are both thermodynamically and kinetically accessible from their isomeric alkyl structures, they are not *required* intermediates in CO insertion chemistry. Bidentate acyl coordination reversibly traps the intermediate, producing an observable species in sterically conjested systems.[23] Reversion to a monodentate coordination mode precedes conversion to the six-coordinate product in a manner analogous to the "dissociative trapping" mechanism demonstrated by Halpern[24] for nucleophilic catalysis of migratory CO insertion.

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(23) We thank a referee for pointing out that other factors such as solvation may also be important in determining the position of the methyl ↔ η^2-acyl equilibrium, particularly when the energy change is very small. Examination of **6b** in THF shows that the equilibrium is shifted significantly toward the alkyl isomer **5b** compared to methylene chloride.

(24) Webb, S. L.; Giandomenico, C. M.; Halpern, J. *J. Am. Chem. Soc.* **1986**, *108*, 345-347.

Structural Consequences of Nickel versus Macrocycle Reductions in F430 Models: EXAFS Studies of a Ni(I) Anion and Ni(II) π Anion Radicals

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Factor 430 (F430) is a nickel tetrapyrrole (hydrocorphin) found in methyl coenzyme M reductase, the enzyme that catalyzes the final stages of the reduction of carbon dioxide to methane in methanogenic bacteria.[2] Detection of EPR signals attributable to Ni(I) in the catalytic cycle of *Methanobacterium thermoautotrophicum*[3] has led to intensive investigations of the reductive chemistry of F430 and of nickel porphyrins and hydroporphyrins.[4-8] Reduction of Ni(II) F430[4] and isobacteriochlorins[5,6] unambiguously results in Ni(I) species whereas porphyrins,[5-9] chlorins,[5,6] and hexahydro- and octahydroporphyrins[6] yield anions variously ascribed to Ni(I) or Ni(II) π radicals with some metal character.

The structural consequences associated with the reduction of Ni(II) to Ni(I) in porphyrin derivatives are unknown.[9] Changes as large as 0.2 Å in Ni–N distances have been suggested by Stolzenberg and Stershic for isobacteriochlorins.[5] They and Renner et al.[6] further suggested that, in addition to the relative ordering of the Ni(II) and π^* orbitals, the ability of the macrocycle to accommodate the larger Ni(I) controlled the sites of reduction, i.e., Ni(I) versus π anion radical.

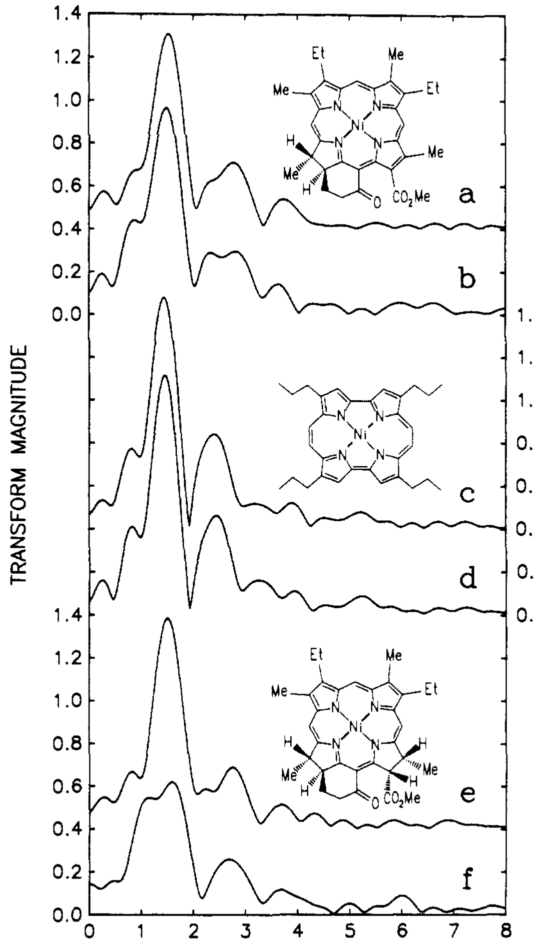

Figure 1. Chemical structures and Fourier transforms of k^2 weighted EXAFS oscillations for (a) Ni(II) chlorin, (b) Ni(II) chlorin π anion radical, (c) Ni(II) porphycene, (d) Ni(II) porphycene π anion radical, (e) Ni(II) iBC,and (f) Ni(I) iBC anion. Comparable spectra are offset for clarity (in THF; Bu_4N^+ is the counterion in all reduced species; T = 298 K).

We present here EXAFS results for the Ni(II) radical anions of a chlorin and a porphycene and for the Ni(I) anion of an isobacteriochlorin (iBC) that clearly demonstrate the structural consequences of metal versus macrocycle reductions.

Low-spin Ni(II) chlorin,[10] porphycene[11] and iBC[10] (see Figure 1 for structures) undergo reversible one-electron electrochemical reductions in tetrahydrofuran[6,11] ($E_{1/2}$ = −1.04, −0.80, and −1.33 V, respectively, in the presence of 0.1 M $(Bu)_4NClO_4$ vs SCE). Upon reduction, the chlorin and the porphycene exhibit optical spectra diagnostic of π anion radicals: loss of the visible bands and the appearance of weak broad bands stretching into the near infrared region.[6,11-13] In frozen THF, at 115 K, the reduced species display EPR spectra typical of free radicals[6,11,13] (the chlorin spectrum includes a shoulder on the high-field side,[6,13] also noted by Kadish et al.[8] for the π anion of a Ni porphyrin, sug-

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(1) (a) Brookhaven National Laboratory. (b) University of California, Davis.

(2) Ellefson, W. L.; Whitman, W. B.; Wolfe, R. S. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3707. Hausinger, R. P.; Orme-Johnson, W. H.; Walsh, C. *Biochemistry* **1984**, *23*, 801. Daniels, L.; Sparling, R.; Sprott, G. D. *Biochim. Biophys. Acta* **1984**, *768*, 113. Fässler, A.; Kobelt, A.; Pfaltz, A.; Eschenmoser, A.; Bladon, C.; Battersby, A. R.; Thauer, R. K. *Helv. Chim. Acta* **1985**, *68*, 2287 and references therein.

(3) Albracht, S. P. J.; Ankel-Fuchs, D.; Van der Zwaan, J. W.; Fontjin, R. D.; Thauer, R. K. *Biochim. Biophys. Acta* **1986**, *870*, 50. Albracht, S. P. J.; Ankel-Fuchs, D.; Böcher, R.; Ellerman, J.; Moll, J.; Van der Zwaan, J. W.; Thauer, R. K. *Biochim. Biophys. Acta* **1988**, *955*, 86.

(4) Jaun, B.; Pfaltz, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1327.

(5) Stolzenberg, A. M.; Stershic, M. T. *Inorg. Chem.* **1987**, *26*, 1970; *J. Am. Chem. Soc.* **1988**, *110*, 6391 and references therein.

(6) Renner, M. W.; Forman, A.; Fajer, J.; Simpson, D.; Smith, K. M.; Barkigia, K. M. *Biophys. J.* **1988**, *53*, 277.

(7) Lexa, D.; Momenteau, M.; Mispelter, J.; Saveant, J. M. *Inorg. Chem.* **1989**, *28*, 30.

(8) Kadish, K. M.; Sazou, D.; Maiya, G. B.; Han, B. C.; Liu, Y. M.; Saoiabi, A.; Ferhat, M.; Guilard, R. *Inorg. Chem.* **1989**, *28*, 2542.

(9) Ni(I) and high spin Ni(II) thiaporphyrins have been reported recently: Latos-Grazynski, L.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1989**, *28*, 4066. However, comparison with porphyrins is complicated by the sulfur ligated to Ni.

(10) Chlorin: anhydromesorhodochlorin XV methyl ester. iBC: ring C of the chlorin also saturated. Smith, K. M.; Simpson, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 6326.

(11) Porphycene: 2,7,12,17-tetrapropylporphycene. Renner, M. W.; Forman, A.; Wu, W.; Chang, C. K.; Fajer, J. *J. Am. Chem. Soc.* **1989**, *111*, 8618.

(12) Fujita, I.; Davis, M. S.; Fajer, J. *J. Am. Chem. Soc.* **1978**, *100*, 6280.

(13) Data are included in the supplementary material.

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gesting some degree of interaction of the radical with the metal). In contrast to these results, reduction of the iBC yields only a blue shift of the visible absorption band and an EPR spectrum diagnostic of Ni(I) with the electron added to the $d_{x^2-y^2}$ orbital: g = 2.064, 2.076, and 2.199 with average nitrogen hyperfine splittings of 11 G (four nitrogens).[13] These values are similar to those found for the Ni(I) complexes of F430 pentamethyl ester,[4] octaethyl iBC,[5] and tetraaza derivatives.[14]

The very negative reduction potentials of the compounds required that EXAFS measurements be carried out under strictly anaerobic conditions. This was accomplished with electrochemical cells[15] equipped with side arms for optical, EPR, and EXAFS measurements. The EXAFS arm is analogous to an optical cell but with aluminized Mylar windows epoxied to a glass frame. Such a cell readily held high vacuum, and optical, EPR, and EXAFS data could be acquired on the same sample.[13,16]

EXAFS data for the Ni(II) complexes and their reduction products are shown in Figure 1. Analysis[17] of the parent porphycene results yields Ni(II)-N distances of 1.89 (±0.02) Å, in good agreement with single-crystal X-ray data of 1.896 (±0.002) Å.[18] Reduction of the porphycene to its π anion radical leaves the geometry around the Ni virtually unchanged, as evidenced by the close similarity of the EXAFS spectra before and after reduction (Figure 1c,d). Not surprisingly, there is no evidence of coordination of the anion by the bulky Bu_4N^+ counterion. Similarly, the spectra of the chlorin and its anion radical do not differ, again indicating that the Ni environment remains unperturbed upon reduction (Figure 1a,b). Analysis of the parent chlorin spectrum yields average Ni-N distances of 1.95 (±0.02) Å. X-ray data for the compound are not available, but other Ni(II) chlorin structures have been reported:[19] Ni-N(pyrrole) distances range between 1.92 and 1.97 Å and Ni-N(pyrroline) bonds between 1.94 and 2.04 Å. The shorter distances are typically found in distorted chlorins.

Analysis[17] of the Ni(II) iBC EXAFS data yields average Ni-N distances of 1.93 (±0.02) Å. X-ray diffraction[6,20] data show the molecule to be severely distorted, with Ni-N distances of 1.920 (7), 1.902 (6), 1.925 (6), and 1.910 (7) Å, for an average distance of 1.915 Å. The EXAFS data for the Ni(II) iBC thus agree well with the crystallographic results. (No difference was found between the iBC in solution and amorphous samples.)

In contrast to the results obtained for the Ni(II) π radicals of the porphycene and the chlorin, the EXAFS spectra of the Ni(I) iBC differ significantly from those of the Ni(II) compound (Figure 1e,f). A satisfactory fit to the data[17] requires two sets of nitrogen distances of 1.85 (±0.05) and 2.00 (±0.03) Å. Hence, reduction to Ni(I) induces a distortion in the macrocycle core rather than a simple expansion.[21] X-ray results for another d^9 system, Cu(II) dioxo iBC,[22] show a similar bonding pattern: Cu-N distances = 2.035 (5), 2.053 (5), 2.006 (5), and 1.992 (5) Å.

Reduction of Ni(II) to Ni(I) thus requires that the macrocycle accommodate a change of ±0.1 Å in Ni-N bonds. Structural data certainly provide examples of such flexibility in hydroporphyrins.[19,23] Noteworthy, however, is our observation[6] that the hexahydro and octahydro derivatives in the homologous series[10] represented by the chlorin and iBC discussed above are *not* reduced to Ni(I), although the compounds are harder to reduce than the iBC. More extensive saturation may therefore render the macrocycles too rigid to accommodate the Ni(I) ion. This structural constraint may be less crucial in F430 itself. EXAFS studies[24] of the complex and its epimers yield Ni(II)-N distances ranging between 1.9 and 2.1 Å. Such macrocycle cores would thus readily accommodate the Ni(I)-N distances reported here.

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Supplementary Material Available: Details of the EXAFS experiments and fits and optical and EPR spectra of the Ni(II) chlorin anion radical and Ni(I) iBC anion (10 pages). Ordering information is given on any current masthead page.

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(14) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109.

(15) Fajer, J.; Fujita, I.; Davis, M. S.; Forman, A.; Hanson, L. K.; Smith, K. M. *Adv. Chem. Ser.* **1982**, *201*, 489.

(16) Furenlid, L. R.; Renner, M. W.; Fajer, J. *Rev. Sci. Instrum.* In press.

(17) EXAFS data were analyzed by standard methods. See, for example: Stern, E. A.; Heald, S. M. *Handbook on Synchrotron Radiation*; Koch, E. E., Ed.; North Holland: Amsterdam, 1983; Vol. 1 and references therein. Additional details are provided in the supplementary material.

(18) Vogel, E.; Balci, M.; Pramod, K.; Koch, P.; Lex, J.; Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 928.

(19) Suh, M. P.; Swepston, P. N.; Ibers, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 5164. Stolzenberg, A. M.; Glazer, P. A.; Foxman, B. M. *Inorg. Chem.* **1986**, *25*, 983. Barkigia, K. M.; Smith, K. M.; Fajer, J. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 218.

(20) Barkigia, K. M.; Simpson, D. J.; Smith, K. M.; Fajer, J. Unpublished results.

(21) We have considered the possibility of two conformers with all short and all long distances. However, NMR data for the Ni(II) iBC indicate only one conformer, and the X-ray absorption edges of the Ni(I) iBC show no evidence of broadening expected from such different Ni(I)-N distances. Note also the results for the hexahydro and octahydro derivatives (vide infra).

(22) Chang, C. K.; Barkigia, K. M.; Hanson, L. K.; Fajer, J. *J. Am. Chem. Soc.* **1986**, *108*, 1352.

(23) Kratky, C.; Waditschatka, R.; Angst, C.; Johansen, J. E.; Plaquerent, J. C.; Schreiber, J.; Eschenmoser, A *Helv. Chim. Acta* **1985**, *68*, 1312. Strauss, S. H.; Silver, M. E.; Long, K. M.; Thompson, R. G.; Hudgens, R. A.; Spartalian, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4207. Barkigia, K. M.; Fajer, J.; Chang, C. K.; Williams, G. J. B. *J. Am. Chem. Soc.* **1982**, *104*, 315. Barkigia, K. M.; Chantranupong, L.; Smith, K. M.; Fajer, J. *J. Am. Chem. Soc.* **1988**, *110*, 7566.

(24) Shiemke, A. K.; Hamilton, C. L.; Scott, R. A. *J. Biol. Chem.* **1988**, *263*, 5611. Shiemke, A. K.; Kaplan, W. A.; Hamilton, C. L.; Shelnutt, J. A.; Scott, R. A. *J. Biol. Chem.* **1989**, *264*, 7276.

Bilayer-Forming Ion-Pair Amphiphiles from Single-Chain Surfactants[1]

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In this paper we show that amphiphilic ion pairs, derived from a series of trimethyl-*n*-alkylammonium bromides and saturated fatty acids, form vesicles upon sonic dispersal in water. We further show that the ability of such "ion-pair amphiphiles" (IPAs) to form a lamellar phase is critically dependent upon the absence of salts which can compete, effectively, for binding. Ion-pair amphiphiles of the type described herein are proposed as a novel class of vesicle-forming material for both theoretical investigations and practical device applications.[2]

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(2) A recent report by Kaler et al. confirms our present findings that vesicles can be produced from mixtures of oppositely charged, single-chain surfactants: Kaler, E. W.; Murthy, A. K.; Rodriguez, B. E.; Zasadzinski, J. A. N. *Science* **1989**, *245*, 1371. Earlier work, with oppositely charged, single-chain surfactants, has also supported the existence of a lamellar phase: Jokela, P.; Jonsson, B.; Khan, A. *J. Phys. Chem.* **1987**, *91*, 3291.

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