Figure 4. Dependence of $k_q - k_{en}$, where this is equal to the rate constant for quenching due to electron transfer on $\Delta G^{\ominus}_{el}$, the free-energy change for electron transfer from the triplet donor to $Cr(hfac)_3$.

a correlation as expected, and thus from the rate constant obtained for the quenching of triplet β-carotene and Figure 4 one obtains an estimate of E_D^{ox} for β-carotene equal to 0.35 ± 0.03 V (vs. SCE). This estimate for the half-wave oxidation potential of β-carotene agrees within experimental error with the value of 0.39 ± 0.04 V obtained from eq 15. This work demonstrates that charge-transfer quenching of excited states could occur in addition to energy-transfer quenching for carotenoids in many biological systems. It is worth noting that electrochemical measurements on β-carotene have revealed only two-electron oxidation for which the reported oxidation potentials are 0.51[49] and 0.74 V[50] in acetonitrile and benzene (2:1 vol) and in vigorously dried tetrahydrofuran, respectively.

Figure 4 and Table IV demonstrate that the electron-transfer part of the quenching constant correlates well with $\Delta G^{\ominus}_{el}$, the free energy for electron transfer as estimated from oxidation and reduction potentials of the donors and $Cr(hfac)_3$, respectively. The best fit to the experimental data for the "intrinsic barrier", $\Delta G^{\ominus \ast}_{el}(0) = 0.16$ eV, lies between the values for the intrinsic barriers for energy transfer to Cr(III) β-diketonates which are ~ 0.03 and ~ 0.25 eV for energy transfer to the nondistorted ^2E_g state and the highly distorted $^4T_{2g}$ excited states, respectively. It is interesting to note that the transmission coefficient for electron transfer, $\kappa_{el} = 0.016$, is three times that for energy transfer to produce the ^2E_g state which reflects the more stringent orbital overlap requirements for exchange energy transfer to produce the metal-centered ^2E_g state.

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Correlation between Metal Stability, Charge Transfer, and Raman Frequencies in Metalloporphyrins and Their π–π Complexes[†]

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Abstract: The frequencies of the Raman core-size and oxidation-state marker lines of metalloporphyrins are found to be related to the electronegativity and ionic radius of the metal ion. The frequencies correlate with a stability index for the metalloporphyrins toward acid demetalation that is based on these properties. Higher electronegativity and smaller ionic radius of the metal increase conjugation of the $a_{2u}(\pi)$ orbital with the metal $4p_z$ orbital. The result is to lower the charge density and energy of the $a_{2u}(\pi)$ orbital. Stabilization of the $a_{2u}(\pi)$ orbital, which mainly affects charge density at the meso carbons and pyrrole nitrogens of the macrocycle, apparently increases the C_m-C_α stretching force constant and, therefore, accounts for the metal-dependent shifts in the Raman lines. The pattern of shifts in the core-size and oxidation-state marker lines observed when phenanthroline binds to metalloporphyrins is strikingly similar to the shifts induced by metal substitution. Raman difference spectroscopy shows that phenanthrolines form π–π donor/acceptor complexes with metallouroporphyrins in water. The $a_{2u}(\pi)$ orbital is the highest occupied molecular orbital of the macrocycle and is expected to be the principal donor orbital in a π–π charge-transfer complex. The Raman line shifts are entirely consistent with phenanthroline accepting charge density from the $a_{2u}(\pi)$ orbital. Moreover, these dissimilar phenomena affect the same porphyrin orbital, so the metal ion can easily modify the effect of π–π complexation, thus explaining both the similarity in the pattern of Raman line shifts and the effect of the metal on the shifts induced by complexation.

The mechanisms by which reactants are catalytically activated by metalloporphyrins are not well understood in either biological or other chemical reactions. A molecular basis of catalytic activation and control must include an understanding of the function of intermediate complexes in the activation process and, in particular, an understanding of the role of the various interactions that stabilize these molecular complexes.

Many of the reactions catalyzed by the metalloporphyrins are redox reactions, so an understanding of the role of charge transfer in these molecular complexes is paramount. In this regard the effects on ligation of cis electron-withdrawing substituents on the macrocycle and of trans axial ligands at the metal site have been examined.[1–4] Charge-donating groups at the porphyrin periphery

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influence the σ-donor and π-acceptor properties of the metal d orbitals and thus affect ligand binding.[1-4] Similarly, a sixth metal ligand affects the charge density in the d orbitals of the metal and consequently influences the charge transfer to and reactivity of a trans ligand of the metal.[1]

Recently, porphyrins and metalloporphyrins have been found to form π–π complexes with many aromatic heterocycles in an aqueous environment.[5-8] The metalloporphyrins are known to catalytically activate aromatic rings in redox reactions,[9] and so charge transfer between the two ring systems in the π–π complex might lower the transition state in which a whole electron is transferred and, thus, influence catalytic activity.

Previous work has demonstrated the role of charge transfer in some of these molecular complexes. In particular, Shelnutt[6-8] found shifts in two Raman lines of the porphyrin macrocycle that correlate with the acceptor properties of a series of substituted phenanthrolines (phen). These two plus another of the Raman lines shift to higher frequency for the phenanthroline complexes and were identified previously as marker lines of the oxidation state of the metal for iron(II, III, and IV) porphyrins,[10-12] as ring electron-density marker lines in a series of iron(II) porphyrin-bis-axial ligand complexes,[13,14] and as ring oxidation-state marker lines in the VO and Zn porphyrin π anions.[15]

The structure of the metallouroporphyrin (MURO) complexes with the phenanthrolines seems to have the ring systems stacked. The evidence for this geometry as opposed to axial ligation of the nitrogen lone pair at the metal is as follows: (1) The 2,9-dimethylphenanthroline complex gives shifts in the Raman lines that are expected on the basis of the acceptor ability of this derivative in spite of its possession of sterically hindered nitrogen lone pairs that prevent axial ligation. (2) The binding energy (ΔG) for the phen–CuURO complex (4.2 kcal/mol) is approximately equal to ΔG for the phen–Fe^{III}URO complex (4.4 kcal/mol), and ΔG is only slightly less for the complex with metal-free uroporphyrin (3.5 kcal/mol). (3) The metal has no effect on ΔG for the 2,9-Me$_2$phen complexes (4.5 kcal/mol) with CuURO and FeURO. (4) Phenanthroline derivatives that are sterically hindered from lying flat on the porphyrin ring do not fall on the linear relationship that is observed for the unhindered derivatives, i.e., the correlation between the acceptor properties (the sum of Hammett constants for the phen substituents) and the shifts in the Raman lines. (5) Preliminary NMR results have confirmed that the complexes do not involve interaction with the metal (Fe^{III}) in solution.[16]

Although the interaction of the lone pairs on the nitrogens of phenanthroline with the metal ion could be ruled out by the above arguments, different metal atoms in the porphyrin core do affect the pattern of shifts in the Raman lines.[7,8] In an effort to understand the effect of the metal on the electronic structure of the porphyrin in π–π molecular complexes with the phenanthrolines, these complexes were studied for a variety of metal porphyrins by Raman difference spectroscopy (RDS).[6-8,17-21] The complexes

Table I. Metallouroporphyrin Raman Line Frequencies and Shifts[a] on Formation of Complex with 1,10-Phenanthroline in 0.1 N NaOH[b]

CuURO		NiURO		Fe^{III}URO		CoURO	
ν	Δν	ν	Δν	ν	Δν	ν	Δν
1310	0.2	1300	1.4	1307			1309	-0.4
1379	0.4	1383	0.4	1376	0.6		
1403		1406		1402		1402	>0
1499	1.9	1518	2.9	1489	2.0^c	1510	4.0
1582	>0	1602	2.8	1581	>0	1598	3.0
1637	2.0	1656	5.3	1627	2.0^c	1647	4.4

[a] Corrected for incomplete formation. [b] ν (cm^{-1}) is the frequency of the uncomplexed MURO and Δν is the shift on binding 1,10-phen. [c] Slight line shape change may make calculated shifts larger than the actual shifts.

of phenanthroline with copper(II), nickel(II), cobalt(II), iron(III), and free-base uroporphyrin are compared. Differences in the shifts in the Raman lines of the porphyrin for these metalloporphyrin-phenanthroline complexes are related to differences in the electronic structure of the porphyrin ring that are brought about by differences in the metal–porphyrin bond. In addition, the frequencies of three Raman lines, previously identified as oxidation-state marker lines, are found to be a monotonic function of the σ-electron density in the macrocycle (and roughly the π-electron density).

Materials and Methods

The metallouroporphyrins were obtained commercially (Porphyrin Products) and further purified by column chromatography.[6-8] The Raman and absorption measurements were performed on solutions of the metalloporphyrin (≲5 × 10^{-5} M) in either 0.1 N NaOH or 50 mM Tris buffer (pH 7.8).

The instrumentation for Raman difference spectroscoy has been previously described.[7,19,20] Briefly, a spinning partitioned Raman cell allows the Raman spectrum of two similar samples to be collected simultaneously so that accurate comparisons of the frequencies can be made. For example, one side of the cell might contain the metalloporphyrin–phenanthroline complex and the other compartment might contain the metalloporphyrin. The frequency shifts resulting from complex formation are determined from the difference spectrum.[7,19,20] The errors in the reported frequency shifts are no greater than 0.2 cm^{-1} and typically are ±0.1 cm^{-1}.

Results and Discussion

Table I gives the frequencies of the Raman lines of the uncomplexed metalloporphyrins and the shifts in these lines that occur for the different metallouroporphyrin–phenanthroline complexes. First, note that the shifts in the Raman lines are to higher frequency for the complex for almost all lines. This pattern of shifts is general, since of eight other Raman lines of CuURO not listed in Table I, only three (at 752, 1102, and 1245 cm^{-1}) shift to lower frequency. This general pattern of shifts is expected when electron density in an aromatic π-electron system is modified. It is significant that the three oxidation-state marker lines at 1379, 1499, and 1637 cm^{-1} in CuURO always shift to higher frequency for the phenanthroline complexes.

The significance of the positive shift in this group of Raman lines on complex formation can be established from a study of the metal-dependent shifts in these lines of the uncomplexed metalloporphyrins. When the frequencies of the oxidation-state marker lines are compared for the different metal porphyrins, we observe that the frequencies of these lines vary as a group. The absorption bands of the metalloporphyrin also shift systematically

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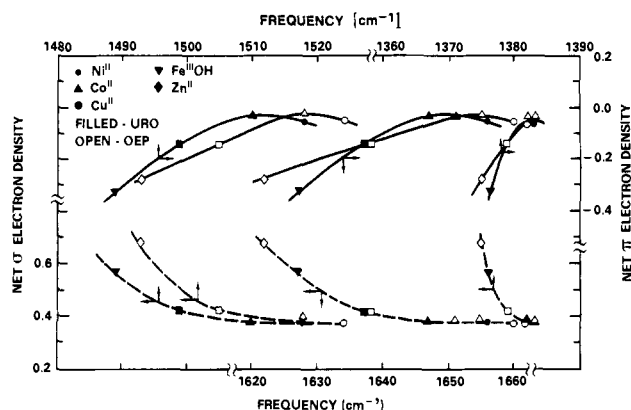(20) Rousseau, D. L. *J. Raman Spectrosc.* **1981**, *10*, 94.

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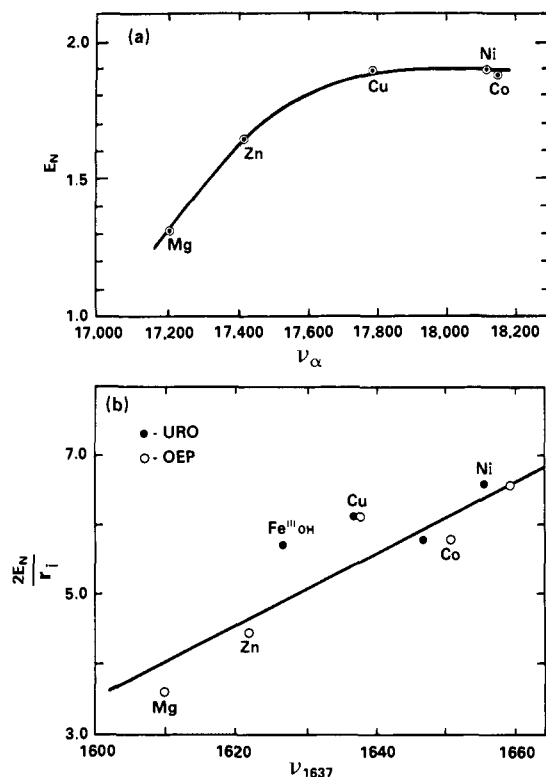
Figure 1. (a) The relationship between electronegativity E_N of the central metal and the frequency of maximum absorbance of the α band of metallouroporphyrins. (b) Linear correlation between Buchler's stability index ($=ZE_N/r_i$) and the frequency of the 1637-cm^{-1} core-size and oxidation-state marker line. Raman frequencies other than from the present work were taken from ref 6–8 and 22.

Figure 2. Relationships between frequencies of the 1379-, 1499-, and 1637-cm^{-1} Raman lines (CuURO) for uroporphyrins and octaethylporphyrins and the calculated π- (top) and σ- (bottom) electron densities. The electron densities were obtained from MO calculations published by Gouterman and co-workers.[31-33]

as the metal ion is varied, so it is useful to look for a connection between these spectroscopic changes. Indeed, Kitagawa et al.[22] have noted that the frequencies of several Raman lines of metallooctaethylporphyrins correlate well with the frequency of the α-band absorption. This relationship holds for the series of metals Mg^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, and Ni^{2+}, and it is also valid for the 1499-, 1582-, and 1637-cm^{-1} lines of the metallouroporphyrins as well.

The metal ion influences the absorption bands of the porphyrin by interaction with its frontier orbitals. For example, the α band, which corresponds to the $\pi \rightarrow \pi^*$ transition from the highest occupied porphyrin orbitals $a_{1u}(\pi)$ and $a_{2u}(\pi)$ to the unoccupied $e_g(\pi^*)$ orbital, could be shifted by differences in the interaction of the metals with any of these orbitals. Several workers[22-24] have pointed out that the frequency of the maximum of the α-band absorption ν_α is proportional to the electronegativity of the metal ion. Figure 1a shows that this relationship roughly holds for the Mg, Zn, Cu, Co, Ni series but is apparently not linear. Considering the symmetry of the frontier orbitals, Gouterman[24] concluded that it is increased conjugation of the metal with the porphyrin ring that lowers the energy of the $a_{2u}(\pi)$ orbital relative to the $e_g(\pi^*)$ orbital, thereby causing the shifts of the absorption bands to higher frequency for the more electronegative metals. This stabilization of the $a_{2u}(\pi)$ orbital would lower the bond energies of the porphyrin ring and would likely increase the force constants of ring vibrations. Stronger conjugation with the unoccupied metal p_z orbital also lowers the charge density in the $a_{2u}(\pi)$ orbital. Since the $a_{2u}(\pi)$ orbital has electron density mainly on the meso carbons and pyrrole nitrogens, it is reasonable that vibrations associated with bonding to these atoms are most affected. It is interesting that the vibrations at 1499, 1582, and 1637

cm^{-1} are the ones that primarily involve C_α–C_{meso} stretching;[25] these lines show the largest shifts.

The 1499-, 1582-, and 1637-cm^{-1} lines (of CuURO) are also markers of the size of the core of the porphyrin.[26] As well-characterized marker lines of the structure of the metal site in the porphyrin, it is not unexpected that they would reflect differences in the metal–porphyrin bond. The 1582-cm^{-1} line increases in frequency along the series $Fe^{III}OH < Cu < Co < Ni$ by 21 cm^{-1}. The correlation between the frequency of the 1582-cm^{-1} Raman line and the core size[26] indicates a reduction in the center-to-nitrogen (pyrrole) distance by 0.04 Å in the series. A decrease in core size might be expected as the metal–porphyrin bond becomes more covalent. A decrease in core size is also consistent with the "tightening" of the porphyrin ring evidenced by the increase in the force constants of roughly 75% of the Raman active vibrational modes. For the more electronegative metals, it appears that stronger conjugation between the metal $4p_z$ orbital and the $a_{2u}(\pi)$ orbital allows the π electrons to be more delocalized, consequently leading to stronger coordination to the metal as well as stronger bonds in the porphyrin macrocycle.

Stronger coordination to the metal should be reflected in the resistance of the metalloporphyrins to demetalation. Indeed, Buchler[27] has suggested that the resistance to demetalation by protic acids can be described by a stability index $S = (Z/r_i)E_N$ where Z/r_i, the charge-to-ionic radius ratio, describes the ionic-bonding ability and E_N the covalent-bonding ability of the metal. The order of the stability index for the metal–porphyrin bond is $Mg < Zn < Fe^{III}OH \lesssim Co < Cu < Ni$. Therefore, a roughly linear correlation of the stability index with the frequencies of the 1637-cm^{-1} Raman line exists for these metals and is illustrated in Figure 1b. The wavelength (or ν_α) of the lowest-energy absorption band has also been suggested[23,28-30] as a spectral measure of stability of the metal–porphyrin bond, so the correlation[22] between ν_α and the frequency of the core-size marker lines for the metal–porphyrin complexes should not be unexpected for metals with constant Z.

Since the 1499- and 1637-cm^{-1} Raman lines as well as the line at 1379 cm^{-1} are oxidation-state marker lines and since they also depend on electron density in the ring in some cases, it was thought that the metal atom itself might modify the electron density in the ring in a systematic manner that would be reflected in the molecular-orbital calculations. The σ- and π-electron densities

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in the macrocycle can be obtained from published[31-33] iterative extended Hückel MO calculations for the transition-metal complexes. Figure 2 shows a plot of the frequencies of the three oxidation-state marker lines as a function of the calculated π- (top) and σ- (bottom) electron densities for several metalloporphyrins. Published[26] Raman frequencies for the metal octaethylporphyrins are also plotted. It is clear that the frequencies of the oxidation-state marker lines are monotonic functions of the σ-electron density. The 1499- and 1637-cm^{-1} lines show a stronger dependence on electron density than the 1379-cm^{-1} line. (Also note the apparent constant increase (6–8 cm^{-1}) in the frequency of the 1499-cm^{-1} line for the octaethylporphyrins relative to the corresponding metal uroporphyrin derivatives.) The frequencies roughly follow the π-electron density as well. However, the frequencies do not correlate with *total* electron density, since Zn falls well off any possible curve.

From Figure 2 one can see that the frequency of the three Raman lines increases with increasing covalency of the metal–porphyrin bond. The calculated electron densities reflect the degree of covalency through an increase of σ donation to the metal and a concomitant increase in π acceptance by the porphyrin in the series Zn < Fe^{III}OH < Cu < Co $\lesssim$ Ni. The electron densities for two other metalloporphyrins, Mg[33] and VO,[32] as well as various Fe^{II} and Fe^{III} axial ligand complexes, have also been calculated. The point for magnesium porphyrin, which does not have d and $3p_z$ electrons, falls off the 1379-cm^{-1} line curve but close to the extrapolated curves for the other two Raman lines. The electron densities for the magnesium and iron porphyrins are very sensitive to axial ligation and axial ligands were not included in the Mg calculations. Vanadylporphyrin does not obey the relationship shown in Figure 2, but the correct distance of VO from the ring plane was not known at the time the calculation was done and the electron densities may be sensitive to the out-of-plane distance.

In changing from one metal in the porphyrin to another, the change in the frequency of the 1379-cm^{-1} Raman line is always smaller than the change in the 1637-cm^{-1} line. For example, the $\Delta\nu_{1379}$ (Fe^{III}OH → Cu) is 3 cm^{-1}, whereas $\Delta\nu_{1637}$ (Fe^{III}OH → Cu) is 10 cm^{-1}; the ratio is 3.3. For the Cu → Ni substitution $\Delta\nu_{1379}$ is 4 cm^{-1} and $\Delta\nu_{1637}$ is 19 cm^{-1}, and the ratio is 4.8. In addition, the ratio tends to increase in the order Fe^{III}OH → Cu → Ni for the metal-dependent shifts. The frequency of the 1379-cm^{-1} Raman line, which is predominately the C$_\alpha$–N(pyrrole) stretch,[25] is commonly used as a marker of electron density in the e$_g(\pi^*)$ orbitals of the porphyrin ring.[13] Shifts to higher frequency in this line result from lower electron density in the e$_g(\pi^*)$ antibonding orbital. If the above discussion relating the shifts in the core-size marker lines primarily to the depletion of electron density from the ring a$_{2u}(\pi)$ orbital is correct, then it is not surprising that the shifts in the 1379-cm^{-1} line and the core-size marker lines are considerably different. Clearly for these metalloporphyrins the dominant effect of metal substitution is to change the density in a$_{2u}(\pi)$ by interaction with the 4p$_z$ metal orbital. This trend is also seen in Gouterman's MO calculations.[31] The result is larger shifts in the core-size marker lines than in the 1379-cm^{-1} line. The 4p$_z$ orbital does not have the proper symmetry to interact with the e$_g(\pi^*)$ orbitals, so either there is a smaller effect of the electron density in the a$_{2u}(\pi)$ orbital on the 1379-cm^{-1} vibration or there is a weak interaction between the metal d$_\pi$ orbitals and the e$_g(\pi^*)$ orbitals that is systematically influenced by the electronegativity of the metal.

Amazingly, the metal ion also seems to control the relative magnitudes of the Raman shifts observed on formation of the π–π complex with phenanthroline. The ratios of the shifts on complexation for the 1637- and 1379-cm^{-1} lines ($\Delta\nu_{1637}/\Delta\nu_{1379}$) are 3.3 for Fe^{III}URO, 5.0 for CuURO, 13.3 for NiURO, and >10 for CoURO. Thus, the order of increasing $\Delta\nu_{1637}/\Delta\nu_{1379}$ is Fe^{III}OH < Cu < Co $\approx$ Ni.

The striking similarity between the metal-dependent shifts and the smaller shifts on formation of the phen complex suggests a common interpretation for the two seemingly unrelated phenomena. The a$_{2u}(\pi)$ orbital must lose electron density to explain the shifts of the core-size marker lines on binding phen. Therefore, either (1) an interaction between a π *orbital* of phen and the p$_z$ orbital of the metal increases its apparent electronegativity by removing charge (and increasing the conjugation between the metal and the porphyrin ring) or else (2) the phen molecule interacts directly with the a$_{2u}(\pi)$ orbital, or both interactions may occur. Either interaction would lower the a$_{2u}(\pi)$ orbital and decrease its electron density. Since π-electron density is removed in either case, this is consistent with phen acting as an acceptor and would also explain the correlation between the acceptor ability of a series of phen derivatives and $\Delta\nu_{1637}$.[6-8]

In summary, regardless of whether the metal or porphyrin ring interacts with phen, it is clear that the effect on the vibrational frequencies is identical with the effect of changing the metal ion to one with a higher electronegativity. Complex formation, like changing metals, appears to decrease σ-electron density and to increase π-electron density in the macrocycle, that is it increases the covalency of the metal bond to the ring. In both cases, increased covalency strengthens the metal–porphyrin bond and decreases the core size, thereby enhancing the overlap between the a$_{2u}(\pi)$ orbital and the metal 4p$_z$ orbital. The interaction of the filled porphyrin orbital with the empty metal orbital stabilizes and lowers the charge density of the a$_{2u}(\pi)$ orbital. Evidently this electronic redistribution raises the force constants of the methine bridge carbon–carbon stretching vibrations and hence the frequencies of the core-size marker lines.

Therefore, an interaction of phenanthroline with the a$_{2u}(\pi)$ orbital of the macrocycle that is further modulated by the metal–porphyrin interaction seems likely. When phenanthroline complexes with the porphyrin, the electron density and energy of its donor a$_{2u}(\pi)$ orbital decreases, as was the case for a more electronegative metal. A direct interaction of phenanthroline with the porphyrin moiety seems reasonable. However, an interaction between phen and the metal that increases the apparent electronegativity of the metal cannot be dismissed, although such a mechanism seems inconsistent with the strong binding of phen to free-base uroporphyrin and with its lack of sensitivity to the electronic configuration of the transition metals. In either case the phen molecule is parallel to the porphyrin ring.

Although there is great similarity in the effects of metal substitution and phen binding on the Raman frequencies, the effect on the absorption spectrum is quite different. For metal substitution, the frequencies of the 1499-, 1582-, and 1637-cm^{-1} Raman lines are proportional to the frequency of the α-band absorption. For phen binding, the shift in the α-band frequency is opposite the shift in the Raman lines. Hence, the affect of complex formation on the excited states is different from that of metal substitution. This result also suggests the metal is not directly interacting with phen.

These electronic differences give rise to structural differences as well. Binding of a phenanthroline molecule to the porphyrin apparently reduces the core size[26] by up to 0.01 Å. Also, the decrease in the core size on binding phenanthroline is larger for the metalloporphyrins with the smallest core, i.e., the Co and Ni porphyrins. This fact is somewhat surprising, since Ni porphyrin already has one of the smallest center-to-nitrogen distances of any metalloporphyrin. As far as the structure of the complex is concerned, it is difficult to see how simple ligation at the metal can make the core size smaller, since nonbonding interaction of phenanthroline with the pyrrole nitrogens would tend to increase the core size instead of decreasing it.

Due to the similarity of the present analysis of the shifts in the core-size marker lines and the earlier interpretation of the absorption-band shifts for metalloporphyrins, we can predict that the frequency of the core-size marker lines will be proportional to the stability of the metal–porphyrin bond. Such a marker of stability is useful when the normal absorption bands are obscured or shifted by overlapping charge-transfer bands as in the Fe^{III}

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porphyrins and that spectral measure of stability cannot be applied.

The phenanthroline complexes produce a pattern of shifts in the Raman lines of the porphyrin that is quite different from that observed for the complexes with the viologen dications or for dimerization of the porphyrin.[6-8] Viologen is strongly bound electrostatically to the metallouroporphyrin anion which has a charge of 8–. In both cases, the shift in the oxidation-state marker line and those of the two oxidation and core-size marker lines are nearly equal. The shifts are to lower frequency for methyl viologen and to higher frequency for dimerization. Therefore, different patterns of shifts are observed for these intermolecular complexes, and the electronic structure of the macrocycle is presumably affected in some other fashion. Further RDS studies of these complexes are necessary to resolve these differences in electronic structure of the porphyrin. The patterns of the Raman line shifts

for metalloporphyrins in different environments, such as in the heme proteins,[18,19,34] may then be interpreted more reliably.

Registry No. CuURO, 78991-92-1; NiURO, 84098-84-0; Fe^{III}(OH)-URO, 84254-29-5; CoURO, 84254-30-8; phen CuURO, 78803-43-7; phen NiURO, 84254-31-9; phen Fe^{III}(OH)URO, 84254-33-1; phen CoURO, 84254-35-3; MgURO, 84254-36-4; ZnURO, 55972-25-3; MgOEP, 20910-35-4; ZnOEP, 17632-18-7; CuOEP, 14409-63-3; CoO-EP, 17632-19-8; NiOEP, 24803-99-4.

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Preparation and Molecular Stereochemistry of Anionic Difluoro(*meso*-tetraphenylporphinato)iron(III), a High-Spin Six-Coordinate Iron(III) Porphyrinate with an Unusually Expanded Core and a Hydrogen-Bonded "Distal" Imidazole

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Abstract: The preparation and molecular stereochemistry of the six-coordinate high-spin anionic complex difluoro(*meso*-tetraphenylporphinato)iron(III) are described. The complex is isolated as the 2-methylimidazolium salt. The [Fe(TPP)(F)$_2$]$^-$ anion has a crystallographically required center of symmetry at the iron(III) atom; hence, the iron atom is centered in the porphinato plane. The planar porphinato core is radially expanded with Fe–N$_p$ = 2.064 (3) Å; this equatorial distance is substantially larger ($\sim$0.02 Å) than that observed in related species. The axial Fe–F bond distance is 1.966 (2) Å. The 2-methylimidazolium counterion is hydrogen bonded to the fluoride ions of two adjacent [Fe(TPP)(F)$_2$]$^-$ anions to form a quasi-linear hydrogen-bonded chain. The F$\cdots$N(im) separations are 2.622 (7) and 2.695(7) Å. The compound is crystallized as the dichloroform solvate. Crystal data: triclinic, space group $P\bar{1}$, Z = 1, a = 10.363 (3) Å, b = 12.382 (3) Å, c = 10.094 (3) Å, α = 103.47 (3)°, β = 107.68 (3)°, and γ = 72.90 (2)°. Diffraction data were collected by the θ–2θ scan method on a four-circle diffractometer; all unique data to $2\theta \leq 59.7$ were measured. A total of 4597 data points were used in the structure determination; final discrepancy indices are R_1 = 0.078 and R_2 = 0.095.

Ferric porphyrinates have a rich and varied spin-state/stereochemistry that can be controlled by manipulation of axial ligation.[3] One important class is the high-spin six-coordinate species which have radially expanded porphinato cores.[4] The radial expansion of the core is conveniently measured by changes in the "radius of the central hole", or Ct$\cdots$N distance. Relative to low-spin ferric species, the radial expansion is about 0.055 Å, the difference between the low-spin 1.990-Å value and the 2.045-Å value for high-spin species having an in-plane iron(III) atom.[3] The importance of a radially expanded porphinato core in the stereochemistry of the heme group of a number of hemoproteins has

been demonstrated by resonance Raman studies.[5]

We now report the structural characterization of a six-coordinate high-spin species, the ionic complex difluoro(*meso*-tetraphenylporphinato)iron(III), [Fe(TPP)(F)$_2$]$^-$.[6] Our characterization demonstrates that the species exhibits an unexpected and unusually large porphinato core expansion. The radial expansion

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(6) Abbreviations used: TPP, the dianion of *meso*-tetraphenylporphyrin; 2MeHIm, 2-methylimidazolium cation; N$_p$, porphinato nitrogen atom; Ct, center of the porphinato ring.