catalysts might be that shown in Scheme I.

In conclusion, bimetallic Rh–Fe^{3+} ensembles appeared to be generated from Rh–Fe carbonyl clusters supported on SiO_2. They are active for migratory CO insertion as judged by selectivity toward olefin hydroformylation. This activity and selectivity may be due to the bi-site interaction with C- and O-bonded CO. This is reflected in Fe promotion for C_1–C_2 alcohol production from CO + H_2 catalyzed on Rh–Fe catalysts.

Acknowledgment. We thank Professor T. Tominaga and Dr. Y. Minai of the University of Tokyo for measurements of Mössbauer spectroscopy and helpful discussion on the evaluation of Mössbauer data. The portion of this research performed at Hokkaido University was supported by the Iwatani Naoji Foundation and the portion at Northwestern University was supported by Department of Energy Grant No. DE-FG02-86ER13640.

Registry No. $Rh_4(CO)_{12}$, 19584-30-6; $[TMBA][FeRh_5(CO)_{16}]$, 87824-94-0; $[NMe_4]_2[FeRh_4(CO)_{15}]$, 87824-95-1; $[TMBA]_2[Fe_2Rh_4(CO)_{16}]$, 83971-74-8; $Fe_3Rh_2(CO)_{14}C$, 109864-06-4; $[TMBA]_2[Fe_3(CO)_{11}]$, 83971-68-0; ethylene, 74-85-1; propylene, 115-07-1.

Supplementary Material Available: A table listing the results for ethylene hydroformylation and a figure showing the Mössbauer spectrum (2 pages). Ordering information is given on any current masthead page.

---

(20) Richmond, T. G.; Basolo, F.; Shriver, D. F. *Inorg. Chem.* **1982**, *21*, 1272.

Research Institute for Catalysis
Hokkaido University
Sapporo 060, Japan
Atsushi Fukuoka
Masaru Ichikawa*

Department of Chemistry
Northwestern University
Evanston, Illinois 60201
Joseph A. Hriljac
Duward F. Shriver

Received May 19, 1987

Stabilization of Nickel(III) in a Classical N_2S_2 Coordination Environment Containing Anionic Sulfur

Sir:

Current interest in the factors stabilizing Ni(III)[1] derives in substantial measure from the presence of this oxidation state in many hydrogenases,[2] in which nickel has been suggested to function in catalytic dihydrogen activation.[3] In the enzymes, the Ni(II/III) potential is remarkably negative, falling in the ca. −150 to −400 mV range vs NHE.[3] In synthetic complexes, the higher oxidation states of nickel can often be stabilized by anionic polarizable ligands containing deprotonated amides[4–6] or oximes.[7] Thiolate being a polarizable ligand, it is perhaps not unexpected that the Ni EXAFS of several hydrogenases reveals the presence of (at least three) anionic sulfur ligands.[8,9] Classical nickel(II) thiolate complexes (the non-dithiolene type) can be oxidized,[10] but always irreversibly thus far, and the description of certain products as containing Ni(III) is without substantiation. Our study of this problem has revealed no cases in which the ligand is not irreversibly oxidized to a disulfide,[11] a behavior also demonstrated by others.[10e] We report here one means of effecting *metal*-centered oxidation in a classical (innocent) ligand system containing thiolates and a measure of the relative effect of anionic oxygen and sulfur ligands on nickel redox potentials.

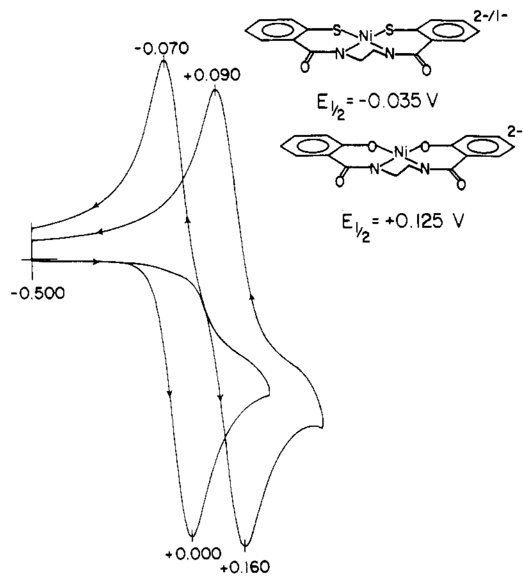


Figure 1. Cyclic voltammograms (100 mV/s) of 1 mM $[\mathbf{1}]^{2-}$ and $[\mathbf{2}]^{2-}$ in DMF solutions at 25 °C. Peak and half-wave potentials vs SCE are indicated.

Treatment of *N,N'*-ethylenebis(*o*-hydroxybenzamide)[12] (2 equiv of Et_4NOH) and *N,N'*-ethylenebis(*o*-mercaptobenzamide)[13] (4 equiv of NaH) in DMF with the indicated bases followed by 1 equiv of $Ni(OAc)_2\cdot 4H_2O$, and in the latter case also by 2 equiv of Et_4NCl, afforded in good yields red $(Et_4N)_2[\mathbf{1}]$ and red-green dichroic $(Et_4N)_2[\mathbf{2}]$,[14,15] respectively. ${}^1H$ NMR spectra were

---

[1] (a) Nag, K.; Chakravorty, A. *Coord. Chem. Rev.* **1980**, *33*, 87. (b) Haines, R. I.; McAuley, A. *Coord. Chem. Rev.* **1981**, *39*, 77.

[2] Hausinger, R. P. *Microbiol. Rev.* **1987**, *51*, 22.

[3] (a) van der Zwaan, J. W.; Albracht, S. P. J.; Fontijn, R. D.; Slater, E. C. *FEBS Lett.* **1985**, *179*, 271. (b) Teixeira, M.; Moura, I.; Xavier, A. V.; Huynh, B. H.; DerVartanian, D. V.; Peck, H. D., Jr.; LeGall, J.; Moura, J. J. G. *J. Biol. Chem.* **1985**, *260*, 8942. (c) Cammack, R.; Fernandez, V. M.; Schneider, K. *Biochimie* **1986**, *68*, 85. (d) Cammack, R.; Patil, D. S.; Hatchikian, E. C.; Fernandez, V. M. *Biochim. Biophys. Acta* **1987**, *912*, 98.

[4] (a) Bossu, F. P.; Margerum, D. W. *Inorg. Chem.* **1977**, *16*, 1210. (b) Bossu, F. P.; Paniago, E. B.; Margerum, D. W.; Kirksey, S. T., Jr.; Kurtz, J. L. *Inorg. Chem.* **1978**, *17*, 1034. (c) Lappin, A. G.; Murray, C. K.; Margerum, D. W. *Inorg. Chem.* **1978**, *17*, 1630. (d) Margerum, D. W. *Pure Appl. Chem.* **1983**, *55*, 23. (e) Kirvan, G. E.; Margerum, D. W. *Inorg. Chem.* **1985**, *24*, 3245. (f) Subak, E. J., Jr.; Loyola, V. M.; Margerum, D. W. *Inorg. Chem.* **1985**, *24*, 4350. (g) Pappenhagen, T. L.; Kennedy, W. R.; Bowers, C. P.; Margerum, D. W. *Inorg. Chem.* **1985**, *24*, 4356.

[5] (a) Fabbrizzi, L.; Perotti, A.; Poggi, A. *Inorg. Chem.* **1983**, *22*, 1411. (b) Fabbrizzi, L.; Licchelli, M.; Perotti, A.; Poggi, A.; Soresi, S. *Isr. J. Chem.* **1985**, *25*, 112.

[6] (a) Kimura, E.; Sakonaka, A.; Machida, R.; Kodama, M. *J. Am. Chem. Soc.* **1982**, *104*, 4255. (b) Kimura, E. *Coord. Chem. Rev.* **1986**, *15*, 1. (c) Machida, R.; Kimura, E.; Kushi, Y. *Inorg. Chem.* **1986**, *25*, 3461.

[7] (a) Chakravorty, A. *Isr. J. Chem.* **1985**, *25*, 99. (b) Bemtgen, J.-M.; Gimpert, H.-R.; von Zelewsky, A. *Inorg. Chem.* **1983**, *22*, 3576.

[8] (a) Lindahl, P. A.; Kojima, N.; Hausinger, R. P.; Fox, J. A.; Teo, B. K.; Walsh, C. T.; Orme-Johnson, W. H. *J. Am. Chem. Soc.* **1984**, *106*, 3062. (b) Scott, R. A.; Wallin, S. A.; Czechowski, M.; DerVartanian, D. V.; LeGall, J.; Peck, H. D., Jr.; Moura, I. *J. Am. Chem. Soc.* **1984**, *106*, 6864. (c) Scott, R. A.; Czechowski, M.; DerVartanian, D. V.; LeGall, J.; Peck, H. D., Jr.; Moura, I. *Rev. Port. Quim.* **1985**, *27*, 67.

[9] EPR spectra of *Wolinella succinogenes* hydrogenase enriched in ${}^{33}S$ indicate at most two sulfur atoms bound to Ni(III): Albracht, S. P. J.; Kröger, A.; van der Zwaan, J. W.; Unden, G.; Böcher, R.; Mell, H.; Fontijn, R. D. *Biochim. Biophys. Acta* **1986**, *874*, 116.

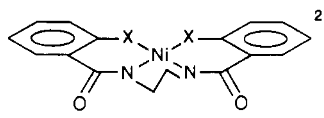
[10] (a) Yamamura, T.; Miyamae, H.; Katayama, Y.; Sasaki, Y. *Chem. Lett.* **1985**, 269. (b) Yamamura, T. *Chem. Lett.* **1986**, 801. (c) Fabre, P.-L.; Poilblanc, R. *Bull. Soc. Chim. Fr.* **1986**, 740. (d) Snyder, B. S.; Rao, Ch. P.; Holm, R. H. *Aust. J. Chem.* **1986**, *39*, 963. (e) Nakabayashi, Y.; Masuda, Y.; Sekido, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1986**, *205*, 209.

[11] Krüger, H.-J.; Holm, R. H., unpublished results.

[12] (a) Van Allan, J. A. *J. Am. Chem. Soc.* **1947**, *69*, 2913. (b) Ojima, H. *Nippon Kagaku Zasshi* **1967**, *88*, 329. This paper describes the preparation of the disodium salt of $[\mathbf{1}]^{2-}$ and its IR and UV/visible spectra.

[13] Tanaka, H.; Yokoyama, A. *Chem. Pharm. Bull.* **1962**, *10*, 556.

0020-1669/87/1326-3645$01.50/0



X=O([1]), S([2])

consistent with the indicated structures. The compounds are planar (diamagnetic) and, unlike some Ni(II) deprotonated amide complexes,[4b,6c] do not react with dioxygen for at least 24 h. They are, however, readily oxidized electrochemically, as shown by the cyclic voltammograms in Figure 1 recorded at v = 100 mV/s. The reactions $[\mathbf{1}]^{2-} \rightleftharpoons [\mathbf{1}]^- + e^-$ and $[\mathbf{2}]^{2-} \rightleftharpoons [\mathbf{2}]^- + e^-$ in DMF and acetonitrile are chemically reversible ($i_{p,a}/i_{p,c} \approx 1$) and approach electrochemical reversibility (ΔE_p = 70 mV, $i_p \propto v^{1/2}$). Addition of ligands such as PhS$^-$, PhO$^-$, py, and OAc$^-$ showed little if any effect on the potentials.

Electrolysis of DMF solutions of $[\mathbf{1}]^{2-}$ (+0.40 V) and $[\mathbf{2}]^{2-}$ (+0.17 V) at −30 °C resulted in the development of green and blue-green colors, respectively. These solutions were immediately frozen and examined by EPR spectroscopy. The spectra, presented in Figure 2, with substantial g-tensor anisotropies and average g values in excess of 2.00, demonstrate metal-centered oxidation products. Because the spectral features cannot be assigned to specific principal components of the g tensor without further information, the orbital of the odd electron remains unidentified at present. However, the configuration $...(d_{z^2})^1$ is unlikely for the oxidation product of $[\mathbf{2}]^{2-}$ inasmuch as no g value is close to 2.[16] With 1 mM solutions at −30 °C and the passage of 1 faraday on oxidation, the first electrolytic oxidation–reduction cycle was completed with ca. 85% and 80% recoveries of $[\mathbf{1}]^{2-}$ and $[\mathbf{2}]^{2-}$, respectively. Cyclic voltammetry of these solutions revealed the presence of these complexes at concentrations consistent with the coulometric results. At room temperature, 1 mM solutions of the oxidized forms decayed completely within 4 h to EPR-silent species that have not been identified. This decay, which occurred much more slowly at −30 °C, appears to be the reason for the small residual currents observed after the passage of 1 faraday at either temperature and the less than quantitative recoveries of the initial compounds in the redox cycle at −30 °C. A combination of OTTLE experiments and analysis of the time-dependent EPR and UV–visible spectral intensities has further substantiated assignment of the EPR-active complexes having intense LMCT bands at 840 and 718 nm as the Ni(III) primary oxidation products $[\mathbf{1}]^-$ and $[\mathbf{2}]^-$, respectively.

When the electrolysis is carried out in 4:1 DMF/py (v/v) as above and the solutions immediately frozen, the reaction products afford EPR spectra (Figure 2) consistent with the formulations $[\mathbf{1}(\mathrm{py})_2]^-$ and $[\mathbf{2}(\mathrm{py})]^-$. The spectrum of $[\mathbf{1}(\mathrm{py})_2]^-$ is axial with $g_\perp > g_\parallel$ and a superhyperfine quintet from two axial pyridine ligands with a_N = 18.5 G. The spectrum of $[\mathbf{2}(\mathrm{py})]^-$ is rhombic, but with the extent of rhombicity much reduced compared to that of $[\mathbf{2}]^-$, and has a triplet with a_N = 21.0 G. These results require the $...(d_{z^2})^1$ configuration in each case.[16] The coupling constants are within the ranges for other Ni(III) complexes with one (20–25 G) and two (18–20 G) axial nitrogen ligands.[4c,e–g,6a] Rhombic spectra of Ni(III) peptide complexes have been observed when a sulfur ligand is substituted for nitrogen,[17] presumably at an in-plane position.

The results constitute the initial demonstration with synthetic complexes that Ni(II) at least partly in a thiolate coordination environment can be oxidized to the Ni(III) state with a stability sufficient to permit its detection. Further, the in-plane ligand change 2 RO$^-$ → 2 RS$^-$ results in a *decrease* in potential by 0.160 V,[18] or a 3.7 kcal/mol relative stabilization in the N_2S_2 unit. The −0.035 V potential for the $[\mathbf{2}]^{2-}/[\mathbf{2}]^-$ couple is one of the lowest recorded for a nonbiological Ni(II)/Ni(III) couple. In contrast, the great majority of Ni(II,III) potentials are $\gtrsim$+0.50 V vs SCE,[1] with cationic complexes generally having the higher values. The apparently lowest value is −0.20 V, for a NiN_6 complex derived from dioximate ligand;[7a] several tetraaza macrocyclic species are reported to have potentials just below 0 V vs SCE.[19] Potentials

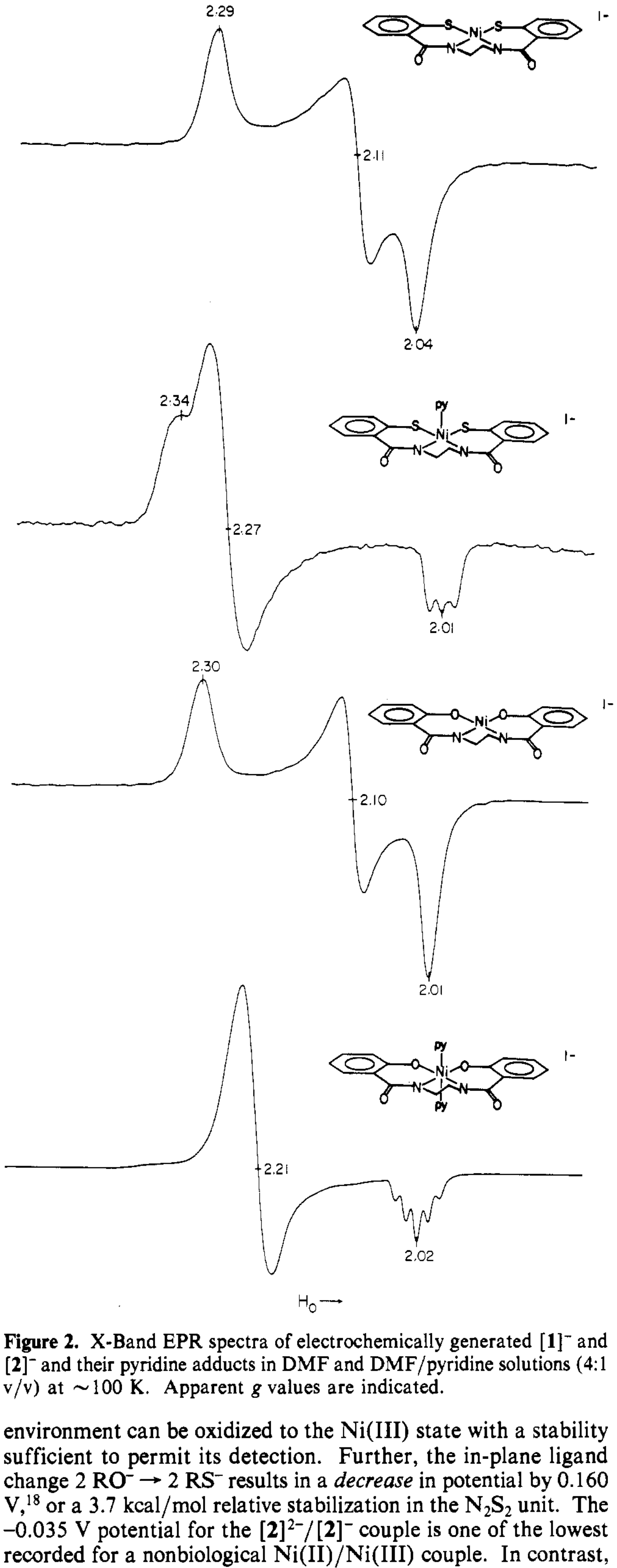


Figure 2. X-Band EPR spectra of electrochemically generated $[\mathbf{1}]^-$ and $[\mathbf{2}]^-$ and their pyridine adducts in DMF and DMF/pyridine solutions (4:1 v/v) at ~100 K. Apparent g values are indicated.

---

(14) Experimental details: All reactions and measurements were performed under anaerobic conditions. New compounds gave satisfactory elemental analyses. Electrochemical experiments were performed with a Pt working electrode and ~0.2 M (n-Bu$_4$N)(ClO$_4$) supporting electrolyte; potentials are referenced to the SCE. Under these conditions, $E_{1/2}$ = 0.48 V for the ferrocenium/ferrocene couple in DMF.

(15) λ_{max} in EtOH (ϵ_M): $(Et_4N)_2[\mathbf{1}]$, 548 (75.8), 459 (223), 361 (sh, 3550), 327 (sh, 8060), 308 (9050) nm; $(Et_4N)_2[\mathbf{2}]$, 581 (176), 502 (sh, 132), 360 (sh, 6480), 316 (sh, 16600), 287(25200), 253 (35600) nm.

(16) Maki, A. H.; Edelstein, N.; Davison, A.; Holm, R. H. *J. Am. Chem. Soc.* **1964**, *86*, 4580.

(17) Sugiura, Y.; Kuwahara, J.; Suzuki, T. *Biochem. Biophys. Res. Commun.* **1983**, *115*, 878.

(18) A previous attempt to address this point utilized thioether vs ether ligand functionalities and showed that the former promoted reversible oxidation whereas the latter did not: Ray, D.; Pal, S.; Chakravorty, A. *Inorg. Chem.* **1986**, *25*, 2674.

(19) Busch, D. H. *Acc. Chem. Res.* **1978**, *11*, 392.

for certain $[Ni(S_2C_2R_2)_2]^{1-,2-}$ couples are even more negative,[20] but these dithiolene monoanions are extensively delocalized. Manifestations of this include a pronounced dependence of potential on substituent R and a relatively small g anisotropy (e.g., $g_x = 2.160$, $g_y = 2.042$, $g_z = 1.998$ in $[Ni(mnt)_2]^{-}$ [16]). The existence of a dithiolene structure in the enzymes is implausible given the highly anisotropic, nearly invariant Ni(III) EPR spectra ($g \approx 2.3, 2.2, 2.0$) of the "as prepared" state of most hydrogenases.[2] The present complexes when oxidized resemble this state in terms of g anisotropy but are not considered as site models owing to the lack of precedence of deprotonated amide as a physiological ligand. Rather, they do emphasize the role of anionic polarizable ligands, including thiolate, and the attendant net negative charge of the reduced species in markedly lowering redox potentials. Thiolate ligands at biological nickel sites doubtless modulate potentials by virtue of these properties. Indeed, Co(III) has recently been stabilized in a classical tetrathiolate environment[21,22] and in one case reversibly linked to Co(II) at a potential of −1.16 V vs SCE.[21b]

Future reports will deal with the redox processes of Ni(II) thiolate complexes and further investigations of anionic N_2S_2 ligand complexes of nickel and other metals.[11] As will be shown, ligand structural variation can afford even lower Ni(III)/Ni(II) potentials than that reported here.

Acknowledgment. This research was supported by National Science Foundation Grant CHE 85-21365.

---

(20) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, *10*, 49. McCleverty, J. A. In *Reactions of Molecules at Electrodes*; Hush, N. S., Ed.; Wiley-Interscience: New York, 1971; pp 403–492.

(21) (a) Rao, Ch. P.; Dorfman, J. R.; Holm, R. H. *Inorg. Chem.* **1986**, *25*, 428. (b) Mukherjee, R. N.; Rao, Ch. P.; Holm, R. H. *Inorg. Chem.* **1986**, *25*, 2979.

(22) Fikar, R.; Koch, S. A.; Millar, M. M. *Inorg. Chem.* **1985**, *24*, 3311.

Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

H.-J. Krüger
R. H. Holm*

Received June 10, 1987

Pincer Porphyrin: X-ray Crystal Structure of a Binuclear Zinc/Copper Complex[1]

Sir:

Binucleating porphyrins are receiving considerable current attention as active-site models for multimetal proteins and for exploiting chemistry that is distinctive to binuclear complexes.[2-9] A critical aspect of such systems is achieving a well-defined geometric arrangement of the metal sites. For this reason relatively rigid urea[3] or arene[6,7] links between cofacial porphyrins have been favored as have multiple links in face-to-face porphyrins[5] and ligating superstructures.[2,4,8] The merits of these approaches are borne out in the few x-ray crystal structures that have successfully been determined on binuclear systems,[3,5,6] but even so, it is clear that "rigid" systems have important and subtle flexibility. Also, although large molecules that are rigid and symmetrical often crystallize well this can lead to unworkable solubility. Binucleating porphyrins with relatively flexible superstructures are synthetically accessible[8,10] and can be expected to have good solubility but in the absence of single-crystal x-ray data there will always remain uncertainty about the structures of their binuclear complexes. This leads us to communicate the first structural characterization of a binuclear complex of "pincer porphyrin", a binucleating porphyrin whose design is tailored to provide flexibility, solubility, and crystallizability.[9]

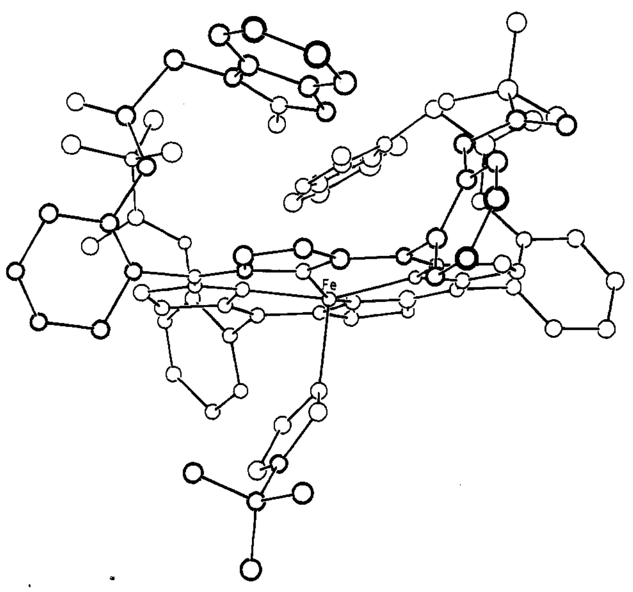
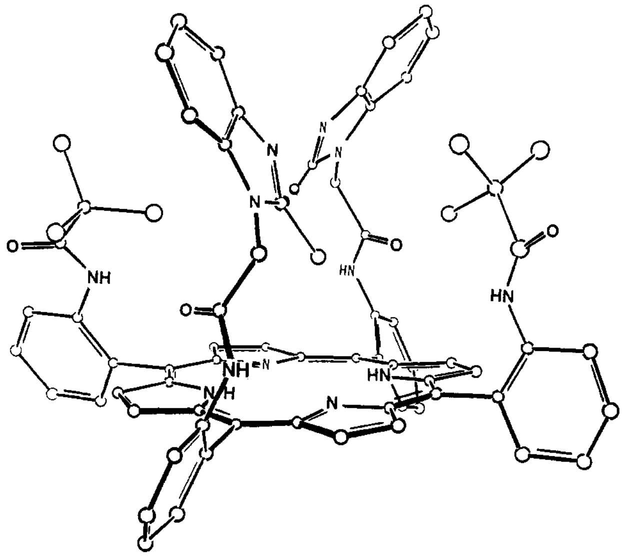


Figure 1. ORTEP drawing of the [Fe(PincerP)(4-*t*-BuHIm)] molecule illustrating how the two attached benzimidazole groups block access to one face of the porphyrin. The two benzimidazole planes make dihedral angles of 26.7 and 23.0° with the porphinato core.



In the structures of the mononuclear [Fe(4-*t*-BuHIm)(PincerP)][11] and the dinuclear $[(DMF)ZnCu(PincerP)]PF_6$ we have the elements of a model for the heme/copper active site of cytochrome oxidase. The structures reveal interesting conformational aspects

---

(1) This paper is dedicated to the memory of Steven (Rodj) J. Rodgers (1957–1986).

(2) Elliott, C. M.; Arnette, J. K.; Krebs, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 4904. Recent representative references include this reference and ref 3–9. Further citations can be found within these references.

(3) Landrum, T.; Grimmett, D.; Haller, K. J.; Scheidt, W. R.; Reed, C. A. *J. Am. Chem. Soc.* **1981**, *103*, 2640.

(4) Hamilton, A. D.; Rubin, H.-D.; Bocarsly, A. B. *J. Am. Chem. Soc.* **1984**, *106*, 7255.

(5) Collman, J. P.; Chong, A. O.; Jameson, G. B.; Oakley, R. T.; Rose, E.; Schmittou, E. R.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 516.

(6) Fillers, J. P.; Ravichandran, K. G.; Abdalmundi, I.; Tulinsky, A.; Chang, C. K. *J. Am. Chem. Soc.* **1986**, *108*, 417.

(7) Tabushi, I.; Sasaki, T. *J. Am. Chem. Soc.* **1983**, *105*, 2901.

(8) Gunter, M. J.; Mander, L. N.; Murray, K. S.; Clark, P. E. *J. Am. Chem. Soc.* **1981**, *103*, 6784.

(9) Larsen, N. G.; Boyd, P. D. W.; Rodgers, S. J.; Wuenschell, G. E.; Koch, C. A.; Rasmussen, S.; Tate, J. R.; Erler, B. S.; Reed, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 6950.

(10) Young, R.; Chang, C. K. *J. Am. Chem. Soc.* **1985**, *107*, 898.

(11) Abbreviations used in this paper: 4-*t*-BuHIm = 4-*tert*-butylimidazole; PincerP = dianion of 5α,15α-bis[(*N*-(2-methylbenzimidazolyl)acetamido)phenyl]-10α,20α-bis(pivalamidophenyl)porphine = trans-L of ref 9; DMF = *N*,*N*′-dimethylformamide; THF = tetrahydrofuran; PincerP′ = 5,6-dimethylbenzimidazole analogue of PincerP.

0020-1669/87/1326-3647$01.50/0