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In Situ FT-IR and UV–vis Spectroscopy of the Low-Temperature NO Disproportionation Mediated by Solid State Manganese(II) Porphyrinates

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The heterogeneous reaction between NO gas and sublimed layers of manganese(II) porphyrinato complexes Mn(Por) (Por = TPP (tetraphenylporphyrinato dianion), TMP (tetramesitylporphyrinato dianion), or TPP_{d20} (perdeuterated tetraphenylporphyrinato dianion)) has been monitored by IR and optical spectroscopy over the temperature range of 77 K to room temperature. These manganese porphyrins promote NO disproportionation to NO_2 species and N_2O, and the reaction proceeds via several distinct stages. At 90 K, the principal species observed spectrally are the nitric oxide dimer, *cis*-ONNO, two manganese nitrosyls, the simple NO adduct Mn(Por)(NO), and another intermediate (**1**) that is apparently critical to the disproportionation mechanism. This key intermediate is formed prior to N_2O evolution, and proposals regarding its likely structure are offered. When the system is warmed to 130 K, the disproportionation products, N_2O and the O-coordinated nitrito complex Mn(Por)(NO)(*O*NO) (**2**), are formed. IR spectral changes show that, upon further warming to 200 K, **2** isomerizes into the N-bonded nitro linkage isomer Mn(Por)(NO)(*N*O_2) (**3**). After it is warmed to room temperature, the latter species loses NO and converts to the known 5-coordinate nitrito complex Mn(Por)(ONO) (**4**).

Introduction

The reactions of metal complexes with nitric oxide (nitrogen monoxide) and the metal-mediated transformations of NO to other NO_x species have long been of interest. While these reactions have demonstrated importance in biological media,[1] they have also drawn considerable attention in catalytic chemistry where oxygen atom transfers from metal-coordinated NO_x may have utility in the selective oxidations of organic substrates[2] and in environmental chemistry where of NO_x removal from effluent gas streams has importance.[3] One such reaction is the disproportionation of NO to nitrous oxide and nitrogen dioxide (eq 1). Disproportionation, the source of major impurities in gaseous NO commercially supplied in high-pressure steel tanks, is relevant to mechanisms for the enzymatic reduction of NO to N_2O and is likely to influence catalytic cycles dependent on the transformations among various NO_x.[4]

$$3NO \rightarrow N_2O + NO_2 \qquad (1)$$

There are numerous literature reports describing activation of NO disproportionation by metal complexes to give N_2O and metal nitrite complexes.[5] For example, Tolman and co-workers have described the reaction of NO with copper(I) tris(pyrazolyl)borate to give N_2O and a Cu(II) nitrito species.[5f] Similar reactivity has been described by Franz and Lippard for manganese and iron tropocoronand complexes.[6]

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The critical step of NO disproportionation reactions appears to be the N−N coupling required to form a precursor of N_2O. It has been proposed in those studies that metal nitrosyls reacted with NO to form a *cis*-dinitrosyl intermediate, which then converts into a hyponitrito $M(N_2O_2)^{2-}$ complex, followed by O-atom abstraction by a third NO. Among metal porphyrins NO disproportionation has been reported for ruthenium and osmium complexes, M(Por)(CO), which react with NO to give N_2O and the nitrosyl nitrito complexes M(Por)(NO)(ONO) (M = Ru, Os; Por = TPP, OEP).[7] Although these systems were the subjects of kinetics studies, the detailed mechanisms of the N−N bond formation leading to N_2O have not been fully characterized.

This paper reports the IR and UV−vis spectroscopic studies monitored over the temperature range from 77 K to room temperature (RT) for the reaction of NO with films of the manganese(II) porphyrinato complexes Mn(Por) (Por = TPP (tetraphenylporphyrinato dianion), TMP (tetramesitylporphyrinato dianion), or TPP_{d20} (perdeuterated tetraphenylporphyrinato dianion)) that promote NO disproportionation. In this work, we report vibrational and optical spectra of an intermediate that is apparently the direct precursor of the N−N bond formation, and we also report the IR spectra of several other previously unknown $Mn-NO_x$ complexes.

Experimental Section

Complexes Mn(TPP)(Pip) and Mn(TMP)(Pip) (Pip = piperidine), synthesized according to published methods,[8] were the precursors of the manganese(II) porphyrinato complexes Mn(Por) used to prepare the sublimed layers. $Mn(TPP_d20)(Pip)$ was synthesized following the procedure reported in ref 9. The Mn(Por) sublimates on the KBr or CaF_2 substrates of the optical cryostats were prepared under continuous vacuum conditions, according to a procedure described elsewhere.[10] Such thin layers of metallo-tetraarylporphyrins sublimed onto a low-temperature (77 K) surface are spongelike and have high microporosity that allows potential ligands to diffuse easily across the bulk.[10b,c] The species thus formed are convenient for spectroscopic studies because of the absence of solvent interference. After sample preparation, a known quantity of NO measured by a mercury manometer was slowly deposited onto the 77 K Mn(Por) layers. IR or UV−vis spectra were measured for these mixtures at different substrate temperatures controlled by a thermocouple.

The nitric oxide and ^{15}NO (Institute of Isotopes, Republic of Georgia, with isotopic enrichment 98.5%) were purified as follows. First, NO was passed multiple times through a column containing KOH pellets and through butylbromide/liquid N_2 (−119 °C) cooled traps to remove N_2O and NO_2 impurities. Although the N_2O contamination after this procedure was estimated to be less than 0.2%, this level of purity was not satisfactory for the low-temperature FTIR experiments. Weak bands at 2240 and 1290 cm^{-1} attributed to N_2O were still seen after NO deposition on the KBr substrate at 7 K, so additional purification was necessary to eliminate interference from N_2O impurities. In the second step, the glassy bulb containing prepurified NO was submerged into a dewar flask filled with liquid N_2 and connected with cryostat cooled by a helium closed-cycle refrigeration system (ARS DE202). NO evaporating from the 77 K bulb was deposited onto the 7 K substrate of the cryostat (at 77 K, the NO vapor pressure is about 10^{-1} Torr while that for N_2O is 10^{-6} Torr),[11] and the purity of the condensate was checked by IR spectroscopy. Then the cryostat was allowed to warm to 110 K, and the NO was condensed into another glass bulb submerged in liquid N_2. Considerable precautions were taken to prevent inadvertent air contamination during the gas transfers and purification steps for each experiment described here.

Gas analyses were performed by gas chromatography on a GCHF 18.3 instrument equipped with a thermal conductivity detector and a 300 cm column packed with Porapac Q (80−100 mesh). The retention times (min) for various gases were NO (1.11), NO_2 (3.6), and N_2O (4.6−4.8), using H_2 as a carrier gas with flow rate 40 mL/min at 40 °C. In a typical experiment, the cryostat with prepared Mn(TPP) sample was attached to a high-vacuum line; a known quantity of NO measured with a mercury manometer was added, and the unit was sealed with a vacuum valve. After the reaction, the headspace gas of the cryostat was carefully transferred under vacuum into a flask fitted with liquid nitrogen finger, manometer, and adapter, which allowed for syringe access and protected the sample from air with a rubber septum. The pressure was equilibrated to atmospheric pressure with H_2, and the gas mixture was sampled with a Hamilton gastight syringe for GC injections.

Quantitative analysis of the N_2O content in the headspace was performed by comparison of the average peak areas of three injections with previously prepared standard curves with CO_2 used as an internal standard. The standards were analyzed in the same way as the reaction samples. Three injections were made for each standard to obtain GC calibration curves for NO or N_2O. Infrared spectra were measured on Specord M-80 and Nicolet "Nexus" FTIR spectrometers. The UV−vis spectra were measured on a Specord M-40 spectrophotometer.

Results and Discussion

Low-Temperature Reaction of Mn(TPP) with NO. When sublimed layers of Mn(TPP) at 77 K were exposed to excess NO that had been carefully purified in the manner described above, new absorption bands were observed at 1853 s and 1752 vs. We have assigned these bands to the

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symmetric and asymmetric NO stretching modes of the *cis*-ONNO dimer on the basis of the following reasoning. The NO dimers have been extensively studied in gas and condensed phases, as well as in different low-temperature matrixes.[12] In the pure solid at 12 K, the $\nu(\mathrm{NO})_{\mathrm{sym}}$ and $\nu(\mathrm{NO})_{\mathrm{asym}}$ bands of the more stable *cis*-ONNO isomer were identified as appearing at 1865 and 1760 cm^{-1}, respectively. In contrast, the trans dimer, having the center of symmetry, exhibits only a single infrared active ν(NO) band, which has been observed at 1760 cm^{-1} in a dinitrogen matrix[13] and at 1740 cm^{-1} in a carbon dioxide matrix;[14] however, the sensitivity of these bands to the environment is well-known.[15] It is significant that the positions of the two bands seen upon deposition of NO on 77 K Mn(TPP) layers are quite similar to those seen in our experiments with metallo porphyrinato layers of other metals (Co-, Fe-, Cu-, Ni-, and Zn(TPP)) under analogous conditions. This indicates that the bands seen in the Mn(TPP) layers are independent of the metal center and, hence, are characteristic of *cis*-ONNO itself in these media and not of coordinated $(\mathrm{NO})_2$ dimers.

Subsequent warming of the samples to ~90 K resulted in the formation of a new band at 1712 cm^{-1} and a very weak one near 1820 cm^{-1}, in addition to the bands at 1853 s and 1752 vs attributed to *cis*-ONNO (Figure 1a). It should be noted that the band at 1820 cm^{-1} overlaps with another small absorbance at 1812 cm^{-1}, which belongs to a porphyrin moiety overtone and occurs in the IR spectra of all tetraaryl-substituted MPs. When this experiment was carried out with ^{15}NO, the same pattern of NO-dependent bands was seen but with the frequencies shifted to 1820 s, 1716 vs, 1784 vw, and 1680 m cm^{-1}, respectively. The intensity ratio of the asymmetric/symmetric bands (integrated absorbances) seen in Figure 1a is ~4, which is somewhat higher than the reported intensity ratio (~2.8) of these IR bands for *cis*-ONNO;[15] however, the higher relative intensity of the 1752 cm^{-1} band in Figure 1a may be caused by an overlap with the ν(NO) band 1740 cm^{-1} (1705 cm^{-1} for ^{15}NO) of Mn(TPP)(NO),[16] or another 6-coordinate species containing coordinated NO (see below), which is also formed under these conditions. In our control experiments with M(TPP) (M = Zn, Ni) that do not form nitrosyls or for those where the ν(NO) of M(TPP)(NO) (Co and Fe) do not overlap the $\nu(\mathrm{NO})_{\mathrm{asym}}$ band of *cis*-ONNO, this ratio is closer to the reported value.

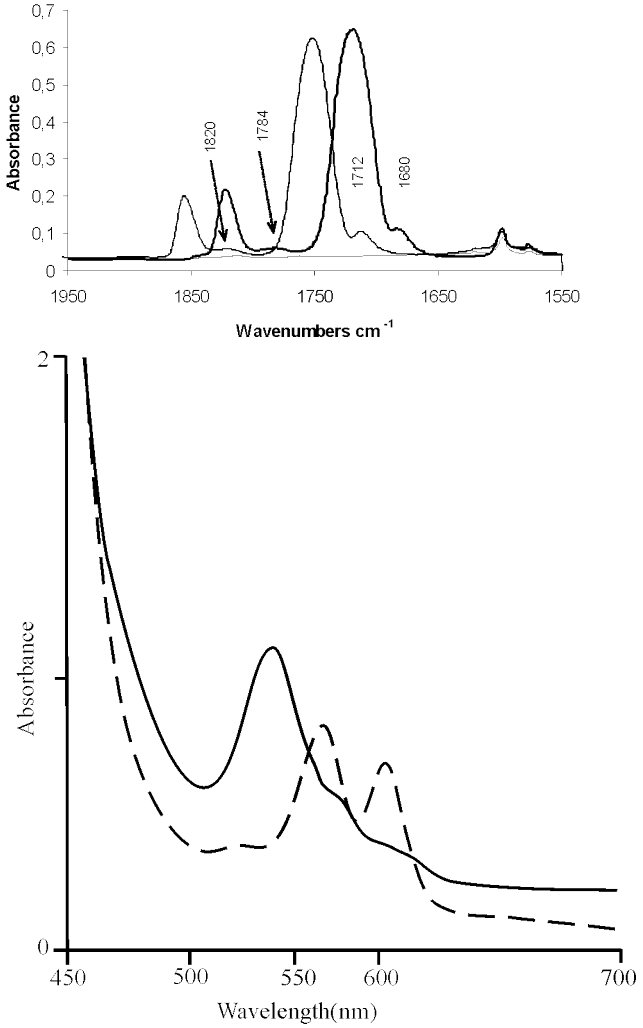

Figure 1. IR and UV−vis spectra of the same sample of Mn(TPP) before and after treatment with NO. In the top panel, the dashed line represents Mn(TPP) at 77 K, the thin line indicates the spectrum after the sample was exposed to NO and warmed to 90 K, and the thick line shows the same for ^{15}NO. In the bottom panel, the dashed line shows Mn(TPP) and the solid line shows it after it was exposed to NO and warmed to 90 K.

The bands at 1820 and 1712 cm^{-1} (1784 and 1680 for ^{15}NO) are attributed to the formation of a new intermediate **1**. The difference between spectra recorded before and after the addition of approximately 1 equiv of NO to the Mn(TPP) layers at ~90 K shows initial formation of a nitrosyl band at 1740 cm^{-1}, assigned to the mononitrosyl complex Mn(TPP)(NO). As more NO equivalents were added, there was concomitant formation of bands at 1820 and 1712 cm^{-1} (**1**) and at 1853 and 1752 cm^{-1} (*cis*-ONNO). The difference between the spectra recorded before and after this step also showed the decrease in the 1740 cm^{-1} band of the mononitrosyl complex. This indicates that the latter underwent conversion to **1** when the system was exposed to the additional NO under these conditions. Cooling of this sample to 77 K, followed by a prolonged evacuation, ultimately results in decreased intensities of the bands attributed to the dimer and to **1**. Attempts to completely remove the *cis*-ONNO dimer by evacuating the system, without disruption of intermediate **1** were unsuccessful.

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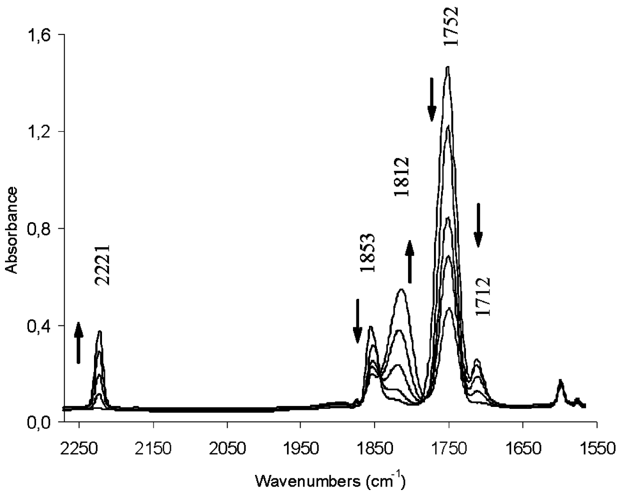

Figure 2. FT-IR monitoring of N_2O and Mn(TPP)(NO)(ONO) formation upon warming of the Mn(TPP) sample from 100 to 130 K under excess NO (ca. $P = 15$ Torr).

When a sample prepared by stepwise addition of NO to Mn(TPP) layers at ~90 K instead was warmed to $T > 100$ K, the bands attributed to the NO dimer and that at 1712 cm^{-1} underwent a gradual disappearance. At the same time, formation of N_2O was detected by the appearance of the characteristic IR band at 2221 cm^{-1}. Notably, under analogous experimental conditions, the other metalloporphyrins listed above do not display an IR band similar to that of **1** nor the formation of N_2O. This circumstantial evidence suggests that chemical involvement of manganese center is necessary requirement for formation of **1**, which plays a role in the production of N_2O.

Optical spectroscopy is a sensitive probe of the metal oxidation state in manganese porphyrin complexes because of the extensive mixing of the metal e_g and porphyrin ring $e_g(\pi)$ orbitals.[17a-c] Figure 1b shows the optical spectra of the material obtained by exposure of Mn(TPP) to excess NO at 77 K and slowly warmed to 90 K. The IR spectrum of this same material is dominated by the band at 1820 and 1712 cm^{-1}; in other words, it is intermediate **1**. Notably, the optical spectrum is close to that reported for the mononitrosyl complex Mn(TPP)(NO) in frozen solutions;[16a] thus it appears that the oxidation state in **1** is the same as that in Mn(TPP)(NO), since oxidation to Mn(III) should show an absorption at $\lambda_{max} = 480$ nm.

Figure 2 shows the IR spectral changes upon warming a Mn(TPP) sample under excess NO from 100 to 130 K, where it is seen that decreases in the bands attributed to *cis*-ONNO and **1** are accompanied by the emergence of new bands centered at 2221 and 1812 cm^{-1}. The former band undoubtedly represents the formation of N_2O, while the latter band was assigned to the ν(NO) of the linear nitrosyl in the nitrosyl-nitrito species Mn(TPP)(NO)(ONO) (**2**), which was characterized in an earlier communication.[10a] IR spectral changes in the region characteristic to the ONO$^-$ vibrations are shown in Supporting Information Figure S1. Three new bands appear at 1488, 970, and 821 cm^{-1}, and they are consistent with the ν(N=O), ν(N−O), and δ(ONO) modes of an oxygen-coordinated ONO moiety. When the experiment was carried out with ^{15}NO, the nitrosyl and nitrito ligand bands were located at 1778, 1450, 950, and 818 cm^{-1}, respectively.

Table 1. IR Frequencies (cm^{-1}) of Mn(Por)(NO)(ONO) Complexes[a]

compound	ν(NO)	ν(N=O)	ν(N−O)	δ(ONO)
Mn(TPP)(NO)(ONO)	1812 (1778)	1480 (1454)	971 (952)	822 (817)
Mn(TPP$_{d20}$)(NO)(ONO)	1811 (1778)	1481 (1453)	976 (957)	
Mn(TMP)(NO)(ONO)	1809 (1777)	1484 (1455)	968 (948)	822 (818)

[a] Values in parentheses represent the frequencies observed after the reaction with ^{15}NO.

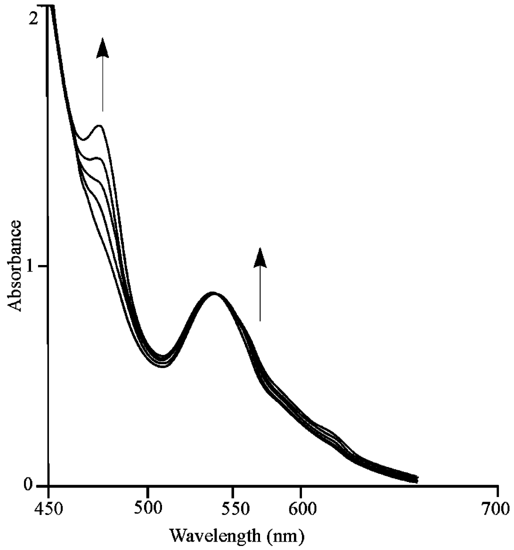

Figure 3. In situ UV−vis reaction spectra of Mn(TPP) under excess NO when the sample was warmed from ~90 to ~130 K. The appearance of the absorbance band at 480 nm upon formation of **2** indicates oxidation of the metal center to Mn(III) state.

Analogous infrared spectral changes were also observed when the same reactions with NO were carried out with sublimed layers of Mn(TPP$_{d20}$) and Mn(TMP). Frequencies observed for the nitrosyl and nitrito groups in the various Mn(Por)(NO)(ONO) products are listed in Table 1.

Irreversible conversion of intermediate **1** to Mn(Por)(NO)(ONO) was also indicated by the changes in the visible spectra (Figure 3). When the sample was warmed to 130 K, the absorption band of **1** at 539 nm shifted to 546 nm, together with formation of a broad shoulder at 560 nm and a new band at 478 nm. The latter suggests oxidation of the metal center upon formation of **2**, since this absorption is characteristic of other Mn(III) porphyrin nitrosyl complexes.[16a]

Figure 4 shows the temporal progression of the integrated IR absorbance peak of N_2O produced by a sample maintained at 130 K. The highest yield of nitrous oxide was found by keeping the sample at 130 K from 2 to 3 h. Spontaneous warming of the sample from 80 K to room temperature gives decreased yields of N_2O. The formation of N_2O was confirmed by gas chromatography. Quantitative analysis of the reaction gas revealed formation of 0.4−0.7 equiv of N_2O

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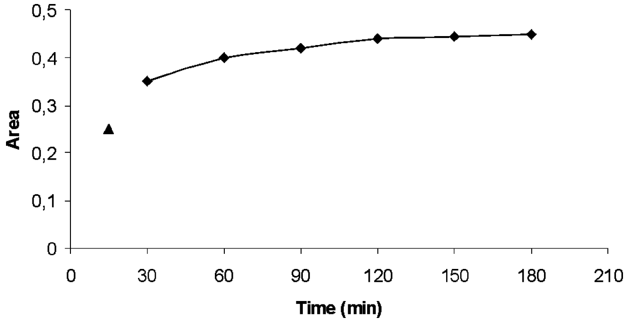

Figure 4. Production of N_2O (integrated IR absorbances of the band at 2221 cm^{-1}) depending on the time that the sample was maintained at 130 K. The N_2O produced when the cryostat spontaneously warmed to RT is denoted by triangle.

per manganese, depending on the reaction conditions. However, such analysis revealed negligible N_2O formation when the same system was studied at room temperature.

Isotope Exchange Experiments. We also studied the reaction of Mn(^{15}NO)(TPP) with an excess of ^{14}NO at 77–130 K. Upon exposure to excess ^{14}NO, the ν(NO) band of Mn(^{15}NO)(TPP) at 1707 cm^{-1} decreased rapidly and, finally, almost completely disappeared, and according to the IR spectra, the major products were Mn(TPP)(^{14}NO)(O^{14}NO) and $^{14}N_2O$. Thus, the ^{15}NO/^{14}NO exchange on the metal center must be much faster than the subsequent disproportionation. Furthermore, although the nitrosyl complex Mn(TPP)(NO) is labile in room-temperature solutions,[18] in sublimed layers, it does not lose NO under long-term continuous evacuation, even when the sample was heated to ~350 K. In this context, an NO exchange mechanism dependent upon the presence of excess NO must be in effect under these low *T* conditions.

Such a mechanism might be functioning via the formation of a dinitrosyl intermediate Mn(Por)$(NO)_2$ analogous to those reported for Ru– and Fe–porphyrins.[19a,b] To test this hypothesis, the reaction of Mn(TPP) with a 1:1 mixture of ^{15}NO and ^{14}NO was examined at low-temperature (77–100 K). It was anticipated that under these conditions a dinitrosyl complex Mn(TPP)$(NO)_2$ would demonstrate ν(NO) bands[20] because of the formation of Mn(TPP)$(^{14}NO)_2$, Mn(TPP)$(^{15}NO)_2$, and Mn(TPP)(^{14}NO)(^{15}NO). Unfortunately, interference from the broad bands of the mixed $(NO)_2$ dimers prevented this assessment. On the other hand, the IR spectrum from this experiment displayed four bands of equal intensity in the nitrous oxide region at 2221 ($^{14}N_2O$), 2199 ($^{14}N^{15}NO$), 2175 ($^{15}N^{14}NO$), and 2152 ($^{15}N_2O$) cm^{-1},[21] consistent with complete scrambling of the nitrogen labels in this disproportionation product (Figure S2).

Further Reactivity. The FTIR spectral changes during further warming of **2** from 130 K to RT are shown in Figure 5. All bands attributed to Mn(TPP)(NO)(ONO) diminished in intensity and finally disappeared, while new bands developed at 1448 cm^{-1} (1425 cm^{-1} for the reaction with ^{15}NO) and ~1000 cm $^{-1}$. This spectral behavior is consistent with the loss of NO from **2** upon warming of the sample to give the previously characterized[22] nitrito complex Mn(TPP)(ONO) (**4**), which displays IR bands at 1444 and 1029 cm^{-1} assigned to the ν(N=O) and ν(N–O) of the coordinated nitrito ligand. However, the latter band is not well resolved in the spectrum of our amorphous sample. The assignment of the final product as Mn(TPP)(ONO) was strengthened by reacting the Mn(TPP) layers with very low concentrations of NO_2 at RT. The result was an FT-IR spectrum identical to that obtained after the products of the low-temperature reaction of Mn(TPP) with excess NO were warmed to room temperature.

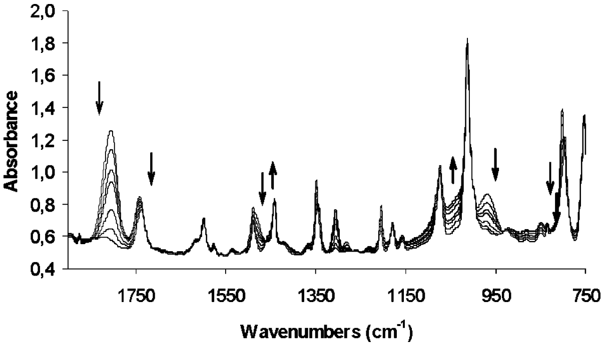

Figure 5. Changes in the IR spectrum of **2** upon the increase of *T* from 130 K to RT. (P_{NO} = 5 Torr).

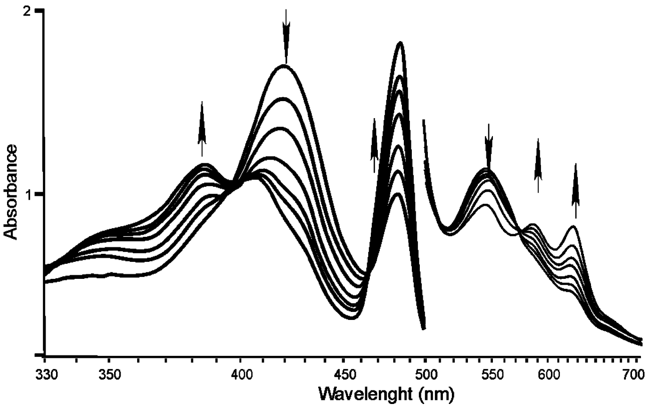

Figure 6. Changes in the UV–vis spectra of the NO/Mn(TPP) system as the temperature was increased from 200 K to RT.

The changes in the optical spectrum are in agreement with this conclusion. The UV–vis spectrum displayed, upon warming of **2** to room temperature, new bands at ~385, 476, 583, and 620 nm (Figure 6), consistent with those of Mn(TPP)(ONO).[22] The remaining absorbance at 540 nm is the result of the incomplete conversion of Mn(TPP)(NO) into **2** during the low *T* reaction; this feature is also shown by the small 1740 cm^{-1} band seen in the IR spectra after the sample reached RT.

The conversion of **2** to **4** described above might be accomplished by the simple dissociation of NO from

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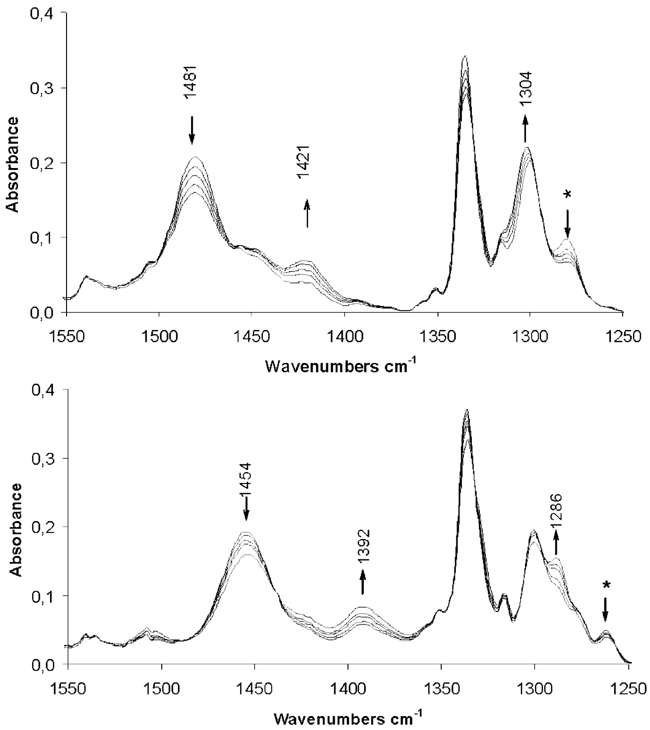

Figure 7. FT-IR spectra when **2** was warmed from 130 to 200 K: (top) Mn(TPP$_{\mathbf{d20}}$)(^{14}NO)(O^{14}NO) and (bottom) same process for Mn(TPP$_{\mathbf{d20}}$)(^{15}NO)(O^{15}NO) (ν_1 vibration of N_2O is denoted by *).

Mn(TPP)(NO)(ONO) (eq 2). However, careful inspection of the temporal IR spectra upon warming of **2** revealed the formation of another transient species.

$$\underset{(\mathbf{2})}{\text{Mn(Por)(NO)(ONO)}} \rightarrow \underset{(\mathbf{4})}{\text{Mn(Por)(ONO)}} + \text{NO} \qquad (2)$$

Figures 7 and 8 show the temporal IR spectral changes in the region corresponding to ONO$^-$ vibrations, upon warming of the sample from 130 K to RT. As can be seen from Figure 7, warming of **2** from 130 to 200 K led to a gradual decrease in the intensity of the bands at 1481 and 970 cm^{-1} (1454 and 950 cm^{-1} for ^{15}NO) (the 970 band is not shown). Concomitantly, two new bands, correlated in intensity, appeared at 1421 and 1304 cm^{-1} (1392 and 1286 cm^{-1} for ^{15}NO), reaching their maximal intensities at 200 K. This conversion was irreversible; cooling of the sample did not lead to an increase of the intensities of the bands of **2**.

Spectral changes observed upon further warming of the sample from 200 K to RT are shown in Figure 8. The new bands at 1421 and 1304 cm^{-1},^{23} together with bands assigned to the nitrito vibrations of **2**, disappeared, while two other new bands appeared at 1448 cm^{-1} (1425 cm^{-1} for ^{15}NO) and in vicinity of 1000 cm^{-1}. These bands and a small one at 1740 cm^1 indicate that some Mn(TPP)(NO) persisted after the sample reached RT.

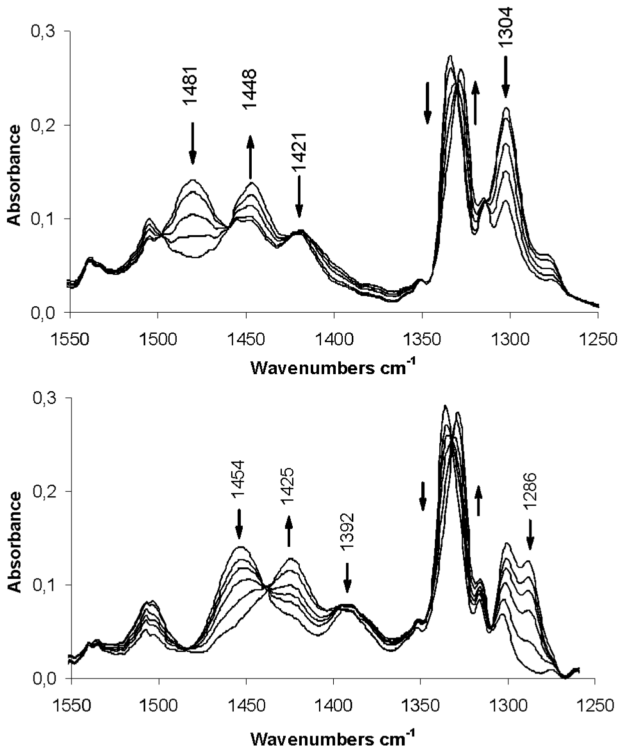

Figure 8. FT-IR spectral changes observed when **2** was warmed from 200 K to RT: (top) Mn(TPP$_{d20}$)(^{14}NO)(O^{14}NO) and (bottom) Mn(TPP$_{d20}$)(^{15}NO)(O^{15}NO).

The appearance of the transient IR bands at 1421 and 1304 cm^{-1} is consistent with the linkage isomerization of the O-coordinated nitrito ligand of **2** to give an N-bonded nitro complex Mn(TPP)(NO)(NO$_2$) (**3**) (eq 3). Similar nitrito−nitro isomerizations are known for pentaammine and ethylenediamine cobalt complexes in the solid state^{24} and proposed in the recombination processes after photodissociation of NO$_2$ from Co(TPP)(NO$_2$) in solution.^{25} An analogous isomerization has been recently documented for Fe (Por)(NO)(ONO) complexes.^{26} A nitrosyl nitro complex analogous to **3** is the iron(III) species Fe(TPP)(NO)(NO$_2$), which displays IR bands for the asymmetric and symmetric modes of coordinated NO$_2$ at 1450 and 1300 cm^{-1},^{27a} close to the positions of the bands attributed to **3**. Other six-coordinate porphyrin nitro complexes show similar IR bands. For example, in sublimed films, those for Co(TPP)(NO$_2$) are located at 1468 and 1280 cm^{-1}, while the addition of piperidine or pyridine (to give six-coordinate complexes) shifts these bands to 1437 and 1308 cm^{-1} or 1439 and 1310 cm^{-1}, respectively.^{28}

$$\underset{(\mathbf{2})}{\text{Mn(Por)(NO)(ONO)}} \rightarrow \underset{(\mathbf{3})}{\text{Mn(Por)(NO)(NO}_2)} \qquad (3)$$

The apparent isomerization of **2** to **3** is reflected in a shift of ν(NO) to ~1805 cm^{-1} (1770 cm^{-1}for ^{15}NO), as the bands

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(23) The band at 1304 cm^{-1} appears as a shoulder of porphyrin band at 1300 cm^{-1}, the intensity of which (as well as the intensities of few other porphyrin bands 1600, 1233, 1204 cm^{-1}) shows temperature dependence. The same behavior of the 1300 cm^{-1} band (more intensive at lower temperatures) for ^{15}NO can be seen in Figures 7 and 8.

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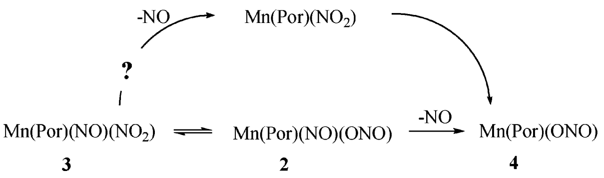
at 1421 and 1304 cm^{-1} (1392 and 1286 cm^{-1} for ^{15}NO) reach their maxima. Although the exact ν(NO) position might be affected by overlap with the ν(NO) band of **2** still present in sample, the shift to lower frequency is in agreement with the trend reported for Fe(TPP) complexes. The Fe(TPP)(NO)(ONO) generated by UV photolysis at low temperature displayed a higher frequency ν(NO) band than did the Fe(TPP)(NO)(NO_2) precursor.[29]

Assignment of **3** as Mn(TPP)(NO)(NO_2) is further supported by experiments where increments of O_2 were deliberately added into a cryostat containing Mn(TPP)(NO) prepared under excess NO at 200 K (Figure S3).[30] The incremental O_2 resulted in decreased intensity of the nitrosyl band and the appearance of small absorbances at 1860, 1590, and 1295 cm^{-1}, characteristic of N_2O_3.[31] The sample was kept at 200 K for a several hours which led to complete consumption of N_2O_3 and the appearance of three new bands at 1806, 1422, and 1304 cm^{-1} (1771, 1392 and 1286 cm^{-1} for ^{15}NO), indicating the formation of **3**. Warming of the sample to room temperature shows conversion of **3** into Mn(TPP)(ONO). However, we were unable to obtain a pure material because of the incomplete conversion of Mn(TPP)(NO) into Mn(TPP)(NO)(NO_2). The addition of more O_2 ultimately results in the complete disappearance of the nitrosyl band and formation of a nitrate complex with IR bands at 1470 and 1284 cm^{-1}.[22]

The above results clearly suggest that the transformation of **2** to **4** upon warming of samples of **2** from 130 K to room temperature may be more complicated than the simple NO dissociation depicted in eq 2. The nitrosyl nitro species **3** is formed as a transient species, and it is possible that at least part of the **2** to **4** transformation occurs via the sequence **2** → **3** → **4** (eq 4). Alternatively, the formation of **3** may be a "dead-end" equilibrium.



(4)

The formation of **3** from **2** might have several routes, one being an intramolecular nitrito- to nitro- linkage isomerization, the other being NO_2 dissociation from **2** to give Mn(Por)(NO) followed by reaction of the latter with NO_2 or with N_2O_3 under excess NO (the typical experimental condition) to give **3**. The following experiments were initiated to test the likely mechanism. A sample of Mn(TPP)(NO)(ONO) (**2**) was evacuated at 130 K; then ^{15}NO was introduced into the cryostat, and that sample was allowed to warm to RT. If eq 5 were operational, Mn(TPP)(O^{15}NO) should be formed as one of the final products; however, none was detected. In a separate experiment, a sample of **2** was warmed from 130 to 200 K during continuous high-vacuum evacuation and the IR spectrum monitored. Spontaneous NO_2 dissociation from **2** should result in the appearance of Mn(TPP)(NO), but this was not seen. Instead, the IR spectral changes were consistent with the intramolecular transformation of **2** to **3**. The stable nitrito product Mn(TPP)(ONO) (**4**) is formed upon further warming to RT. If an Mn(III) nitro species were the result of NO dissociation from **3**, this would initially give the pentacoordinate nitro intermediate Mn(TPP)(NO_2) which would undergo linkage isomerization to the more stable nitrito form. The same intermediate has been invoked in solution-phase flash photolysis of Mn(TPP)(ONO) under excess NO where time-resolved UV−vis spectroscopy detected a species thought to be Mn(TPP)(NO_2), which underwent unimolecular isomerization to **4** ($k_{\mathrm{isom}} =$ 14 s^{-1} in 298 K toluene).[32] Notably, the loss of NO from **2** (or **3**) appears to be irreversible, since recooling of the Mn(TPP)(ONO) sample under excess NO does not reform **2**.

$$\mathbf{2} \rightarrow \mathrm{Mn(Por)(NO)} + \mathrm{NO_2}\,(\mathrm{N_2O_3}\ \text{under excess NO}) \rightarrow \mathbf{3} \quad (5)$$

Some additional information can be also drawn from Figures 7 and 8. Earlier studies established that several IR and Raman bands for Fe(TPP) axial complexes are sensitive to the spin and oxidation states of iron center.[33] The bands in the ranges of 1350−1330 cm^{-1} (ν(C_a−C_m) mixed with ν(C_m−phenyl)) and 469−432 cm^{-1} (porphyrin core deformation mode) lie at higher frequencies in low-spin complexes. Similar behavior of these bands was noted in studies of dioxygen and nitrate complexes of Mn(TPP).[34] For Mn^{II}(TPP_{d20}), these bands lie at 1326 and 422 cm^{-1}. Formation of the nitrosyl complex Mn(TPP_{d20})(NO) is accompanied by transition from the high- to low-spin state,[16a] and this is accompanied by shifts of these bands to 1336 and 450 cm^{-1}, respectively. No further shifts of these bands were observed upon generation of **2**, indicating that the Mn center remains in the low-spin state, in agreement with other 6-coordinate manganese nitrosyl porphyrinato complexes.[16a] These bands do not shift further when the samples are warmed from 130 to 200 K, thus **3** is also likely to be in a low-spin state. However, upon formation of the nitrito complex **4**, the band at 1336 cm^{-1} shifts back to 1326 cm^{-1} (Figure 8), suggesting that this species is high spin as has been reported for the nitrato analogue Mn(TPP)(ONO_2).[22]

Possible Disproportionation Mechanisms. There are several key observations that need to be addressed when speculating about prospective mechanisms for NO disproportionation.

(a) At low *T*, intermediate **1** is formed upon exposure of Mn(Por) to NO prior to formation of N_2O, and it displays

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(30) Exposure of the Mn(TPP) to excess NO at room temperature followed by slow cooling to 200 K gave an IR spectrum (ν(NO) ~1740 cm^{-1}) showing only the formation of Mn(TPP)(NO).

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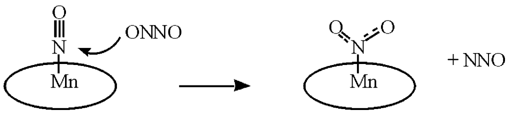
Scheme 1. Hypothetical O-Atom Transfer from Dinitrogen Dioxide to Coordinated NO



isotope sensitive IR bands at 1820 and 1712 cm^{-1}. The formation of **1** is somewhat reversible, since evacuating the system not only removes the NO dimers present at these temperatures but also depletes **1**.

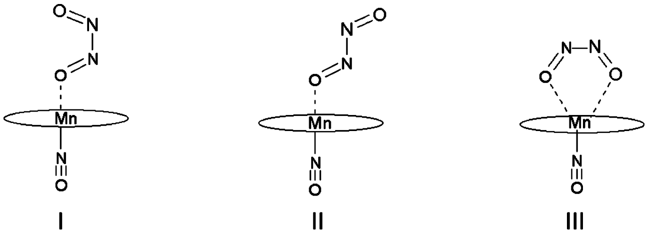
(b) At room temperature, sublimed layers of Mn(Por) form Mn(Por)(NO) (ν(NO) = 1740 cm^{-1}) when exposed to NO but do not promote NO disproportionation. No evidence of the nitrito complex was observed in the FT-IR or UV−vis spectra of Mn(Por) exposed to excess NO at RT.

(c) The nitrito nitrosyl complex Mn(Por)(NO)(ONO) (**2**) undergoes linkage isomerization to give the nitro complex Mn(Por)(NO)(NO_2) (**3**) as T is increased, but the reverse was not seen. This suggests that the disproportionation mechanism must lead directly to the O-bound nitrito complex, since **2** is formed concurrently with the appearance of N_2O.

The key step for NO disproportionation is the N−N coupling to form N_2O. Various scenarios can be envisioned. One might involve oxygen atom transfer from the dinitrogen dioxide dimer to a coordinated NO as illustrated in Scheme 1 and as suggested in solution studies for the reaction of NO with Ru(Por)((CO).[35] However, such a pathway would immediately generate an N-coordinated nitro complex. If this were 5-coordinate, isomerization to the pentacoordinate nitrito complex **4** would be favorable, but the rate should be slow at low T, and a nitro intermediate would be observed. Furthermore, point c discounts the possibility of the direct formation of **3** at low T. Nonetheless, the unusual feature of the disproportionation being observable at low T but not at RT argues for a key species having a negative enthalpy but a very positive entropy of formation. This would be a likely characteristic of intermediates involving two or more moles of NO gas, such as the NO dimer or a complex thereof.

In this context, the metal center is a possible template for the formation of a hyponitrite complex, M(N(O)NO). An intermediate might be the dinitrosyl species *cis*-Mn(Por)-$(NO)_2$, although the hyponitrito ligand could also be formed by direct attack of free NO on a coordinated NO. A hyponitrito complex that has been rigorously established is $[Co(NH_3)_5(N_2O_2)]_2^{4+}$,[36] and this displays IR bands at 1136, 1046, and 932 cm^{-1}.[37] Another, $Pt(N_2O_2)(PPh_3)_2$, is reported to show strong bands at 1285 and 1240 cm^{-1}.[38] In sodium hyponitrite, where the $N_2O_2^{2-}$ anion has a trans configuration, the corresponding bands occur at 1383, 1115 (Raman), and 1020 cm^{-1} (IR).[39] In the present study, we used different porphyrins to free the spectral ranges where hyponitrito bands might be expected but did not detect isotope sensitive bands in these regions. As discussed below, a complex of dinitrogen dioxide is a likely candidate for **1**, but the IR spectra suggest the extent of charge transfer from the metal is too small to consider the resulting ligand to be a hyponitrite anion.

Scheme 2. Possible Geometries of O-Coordinated Dinitrogen Dioxide



Intermediate **1** appears prior to N_2O formation and shows isotope-sensitive IR bands at 1820 and 1712 cm^{-1} in the region associated with terminal nitrosyls.[40] For a dinitrosyl complex, the competition between the two π-acceptor ligands would shift the ν(NO) frequencies to higher values relative to the mononitrosyl analogue Mn(TPP)(NO) (1740 cm^{-1}). For example, Fe(TPP)(NO) shows ν(NO) at 1681 cm^{-1} in $CHCl_3$, while cooling to 213 K resulted in the appearance of a new band at 1695 cm^{-1} with twice the intensity and another much weaker band at 1776 cm^{-1} attributed to $Fe(TPP)(NO)_2$.[19b] A similar spectrum (1692 s and 1772 w cm^{-1}) was obtained in solid-state conditions at low T.[19c] The pattern for **1** is different, so it seems unlikely that this species is a dinitrosyl complex.

A plausible alternative for **1** would be the Mn(II) complex of a nearly neutral dinitrogen dioxide ligand, since **1** is generally observed under conditions where the nitric oxide dimers are also seen. Modest charge transfer from the electron-rich metal center to the π^* orbitals of ONNO should result in lowered frequencies for the NO stretches of that ligand.[41] However, since the electronic spectrum of this complex appears to be that of a Mn(II) porphyrin complex, we would argue that such charge transfer is much less than implied by designating this ligand as hyponitrite. Furthermore, **1** might be a six-coordinate nitrosyl adduct of the type *trans*-Mn(Por)(NO)(ONNO). In analogy, an EPR study of the reaction of NO with Co(TPP)(NO) in toluene solution has been interpreted in terms of the initially formed Co(TPP)-$(NO)_2$ converting to Co(TPP)(NO)(N_2O_2) upon an increase in NO pressure.[42] As noted in point c, the product formed initially is the O-bonded nitrito complex Mn(Por)(NO)-(ONO), and since nitro to nitrito isomerization does not appear to be facile under these conditions, it seems likely that the precursor to **2** is also an O-coordinated adduct. Scheme 2 displays some possible structures of O-coordinated dinitrogen dioxide complexes.

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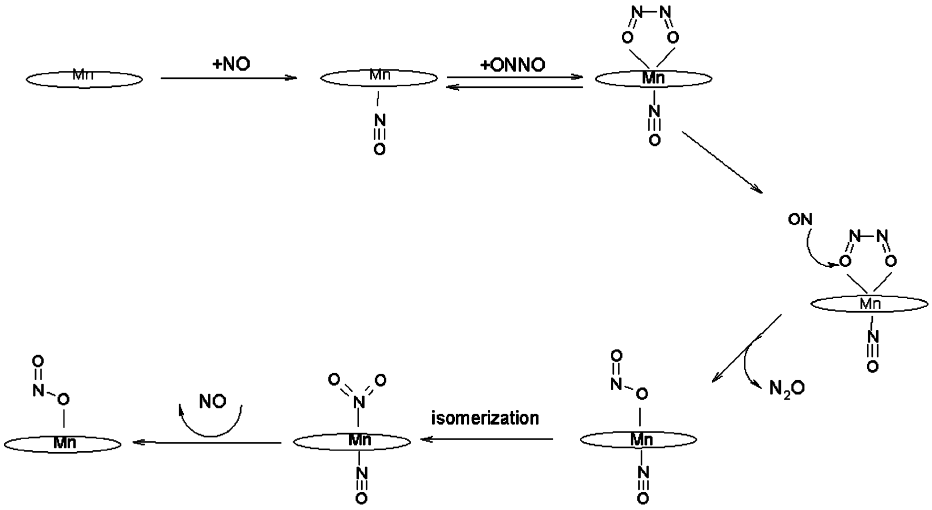
Scheme 3. Prospective Sequence of Reactions in the Course of the Disproportionation of NO by Mn(Por) to Give N_2O and Mn(Por)(ONO) in Low-Temperature Sublimed Layers



Six-coordinate complexes, as shown in Scheme 2, would be expected to display an ν(NO) band for the coordinated nitrosyl. As noted above, the overlap of other absorbances with this $(NO)_2$ band is a likely reason for the unusually high-intensity ratio of asymmetric/symmetric bands for the NO dimers in the present experiments. Among these, **III** would appear to be the more consistent with the IR bands attributed to **1** given that peak separation and relative intensities are similar to those of the *cis*-ONNO dimer. Such a coordination mode, however, might be expected to pull the Mn away from the mean porphyrin plane toward the $(NO)_2$ ligand, weakening the Mn−NO bond and thereby changing the ν(NO) frequency. However, in contrast to the other metal porphyrin systems, the addition of trans ligand to the Mn(II) porphyrin nitrosyls does not significantly changes the ν(NO) frequency (1).[16c,d]

Scheme 3 is a proposed mechanism for the transformations taking place in the course of the interaction of excess NO with sublimed layers of Mn(Por) at low *T*. Intermediate **1** is believed to be responsible for the assembly of 3 equiv of NO: two as the ONNO ligand and one as a nitrosyl ligand. The formation of the nitrito nitrosyl complex **2** is thought to be the result of the attack of free NO on the O atom of the coordinated dimer with concomitant formation of N_2O. This would satisfy the apparent requirement that a metastable O-coordinated nitrito product, **2**, is initially formed in the disproportionation sequence, but this is quite speculative. The data do clearly show that as the temperatures of solids containing **2** are slowly increased, linkage isomerization occurs to give the nitro isomer **3.** Further temperature increases lead to NO loss, giving the pentacoordinate nitrito complex Mn(TPP)(ONO) (**4**); however, it is not clear whether this occurs directly from **2** or via the intermediacy of **3**.

Summary

The sublimed layers of manganese(II) porphyrins display interesting reactivity with NO. The room temperature reaction of Mn(Por) with excess NO leads only to the known nitrosyl complex Mn(Por)NO; however, when the same reaction is executed at low temperature, NO disproportionation occurs. We have used in situ FTIR and optical spectroscopy to monitor these transformations from 77 K to RT. A reaction intermediate spectrally characterized at 90 K is thought to be an O-coordinated dinitrogen dioxide complex Mn(Por)-(NO)(ONNO) (**1**). Further reaction with NO shows evolution of N_2O and formation of the nitrosyl nitrito complex Mn(Por)(NO)(ONO) (**2**), which is stable at 130 K. The latter undergoes linkage isomerization into the N-bounded nitrosyl nitro form Mn(TPP)(NO)(NO_2) when the sample warms from 130 to 200 K, but the reverse process was not seen. When the system was warmed further (to room temperature), the known nitrito complex Mn(TPP)(ONO) is the final manganese product.

Acknowledgment. Financial support from CRDF (Grant AC2-2520-TB-03) is gratefully acknowledged. P.C.F. also acknowledges a grant (DE-FG02-04ER15506) from the Chemical Sciences Division, Office of Basic Energy Sciences, U.S. Department of Energy.

Supporting Information Available: Figures showing the IR spectra of the formation of **2**, the IR spectra of a sample with an excess of a 1:1 mixture of $^{15}NO/^{14}NO$, and the FT-IR spectra of Mn(TPP)(NO)(NO_2) derivatives in the sublimed layers. This material is available free of charge via the Internet at http://pubs.acs.org.

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