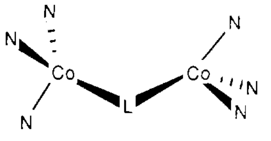

II

Oxygenation of CoHcy. The spectroscopy and chemistry of the reaction product of CoHcy with dioxygen is quite similar to that of the (μ-hydroxo)(μ-peroxo)dicobalt(III) species;[24,26] these similarities strongly support a μ-hydroxo, μ-peroxo structure for oxyCoHcy. When peroxide forms a bridge, the degeneracy of the two π^* orbitals is removed; therefore, two $O_2^{2-} \rightarrow$ Co(III) charge-transfer transitions are expected from the dibridged species due to $\pi_a^* \rightarrow d_\sigma^*$ and $\pi_b^* \rightarrow d_\sigma^*$. These are observed at 300 and 372 nm in the L-histidine (μ-OH$^-$)(μ-O_2^{2-})Co^{III} dimer.[24a] The intensities and energies of the peaks are sensitive to the angle of the peroxide relative to the plane defined by the two cobalts and hydroxide. The 319- and 404-nm bands observed in oxygenated CoHcy can be assigned to the two $O_2^{2-} \rightarrow$ Co(III) LMCT's.

Preliminary kinetics analysis of the oxygenation of CoHcy yielded a second-order rate constant of 11 $M^{-1}\ s^{-1}$ at pH 8.13 and 170 $M^{-1}\ s^{-1}$ at pH 9.4. This assumed a rate law of rate = k[CoHcy][O_2], where k is dependent on the [OH$^-$] to the first order. (These rate constants are much slower than in native hemocyanin, which has a rate constant for the oxygenation of approximately $10^7\ M^{-1}\ s^{-1}$.) This first-order dependence on [OH$^-$] was first observed in the formation of μ-hydroxo, μ-peroxo dimers of cobalt(III) glycylglycine complexes.[26a] The stabilizing effect of hydroxide in the formation of a large number of (μ-peroxo)-cobalt(III) dimers has been reported.[26e,f] The rate constant for oxygenation of CoHcy is significantly lower than that observed for the oxygenation of octahedral Co(II) complexes,[26f] which are typically in the range of 10^3–$10^4\ M^{-1}\ s^{-1}$. The rates do vary with steric influences,[26f] and the coordination number change that must take place upon oxygenation of CoHcy is not represented by these models. Oxygenation of tetrahedral Co(II) complexes in concentrated base has been reported but without any rate data.[26d]

The chemistry and structure of the active site in CoHcy seems to mimic that the deoxyhemocyanin: two four-coordinate distorted tetrahedral metals that upon oxygenation become six-coordinate with μ-peroxo, μ-hydroxo ligands. The two Co(II)'s in the active site of *L. polyphemus* CoHcy bind equivalently as determined by the equilibrium with apohemocyanin and spectroscopy of exogenous ligand binding. More detailed spectroscopic, equilibrium, and kinetics studies of CoHcy will certainly add to our understanding of the structure and function of hemocyanin active sites.

Acknowledgment. This work was supported by the National Science Foundation (Grants R II 8610679 and DMB-8807718) and a William and Flora Hewlett Foundation Grant of the Research Corp.

Registry No. Co, 7440-48-4; OH, 14280-30-9; Cl, 16887-00-6; N_3, 14343-69-2; O, 7782-44-7.

Contribution from the Department of Chemical and Biological Sciences, Oregon Graduate Institute of Science and Technology, Beaverton, Oregon 97006-1999, and Department of Chemistry, Brandeis University, Waltham, Massachusetts 02254

Spectral Properties of *cis*- and *trans*-Metallooctaethylchlorins: Effects of Pyrroline Ring Stereochemistry and Macrocyclic Conformation

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Received July 19, 1989

We recently observed that differences in the structure of *nonconjugated* substituents on the pyrroline ring of metallochlorins had a dramatic effect on the resonance Raman (RR) spectral frequencies. To explore this novel finding, we have compared the spectral properties of the cis and trans stereoisomers of planar copper(II) octaethylchlorin [Cu(OEC)] and of S_4-ruffled nickel(II) octaethylchlorin [Ni(OEC)], where only the configuration of the nonconjugated substituents is varied. Study of these complexes addresses both stereochemistry at the pyrroline ring and the macrocyclic conformation of hydroporphyrins as modulators of the spectral properties. (1) Electronic absorption transitions of the *cis*-M(OEC) complexes are red-shifted from those of *trans*-M(OEC), whereas the Soret/Q_y intensity ratio of S_4-ruffled Ni(OEC) complexes is less than that for the planar Cu(OEC) complexes. (2) The infrared frequencies of C_b–H deformation modes of *cis*-M(OEC) are higher than those of *trans*-M(OEC). (3) The RR band at ~745 cm^{-1} is lower in *frequency* for *cis*-M(OEC) than for *trans*-M(OEC), whereas this band exhibits increased *intensity* for S_4-ruffled Ni(OEC) vs planar Cu(OEC) complexes. (4) Extension of the core size/RR frequency correlation of metalloporphyrins to the -chlorins indicates that *cis*-M(OEC) complexes are smaller in core size than *trans*-M(OEC), whereas the Ni(OEC) complexes are smaller in core size than Cu(OEC). These data demonstrate that structural variations on the pyrroline ring of chlorins have a marked effect on the spectral properties and that macrocyclic conformation also has a significant influence. Thus, apparently localized changes in the macrocyclic structure strongly perturb the overall properties of chlorins and should be considered in spectral analyses of novel biological and model hydroporphyrins.

Introduction

For biological hydroporphyrins[2] of known structure (e.g., chlorophylls,[3] sulfite reductases,[4] and factor F-430 of methanogenic bacteria[5,6] the stereochemistry of the substituents on the sp^3-hybridized carbons of the pyrroline ring is trans. The trans configuration is thermodynamically favored for hydroporphyrins with two hydrogen substituents on the pyrroline ring. Oxidative dehydrogenation of a *cis*-pyrroline ring is often facile.[7] Thus, trans stereochemistry at the pyrroline may stabilize biological macrocycles against reversion to the porphyrin.

Recently, however, a *cis*-pyrroline configuration has been suggested for the heme *d* prosthetic chlorin of the *Escherichia coli* terminal oxidase.[8-10] A cis configuration is also indicated for the chlorin catalase of *E. coli*.[11] In both of these cases, the proposed in vivo iron chlorin has no hydrogen substituents on the saturated ring, thereby eliminating the potential for oxidative

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[2] Hydroporphyrins differ from the parent porphyrin by saturation of one or more pyrrole rings. The pyrroline (reduced) ring does not necessarily have hydrogen substituents. Biological hydroporphyrins include dihydroporphyrins (chlorins), isobacteriochlorin (iBC) tetrahydroporphyrins (two adjacent pyrroline rings), bacteriochlorin (BC) tetrahydroporphyrins (two opposite pyrroline rings), and the more highly saturated and modified corphinoid macrocycle of factor F-430.

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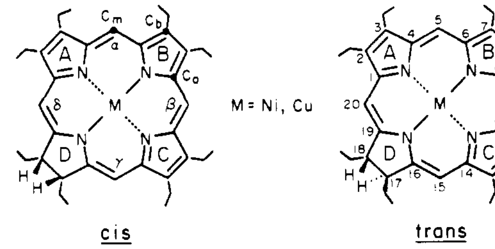

Figure 1. Structures. The primary structural difference between the macrocycle lies in the stereochemistry of the substituents on the saturated (D) ring.

dehydrogenation. However, functional consequences and/or advantages of cis vs trans stereochemistry at the pyrroline ring(s) of hydroporphyrins have not been evaluated.

We decided to examine the spectral effect(s) of stereochemical variations for metallochlorins as a consequence of previous work. In a study of models for the heme *d* prosthetic group, we noted that the resonance Raman (RR) spectral properties varied remarkably between chlorins differing *only* in the structure of *nonconjugated* substituents on the pyrroline ring.[9] Thus, the RR spectra of Cu–diol chlorin,[12] Cu–lactone chlorin, and Cu–Me$_7$ chlorin were distinct from one another with respect to frequencies, intensities, and total number of bands.[9] To test the limits of these observations, we sought to compare chlorins having a high degree of structural similarity except on the saturated ring. Comparison of the cis and trans stereoisomers[13] of metallooctaethylchlorin complexes (M[OEC]) directly tests the influence of nonconjugated substituents on the spectral properties of hydroporphyrins. It also evaluates the spectral effects of stereochemical modifications at the pyrroline ring. As shown herein, seemingly minor structural alterations have a profound effect on both the electronic absorption and vibrational spectra.

The second common structural property of hydroporphyrins is the loss of planarity at the pyrroline ring(s), occurring with a concomitant increase in macrocyclic flexibility. This is exemplified by iron(II) hydroporphyrins[14] and particularly by nickel(II) hydroporphyrins.[6a,13,15-18] The preferred short Ni–N$_{\text{pyrrole}}$ bonds of nickel porphyrins[19] and nickel hydroporphyrins are best accommodated by a nonplanar, e.g., S_4-ruffled, macrocycle. However, the spectral effects of this deviation from planarity have not fully been evaluated for hydroporphyrins. This is surprising, given that RR spectra of nickel porphyrins are extremely sensitive to macrocyclic deviations from planarity.[20-24] Furthermore, in the case

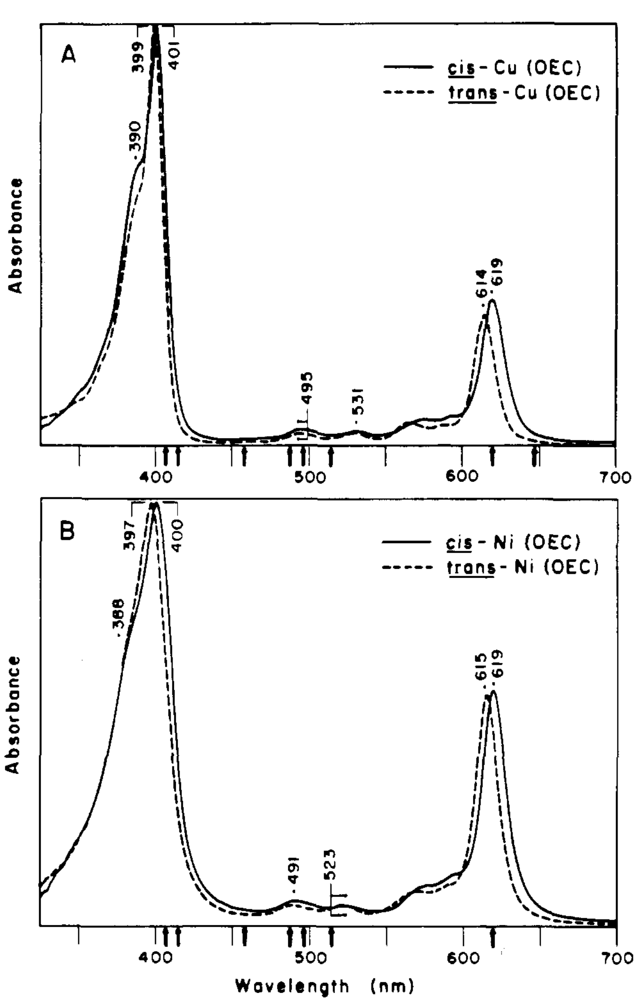

Figure 2. Electronic absorption spectra (samples in CH_2Cl_2 solution): (A) *cis*-Cu(OEC) and *trans*-Cu(OEC); (B) *cis*-Ni(OEC) and *trans*-Ni(OEC). Arrows indicate the wavelengths of RR excitation lines used.

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(12) Abbreviations used: Cu–diol chlorin, copper(II) *cis*-3′,4′-dihydroxy-2,4-dimethyldeuterochlorin IX dimethyl ester;[9] Cu–lactone chlorin, copper(II) 5′-hydroxy-6,6′-*trans*-γ-spirolactone-2,4-dimethyldeuterochlorin IX monomethyl ester;[9] Cu–(Me)$_7$ chlorin, copper(II) 3′-hydro-4′-methyl-2,4-dimethyldeuterochlorin IX dimethyl ester;[9] OEC, octaethylchlorin; RR, resonance Raman; IR, infrared; OEP, octaethylporphyrin; SERRS, surface enhanced resonance Raman scattering; *meso*-Ni(TMC), nickel(II) *meso*-tetramethylchlorin.

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Table I. FTIR C–H Stretching Frequencies (cm^{-1}) for M(OEP) and M(OEC) Complexes

planar				S_4 ruffled			
Cu(OEP)	*cis*-Cu(OEC)	*trans*-Cu(OEC)	D_{4h} Ni(OEP)^a	D_{2d} Ni(OEP)	*cis*-Ni(OEC)	*trans*-Ni(OEC)	assignment
3053	3058	3047	3076	3058	3058	3061	C_m–H
2962	2961	2962	2968	2963	2958	2960	ethyl
2928	2927	2927	2936	2930	2928	2930	ethyl
2868	2867	2866	2872	2868	2868	2868	ethyl

^{a} IR frequencies for planar (D_{4h}) Ni(OEP) from Kincaid et al.[38] All other data from this work.

of F-430, even the biological activity is lost upon modification of the macrocycle to yield its strongly ruffled 12,13-diepimer.[5,6] Thus, comparison of the S_4-ruffled Ni(OEC) and planar Cu(OEC) complexes[13] permits evaluation of macrocyclic conformation as a modulator of hydroporphyrin spectral properties.

Resonance Raman spectroscopy has been a valuable adjuct to the study of both biological and model metalloporphyrins.[25,26] Its extension to metallochlorins has led to diagnostic spectral characteristics useful in the study of novel hydroporphyrins[9,26-33] and has also provided new insight into well-characterized systems such as the chlorophylls.[30-34]

We report herein the resonance Raman, electronic absorption, and Fourier transform infrared (IR) spectra of tetracoordinate Cu^{II} and Ni^{II} complexes of *cis*- and *trans*-octaethylchlorin[13] (Figure 1). Both the stereochemistry at the pyrroline ring and the macrocyclic conformation (planar vs S_4-ruffled) are clearly shown to influence the spectral properties of the M(OEC) complexes. It is thus evident that the general properties of metallochlorins are strongly perturbed by apparently "local" structural alterations.

Experimental Section

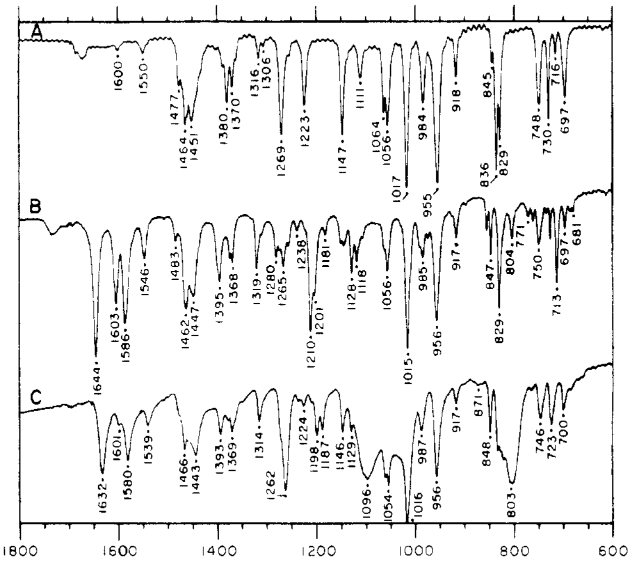

Figure 3. FTIR spectra of (A) Cu(OEP), (B) *cis*-Cu(OEC), and (C) *trans*-Cu(OEC) (samples ~1:150 mg in KBr).

Cu(OEP).[12] *cis*-Cu(OEC), *trans*-Cu(OEC), Ni(OEP), *cis*-Ni(OEC), and *trans*-Ni(OEC) were prepared and characterized by published methods.[13] The crystalline complexes were further purified by chromatography on grade 3 alumina (99:1 benzene/methanol), and were recrystallized from chloroform/hexane to remove trace levels of fluorescent free-base macrocycles. Absorption spectra were recorded on a Perkin-Elmer Lambda 4C spectrophotometer from solutions prepared anaerobically with dry benzene.[13] Fourier transform IR spectra (Perkin-Elmer 1800 spectrometer) were obtained from pellets prepared as an ~1:150 mg ratio of sample:KBr. Resonance Raman spectra were obtained from a mixture of solids prepared in an ~1:150 mg ratio of sample:KBr that was gently hand-compressed into the groove of a sample holder that was subsequently mounted on the spindle of a motor and spun during laser irradiation.[9,31] No evidence of photodecomposition was observed. Spectra-Physics 164-05 Ar and 2025-11 Kr ion lasers and a Coherent Innova 90-6 Ar ion laser pumping a Coherent 599-01 dye laser were used as excitation sources. The computer-controlled Jarrell-Ash Raman spectrophotometer and data reduction programs have been reported.[35] The computer system for the spectrophotometer has recently been upgraded to an RMX86-based Intel 310 running our own revised Fortran 77 data collection and analysis programs.[36]

Results

1. Electronic Absorption Spectroscopy. Absorption spectra of *cis*- and *trans*-Cu(OEC) and of *cis*- and *trans*-Ni(OEC) are shown in Figure 2. All of the transitions of *cis*-Cu(OEC) (with the exception of the 495-nm band) are to the red of those of *trans*-Cu(OEC). The electronic transitions of *cis*-Ni(OEC) are also all to the red of those of *trans*-Ni(OEC). Undoubtedly, the stereochemistry of the nonconjugated substituents on the pyrroline ring influences the electronic transitions.

Figure 2 also illustrates the spectral effects of macrocyclic conformation. The intensity ratio of the ~400-nm Soret band with respect to the ~617-nm $Q_y(0,0)$ band is ~3:1 for the planar Cu(OEC) complexes, a value generally typical of metallochlorins.[37]

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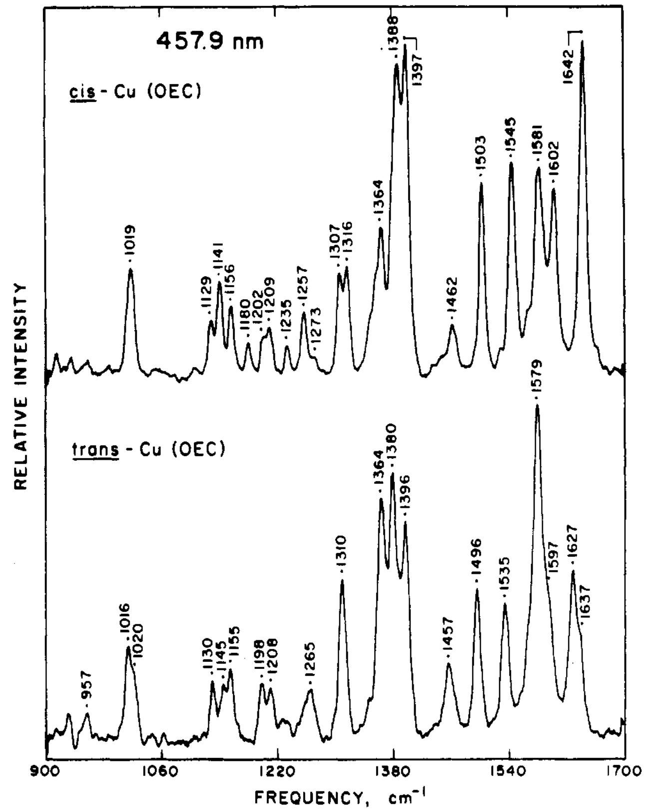

Figure 4. High-frequency 457.9-nm excitation RR spectra of *cis*-Cu(OEC) and *trans*-Cu(OEC). Conditions: laser power, 50 mW; sample, ~1:150 mg in KBr matrix; spinning sample cell; backscattering geometry.

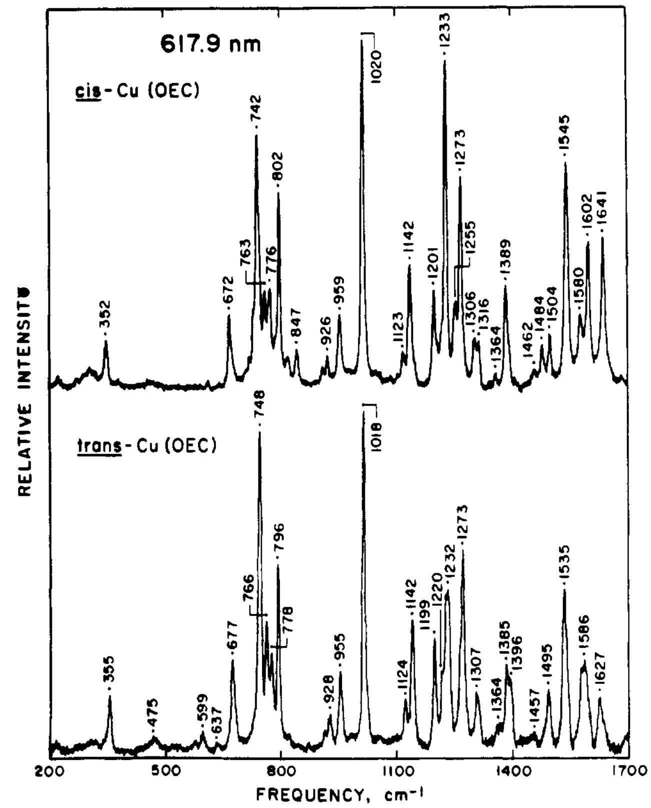

Figure 5. Q_y excitation RR spectra of *cis*-Cu(OEC) and *trans*-Cu(OEC): laser power, 110 mW; other conditions as in Figure 4.

In contrast, the Soret/Q_y ratio of the S_4-ruffled Ni(OEC) complexes is only ~2:1 because the Soret absorptivity of the Ni(OEC) complexes is decreased.[13]

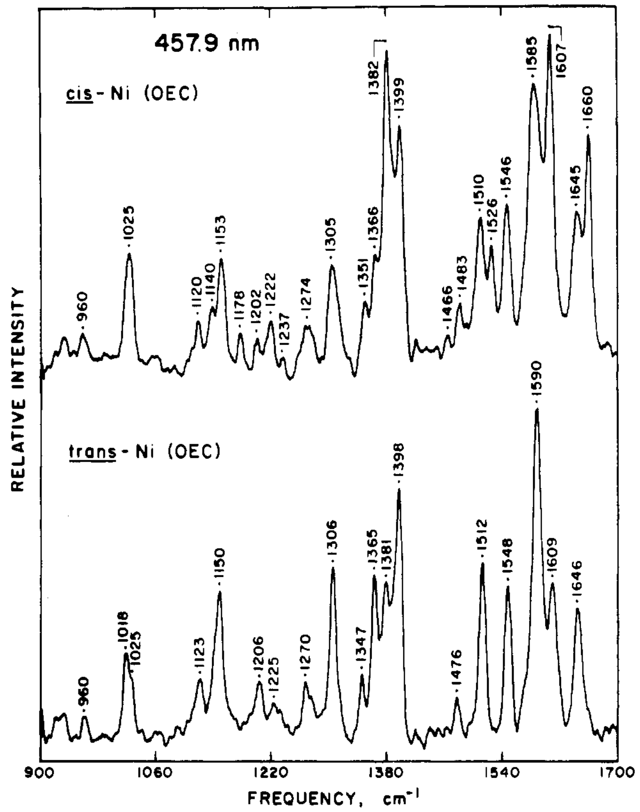

Figure 6. High-frequency 457.9-nm excitation RR spectra of *cis*- and *trans*-Ni(OEC): laser power, 50 mW; other conditions as in Figure 4.

2. Fourier Transform Infrared Spectroscopy. Table I presents the C–H stretching modes observed in the IR spectra of the M(OEC) and M(OEP) complexes. The 600–1800-cm^{-1} IR spectra of *cis*- and *trans*-Cu(OEC) are shown in Figure 3, along with that of the Cu(OEP) parent. This is the first complete report of the *cis*-Cu(OEC) infrared spectrum.[39] However, Mason[40] tabulated IR frequencies for *trans*-Cu(OEC), and portions of the *trans*-Cu(OEC) IR spectrum have been discussed.[41]

The IR spectra of both *cis*- and *trans*-Cu(OEC) are considerably more intricate than that of Cu(OEP), a consequence of the decreased molecular symmetry.[9,27c,31] IR features assigned to porphyrin $-CH_3$ and $-CH_2$ deformation modes[38b] are similar for the Cu(OEC) complexes. The infrared bands of *cis*- and *trans*-Cu(OEC) obviously differ from one another. For example, *cis*-Cu(OEC) has IR bands at 1586, 1603, and 1644 cm^{-1} that are at 1580, 1601, and 1632 cm^{-1}, respectively, for *trans*-Cu(OEC), and especially differ in relative intensity (Figure 3). In the ~1150–1220-cm^{-1} region, *cis*- and *trans*-Cu(OEC) have IR features corresponding with the sp^3 C_b–H deformation modes of metallochlorins calculated by Boldt et al.[30] The C_b–H deformations differ in frequency between *cis*-Cu(OEC) and *trans*-Cu(OEC), but these bands are absent from the spectrum of Cu(OEP), as expected for pyrroline C_b–H modes.

3. Resonance Raman Spectroscopy. Representative resonance Raman spectra of *cis*- and *trans*-Cu(OEC) and of *cis*- and *trans*-Ni(OEC) are shown in Figures 4–7.[42] The characteristic

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(38) (a) Kincaid, J. R. Unpublished results. (b) Kincaid, J. R.; Urban, M. W.; Watanabe, T.; Nakamoto, K. *J. Phys. Chem.* **1983**, *87*, 3096–3101.

(39) The IR "chlorin band" for both *cis*- and *trans*-Cu(OEC) was discussed previously.[31]

(40) Mason, S. F. *J. Chem. Soc.* **1958**, 976–982.

(41) Ogoshi, H.; Watanabe, E.; Yoshida, Z.; Kincaid, J. R.; Nakamoto, K. *Inorg. Chem.* **1975**, *14*, 1344–1350.

(42) RR spectra of *cis*- and *trans*-Cu(OEC), obtained with rigorous resonance (617.9 nm) vs preresonance (647.1 nm) excitation, were compared to evaluate the wavelength dependence of Q_y enhancement (see Figure 5). RR frequencies and relative intensities for each Cu(OEC) complex were identical for the entire 200–1700-cm^{-1} spectral range. This observation facilitates cross-comparison of RR spectra of metallochlorins.

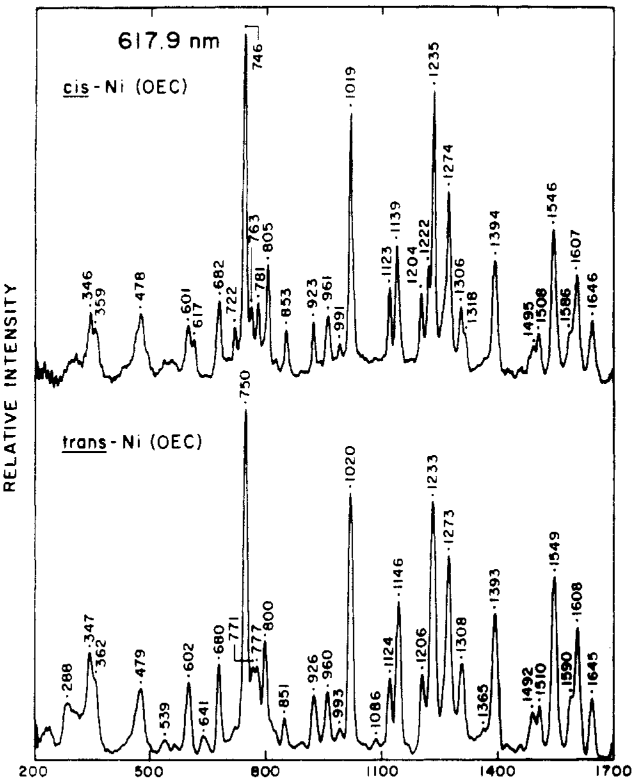

Figure 7. Q$_y$ excitation RR spectra of *cis*- and *trans*-Ni(OEC): laser power, 110 mW; other conditions as in Figure 4.

chlorin RR spectral pattern[9,27-34] is seen for the M(OEC) complexes. However, RR spectra of the stereoisomers exhibit clear differences at every excitation line examined[43] with respect to (a) the frequencies of the RR bands, (b) the number of RR bands, and (c) the patterns of relative intensity.

With 457.9-nm excitation, the RR spectrum of *cis*-Cu(OEC) has bands at 1462, 1503, 1545, 1581, 1602, and 1642 cm^{-1} that shift for *trans*-Cu(OEC) to 1457, 1496, 1535, 1579, 1597, and a poorly resolved doublet at 1627/1637 cm^{-1}, respectively (Figure 4). Resonance Raman frequencies of *cis*-Ni(OEC) are also shifted from those of *trans*-Ni(OEC). For example, with 457.9-nm excitation (Figure 6), the RR spectrum of *cis*-Ni(OEC) has bands at 1483, 1510, 1546, and 1585 cm^{-1} that are at 1476, 1512, 1548, and 1590 cm^{-1}, respectively, for *trans*-Ni(OEC). The RR spectrum of *cis*-Ni(OEC) also has features at, e.g., 1526 and 1660 cm^{-1} that are absent from the *trans*-Ni(OEC) spectrum.

The highest energy RR band of *trans*-Cu(OEC) and *cis*-Ni(OEC) is absent from spectra obtained with red excitation (Figure 5 and 7). We noted this phenomenon previously.[31] The Q$_y$-excitation RR spectra of the planar Cu(OEC) stereoisomers remain very different from one another. In contrast, Q$_y$-excitation RR spectra of S_4-ruffled *cis*- and *trans*-Ni(OEC) are more similar to one another than is the case for 457.9-nm excitation.

Discussion

The NMR (^{1}H and ^{13}C) spectral properties of M(OEC) complexes are perturbed both by the stereochemistry at the pyrroline ring and by the overall macrocyclic conformation.[13] Where M = H$_2$, Mg, Zn, and (presumably) Cu, the NMR spectra indicate a planar macrocycle. In contrast, the NMR results strongly support S_4-ruffling of the *cis*- and *trans*-Ni(OEC) macrocycles.[13]

The specific molecular conformations of planar *cis*- and *trans*-Cu(OEC) complexes are not identical. For *cis*-Cu(OEC), the conformation of the pyrroline ring substituents destroys the expected mirror plane, leaving the complex with little or no symmetry. For *trans*-Cu(OEC), the C_2 axis through the pyrroline ring of *trans*-Cu(OEC) is preserved.[13] In the case of *trans*-Ni(OEC), the shallow half-chair conformation of the pyrroline ring and overall S_4-ruffling of the macrocycle apparently destroy any symmetry elements. Surprisingly, for *cis*-Ni(OEC) the NMR data indicate retention of the mirror plane through the pyrroline ring, presumably due to a low barrier to inversion of the sense of ruffling.[13] These factors combine to increase the relative symmetry of the *cis*-Ni(OEC) complex.

As shown by Kratky et al.[16] hole contraction and ruffling induced by Ni^{II} appears to affect the stereochemistry at the periphery of the macrocycle. Alternatively, Stolzenberg and Stershic[17b] suggest that it may be the substituent stereochemistry that controls the extent of ruffling. Clearly, isolating the spectral effects of stereochemistry at the pyrroline ring from the effects of a planar vs ruffled macrocyclic conformation is not trivial.

For metallochlorins, the RR and IR spectra are now relatively well characterized and provide a rich source of structural information.[9,27-34] The vibrational properties of chlorins include (1) a diagnostic cluster of bands in the ~1340–1400-cm^{-1} region of the RR spectra,[44] (2) loss of mutual exclusion, causing an increase in the number of RR and IR features and significant IR and RR frequency matching, and (3) strong C_a–C_m modes above ~1600 cm^{-1} in both the IR and RR spectra.[9,27-34]

Two fundamental structural properties of metallochlorins have not been considered previously as potential modulators of the spectra, despite their obvious biological relevance. The spectral effects of (A) the stereochemistry at the pyrroline ring and (B) the overall macrocyclic conformation are discussed herein.

A. Spectral Effects of Pyrroline Stereochemistry. There are several clear-cut differences between spectral properties of the *cis*-M(OEC) complexes and their trans analogues that appear to be responsive to stereochemistry at the pyrroline ring. They include (1) a bathochromic shift of the electronic transitions of *cis*-M(OEC) relative to those of *trans*-M(OEC), (2) altered C_b–H deformation frequencies in the IR spectra, and (3) alterations in the frequencies, intensities, and number of bands in the RR spectra.

1. Electronic Absorption Spectroscopy. The stereochemistry at the pyrroline ring of metallochlorins clearly affects the π-orbital energies, even though the pyrroline substituents are nonconjugated. This is exemplified by the 4–5-nm red shift of the Q$_y$ transitions of *cis*-Cu(OEC) and *cis*-Ni(OEC) vs those of *trans*-Cu(OEC) and *trans*-Ni(OEC), as shown in Figure 2. Although the magnitude of the red shift induced by a cis configuration at the pyrroline ring is relatively minor, it is consistently observed between all of the *cis*-M(OEC) and *trans*-M(OEC) complexes, where M = Cu^{II}, Ni^{II}, Mg^{II}, Zn^{II}, and Sn^{II}.[13] The electronic transitions of *cis*-H$_2$(OEC) are also red-shifted from those of *trans*-H$_2$(OEC).[45] Similarly, the ttct isomer of a free-base hexahydroporphyrin has a 642-nm absorption band that shifts to 634 nm for the tttt isomer.[46] This pattern does not appear to be limited to model hydroporphyrins. For the chlorin catalase from *E. coli*,[11a] having a *cis*-γ-spirolactone on the pyrroline ring,[11b] the Q$_y$ transition is ~5 nm red-shifted from that of the heme *d* chlorin of the *E. coli* terminal oxidase (*trans*-γ-spirolactone[8-10,47]). The direction and magnitude of the red shift observed for *cis*-chlorins is similar to that observed upon addition of a conjugated (e.g., vinyl or formyl) substituent for metalloporphyrins[48] and -chlorins.[27b,30,31] Thus, one definitely should be cautious in using the

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(43) The 496-nm excitation RR spectra of *cis*- and *trans*-Cu(OEC), where the complexes have a common electronic transition, were distinct from one another. Thus, differences in RR spectral properties between the Cu(OEC) stereoisomers are not a simple consequence of the shift in electronic transitions relative to the Raman exciting line.

(44) This property is often *least* evident with Soret excitation.

(45) Whitlock, H. W., Jr.; Hanauer, R.; Oester, M. Y.; Bower, B. K. *J. Am. Chem. Soc.* **1969**, *91*, 7485–7489.

(46) Johansen, J. E.; Angst, C.; Kratky, C.; Eschenmoser, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 141–143.

(47) A *trans*-lactone chlorin will arise in a facile manner from a *cis*-diol chlorin;[9] the precursor of the proposed *cis*-lactone chlorin in the *E. coli* catalase is unknown.[11]

(48) Smith, K. M., Ed. *Porphyrins and Metalloporphyrins*; Elsevier Scientific: Amsterdam, 1975.

electronic absorption spectra of unknown chlorins as the basis for structural predictions.

2. Fourier Transform Infrared Spectroscopy. A second difference between *cis*- and *trans*-M(OEC) is apparent in the ~1150–1220-cm^{-1} IR spectra (Figure 3). The increased frequency of the C$_b$–H deformation[30] modes of *cis*-M(OEC) relative to *trans*-M(OEC) occurs for both the Cu(OEC) and Ni(OEC) pairs. The *cis*-Cu(OEC) IR spectrum has a strong band at 1210 cm^{-1}, a sideband at ~1201 cm^{-1}, and much weaker flanking bands at ~1238 and 1181 cm^{-1}. The IR bands of *cis*-Ni(OEC) in this region (not shown) are very similar to those of *cis*-Cu(OEC). In contrast, the *trans*-Cu(OEC) IR spectrum displays medium-intensity bands at 1198 and 1187 cm^{-1}, with a weaker high-frequency sideband at 1224 cm^{-1}. The IR bands of *trans*-Ni(OEC) are very close in frequency to those of *trans*-Cu(OEC). These data suggest that IR-active C$_b$–H deformation modes of chlorins are sensitive to the stereochemistry at the pyrroline ring.

For chlorophylls (trans hydrogens at pyrroline ring D), the IR spectra also display 1185–1192-cm^{-1} bands[49] similar to those of *trans*-Cu(OEC) and *trans*-Ni(OEC) but distinct from those of *cis*-M(OEC). The IR spectrum of *trans*-Fe^{II}(OEC)[50] in this region is also similar to IR spectra of *trans*-Cu(OEC) and *trans*-Ni(OEC). Thus, the ~1150–1220-cm^{-1} IR spectra may be useful in identification of stereochemistry for chlorins with two hydrogen substituents on the pyrroline ring. Because only one or two of the C$_b$–H deformation modes was observed in RR spectra of *trans*-Ni(OEC),[30] these data exemplify the utility of a combined IR and RR approach to the study of hydroporphyrins.

3. Resonance Raman Spectroscopy. a. High-Frequency Region. The single sharp ~1642-cm^{-1} RR band of *cis*-Cu(OEC), shown in Figure 4, is similar to the "ν_{10}" C$_a$–C$_m$ mode[51] of other copper chlorins, assigned on the basis of isotopic substitution.[9] In comparison, the 1627-cm^{-1} band of *trans*-Cu(OEC) is anomalously low in frequency,[52] and the RR doublet at 1627 and 1637 cm^{-1} is also unusual for copper(II) chlorins.[9] This difference between the Cu(OEC) stereoisomers is also apparent in their IR spectra (Figure 3): *cis*-Cu(OEC) has a strong sharp 1644-cm^{-1} band, whereas *trans*-Cu(OEC) has a broad band at 1632 cm^{-1}, also suggesting two components.

Resonance Raman frequencies of *trans*-Ni(OEC) also differ from those of *cis*-Ni(OEC), as shown for the highest energy band (Figure 6). Whereas the 457.9-nm excitation RR spectrum of *trans*-Ni(OEC) has a single feature at 1646 cm^{-1}, the RR spectrum of *cis*-Ni(OEC) has a doublet at 1645 and 1660 cm^{-1}. The normal mode analysis for *trans*-Ni(OEC) includes a doublet in this region, at 1648 and 1644 cm^{-1}, assigned respectively as "ν_{10}" plus "ν_{37a}" and "ν_{37b}" plus "ν_{19}".[30] These bands arise from extensive mixing of the former porphyrin IR-active E$_u$ and Raman-active modes.[30] Although the 1660- and 1645-cm^{-1} bands of *cis*-Ni(OEC) may correspond directly with those of *trans*-Ni(OEC), the overall IR spectral features of *cis*-Ni(OEC) differ sufficiently from those of *trans*-Ni(OEC) that a one-to-one transferral of RR assignments between the two does not seem probable. Confirmation of this point and a precise characterization of the vibrational modes for *cis*-M(OEC) would require specific labeling. However, synthetic considerations currently preclude this because methods of specific labeling for *cis*-chlorins without loss of stereochemistry or oxidation to the porphyrin have not yet been developed.

b. Core Size. The resonance Raman frequencies of the C$_a$–C$_m$ modes of porphyrins are sensitive to the oxidation state, spin state, and coordination number of the central metal ion. They also display a negative linear correlation with porphyrin core size (C$_t$–N, Å).[25,26] Kitagawa and Ozaki[26] proposed that this correlation was transferable to M(OEC) complexes. This proposal is generally supported by our RR spectral analysis of solid-state samples of crystallographically defined tetracoordinate Fe^{II}(OEC), although the effect of macrocyclic ruffling is not negligible.[50]

The RR bands of the *cis*-M(OEC) complexes are generally higher in frequency than those of *trans*-M(OEC). Thus, use of the core size/RR frequency correlation implies that *cis*-M(OEC) complexes have a smaller core size than the respective *trans*-M(OEC) complexes. At present, there is no independent evidence with which to verify this intriguing proposal. One may, however, draw parallels to numerous other hydroporphyrins studied by Eschenmoser and colleagues. An inverse relationship between saddle steepness and M–N distance was observed, where the steepest saddle (and smallest M–N distance) was observed in the case of all-cis complexes.[6a,16]

c. Low-Frequency Region. Another obvious difference between the RR spectra of the *cis*- and *trans*-M(OEC) complexes is seen for the ~740–750-cm^{-1} "ν_{15}" mode,[53-55] maximized for metallochlorins with Q$_y$ excitation (Figures 5 and 7). The frequency of the "ν_{15}" band of *cis*-M(OEC) is decreased relative to that of the *trans*-M(OEC) complexes. It appears at 742 cm^{-1} for *cis*-Cu(OEC) vs 748 cm^{-1} for *trans*-Cu(OEC) and at 746 cm^{-1} for *cis*-Ni(OEC) vs 750 cm^{-1} for *trans*-Ni(OEC). These data clearly indicate that the "ν_{15}" band of metallochlorins is sensitive to the stereochemistry at the pyrroline ring.

B. Spectral Effects of Macrocyclic Conformation. The central metal ion and its consequent influence on macrocyclic conformation also affect the spectral properties of metallochlorins, as shown herein by differences between the planar Cu(OEC) and S_4-ruffled Ni(OEC) complexes. This is most clearly illustrated by (a) alterations in the Soret/Q$_y$ ratio of the electronic absorption spectra, (b) RR frequency shifts, and (c) intensity changes in the low-frequency region of the RR spectra.

1. Electronic Absorption Spectroscopy. The Soret/Q$_y$ ratio of extinction coefficients for *cis*- and *trans*-Ni(OEC) is only ~1.8 (Figure 2[13]). This is in contrast to a Soret/Q$_y$ ratio of ~3 for the Cu(OEC) complexes or for other M(OEC) complexes where M = Mg, Sn, and Sn.[13] Chlorophyll derivatives (phorbins) also have a low Soret/Q$_y$ ratio relative to other chlorins. Weiss attributed this to distortion of the chlorin macrocyclic π-system by the phorbin isocyclic ring.[56] We infer that introduction of Ni^{II} and the consequent ruffling of the macrocycle[13,18] have a similar perturbing effect on the Ni(OEC) π-system. Clearly, then, conformational distortions at the pyrroline ring of metallochlorins are not simply localized, but are transmitted throughout the macrocycle.

2. Fourier Transform Infrared Spectroscopy. Table I lists spectral features for the 2600–3200-cm^{-1} region of the IR spectra. Strong ν(C–H) modes of the ethyl substituents[57] apparently obscure the pyrroline C$_b$–H stretching modes of the chlorins, expected at ~2880–2920 cm^{-1}.[58] The ~3075-cm^{-1} band of planar (D_{4h})

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(49) Katz, J. J.; Dougherty, R. C.; Boucher, L. J. In *The Chlorophylls*; Vernon, L. P., Seely, G. R., Eds.; Academic Press: New York, 1966; Chapter 7.

(50) Mylrajan, M.; Andersson, L. A.; Loehr, T. M.; Sullivan, E. P., Jr.; Strauss, S. H. Manuscript in preparation.

(51) Use of the phrase "ν_x" does not imply identical origins for vibrational features of chlorins and porphyrins. As Bocian and co-workers have shown, this is clearly not the case.[30] Rather, it is used to simplify comparisons, facilitating discussion of vibrational properties for novel hydroporphyrins relative to the well-understood spectra of porphyrins.[25,26] This is warranted because similar vibrational behavior is generally observed between chlorins and porphyrins, such as the response to isotopic substitution.[9]

(52) Indeed, our first thought upon observing the abnormally low frequency of this feature was that we were mistakenly examining a high-spin, pentacoordinate iron(III) chlorin (as opposed to a Cu^{II} complex).

(53) The ~750-cm^{-1} feature of planar and ruffled Ni(OEP), formerly assigned as ν_{16},[54,55] was recently reassigned as ν_{15}.[24] In the case of metallochlorins, the relatively weak ~740–750-cm^{-1} feature observed with Soret and near-Soret excitation is not isotope sensitive,[26] whereas the strong ~740–750-cm^{-1} feature observed with Q$_y$ excitation is clearly shifted upon *meso*-d_4-deuteriation.[9] The latter feature, formerly assigned by us as "ν_{16}"[9] is, then, "ν_{15}".[24]

(54) The ν_{16} mode of metalloporphyrins was assigned as a C$_a$–N–C$_a$ mode for D_{4h} Ni(OEP) and shifts down 72 cm^{-1} for *meso*-d_4-Ni(OEP).[55]

(55) Abe, M.; Kitagawa, T.; Kyogoku, Y. *J. Chem. Phys.* **1978**, *69*, 4526–4534.

(56) (a) Weiss, C. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, Chapter 3. (b) Weiss, C. *J. Mol. Spectrosc.* **1972**, *44*, 37–80.

(57) Caughey, W. S.; Alben, J. O.; Fujimoto, W. Y.; York, J. L. *J. Org. Chem.* **1966**, *31*, 2631–2640.

Ni(OEP) was assigned as the C_m–H stretching mode.[38] In contrast, the $\nu(C_m–H)$ mode of S_4-ruffled (D_{2d}) Ni(OEP), not reported previously, is at 3058 cm^{-1} (Table I). The 17-cm^{-1} downshift of $\nu(C_m–H)$ between planar and ruffled Ni(OEP) suggests that the meso carbons of nickel(II) tetrapyrroles are sensitive to the macrocyclic conformation. The $\nu(C_m–H)$ modes of the S_4-ruffled *cis*- and *trans*-Ni(OEC) complexes are also at ~3060 cm^{-1}. In contrast, the frequency of $\nu(C_m–H)$ for the Cu(OEC) complexes appears to depend on the pyrroline stereochemistry (Table I). Ring strain, steric congestion, and conformational alterations are known to affect C–H stretching mode frequencies.[58] Apparently in the case of the Ni macrocycles, S_4-ruffling allows adjustments and may relieve steric congestion at the periphery of the macrocycle.[13]

3. Resonance Raman Spectroscopy. a. Core Size. Resonance Raman features of *cis*- and *trans*-Ni(OEC) are generally higher in frequency than those of *cis*- and *trans*-Cu(OEC). If the core size/RR frequency inverse correlation is indeed transferable to metallochlorins,[26,50] this implies that Ni(OEC) complexes are smaller in core size than Cu(OEC) complexes. Given the tendency of the nickel(II) porphyrins and nickel(II) hydroporphyrins to have a shorter M–N distance (~1.92 Å[16,19]) than is observed for copper(II) porphyrins (~2.00 Å[59]), this finding is not unexpected and may also reflect the macrocyclic ruffling. In fact, for metal pyrrocorphinates, differences in M–N distances between Cu^{II} and Ni^{II} complexes are associated with the saddle steepness and extent of ruffling for the latter.[16]

b. Low-Frequency Spectra. The intensity of the 740–750-cm^{-1} "ν_{15}" band[53-55] (as observed with Q_y excitation) appears to be responsive to macrocyclic deformation from planarity for metallochlorins. For example, "ν_{15}" of S_4-ruffled Ni(OEC) is the strongest feature in the entire 200–1700-cm^{-1} spectrum (Figure 7). In contrast, for the planar Cu(OEC) complexes, the intensity of "ν_{15}" is less than that of the ~1020-cm^{-1} band (Figure 5).[60] In the case of structurally perturbed[20] nickel(II) pyropheophorbide *a*, "ν_{15}" is also dominant in the Q_y-excitation RR spectrum.[30,31] This band is considerably more intense than that of chlorophyll *a* or the methyl chloroiron(III) pheophorbides.[31] For S_4-ruffled tetracoordinate Fe^{II}(OEC),[14] "ν_{15}" is also the dominant band in the RR spectra.[50] Thus, the relative intensity of the "ν_{15}" band of metallochlorins appears to be sensitive to the overall conformation of the macrocycle.[31] Ozaki et al.[61] first noted that the intensity of the ~750-cm^{-1} low-frequency RR band of M(OEP) complexes was dependent upon the macrocycle planarity. Comparison of the relative intensity of ν_{15} in RR spectra of planar, ruffled, and solution samples of Ni(OEP)[24] also supports our proposal that its intensity is related to macrocycle conformation. Because the "ν_{15}" feature of metallochlorins is responsive to both macrocyclic deformation and stereochemistry, it appears to be an important structural marker. No low-frequency red-excitation RR spectra of biological metallochlorins (other than the SERRS[12] spectrum of Chl *a*[31]) have yet been reported.

Other low-frequency bands in the Q_y-excitation RR spectra of planar Cu(OEC) and S_4-ruffled Ni(OEC) also differ (Figures 5 and 7): (1) The ~478-cm^{-1} band of *cis*- and *trans*-Ni(OEC) is considerably stronger than that of the Cu(OEC) complexes. (2) The single ~352-cm^{-1} feature of the Cu(OEC) complexes is an ~346- and 360-cm^{-1} doublet for the Ni(OEC) complexes. (3) Ni(OEC) spectra have an ~600-cm^{-1} band that is very weak or absent from Cu(OEC) spectra. Low-frequency features of Ni(OEP), from which these features of Ni(OEC) are presumably derived, were recently assigned in some detail by Spiro and coworkers.[24] Because the Ni(OEC) and Cu(OEC) complexes are four-coordinate, the low-frequency spectral differences are clearly not axial ligand modes. Instead, they appear to be further consequences of ruffled vs planar conformation for the M(OEC) macrocycles.

Table II. Selected RR Frequencies (cm^{-1}) of Nickel(II) hydroporphyrins

complex	macrocyclic conformation	coordn no.	RR bands	
cis-(OEC)[a]	S_4-ruffled[b,c]	4	1660 1645	1585
trans-(OEC)[a,d]	S_4-ruffled[b]	4	1646	1590
pyropheophorbides[d,e] (trans)	ruffled[f]	4	1660	1590
methylreductase[g]		5?	1652	1575
extracted F-430[g,h]	~planar[i]	major, 6	1629	1556
		minor, 4	1622–1632	1534
F-430, diepimer[g]	saddle-shaped[i]	4	1623	1529
corphinoid models[j]	saddle[i]	4	1640	1547
corphinoid models[j]	saddle[i]	5	1631	1550
corphinoid models[j]	saddle[j]	6	1620–1630	~1550

[a] This work. [b] Reference 13. [c] Low barrier to inversion of sense of ruffling.[13] [d] Reference 30. [e] Reference 31. [f] Reference 16. [g] Reference 64. [h] Reference 63. [i] Reference 6a. [j] Reference 62.

C. Extension to Other Hydroporphyrins. Nickel(II) hydroporphyrins examined by RR spectroscopy now include *meso*-tetramethylchlorin,[27c] *cis*- and *trans*-(OEC) complexes (this work and ref 27c), methyl pyropheophorbides (trans at pyrroline ring D),[30,31] model corphinoids,[62] F-430 and its 12,13-diepimer (trans at the pyrroline rings, but different macrocyclic conformations),[63,64] and the *Methanobacterium thermoautotrophicum* methylreductase[64] (pyrroline stereochemistry and macrocyclic conformation *presumed* to be analogous with extracted F-430).

No clear consensus with respect to the overall IR spectral effects of pyrroline stereochemistry, macrocyclic conformation, or coordination number for these nickel(II) hydroporphyrins is yet possible (Table II). For example, the 1660-cm^{-1} ("ν_{10}") band of four-coordinate *cis*-Ni(OEC) is similar in frequency to "ν_{10}" of four-coordinate nickel(II) *trans*-pyropheophorbides and also to "ν_{10}" of the five-coordinate methylreductase enzyme (Table II). In contrast, the 1646-cm^{-1} "ν_{10}" band of four-coordinate *trans*-Ni(OEC) is similar to that of four-coordinate F-430 model compounds but differs from that of the tetracoordinate F-430 diepimer or that of the extracted F-430 macrocycle. Thus, the "ν_{10}" frequency of nickel(II) hydroporphyrins clearly varies considerably, depending upon as yet undefined details of macrocyclic structure.[65]

Resonance Raman frequencies of Ni(OEC) do not appear to be directly transferable to model nickel corphinoids. The complex variations in frequencies of nickel(II) hydroporphyrins with alteration of pyrroline stereochemistry, macrocyclic conformation, and coordination number undoubtedly indicate a need for more extensive work on structurally well-defined systems.

Conclusions

Comparative spectral analysis of cis- and trans complexes of planar Cu(OEC) and of S_4-ruffled Ni(OEC) demonstrates distinct electronic absorption, IR, and RR spectral patterns responsive to the pyrroline stereochemistry or the macrocyclic conformation,

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(58) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 3rd ed.; Chapman & Hall: London, 1975; Vol. I.

(59) (a) Fleischer, E. B. *J. Am. Chem. Soc.* **1963**, *85*, 1353–1354. (b) Moustakali, I.; Tulinsky, A. *J. Am. Chem. Soc.* **1973**, *95*, 6811–6815.

(60) The ~1020-cm^{-1} RR band, maximally enhanced with Q_y excitation, is only present in RR spectra of chlorins having the octaethyl-substituent pattern. It is also present in RR spectra of iron(II) octaethylisobacteriochlorin.[50]

(61) Ozaki, Y.; Kitagawa, T.; Kyogoku, Y. *FEBS Lett.* 1976, *62*, 369–372.

(62) (a) Shelnutt, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 4169–4173. (b) Crawford, B. A.; Findsen, E. W.; Ondrias, M. R.; Shelnutt, J. A. *Inorg. Chem.* **1988**, *27*, 1846–1848.

(63) Shiemke, A. K.; Eirich, L. D.; Loehr, T. M. *Biochim. Biophys. Acta* **1983**, *748*, 143–147.

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(65) The 1585- and 1660-cm^{-1} RR bands of *cis*-Ni(OEC) are closer to those of the methylreductase enzyme of *M. thermoautotrophicum* than are the RR bands of any nickel corphinoid model studied (Table II). One might then speculate that extraction of the F-430 macrocycle from the methylreductase enzyme results in alteration of the stereochemistry at one of the pyrroline rings.

or both. (1) The $\sim$740–750-cm^{-1} "ν_{15}" RR band (maximized with Q_y excitation) is sensitive to both pyrroline stereochemistry and to macrocyclic conformation: the *frequency* observed for *trans*-M(OEC) is greater than that of *cis*-M(OEC), whereas the *intensity* observed is greater for S_4-ruffled Ni(OEC) than for planar Cu(OEC). (2) The frequencies of bands in the $\sim$1150–1220-cm^{-1} IR spectra are sensitive to pyrroline stereochemistry: the C_b–H deformation modes of *cis*-M(OEC) are higher in frequency than those of *trans*-M(OEC). (3) Extension of the core size/RR frequency inverse correlation of metalloporphyrins to the -chlorins indicates sensitivity to both stereochemistry and macrocyclic conformation: RR frequencies of *cis*-M(OEC) are higher than those of *trans*-M(OEC); thus, *cis*-M(OEC) complexes have a smaller core size than *trans*-M(OEC). Similarly, RR frequencies of *cis*- and *trans*-Ni(OEC) are higher than those of the Cu(OEC) complexes; thus, S_4-ruffled Ni(OEC) complexes have a smaller core size than planar Cu(OEC) complexes. (4) The electronic absorption spectra of M(OEC) are also sensitive both to the stereochemistry at the pyrroline ring and to the macrocyclic conformation: the Q_y transitions of *cis*-M(OEC) are red-shifted from those of *trans*-M(OEC), whereas the Soret/Q_y intensity ratio of the planar Cu(OEC) complexes is greater than that of the ruffled Ni(OEC) complexes.

Thus, "local" structural modifications have a significant effect on both the vibrational modes of chlorins and their electronic absorption properties. Consequently, the influences of nonconjugated substituents and their conformation and stereochemistry, as well as the overall macrocyclic conformation of chlorins and other hydroporphyrins, should be considered in the analysis of their spectral properties.

Acknowledgment is made to the donors of the Petroleum Research Fund (L.A.A.), administered by the American Chemical Society, for partial support of this research. This work was also supported by the National Institutes of Health (Grant GM 34468 to T.M.L. and L.A.A. and Grant GM 33882 to A.M.S.) and by the Camille and Henry Dreyfus Foundation (Distinguished New Faculty Award to A.M.S.). We thank Professor James Kincaid for sharing unpublished data and Ron Shigeta for technical assistance.

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Synthetic Control of Excited-State Properties in Ligand-Bridged Complexes of Rhenium(I). Intramolecular Energy Transfer by an Electron-Transfer/Energy-Transfer Cascade

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Received August 15, 1989

In the series of complexes $[(4,4'\text{-}(X)_2\text{-}2,2'\text{-bpy})(CO)_3Re^I(4,4'\text{-bpy})Re^I(CO)_3(4,4'\text{-}(Y)_2\text{-}2,2'\text{-bpy})]^{2+}$ (X, Y = H, CH_3, NH_2, CO_2Et), the ultimate site of the excited electron following metal-to-ligand charge-transfer (MLCT) excitation has been studied by transient absorbance and emission spectroscopies in polar organic solvents. The electron-donating groups NH_2 and Me increase the energy of the π^* levels of the 2,2′-bpy ligand. They lead to localization of the excited electron on the bridging 4,4′-bpy ligand, as shown by the appearance of an absorption feature at 570–610 nm in CH_3CN in transient absorbance difference spectra. Electron-withdrawing CO_2Et groups lower the energy of the π^* levels and lead to localization of the excited electron on the 2,2′-bpy ligand, as shown by the appearance of a narrow transient absorption feature at 380–385 nm in CH_3CN. With X = Y = H, a solvent-dependent equilibrium exists between the 2,2′-bpy and 4,4′-bpy states. In the asymmetrical complexes with X = NH_2 or H and Y = CO_2Et, rapid ($k > 2 \times 10^8$ s^{-1}) intramolecular energy transfer occurs following Re → 4,4′-$(X)_2$-bpy MLCT excitation in CH_3CN. Intramolecular energy transfer continues to occur in a 4:1 (v/v) ethanol/methanol glass at 77 K. With 3,3′-$(Me)_2$-4,4′-bpy as the bridging ligand, the rate constant for energy transfer is far slower ($k < 4 \times 10^6$ s^{-1}), suggesting that energy transfer in the 4,4′-bpy bridged complex may occur by an electron-transfer/energy-transfer pathway.

Introduction

Ligand-bridged metal complexes have provided a useful basis for theoretical and experimental studies on light-induced intramolecular electron and energy transfer.[1,2] For example, in mixed valence complexes such as $[(NH_3)_5Ru^{II}(L)Ru^{III}(NH_3)_5]^{5+}$ or $[(bpy)_2ClRu^{II}(L)Ru^{III}Cl(bpy)_2]^{3+}$ (L is 4,4′-bipyridine (4,4′-bpy) or pyrazine (pz); bpy is 2,2′-bipyridine), the existence of light-induced electron transfer is evidenced by the appearance of intervalence transfer absorption bands.[3,4] In complexes such as $[(NH_3)_5Ru^{II}(pz)Ru^{III}(edta)]^5$ or $[(bpy)_2(CO)Os^{II}(4,4'\text{-bpy})Os^{II}(phen)(dppe)(Cl)]^{3+}$ (phen is 1,10-phenanthroline, dppe is *cis*-$Ph_2PCH{=}CHPPh_2$),[6] metal-to-ligand charge-transfer (MLCT) excitation is followed by electron transfer across the ligand bridge.[7,8]

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