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the incident microwave power was kept less than 10 mW (−13 dB) for the ESR measurement. The temperature was controlled by a Bruker VT4211 variable-temperature unit.

Determination of Association Constants, ΔH°, and ΔS°. Association constants were determined by assuming the following equilibrium:

$$R + CD \rightleftharpoons R\text{–}CD$$

where R, CD, and R–CD denote the probe, the cyclodextrin, and the inclusion complex, respectively. Thus the association constant is

$$K_a = [R\text{–}CD]/[R][CD] = (r_1/r_2)(C - R_0 r_1/(r_1 + r_2))^{-1}$$

whwere R_0 and C denote the initial concentrations of R and CD, and r_1 and r_2 show the relative concentrations of included and nonincluded species, respectively. R_0 was estimated to be less than 10^{-4} M from ESR intensity, which is much smaller than C. Thus, K_a is calculated by using $K_a = (r_1/r_2)/C$. The relative concentrations were determined by the area intensity measured from the spectrum simulation. Due to the difficulty in exact fitting of the simulated spectrum to that of observed, the maximum error estimated for r_1/r_2 is ±10%.

The temperature dependence of the association constants was observed from 290 to 340 K at every 10 K. ΔH° and ΔS° were determined by using a Van't Hoff plot of K_a at these temperatures.

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Ruffling of Nickel(II) Octaethylporphyrin in Solution

R. G. Alden,[†] B. A. Crawford,[†] R. Doolen,[†] M. R. Ondrias,[†] and J. A. Shelnutt[*,‡]

Contribution from the Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131, and Fuel Science Division 6211, Sandia National Laboratories, Albuquerque, New Mexico 87185. *Received August 15, 1988*

Abstract: Nickel(II) octaethylporphyrin (NiOEP) plays a central role in studies of the molecular properties of tetrapyrroles and tetrapyrrole-containing enzymes. NiOEP in noncoordinating solvents is found to be a mixture of planar and nonplanar, ruffled species. At 77 K in frozen solutions, the S_4 ruffled form is more prominent than at room temperature. The ruffled form is most prominent for laser excitation to the red of the Soret absorption maximum, suggesting that the ruffled form has a red-shifted Soret band. The presence of multiple forms coexisting in solution requires that normal coordinate analyses based on NiOEP spectra be reexamined.

Nickel(II) octaethylporphyrin (NiOEP) plays a central role in studies of the molecular properties of porphyrins and porphyrin-containing enzymes. NiOEP's importance stems from its use in isotopic substitution work for vibrational analysis of porphyrins[1-3] molecular orbital calculations,[4] X-ray crystallographic structural studies,[5-7] and many structural studies using a variety of spectroscopic techniques.[8] These fundamental studies have had a significant influence on the development of our understanding of metalloporphyrin structure and bonding. The work with the nickel derivative has taken on added significance with the recent discovery of an enzyme (methylreductase) that contains a nickel tetrapyrrole as a prosthetic group.[9]

One aspect of porphyrin structure that is of current interest is the propensity for forming nonplanar structures. These nonplanar ruffled, domed, or flexed conformations may influence many chemical and photochemical properties of porphyrins in biological reactions. Specifically, nonplanar conformations have been proposed to play a role in reactions catalyzed by vitamin B_{12},[10] in the function of cofactor F_{430} in methylreductase,[11] and in the photophysics of tetrapyrrole pigments of photosynthetic reaction centers.[12]

Nickel octaethylporphyrin is known to crystallize in three dramatically different structures, one of which is nonplanar.[5-7] Consequently, NiOEP again provides an interesting test case for studies of nonplanar porphyrin macrocycles. Two of the NiOEP structures are planar triclinic forms (here designated A and B),[7] and the third is a ruffled tetragonal form. The most striking difference between the triclinic and tetragonal forms is the pronounced nonplanarity of the macrocycle in the tetragonal form. The methine bridge carbons are 0.5 Å out of the mean macrocycle plane. There is a marked S_4 symmetry ruffling of the macrocycle wherein adjacent pyrrole rings are tilted in opposite directions with respect to the mean plane of the pyrrole nitrogens. The ruffling effectively reduces the molecular symmetry from D_{4h} to D_{2d}. The angle between adjacent pyrrole planes is 32.8° for the tetragonal structure, but only 2.1° for the triclinic A structure.[5]

Single-crystal resonance Raman spectra clearly distinguish among the three crystalline forms.[7,13] In particular, differences in the frequencies of the Raman core-size (center-to-nitrogen-(pyrrole) distance) marker lines are observed.[13] Further, previous resonance Raman results have shown that the frequencies of the Raman core-size marker lines of NiOEP in noncoordinating solvents are closest to those of the Raman spectrum of the triclinic forms, indicating that NiOEP is planar in solution.[13]

We present new resonance Raman spectra of NiOEP obtained in noncoordinating solvents at 295 K and at 77 K, using a variety of excitation wavelengths near resonance with the Soret absorption

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[†] University of New Mexico.

[‡] Sandia National Laboratories.

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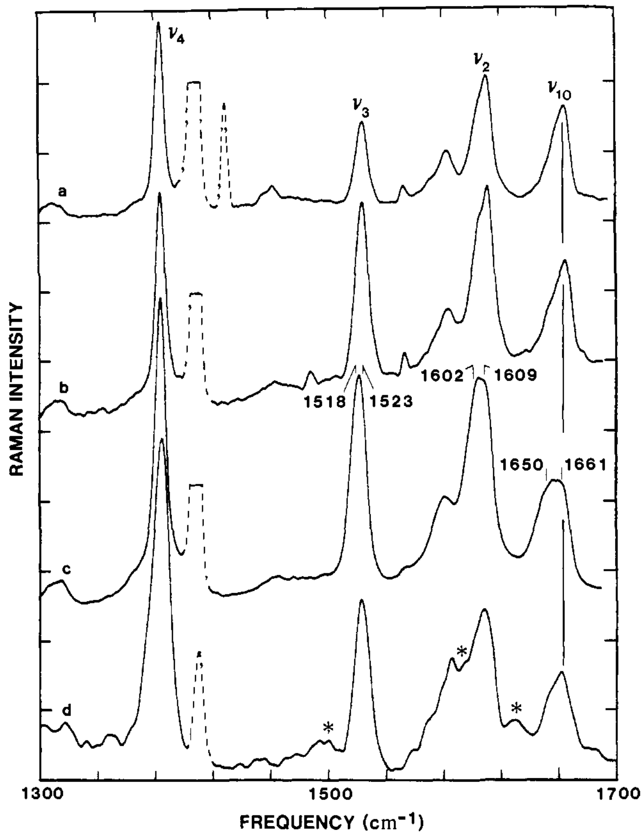

Figure 1. Raman spectra of NiOEP in methylene chloride at 77 K taken with excitation at (a) 441.6 nm, (b) 413.1 nm, (c) 406.7 nm, and (d) 392 nm. The spectrum obtained with 392-nm excitation shows evidence (new lines at approximately 1630, 1590, and 1495 cm^{-1} and broadening of ν_4) of formation of a transient d–d excited state even at low peak power for the pulsed dye laser.[26]

band at 393 nm. The new Raman spectra indicate the presence of temperature-dependent shoulders on the low-frequency side of each of the core-size marker lines. We interpret these shoulders to indicate the presence of multiple conformations of NiOEP in solution. The presence of multiple forms at room temperature suggests that previous vibrational analysis work based on nickel octaethylporphyrin may require reinterpretation. This is particularly true for the low-frequency portion of the spectrum where large differences in frequencies of the Raman lines are noted.[7]

Materials and Methods

NiOEP was purchased from Porphyrin Products and further purified by column chromatography on alumina. Benzene and methylene chloride were obtained from Aldrich Chemicals. The sample integrity and purity was monitored by absorption spectra and individual scans of the signal averaged Raman spectra. No free-base impurity, other contaminants, or aggregation effects were observed in the absorption spectra obtained either at room temperature or at 77 K. The absorption spectra were obtained with commercial UV–visible–near IR (Perkin-Elmer Model 330 or Hewlett-Packard Model 8452) spectrophotometers.

Raman spectra of NiOEP in methylene chloride were obtained by using spectrometers described previously.[14,15] The room-temperature solutions were contained in a cylindrical cell partitioned into two compartments and rotated at 100 Hz. The solutions contained in each compartment are alternately probed by the laser, and the photon counts are gated from each sample. In this way, the Raman spectra of the two solutions are generated simultaneously. In this case a NiOEP solution was in one chamber, while the second chamber housed the neat solvent. Subtraction of the solvent Raman spectrum could then be accurately accomplished. Raman spectra obtained at 77 K were obtained on the difference spectrometer used in the conventional ungated mode of operation. An EPR tube containing the NiOEP sample was maintained at 77 K by using an EPR dewar (Wilmad) filled with liquid nitrogen.

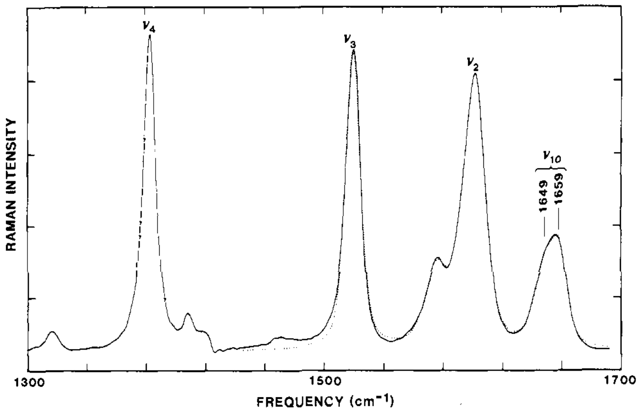

Figure 2. Raman spectrum of NiOEP in methylene chloride at 295 K taken with 406.7-nm excitation (solid line). The fit for the Voigt decomposition of the peaks is also shown (dotted line). The least-squares fit assumes only seven lines, two each in the region of the ν_2 and ν_{10} spectral features. The low-frequency component of ν_{10} (1659 cm^{-1}) is found at 1649 cm^{-1}. The lines are about 50% Gaussian.

Excitation of the samples was accomplished by using either the 441.6-nm line of a He Cd laser (Omnichrome), the 413.1- and 406.7-nm lines of a Kr$^+$ laser (Coherent), or 392-nm radiation of a 10-ns, N$_2$-laser pumped dye laser (Molectron). The spectral resolution was 4 cm^{-1} or better.

Results and Discussion

Figure 1 shows the Raman spectra of NiOEP obtained at 77 K by using four different excitation frequencies near the Soret absorption region. It is clear that low-frequency shoulders occur for ν_3 (1523 cm^{-1}), ν_2 (1609 cm^{-1}), and ν_{10} (1661 cm^{-1}). The low-frequency shoulders are resonantly enhanced the most at 406.7-nm excitation (Figure 1c), where they are almost equal in intensity to the main peak. The positions of these shoulders correlate well with the Raman spectra of the tetragonal form, although they are somewhat higher in frequency. For the tetragonal form, ν_3, ν_2, and ν_{10} are located at 1514, 1595, and 1641 cm^{-1}, respectively.[7] (The line identified as ν_{19} is a mixture of ν_{19} and ν_2 at 501.7-nm excitation. The frequencies of ν_2, observed for the crystals with Soret excitation at 406.7-nm, are the same as reported[7] for ν_{19} within experimental error.)

Curve fitting with Voigt line shapes gives estimates of 1518, 1602, and 1650 cm^{-1} for the shoulders.[16] The marker line region of the spectra was decomposed into component Lorentzian–Gaussian lines (Voigt line shapes, for which the amount of Gaussian character was allowed to vary) by using a nonlinear least-squares program in which the frequency, peak intensity, and line width were varied. The flat background was also allowed to vary. The Gaussian contribution to the lines was typically 50 ± 10%. This is surprising in view of the fact that Raman lines under these experimental conditions routinely contain only about 5% Gaussian character. The strong Gaussian character suggests that multiple nonplanar conformational substates exists. Also, the distribution of conformations is large for the ruffled form based on the broader line width required to fit the low-frequency shoulders. Errors in the peak positions are estimated to be less than 0.5 cm^{-1} for the data cited.

It is also noted that ν_4 at 1382 cm^{-1} has a line width of 10 ± 1 cm^{-1} and shows no appreciable broadening or asymmetry even at 406.7-nm excitation. This behavior is consistent with the ruffling interpretation since ν_4 has virtually the same frequency for both the tetragonal (1383 cm^{-1}) and triclinic crystalline forms (A, 1380 cm^{-1}; B, 1383 cm^{-1}).[7] Thus, only one narrow (~10-cm^{-1}) line would be detected for a mixture of the two forms.

The Raman data shown in Figure 2 demonstrate that the ruffled NiOEP solution form is less prominent at room temperature, based on the decreased intensity of the shoulders on ν_3, ν_2, and ν_{10} for the 406.7-nm spectrum. The fit for the Voigt decomposition of

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the lines is also illustrated in Figure 2. The two components of ν_{10} are separated by 10 ± 1 cm^{-1}, in agreement with the low-temperature data.

An interpretation based on a core-size difference rather than a difference in planarity of the macrocycle is unlikely because the shifts in ν_3, ν_2, and ν_{10} (−5, −7, −11 cm^{-1}) of the ruffled form relative to the planar form in solution are proportional to the shifts of the tetragonal crystalline form relative to either the triclinic A form (−7, −11, −18 cm^{-1}) or the B form (−11, −13, −21 cm^{-1}). Also, the shift in ν_2 is larger than the shift in ν_3. In contrast, the shifts predicted from an increase in core size are smaller for ν_2 than for ν_3;[17] thus, the observed pattern of shifts in the core-size markers favors the ruffling interpretation. The differences in core-size marker line frequencies for the two solution forms comprise 50–70% of the differences observed for the two crystalline forms. The smaller frequency differences observed in solution suggest that the degree of ruffling is less in solution.

The enhanced contribution from the ruffled form at 406.7 nm indicates a red shift in the Soret absorption maximum for the ruffled form of NiOEP, relative to the absorption maximum of the planar solution form at 393 nm. Although we have not detected a shoulder in the absorption spectrum at 295 K or at 77 K, iterative extended Hückel calculations for the planar and the ruffled structures predict a red shift for the Soret and α bands of 410 and 360 cm^{-1}, respectively. IEH MO calculations were carried out with a program provided by M. Gouterman and E. R. Davidson. The molecular geometries used were those of the triclinic A and tetragonal crystal structures. The shift in the positions of the observed Q (α) and B (Soret) transitions was determined by using the predicted energies of the four frontier orbitals (a_{1u}, a_{2u}, and $e_g{}^*$). The shifts were calculated by the method of Gouterman[18] and Shelnutt.[19] The primary effect of ruffling is destabilization of all of the frontier orbitals. In detail, both the a_{1u} and a_{2u} orbitals are destabilized more than the $e_g{}^*$, so that the separation between the HOMOs and LUMOs is smaller for the ruffled structure. This accounts for the red shift in the spectrum.

The full implication of ruffled conformations on nickel–tetrapyrrole chemistry is unclear at present. Multiple forms have recently been detected in nickel tetrapyrroles related to cofactor F_{430}.[22,23] Native F_{430} is expected to be more planar than its heat-extracted form, the 12,13-diepimer.[11,24] It is thought that the degree of planarity in these two F_{430} forms determines their relative axial ligand affinities[11] and may affect other properties including catalytic activity. An increased degree of ruffling can also explain the observed differences in the dynamics of axial ligand photodissociation for the reduced nickel tetrapyrroles (such as the F_{430} model compound)[23,25] compared with the more planar nickel porphyrins.[26]

In particular, for NiOEP the presence of multiple forms at room temperature strongly suggests that a reinterpretation of previous work on the vibrational analysis of porphyrins may be necessary, especially since NiOEP has been used as a reference structure. Because of the existence of multiple forms in solution and because of the large differences between the low-frequency vibrations of the tetragonal and triclinic forms,[7] some vibrations may have been identified incorrectly in the past. Also, the existence of a ruffled equilibrium conformation suggests that a normal coordinate analysis based on the nonplanar structure might aid in assignment of the out-of-plane vibrational modes.[3] The existence of both planar and ruffled species in solution also explains some of the anomalous spectroscopic behavior of nickel porphyrins that occurs upon aggregation[27] and upon π–π complex formation.[28]

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New Molecular Hydrogen Iron(II) Complexes: Synthesis, Characterization, and Reactivity with Aryldiazonium Cations

Gabriele Albertin,* Stefano Antoniutti, and Emilio Bordignon*

Contribution from the Dipartimento di Chimica dell'Università di Venezia, Dorsoduro 2137, 30123 Venice, Italy. *Received April 29, 1988*

Abstract: Dihydrogen complexes of the type $[FeH(\eta^2\text{-}H_2)P_4]BPh_4$ [P = $PhP(OEt)_2$ and $P(OEt)_3$] were prepared by allowing the dihydride FeH_2P_4 to react at −80 °C with $HBF_4{\cdot}Et_2O$ in ethanol. Variable-temperature ^1H and $^{31}P\{^1H\}$ NMR spectra and T_1 measurements of the complexes are reported. Ligand-substitution reactions with CO, isocyanide, nitrile, and phosphite afforded the new monohydrides $[FeHLP_4]BPh_4$ [L = CO, $4\text{-}CH_3C_6H_4NC$, $4\text{-}CH_3OC_6H_4NC$, $4\text{-}ClC_6H_4NC$, $2,6\text{-}(CH_3)_2C_6H_3NC$, $4\text{-}CH_3C_6H_4CN$, $CH_3(CH_2)_2CN$, $P(OEt)_3$, and $PhP(OEt)_2$]. Furthermore, the reactivity with aryldiazonium cations of both molecular hydrogen $[FeH(\eta^2\text{-}H_2)P_4]^+$ and hydride $[FeHLP_4]^+$ derivatives was examined and led to the synthesis of bis(aryldiazenido) $[Fe(ArN_2)_2P_3]^{2+}$ (Ar = $4\text{-}CH_3C_6H_4$ and $4\text{-}CH_3OC_6H_4$) and monodiazene $[Fe(ArN{=}NH)LP_4]^{2+}$ (L = nitrile) complexes, respectively. Their characterization by infrared, ^1H, and $^{31}P\{^1H\}$ NMR data is also reported.

There has recently been considerable interest in the chemistry of dihydrogen complexes of the transition metals, not only because they may serve as models for the important process of oxidative addition of the dihydrogen, but also because of their relevance

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