

- E. C. J.; Watkins, G. L. *Tetrahedron Lett.* **1974**, 585. (e) Sodium diethylaluminumhydride in the presence of 2,6-di-*t*-butylphenoxydiethylaluminum: Yoon, N. M.; Kim, S. K.; Gyong, Y. S. *Bull. Korean Chem. Soc.* **1986**, 7, 323. (f) Hydrogenation: Peitra, S.; Trinchera, C. *Gazz. Chim. Ital.* **1955**, 85, 1705; Gaiffe, A.; Pallaud, R. *Compt. Rend.* **1961**, 252, 1339, **1962**, 254, 486; Plieninger, H.; Werst, G. *Angew. Chem.* **1955**, 67, 156; *Chem. Ber.* **1955**, 88, 1965; Coker, J. N.; Kohlhasse, W. L.; Fields, M.; Rogers, A. O.; Stevens, M. A. *J. Org. Chem.* **1962**, 27, 850; Staskun, B.; Backeberg, O. G. *J. Chem. Soc.* **1964**, 5880; van Es, T.; Staskun, B. *J. Chem. Soc.* **1965**, 5775; *Org. Syn.* **1971**, 51, 20. (g) Organosilicon hydride: Fry, J. L. *Chem. Comm.* **1974**, 45; Fry, J. L.; Ott, R. A. *J. Org. Chem.* **1981**, 46, 602. (h) Thexylbromoborane-dimethyl sulfide: Cha, J. S.; Oh, S. Y.; Kim, J. E. *Bull. Korean Chem. Soc.* **1987**, 8, 301.
- Cha, J. S.; Yoon, M. S. *Tetrahedron Lett.* **1989**, 30, 3677.
  - (a) Cha, J. S.; Lee, S. E.; Lee, H. S. *Org. Prep. Proced. Int.* **1992**, 24, 331. (b) Cha, J. S. *Bull. Korean Chem. Soc.* **1992**, 13, 670.
  - Cha, J. S.; Jeung, M. K.; Kim, J. M.; Kwon, O. O.; Lee, J. C. *Org. Prep. Proced. Int.* **1994**, 26, 552.
  - Cha, J. S.; Jeung, M. K.; Kwon, O. O.; Lee, K. D. Lee, H. S. *Bull. Korean Chem. Soc.* **1994**, 15, 873.
  - Yoon, N. M.; Gyong, Y. S. *J. Org. Chem.* **1985**, 50, 2443.
  - CRC Handbook of Tables for Organic Compound Identification*; 3rd ed.; CRC Press, Inc.: Cleveland, 1967.

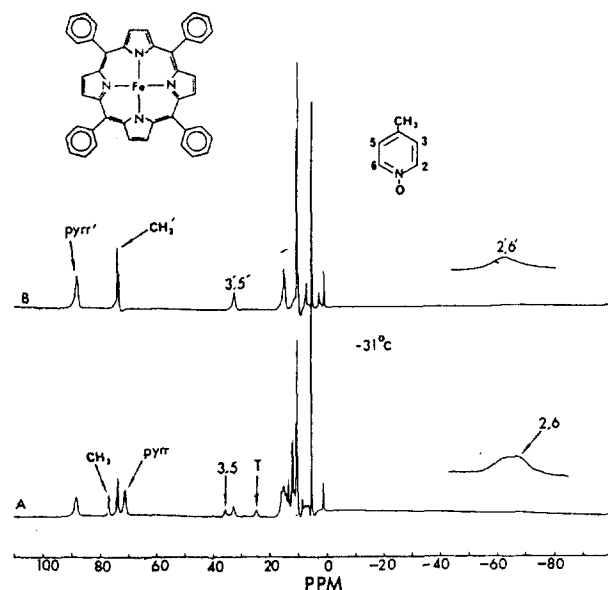
## Evidence for Coordination of Picoline N-oxides to Iron(III) Porphyrin Complexes

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Metalloporphyrins have been found as effective catalysts for the chemical oxidation of organic and inorganic compounds in the presence of oxygen donors.<sup>1</sup> As an oxygen donating reagent, iodosylbenzene, organic perbenzoic acid, hydrogen peroxide, sodium hypochlorite, potassium persulphate, molecular oxygen and amine N-oxide have been used.<sup>2</sup> Bruce and coworkers primarily showed the oxygen donation ability of *N,N*-dimethylaniline N-oxide to an iron(III) porphyrin catalyst.<sup>3</sup> Advantages of N-oxides over other chemical oxidants are their higher solubility in organic solvents, their monomeric nature, and their inability to oxidatively destroy the porphyrin ring. Hirobe and coworkers have also reported that iron(III) porphyrins serve to deoxygenate tertiary amine N-oxide compounds.<sup>4</sup> The high-spin six coordinate complex, [(TPP)Fe(III)(PNO)<sub>2</sub>]ClO<sub>4</sub>, (TPP=dianion of tetraphenyl porphyrin PNO=4-picoline N-oxide), has been prepared and purified by Reed, Scheidt, and coworkers.<sup>5</sup> They characterized



**Figure 1.** <sup>1</sup>H NMR Spectra of Titration of (TPP)Fe(III)SO<sub>3</sub>CF<sub>3</sub>. Both spectra were taken in CD<sub>2</sub>Cl<sub>2</sub> at -31 °C: (A) in the presence of 2.0 equiv of PNO, (B) in the presence of 5.0 equiv of PNO. T represents a pyrrole resonance of the initial iron(III) triflate complex.

this complex by infrared spectroscopy, magnetic susceptibility and elemental analysis, but not NMR spectroscopy. In this paper an evidence for coordination of PNO to the iron(III) porphyrins by <sup>1</sup>H NMR measurements is described.

## Experimental

PNO was purchased from Aldrich and recrystallized from acetone and diethyl ether. As reported previously, the triflate complex, (TPP)Fe(III)SO<sub>3</sub>CF<sub>3</sub>, was prepared by dissolving the [(TPP)Fe(III)]<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub> and stirring with 1 M aqueous HSO<sub>3</sub>CF<sub>3</sub> (Aldrich) for several hours.<sup>6</sup> <sup>1</sup>H NMR spectra were recorded on Bruker AC-200 Fourier transform spectrometer. All NMR signal positions were obtained through the use of the solvent as a reference. The solvent signal for CH<sub>2</sub>Cl<sub>2</sub> (CDHCl<sub>2</sub>) was assigned as 5.32 ppm vs TMS. NMR measurements were performed at 25 °C or -31 °C.

## Results and Discussion

Coordination of picoline N-oxide in CH<sub>2</sub>Cl<sub>2</sub> solution to the iron(III) porphyrin containing a very weak ligand, (triflate anion CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>), is evident by NMR spectroscopy. A pyrrole proton resonance of the iron(III) triflate porphyrin, (TPP)Fe(III)SO<sub>3</sub>CF<sub>3</sub>, in CD<sub>2</sub>Cl<sub>2</sub> was observed at 39.6 ppm in the <sup>1</sup>H NMR spectrum at room temperature.<sup>6</sup> Titration of the triflate complex with PNO in a non-coordination solvent results in the following observation. Addition of 1.0 equiv of PNO gives a very broad pyrrole signal at -48.5 ppm at room temperature. This 48.5 ppm signal shifts further downfield to 60.1 and 68.4 ppm with addition of 2.0 and 5.0 equiv of PNO. The shift downfield and broadness of the pyrrole proton resonance in the <sup>1</sup>H NMR spectrum probably indicates a fast exchange process for the triflate ligand and PNO

on the NMR time scale.<sup>7</sup> As the temperature was lowered, the pyrrole proton resonance at 60.1 ppm in the presence of 2.0 equiv of PNO split at  $-31\text{ }^{\circ}\text{C}$  near the slow exchange limit and three individual pyrrole signals were seen (Figure 1-A). Three pyrrole resonances at 88.4, 73.8 and 24.5 ppm were assigned to bis PNO, mono PNO and unreacted iron (III) triflate complex, respectively. The  $^1\text{H}$  NMR spectrum of a triflate complex with 5.0 equiv of PNO shows only the species bis PNO complex,  $[(\text{TPP})\text{Fe}(\text{III})(\text{PNO})_2]\text{SO}_3\text{CF}_3$ , at  $-31\text{ }^{\circ}\text{C}$  (Figure 1-B). The pyrrole resonance was observed at 88.4 ppm at  $-31\text{ }^{\circ}\text{C}$  and was confirmed with  $\beta$ -pyrrole deuterated  $(\text{TPP}-d_3)\text{FeSO}_3\text{CF}_3$  in the  $^2\text{H}$  NMR spectrum.

Ortho-, meta-protons and 4-methyl peaks of coordinated PNO in the bis PNO complex were observed at  $-63.4$ ,  $32.5$  and  $73.8$  ppm in  $\text{CD}_2\text{CCl}_2$  solution at  $-31\text{ }^{\circ}\text{C}$ . These peak assignments are based on the intensity and shift pattern. The alternating shifts and large isotropic shifts imply the involvement of a  $\pi$ -spin delocalization pathway through the axial ligand.<sup>8</sup> This observation bears a similarity to the previously characterized phenolate axial ligand resonance position in an iron(III) porphyrin complex.<sup>9</sup> From the knowledge of axial ligand PNO chemical shifts for the bis PNO complex, assignment of axial ligand PNO signals for the mono PNO complex was carried out for the  $^1\text{H}$  NMR spectrum of the mixture. Ortho-, meta-protons and 4-methyl resonance for the mono axial ligated PNO were detected at  $-67.4$ ,  $35.5$  and  $77.0$  ppm in  $\text{CD}_2\text{CCl}_2$  at  $-31\text{ }^{\circ}\text{C}$ , respectively.

The iron(III) triflate complex has an admixed spin state ( $S=5/2$  and  $3/2$ ) in solution.<sup>6</sup> The pyrrole proton resonances for the triflate complex show non-Curie law behavior in moving upfield as the temperature is lowered. The pyrrole proton signal at 39.6 ppm at room temperature is shifted to 24.5 ppm at  $-31\text{ }^{\circ}\text{C}$ . Appearance of the pyrrole resonance for the mono PNO complex at 73.8 ppm at  $-31\text{ }^{\circ}\text{C}$  implies the high-spin iron(III) state, as the pyrrole chemical shift values for the high-spin iron(III) tetraarylporphyrins range

from approximately 60 to 80 ppm.<sup>10</sup> Appearance of the pyrrole proton signal at 88.4 ppm for bis PNO complex also indicates the high-spin state, and this is consistent with the previously reported result.<sup>5</sup>

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## References

1. (a) Sheldon, R. A.; Kochi, J. A. *Metal-Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981. (b) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401.
2. Meunier, B. *Chem. Rev.* **1992**, *92*, 1411 and references therein.
3. (a) Schannon, P.; Bruice, T. C. *J. Am. Chem. Soc.* **1981**, *103*, 4580. (b) Powell, M. F.; Pai, E. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 3277. (c) Dicken, C. M.; Lu, F. -L.; Nee, M. W.; Bruice, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 1636.
4. Miyata, N.; Santa, T.; Hirobe, M. *Chem. Pharm. Bull.* **1984**, *32*, 377.
5. Mashiko, T.; Kastner, M. E.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1978**, *100*, 6354.
6. Boersma, A.; Goff, H. M. *Inorg. Chem.* **1982**, *21*, 581.
7. Drago, R. S. *Physical Methods in Chemistry*; W. B. Saunders Company: Philadelphia, London, Toronto, 1977, p 436-466.
8. La Mar, G. N.; Horrocks, W. D.; Holm, R. H. *NMR of Paramagnetic Molecules*; Academic Press: New York and London, 1973.
9. Goff, H. M.; Shimmomura, E. T.; Lee, Y. J.; Scheidt, W. R. *Inorg. Chem.* **1984**, *23*, 315.
10. Goff, H. M. in *Iron Porphyrins*; Part I, Lever, A. B. P.; Gray, H. B. eds.; Addison-Wesley: Reading MA, 1983, p 237-281.