Inorg. Chem. **2003**, *42*, 4902–4908

Inorganic Chemistry
Article

Spectroscopic and Density Functional Studies of the Dinitrosyl Metalloporphyrin Complexes $Fe(P)(NO)_2$ and $Ru(P)(NO)_2$

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Received January 24, 2003

Experimental evidence including infrared spectra for the formation of the dinitrosyl metalloporphyrin complexes $M(P)(NO)_2$ (M = Ru or Fe, P = tetraphenylporphyrin (TPP), octaethylporphyrin (OEP), or tetra-*m*-tolylporphryin (TmTP)) is described. Although observation of a single NO stretching band in the IR spectrum of each $M(P)(NO)_2$ complex first suggested a centrosymmetric (D_{4h} or C_{2h}) structure, DFT geometry optimizations and frequency calculations of model complexes indicate that the *trans-syn* (C_{2v}) conformation should be more stable. The frequency calculations resolve the apparent ambiguity in the IR spectra in terms of the relative oscillator strengths of the predicted IR bands.

Introduction

Studies in this laboratory have been concerned with the reactivity of the ubiquitous bioregulatory molecule nitric oxide (NO, also known as nitrogen monoxide)[1] with heme proteins and models.[2−5] In the course of these investigations we have reported the reactions of the NO with the ruthenium porphyrin complexes Ru(P)(CO) (P = tetraphenylporphyrin (TPP), octaethylporphyrin (OEP), or tetra-*m*-tolylporphryin (TmTP)) and with several iron(II) analogues. For the reaction of NO with Ru(P)(CO), infrared and optical spectroscopic evidence obtained by stopped flow techniques demonstrated the ambient temperature formation of a reactive intermediate concluded to be the dinitrosyl complex $Ru(P)(NO)_2$.[3c,d] This underwent further reaction with NO to give the nitrosyl nitrito complexes Ru(P)(NO)(ONO) (eqs 1 and 2). The analogous intermediate was seen in time-resolved infrared (TRIR) studies of intermediates generated in the flash photolysis of Ru(TmTP)(NO)(ONO).[3b]

$$\mathrm{Ru(P)(CO)} + 2\mathrm{NO} \rightleftharpoons \mathrm{Ru(P)(NO)_2} + \mathrm{CO} \tag{1}$$

$$\mathrm{Ru(P)(NO)_2} + 2\mathrm{NO} \rightleftharpoons \mathrm{Ru(P)(NO)(ONO)} + \mathrm{N_2O} \tag{2}$$

In contrast, there was no directly observable further reaction of solutions of the stable mononitrosyl iron complexes Fe(P)(NO) with clean NO ($P_{NO} < 1$ atm) at ambient temperature.[5] However, when T was lowered to ∼180 K, NMR, optical, and IR spectral changes proved to be consistent with the reversible formation of a dinitrosyl complex (eq 3) analogous to that seen for the Ru(II) species.[5b] Notably, characterizing the properties of dinitrosyl iron(II) porphyrin complexes gains further relevance with the recent proposal

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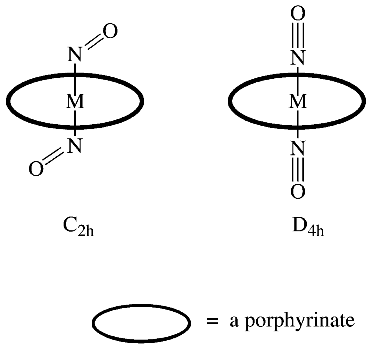

Figure 1. Possible centrosymmetric structures for *trans*-$M(P)(NO)_2$ intermediate based on spectroscopic evidence.

that the principal target of this bioregulatory molecule, soluble-guanylyl cyclase, may require two NO equivalents for activation.[6]

$$Fe(P)(NO) + NO \rightleftharpoons Fe(P)(NO)_2 \qquad (3)$$

Only a single IR band in the ν(NO) region was observed for each of the $Fe(P)(NO)_2$[5b] and $Ru(P)(NO)_2$[3b,d] complexes characterized spectroscopically, and on this basis, it was suggested that these complexes have *trans* centrosymmetric structures (Figure 1). In such a geometry the two NO oscillators should couple to give symmetric and antisymmetric vibrations ν_s(NO) and ν_{as}(NO), only the latter being an allowed IR band. However, simple molecular orbital arguments[7] appear to be inconsistent with such complexes having two linearly coordinated NO's in a mutually *trans* configuration (i.e., a *trans*-collinear geometry). Instead bending of at least one of the nitrosyls might be anticipated, and the relatively low values seen for the ν_{NO} bands for respective complexes appear to be consistent with this view (see below). A centrosymmetric configuration could alternatively involve two nonlinear M−NO groups with a 180° dihedral angle between the respective planes defined by each MNO, but it was not obvious why such a *trans-anti* conformation would be favored over other possibilities. In this context, we initiated an investigation of the electronic nature of such $M(P)(NO)_2$ complexes using density functional[8] (DFT) methods. Described in this report are some experimental details regarding the IR and other spectral characterizations of several such $Fe(P)(NO)_2$ and $Ru(P)(NO)_2$ complexes and the results of these DFT studies of model systems.

Experimental Section

Materials and Techniques. The ruthenium and iron porphyrin complexes used were all known compounds prepared and purified by established procedures. Reagent or higher grade solvents were purified, dried, and distilled by published methods. Nitric oxide (99%, Aire Liquide) was purified by passage through a stainless steel column containing Ascarite II (Thomas Scientific), and led into the vacuum line by stainless steel (316) tubing connected via an O-ring seal (Viton) to a greaseless vacuum line. ^{15}NO was prepared by ascorbate reduction of $Na[^{15}NO_2]$. Solutions of known [NO] were prepared in a VAC inert atmosphere glovebox and/or by established anaerobic techniques on a glass/stainless steel/Teflon greaseless vacuum line, and solutions were transferred without exposure to air to sealed spectrometer cells. IR spectra were recorded on a Bio-Rad model FTS-60 FTIR spectrophotometer. Low-temperature spectra were recorded in a pour-fill cryostat (R. G. Hansen & Associates). In the case of short-lived reactive intermediates, the FTIR spectrum was recorded for a flowing sample solution using a custom-designed continuous flow system to mix the solutions.

Computational Details. Geometry optimizations and frequency calculations were performed at the density functional level of theory using the split valence 3-21g basis set[9−11] and Becke's three-parameter hybrid exchange functional[12] with Lee, Yang, and Parr's correlation functional (B3LYP).[13,14] Such B3LYP/3-21g calculations were performed on the model structures $[M(NH_3)_4(NO)_2]^{2+}$ and $M(porphine)(NO)_2$ using Gaussian 98.[15] Optimizations and frequency calculations on the $[M(NH_3)_4(NO)_2]^{2+}$ structures were accomplished using default convergence criteria, while the calculations on the porphine structures were performed using tighter convergence criteria due to their shallow potential energy surfaces. In order to verify the quality of the optimized structures for the model systems, geometry optimizations were performed on $[Ru(NH_3)_5(NO)]^{3+}$ using tight convergence criteria and compared to literature values. A similar calculation was carried out on the analogous dication $[Ru(NH_3)_5(NO)]^{2+}$ to evaluate the effect of added electron density on the structure. Unless otherwise noted the DFT calculations reported are full optimizations without symmetry constraints.

Results and Discussion

Spectroscopic Evidence for Dinitrosyl Complexes. We have previously communicated[3,5] spectroscopic data sup-

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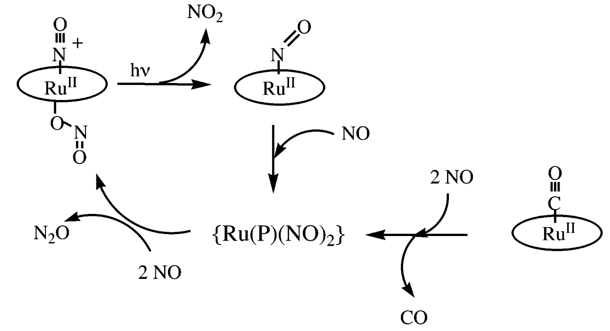
Scheme 1. Formation of the Common Intermediate Ru(TPP)(NO)$_2$ in Photochemical and Thermal Mechanisms



porting formation of dinitrosyl complexes of the types Ru(P)(NO)$_2$ and Fe(P)(NO)$_2$, and for this reason, these experiments will be summarized here with only limited supporting data.

For ruthenium, a key indication of the dinitrosyl porphyrins Ru(P)(NO)$_2$ was the observation of an intermediate in the NO disproportionation resulting from the reaction of Ru(P)(CO) (P = TmTP or OEP) and excess nitric oxide.[3c] In stopped-flow kinetics studies, this species was found to be reversibly formed according to a rapidly established equilibrium second order in [NO] and inverse first order in [CO]. Further reaction of this intermediate with NO leads to formation of N$_2$O plus Ru(P)(NO)(ONO). An intermediate with the same spectral and reactivity properties was also observed in a very different experiment, namely, a photochemical study of the nitrosyl nitrito complexes Ru(P)(NO)(ONO) (P = OEP, TPP, or TmTP).[3b] When this species was subjected to flash photolysis, the competing primary photoreactions were NO loss to give Ru(P)(ONO) and NO$_2$ loss to give Ru(P)(NO). In the presence of excess NO, the former is rapidly trapped to regenerate the starting complex, but the latter gives another species with the same properties as that seen in the disproportionation mechanism and attributed to Ru(P)(NO)$_2$ (Scheme 1).

In order to interrogate this transient species, flow reactor techniques were used to mix Ru(TmTP)(CO) with NO and to record the FTIR spectrum at a time delay (0.2 s) where the optical spectral data indicated this intermediate to be at its maximum concentration under the reaction conditions.[3d] In ambient temperature cyclohexane, the flow reactor experiment demonstrated the formation of a reactive intermediate with a ν(NO) band at 1642 cm^{-1} which was attributed to Ru(TmTP)(NO)$_2$. When the flash photolysis of Ru(TmTP)(NO)(ONO) was carried out in cyclohexane solution under excess NO, the same 1642 cm^{-1} band was seen in the time-resolved infrared spectrum recorded using step-scan FTIR techniques.[3b]

A different situation was demonstrated by the related iron(II) system. Reaction of Fe(P) with excess *clean* NO in ambient temperature solutions gives a solution where the only detectable ferroheme complex is the mononitrosyl Fe(P)(NO) (P = TPP or TmTP).[5a,c] Spontaneous disproportionation was not seen under these conditions. However, when a toluene-d_8 solution of Fe(TmTP)(NO) containing 10 mM NO was cooled to 179 K, the reversible formation of Fe(TmTP)(NO)$_2$ was apparent (eq 4).[5b] The key observations in support of this formulation were [NO] dependent changes in the ^{1}H NMR spectrum. Although Fe(P)(NO) is low spin, the {MNO}^{7} electronic configuration is paramagnetic and the ^{1}H NMR spectrum is correspondingly broadened and shifted. Coordination to a second NO gives a diamagnetic {M(NO)}^{8} species, which displays markedly sharpened ^{1}H resonances.[5b] The equilibrium constant K_4 for eq 4 was evaluated from the temperature dependence of the NMR spectra as 3100 M^{-1} at 179 K with $\Delta H°_4 = -6.7$ kcal mol^{-1} and $\Delta S°_4$ as -21 cal mol^{-1} K^{-1}.

$$\text{Fe(TmTP)(NO)} + \text{NO} \overset{K_4}{\rightleftharpoons} \text{Fe(TmTP)(NO)}_2 \qquad (4)$$

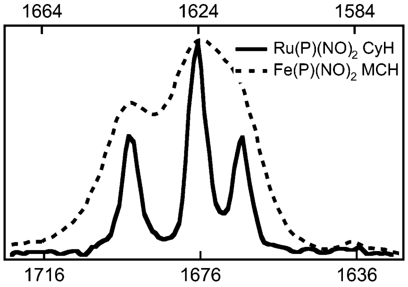


Figure 2. IR spectra of the mixed labeled (1:1 ^{15}NO:^{14}NO) dinitrosyls Ru(TmTP)(NO)$_2$ in ambient cyclohexane and Fe(TmTP)(NO)$_2$ in 179 K methylcyclohexane. The frequency scale at the top is for the ruthenium complex while the frequency scale at the bottom is for the iron analogue.

At ambient temperature, solutions of Fe(TPP)(NO) in CHCl$_3$ displayed a single IR band at 1681 cm^{-1} ($\epsilon = 800$ M^{-1} cm^{-1}) which was little affected by lowering the T to 213 K. Adding NO (8 mM) did not change this band at ambient T; however, at 213 K, the solution displayed a new, more intense ν(NO) band at 1695 cm^{-1} ($\epsilon = 1600$ M^{-1} cm^{-1}) (Supporting Information Figure S-1) apparently corresponding to the dinitrosyl Fe(TPP)(NO)$_2$. When an analogous experiment was performed with a methylcyclohexane (MCH) solution of Fe(TmTP)(NO) in the presence of a 1:1 mixture of ^{14}NO:^{15}NO, equal intensity bands at 1683 and 1654 cm^{-1} were observed at room temperature and interpreted as corresponding to the ν(NO) bands for Fe(TmTP)(^{14}NO) and Fe(TmTP)(^{15}NO), respectively. At 173 K, the IR spectrum displayed three new bands at 1696, 1676, and 1665 cm^{-1} in an approximately 1:2:1 intensity distribution (Figure 2). The latter spectrum can be easily rationalized as corresponding to the unlabeled, singly labeled, and doubly labeled dinitrosyl Fe(TmTP)(NO)$_2$. In contrast, the IR spectra of 173 K MCH solutions displayed a single ν(NO) band in each case when isotopically pure NO was used (1696 cm^{-1} for Fe(TmTP)(^{14}NO)$_2$, 1665 cm^{-1} for Fe(TmTP)(^{15}NO)$_2$). Upon warming, the solutions re-formed the mononitrosyls quantitatively.

Figure 2 displays the IR spectra of the mixed labeled (^{14}NO:^{15}NO 1:1) Fe(TmTP)(NO)$_2$ in 173 K MCH and that of Ru(TmTP)(NO)$_2$ in ambient cyclohexane. Although the Fe(TmTP)(NO)$_2$ peaks are broadened in the glassy MCH, the spectral patterns are similar with the ruthenium ν(NO) bands at somewhat higher frequency. An interesting feature is that the singly labeled peak shifts further (~3 cm^{-1}) than the weighted mean of the unlabeled and doubly labeled com-

Table 1. Comparison of Selected Parameters Calculated by DFT Optimization (B3LYP/3-21g) for $[Ru(NH_3)_5(NO)]^{3+}$ and for $[Ru(NH_3)_5(NO)]^{2+}$ with the Known X-ray Structural Data for $[Ru(NH_3)_5(NO)]Cl_3$

	$[Ru(NH_3)_5(NO)]^{3+}$			$[Ru(NH_3)_5(NO)]^{2+}$
param	exptl (X-ray)[a]	lit. (DFT)[b]	this work (DFT)	this work (DFT)
		Bond Lengths (Å)		
Ru−N(O)	1.770	1.811	1.808	1.894
$Ru-N(H)_{eq}$	2.042−2.133	2.200−2.201	2.198−2.199	2.195
$Ru-N(H)_{ax}$	2.017	2.181	2.186	2.250
N−O	1.172	1.153	1.153	1.216
		Bond Lengths (Å)		
Ru−N−O	172.8	178	176.9	137.1
		Frequency (cm^{-1})		
ν(NO)	1913		1810	1504

[a] Crystal structure data is for the $[Ru(NH_3)_5(NO)]Cl_3$ salt.[16] [b] Reference 17. [c] Frequency obtained from the $[Ru(NH_3)_5(NO)](PF_6)_2$ compound.[19]

plexes (see Supporting Information Table S-1). Other workers have seen similar effects in non-centrosymmetric transition metal polynitrosyls[16] for which the ν_s(NO) and ν_{as}(NO) bands are both IR-active, and this may be the result of some mixing and splitting of the symmetric and antisymmetric stretches in the lower symmetry mixed labeled species. A very similar pattern (with higher frequency ν(CO) values) was seen for the spectrum of the analogously mixed labeled (^{12}CO:^{13}CO 1:1) ruthenium dicarbonyl complex Ru(OEP)-$(CO)_2$ in ambient *T* cyclohexane (Table S-1). Since the latter is anticipated to have *trans*-collinear RuCO orientations, this analogy led us to consider centrosymmetric $M(P)(NO)_2$ structures as likely; however, the DFT calculations described below offer a somewhat different perspective.

DFT Geometry Optimizations. DFT computations were first carried out for the mononitrosyl trication $[Ru(NH_3)_5(NO)]^{3+}$ using the B3LYP density functionals and 3-21g basis set as a model in order to evaluate the quality of our application of these techniques. The bond lengths and bond angles from the optimized structure (see Table 1) match well those of previously reported computational results.[17] They also show reasonable agreement with crystal structure data,[18,19] although the experimental N−O bond length is ~0.019 Å shorter and the experimental Ru−N−O bond angle (172.8°) is several degrees smaller than calculated (179.1°). Nonetheless, the differences are relatively small. The linear RuNO angle is appropriate for the $\{MNO\}^6$ electronic configuration[7] of this complex, which can formally viewed as a $Ru^{II}(NO^+)$ species. The DFT calculation also predicts that coordination of NO in this case will lead to modest shortening of the $Ru-N(H)_{ax}$ bond relative to the $Ru-N(H)_{eq}$ bond (−0.012 Å) as was also seen in the X-ray structure, although the experimental difference between the bond lengths of the axial and equatorial ammines is significantly more accentuated.

An analogous DFT (B3LYP/3-21g) optimization was carried out for the unknown dication $[Ru(NH_3)_5(NO)]^{2+}$, and key parameters are listed in Table 1. The $(O)N-Ru-N(H)_{ax}$ angle is calculated to be nearly linear (177.5°), but as expected for a $\{MNO\}^7$ complex ion, the Ru−N−O now shows a considerable bend to 137.1° and the N−O bond is longer by 0.063 Å, consistent with the added electron having considerable population in the π^* orbitals of the RuNO unit. It is also notable that there is little effect of the additional electron (relative to the trication) on the $Ru-N(H)_{eq}$ bond lengths. Indeed these are slightly shorter (−0.004 Å) in the dication. However, there is measurable lengthening of the axial bonds: the Ru−N(O) bond is calculated to be 0.086 Å longer and the $Ru-N(H)_{ax}$ bond to be 0.064 Å longer than in the trication. The latter is thus 0.055 Å longer than the $Ru-N(H)_{eq}$ bond in the same species, consistent with the expected labilization of the ligand *trans* to the nitrosyl in hexacoordinate $\{MNO\}^7$ complexes.[20]

Species closer to the $M(P)(NO)_2$ complexes of interest discussed in the Introduction would be the (unknown) model *trans*-dinitrosyl ruthenium(II) and iron(II) complexes *trans*-$[Ru(NH_3)_4(NO)_2]^{2+}$ and *trans*-$[Fe(NH_3)_4(NO)_2]^{2+}$. B3LYP/3-21g geometric optimizations were carried out for each of these, and the relevant computed parameters are listed in Table 2. For the $\{M(NO)_2\}^8$ complex *trans*-$[Ru(NH_3)_4(NO)_2]^{2+}$ the two extra electrons in the M−NO π-symmetry orbitals lead to substantial lengthening of the Ru−N(O) and N−O bond lengths (relative to $[Ru(NH_3)_5(NO)]^{3+}$) and bending of the Ru−N−O bond angle to a rather acute 132° in the computed structure. Comparable structures were computed for the unknown species *trans*-$[Fe(NH_3)_4(NO)_2]^{2+}$, and both are illustrated in Figure 3. Notably, in both cases, the computations adopt the *trans-syn* conformation (C_{2v}), i.e., the two NO's bend in the same direction with a very small dihedral angle between the planes defined by the two M−N−O angles, 2.2° and 2.1°, respectively.

Single-point calculations to determine energies of the alternative *trans-anti* conformations of the two $[M(NH_3)_4(NO)_2]^{2+}$ complexes were carried out for structures generated by rotating one of the MNO planes in the optimized structure to give a dihedral angle of 180°. The respective energies for the Fe(II) and Ru(II) species were 29.4 and 25.6 kcal mol^{-1} higher, respectively, for the *trans-anti* than the favored (optimized) *trans-syn* conformations. Attempts to begin the optimization calculations with either compound in the *trans*-collinear geometry did not converge, indicating that this geometry is not at or near an energy minimum. We have carried out similar calculations on the diimine complexes *trans*-$[ML_2(NO)_2]^{2+}$ (where M is Fe or Ru and L is 1,2-diiminoethane) and have come to the same conclusion, namely, that the respective *trans-anti* conformations are substantially higher in energy than the *trans-syn* analogues and that the *trans*-collinear configuration is not stable.[21] Thus,

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Table 2. Parameters for DFT Optimized (B3LYP/3-21g) Structures for $[Fe(NH_3)_4(NO)_2]^{2+}$ and $[Ru(NH_3)_4(NO)_2]^{2+}$

complex	bond length (Å)		bond angle (deg)		frequency (cm^{-1})		intensity
t-$[Fe(NH_3)(NO)_2]^{2+}$	Fe−N(O)	1.731[a]	Fe−N−O	134.3	ν_{as}(NO)	1513	972.0
	Fe−N(H)$_3$	2.026, 2.040[b]	(O)N−Fe−N(O)	170.3	ν_s(NO)	1612	3.6
	N−O	1.202[a]					
t-$[Ru(NH_3)(NO)_2]^{2+}$	Ru−N(O)	1.946[a]	Ru−N−O	132.3[a]	ν_{as}(NO)	1509	1152.7
	Ru−N(H)$_3$	2.196[a]	(O)N−Ru−N(O)	167.0	ν_s(NO)	1589	29.9
	N−O	1.196[a]					

[a] Values averaged. [b] Amine nitrogens closest to the nitrosyl oxygens exhibit slightly shorter M−N bonds.

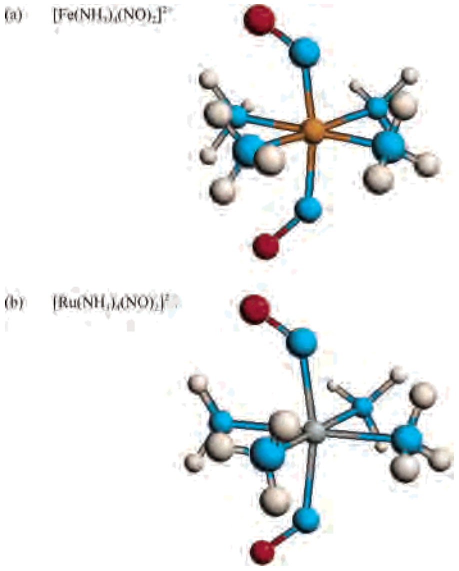

Figure 3. Computed *trans*-tetraammine dinitrosyl structures optimized using DFT with a 3-21g basis set and B3LYP functionals: (a) $[Fe(NH_3)_4(NO)_2]^{2+}$; (b) $[Ru(NH_3)_4(NO)_2]^{2+}$.

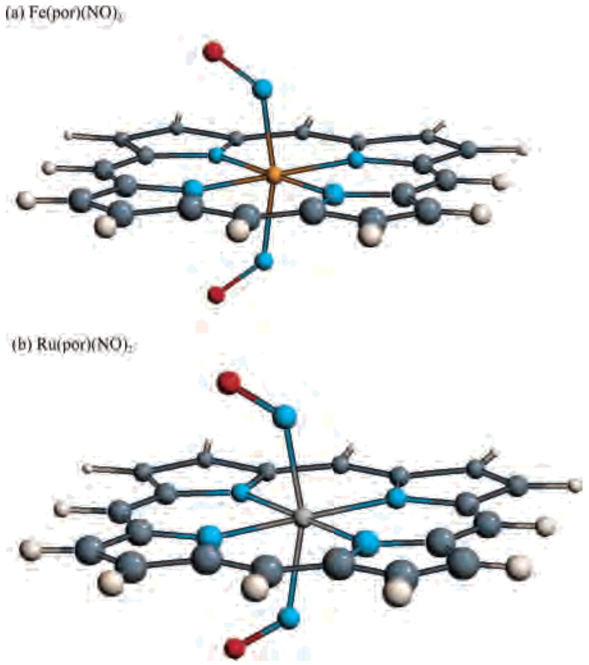

Figure 4. Computed porphine dinitrosyl structures optimized using DFT (B3LYP/3-21g): (a) $Fe(por)(NO)_2$; (b) $Ru(por)(NO)_2$.

while *trans*-$(NH_3)_4$ is limited as a model for a porphyrinato ligand, since the latter is both unsaturated and dinegatively charged, observation of the *trans-syn* conformation with relatively acute M−N−O bond angles indicates that there is no unexpected minimum with the *trans* nitrosyls oriented in a collinear configuration or otherwise centrosymmetric geometry of the ON−M−NO unit. Computational results with the diimine complexes *trans*-$[ML_2(NO)_2]^{2+}$ further confirm that replacing the sp^3-hybridized ammine ligands by sp^2-hybridized imines does not change this qualitative conclusion.

In this context, computations were initiated on the complexes *trans*-M(por)$(NO)_2$, where M = Fe or Ru and por^{2-} is the dianion of the unsubstituted porphyrin, porphine. Figure 4 illustrates the B3LYP/3-21g computed optimized structures of *trans*-Fe(por)$(NO)_2$ and *trans*-Ru(por)$(NO)_2$. Table 3 summarizes key calculated bond length and bond angle results and compares these to X-ray crystallographic data for analogous bond lengths and bond angles for the 6-coordinate mononitrosyl complex Fe(TPP)(1-MeIm)(NO) (1-MeIm = 1-methylimidazole) and the 5-coordinate analogue Fe(TPP)(1-MeIm)(NO).[20] For Fe(por)$(NO)_2$, the Fe−N(por) calculated bond lengths are comparable to the experimental bond lengths in the mononitrosyl complexes, but as expected, much greater differences were seen when the FeNO units in the mono- and dinitrosyl structures were compared. Most significantly, the computed Fe−N−O bond angles for the dinitrosyl are more acute and the NO bonds are ∼0.08 Å longer. Another notable feature also seen for the *trans*-tetraammines is that the M−N(O) bonds display an off-axis tilt of the nitrosyl coordination from the normal to the porphyrin plane as evidenced by the (O)N−M−N(O) angles of 165.9° and 162.1° computed for *trans*-Fe(por)$(NO)_2$ and *trans*-Ru(por)$(NO)_2$, respectively.

The most striking features of the *trans*-M(por)$(NO)_2$ optimized structures are the *trans-syn* conformations of the ON−M−NO coordination with dihedral angles between the two M−N−O planes computed to be 4.2° and 3.1°, respectively (Figure 4). Single-point calculations to determine energies of the alternative *trans-anti* conformers of the two M(por)$(NO)_2^{2+}$ complexes were carried out for structures generated by rotating one of the MNO planes in the optimized structure to give a dihedral angle of 180°. The respective energies for the Fe(II) and Ru(II) species were +65 and +69 kcal mol^{-1} higher, respectively, for this *trans-anti* species over the favored (optimized) *trans-syn* conformations. However, since the *trans-anti* conformer calculations did not allow for relaxation of other bonds, the energy difference would not be an appropriate estimate for the barrier of rotation of one MNO plane vs the other. Ghosh and coworkers[22] have used DFT calculations to come to a similar

Table 3. Selected Parameters Calculated by DFT Optimization (B3LYP/3-21g) for Fe(por)$(NO)_2$ and Ru(por)$(NO)_2$

complex	bond length (Å)		bond angle (deg)		frequency (cm^{-1})		intensity
Fe(por)$(NO)_2$ (DFT)	Fe−N(O)	1.754[a]	Fe−N−O	133.6[a]	ν_{as}(NO)	1503	1019.1
	Fe−N(por)	1.991, 1.998[b]	(O)N−Fe−N(O)	165.9	ν_s(NO)	1582,1583	19.2, 4.1
	N−O	1.203[a]					
Fe(TPP)(NO) (X-ray)[c]	Fe−N(O)	1.717	Fe−N−O	1.49.3	ν(NO)	1670	
	Fe−N(TPP)	2.001					
	N−O	1.122					
Fe(por)(1-MeIm)(NO) (X-ray)[c]	Fe−N(O)	1.743	Fe−N−O	142.1	ν(NO)	1625	
	Fe−N(TPP)	2.008					
	N−O	1.121					
Ru(por)$(NO)_2$ (DFT)	Ru−N(O)	1.956[a]	Ru−N−O	129.8[a]	ν_{as}(NO)	1480	1120.6
	Ru−N(por)	2.078, 2.075[b]	(O)N−Ru−N(O)	162.1	ν_s(NO)	1546	31.9
	N−O	1.204[a]					

[a] Values averaged [b] Porphine nitrogens closest to the nitrosyl oxygens exhibit slightly shorter M−N bonds. [c] Reference 20.

conclusion that the lowest energy structure of the dinitrosyl iron(II) porphyrins is the *trans-syn* conformation.

Frequency calculations were carried out for all optimized structures and gave positive frequencies for all vibrations. The nitrosyl stretching frequencies (ν(NO)) were assigned by analysis of the displacement vectors for each normal mode in the Gaussian 98 output and use of Jmol visualization software.[23] In each case, frequencies identified as ν(NO) showed considerable displacement along N−O bond, although it is prudent to remember that such normal modes are not localized to those oscillators. For $[Ru(NH_3)_5(NO)]^{3+}$ the computed ν(NO) is relatively high frequency (1810 cm^{-1}, Table 1) consistent with the representation of this as $Ru^{II}(NO^+)$. This result is about 100 cm^{-1} lower than the experimental ν(NO) recorded for solid $[Ru(NH_3)_5(NO)](PF_6)_3$ in a KBr pellet (Table 1). Notably, frequency calculation for the one-electron-reduced species, i.e., the dication $[Ru(NH_3)_5(NO)]^{2+}$, gives a significantly lower ν(NO) (1504 cm^{-1}) than does the trication, again supporting the view that much of the added electron density appears in the RuNO π* orbital.

As anticipated there are two NO stretching frequencies calculated for the optimized structures of *trans-syn*-$[Ru(NH_3)_4(NO)_2]^{2+}$ and *trans-syn*-$[Fe(NH_3)_4(NO)_2]^{2+}$). By analyzing the displacement vectors along the NO bonds during such vibrations these can be assigned as the symmetric and asymmetric stretches, ν_s(NO) and ν_{as}(NO), and these were found at 1612 and 1513 cm^{-1}, respectively, for the Fe dinitrosyl and at 1589 and 1509 cm^{-1}, respectively, for the Ru dinitrosyl. In a centrosymmetric complex, group theory predicts that the ν_s(NO) vibration would be infrared inactive and the ν_{as}(NO) would be infrared active, while one expects both to be active in C_{2v} symmetry such as the *trans-syn* conformation. However, the calculated relative intensities of these predicted frequencies offer an interesting insight. For both complexes, the asymmetric stretching mode ν_{as}(NO) is more than an order of magnitude more intense than is ν_s(NO) (Table 2) despite the absence of a center of symmetry.

Similarly, the frequencies calculated for the optimized *trans-syn*-Ru(por)$(NO)_2$ model displays two NO stretching modes, a strong ν_{as}(NO) band at 1480 cm^{-1} and a nearly 40-fold weaker ν_s(NO) band at 1546 cm^{-1}. Although both of these are considerably lower frequency than the single ν(NO) band at 1642 cm^{-1} seen for the ruthenium dinitrosyl Ru(TmTP)$(NO)_2$ in cyclohexane, the lower frequency is consistent with differences between DFT calculated and experimental IR frequencies for the $[Ru(NH_3)_5(NO)]^{3+}$ ion noted above. Furthermore, the prediction that the *trans-syn* conformation gives only one strong band in the nitrosyl stretching region resolves what had seemed to be an ambiguity in the spectroscopic properties of Ru(TmTP)$(NO)_2$.

Frequency calculation for the optimized *trans-syn*-Fe(por)$(NO)_2$ conformation adds a small twist to the story since three frequencies were found, a strong ν_{as}(NO) band at 1503 cm^{-1}, a 40-fold weaker ν_s(NO) band at 1582 cm^{-1}, and a 250-fold weaker ν_s(NO) band at 1583 cm^{-1}. Of the latter two, the former shows considerable displacement along the NO bond vectors while the latter shows a much smaller, but real, displacement of the NO bond vectors coupled to much greater displacements in the porphyrin ring. These appear to represent an accidental degeneracy of ring and NO vibrations. The predicted strong band at 1503 cm^{-1} is consistent with the spectrum of Fe(TPP)$(NO)_2$, which shows a single band at 1695 cm^{-1} in 213 K chloroform. Although the predicted frequency is much lower than the observed, the pattern is self-consistent with our other observations regarding the direction and magnitude of the differences between calculated and observed frequencies.[24]

Summary. In conclusion, the spectroscopic and equilibrium evidence clearly points to the formation of dinitrosyl complexes of the type M(P)$(NO)_2$ when solutions of Fe(P)NO and Ru(P)(CO) are exposed to excess NO. The observation of a single ν_{NO} band was initially interpreted in terms of the M(P)$(NO)_2$ species being centrosymmetric although molecular orbital considerations as well as the relatively low

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(22) (a) Ghosh, A. Personal communication. Subsequent to submission of the present article, Ghosh et al. published their conclusion based on a DFT (PW91/TZP) computation of Fe(P)$(NO)_2$ that the *trans-syn* conformation is more stable but did not address the ambiguity resulting from experimental observation of a single ν(NO) frequency.[22b] (b) Conradie, J.; Wondimagegn, T.; Ghosh, A. *J. Am. Chem. Soc*. **2003**, *125*, 4968−4969.

(23) Jmol is open-source software which can be obtained at http://jmol.sourceforge.net/. (June 17, 2003).

(24) Our DFT computed ν(NO) frequencies for the model compounds were consistently lower than the experimental values although the patterns observed were entirely self-consistent. We attribute these differences to the relatively small basis set (3-21g) used.

frequency of this band for individual complexes suggested that the M−N−O angles were likely to be nonlinear. This latter view is confirmed by the DFT optimizations carried out on *trans*-$[M(NH_3)_4(NO)_2]^{2+}$ and on *trans*-$M(por)(NO)_2$ models (M = Fe and Ru), which showed in each case that the *trans-syn* conformations are considerably more stable than either the *trans-anti* conformation with acute M−N−O angles or the *trans*-collinear structures. A similar conclusion has been reached by Ghosh et al. for an $Fe(P)(NO)_2$ computation.[22] The seeming ambiguity regarding the experimental observation of only a single ν(NO) band in the FTIR spectra of several $Ru(P)(NO)_2$ and $Fe(P)(NO)_2$ complexes appears to be resolved by frequency calculations which demonstrate that only the ν_{as}(NO) band appears to be strong for these complexes in the *trans-syn* conformation.

Acknowledgment. This research was supported by grants from the National Science Foundation (CHE-0095144) and the ACS Petroleum Research Fund. Support for the UCSB Origin 2000 computer was provided by the National Science Foundation (CDA96-01954) and by Silicon Graphics Inc.

Supporting Information Available: Table of observed ν(NO) and ν(CO), and reduced mass functions for the *trans*-dicarbonyl $Ru(OEP)(CO)_2$ and the *trans*-dinitrosyls $Fe(TmTP)(NO)_2$ and $Ru(TmTP)(NO)_2$. Tables of Cartesian coordinates and energies (in hartrees) of the complexes $[Ru(NH_3)_5(NO)]^{3+}$, $Ru(NH_3)_5(NO)]^{2+}$, $[Ru(NH_3)_4(NO)_2]^{2+}$, $[Fe(NH_3)_4(NO)_2]^{2+}$, Ru(porphine)$(NO)_2$, and Fe(porphine)$(NO)_2$ optimized at the B3LYP/3-21g level. Supplemental figure showing ν(NO) band of $Fe(TmTP)(NO)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

IC034079V