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Formation and Characterization of Sulfur-ligated Iron(III) Porphyrin Complexes: Correlation of Coordination and Magnetic Behavior

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Axial thiolate ligands occur in a number of iron(III) heme protein systems.[1-3] The study of iron porphyrin complexes with sulfur donor ligands is therefore of considerable importance to an understanding of the biological role of the sulfur-ligated heme units.[4-7]

Only limited data are available concerning the thio- or dithio- derivatives of iron porphyrins.[8] in part due to a facile oxidation-reduction reaction. Collman and Holm were the first to isolate and characterize the thiolate iron(III) porphyrin complexes.[6-8] Their measurements (electron magnetic resonance (EPR), Mossbauer spectroscopy, magnetic susceptibility, and X-ray crystal analysis) indicated the presence of both low-spin (bis-ligated) and high-spin (mono-ligated) iron(III) porphyrin complexes. The goal of the present work is the synthesis and characterization of iron porphyrins with a new sulfur ligand: Dithiocarbamatoiron(III) Porphyrin complex((Por)Fe(III)(Dtc)). The bis-ligated complex can be obtained through the modulation of the porphyrin ring basicity and reaction temperature.

Studies of many iron(III) dithiocarbamate complexes[2,9] have focused on the existence of "spin equilibria" in these complexes. But no "spin equilibria" was observed in iron (III)(Dtc) porphyrin complex. Both NMR and EPR spectroscopies were used to monitor the formation, magnetic behavior, and spin states of the new complexes. Correlation of pyrrole ^1H chemical shifts at various temperatures with the electronic structure of the iron porphyrin is diagnostic of the "spin-equilibria" phenomenon.

Experimental Section

The ammonium salt of diethyldithiocarbamic acid, $[NH_4]^+$ $[(C_2H_5)_2NCS_2]^-$ 98%, was obtained from Aldrich Chemical Co (Milwaukee, WI) and used as received. Stock solutions of the salts were prepared with 1.0 M in tetrahydrofuran. Tetraarylporphyrins were prepared by aldehyde/pyrrole condensation, and pyrrole deuterated derivatives were prepared by pyrrole deuterium exchange before macrocycle conden-

sation.[10a] Standard metal incorporation and purification methods were employed.[10b] Trifluoromethanesulfonate (triflate) complexes of iron(III) porphyrins, $TPPFe(III)O_3SCF_3$, were prepared by acid cleavage of the appropriate μ-oxo iron(III) porphyrin dimer.[11] Chlorinated solvents were washed successively with concentrated sulfuric acid, water, and aqueous sodium carbonate, dried over solid calcium chloride, and distilled from solid P_4O_{10}. Deuterated NMR solvents (Aldrich) were used as received.

Proton (360 MHz) and deuterium (55 MHz) NMR spectra of dichloromethane solutions of iron porphyrins with a concentration range of 2.0-6.0 mM were recorded on a Bruker WM-360 spectrometer. Tetramethylsilane was used as an internal reference, and downfield chemical shifts were given a positive sign. Temperature calibration was carried out by the Van Geet method.[12] EPR spectra were recorded on frozen solutions at 77 K, following NMR spectroscopic examination.

Results and Discussion

The previously unreported iron(III) porphyrin Dtc complexes examined here were characterized by NMR and EPR spectroscopic methods. Reaction of iron(III) porphyrin complexes with $[NH_4]^+Dtc^-$ was carried out under inert atmosphere. Titrations of various chloroiron(III) porphyrin complexes with Dtc^- indicated that the reaction did not go to completion with the addition of one equivalent of ligand. For example, approximately 2.0 equivalents of Dtc^- were required to convert $(d_8$-TPP)Fe(III)Cl to a complex with a single distinctive pyrrole deuterium resonance at 77.6 ppm. Chloride ion competition with Dtc^- binding accounted for the non-stoichiometric ratio of Dtc^- to iron porphyrin. Thus, iron porphyrin complexes with the weakly bound triflate ligand were used.

Titration of the iron porphyrin triflate complex $((d_8$-TPP) Fe(III)O_3SCF_3)$ with Dtc^- in non-coordinating solvents gave different results. The pyrrole resonance for $(d_8$-TPP)Fe(III) (O_3SCF_3) in CH_2Cl_2 was observed at 34.2 ppm in the ^2H NMR spectrum at room temperature (Figure 1A). Addition of 1.0 equiv of Dtc gave pyrrole resonances at 77.6 and 13.6

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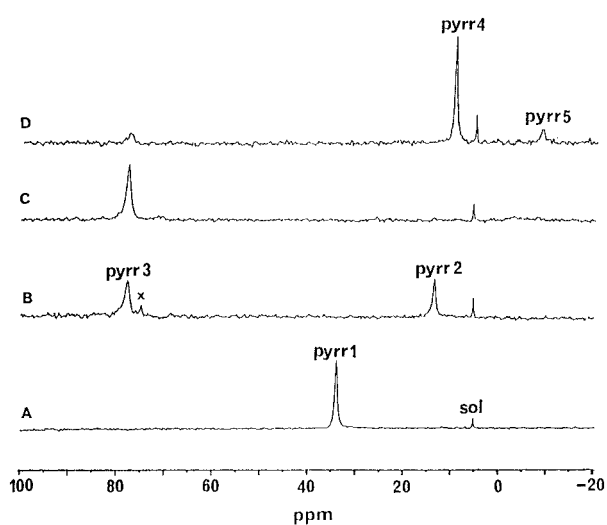
Figure 1. Deuterium NMR (55 MHz) spectra for Dtc⁻ reaction with 4.0 mM (d₈-TPP)Fe(III)O₃SCF₃ in dichloromethane solution at room temperature. (A) (d₈-TPP)Fe(III)O₃SCF₃, (B) addition of 1.0 equiv. Dtc⁻, (C) addition of 1.7 equiv. Dtc⁻, (D) addition of 10.0 equiv. Dtc⁻. The pyrrole resonance is denoted as "pyrr". The signal denoted as x might be due to the pyrrole resonance of Dtc impurity.

ppm with complete disappearance of pyrrole resonance for the triflate complex (Figure 1B). The 13.6 ppm signal disappeared with additional excess Dtc (1.5-2.5 equiv.), having a single pyrrole resonance at 77.6 ppm. (Figure 1C) The 13.6 ppm pyrrole signal resulted from formation of the μ-oxo dimeric species. (TPP)Fe-O-Fe(TPP). since ammonium salt of Dtc is extremely hygroscopic. Further titration with Dtc⁻ generated a new pyrrole signal at 8.9 ppm and a very small peak at -8.4 ppm. The diamagnetic pyrrole signal at 8.9 ppm was assigned to a low-spin (d⁶, S=0) iron(II) complex. The upfield signal corresponds to the generation of a small amount of iron(III)(Dtc)₂⁻ porphyrin complex, *vide infra*.

The 77.6 ppm pyrrole resonance generated by the addition of Dtc⁻ is indicative of a high-spin monomeric Dtc-iron(III) porphyrin complex. as the pyrrole chemical shift value for high-spin iron(III) tetraphenylporphyrins ranges from approximately 60 to 80 ppm (25 °C, TMS ref.).[13] The deuterium NMR spectra of the pyrrole-deuterated iron(III) porphyrin Dtc complex was recorded from 200 K to 298 K. A plot of chemical shift *vs* 1/T was linear, which confirmed that the pyrrole signal at 77.6 ppm represents a single species and is not a dynamically averaged resonance.

The proton NMR spectrum for iron(III)(Dtc) porphyrin complex was acquired (Figure 2). The linewidth for the pyrrole signal of (TPP)Fe(III)(Dtc) is relatively larger, *ca.* 2000 Hz, than the pyrrole signal of (TPP)Fe(III)Cl. *ca.* 500 Hz. The coordinated β-CH₃ ligand signal of Dtc was observed in the diamagnetic region. The α-CH₂ ligand signal was not observed due to line broadness. No signal related to free Dtc⁻ was detected. A variable-temperature study to elucidate the proton NMR signal of the ligand and free Dtc indicates that there might be fast exchange between ligand and free Dtc. since the very broad signal was obscured in the diamag-
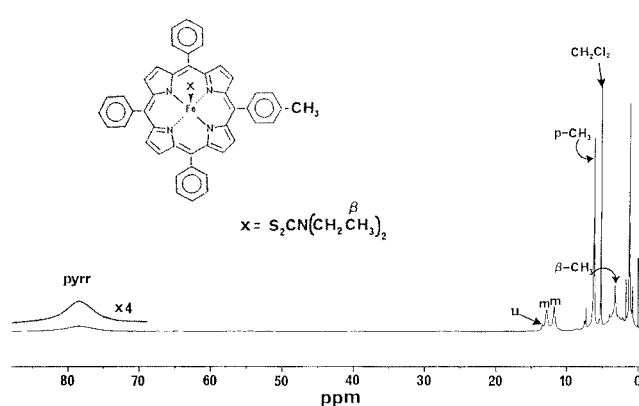

Figure 2. Proton NMR (360 MHz) spectrum for 1.5 equiv. Dtc⁻ addition to (p-FTPP)Fe(III)O₃SCF₃ in dichloromethane solution at room temperature. The "pyrr" corresponds to pyrrole resonance of (p-FTPP)Fe(III)(Dtc). "m" to meta phenyl proton resonance, and "" to μ-oxo dimer.

netic region. Assignments of the phenyl proton NMR signals of the iron(III)(Dtc) porphyrin complexes were based on the peak intensity and on splitting upon variation of the phenyl ring substituents. as shown in Table 1. Spectra of the (TPP)-Fe(III)-Dtc complex in dichloromethane solution exhibited meta phenyl proton signals at 12.78 and 11.73 ppm (13.35 ppm, 12.20 ppm for (TPP)Fe(III)Cl). and para phenyl proton at 3.25 ppm (6.51 ppm for (TPP)Fe(III)Cl)). The ortho phenyl proton signals were not detected. again probably due to large linewidth. The phenyl moieties lie nearly orthogonal to the porphyrin ring, and thus the split meta-phenyl signal is indicative of non-equivalent occupation of the axial ligand positions.

The ²H NMR spectrum of the iron(III) porphyrin triflate complex with approximately 15 fold excess Dtc⁻ at 200 K temperature contained a pyrrole deuteron resonance located at -16.0 ppm. The sixth axial position is believed to be occupied by a second molecule of Dtc. Hexa-coordination is indicative of a low-spin (S=1/2) configuration except for very weak ligands. such as F⁻ and H₂O.[14] The liquid nitrogen temperature EPR spectrum for this complex is clearly consistent with low-spin character. with absorption bands at g = 2.43, 2.28. and 1.91. (TPP)Fe(III)(Dtc) without excess Dtc⁻ in solution exhibits a high-spin EPR spectrum with a g = 5.86. The addition of 1.0 equiv. of Dtc⁻ to the TPPFe(III)-

Table 1. Phenyl proton Chemical shift values for iron(III) porphyrin Dtc complexes

Species[a]	Phenyl protons (ppm)		
	ortho[b]	*meta*	*para*
(p-CH₃TPP)Fe(III)Dtc	12.88	11.88	6.27 (CH₃)
(TPP)Fe(III)Dtc	12.78	11.73	3.25
(F₄-TPP)Fe(III)Dtc	12.20	11.29	
(F₈-TPP)Fe(III)Dtc	12.81	11.76	3.15

[a]All Dtc complexes were prepared in CD₂Cl₂ solution. [b]Ortho phenyl protons in the Dtc-iron(III) porphyrin complexes are not detected in the proton NMR due to large linewidths.
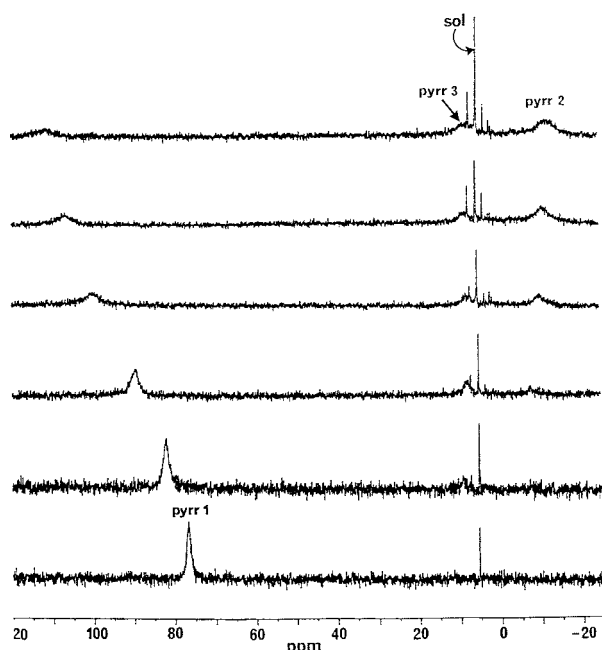
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Figure 3. Deuterium NMR spectra for reaction of 3.5 equiv. Dtc⁻ with 4.0 mM (d₈-*p*-OCH₃TPP)Fe(III)Cl in dichloromethane solution. A) 298 K, B) 271 K, C) 252 K, D) 229 K, E) 209 K, and F) 200 K. The "pyrr 1" corresponds to pyrrole resonance of (d₈-*p*-OCH₃TPP)Fe(III)(Dtc), "pyrr 2" to that of (d₈-*p*-OCH₃TPP)-Fe(III)(Dtc)₂⁻, and "pyrr 3" to that of (d₈-*p*-OCH₃TPP)Fe(II)(Dtc)ₓ. The subscript x is due to the possible five- or six-coordination.

Figure 4. EPR spectra for reaction of 4.0 mM TPPFe(III)O₃SCF₃ with Dtc⁻ in dichloromethane solution at 77 K. A) addition of 1.0 equiv. Dtc⁻ B) addition of 15.0 equiv. Dtc⁻ at dryice temperature and acquired at 77 K. The "*" is due to minor amount of the low-spin complex.

O₃SCF₃ did not produce a low-spin complex. as revealed by NMR and EPR spectroscopic methods. As soon as an additional equivalent of Dtc⁻ was added to this solution. a low-spin absorption band appeared in the EPR spectrum (Figure 4). Further structural characterization was unsuccessful due to the instability of the resulting complex.

A reaction was carried out by addition of several equivalents of Dtc⁻ to solutions of the relatively basic porphyrins, such as (*p*-OCH₃TPP)Fe(III)Cl and (3,4,5-OCH₃TPP)-Fe(III)Cl. In this case shown in Figure 3. reduction was less problematic. affording the observation of the pyrrole resonance change with intensity conversion of the complex from a five-coordinate high-spin to a six-coordinate low-spin species. Upon lowering the solution temperature, a new pyrrole signal (pyrr. 2 at Figure 3) in the upfield region started to grow. However, this low-spin complex was unstable at elavated temperature and converted to the iron(II) complex. which gave a pyrrole resonance at 8.9 ppm. The low-spin iron(III)(Dtc)₂⁻ porphyrin complex is stabilized only at low temperature. The pyrrole signal at 8.9 ppm started to grow even for the basic porphyrins as the temperature was raised. At a temperature of 298 K. the -16.0 ppm pyrrole peak (-8.4 ppm at 25 °C) is totally converted to the 8.9 ppm pyrrole signal (Figure 4). This chemical shift is identical with the pyrrole signal generated by titration of iron(III) triflate porphyrin with excess Dtc⁻ at 25 °C. The excess free thiolate or bis-ligated Dtc ligands probably reduced the iron(III) to iron(II). Also. over a period of hours the iron(II) Dtc com-
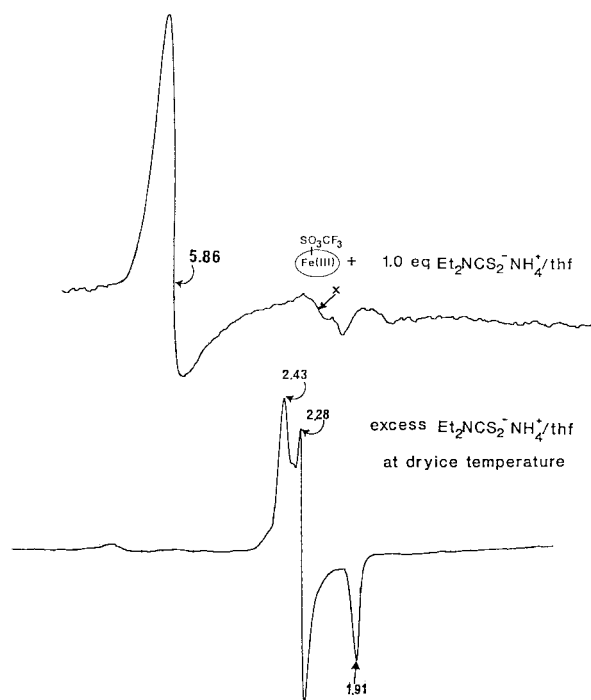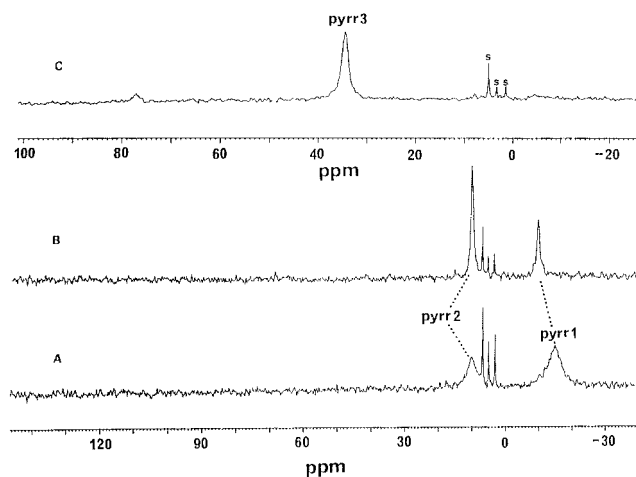

Figure 5. Dueterium NMR spectra for reaction of 15.0 equiv. of Dtc⁻/thf with 4.0 mM (d₈-*p*-OCH₃TPP)Fe(III)Cl in dichloromethane solution. A) 200 K, B) raised to 256 K, and C) after 5 hours at 298 K. The "pyrr 1" correspond to the pyrrole resonance of iom(III)(Dtc)₂, "pyrr 2" to iron(II)(Dtc)ₓ, and "pyrr 3" to iron(II)(thf)ₓ porphyrin complexes.

plex decomposed to produce a partially solvated iron(II)-(thf)ₓ porphyrin complex (Figure 4C). The pyrrole resonance of this complex was dependent upon the amount of added thf from the titrated Dtc⁻/thf solution. For example. for the reaction of (d₈-TPP)Fe(III)Cl with 15.0 equiv. Dtc⁻, a 35 ppm pyrrole deuteron signal was observed after complete decom-

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Scheme 1

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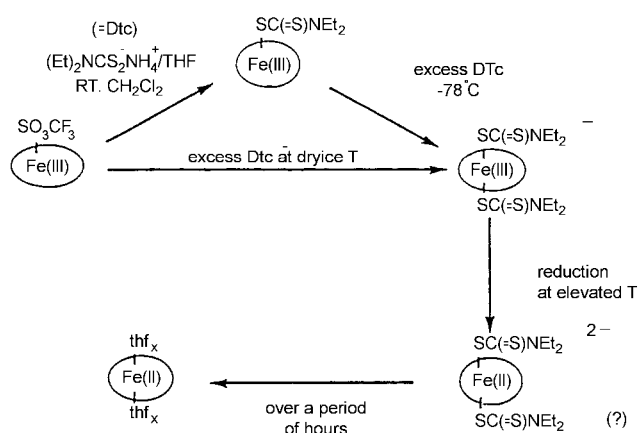
position (5 hours at 298 K). This 35 ppm pyrrole resonance moved in a downfield direction upon titration with thf and finally appeared at 48 ppm in the presence of a large excess of thf. The 48 ppm resonance is assignable to the pyrrole signal of TPPFe(II)(thf)$_2$. The 35 ppm pyrrole signal was independently confirmed by the titration of square-planar iron(II) with thf in toluene solution. The general reaction process is illustrated in Sheme 1.

Conclusions

The first characterization of iron-sulfur bonded porphyrin complexes of Dtc has been presented. Although the bonding configuration for the iron(III)(Dtc) is not clear at present due to its instability, the formation of monomeric iron(III)(Dtc) was evident by spectroscopic results. The ligand underwent a high-spin to low-spin transformation upon addition of second ligand sources. While this ligand does not exist in proteins, the results could allow an assessment of the influence of sulfur ligation on the magnetic and electronic properties of bound hemes in a relatively stable five-coordinate iron (III) complexes and serve as a model for the thiolate ligand, which is the essential component of cytochrome P-450. The present information (high-spin and low-spin interconversion) may provide a dynamic model for the transformation associated with the substrate binding in the catalytic cycle of P-450 enzymes in which the low-spin, six-coordinate resting form is converted to a high-spin, five-coordinate species.

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References

1. (a) Suzuki, N.; Higuchi, T.; Urano, Y.; Kikuchi, K.; Uekusa, H.; Ohashi, Y.; Uchida, T.; Kitagawa, T.; Nagano, T. *J. Am. Chem. Soc.* **1999**, *121*, 11571. (b) Sono, M.; Roach, M. P.; Coulter, E. D.; Dawson, J. H. *Chem. Rev.* **1996**, *96*, 2841. (c) Wagenknecht, H. A.; Woggon, W. D. *J. Am. Chem. Soc.* **1997**, *36*, 390 (d) Dawson, J. H. *Science* **1988**, *240*, 433 (e) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49.
2. (a) Sundamoorthy, M.; Terner, J.; Poulos, T. L. *Structure* **1995**, *3*, 1367. (b) Crane, B. R.; Arvai, A. S.; Gachhui, R.; Wu, C.; Ghosh, D. K.; Getzoff, E. D.; Steuhr, D. J.; Tainer, J. H. *Science* **1997**, *278*, 425. (c) Coucouvanis, D. *Prog. Inorg. Chem.* **1970**, *11*, 233.
3. Burns, R. P.; Macullough, F. P.; McAuliffe, C. A. *Adv. in Inorg. Chem. Radiochem.* **1980**, Vol 23, 211.
4. (a) Reisach, J.; Gersonde, K. *Biochemistry* **1977**, *16*, 2539. (b) Ortiz de Montello, P. R. In *Cytochrome P-450, Structure, Mechanism, and Biochemistry*; Plenum Press: New York, 1986.
5. Collman, J. P.; Hoard, J. L.; Kim, N.; Lang, G.; Reed, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 2676.
6. (a) Mashiko, T.; Reed, C. A.; Haller, K. J.; Kastner, M. E.; Scheidt, W. R. *J. Am. Chem. Soc.* **1981**, *103*, 5758. (b) Caron, C.; Mitscher, A.; Riviere, G.; Ricard, L.; Schappacher, M.; Weiss, R. *J. Am. Chem. Soc.* **1979**, *101*, 7401.
7. Reed, C. A.; Mashiko, T.; Bentley, S. P.; Kastner, M. E.; Scheidt, W. R.; Spartalian, K.; Lang, G. *J. Am. Chem. Soc.* **1979**, *101*, 2948.
8. (a) Tang, S. C.; Koch, S.; Papaefthymiou, G. C.; Foner, S.; Frankel, R. B.; Ibers, J. A.; Holm, R. H. *J. Am. Chem. Soc.* **1976**, *98*, 2414. (b) Collman, J. P.; Sorell, T. N.; Hodgson, K. O.; Kulshrestha, A. K.; Strouse, C. E. *J. Am. Chem. Soc.* **1977**, *99*, 5158. (c) Schappacher, M.; Ricard, L.; Weiss, R.; Montiel-Montoya, R.; Gonser, U.; Bill, E.; Trautwein, A. *Inorg. Chim. Acta* **1983**, *78*, L9.
9. (a) Martin, R. L.; White, A. H. *Transition Metal Chem.* **1968**, *4*, 113. (b) Barefield, E. K.; Busch, D. H.; Nelson, S. M. *Q. Rev. Chem. Soc.* **1968**, *22*, 457. (c) Konig, E. *Coord. Chem. Rev.* **1968**, *3*, 471. (d) Sacconi, L. *Pure. Appl. Chem.* **1972**, *76*, 975. (e) Hall, G. R.; Hendrickson, D. N. *Inorg. Chem.* **1976**, *15*, 607. (f) Flick, C.; Gelerinter, E. *Chem. Phys. Lett.* **1973**, *23*, 422.
10. (a) Shirazi, A.; Goff, H. M. *J. Am. Chem. Soc.* **1982**, *104*, 6318. (b) Alder, A. D.; Longo, F. R.; Kampus, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.
11. Boersma, A. D.; Goff, H. M. *Inorg. Chem.* **1982**, *21*, 581.
12. Van Geet, A. C. *Ana. Chem.* **1968**, *40*, 2227.
13. Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543.
14. Deatherage, J. F.; Loe, R. S.; Moffat, K. *J. Mol. Biol.* **1976**, *104*, 723.