub>]<sup>+</sup> plus free NO<sub>2</sub><sup>-</sup> as illustrated by Scheme 4.

When the layer is warmed to higher *T*, the intensity of the  $\nu_a(\text{NO}_2^-)$  band of the free ion begins to decrease with concomitant intensity increase of the bands of Mn(TPP)(NH<sub>3</sub>)(ONO) demonstrating reverse binding of NO<sub>2</sub><sup>-</sup> after the loss of one NH<sub>3</sub> from the thermally unstable diammine complex. However, not all the diammine complex is converted back to the mixed six-coordinate species, since some of the latter releases NH<sub>3</sub> to restore the parent O-nitrito complex I. These data indicate that complex equilibria depending on the pressure of NH<sub>3</sub> and temperature exists between the species represented on Scheme 4.

None of the 6-coordinate nitrito complexes studied were thermally stable at higher *T*, and each slowly decomposes by losing L upon warming to RT. The adducts with less volatile Py and 1-MeIm ligands are more stable. Pumping overnight leads to complete decomposition of the Py complex while about half of the 1-MeIm complex still is present in the layer after this procedure.

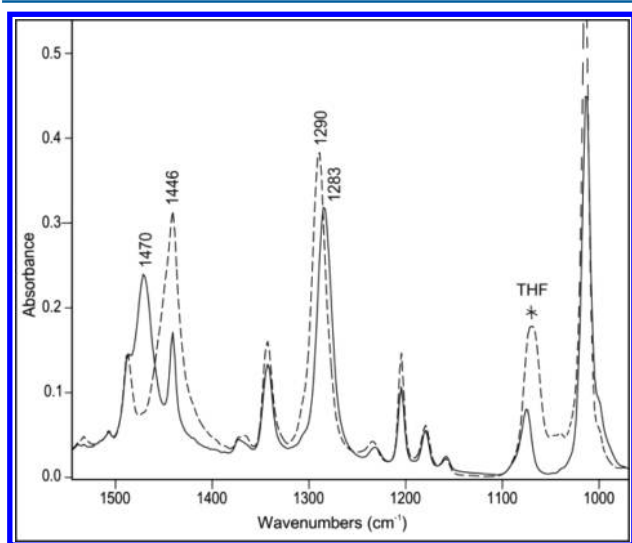


Scheme 4



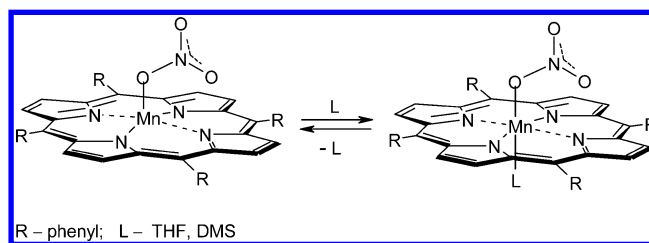
**Six-Coordinate Nitrate Complexes of Mn(TPP) with THF and DMS.** Introduction of small increments of THF vapor into the cryostat containing thin layers of **II** at LN<sub>2</sub> temperature followed by slow warming leads to shifts of the IR bands of the coordinated nitrate group. The high-frequency  $\nu_3(\text{NO}_2)$  band shifts noticeably to lower frequency, while the  $\nu_2(\text{NO}_2)$  band undergoes a minor shift to higher frequency (Figure 10, dashed line). The low-intensity  $\nu(\text{O}-\text{N})$  band also

undergoes a shift to higher frequency as seen in Figure 4. The above-mentioned bands show the appropriate isotopic shifts when <sup>15</sup>N- or <sup>18</sup>O-labeled nitrate complexes were used, confirming their assignment to the coordinated nitrate group (Supporting Information Figure S6, Table 3). These spectral changes are analogous to those observed upon formation of the six-coordinate iron-porphyrins nitrate complex with a *trans*-THF ligand<sup>3b</sup> consistent with formation of the 6-coordinate nitrate-complex Mn(TPP)(THF)( $\eta^1$ -ONO<sub>2</sub>) (Scheme 5). The Q bands in the electronic absorption spectrum shift to higher energy upon coordination to THF (Figure 11).



**Figure 10.** FTIR spectral changes of layered Mn(TPP)( $\eta^1$ -ONO<sub>2</sub>) (solid) upon supplying the cryostat with 0.3 Torr equivalent of THF at LN<sub>2</sub> temperature and slow warming to 180 K. to give Mn(TPP)(THF)( $\eta^1$ -ONO<sub>2</sub>) (dashed line). The THF excess was mostly pumped out at 180 K.

Scheme 5



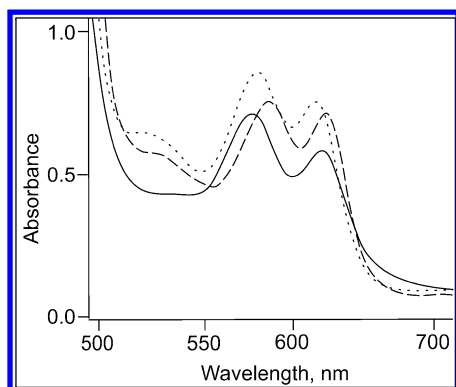
The THF adduct Mn(TPP)(THF)( $\eta^1$ -ONO<sub>2</sub>) can also be obtained at room temperature by exposure of **II** to THF vapor (a few tens of torr). It is stable at room temperature when a few torr of THF are present in cryostat, but it slowly loses the THF ligand in the course of pumping to restore the spectrum of the initial nitrate complex **II**. The THF complex readily decays when it is dissolved in noncoordinating solvent (Supporting Information, Figure S7).

Interaction of the S-donor ligand DMS with **II** leads to the same spectral changes as in the case of THF manifesting the formation of the 6-coordinate complex Mn(TPP)(DMS)( $\eta^1$ -ONO<sub>2</sub>) (Supporting Information, Figure S8). In this case,

**Table 3.** IR Frequencies (cm<sup>-1</sup>) of Differently Labeled Nitrate Group in 6-Coordinate Complexes of Metalloporphyrins with the Various Trans Electron Donor Ligands<sup>a</sup>

adduct	$\nu_a(\text{NO}_2)$ (cm <sup>-1</sup> )	$\nu_s(\text{NO}_2)$	$\nu(\text{O}-\text{N})$	Q bands (nm)	refs
Mn(TPP)(DMS)( $\eta^1$ -ONO <sub>2</sub> )	1451 (1407)	1289 (1263)		583, 618	this work
Mn(TPP)(THF)( $\eta^1$ -ONO <sub>2</sub> )	1446 (1410)	1290 (1262)		575, 610	this work
Mn(TPP)(THF)( $\eta^1$ - <sup>15</sup> N <sup>18</sup> O <sup>18</sup> O <sub>2</sub> )	1419	1269	969		this work
Mn(TPP)(Py)( $\eta^1$ -ONO <sub>2</sub> )	1427 (1393)	1393 (1269)		578, 614	this work
Mn(TPP)(1-MeIm)( $\eta^1$ -ONO <sub>2</sub> )	1418 (1390)	1293 (1264)			this work
Mn(TPP)(NH <sub>3</sub> )( $\eta^1$ -ONO <sub>2</sub> )	1426 (1403)	1290 (1260)			this work
Fe(TPP)(NO)( $\eta^1$ -ONO <sub>2</sub> )	1505 (1472)	1265 (1246)	969 (954)	547, 582	12a
Fe(TPP)(THF)( $\eta^1$ -ONO <sub>2</sub> )	1491 (1457)	1280 (1258)	~997 (986)		12b
Fe(TPP)(NH <sub>3</sub> )( $\eta^1$ -ONO <sub>2</sub> )	1499 (1472)	1268 (1249)	938 (925)		12
Co(TPP)(NH <sub>3</sub> )( $\eta^1$ -ONO <sub>2</sub> )	1484 (1459)	1270 (1248)	983 (970)	558, 597	13a
Co(TPP)(Py)( $\eta^1$ -ONO <sub>2</sub> )	1477 (1449)	1270 (1247)	985 (979)	549	13b

<sup>a</sup>The data for <sup>15</sup>N labeled nitrate group are given in parentheses.



**Figure 11.** Visible spectra of Mn(TPP) sublimed layer (solid line) after interaction with  $\text{NO}_2$  to form II (dashed line), then interaction with THF at 180 K (dotted line) (all on a  $\text{CaF}_2$  substrate).

however, the complex is less stable and begins to decompose at temperatures above  $-30^\circ\text{C}$  (Scheme 5).

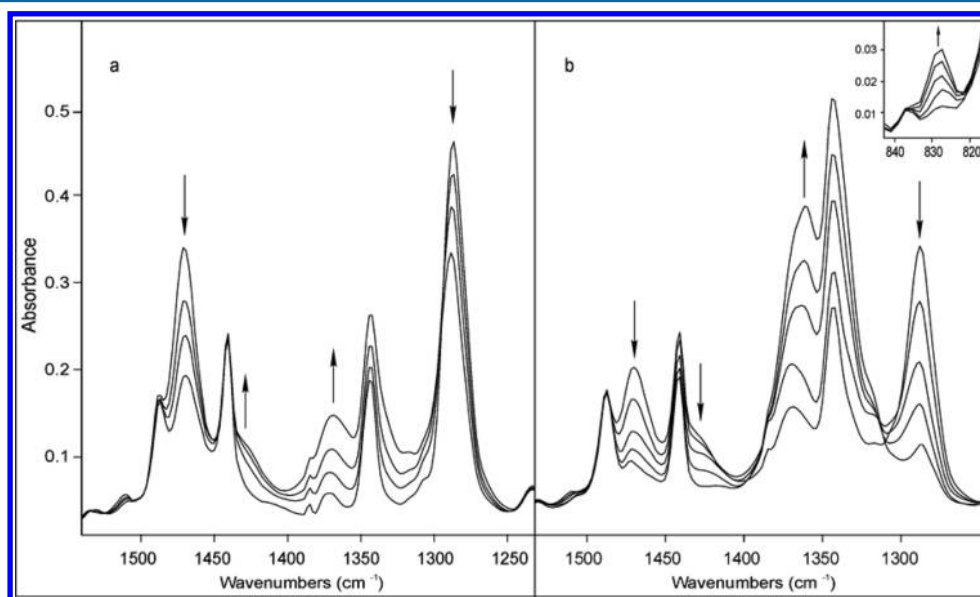
**Interaction of N-Donor Ligands with II.** When small quantity ( $\sim 0.5$  Torr equivalent) of  $\text{NH}_3$  was introduced into the cryostat with layered II at  $\text{LN}_2$ , and layer was slowly warmed to 130 K, the FTIR spectral changes shown in Figure 12a were observed. The bands of II at 1470 and 1284  $\text{cm}^{-1}$  decreased in intensity, and new bands at  $\sim 1427$  and 1360  $\text{cm}^{-1}$  emerged. Their intensities do not correlate, indicating that these new bands belong to different species. From the results described above for the THF and DMS ligands it is reasonable to suggest that the band at  $\sim 1427$   $\text{cm}^{-1}$  is the nitrate  $\nu_a(\text{NO}_2)$  of  $\text{Mn}(\text{TPP})(\text{NH}_3)(\eta^1\text{-ONO}_2)$  while the shift of the band at 1284  $\text{cm}^{-1}$  to higher frequency may involve the overlapping of  $\nu_s(\text{NO}_2)$  bands of II and the 6-coordinate species.

The spectral changes observed upon addition of more  $\text{NH}_3$  (1 Torr equivalent) at  $\text{LN}_2$  T and warming to 130 K are represented in Figure 12b. The bands of coordinated nitrate group disappear and the broad band near 1360  $\text{cm}^{-1}$  and overlapping with the porphyrin band at 1350  $\text{cm}^{-1}$  continues to grow. This band has its isotopic analogs in the experiments with

$^{15}\text{N}$ - and  $^{18}\text{O}$ -containing species and unambiguously can be assigned to the degenerate asymmetric stretching mode  $\nu_3(\text{E})$  of the nitrate anion.<sup>18</sup> Consistent with this interpretation a weak, isotopically sensitive band also grows in the vicinity of 830  $\text{cm}^{-1}$  where the out-of-plane deformation mode  $\nu_2(\text{A}_2)$  of  $\text{NO}_3^-$  anion is disposed (Figure 12b, inset).<sup>18</sup> For this system the doubly degenerate  $\nu_3(\text{E})$  band is not a single band but has complex shape (the shoulder at  $\sim 1320$   $\text{cm}^{-1}$  can be noticed in Figure 12b) that is certainly connected with the H-bonding of  $\text{NO}_3^-$  with  $\text{NH}_3$  (coordinated or solvated) that lowers the  $D_{3h}$  symmetry of nitrate-anion and removes the degeneracy of  $\nu_3(\text{E})$  mode. Such splitting was described in the literature<sup>27</sup> for the  $\text{NO}_3^-/\text{H}_2\text{O}$  system. Depending on the quantity of the  $\text{H}_2\text{O}$  molecule per an  $\text{NO}_3^-$  ion and the symmetry of H-bonding the different characteristics of  $\nu_3$  splitting into two components was observed with separation of the bands as much as 43  $\text{cm}^{-1}$  in some cases.<sup>27</sup> The same pattern is apparently true for  $\text{NO}_3^-/\text{NH}_3$ . This interpretation gains additional support in the experiments with Py ligand (see below) where the same band manifests itself as a single unperturbed curve.

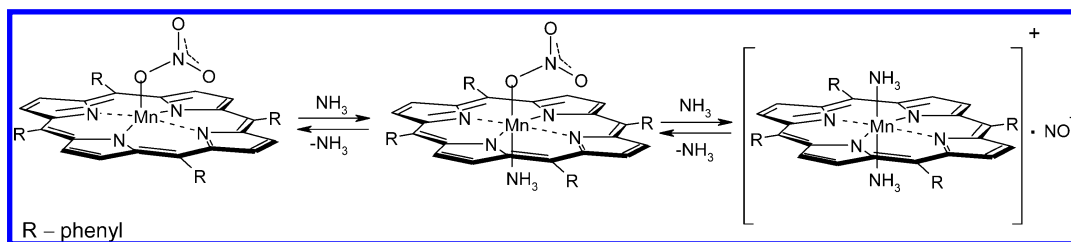
It can be concluded from this data that when excess  $\text{NH}_3$  is present, the nitrate ion can be readily displaced to form the cationic complex  $[\text{Mn}(\text{TPP})(\text{NH}_3)_2]^+$  plus free nitrate anion  $\text{NO}_3^-$ .

Further warming of this system to room temperature led to partial loss of  $[\text{Mn}(\text{TPP})(\text{NH}_3)_2]^+$  cation accompanied by the reformation of 6-coordinate nitrate-complex  $\text{Mn}(\text{TPP})(\text{NH}_3)(\eta^1\text{-ONO}_2)$  and II. Thus, it appears that equilibrium between three different species represented in Scheme 6 is responsible. The relative quantities of these complexes depend on the temperature and  $\text{NH}_3$  pressure. Our attempts to find conditions where only the 6-coordinate nitrate-complex was present in layered medium were unsuccessful. The FTIR spectrum of one of such a system is demonstrated in Supporting Information, Figure S9. Although this sample mostly contains the nitrate-ammine complex  $\text{Mn}(\text{TPP})(\text{NH}_3)(\eta^1\text{-ONO}_2)$  (bands at 1427 and 1290  $\text{cm}^{-1}$ ), there are also noticeable quantities of

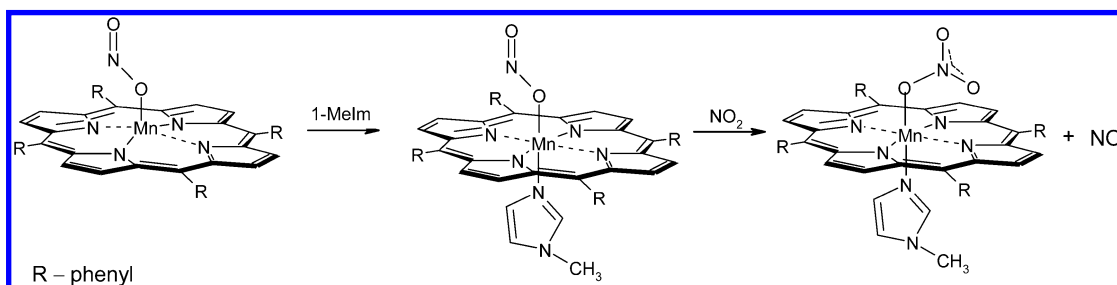


**Figure 12.** FTIR spectral changes upon supplying (a) 0.5 Torr equivalent  $\text{NH}_3$  into layered II at  $\text{LN}_2$  T and slow warming to 130 K. (b) The same procedure with the additional 1 Torr equivalent  $\text{NH}_3$ .

Scheme 6



Scheme 7



diammonia cationic complex  $[\text{Mn}(\text{TPP})(\text{NH}_3)_2]^+\cdot\text{NO}_3^-$  (band at  $1360\text{ cm}^{-1}$ ) and **II** (band at  $1470\text{ cm}^{-1}$ ).

Long-time pumping of the system at RT leads eventually to the complete restoration of **II** demonstrating that neither cationic  $[\text{Mn}(\text{TPP})(\text{NH}_3)_2]^+\cdot\text{NO}_3^-$  nor the nitrate-ammine  $\text{Mn}(\text{TPP})(\text{NH}_3)(\eta^1\text{-ONO}_2)$  complexes are stable in the absence of excess  $\text{NH}_3$ . Similar behavior was seen for the Fe-porphyrin nitrate complexes.<sup>12b</sup>

Experiments with the less volatile ligand Py gave somewhat different results. Although the presence of excess Py leads to formation of the cationic  $\text{Mn}(\text{TPP})(\text{Py})_2^+$  and  $\text{NO}_3^-$  ion, the latter complex could be transformed to the six-coordinate nitrate-pyridyl complex  $\text{Mn}(\text{TPP})(\text{Py})(\eta^1\text{-ONO}_2)$  by pumping out the cryostat at RT to give the IR spectrum shown in Supporting Information, Figure S10. This result implies that the cationic bis(pyridyl) complex  $[\text{Mn}(\text{TPP})(\text{Py})_2]^+$  is not very stable at RT.

Another ligand of considerable interest is 1-methyl-imidazole (1-MeIm), which is a mimic of the histidine imidazole in hemoproteins. When layers of **II** in the cryostat were treated with saturated vapors of 1-MeIm, the IR bands of **II** disappeared with the concomitant growth of bands characteristic of a 6-coordinate species. However, a significant quantity of  $[\text{Mn}(\text{TPP})(1\text{-MeIm})_2]^+\cdot\text{NO}_3^-$  is also formed. The latter does not transform back to the six-coordinate nitrate complex  $\text{Mn}(\text{TPP})(1\text{-MeIm})(\eta^1\text{-ONO}_2)$  upon high-vacuum pumping. Thus, the binding of two axial 1-MeIm ligands in bis-ligated cationic complex is stronger than for Py. The  $[\text{Mn}(\text{TPP})(1\text{-MeIm})_2]^+$  complex has been isolated and structurally characterized.<sup>28b</sup>

The strategy demonstrated in Scheme 7 was applied to obtain the 6-coordinate nitrate-complex with a *trans*-1-MeIm ligand (details of experiment and spectral evidence for formation of the  $\text{Mn}(\text{TPP})(1\text{-MeIm})(\eta^1\text{-ONO}_2)$  are represented in Supporting Information, Figure S11).

The 6-coordinate nitrate complexes with Py and 1-MeIm are stable in the solid state at RT, but dissolution in non-coordinating solvent leads to their decomposition.

In Table 3 the data on FTIR and UV-vis spectra of six-coordinated nitrate-complexes with the various trans ligands

are summarized. As can be seen in all these complexes, 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 (compare with the data of Table 1). The magnitudes of these shifts correlate with the donor strengths of the trans ligands: stronger  $\sigma$ -donors result in bigger shifts of these bands from the values of the five-coordinate species. It is noteworthy that a number of 6-coordinate nitrate complexes of Mn(TPP) obtained in this work were thermally stable in the solid state in contrast to the nitrate-complexes of iron and cobalt-porphyrins.<sup>3c,4</sup> Assuming that Mn-porphyrins promotes the NOD-reaction it is reasonable to expect that the resulting species might contain 6-coordinate nitrate-complexes at ambient conditions in contrast to Fe or Co analogs that eliminate the nitrate anion upon warming to RT.

In summary, formation of **II** by interaction of  $\text{NO}_2$  gas with amorphous layer of Mn(TPP) proceeds via two distinct stages. At very low  $P_{\text{NO}_2}$ ,  $\text{NO}_2$  coordination to give the 5-coordinate O-nitrito complex **I** occurs. Subsequent reaction at higher  $P_{\text{NO}_2}$  leads to formation of the nitrate complex **II**, with the concomitant formation of NO. A plausible mechanism for this stage of reaction is offered based on the spectral changes observed upon subsequent interaction of  $^{15}\text{NO}_2$  and  $\text{NO}_2$  with the layered Mn(TPP). Reaction of electron donor ligands (L) with **I** leads to formation of the 6-coordinate O-nitrito complexes  $\text{Mn}(\text{TPP})(\text{L})(\text{ONO})$  that are mostly thermally unstable. Formation of these 6-coordinated complexes is accompanied by the low- and high-frequency shifts of the  $\nu(\text{N}=\text{O})$  and  $\nu(\text{N}-\text{O})$  bands, correspondingly, of the coordinated nitrite. The magnitudes of the shifts depend on the nature of trans ligand and is higher for stronger Lewis base donors. With ammonia the displacement of the coordinated nitrite by the excess  $\text{NH}_3$  was observed leading to formation of the cationic diammine complex  $[\text{Mn}(\text{TPP})(\text{NH}_3)_2]^+$  and free nitrite anion  $\text{NO}_2^-$ .

Reaction of electron donor ligands with layered **II** results in formation of six-coordinate nitrate-complexes  $\text{Mn}(\text{TPP})(\text{L})(\eta^1\text{-ONO}_2)$  that display different stabilities depending on the donor strength of L. Although relatively stable in the solid state, these species decompose upon dissolution to yield initial 5-



coordinate nitrate complex **II**. It is also shown that strong N-donor ligands are able to reversibly display weakly bound nitrate ligand to form bis-ligated cationic complex  $[\text{Mn}(\text{TPP})\text{-}(\text{N-donor})_2]^+$  and nitrate anion  $\text{NO}_3^-$ .

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

FTIR spectrum of  $\text{Mn}(\text{TPP})(\eta^1\text{-}^{18}\text{O}^{15}\text{N}^{18}\text{O})$ , shifts of porphyrin vibrational modes upon metal oxidation, FTIR spectra of  $\text{Mn}(\text{TPP})(\eta^1\text{-ONO}_2)$  and  $\text{Mn}(\text{TPP})(\eta^1\text{-O}^{15}\text{NO}_2)$ , FTIR spectral changes upon addition of  $\text{NO}_2$  to the layered  $\text{Mn}(\text{TPP})(\eta^1\text{-O}^{15}\text{NO})$ , FTIR spectra of  $\text{Mn}(\text{TPP})(\eta^1\text{-O}^{15}\text{NO})$  and  $\text{Mn}(\text{TPP})(\text{DMS})(\eta^1\text{-O}^{15}\text{NO})$  at 170 K, FTIR spectra of  $\text{Mn}(\text{TPP})(\text{THF})(\eta^1\text{-ONO}_2)$  and  $\text{Mn}(\text{TPP})(\text{THF})(\eta^1\text{-O}^{15}\text{NO}_2)$ , decomposition of  $\text{Mn}(\text{TPP})(\text{THF})(\eta^1\text{-O}^{15}\text{NO}_2)$  upon dissolution in  $\text{CCl}_4$ , FTIR spectrum of  $\text{Mn}(\text{TPP})(\text{DMS})(\eta^1\text{-ONO}_2)$ , FTIR spectrum of layered **II** after reaction with  $\text{NH}_3$ , FTIR spectra of layered **II** after exposure under vapors of Py, FTIR spectral changes upon addition  $^{15}\text{NO}_2$  on layered  $\text{Mn}(\text{TPP})(1\text{-MeIm})(\text{O}^{15}\text{NO})$  demonstrating formation of the  $\text{Mn}(\text{TPP})(1\text{-MeIm})(\text{O}^{15}\text{NO}_2)$ , and experimental details for obtaining  $\text{Mn}(\text{TPP})(1\text{-MeIm})(\eta^1\text{-ONO}_2)$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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