Comparative IR Study of Nitric Oxide Reactions with Sublimed Layers of Iron(II)- and Ruthenium(II)-*meso*-Tetraphenylporphyrinates

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Abstract: The interactions of nitric oxide gas with thin layers of $Fe^{II}(TPP)$ and $Ru^{II}(TPP)$, obtained by sublimation onto low-temperature substrate (77 K), has been investigated by means of IR spectroscopy (TPP = *meso*-tetraphenylporphyrinate). Only simple addition of NO to form Fe(TPP)(NO) is observed for the iron–porphyrin $Fe^{II}(TPP)$, while, in contrast, $Ru^{II}(TPP)$ promotes NO disproportionation to form the nitrosyl–nitrito complex Ru(TPP)(NO)(ONO) and N_2O. Thin layers of Fe(TPP)(NO) are inert to further reaction with excess NO; however, the nitrosyl–nitro complex Fe(TPP)(NO)(NO$_2$) is readily formed when traces of dioxygen are added to the NO atmosphere. When the NO_2 concentrations in the NO/NO$_2$ mixture are relatively high, the nitrato complex Fe(TPP)(NO$_3$) is also formed. Spectral data are given indicating that moderate shifts in the nitrosyl stretching frequency of Fe(TPP)(NO) are due to crystal packing effects, rather than to the H-bonding of coordinated NO with protic contaminants suggested in an earlier publication. Removal of NO by exhaustive evacuation from layers containing Fe(TPP)(NO)(NO$_2$) leads to formation of Fe(TPP)(NO) and Fe(TPP)(NO$_3$).

Introduction

The interaction of Fe(TPP)(NO) (**1**, TPP = *meso*-tetraphenylporphyrinate) with excess NO has been the subject of some recent disagreement.[1,2] According to one laboratory,[1] this reaction in solution and in thin films leads to NO disproportionation to give the nitrosyl–nitro product Fe(TPP)(NO)(NO$_2$) (**2**), as had been previously reported by others.[3,4] In contrast, solution experiments by another laboratory[2] arrived at the conclusion that this formation of **2** from **1** was the result of trace NO$_2$ in the nitric oxide sources. With clean NO, **2** was not observed; although at low temperature a *trans*-dinitrosyl species Fe(TPP)(NO)$_2$ was seen.[5] To explain this discrepancy, it was suggested[1] that water molecules H-bonded to the coordinated NO of **1** may inhibit disproportionation.

Here we address these discrepancies by using infrared spectroscopy to examine NO reactions with sublimed layers of Fe(TPP) in a high-vacuum system where the compositions of the reactant gases can be carefully controlled. This methodology is very informative for the spectral investigations of ligand–metalloporphyrin interactions.[6] Tetraarylporphyrins can form microporous "porphyrin sponges", which allow incorporation of guest molecules with different shapes and sizes.[7a,b] Sublimed layers of metal–*meso*-tetraphenylporphyrinates are also sponge-like,[8a] and amorphous layers of M(TPP) obtained by sublimation on a low-temperature (77 K) surface have high microporosity. In these layers, potential reagents can easily diffuse across the thickness, and adducts thus formed can be studied by IR spectroscopy without solvent interference. We also describe a comparative study of the interaction of NO with sublimed layers of Ru(TPP) (**3**). It has been shown that NO reacts with Ru(TPP)(CO) in solution to give the nitrosyl–nitrito complex Ru(TPP)(NO)(ONO) (**4**)[9,10] and that this reaction proceeds via the intermediacy of the dinitrosyl complex Ru(P)(NO)$_2$.[10]

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Experimental Section

Since iron(II) porhyrinates are very sensitive to oxygen and readily transform to Fe(III) derivatives, the more stable Fe(TPP)(B)$_2$ complexes with nitrogen bases (B is pyridine or piperidine) were prepared[11] to use as parent compounds. The low-temperature sublimate was prepared[12] by placing an Fe(TPP)(B$_2$) sample in a Knudsen cell and heating it to about 470 K under high vacuum ($P = 10^{-5}$ mmHg). Evacuation for 3 h resulted in the complete elimination of the coordinated axial ligands B, as monitored by measuring the pressure at the cryostat outlet. Then liquid nitrogen was poured into the cryostat, and the Knudsen cell was heated to 520 K, at which temperature sublimation of Fe(TPP)(NO) on the KBr substrate occurred. For obtaining layers with thicknesses convenient for IR spectral studies, sublimation was carried out for about 2 h.

The precursor for preparing Ru(TPP) thin layers was Ru(TPP)(CO).[9b] In this case, elimination of CO was carried out at 520 K, and sublimation with an appropriate rate required heating to about 570 K. The sublimed low-temperature layers of Fe(TPP) and Ru(TPP) were heated to room temperature under dynamic vacuum, and nitric oxide was fed to the cryostat from a vessel provided with a mercury manometer to measure the equilibrium pressure of NO. In experiments with the addition of low-pressure O$_2$, the thoroughly dried dioxygen was introduced into the cryostat from a small glass flask (10 mL). The same procedure was carried out with the layers obtained by sublimation on to the room temperature substrate.

Nitric oxide was purified by passage through KOH pellets and a cold trap (dry ice/acetone) to remove higher nitrogen oxides and trace quantities of water. The purity was checked by IR measurements of the layer obtained by slow deposition of NO on the cooled substrate of the optical cryostat (77 K). The IR spectra did not show the presence of N$_2$O, N$_2$O$_3$, or H$_2$O. ^{15}NO with 98.5% enrichment was purchased from the Institute of Isotopes and was purified by the same procedures.

IR spectra were obtained on a Specord M-80 spectrophotometer equipped with a polarizer and on a Perkin-Elmer 1600 FTIR spectrometer.

Results and Discussion

IR experiments have previously demonstrated the ready formation of Fe(TPP)(NO) (**1**) by interaction of NO gas with a thin layer of Fe(TPP) obtained by sublimation onto low temperature (77 K) substrate.[13a] In this process (Figure 1b), although a large excess of NO was used, no products beside **1** were observed. This raised the following question: If disproportionation can proceed in such films as reported,[1] why should the nitrosyl–nitro complex **2** be formed from reaction of Fe(TPP)(NO) with excess NO, but not by direct interaction of excess NO with Fe(TPP)? Under our experimental conditions, exposure of dry Fe(TPP)(NO) layers to a NO atmosphere does not lead to formation of Fe(TPP)(NO)(NO$_2$).

Solid-State Effects on IR Bands. It has been suggested[1] that protic impurities such as water inhibit promotion of NO disproportionation by Fe(TPP)(NO). The main evidence in support of this argument[1] was the upward shift of ν(NO) in

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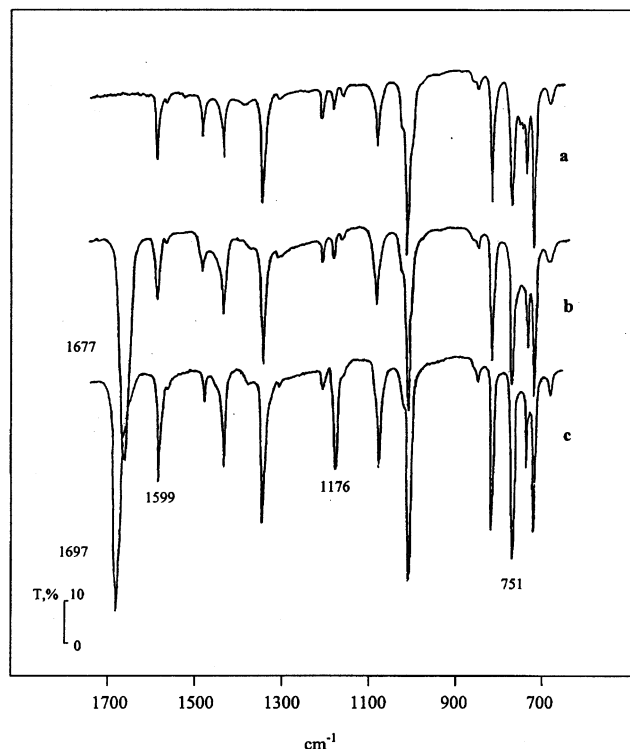
Figure 1. IR spectra (a) of a thin layer of Fe(TPP) obtained by sublimation onto a low-temperature (77 K) substrate and heated to 293 K, (b) after interaction with excess NO, and (c) after annealing by heating to 353 K for 2 h and then cooling to 293 K.

FTIR ATR spectra upon the treatment of Fe(TPP)(NO) thin films by acetone followed by purging with N$_2$. In very dilute solutions of **1**, quantities of protonic impurities of comparable concentrations are certainly possible despite considerable efforts to maintain "dry" conditions.[2] In contrast, the presence of stoichiometric quantities of water in sublimed layers obtained by deposition onto a room temperature substrate under high vacuum described here is very unlikely. The only likely H$_2$O source is the nitric oxide, which, in turn, was thoroughly dried.

We have observed similar shifts of ν(NO) just from annealing sublimed layers of **1** in a vacuum (Figure 1c) as well as for layers of cobalt– and manganese–nitrosyls (with $\Delta\nu$(NO) equal to 20, 16, and 13 cm^{-1}, respectively).[13] Although such shifts could be related to intercalated solvent molecules that are eliminated upon heating the layered sample, there was no IR evidence for water in the spectral range 3100−3500 cm^{-1}, where the stretching of H-bonded water appears. Furthermore, several other experimental observations support the more likely explanation that the ν(NO) band shifts are due to crystal packing effects.

(i) From Figure 1c it is seen that the ν(NO) shift is accompanied by the marked enhancement in the porphyrin band intensities at 1598, 1178, and 750 cm^{-1} assigned to phenyl group vibrations.[14] Some changes in band intensities occur also in the range 3000−3100 cm^{-1} containing weak CH stretching bands.

(ii) Sublimation of Fe(TPP) onto the freshly polished KBr substrate, maintained at room temperature, leads to formation of oriented samples with the plane of macrocycle parallel to the substrate plane[8b,c] (Supporting Information Figure S1).

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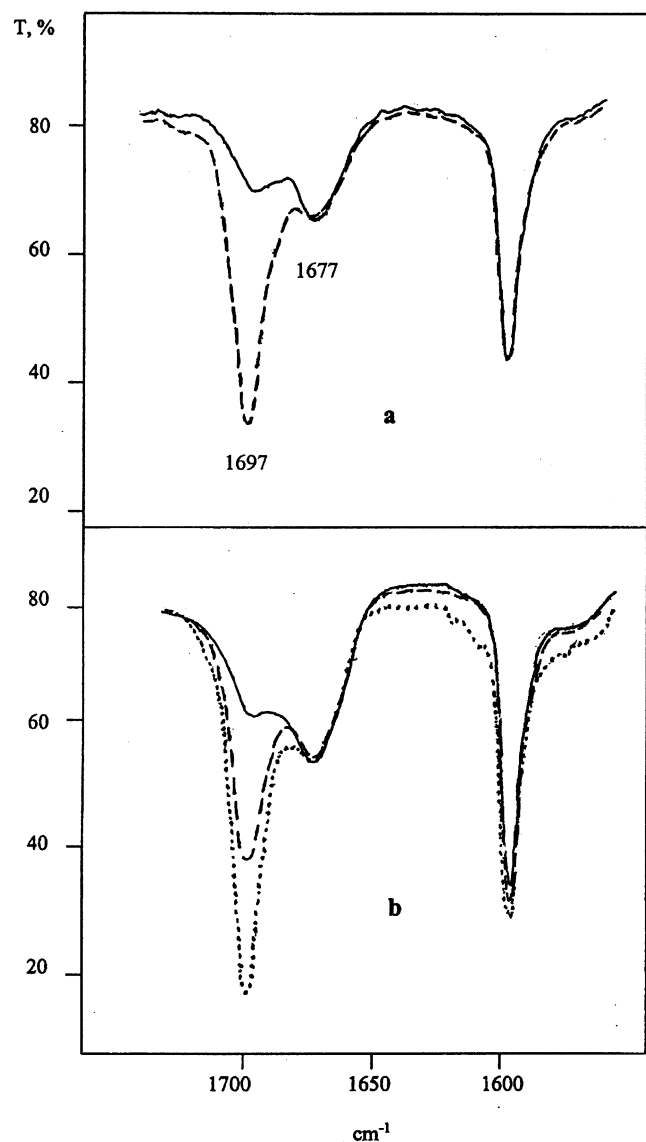
Figure 2. IR spectra in the nitrosyl stretching range of partially oriented Fe(TPP) layer after interaction of excess NO: (a) with substrate normal to the incident beam (solid line) and with substrate tilted to 40° (dashed line); (b) for tilted substrate and polarized IR radiation (s-polarization (solid line), p-polarization (dotted line), polarization angle = 45° (dashed line)).

Interaction of NO with this type of layer leads to a sample for which the NO stretching band at 1697 cm^{-1} is weak when the substrate is perpendicular to the IR beam. Tilting the substrate sharply enhances the intensity of this band and reveals strong dependence on the polarization angle, when polarized IR radiation is used (Supporting Information Figures S-2 and S-3). The spectra of layers containing both types of nitrosyl complexes (with ν(NO) at 1677 and 1697 cm^{-1}) are more pronounced. The lower frequency ν(NO) band does not reveal any dependence on the tilting angle of the substrate and the polarization direction (Figure 2a,b), while the high-frequency band shows strong dependence on both parameters.

(iii) In the sublimed layers of *meso*-4-pyridyltriphenylporphyrinatoiron(II) [Fe(MPyTPP)], coordination of a pyridyl to the metal ion of an adjacent molecule leads to oligomers with perpendicularly oriented porphyrins[15a] and a solid-state structure significantly distinct from that of Fe(TPP). Interaction of these layers with NO results in formation of five- and six-coordinated

complexes with ν(NO) at 1678 and 1650 cm^{-1}, respectively.[15b] In the latter, the pyridyl group of the adjacent molecule occupies the sixth coordination site. Annealing such layers did not shift the 1678 cm^{-1} band.

These observations can be explained in terms of crystal packing effects. It is reasonable to suggest that in amorphous layers there are few close contacts between coordinated NO and adjacent molecules. For this reason the value of ν(NO) is close to that observed in solution.[3,5] As is seen from Figure 1c sample annealing results in some enhancement of peak intensity of all the IR bands. However, the characteristic bands that belong to the groups situated on the periphery of molecules, i.e., phenyl group vibrations, reveal large intensity enhancement due to close packing upon crystallization.

In oriented samples the *ab* plane of crystallites[6] is disposed parallel to the substrate plane. In this case the out-of-plane vibrations of porphyrin are not active in the IR spectrum, because the electric vector and transition dipole moments of these vibrations are orthogonal. However, they become active when the substrate is tilted. In the case of a linear Fe−N−O moiety, the NO stretching is akin to an out-of-plane vibration and also should be inactive. Since the angle[16] between the coordinated NO and the normal to the porphyrin plane is about 30°, nitrosyl stretching will be only partially active and will enhance its intensity with tilting of the substrate. The intensity of the 1697 cm^{-1} band strongly depends on both the tilting and polarization angles. Partially oriented sublimed layers containing oriented and disoriented domains show two nitrosyl stretching bands that reveal substantially different orientation/polarization properties. This result is easy to interpret by concluding that Fe(TPP)(NO) molecules with the low ν(NO) are in the amorphous regions of the layer.

Prolonged exposure (several days) of annealed layers of **1**, which display the higher frequency ν(NO) bands, to gaseous H$_2$O or CH$_3$OH with pressures close to their saturation values does not shift ν(NO) to lower frequency. On the other hand, these same layered materials readily form the nitrosyl−nitro complex **2** upon exposure to NO$_2$ (see below); thus, the crystalline films have enough porosity for diffusion of NO$_2$ into the layers.

Fe(MPyTPP) does not form layers with oriented molecules under the experimental conditions that give oriented sublimed layers of Fe(TPP). This can be attributed to the pyridyl-substituted metalloporphyrins forming coordination oligomers and polymers as described above.[17] This prevents the close packing of molecules in crystallites and assists creation of a porous network material.[18,19] If the ν(NO) shift to high frequency upon annealing were the result of eliminating a hydrogen-bonding impurity, the same pattern would be expected for five-coordinated Fe(MPyTPP)(NO). The absence of such behavior argues that other intermolecular interactions are responsible. The high sensitivity of ν(NO) to the environment has repeatedly been observed,[4a,b] an example being Fe(TPP)(NO) itself, for which

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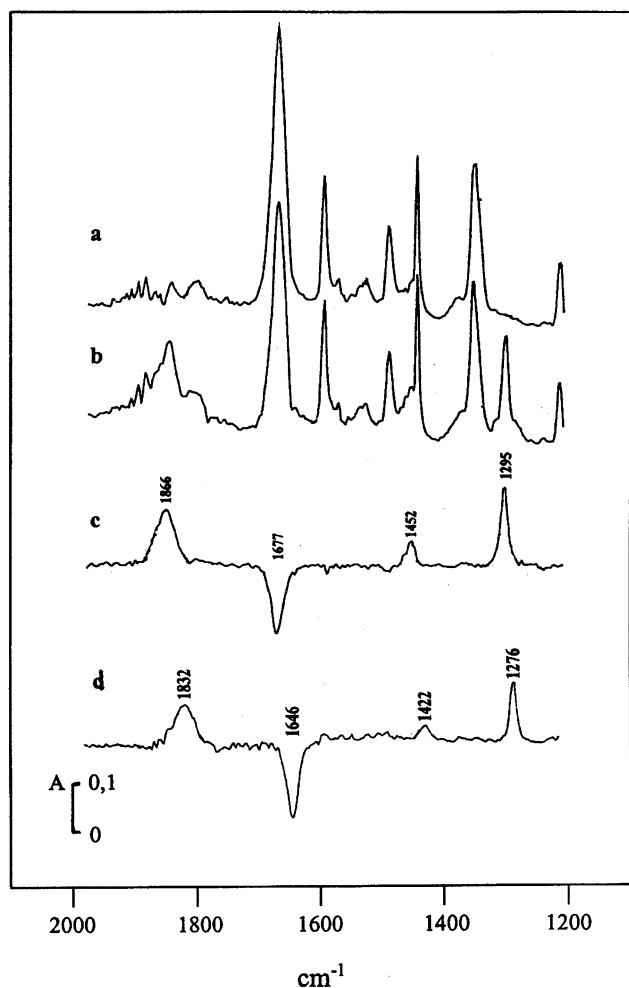
Figure 3. Sequential IR spectra of the Fe(TPP) film kept (a) under 30 mmHg NO atmosphere (ca. 2 mmol) over 3 h and (b) after addition in to the cryostat of 2.6 μmol of O_2; (c) the difference IR spectrum of b minus a. Spectrum d is the same as c with ^{15}NO.

ν(NO) values from 1670 to 1700 cm^{-1} have been reported in different media.[16,3,5,20,21]

Reaction of Fe(TPP)(NO) with NO₂. Despite the above observations, our experimental data cannot completely preclude the presence of an H-bonded form of **1** within the solid films. However, neither the samples displaying the lower ν(NO) values nor those with the higher ν(NO) form spectrally measurable quantities of Fe(TPP)(NO)(NO₂) even after 3 days of contact with NO at pressures up to 300 mmHg. Moreover, when the NO gas in contact with the solid Fe(TPP)(NO) was deposited on the cold surface (77 K) of a second cryostat, no detectable quantities of N₂O were observed in the IR spectra. These results are consistent with solution studies at University of Santa Barbara (UCSB) examining the reaction of **1** with clean NO.[2]

The addition of small quantities of O₂ to the cryostat leads to formation of Fe(TPP)(NO)(NO₂) irrespective of whether the solid sample of **1** displayed a low or a high ν(NO). Figure 3a represents the IR spectrum of Fe(TPP)(NO) under 30 mmHg of ^{14}NO. The features in the 1800−1900 cm^{-1} spectral range are caused by the presence of gas phase and adsorbed NO. This spectrum does not change for 3 h. However, addition of a small

quantity of O₂ led to the appearance of the new band at 1295 cm^{-1} and to decreased intensity at 1677 cm^{-1} (Figure 3a,b). Three new bands at 1866 {ν(NO)}, 1452 {ν_a(NO₂)}, and 1295 cm^{-1} {ν_s(NO₂)} are easily seen in the difference spectra (Figure 3a,c) and unambiguously indicate formation of the nitrosyl−nitro complex **2**. Experiments with ^{15}NO (Figure 3d) reveal the isotopic shifts consistent with this conclusion. Adding more O₂ into the cryostat leads to formation of more **2**. Annealing the sample leads to high-frequency shifts of bands characteristic of the coordinated nitrosyl and nitro groups to 1877 {ν(NO)}, 1464 {ν_a(NO₂)}, and 1300 cm^{-1} {ν_s(NO₂)}, the value of ν(NO) coinciding with that reported for solid Fe(TPP)(NO)-(NO₂).[4a] Hence in this case we also observe high environmental sensitivity of axial ligand vibrations,[4a,b] and these frequency shifts were accompanied by sharply enhanced intensities of phenyl vibrations.

The reaction described above is very sensitive to the relative concentrations of NO and NO₂ in gas phase. At relatively high concentrations of NO₂ the nitrato complex Fe(TPP)(NO₃) (**3**) is also formed (Supporting Information Figure S-4) and is the major product at higher NO₂ concentrations.

Reaction of NO with Ru(TPP). The possibility that the solid state may inhibit the NO disproportionation was addressed by the experiments with Ru(TPP). In this case NO addition to a sublimed layer containing predominantly Ru(TPP) (in the sublimate there is also some Ru(TPP)(CO)) leads to ready formation (within a few minutes) of a material with an IR spectrum consistent with the known nitrosyl−nitrito complex Ru(TPP)(NO)(ONO) (Figure 4).[9,10] Experiments with ^{15}NO support this conclusion. The spectrum of the head gas deposited on the frozen surface of a second cryostat displayed intense IR bands characteristic of N₂O (^{15}N₂O) at 2242 (2170) {ν_a(NNO)} and 1294 (1276) cm^{-1} {ν_s(NNO)}. Hence the disproportionation reaction given in eq 1 readily occurs in this case.

$$Ru(TPP) + 4NO \rightarrow Ru(TPP)(NO)(ONO) + N_2O \quad (1)$$

Stability of Fe(TPP)(NO)(NO₂). In solution **2** is stable only under an NO atmosphere,[2b,3] and recent data[1,2] based on UV−vis spectral changes suggested that removal of NO head gas leads to formation of Fe(TPP)(NO₂), although this species has been shown to be unstable.[2b] The spectral properties of a bona fide example of Fe(TPP)(NO₂) have not been reported,[22] so an attempt to obtain this species by NO elimination from **2** might provide the opportunity for such spectral characterization. However, exhaustive evacuation of NO at elevated temperature from a layered sample of Fe(TPP)(NO)(NO₂) gave a material displaying an IR spectrum consistent with a mixture of the nitrosyl complex Fe(TPP)(NO) and a new species with the bands at 1526 and 1271 cm^{-1} (Figure 5b). The second product appears to be the nitrato complex Fe(TPP)(NO₃), since these bands are close in energy to those reported by Goff and co-workers for Fe(TPP)(NO₃) (1544 and 1275 cm^{-1})[23] and Scheidt and co-workers for Fe(TpivPP)(NO₃) (1520 and 1250 cm^{-1}).[24] Thus, NO removal leads to the tranformation described by eq 2, apparently via NO dissociation from **2** (eq 3) to give the five-

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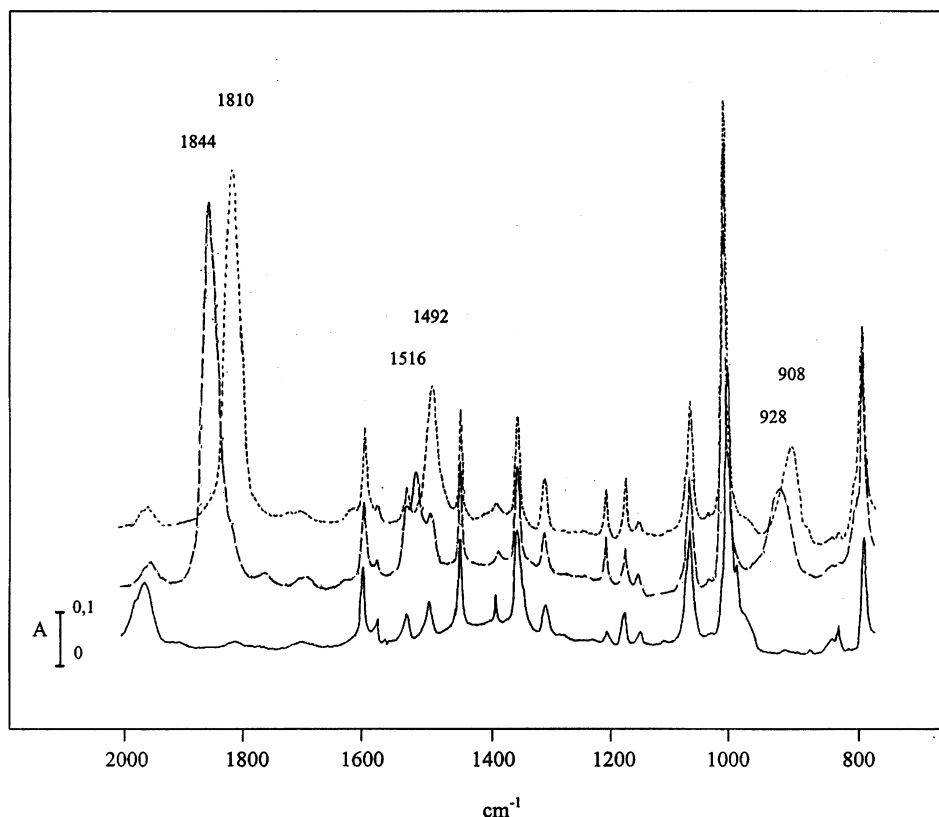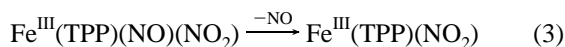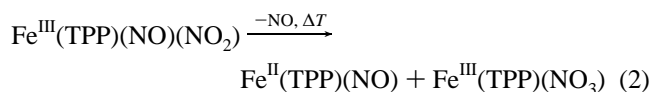(24) Munro, O. Q.; Scheidt, R. W. *Inorg. Chem.* **1998**, *37*, 2308−2316.

Figure 4. IR spectra of Ru(TPP) layers obtained by sublimation on to the low-temperature (77 K) substrate and heated to 293 K before (solid line) and after interaction with excess NO (dashed line) and ^{15}NO (dotted line).

coordinate nitro complex Fe(TPP)(NO$_2$), which is very reactive and readily undergoes disproportionation to form Fe(TPP)(NO) and Fe(TPP)(NO$_3$) according to eq 4.

$$Fe^{III}(TPP)(NO)(NO_2) \xrightarrow{-NO, \Delta T}$$

$$Fe^{II}(TPP)(NO) + Fe^{III}(TPP)(NO_3) \quad (2)$$

$$Fe^{III}(TPP)(NO)(NO_2) \xrightarrow{-NO} Fe^{III}(TPP)(NO_2) \quad (3)$$

$$2Fe^{III}(TPP)(NO_2) \rightarrow Fe^{II}(TPP)(NO) + Fe^{III}(TPP)(NO_3) \quad (4)$$

This disproportionation described by eq 4 could occur by a "bimolecular" oxygen transfer from one coordinated nitro group to another. An alternative mechanism might involve dissociation of NO$_2$ followed by O atom transfer to a coordinated nitro group and reaction between the resulting NO and Fe(TPP). The rationale for the latter proposal is the observation that free NO$_2$ readily oxidizes Fe(TPP)(NO$_2$) to Fe(TPP)(NO$_3$) in solution.[2b] That the same type of reaction may also proceed in the sublimed layer is attested by the present study and previous observation that interaction of NO$_2$ gas with the Fe(TPP) sublimed layer led to formation of nitrato complex.[14a]

Summary

Recent solution studies at UCSB[2a,b] demonstrated that scrupulously purified NO does not react with Fe(TPP)(NO) (**1**) to give Fe(TPP)(NO)(NO$_2$) (**2**). This interaction led only to formation of the unstable *trans*-dinitrosyl complex Fe(TPP)-(NO)$_2$, which could spectrally characterized at low temperature. The present investigation was stimulated in part by a recent

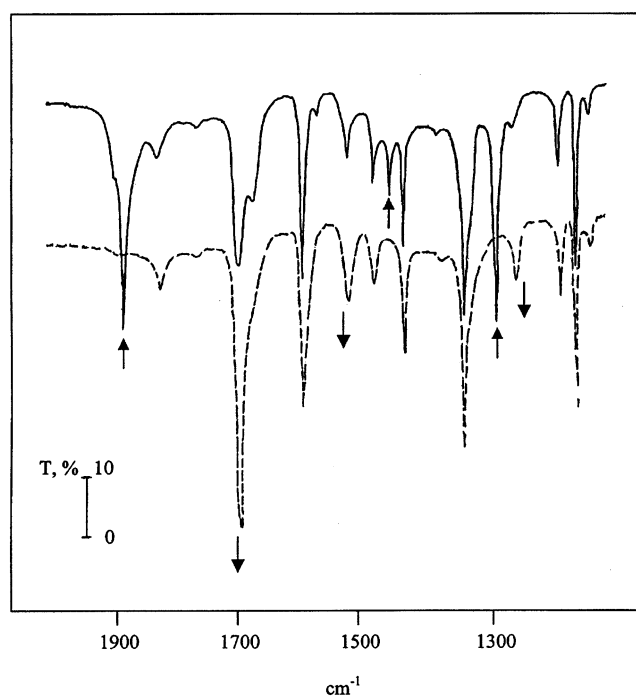**Figure 5.** IR spectrum of the Fe(TPP) sublimed layer that has been exposed to partially oxidized NO to give Fe(TPP)(NO)(NO$_2$) (solid line). The same after exhaustive evacuation at 80 °C over 1 h (dashed line).

report[1] which concluded on the basis of FTIR ATR spectral measurements that the reaction of NO with thin films of **1** leads to NO disproportionation and formation of **2**. The solid-state transmission/absorption IR spectroscopic data reported here are, in contrast, completely consistent with conclusions obtained

from solution studies[2a,b], namely, NO disproportionation is not promoted by **1** under clean NO at ambient temperature. The reliability of these conclusions is enhanced by the observation that in the same experimental conditions sublimed layers of Ru-(TPP) do easily react with excess of NO to form nitrosyl−nitrito complex Ru(TPP)(NO)(ONO) and N_2O. We attribute the difference in reactivity to the much greater propensity of the ruthenium complex to form dinitrosyl complexes at ambient temperature.

We have also demonstrated that $\nu(NO)$ shifts seen for Fe(TPP)(NO) thin films are not due to protic impurities (also proposed[1] to inhibit promotion of NO disproportionation) but instead likely to be due to crystal packing effects. Furthermore, neither the samples displaying the lower $\nu(NO)$ values (those attributed to contamination by protic impurities) nor those with the higher $\nu(NO)$ form spectrally measurable quantities of **2**, even after several days of contact with excess clean NO. However, formation of **2** in thin films readily occurs when **1** is exposed to a partially oxidized atmosphere of NO. These observations further support the conclusion that earlier reports that **2** is formed by the direct interaction of **1** with NO may have been compromised by trace impurities of NO_2. The stability of **2** formed in layered samples is strongly dependent on the head-gas composition. At relatively high gas-phase concentrations of NO_2, the nitrato complex Fe(TPP)(NO₃) (**3**) is also formed, while evacuation of head gas at elevated temperatures leads to disruption of **2** and formation of **1** together with **3**. These observations are in parallel with those obtained in solution[2b].

Supporting Information Available: Figure S-1 displaying the IR spectra of partially oriented sublimed film of Fe(TPP) in the range of out-of-plane deformation modes, Figure S-2 displaying dependence of nitrosyl stretching band intensity on the substrate tilting angle for oriented layers of Fe(TPP)(NO), Figure S-3 displaying the dependence of the nitrosyl stretching band intensity on the polarization direction for oriented layers of Fe(TPP)(NO), and Figure S-4 displaying formation of the nitrato complex Fe(TPP)(NO₃) at high concentrations of NO_2 in the gas phase (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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