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Density Functional Studies of the Structure and Bonding of Nitrosyl Metalloporphyrin Complexes

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Abstract.—Density functional calculations were used to determine optimized geometries for nitrosyl-metalloporphyrin complexes of Fe(II), Co(II) and Mn(II). The optimized structures were found to be consistent with experimental data and previous computational predictions using single point density functional calculations. Vibrational frequencies for the N-O stretching mode were also calculated and shown to be consistent with experimental data. The nature of the bonding between the metal center and nitrosyl ligand is discussed in relation to the structure of the M-N-O linkage. The results were found to be consistent with previous descriptions derived from the Fenske-Hall approximate molecular orbital method. Other interesting structural features in the optimized geometries are noted.

Key words:—Density functional calculations, optimized geometries, nitrosyl-metalloporphyrin complexes, Fe(II), Co(II), Mn(II), Fenske-Hall approximate molecular orbital method.

Introduction

The calculations presented in this paper focus on the structure of the metal-nitrosyl unit in porphyrin complexes of Fe(II), Co(II), and Mn(II) (indicated as M(PP)NO). It has been shown experimentally that the M-N-O linkage in Mn(II) porphyrin complexes is essentially linear (Scheidt and Frisse 1975) while the structures in Fe(II) and Co(II) complexes are bent (Scheidt and Hoard 1973, Scheidt and Piciulo 1976). Approximate molecular orbital calculations have been used to explain this trend, which primarily arises as a result of a change in the number of electrons available for bonding on the metal center (Graham and Brown 2001). Bending of the M-N-O linkage allows for orbital mixing, resulting in a lowering of the energy of the highest occupied molecular orbital (HOMO) in complexes of Iron (II) and Cobalt (II). A qualitative MO diagram describing the interactions between linear and bent NO and a metal porphyrin fragment is given in Fig. 1.

The $2a_1$ molecular orbital for the linear NO complex in Fig. 1 can be described as primarily the nitrosyl 5 – metal $d_z{}^2$ antibonding interaction. For Co(II) and Fe(II) this is the HOMO of the complexes. In the case of Co(II) this orbital is doubly occupied, in the Fe(II) complex it is singly occupied, and in the Mn(II) complex it is empty. Bending of the M-N-O linkage allows mixing between the metal $d_z{}^2$ and NO 2π orbitals and a decrease in overlap between the NO5 and metal $d_z{}^2$ resulting in stabilization of the $2a_1$ orbital. Bending also results in some destabilization of the 1e orbitals (largely metal based orbitals with metal $d\pi$-NO2π back-donation) and hence is favored only when $2a_1$ is occupied. Qualitative molecular orbital theory predicts a linear NO in the Mn(II) complex and a bent NO in Fe(II) and Co(II) complexes. The degree of bending in the Co(II) complex is expected to be greater than that in the Fe(II) complex as the $2a_1$ orbital is only singly occupied in the Fe(II) case. These qualitative descriptions of bonding provide a simple explanation of the reasons for NO bending. However, the method used to generate these descriptions (Fenske-Hall Approximate Molecular Orbital Method) cannot be used to quantitatively predict the degree of bending that will occur.

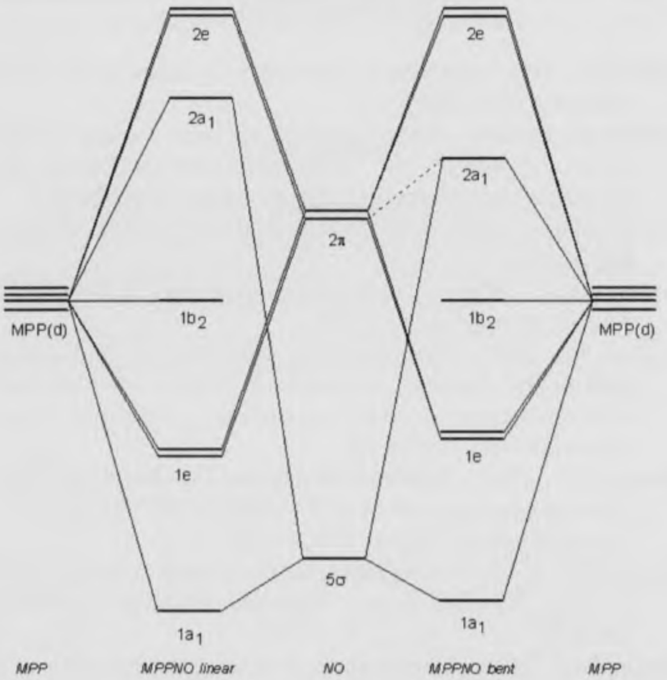

Fig. 1. Qualitative Molecular Orbital Description of Linear and Bent Nitrosyl Metalloporphyrin Complexes.

Because of the large size of the systems of interest, full geometry optimizations using ab initio or DFT (Density Functional Theory) methods were not practical until recently. Hence to obtain a quantitative prediction of the degree of bending of the M-N-O linkage in each complex, previous studies used a series of single point density functional calculations to estimate the optimal M-N-O angle (Graham and Brown 2001). The degree of bending predicted in these studies was found to be in good agreement with experimental data. Due to the rapid development in processing speed of modern computers, full optimization calculations on large molecules are now possible even on relatively inexpensive personal computers. In the current paper we present the results of full geometry optimization and vibrational analysis calculations on the nitrosyl-porphyrin complexes of iron(II), manganese(II), and cobalt (II).

Methods

All calculations were performed using Gaussian 03W on IBM compatible PCs (Fritch et al. 2003). The non-local density functional method BPW91 was used for all calculations. Geometry optimizations were performed using both 6-31G and 6-31G(d) basis sets. Vibrational frequencies were calculated using the 6-31G(d) basis set, except for the manganese complex for which frequencies were calculated using 6-31G.

Results and Discussion

The geometries of the metal nitrosyl-porphyrin complexes were optimized using the non-local density functional method BPW91 and the basis sets 6-31G and 6-31G(d). Ball and stick representations of the optimized complexes of Mn, Fe and Co are given in Figs. 2, 3 and 4, respectively.

Table 1. Calculated M-N-O angles for nitrosyl porphyrin complexes of Mn(II), Fe(II) and Co(II)

M-N-O angle	Mn	Fe	Co
Experiment	*176*	*149*	*135*
ADF single point calculations	180.0	144	128
BPW91/6-31G optimization	180.0	143	125
BPW91/6-31G(d) optimization	180.0	144	123

A comparison of calculated and experimental M-N-O angles for each complex is given in Table 1. It is observed that the predicted M-N-O angles are in good agreement with both experimental data and previously predicted values from single point DFT calculations. The addition of d-polarization functions to the 6-31G basis set (6-31G(d)) did not significantly change the calculated M-N-O angles. Both the single point DFT calculations and the full geometry optimization calculations appear to slightly overestimate the degree of bending in the iron and cobalt complexes. However, the experimental numbers were determined for complexes in which there are additional functional groups attached to the porphyrin ring (such as in protoporphyrin IX) and also under conditions where intermolecular interactions could produce some variation in structure. Hence, an exact agreement is not expected.

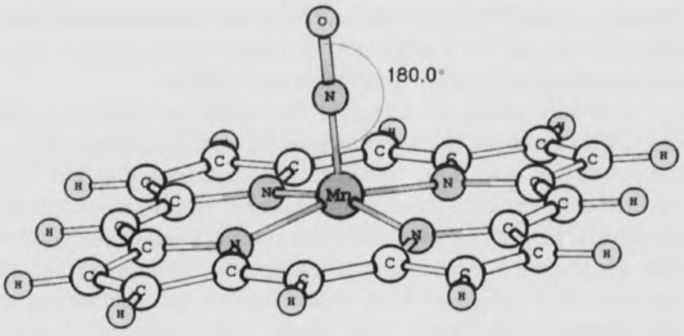

Fig. 2. BPW91/6-31G(d) Optimized Geometry for Mn(PP)NO.

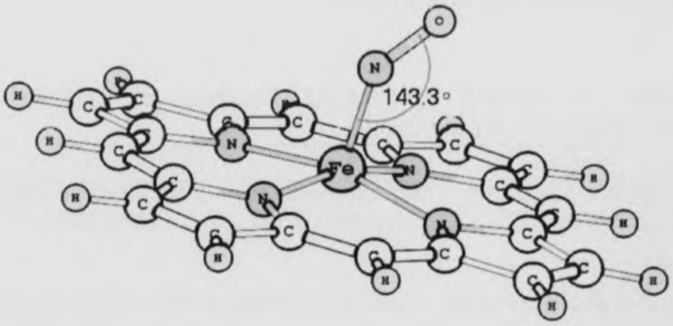

Fig. 3. BPW91/6-31G(d) Optimized Geometry for Fe(PP)NO.

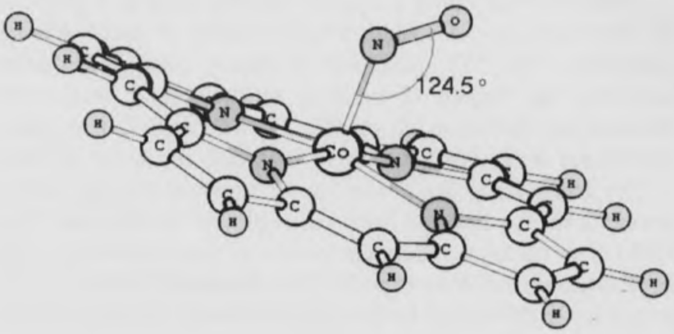

Fig. 4. BPW91/6-31G(d) Optimized Geometry for Co(PP)NO.

As illustrated in Figs. 3 and 4, bending of the NO ligand in the Fe(II) and Co(II) complexes occurs in a plane between nitrogen atoms of the porphyrin ring (a dihedral angle of 45°).

This minimizes repulsive interactions between the NO and ring nitrogen atoms. This is the mode of bending assumed in previous approximate and DFT calculations (Graham and Brown 2001) and consistent with known experimental results.

It is interesting to note that the optimized structure for the Co(II) complex exhibits considerable ruffling distortion of the porphyrin ring. This structure was determined to be 7 kJ/mole lower in energy than an optimized structure in which the porphyrin ring is forced to remain planar. Distortions of this type are known to occur for smaller metal ions and it is believed that the main cause of such distortions is the shortening of the distance between the metal center and porphyrin nitrogen atoms. Table 2 lists metal-porphyrin (N) distances for the three complexes. It is observed that the average metal-N distance in the Co(II) complex is indeed shorter than in the complexes of Fe(II) and Mn(II). The porphyrin rings in the Mn(II) and Fe(II) complexes are essentially planar.

Table 2. Metal-N (porphyrin) distances in M(PP)NO, M = Mn(II), Fe(II) and Co(II)

Mn-N	Fe-N	Co-N
1.997, 1.997, 1.975, 1.975 Average = 1.986	2.027, 2.027, 1.999, 1.999 Average = 2.013	2.018, 2.018, 2.018, 2.018 Average = 2.018

Other interesting structural features noted are that in the complexes of Fe and Co, the metal is slightly displaced from the center of the porphyrin ring and the M-N bond of M-NO is slightly tilted from perpendicular toward the closer side of the porphyrin ring.

The N-O stretching frequency is often used as a probe in the determination of structure and bonding of metal nitrosyl complexes. The NO stretching frequency gives information regarding the degree of bending of the ligand with lower frequencies indicative of smaller M-N-O angles. Calculated vibrational frequencies for the N-O stretch are given in Table 3. The frequencies are scaled using standard scaling factors related to the method and basis set employed (Radom and Scott 1996). The calculated frequencies are in good agreement with experimental values. As expected, the calculated N-O stretching frequency in the series Mn-Fe-Co decreases as the M-N-O angle decreases.

The variation of Co(PP)NO HOMO energy and total energy with M-N-O angle is illustrated in Fig. 5. The energies are relative values, scaled for visualization purposes, and hence no units are given. Consistent with previous calculations, the energy of the HOMO decreases approximately linearly with decreasing M-N-O angle. The total energy of the complex exhibits a minimum at approximately 123°, beyond which further stabilization of the HOMO no longer results in stabilization of the complex. This is expected as bending of the NO results in some destabilization of the $1a_1$ and 1e molecular orbitals (Fig. 1). The resulting optimal angle arises from competing effects of stabilization of $2a_1$ and destabilization of $1a_1$ and 1e. In the Iron (II) complex, a larger M-N-O angle (relative to Co(II)) is expected as the singly occupied $2a_1$ HOMO contributes less influence on the total energy of the molecule.

Table 3. Calculated Vibrational Frequencies for the N-O stretch in M(PP)NO, M = Mn(II), Fe(II) and Co(II).

	Experimental	Calculated Gaussian 03
Co	1680	1661 (6-31G(d))
Fe	1700	1691 (6-31G(d))
Mn	1730	1744 (6-31G)

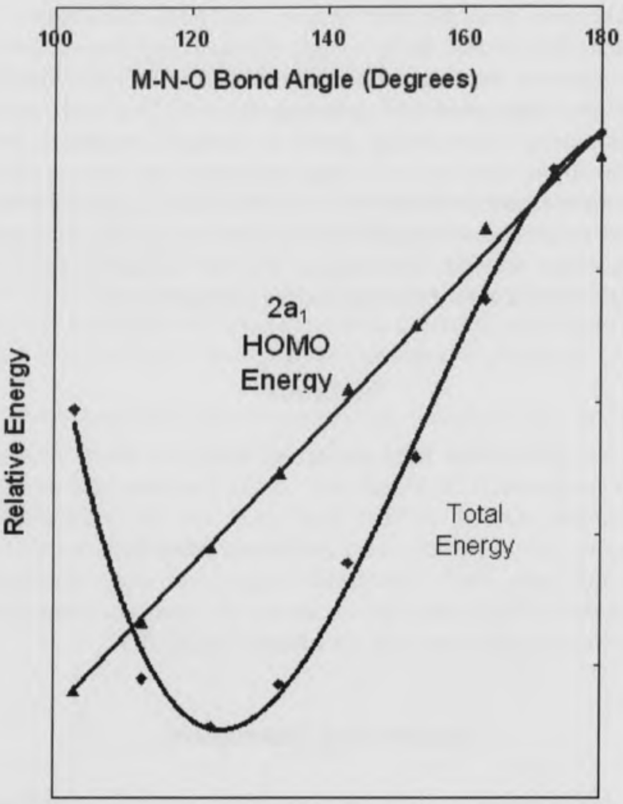

Fig. 5. Variation of Relative Total Energy and HOMO Energy with M-N-O angle for Co(PP)NO.

Conclusions

The results obtained using Gaussian 03 density functional calculations are consistent with those previously derived from Fenske-Hall approximate molecular orbital calculations and Amsterdam Density Functional single point energy calculations

(Graham and Brown 2001). Good agreement is obtained between optimized geometries, previously predicted structures, and experimental structures for the complexes of interest. Calculated vibrational frequencies are also found to be in good agreement with available experimental data. The general nature of the bonding and the influence of the HOMO energy on the structures derived from Gaussian calculations are consistent with previous descriptions derived from approximate molecular orbital calculations.

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