

These M d π -O p π MOs characterize the reactivity of most metal-oxo complexes. Groves¹⁴ has concluded on the basis of stereochemistry that in alkane hydroxylation by the related ferryl porphyrin systems such an approach (i.e. the C-H bond approaches the M-O moiety from the side and is directed at the oxo) is expected. In a linear C-H...oxo pathway the C-H bond to be activated is orthogonal to the RuO π MOs, making direct interaction impossible. Another interesting matter in connection with a seven-coordinate pathway is that once the H⁺ is transferred, the conditions for eq 3, fragmentation of the association complex, are set in place—i.e. a seven-coordinate structure with a d population greater than 4 is formed. Thus, the association complex breaks up and a fast proton transfer occurs to yield products.

The INDO/1 results suggest that a pathway which involves precoordination of the alcohol to the metal is competitive with, if not more favorable than, a pathway which involves C-H activation by the oxo alone. In fact, the INDO/1 analysis indicates that the preferred pathway is a combination of both proposals; i.e. the precoordination of the substrate to the metal activates the MeOH for further reaction. The calculated barrier decreases from 52 kcal mol⁻¹ (linear C-H-oxo) to 16 kcal mol⁻¹ (cyclic C-H/Ru-oxo).

Given the interest in metal-oxo mediated oxidations, largely as a result of the heme monooxygenases cytochromes P-450,^{15,16} the INDO/1 results should serve to remind one that when dealing with the oxidation of substrates which are potentially good donors (e.g. amines and ethers), pathways which involve direct interaction between the substrate and the metal should be considered. Steric requirements brought about by the coordination environment around the metal as well as the substrate must also be considered when one contemplates a direct metal-substrate route. Coordination of the substrate to the metal for those cases in which it occurs will activate the metal toward further reaction.

Acknowledgment. We thank the NSF and Shell Foundation (in the form of a predoctoral fellowship for T.R.C.) for funding and Prof. Michael C. Zerner (Florida) for information about the ZINDO program (written by himself and his collaborators). The assistance of Greg Harris (Florida) in preparing the manuscript and helpful comments by Prof. Thomas J. Meyer (University of North Carolina—Chapel Hill) are gratefully acknowledged.

- (14) Groves, J. T.; Nemo, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 6243.
 (15) *Cytochrome P-450: Structure, Mechanism and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum: New York, 1986.
 (16) *Cytochrome P-450: Structural and Functional Relationships*; Ruckpaul, K., Ed.; Verlag: Berlin, 1984.

Contribution from the Department of Chemistry,
 University of Iowa, Iowa City, Iowa 52242

Characterization of Ammonia-Ligated Low-Spin Iron(III) Porphyrin Complexes

Yunghye Oh Kim and Harold M. Goff*

Received March 3, 1989

Substituted imidazoles or pyridines readily coordinate to iron(III) porphyrins to form stable bis(amine)-ligated low-spin iron(III) species.¹⁻³ Although the analogous bis(aliphatic amine) complexes have been observed at low temperature, these ligands are prone to reduce the iron(III) porphyrin complex to the iron(II)

- (1) Epstein, L. M.; Straub, D. K.; Maricondi, C. *Inorg. Chem.* **1967**, *6*, 1720.
 (2) La Mar, G. N.; Walker, F. A. *J. Am. Chem. Soc.* **1972**, *94*, 8607.
 (3) Satterlee, J. D.; La Mar, G. N.; Frye, J. S. *J. Am. Chem. Soc.* **1976**, *98*, 7275.

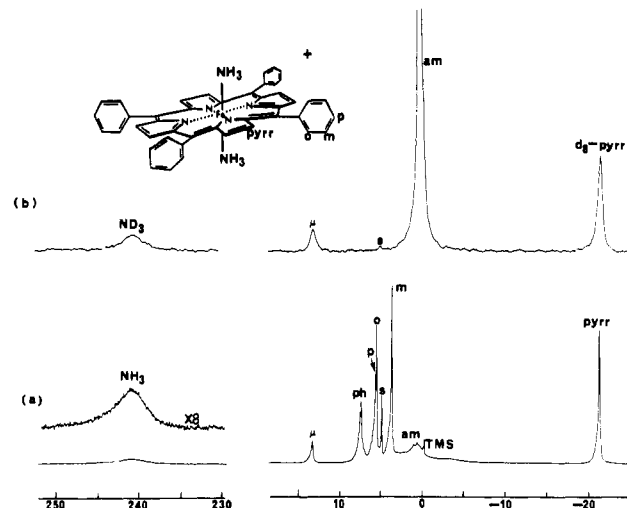


Figure 1. (a) Proton NMR spectrum of a mixture of (TPP)Fe(NH₃)₂·SO₃CF₃ and [(TPP)Fe]₂O in CD₂Cl₂ solution at 25 °C, referenced to tetramethylsilane in ppm. Signals for (TPP)Fe(NH₃)₂⁺ are labeled as follows: pyrrole, "pyrr"; ortho, "o"; meta, "m"; para, "p"; coordinated ammonia, "NH₃". Signals for [(TPP)Fe]₂O are labeled "μ" for pyrrole and "ph" for phenyl protons. The solvent signal is labeled "s", free ammonia, "am", and tetramethylsilane, "TMS". (b) Deuterium NMR spectrum of a mixture of (TPP-d₉)Fe(NH₃)₂·SO₃CF₃, [(TPP-d₉)Fe]₂O, and excess ND₃ in CH₂Cl₂ solution at 25 °C. Signals are labeled as above.

derivative at ambient temperature.⁴ Mixed complexes with cyanide and aliphatic amine ligands exhibit no tendency for auto-reduction.⁴ The ammonia ligand is reportedly inert with respect to reduction of iron(III) to iron(II) porphyrins.⁵ It is surprising, however, that an ammonia-ligated iron(III) complex has not been described. The diamagnetic iron(II) octaethylporphyrin complex (OEP)Fe(NH₃)₂ has been prepared by the reduction reaction of an iron(III) complex, (OEP)FeCl, and hydrazine in 2-picoline.⁶ This report describes the generation of the first low-spin iron(III) porphyrin complex with ammonia ligands.

The ammonia-ligated iron(III) tetraphenylporphyrin (TPP) complex is synthesized by displacement of the weakly coordinated triflate ion in (TPP)FeSO₃CF₃ with anhydrous ammonia gas in dichloromethane, chloroform, or toluene solution. Upon introduction of ammonia into a dichloromethane or chloroform solution of (TPP)FeSO₃CF₃, the color changes from brown to red (optical bands at 414 (Soret) and 546 nm). When ammonia gas is passed into a toluene solution of (TPP)FeSO₃CF₃, the ionic iron porphyrin product precipitates. The solid was recrystallized from dichloromethane and used for NMR and Mossbauer spectroscopic measurements. The iron(III) porphyrin ammonia complex is inevitably contaminated with the thermodynamically stable μ-oxo dimer [(TPP)Fe]₂O due to traces of water in the solvent or ammonia gas.⁷ The ammonia complex is stable in the presence of dry oxygen, but the red solution is immediately changed to that of the green μ-oxo dimer when exposed to a moist atmosphere.

Figure 1a shows the proton NMR spectrum of a CD₂Cl₂ solution that contains the ammonia-ligated iron(III) tetraphenylporphyrin complex contaminated with the [(TPP)Fe]₂O byproduct. Phenyl resonances were assigned as follows: ortho, 5.93 ppm; meta, 3.86 ppm; para, 5.77 ppm.⁸ The pyrrole proton signal is

- (4) Hwang, Y. C.; Dixon, D. W. *Inorg. Chem.* **1986**, *25*, 3716 and references therein.
 (5) Castro, C. E.; Jamin, M.; Yokoyama, W.; Wade, R. *J. Am. Chem. Soc.* **1986**, *108*, 4179.
 (6) Dolphin, D.; Sams, J. R.; Tsin, T. B.; Wong, K. L. *J. Am. Chem. Soc.* **1976**, *98*, 6970.
 (7) Solvents were rigorously dried and manipulated under a nitrogen atmosphere. Chlorinated solvents were distilled from P₂O₅ under a nitrogen atmosphere. Toluene was distilled from sodium/benzophenone under a nitrogen atmosphere.
 (8) These phenyl resonances are assigned from the comparison of the NMR spectra of (2-CH₃TPP)Fe(NH₃)₂⁺, (3-CH₃TPP)Fe(NH₃)₂⁺, and (4-CH₃TPP)Fe(NH₃)₂⁺.

observed at -20.9 ppm, which is a typical value for low-spin iron(III) tetraphenylporphyrin derivatives.^{9,10} A broad resonance for coordinated ammonia is detected at 240.6 ppm in the proton NMR spectrum. This peak is assigned by its appearance in the pyrrole and deuterated (ammonia)iron porphyrin product (Figure 1b).¹¹ Integration of the ammonia and pyrrole proton signals yields an 8:6 intensity pattern. Hence, the product is assigned as a bis(ammonia)-ligated low-spin iron(III) porphyrin derivative, $(\text{TPP})\text{Fe}(\text{NH}_3)_2\text{SO}_3\text{CF}_3$, on the basis of the NMR spectroscopic results. Ammonia ligand exchange is slow on the 55-MHz deuterium NMR time scale ($k_{\text{ex}} < 6 \times 10^4 \text{ s}^{-1}$), as judged by appearance of both coordinated and free ammonia signals.

A plot of pyrrole proton chemical shift vs $1/T$ shows a straight line from 193 to 308 K with an intercept of 15.0 ppm and correlation coefficient of 0.999 . Plots of ammonia and phenyl ortho, meta, and para proton resonances vs $1/T$ also exhibit linearity from 206 to 308 K. This suggests that the signals are from a single species. However, in the proton NMR spectrum at 318 K, a minor pyrrole resonance for a high-spin iron(III) complex is observed at 75 ppm. When the solution temperature is lowered back to 298 K, the 75 ppm peak disappears. Hence, a ligand dissociation reaction occurs in solution at higher temperature to presumably yield a mono(ammonia) complex.

Relative line widths support the far-downfield and near-upfield assignment for respective ammonia and pyrrole proton NMR signals. Under the assumption of dipolar relaxation for protons, the line widths should be proportional to r^{-6} , where r is the iron-proton distance.¹² The pyrrole proton is located 5.1 \AA from the iron center, and on the basis of standard bond distances, the ammonia proton would be 3.0 \AA from the metal center.¹³⁻¹⁵ The 57 -Hz line width pyrrole proton signal would predict a 1380 -Hz ammonia signal. This value is similar to the 1450 -Hz line width value observed in Figure 1a for the coordinated ammonia ligands.

When the relaxation mechanism for a nucleus is limited to that from an unpaired metal spin, the line width is predicted to be proportional to the square of the gyromagnetic constant for the nucleus (γ).¹⁶ Hence, the proton line width could in principle be 42 times as broad as the deuterium line width. Respective proton and deuterium line widths for the ammonia signal in Figure 1 are 154 and 1450 Hz. The 9.4 ratio for these two line widths is considerably less than the possible $(\gamma_{\text{H}}/\gamma_{\text{D}})^2$ value of 42 and presumably reflects a sizable contribution from quadrupolar relaxation by the deuteron.

The solution magnetic moment for $(\text{TPP})\text{Fe}(\text{NH}_3)_2^+$ is $2.3 \pm 0.1 \mu_{\text{B}}$ ¹⁷ at 298 K as obtained from the Evans method.¹⁸ This value is in accord with the reported value for the bis(imidazole)-ligated low-spin iron(III) porphyrin complex.¹⁹

The Mossbauer spectroscopic results for the ammonia adduct of $(\text{TPP})\text{FeSO}_3\text{CF}_3$ also support formulation of a low-spin iron(III) complex. The recrystallized solid material exhibits an isomer shift of 0.21 mm/s (iron metal reference) and a quadrupole splitting of 1.4 mm/s at 80 K. An analogous bis(imidazole) complex exhibits a 0.23 mm/s isomer shift and 2.23 mm/s quadrupole splitting at 77 K, whereas the pyridine complex shows respective values of 0.16 and 1.25 mm/s at the same temperature.²⁰

An interesting feature of the ammonia-iron(III) porphyrin complex is the observation of a strong g_{max} type EPR spectrum. The spectrum for a frozen dichloromethane solution of $(\text{TPP})\text{Fe}(\text{NH}_3)_2\text{SO}_3\text{CF}_3$ at 5.2 K exhibits a prominent signal at $g = 3.75$, a broad feature at $g = 2$, and no clear evidence of another component up to 6000 G. The strong g_{max} type spectrum is observed for the axially symmetric bisligated low-spin iron(III) porphyrin complexes such as those with pyridine, 3- or 4-substituted pyridine, or 2-methylimidazole complexes.^{14,21,22}

In summary, the electronic properties of the first well-characterized ammonia complex of an iron(III) porphyrin largely parallel those of known bis(amine) complexes. The lack of earlier reports on this subject is seemingly a consequence of the competitive hydrolytic chemistry of iron(III) porphyrins in the presence of the basic ammonia ligand. The demonstrated affinity of ammonia for iron porphyrins is of relevance to the coordination chemistry of nitrogen species in turnover of the nitrite reductase enzyme.²³

Acknowledgment. The financial support of National Science Foundation Grant CHE-8705703 is gratefully acknowledged.

(20) Sams, J. R.; Tsin, T. B. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 450-452.

(21) Walker, F. A.; Reis, D.; Balke, V. L. *J. Am. Chem. Soc.* **1984**, *106*, 6888.

(22) Migita, C. T.; Iwaizumi, M. *J. Am. Chem. Soc.* **1981**, *103*, 4378.

(23) Young, L. J.; Siegel, L. M. *Biochemistry* **1988**, *27*, 2790.

Contribution from the Research School of Chemistry,
Australian National University,
Canberra, ACT 2601, Australia

Spectroscopic Verification of a Tetragonal Compression in an Octahedral Copper(II) Compound

Kim Finnie, Lucjan Dubicki,* Elmars R. Krausz,
and Mark J. Riley

Received January 29, 1990

It is well established that six-coordinate copper(II) complexes preferentially adopt a tetragonally elongated geometry although there are several examples of doped Cu(II) crystals having a compressed geometry.¹ Six-coordinate copper(II) complexes are susceptible to tetragonal distortions, as this is the Jahn-Teller active coordinate in the parent octahedral complex. In this work, a series of CuF_6^{4-} complexes has been used to study the spectroscopic implications of such tetragonal distortions.

The crystal structure of the pure K_2CuF_4 compound was originally described as containing compressed octahedra,² but magnetic³ and spectroscopic⁴ studies were incompatible with this geometry. Subsequently, it has been established that the structure of K_2CuF_4 has an "antiferrodistortive" order where elongated octahedra are orthogonally aligned perpendicular to the tetragonal axis of the crystal.³

Recently an X-ray diffraction study has shown that crystals of KCuAlF_6 contain compressed CuF_6^{4-} octahedra.⁵ A spec-

- (9) (a) La Mar, G. N.; Walker, F. A. In *In Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 61-157. (b) Goff, H. M. In *Iron Porphyrins, Part I*; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1983; pp 237-281.
- (10) When ammonia was allowed to react with electron-deficient iron(III) porphyrins such as tetrakis(*o,o'*-difluorophenyl)- or tetrakis(pentafluorophenyl)porphyrin, the pyrrole proton NMR signals were observed in the high-spin iron(III) region at 80 ppm.
- (11) The ND_3 gas was generated by thermal decomposition of deuterated ammonium sulfate, which was made from recrystallization of ammonium sulfate in D_2O three times.
- (12) Swift, T. J. In *NMR of Paramagnetic Molecules*; La Mar, G. N., Horrocks, W. DeW., Jr., Holm, R. H., Eds.; Academic Press: New York, 1973; pp 53-81.
- (13) The iron(III)-pyrrole hydrogen distance of 5.1 \AA is obtained from the X-ray structure of the bis(imidazole) complex $(\text{TPP})\text{Fe}(\text{Im})_2^+$. The iron-ammonia proton distance is calculated from the iron-imidazole nitrogen distance of 2.0 \AA for $(\text{TPP})\text{Fe}(\text{Im})_2^+$,¹⁴ as well as a Co-N 2.0 \AA distance in $\text{Co}(\text{NH}_3)_6^{3+}$,¹⁵ and from a nitrogen-hydrogen distance of 1.0 \AA in the ammonia molecule.
- (14) Walker, F. A.; Huynh, B. H.; Scheidt, W. R.; Osvath, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 5288.
- (15) Schmidt, K. H.; Muller, A. *Coord. Chem. Rev.* **1976**, *19*, 41.
- (16) McGarvey, B. R.; Kurland, R. J. In *NMR of Paramagnetic Molecules*; La Mar, G. N., Horrocks, W. Dew., Jr., Holm, R. H., Eds.; Academic Press: New York, 1973; pp 555-593.
- (17) This value is corrected for the presence of the μ -oxo dimer.
- (18) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Bartle, K. D.; Dale, B. J.; Jones, D. W.; Maricic, S. *J. Magn. Reson.* **1973**, *12*, 286.
- (19) Goff, H. M. *J. Am. Chem. Soc.* **1981**, *103*, 3714.

(1) Reinen, D.; Friebel, C. *Struct. Bonding* **1979**, *37*, 1.

(2) Knox, K. *J. Chem. Phys.* **1959**, *30*, 991.

(3) Khomskii, D. I.; Kugel, I. *Solid State Commun.* **1973**, *13*, 763.

(4) Kleemann, W.; Farge, Y. *J. Phys. (Paris)* **1975**, *36*, 1293.