of two regioisomers. Second, conversion of the alkyl cyanamide **4** to the imidazoline **6** or aziridine **7** was accomplished without the isolation of the isourea salt **5**. This procedure was one of choice rather than need. Third, satisfactory yields were obtained only for the imidazoline adducts **6** in the cis-alkene series (**9** and **11**) by the initial generation of aziridine **7**.[20] Both aziridine ring formation (**5** → **7**) and rearrangement to the imidazoline[21] (**7** → **6**) proceeded stereospecifically. Fourth, the ring-cleavage reaction in the final step can be readily accomplished with $Ba(OH)_2$.[22]

The synthetic technology described herein readily permits stereospecific incorporation of the key vicinal diamino group within the framework of readily accessible molecules. Our approach should compliment existing diamination procedures. Moreover, useful routes for the preparation of both functionalized aziridines **7** and imidazolines **6** have also been developed. Research is now actively in progress to elaborate this method.

Acknowledgment. We thank the National Institutes of Health (Grant NS15604) and The Robert A. Welch Foundation for their support of our research program.

Registry No. 3, 420-04-2; (±)-*trans*-**6** (4,5-dimethyl), 85782-25-8; *cis*-**6** (4,5-dimethyl), 85782-26-9; **6** (4-butyl), 85782-27-0; (±)-*trans*-**6** (4,5-dipropyl), 85782-29-2; *cis*-**7** (dimethyl), 85782-30-5; **8**, 624-64-6; **9**, 590-18-1; **10**, 592-41-6; **11**, 110-83-8; **12**, 14850-23-8; **13**, 20699-48-3; **13**·2HCl, 66427-25-6; **14**, 20759-15-3; **14**·2HCl, 28971-67-7; **15**, 13880-27-8; **15** (diacetyl), 85782-33-8; **16**, 1436-59-5; **16**·2HCl, 10027-80-2; **17**, 4853-59-2; **17**·2HCl, 85782-34-9; NBS, 128-08-5; (±)-(*R**,*S**)-(3-bromo-2-butyl)cyanamide, 85782-20-3; (*R**,*R**)-(3-bromo-2-butyl)cyanamide, 85782-21-4; (1-bromo-2-hexyl)cyanamide, 85782-22-5; (2-bromohexyl)cyanamide, 85782-32-7; *trans*-(2-bromocyclohexyl)cyanamide, 85782-23-6; (±)-(*R**,*S**)-(5-bromo-4-octyl)cyanamide, 85782-24-7; 7-ethoxycarbimidoyl-7-azabicyclo[4.1.0]heptane, 85782-31-6; *cis*-2-ethoxy-3a,4,5,6,7,7a-hexahydrobenzimidazole, 85782-28-1.

Supplementary Material Available: Complete physical and spectral properties observed for all new compounds reported herein (8 pages). Ordering information is given on any current masthead page.

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(18) Satisfactory spectral (^1H NMR, ^{13}C NMR, IR, and MS) data were obtained for all compounds in this procedure. Analytical (elemental analysis or high-resolution MS) data in agreement with the proposed structures were obtained for all new compounds except for the bromocyanamide derived from **10**. See supplementary material for details.

(19) (a) Strack, E.; Schwaneberg, H. *Chem. Ber.* **1934**, *67*, 1006–1011. (b) Minisci, F.; Galli, R.; Cecere, M. *Gazz. Chim. Ital.* **1964**, *94*, 67–90. (c) Brill, E.; Schultz, H. P. *J. Org. Chem.* **1963**, *28*, 1135–1137.

(20) Treatment of the protonated isourea salts derived from **9** and **11** with Et_3N or $NaHCO_3$ led to multiple products (TLC analysis).

(21) Variants of this stereospecific reaction have been previously reported; see: Heine, H. W.; Bender, H. S. *J. Org. Chem.* **1960**, *25*, 461–463. Dermer, O. C.; Ham. G. R. "Ethylenimine and Other Aziridines"; Academic Press: New York, 1969; p 283, and references therein.

(22) Cleavage of the imidazoline ring **6** can also be accomplished with 30% aqueous H_2SO_4 (reflux, 18 h).

Iron(II) Octaethylchlorin: Structure and Ligand Affinity Comparison with Its Porphyrin and Isobacteriochlorin Homologues

Steven H. Strauss*

Department of Chemistry, Colorado State University
Fort Collins, Colorado 80523

Michael E. Silver and James A. Ibers*

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

Received February 22, 1983

A variety of heme-containing oxidoreductase enzymes[1-6] do not contain iron porphyrins but instead contain iron complexes of chlorins[7] or isobacteriochlorins[7] (hereafter collectively referred to as hydroporphyrins). The discovery of iron hydroporphyrins in these enzymes has prompted the examination of the properties of series of iron porphyrins, chlorins, and isobacteriochlorins[8-10] having identical or very similar peripheral substitution. To ascertain whether a given prosthetic group is optimally suited for a particular chemical task, it is necessary (although not sufficient[11]) to discover what features of the chemistry of iron hydroporphyrins differ from iron porphyrins. Metal-centered properties, such as Fe(II)/Fe(III) potentials,[8,9] CO stretching frequencies of carbonylated complexes,[9] and CO affinities of four-coordinate derivatives,[10] are not significantly macrocycle dependent. Here we report the first structure of an iron chlorin, Fe(OEC),[12] and show that the affinity for weak ligands, such as THF or ethanethiol (EtSH), is strongly macrocycle dependent. We further suggest this dependence to be a manifestation of structural relationships among the porphyrins and the hydroporphyrins.

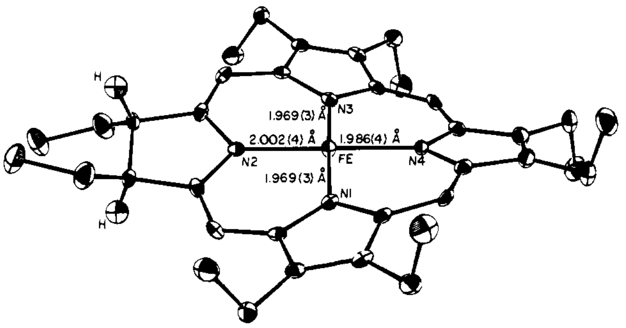

Figure 1. Drawing of the structure of Fe(OEC). Hydrogen atoms, except the two on the pyrroline C_b atoms, have been omitted for clarity. The pyrrole rings containing atoms N1 and N3 are crystallographically related by the 2-fold axis passing through atoms N2, Fe, and N4. Probability ellipsoids are drawn at the 50% level.

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(1) (a) Siegel, L. M.; Singer, T. P.; Ondarza, R. N., Eds. "Mechanisms of Oxidizing Enzymes"; Elsevier: New York, 1978; pp 201–13, and references therein. (b) Janick, P. A.; Siegel, L. M. *Biochemistry* **1982**, *21*, 3538–47. (c) Krueger, R.; Siegel, L. M. *Ibid.* **1982**, *21*, 2892–904. (d) Siegel, L. M.; Rueger, D. C.; Barber, M. J.; Krueger, R. J.; Orme-Johnson, N. R.; Orme-Johnson, W. H. *J. Biol. Chem.* **1982**, *257*, 6343–50.

(2) (a) Payne, W. J. *Bacteriol. Rev.* **1973**, *37*, 409–52. (b) Losada, M. *J. Mol. Catal.* **1975**, *1*, 245–264.

(3) (a) Lemberg, R.; Barrett, J. "Cytochromes"; Academic Press: New York, 1973; pp 217–326, and references therein. (b) Walsh, T. A.; Johnson, M. K.; Barber, D.; Thomson, A. J.; Greenwood, C. *J. Inorg. Biochem.* **1981**, *14*, 15–31 and references therein. (c) Huynh, B. H.; Liu, M. C.; Moura, J. J. G.; Moura, I.; Ljungdahl, P. O.; Munck, E.; Payne, W. J.; Peck, H. D., Jr.; DerVartanian, D. V.; LeGall, J. *J. Biol. Chem.* **1982**, *257*, 9576–81 and references therein.

(4) Jacob, G. S.; Orme-Johnson, W. H. *Biochemistry* **1979**, *18*, 2967–80.

(5) Newton, N.; Morell, D. B.; Clarke, L.; Clezey, P. S. *Biochim. Biophys. Acta* **1965**, *96*, 476–86.

(6) Brittain, T.; Greenwood, C.; Barber, D. *Biochim. Biophys. Acta* **1982**, *705*, 26–32 and references therein.

(7) Porphyrins that contain two reducing equivalents (hydrogen atoms or alkyl groups) across the vicinal C_b atoms of a single pyrrole ring are called chlorins. Porphyrins that contain two adjacent reduced pyrrole rings are called isobacteriochlorins.

(8) (a) Stolzenberg, A. M.; Spreer, L. O.; Holm, R. H. *J. Chem. Soc., Chem. Commun.* **1979**, 1077–8. (b) Richardson, P. F.; Chang, C. K.; Hanson, L. K.; Spaulding, L. D.; Fajer, J. *J. Phys. Chem.* **1979**, *83*, 3420–24. (c) Chang, C. K.; Fajer, J. *J. Am. Chem. Soc.* **1980**, *102*, 848–51. (d) Chang, C. K.; Hanson, L. K.; Richardson, P. F.; Young, R.; Fajer, J. *Proc. Natl. Acad. Sci.* U.S.A. **1981**, *78*, 2652–56.

(9) Stolzenberg, A. M.; Strauss, S. H.; Holm, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 4763–78.

(10) Strauss, S. H.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 863–8.

(11) Ibers, J. A.; Holm, R. H. *Science* (*Washington, D.C.*) **1980**, *209*, 223–35.

(12) Abbreviations: OEP, 2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; OEC, *trans*-7,8-dihydro-2,3,7,8,12,13,17,18-octaethylporphyrinato dianion; OEiBC, 2,3,7,8-tetrahydro-2,3,7,8,12,13,17,18-octaethylporphyrinato dianion, a mixture of the trans,trans,trans and trans,cis,trans isomers; TPP, 5,10,15,20-tetraphenylporphyrinato dianion; TMP, 5,10,15,20-tetramethylporphyrinato dianion; TMC, 7,8-dihydro-5,10,15,20-tetramethylphorphyrinato dianion; P = OEP, OEC, or OEiBC.

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The structure of Fe(OEC),[13] shown in Figure 1, is consistent with earlier spectroscopic deductions.[9,14] The molecule sits on a crystallographic 2-fold axis that passes through atoms N2, Fe, and N4. The iron and four nitrogen atoms are rigorously planar, while the rest of the chlorin macrocycle is significantly S_4 ruffled (the dihedral angles (θ) between the planes of opposite pyrrole rings and the pyrrole and pyrroline rings are 23.3 and 27.4°, respectively). The compound Fe(TPP)[12,15] possesses $\bar{4}$ site symmetry and is ruffled such that θ is 25.6°. The C_a–C_b (1.516 (5) Å) and C_b–C_b (1.508 (7) Å) distances in the pyrroline ring of Fe(OEC) are longer than the usual pyrrole values of ~1.44 and ~1.36 Å, respectively, and reflect the sp^3 hybridization of the pyrroline C_b atoms. The Fe–N_p[16] distance in Fe(TPP), which possesses an $S = 1$ ground state in the solid state,[17] is 1.972 (4) Å. The similar Fe–N_p distances in Fe(OEC) are in harmony with an $S = 1$ ground state for this compound in the solid state.[18] Earlier work has shown that Fe(OEC) probably has an $S = 1$ ground state in solution.[9]

To maintain an optimum M–N_p distance, an increase in S_4 ruffling should occur on going to the more reduced macrocycles of a homologous series. Hydroporphyrins have intrinsically larger cores (longer distances between opposite pyrrole or pyrroline nitrogen atoms) than porphyrins, a function of the more obtuse C_a–N–C_a angle and the longer C_b–C_b distance of the pyrroline ring(s).[19–21] The S_4 distortion from planarity leads to a reduction in core size and shorter metal–nitrogen distances relative to the planar conformation[22] and should be more facile for hydroporphyrins owing to their decreased aromaticity. The triclinic form of Ni(OEP), with an average Ni–N_p distance of 1.96 Å, is planar with $\theta = 0°$.[24] The compound Fe(OEC), despite the S_4 distortion (average $\theta = 25°$), has all Fe–N_p distances >1.96 Å because of the larger core. That such an increased distortion is not observed on going from Fe(TPP) to Fe(OEC) may explain why two of the Fe–N_p distances in the hydroporphyrin are significantly longer than in the porphyrin. However, comparisons with Fe(OEC) should be made with Fe(OEP)[23] and not with Fe(TPP). Consideration of OEP, OEC, and OEiBC structures demonstrates that this distortion is more readily achieved for hydroporphyrins than for porphyrins when the metal has optimum M–N_p distances <1.99 Å, as in Ni(II).[19,20] The tetragonal form of Ni(OEP)[25] and the two isomers of Ni(OEiBC)[19] have average Ni–N_p distances of 1.93 Å. However, in the porphyrin θ is 28° while in the isobacteriochlorins it averages 48°. Similarly, structures of the TMP[12] and TMC[12] complexes of Ni(II)[20b] reveal the porphyrin to be essentially planar while the hydroporphyrin, with θ ranging from 35 to 38°, is highly distorted.

The enhanced ability of hydroporphyrins to distort so as to adjust their core size in response to the needs of the metal may be responsible for the observed dependence on the macrocycle of the affinity of Fe(P)[12] for weak σ-donors. For iron(II) a change in spin state from low or intermediate to high results in the optimum Fe–N_p distances changing from <1.99 to >2.04 Å.[18] Weak σ-donors, such as THF, DMF, and alcohols, are known to form 1:1 (five-coordinate) complexes with Fe(II) porphyrins[26] (equilibrium quotient, K). All known five-coordinate Fe(II) porphyrins are high spin,[27] except when L is a strong π-acceptor, such as CO,[28] CS,[29] a phosphine,[30] or an isocyanide.[30] Since $\mathrm{Fe(TPP)(THF)_2}$ is also high spin,[31] it seems reasonable that Fe(P)(THF) complexes are high spin. Comparison of spectrophotometric titrations of Fe(P) with THF and CO demonstrates that while the affinity for CO is not significantly macrocycle dependent (K is 3.3 (5) × 10^4, 4.5 (1.8) × 10^4, and 7.8 (1.5) × 10^4 M^{-1} for Fe(OEP), Fe(OEC), and Fe(OEiBC), respectively[10]) the affinity for THF of Fe(OEiBC) is 50 times that of Fe(OEP) (K is 0.5–1.0, 15 (3), and 54 (5) M^{-1} for Fe(OEP), Fe(OEC), and Fe(OEiBC), respectively, in benzene at 22 °C). We believe that the structural change on going from four-coordinate, intermediate spin Fe(P) to five-coordinate, low-spin Fe(P)(CO) is small and does not require as much structural compliance of the macrocycle as does the change to five-coordinate, high-spin Fe(P)(THF). The affinity of Fe(P) for EtSH is also macrocycle dependent. While we have not been able to calculate equilibrium quotients for this ligand,[32] the differences are qualitatively the same as for THF.

Thus, the reactivity of Fe(OEC) and its OEP and OEiBC homologues demonstrates that iron hydroporphyrins, while similar to iron porphyrins in their coordination chemistry in many respects, do show significant differences. These differences may have a structural basis whereby reduced macrocycles more easily distort, adjusting their core size to accommodate the requirements of the metal.

Acknowledgment. The crystals of Fe(OEC) used in the present diffraction study were grown during the postdoctoral association of S.H.S. with Professor R. H. Holm. We thank Professor Holm for his support and encouragement. We also thank K. M. Motyl and K. E. Warner for technical assistance. This work was supported by the Research Corp., the National Institutes of Health (HL 13157), a CSU Biomedical Research Support Grant (537272), and the National Science Foundation (CHE 80-06601 and CHE 81-06017).

Supplementary Material Available: Listing of positional and thermal parameters (1 page). Ordering information is given on any current masthead page.

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(13) Diffraction data (Mo radiation) for Fe(OEC) were collected at −150 °C on a Picker four-circle diffractometer, and the structure was solved and refined by standard methods. Space group $D_{2h}{}^{14}$-*Pbcn*, a = 21.880 (9) Å, b = 15.795 (6) Å, c = 8.554 (4) Å, Z = 4. Final anisotropic least-squares refinement of all independent non-hydrogen atoms led to a value of 0.105 for $R(F^2)$ (3419 observations, including those with $F_o{}^2 < 0$, and 187 variables). The conventional R index on F for 1929 reflections having $F_o{}^2 > 3\sigma(F^2)$ is 0.060.

(14) (a) Eisner, U.; Lichtarowicz, A.; Linstead, R. P. *J. Chem. Soc.* **1957**, 733–9. (b) Whitlock, H. W., Jr.; Hanauer, R.; Oester, M. Y.; Bower, B. K. *J. Am. Chem. Soc.* **1969**, *91*, 7485–89. (c) Stolzenberg, A. M.; Spreer, L. O.; Holm, R. H. *Ibid.* **1980**, *102*, 364–70.

(15) Collman, J. P.; Hoard, J. L.; Kim, N.; Lang, G.; Reed, C. A. *J. Am. Chem. Soc.* **1975**, *97*, 2676–81.

(16) In the nomenclature: Hoard, J. L. In "Porphyrins and Metalloporphyrins"; Smith, D. M.; Ed.; Elsevier: New York, 1975; pp 317–380.

(17) Boyd, P. D. W.; Buckingham, D. A.; McMeeking, R. F.; Mitra, S. *Inorg. Chem.* **1979**, *18*, 3585–91.

(18) Scheidt, W. R.; Reed, C. A. *Chem. Rev.* **1981**, *81*, 543–55.

(19) Kratky, C.; Angst, C.; Johansen, J. E. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 211–2.

(20) (a) Ulman, A.; Gallucci, J.; Fisher, D.; Ibers, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 6852–4. (b) Gallucci, J. C.; Swepston, P. N.; Ibers, J. A. *Acta Crystallogr., Sect. B* **1982**, *B38*, 2134–9.

(21) (a) Barkigia, K. M.; Fajer, J.; Spaulding, L. D.; Williams, G. J. B. *J. Am. Chem. Soc.* **1981**, *103*, 176–81. (b) Spaulding, L. D.; Andrews, L. C.; Williams, G. J. B. *Ibid.* **1977**, *99*, 6918–23.

(22) Hoard, J. L. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 18–31.

(23) Red platelets of Fe(OEP) have been obtained but are too thin for diffraction purposes. We are continuing our efforts to grow crystals of Fe(OEP) and Fe(OEiBC).

(24) Cullen, D. L.; Meyer, E. F., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 2095–102.

(25) Meyer, E. F., Jr. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2162–7.

(26) (a) Brault, D.; Rougee, M. *Biochemistry* **1974**, *13*, 4591–7. (b) Rougee, M.; Brault, D. *Ibid.* **1975**, *14*, 4100–6.

(27) (a) Jameson, G. B.; Molinaro, F. S.; Ibers, J. A.; Collman, J. P.; Brauman, J. I.; Rose, E.; Suslick, K. S. *J. Am. Chem. Soc.* **1980**, *102*, 3224–37 and references therein. (b) Caron, C.; Mitschler, A.; Riviere, G.; Ricard, L.; Schappacher, M.; Weiss, R. *J. Am. Chem. Soc.* **1979**, *101*, 7401–2.

(28) Wayland, B. B.; Mehne, L. F.; Swartz, J. *J. Am. Chem. Soc.* **1978**, *100*, 2379–83.

(29) Scheidt, W. R.; Geiger, D. K. *Inorg. Chem.* **1982**, *21*, 1208–11.

(30) Ellis, P. E., Jr.; Jones, R. D.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1980**, 54–5.

(31) (a) Collman, J. P.; Reed, C. A. *J. Am. Chem. Soc.* **1973**, *95*, 2048–9. (b) Reed, C. A.; Mashiko, T.; Scheidt, W. R.; Spartalian, K.; Lang, G. *Ibid.* **1980**, *102*, 2302–6.

(32) Others have noted difficulties in measuring the affinity of iron(II) porphyrins for mercaptans: Ellis, P. E., Jr.; Jones, R. D.; Basolo, F. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 5418–20.