with respect to the Tl and Te atoms. If the $Tl_2Te_2^{2-}$ anion were to undergo a 2e reduction, then a Tl–Tl trans-ring bond might form, since the LUMO in $Tl_2Te_2^{2-}$ is $8a_1$ and is very likely to be Tl-based although it can not be deciphered from the cellular charge distribution for that MO.

At this point in our discussion we may characterize the $Tl_2Te_2^{2-}$ anion as having a significant ionic component to the bonding, which was also found[25] to be true for $HgTe_2^{2-}$. Typically the bonding and/or arrangement of atoms in ionic compounds is dominated by Coulombic repulsions, which tend to maximize the distances between the atoms or groups bonded to the central atom. If the $Tl_2Te_2^{2-}$ anion were truly an ionic system, then one would predict the geometry to be planar (D_{2h}), which would maximize the distances between atoms with the same formal charge. Yet the structure of the $Tl_2Te_2^{2-}$ anion is puckered—a distortion from the anticipated D_{2h} geometry. It is not very likely that the distortion would occur along the Tl–Tl axis, for this would cause the two Te atoms to move closer together and increase their already repulsive interaction. Equivalently, the Te atoms will prefer to be further apart because their formal charge is twice that of the Tl atoms. Therefore, it is more likely that the distortion from D_{2h} symmetry occurs along the Te–Te axis, shortening the Tl–Tl distance only. The puckering of the $Tl_2Te_2^{2-}$ anion is most likely the result of the repulsive interaction of the antisymmetric combination of the Tl 6s AO's ($4b_1$) and the b_1 combination of the Te $5p_x$ AO's ($5b_1$). This interaction in a D_{2h} structure would be minimized by the out-of-plane bending of the Tl atoms to a C_{2v} structure. In order to test this hypothesis, we have performed SW-Xα QR calculations at a D_{2h} geometry.[33] The calculated charge distributions for the $4b_1$ and $5b_1$ MO's in the D_{2h} geometry are the same as those calculated at the C_{2v} geometry to within 1%. However, the $4b_1$–$5b_1$ orbital energy difference increases by $\sim$0.4 eV. This is a clear indication of increased interaction between these two orbitals. In fact, the $4b_1$ MO is actually lower in energy than $5a_1$ (which is the symmetric combination of the Tl 6s AO's) in the planar structure. Confirmation of this effect awaits a structural analysis by a MO method that has a rigorously defined and meaningful total energy.

Conclusions

The SW–Xα method employing quasi-relativistic corrections has been used to study the bonding in the 20-electron tetranuclear heteroatomic Zintl anions $Sn_2Bi_2^{2-}$, $Pb_2Sb_2^{2-}$, and $Tl_2Te_2^{2-}$. The $Sn_2Bi_2^{2-}$ and $Pb_2Sb_2^{2-}$ anions, which both have pseudotetrahedral geometries, have ground-state orbital configurations consistent with a localized valence structure having two-center, two-electron bonds along the six edges of the tetrahedron and one valence lone pair on each atom. The bonding MO's are formed almost entirely from the p AO's on the constituent atoms, while the lone-pair MO's are formed from the valence s AO's and are inert electron pairs. The HOMO's in these two anions are composed primarily of atomic p orbitals of the more electropositive atoms. The LUMO's of the two anions are localized primarily on the more electronegative atoms and are antibonding with respect to them. If the electronegativity differences between the two different atoms become large enough, as in the $Tl_2Te_2^{2-}$ anion, then the HOMO and the LUMO of the chemically bonded anions will interchange, giving a different orbital configuration and cleaving the two homonuclear bonds. The bonding in the $Tl_2Te_2^{2-}$ anion is best described as the result of coordination of two Te^{2-} anions with two Tl^+ cations. This view of the bonding leads to the correct prediction of the ground-state orbital configuration for the anion. Of the four predicted bonding MO's, only three are actually bonding. As for the $Sn_2Bi_2^{2-}$ and $Pb_2Sb_2^{2-}$ anions, the valence atomic s orbitals on the Tl and Te atoms are doubly occupied and are essentially inert. Two additional Te lone-pair orbitals were found. They are formed from the bonding and antibonding combinations of the two Te $5p_\pi$ type AO's. Their interaction is repulsive and is probably responsible for the Te–Te trans-ring distance being longer than the corresponding Tl–Tl distance. Due to the large ionic component to the bonding the $Tl_2Te_2^{2-}$ anion should be planar; however, a repulsive interaction between the antisymmetric combination of the Tl 6s AO's and the b_1 combination of the Te 5p AO's may be responsible for the distortion of the two Tl atoms out of plane.

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Registry No. $Sn_2Bi_2^{2-}$, 113251-42-6; $Pb_2Sb_2^{2-}$, 113273-58-8; $Tl_2Te_2^{2-}$, 77321-80-3.

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(33) The D_{2h} geometry was constructed by bending the Tl atoms in the C_{2v} geometry about the Te–Te axis until all four atoms resided in the same plane. This procedure maintained the original values of the Te–Te and Tl–Te distances. The atomic sphere radii were the same values used in the C_{2v} calculation. The outer sphere and the Watson sphere was subsequently readjusted to be at the center of the anion and to be tangent to the outermost atomic sphere. This calculation was carried out with the C_{2v}-symmetry basis set in order to facilitate our analysis.

Contribution from the Department of Chemistry,
Clemson University, Clemson, South Carolina 29634-1905

Reaction of Certain Nitrogen Oxides with Iron(III) Porphyrin μ-Oxo Complexes

Marc F. Settin and James C. Fanning*

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The nitrogen oxides NO, N_2O_4, and N_2O_3 and the μ-oxo complexes $[Fe(TPP)]_2O$ and $[Fe(OEP)]_2O$, where TPP and OEP are the dianions of *meso*-tetraphenylporphine and octaethylporphyrin, respectively, were reacted in toluene in the absence of O_2. $[Fe(TPP)]_2O$ was reacted with the nitrogen oxides in dimethylacetamide (DMA). All of the reactions were followed by changes in the electronic spectra. The NO reaction with $[Fe(TPP)]_2O$ in toluene yielded a solid product, $Fe(TPP)(NO)(NO_2)\cdot C_7H_8\cdot 2H_2O$. The N_2O_4 and the N_2O_3 reactions in toluene produced $Fe(TPP)NO_3$ and $Fe(OEP)NO_3$, while in DMA these reactions gave an equilibrium amount of $Fe(TPP)(DMA)_x^+$, the solvated complex.

Introduction

For many years studies of iron porphyrin oxynitrogen complexes have been limited to only a variety of nitrosyl hemes.[1-6] A few years ago the nitrate complexes $Fe(TPP)NO_3$ and $Fe(OEP)NO_3$ were prepared and studied.[7] Recently the nature of $Fe(TPP)NO_2$, $Fe(TPP)(NO_2)_2^-$, and $Fe(OEP)(NO_2)_2^-$ has been examined in solution.[8] These types of complexes may be part of a number of processes, such as those involving nitrate and nitrite reductase

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systems[9] as well as certain meat curing processes.[10-12] More information needs to be obtained on such complexes, especially on their modes of formation.

One method that might be used to form these complexes is to react the basic μ-oxo iron(III) complexes $[Fe(TPP)]_2O$ and $[Fe(OEP)]_2O$ and acidic nitrogen oxides, such as N_2O_4 and N_2O_3.[13] Since both the iron complex and the nitrogen oxides are soluble in toluene, it was considered to be the best solvent for these studies. Chlorinated solvents, which dissolve the iron porphyrin complexes well, were not used because of their potential reactivity with the nitrogen oxides[14-16] and because of the low solubility of the gases in these solvents.[17] For a more polar medium, DMA was selected. Dimethylformamide (DMF) had been used for the iron(III) porphyrin nitrite study,[8] but we were concerned that DMF might be more reactive with the nitrogen oxides than the closely related DMA.

These reactions are also being carried out, hopefully to gain some information that might be applicable to the reaction of $[Fe(salen)]_2O$, NO, and O_2 in dichloromethane.[18] The product from this reaction when mixed with secondary amines formed the carcinogenic *N*-nitrosamines in good yield. The C, H, N, and Fe analyses showed the product to be $Fe(salen)NO_3$; yet an authentic nitrate, made by reacting the μ-oxo complex and nitric acid,[19] did not nitrosate amines.[20] Unfortunately, the iron(III) Schiff base μ-oxo complex is insoluble in toluene, and the product from the NO/O_2 reaction, formed in dichloromethane, has been difficult to characterize. By studying the reactivity of the iron(III) porphyrin μ-oxo complexes with the nitrogen oxides, we may be better able to describe the nitrosating material.

Experimental Section

Chemicals. NO (Matheson Gas Products) was passed through a KOH column to remove higher oxides of nitrogen. N_2O_3 was prepared on a vacuum line by adding a slightly less than stoichiometric amount of oxygen to NO and cooling the mixture to −196 °C. Purification of the blue, liquid N_2O_3 was accomplished by a slow trap to trap distillation under static conditions. N_2O_4 was prepared by the addition of a slight excess of oxygen to NO. The white, solid N_2O_4 was purified by pumping off trace gas impurities at −78 °C.

$[Fe(TPP)]_2O$ (Strem Chemical Co.) was recrystallized from a toluene/diethyl ether mixture and dried under vacuum at 60 °C for 24 h. $[Fe(OEP)]_2O$ was prepared from Fe(OEP)Cl (Man-Win Chemical Co.) by the procedure of Fuhrhop et al.[21]

$Fe(TPP)ClO_4$ was prepared by a procedure that did not involve heating a perchlorate in an organic solvent.[22] $[Fe(TPP)]_2O$ (250 mg, 0.18 mmol) was dissolved in 100 mL of dichloromethane. The solution was treated with 50 mL of 8.0 M $HClO_4$(aq). After the mixture was shaken for 5 min and allowed to settle, the solution was poured into a dry container and 400 mL of diethyl ether added. Crystals of the product formed after 3 days at 0 °C. The crystals were dried under vacuum at 25 °C for 24 h. The yield was 72%. The crystals were analyzed for N, Cl, and Fe and gave a satisfactory analysis. The spectral properties matched those given in the literature.[22]

All solvent purification was carried out within an Ar-filled glovebox and the purified solvent used within 24 h. Toluene was mixed with P_2O_5; the mixture was allowed to stand overnight and distilled onto 4-Å molecular sieves. HPLC grade DMA was distilled from CaO onto 3-Å molecular sieves.

Instrumentation. Ultraviolet–visible spectra were recorded by using a Bausch and Lomb Spectronic 200 spectrophotometer. Infrared spectra, magnetic susceptibility measurements, and Mössbauer spectra were recorded on previously described equipment.[19]

Reaction Procedure. A 2.5-μmol sample of the μ-oxo iron(III) porphyrin was dissolved in 50.0 mL of solvent. The electronic spectrum was measured and 25.0 mL of solution transferred to a special vessel attached to a vacuum line. The vessel consisted of a 100-mL chamber containing a stirring bar and fitted with two Teflon valves. One valve was connected to a joint for vacuum line attachment; the other, to a 1.0-cm silica spectrophotometric cell. The solution in the chamber was degassed by three successive freezing, pumping, and thawing cycles. The solution was frozen (−196 °C) and a given amount of the nitrogen oxide transferred onto the solid surface. After warming to room temperature, the solution was stirred for about 30 min. The vessel was removed from the vacuum line and the spectrum obtained; it was then reattached to the vacuum line. This procedure was repeated several times in order to obtain the spectra shown in Figures 1 and 2.

Nitrate/Nitrite Analyses. For those reactions carried out in toluene, 10.0 mL of solution was added to 10.0 mL of a 0.01 M sodium borate buffer solution (pH 9.2) in air and the nitrate and nitrite ions were extracted into the aqueous phase. With DMA solutions, 10.0 mL of the solution was rapidly mixed in air with 10.0 mL of the buffer solution. The mixture was then analyzed directly. A 1.0-mL aliquot of each solution was injected into a Dionex QIC IonChrom analyzer that had an HPIC-A53 column, and 3 mM Na_2CO_3 was used as eluent, producing retention times for nitrite and nitrate of 2.1 and 4.5 min, respectively.

In the analysis any NO present was expected to form initially N_2O_4 and N_2O_3, both of which would produce nitrate and nitrite in solution. The amounts of each ion formed would depend on O_2 in the buffer solution. If all of the oxynitrogen species present yielded nitrate and nitrite, then nitrogen recovery was expected to be total, but if unreactive N_2O formed in the initial reaction, some nitrogen would be lost. Any $Fe(TPP)NO_3$ present should hydrolyze, and the nitrate would be extracted into the aqueous phase.

$Fe(TPP)(NO)(NO_2)\cdot C_7H_8\cdot 2H_2O$. $[Fe(TPP)]_2O$ (500 mg, 0.37 mmol) was added to 100 mL of toluene in a 250-mL round-bottom flask. After 30 min of stirring at room temperature, the solution was saturated with Ar. NO was then blanketed over the surface of the solution and the solution stirred for 12 h. The resulting precipitate was filtered under Ar and washed with three 10-mL degassed portions of toluene. The solid (540 mg) was dried under vacuum at 30 °C for 24 h. Anal. Calcd for $C_{51}H_{40}N_6FeO_5$: C, 70.18; H, 4.62; N, 9.63; Fe, 6.40. Found: C, 69.65; H, 4.04; N, 9.99; Fe, 6.35. Magnetic data (room temperature): χ_m, 4.5 × 10^{-4} cgsu; 1.5 μ_B; diamagnetic correction, −500 × 10^{-6}. Electronic spectrum [λ_{max}, nm (log ϵ_{max})] in toluene: 435 (5.46), 509 (3.97), 540 sh (3.93), 606 sh (3.46), 690 sh (3.10). Mössbauer spectrum (77 K): δ_{Fe}, 0.13 mm s^{-1}; Δ, 1.36 mm s^{-1}.

Results and Discussion

The reactions of the nitrogen oxides with the μ-oxo complexes were carried out by adding incremental amounts of the given nitrogen oxide to the solution of the Fe(III) complex and measuring the visible spectrum after each addition. When an addition produced no further spectral change, the reaction was assumed to be complete. Solutions were prepared with a reactant ratio that was expected to give a complete reaction, and then each solution was subjected to nitrate/nitrite analysis.

NO Reactions in Toluene. The room-temperature visible spectra that resulted after the reaction of 0.05 mM $[Fe(TPP)]_2O$ with 0.1 mM increments of NO in toluene are shown in Figure 1a. As NO was added to the μ-oxo solution, the 567- and 609-nm bands were suppressed, with a new band appearing at 509 nm and broad shoulders at 540, 608, and 684 nm. After four NO additions, there was only a small change in the spectrum with the fifth and final addition. The final spectrum has a shoulder at 570 nm. The collection of spectra does not show clear-cut isosbestic points.

Attempts were made to reverse the NO addition and return to the original spectrum, but neither using three successive freeze-thaw pumping cycles at −95 °C nor bubbling nitrogen

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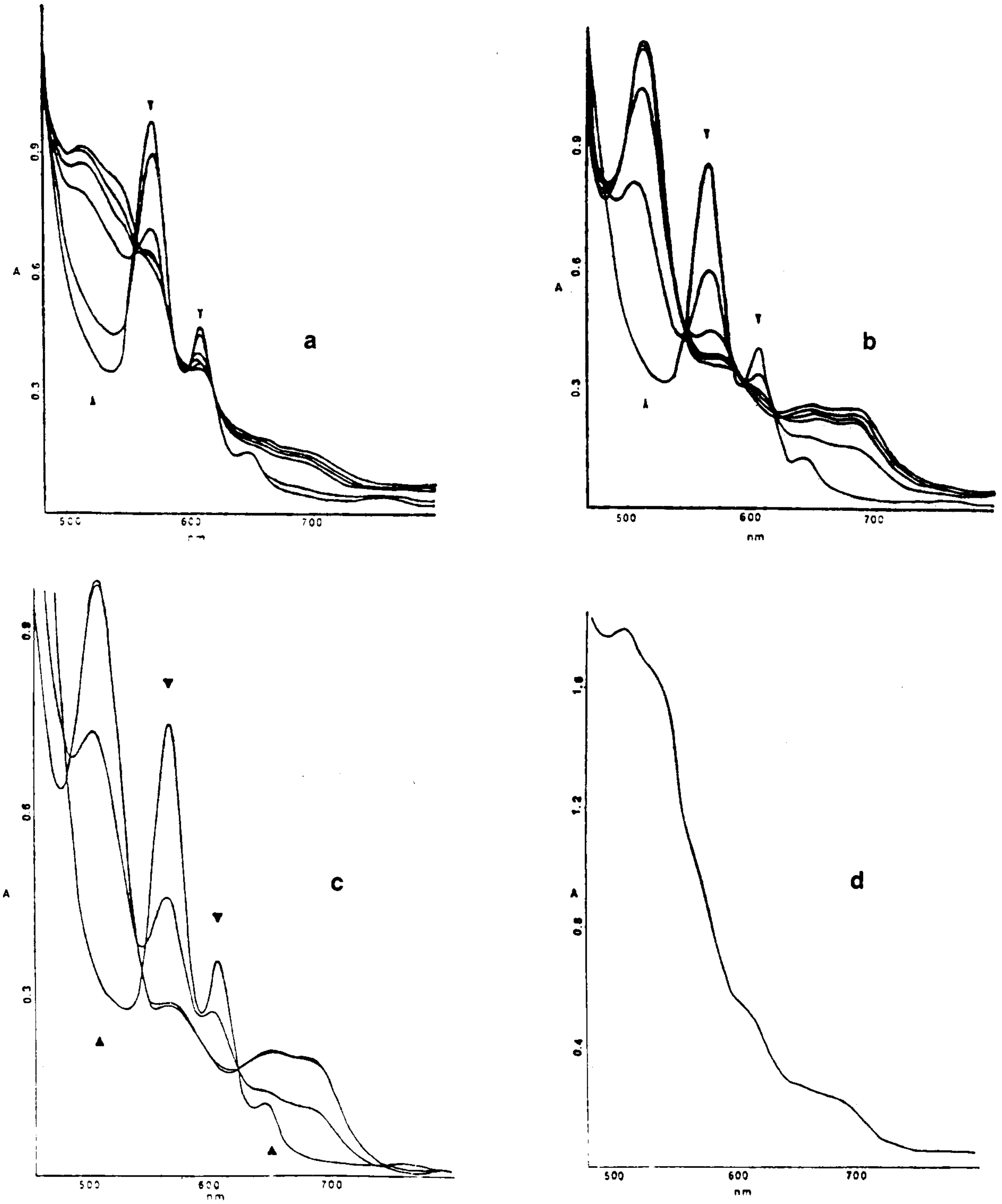

Figure 1. Room-temperature visible spectra of 0.05 mM $[Fe(TPP)]_2O$ in toluene with increments of (a) NO, (b) N_2O_4, and (c) N_2O_3 added. The first spectrum in each case is that of $[Fe(TPP)]_2O$. Each increment of nitrogen oxide increased the N concentration by 0.1 mM. Part d is the spectrum of 0.19 mM $Fe(TPP)(NO)(NO_2)\cdot C_7H_8\cdot 2H_2O$ in toluene.

through the solution at room temperature was successful. The spectrum remained unchanged after both attempts. It appeared that the NO was not bound weakly, as in the case for 1 mol of NO from $Fe(TPP)(NO)_2$ in a toluene solution.[1]

When a large excess of NO was added to a nearly saturated, deoxygenated solution of $[Fe(TPP)]_2O$, a precipitate resulted that was analyzed as $Fe(TPP)(NO)(NO_2)\cdot C_7H_8\cdot 2H_2O$. $Fe(TPP)(NO)(NO_2)$ was proposed to form when Fe(TPP)(NO) and excess NO were reacted together in several solvents at 20 °C.[23] In those instances, no solid could be isolated, so the product was only identified in solution with electronic and IR spectra. The solid product had a strong IR band at 1872 cm^{-1} that differed little from the ν_{NO} (1866 cm^{-1}) found for $Fe(TPP)(NO)(NO_2)$ in benzene.[23] The medium-intensity bands at 1296 and 1176 cm^{-1} are due to the ν_{asym} and ν_{sym} for the bound nitro group.[24] The macrocyclic Fe(II) complex $[Fe([15]aneN_4)(NO_2)(CH_3CN)]PF_6$ has these bands at 1270 and 1180 cm^{-1}.[25] The Mössbauer spectrum indicated the product to be a low-spin Fe(II) complex. Even though the complex should be diamagnetic, there appears to be a small amount of residual paramagnetism, which may be due to the presence of a trace paramagnetic impurity, such as NO.

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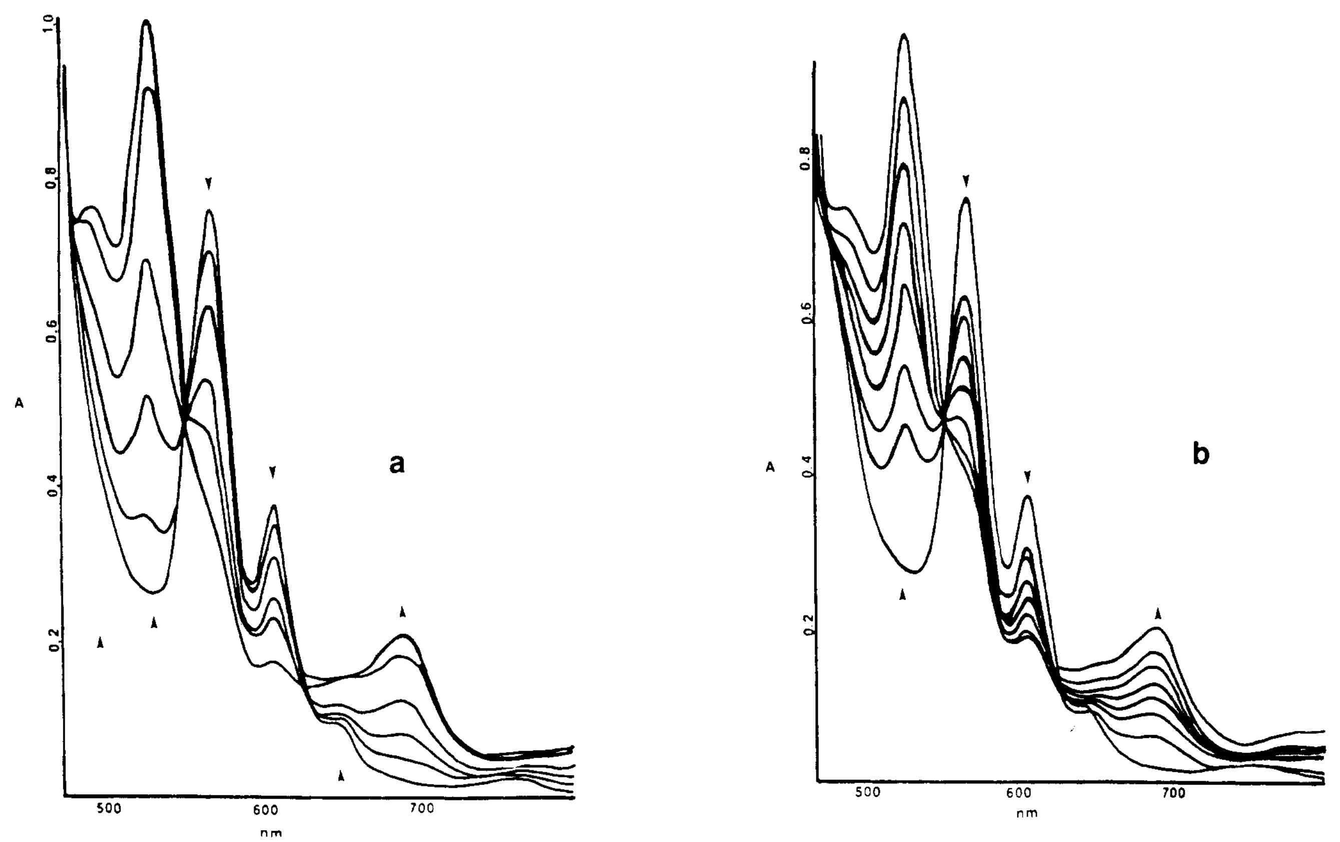

Figure 2. Room-temperature visible spectra of 0.05 mM $[Fe(TPP)]_2$ in dimethylacetamide with increments of (a) N_2O_4 and (b) N_2O_3 added. The first spectrum in each case is that of $[Fe(TPP)]_2O$.

The water of hydration must have come from either the solution or atmosphere, or both.

The solid product $Fe(TPP)(NO)(NO_2)\cdot C_7H_8\cdot 2H_2O$ had a visible spectrum in toluene (Figure 1d) that closely matched that of the product formed when Fe(TPP)NO reacted with excess NO in chloroform[23] and also that of the toluene solution with $[Fe(TPP)]_2O$ and 5 mol of NO (Figure 1a). The latter seems to have an extra shoulder at ca. 570 nm, which might be due to unreacted $[Fe(TPP)]_2O$ or to $Fe(TPP)(NO)_2$. In toluene, $Fe(TPP)(NO)_2$ has bands at 545 and 570 nm, while Fe(TPP)(NO) has them at 545 and 609 nm.[1] It is possible that Fe(TPP)NO or $Fe(TPP)(NO)_2$ is formed as an intermediate:

$$[Fe(TPP)]_2O + 3NO \rightarrow Fe(TPP)(NO)(NO_2) + Fe(TPP)NO$$

$$Fe(TPP)NO + NO \rightleftharpoons Fe(TPP)(NO)_2$$

A large excess of NO is required to convert Fe(TPP)NO to the nitro–nitrosyl product:[23]

$$Fe(TPP)NO + 3NO \rightarrow Fe(TPP)(NO)(NO_2) + N_2O$$

The overall equation for the NO reaction is assumed to be

$$[Fe(TPP)]_2O + 6NO \rightarrow 2Fe(TPP)(NO)(NO_2) + N_2O \quad (1)$$

A 0.05 mM $[Fe(TPP)]_2O$/0.4 mM NO solution showed a 57% N recovery by nitrate/nitrite analysis. If eq 1 was followed, then there should have been a 75% N recovery. The reaction of $Fe(TPP)(NO)(NO_2)$ with the buffer solution in air is no doubt complex, and some nitrogen may have been lost at that point.

A solution made up of 0.5 mM $[Fe(TPP)]_2O$ and 0.40 mM NO was reacted with O_2 to produce a solution with bands at 512, 579, 660, and 688 nm, which are those for $Fe(TPP)NO_3$.[7] The absorbance of the Soret band at 412 nm was measured, and from the literature molar absorbance value (1.12×10^5 M^{-1} cm^{-1}) was calculated the concentration of $Fe(TPP)NO_3$. This indicated that 85% of the original $[Fe(TPP)]_2O$ had been converted to the nitrate.

The reaction of $[Fe(OEP)]_2O$ with NO in toluene followed the same course as that for the TPP complex. A 0.055 mM $[Fe(OEP)]_2O$ solution had bands at 562 and 590 nm with absorbances at 0.65 and 0.53, respectively. The addition of 4 mol of NO/mol of μ-oxo complex resulted in a solution spectrum with bands at 529, 559, and 631 nm having absorbances at 0.92, 0.70, and 0.28, respectively. An additional 1 mol of NO produced no further change in the spectrum. Isolation of a product was not attempted in this case.

N_2O_4 Reactions. In Figure 1b are shown the spectra resulting from 0.05 mM additions of N_2O_4 to a toluene solution of 0.05 mM $[Fe(TPP)]_2O$. The reaction produced only the Fe(III) product $Fe(TPP)NO_3$ and appeared complete after the third addition. A 0.05 mM $[Fe(TPP)]_2O$/0.20 mM N_2O_4 solution showed complete nitrogen recovery by nitrate/nitrite analysis. An equation for the N_2O_4 reaction might be

$$[Fe(TPP)]_2O + {}^3/_2N_2O_4 \rightarrow 2Fe(TPP)NO_3 + NO \quad (2a)$$

An excess of N_2O_4 may be required for complete reaction. An equation for this reaction is

$$[Fe(TPP)]_2O + 2N_2O_4 \rightarrow 2Fe(TPP)NO_3 + N_2O_3 \quad (2b)$$

The addition of O_2 to the solution had no effect on the spectrum of the final solution. The yield of the nitrate complex based upon the Soret band molar absorbance value in the final solution was 93%.

After a 0.05 mM $[Fe(OEP)]_2O$ solution and a 2.5-fold amount of N_2O_4 were reacted, the mixture had the following bands [λ_{max}, nm (log ϵ_{max})]: 634 (3.52), 530 (4.89), 506 (4.90), 384 (5.93). The solution was unaffected by oxygen addition. The N_2O_4 reaction with the μ-oxo complex appeared to produce a quantitative yield of $Fe(OEP)NO_3$. This was unexpected, since the OEP ligand has shown a definite reactivity toward N_2O_4 at the meso position.[14,26] Such reactivity may only occur with an excess of N_2O_4 or with a halogenated solvent present.

N_2O_3 Reaction. The spectra resulting from the reaction of 0.05 mM $[Fe(TPP)]_2O$ with three 0.1 mM increments of N_2O_3 in

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toluene are shown in Figure 1c. Each N_2O_3 addition was carried out at −95 °C and the solution warmed to room temperature to measure the spectrum. The first two additions showed significant changes in the spectrum, with the third showing essentially no further change. The final spectrum was that of $Fe(TPP)NO_3$. There are two possible equations for the reaction:

$$[Fe(TPP)]_2O + 2N_2O_3 \rightarrow 2Fe(TPP)NO_3 + N_2O \quad (3a)$$

$$[Fe(TPP)]_2O + 3N_2O_3 \rightarrow 2Fe(TPP)NO_3 + 4NO \quad (3b)$$

Since a 0.05 mM $[Fe(TPP)]_2O$/0.3 mM N_2O_3 solution showed complete nitrogen recovery by nitrate/nitrite analysis, eq 3b is the preferred one.

$[Fe(OEP)]_2O$ and N_2O_3 were reacted in the same way. A 0.055 mM $[Fe(OEP)]_2O$ solution when made with 0.2 mM N_2O_3 produced a solution with the $Fe(OEP)NO_3$ spectrum.[7]

Reaction of $[Fe(TPP)]_2O$ with Nitrogen Oxides in DMA. The spectrum of $[Fe(TPP)]_2O$ did not change after the solution was made 0.4 mM in NO. However, when oxygen was added, bands at 689 and 530 nm appeared and the μ-oxo bands were reduced in intensity. These two bands also formed and the μ-oxo bands disappeared as increments of N_2O_4 were added to a 0.05 mM $[Fe(TPP)]_2O$ solution (Figure 2a). The set of spectra showed isosbestic points and approached the spectrum of the DMA-solvated complex $Fe(TPP)(DMA)_x^+$. For, when *only* $Fe(TPP)ClO_4$ was dissolved in DMA, the spectrum had bands at 691 (3.40), 527 (4.08), 495 (3.92), 397 (5.03), and 328 nm (4.36) (log ϵ in parentheses). (A dimethyl sulfoxide (DMSO) complex, $Fe(TPP)(DMSO)_x^+$, has been found to have similar bands at 690 (3.54), 531 (4.12), and 490 nm (4.01).[27]) Complete conversion of the 0.05 mM μ-oxo complex to the solvated species did not occur with a N_2O_4 concentration of 0.25 mM. The addition of oxygen to this solution produced no spectral change.

A similar set of spectra was found when 0.05 mM increments of N_2O_3 were added to a 0.05 mM $[Fe(TPP)]_2O$ solution (Figure 2b). A 0.35 mM N_2O_3 concentration did not result in complete conversion to the solvated complex.

The nitrate and nitrite analyses of 0.05 mM $[Fe(TPP)]_2O$ solutions with 0.25 mM N_2O_4 and with 0.35 mM N_2O_3 showed total nitrogen recovery.

For the N_2O_3 reaction the spectral changes may be explained with the equilibria

$$[Fe(TPP)]_2O + N_2O_3 \rightleftharpoons 2Fe(TPP)^+ + 2NO_2^- \quad (4a)$$

$$N_2O_3 \rightleftharpoons NO + {}^1/_2N_2O_4 \quad (4b)$$

where $Fe(TPP)^+$ represents the solvated complex. From the spectral changes at 600 and 698 nm and the dissociation equilibrium (eq 4b) constant at room temperature in ethyl acetate for N_2O_3 (0.024 $M^{1/2}$)[28] may be calculated the equilibrium constant for eq 4a: $(4 \pm 2) \times 10^{-4}$ M^2.

Attempts to make a similar calculation for the N_2O_4 reaction by using the N_2O_4 dissociation equilibrium constant at room temperature in acetonitrile (3×10^{-5})[29] were unsuccessful. This may be the result of trace water contamination forming the strong acid HNO_3 and also HNO_2, a much weaker one. The presence of available protons would result in the acid-catalyzed solvolysis of the μ-oxo complex and a larger amount of the solvated complex. Shaking a 0.05 mM μ-oxo solution with a few microliters of 1:1 aqueous nitric acid resulted in total conversion to $Fe(TPP)^+$.

Final Comments. The reaction of NO, NO/O_2, N_2O_4, and N_2O_3 with the μ-oxo iron(III) porphyrins resulted in no iron(III) porphyrin nitrite as a final product, not even when N_2O_3 was used. Thus, it appears that such complexes cannot be prepared in solution by using nitrogen oxides, at least not under the conditions used here. The nitrite complexes have been prepared only in DMF, DMSO, and dichloromethane solution by reacting tetraphenylphosphonium nitrite with $Fe(TPP)NO_3$.[8]

The reactions in toluene appear to be centered on the μ-oxo bond, since no reaction occurred when $Fe(TPP)ClO_4$ and the gases were mixed under the same conditions as those described for $[Fe(TPP)]_2O$. The reaction is considered to proceed initially by an oxynitrogen species attacking the μ-oxo O atom, breaking one of the Fe–O bonds. Oxynitrogen species would then add to the O and to the Fe. Finally, O atom transfer would take place between the free oxynitrogen species and the Fe-bound oxynitrogen ion to produce the final products. If the iron(III) porphyrin nitrite is formed initially, a further reaction must take place with available nitrogen oxides, possibly by O atom transfer. Reactions involving O atom transfer for cobalt oxynitrogen complexes have been well described[30] and should occur in similar Fe systems.

In DMA the equilibrium reactions proceed with the splitting of the complex followed by solvation, releasing the oxynitrogen ions into the polar solvent. A nitrite concentration large enough to form the nitrite complex is not produced.

Certainly the presence of trace amounts of water would affect the reaction path. Every effort was made to dry the solvents used in the vacuum-line experiments, but water may still have been present at a sufficient level to affect the reaction by forming nitrous and nitric acids with the very reactive N_2O_3 and N_2O_4. A reaction of the acids with the μ-oxo complexes would be expected to form the iron(III) porphyrin nitrite and nitrate.

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Registry No. $[Fe(TPP)]_2O$, 12582-61-5; $[Fe(OEP)]_2O$, 39393-88-9; $Fe(TPP)ClO_4$, 59370-87-5; $Fe(TPP)(NO)(NO_2)\cdot C_7H_8\cdot 2H_2O$, 113380-68-0; $Fe(TPP)NO_3$, 76282-27-4; $Fe(OEP)NO_3$, 113380-69-1; NO, 10102-43-9; N_2O_3, 10544-73-7; N_2O_4, 10544-72-6.

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