high-spin ferric ion. For acidic solution, 1,2-Hopo and its amide derivative are the most effective bidentate chelators yet investigated, while from pH 7 to 9, 8-hydroxyquinoline, 3,4-Hopo, and mimosine are more effective. Macrochelating ligands containing multiple hydroxypyridinone binding groups should have high affinities for Fe(III) and actinide(IV) ions. The syntheses and properties of these ligands are currently under study.

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Supplementary Material Available: Tables X-XIX, containing anisotropic thermal parameters, hydrogen atom parameters, and structure factor listings, and Table XXVII, containing IR, NMR, and mass spectral data for compounds **3-11** (61 pages). Ordering information is given on any current masthead page.

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Molecular Strain in Chelated-Heme Complexes: Evidence from Resonance Raman Spectroscopy

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Resonance Raman spectra with 406.7-nm laser excitation are reported for chelated heme compounds in which an imidazole is covalently bound to a side chain of mesoheme with linkages of different lengths, and with steric strain introduced by a methyl substituent at the imidazole C2 carbon atom. In the Fe^{III} state, Cl^- and F^- appear to bind in preference to the imidazole, while in the presence of sulfate, a mixture of five-coordinate high-spin (imidazole-bound) and intermediate-spin (sulfate-bound) species is suggested by the Raman spectrum. No conditions were found in which the imidazole and fluoride were bound simultaneously; thus the high-spin six-coordinate F^- complex of heme proteins with proximal imidazole ligands could not be modeled and may have limited intrinsic stability outside the proteins. In the reduced chelated hemes, the imidazole is bound to the iron, and the Fe–Im stretching band is seen at the expected frequency, 204 cm^{-1}. No difference is seen for imidazole linkages of different lengths. In the case of 2-methylimidazole-chelated heme, however, this frequency is markedly decreased, reflecting the steric strain. CO binding was monitored via the upshifted porphyrin skeletal frequencies, as well as the appearance of the Fe–CO stretch near 500 cm^{-1}. This frequency is increased for the 2-methylimidazole-chelated heme, as previously observed for CO adducts with hindered imidazoles. In addition an expansion of the porphyrin core, relative to that of the unhindered chelated hemes, is suggested by a frequency lowering observed for skeletal mode ν_3, which is known to be a core-size marker. This expansion is suggested to be the locus of the force associated with the greater than 10-fold enhancement of the CO dissociation rate in the 2-methylimidazole-chelated heme adduct.

Introduction

The existence of heme proteins with a wide range of ligand-binding properties has inspired efforts to create model compounds with which to test ideas about steric and electronic influences on ligand binding.[1] Chelated hemes (Figure 1) have been synthesized, in which an N-alkylated imidazole ring is anchored to the heme periphery with a chain flexible enough to allow coordination of the imidazole as a fifth ligand to the heme Fe, mimicking the proximal imidazole of hemoglobin.[2] The nature of the chain has been varied to test for steric alterations. For example, the number of methylene groups in the side chain has been reduced from three to two in order to strain (i.e. tilt) the iron–imidazole linkage. Another modification involves methylating the imidazole C2 atom, to hinder the Fe atom from moving into the heme plane. Effects of these and other modifications on the CO- and O_2-binding kinetics have been evaluated.[2-4]

Resonance Raman (RR) spectroscopy provides a probe of heme structure.[5] Laser excitation within the porphyrin π–π^* transitions in the visible and in the ultraviolet region provide selective excitation of porphyrin vibrational modes, which are sensitive to structural effects induced by alterations in the state of the central Fe atom and its axial ligands. The technique is equally applicable to heme proteins and to heme model compounds in solution. In this study we examine structural variations in chelated hemes using resonance Raman spectroscopy. In the Fe^{III} state, high-spin adducts have been found to be five-coordinate; there appears to be little propensity to form six-coordinate analogues of metmyoglobin. In the Fe^{II} state, the Fe–imidazole bond strength is apparently unaffected by shortening of the imidazole linkage but is significantly weakened by the introduction of a C2 methyl group on the imidazole. In the CO adduct the steric strain appears to be accommodated by an expansion of the porphyrin core.

Experimental Section

Mesohemin mono-3-(1-imidazolyl)propylamide monomethyl ester (**1**) (see Figure 1), mesohemin mono-2-(1-imidazolyl)ethylamide monomethyl ester (**2**), and mesohemin mono-3-(2-methyl-1-imidazolyl)-propylamide monomethyl ester (**3**) were prepared as mixtures of five-coordinate chelated-imidazole or chloride-bound species.[3,6]

Ferric Porphyrins. Conversion of **1** to a single species was accomplished by dissolving 1 mg in 5 mL of CH_2Cl_2 (reagent grade) and washing three times with equal volumes of 5% Na_2CO_3 to form the μ-oxo dimer. The olive green solution was then washed twice with equal volumes of NaCl/HCl (0.25/0.01 M), NaF/HF (0.25/0.01 M), or 0.01 N H_2SO_4. Absorption spectra for each species are reported in Figure 2. The acid is necessary to cleave the μ-oxo dimer. When the 0.01 N H_2SO_4 washed species was subsequently washed with 50 mM NaF or NaCl, the

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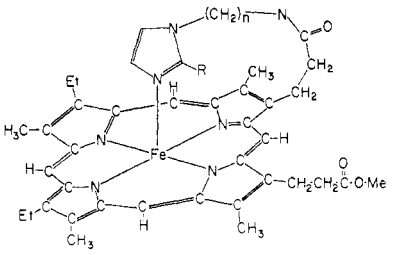

	R	$(CH_2)_n$
1	H	3
2	H	2
3	CH_3	3

Figure 1. Structural diagram of the chelated hemes included in this study.

species gave spectra identical with those of the NaF/HF- and NaCl/HCl-washed species, respectively. The same procedure was applied to mesohemin dimethyl ester chloride (Mid-Century), which was used as received. All solvents and reagents were reagent grade and used without further purification.

Ferrous Porphyrins. A solution of 0.5 mg of **1**, **2**, or **3** in 1 mL of CH_2Cl_2 was degassed by the freeze–pump–thaw method in an NMR tube in which Raman spectra were subsequently obtained. One drop of H_2O and excess solid $Na_2S_2O_4$ were added to the frozen solution under N_2. The NMR tube was sealed with a rubber septum, evacuated, and filled with 1 atm of N_2. The sample was thawed and vigorously shaken, giving a bright reddish solution (λ_{max} = 434 nm). The final volume was ~0.5 mL due to evaporation during the evacuations. Reduction of mesohemin dimethyl ester in the presence of excess 1,2-dimethylimidazole was carried out in the same manner. 1,2-Dimethylimidazole (Sigma) was purified by sublimation two times.

Ferrous CO Porphyrins. The CO adducts were synthesized from a frozen CH_2Cl_2 solution of the reduced heme in an NMR tube. The tube was then opened, flushed with CO, and sealed with a rubber septum under a CO atmosphere. The solution was thawed and vigorously shaken, producing a deeper red solution (λ_{max} = 420 nm).

Spectroscopy. Raman spectra were obtained with a Spex 1401 double monochromator equipped with a cooled photomultiplier and photon-counting electronics. The data were collected digitally with a MINC (DEC) computer. Excitation lines at 406.7 and 413.1 nm were provided by a Spectra-Physics 171 Kr^+ laser. All spectra were recorded by using a back-scattering geometry with a spinning NMR tube.[7] UV–vis absorption spectra were obtained with 1-mm quartz cells with a Hewlett-Packard 8450A diode array spectrophotometer.

Results and Discussion

A. High-Spin Five-Coordinate Fe^{III} Adducts with Weak-Field Ligands. We have examined the extent to which the chelated heme **1** can be induced to form a high-spin six-coordinate species, mimicking aquometmyoglobin, in which a water molecule is bound as a sixth ligand.[8] Such complexes cannot ordinarily be prepared from heme and exogenous imidazole, because of the strong tendency to form a low-spin bis(imidazole) adduct.[9] This problem should be alleviated in chelated hemes, since the imidazole is tethered to the porphyrin.

When a methylene chloride solution of **1** is washed with 5% sodium bicarbonate (forming the μ-oxo dimer) and then with aqueous NaCl/HCl or NaF/HF, absorption spectra are obtained (Figure 2) that resemble those of mesohemin dimethyl ester chloride of fluoride. The RR spectra (Figure 3) have characteristic five-coordinate high-spin Fe^{III} signatures.[10] The most distinctive marker band sensitive to coordination number and spin state is the totally symmetric skeletal mode ν_3, reported previously at 1492 and 1483 cm^{-1} for five- and six-coordinate high-spin Fe^{III} hemes.[11]

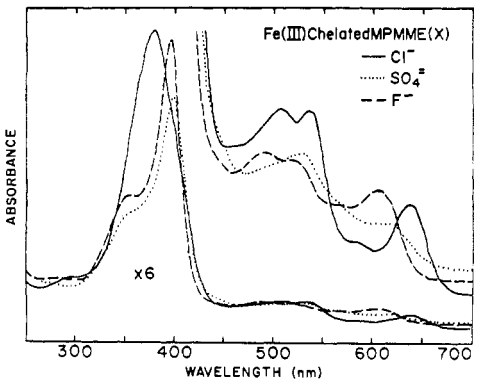

Figure 2. Absorption spectra of CH_2Cl_2 solutions of chelated heme **1** (~1 mM) prepared by washing with 5% Na_2CO_3 aqueous solution and then with aqueous NaCl/HCl (0.25/0.01 M) (—), NaF/HF (0.25/0.01 M) (---), and H_2SO_4 (0.01 N) (···).

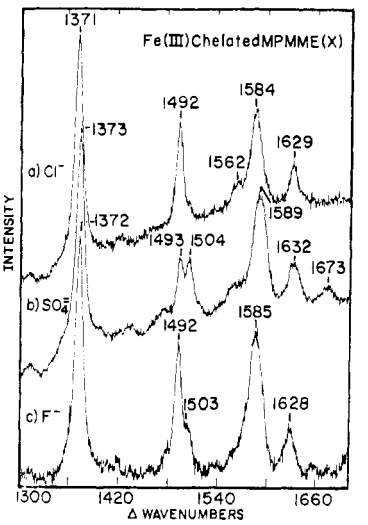

Figure 3. High-frequency RR spectra, with 406.7-nm excitation, for CH_2Cl_2 solutions of **1** (~1 mM) prepared as for Figure 2: (a) NaCl/HCl wash; (b) H_2SO_4 wash; (c) NaF/HF wash. Conditions: 150-mW laser power; 8-cm^{-1} spectral slit width; 5-s/0.5 cm^{-1} collection intervals.

This band is seen at 1492 cm^{-1} for the halide-washed solutions; there is no hint of a band at 1483 cm^{-1}, which would be expected if halide and imidazole were bound simultaneously. Since the absorption spectra resemble those of the mesohemin halides, we conclude that in these solutions halide is bound to the Fe^{III} but imidazole is not.

When the washing solution is dilute (0.01 N) sulfuric acid, the RR spectrum (Figure 3) shows two ν_3 peaks, at 1493 and 1504 cm^{-1}. The latter frequency is characteristic of low-spin or intermediate-spin Fe^{III} hemes.[10-12] Intermediate-spin hemes are known to form when the axial ligand is very weak, e.g. perchlorate. We infer that this solution contains a spin mixture, half of the hemes being high spin and half being intermediate spin. The effect of the intermediate-spin component is also seen in broadening and upshifts of bands at 1585 and 1628 cm^{-1}, arising from skeletal modes ν_2 and ν_{10}.[12] The five-coordinate high-spin component of the spin mixture might be due to sulfate being a ligand of borderline weakness with respect to the high-spin → intermediate-spin transition, or it might be due to imidazole binding, in competition with sulfate binding, for half the hemes. Again there is no hint of a band at 1482 cm^{-1}, which would have been expected had sulfate, or water, been bound simultaneously with imidazole.

It is possible that these attempts to bind imidazole and a sixth ligand simultaneously were complicated by protonation of the imidazole due to the dilute acid wash, which was necessary to break up the μ-oxo dimer that forms in contact with neutral or

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alkaline aqueous solution. Consequently the sulfuric acid washed solution, which gave the mixed-spin RR spectrum, was washed with aqueous NaF to ensure deprotonation of the imidazole and to induce simultaneous binding of F^-. The RR spectrum, however, reverted to one characteristic of five-coordination, and the absorption spectrum was the same as that obtained with NaF/HF washing. Thus, even under these conditions, the Fe^{III} binds preferentially to F^-, and six-coordination is not achieved.

Outside of heme proteins, the only six-coordinate high-spin Fe^{III} complex for which a structure has been reported is the bis(tetramethylene sulfoxide) (TMSO) adduct of iron(III) tetraphenylporphine.[13] In this structure, the Fe atom sits in the plane of the porphyrin, whose central core is somewhat expanded due to the high-spin character of the Fe^{III}, and the TMSO ligands are attached on either side with rather long bonds (2.069 (3) and 2.087 (3) Å). In the more common five-coordinate high-spin Fe^{III} structures, the Fe atom sits out of the porphyrin plane by ~0.4 Å,[14] allowing the porphyrin core to contract somewhat, and the anionic fifth ligand is attached with a short band (1.97 Å). In the case of the fluoride adduct, an unusually high Fe–F stretching frequency, ~600 cm^{-1}, is observed.[15] These structural features may explain the difficulty in binding imidazole as a sixth ligand, even when it is tethered to the porphyrin ring, as in the chelated heme. The stability gained by forming a Fe–imidazole bond is counterbalanced by the losses that would be associated with expansion of the porphyrin core and stretching of the bond to the trans axial ligand due to the nonbonded interactions with the pyrrole N atoms. By the same token, binding of a weak-field ligand to a five-coordinate ImH–Fe^{III} complex is disfavored by the required stretching of the Fe–ImH bond (although displacement of ImH by an anionic ligand is facile in a nonpolar solvent).

Six-coordinate high-spin Fe^{III} structures are, however, found in heme proteins with proximal imidazole ligands. Aquometmyoglobin or hemoglobin have water bound to Fe^{III}; the complexes have a mixed-spin character,[16] with a predominant high-spin component, whose RR signature is characteristic of six-coordination.[10] The water molecule can be replaced by F^-, producing a completely high-spin complex.[17] The Fe–F bond is much longer than in five-coordinate F^- complexes, and a substantially lowered Fe–F stretching frequency, 443 and 471 cm^{-1}, has been reported.[18] Native horseradish peroxidase (HRP), however, contains five-coordinate high-spin Fe^{III} heme, as judged by several spectroscopic criteria;[10] there is no evidence for a bound water molecule. A high-spin six-coordinate complex can be prepared by adding fluoride, but it is significant that the species actually bound is HF.[19] It seems likely that the proton taken up with the F^- resides on a basic residue in the heme pocket, perhaps a distal imidazole, and stabilizes the bound F^- via H bonding. In the case of cytochrome *c* peroxidase (CCP), whose properties are similar to those of HRP, a water molecule is seen in the crystal structure in a position to bind to the heme but is less strongly bound and is in a somewhat different environment than it is in metmyoglobin.[20] RR spectroscopy shows predominant five-coordination at room temperature, but lowering the temperature stabilizes the six-coordinate high-spin structure.[21]

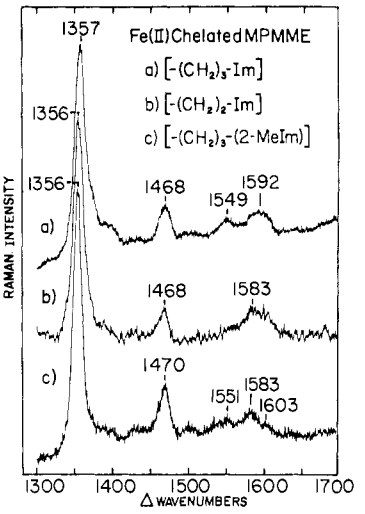

Figure 4. High-frequency RR spectra, with 406.7-nm excitation, for CH_2Cl_2 solutions (~1 mM) of chelated hemes **1**, **2**, and **3** (a, b, and c, respectively) after reduction with aqueous sodium dithionite. Conditions: 150-mW laser power; 8-cm^{-1} spectral slit width; 1 s/0.5 cm^{-1} collection intervals.

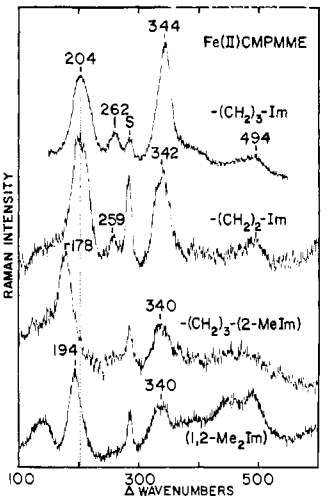

Figure 5. Low-frequency RR spectra, with 413.1-nm excitation, for CH_2Cl_2 solutions (~1 mM) of **1**, **2**, and **3** and of mesoheme dimethyl ester with excess 1,2-dimthylimidazole (~1 mM) (top to bottom) after reduction with aqueous sodium dithionite. Conditions: 150-mW laser power; 7-cm^{-1} spectral slit width; 2 s/0.5 cm^{-1} collection intervals. The solvent band at 285 cm^{-1} was used as an internal standard.

We conclude from these observations that six-coordinate high-spin Fe^{III} heme with imidazole and weak-field ligands is a structure of low intrinsic stability. Its occurrence in heme proteins no doubt reflects stabilization in the protein binding pocket, probably via H-bonding with residues on the distal side as well as constraints on the proximal imidazole.

B. Weakened Fe–Im Bonding to Fe^{II} for Chelated 2-MeIm. When the chelated heme is reduced, a five-coordinate high-spin Fe^{II} heme is formed, as shown by the RR spectra in Figures 4 and 5. The low-frequency spectrum (Figure 5, top spectrum) shows a characteristic band at 204 cm^{-1}, which has been identified[22-24] with the Fe–imidazole stretching vibration. The exact frequency depends on the nature of the imidazole ligand and is quite sensitive to H-bonding of the imidazole N3 proton.[25] In the chelated mesoheme, this proton is replaced by the alkyl chain, so that H-bonding is precluded. The 204-cm^{-1} frequency is in

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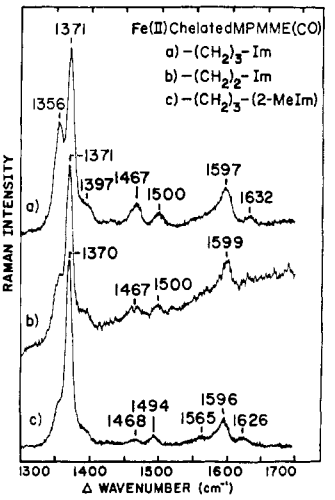

Figure 6. High-frequency RR spectra, with 406.7-nm excitation, for CO adducts of reduced **1**, **2**, and **3** (a, b, and c, respectively) in CH_2Cl_2 solution (~1 mM). Conditions: 150- and 50-mW laser power for (a) and (b, c), respectively; 8-cm^{-1} spectral slit width; 1 s/0.5 cm^{-1} collection intervals.

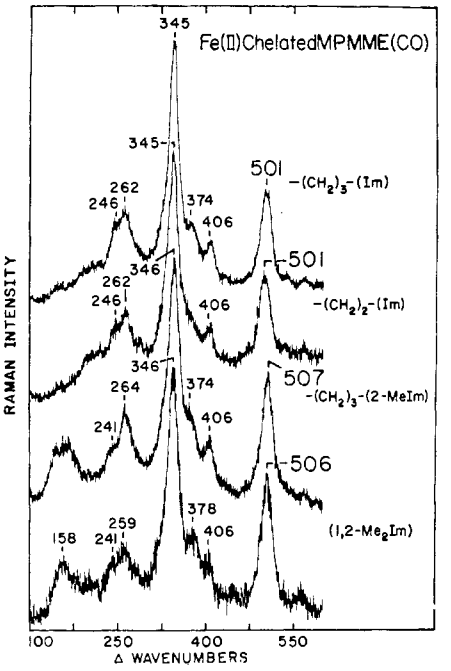

Figure 7. Low-frequency RR spectra, with 406.7-nm excitation, for CO adducts of reduced **1**, **2**, **3**, and mesoheme dimethyl ester with excess 1,2-dimethylimidazole in CH_2Cl_2 solution (~1 mM). Conditions: 50-mW laser power; 5-cm^{-1} spectral slit width; 2 s/0.5 cm^{-1} collection intervals.

the range expected for non-hydrogen-bonded imidazoles. The high-frequency spectrum (Figure 4) is quite similar to that of deoxyhemoglobin and of high-spin Fe^{II} hemes in general.[11] The positions of skeletal modes ν_4 and ν_3, at 1357 and 1468 cm^{-1}, are characteristic. The 1550–1610-cm^{-1} region is complex, and the weak bands are not clearly resolved in these spectra.

When the chelated heme with the shorter chain, **2**, was examined (second spectra in Figures 4 and 5), all of the bands were found at the same frequencies. No difference whatever is seen in the Fe–Im band, 204 cm^{-1}, indicating no detectable difference in the Fe–imidazole bonding. Shortening the chain was expected[3] to induce strain on the Fe–Im bond, but no evidence for strain is seen in ν_{Fe-Im}. We conclude that, at least in the five-coordinate out-of-plane structure, the short and long arms accommodate Fe–imidazole bonding equally well.

The situation is quite different for the 2-methylimidazole-chelated heme, **3**, which shows a marked reduction in the Fe–Im frequency, to 178 cm^{-1}, (Figure 5, third spectrum from the top). For comparison the low-frequency spectrum of the 1,2-dimethylimidazole (1,2-Me_2Im) adduct of iron(II) mesoheme dimethyl ester is shown at the bottom of Figure 5. The 10-cm^{-1} reduction in its Fe–Im frequency (194 cm^{-1}) is attributable to the increased ligand mass and the added steric effect associated with the 2-methyl substituent and its interaction with the pyrrole nitrogens.[26,27] The extra 16-cm^{-1} reduction observed for the 2-methylimidazole-chelated heme must be attributed to an extra steric effect of the 2-methyl group with the side chain since it is directed inside the chelate ring. The high-frequency porphyrin skeletal modes (Figure 4) are, however, unaffected by this steric effect, remaining at essentially the same frequencies as seen for the other chelated hemes.

We note that steric strain has also been invoked[28] to account for the anomalously low Fe–Im stretching frequency in the α chains of deoxyHb,[29] since X-ray crystallography[30] has revealed a tilting of the proximal imidazole, relative to the heme normal, which appears to generate a short nonbonded contact of an imidazole H atom with one of the pyrrole N atoms.[30,31] In the case of hemoglobin, however, an upshift is seen for skeletal mode ν_4, whose frequency has been shown to correlate inversely with ν_{Fe-Im} for a range of hemoglobins.[32] On the basis of this correlation, the 26-cm^{-1} downshift of ν_{Fe-Im} between **1** and **3** should have been accompanied by a 5.5-cm^{-1} upshift of ν_4, whereas no shift in ν_4 (beyond 1 cm^{-1}) is observed (Figure 4). Even if we allow for the likelihood that part of the Fe–Im frequency downshift is due to the increased effective mass of the ligand (less than 10 cm^{-1}, on the basis of the 1,2-Me_2Im mesoheme dimethyl ester frequency), the lack of any detectable effect on ν_4 suggests different mechanisms for the Fe–Im band shifts in hemoglobin and the sterically hindered model.

C. Expanded Core for the 2-MeIm CO Adduct. When carbon monoxide is bound to the reduced chelated hemes, its interaction with the Fe atom can readily be seen in the high-frequency RR spectra (Figure 6) via upshifted frequencies for ν_4, ν_3, and ν_2, to 1370, 1500, and 1598 cm^{-1}, the frequencies expected for a low-spin Fe^{II} heme with a π-acid ligand.[11,33] some high-spin signal remains (ν_4 = 1356 and ν_3 = 1467 cm^{-1}) due to partial photolysis of the bound CO. The extent of the photolysis was reduced in parts b and c of Figure 6 by using lower laser powers. In the case of the 2-methylimidazole-chelated heme, however, ν_3 is observed at a significantly lower frequency, 1494 cm^{-1}, than in the other chelated hemes (1500 cm^{-1}). This band is known to be sensitive to the porphyrin core size,[10,11] and the 6-cm^{-1} decrease implies a ~0.01-Å expansion of the core. Other skeletal modes above 1450 cm^{-1} are also expected to show a core-size effect, but they are too weak and badly overlapped to be accurately assessed in these spectra. An expanded core is plausibly linked to the steric hindrance imposed by the 2-methyl group. The binding of CO enforces a low-spin geometry with six short Fe–ligand bonds. This would necessarily bring the 2-methyl group into steric contact with the pyrrole rings, which could be relieved by an expansion of the core.

In the low-frequency region (Figure 7) CO binding is accompanied by the appearance of a prominent band near 500 cm^{-1}, which has been identified with the Fe–CO stretch via isotropic substitution.[34,35] The band is seen at 501 cm^{-1} for both the long-

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and short-chained chelated hemes, but at a significantly higher frequency, 507 cm^{-1}, for the 2-methylimidazole-chelated heme. Essentially the same frequency, 506 cm^{-1}, is observed for the CO adduct of the 1,2-dimethylimidazole complex of mesoheme dimethyl ester (bottom spectrum). An upshift in the Fe–CO frequency has previously been noted by Yu and co-workers, when the trans-axial ligand is sterically hindered or has a weak field (e.g. tetrahydrofuran).[36] Evidently the Fe–CO bond is strengthened as the bond to the trans ligand is weakened, in contrast to the situation with O_2 adducts, where a small effect in the opposite direction has been observed.[37] We note, however, the recent controversy over the ν_{Fe-O_2} assignment.[38]

The remaining bands in the low-frequency region have been tentatively assigned to both in-plane and out-of-plane porphyrin deformation modes.[39,40] We note that a new band appears, at 158 cm^{-1}, both for the 1,2-Me_2Im mesoheme dimethyl ester adduct and for the 2-methylimidazole-chelated heme. This may be an additional out-of-plane mode, activated by the nonbonded influence of the 2-methyl group, or it may be a mode of the ligand itself, coupled to the porphyrin electronic system via the 2-methyl interaction. A band at 157 cm^{-1} is seen for deoxyhemoglobin[22,32,41] but has not been assigned.

D. Steric Effects and CO Binding. CO dissociation rates have been measured[2-4] for the chelated hemes included in this study. Although the short-chained chelated heme, **2**, is suggested by CPK models to be somewhat strained, the CO off-rate is increased relative to **1** only by a modest factor of 2.[3] We see no evidence for strain in our spectroscopic measurements. All of the RR frequencies are the same for the two chelated hemes, in both ligated and unligated forms. In particular, the Fe–Im stretching frequency in the unligated form and the Fe–CO frequency in the CO adduct are the same.

Addition of a methyl group at the imidazole C2 position, however, produces a dramatic effect, both in the CO off-rate, which is increased by over a factor of 10,[3] and in the RR spectra. It has previously been emphasized[3] that the 2-methyl group has an even larger steric effect on the chelated heme than in the absence of chelation, since the H atom it replaces is inside the chelate ring. Consistent with this view is the large decrease in the Fe–Im frequency in the unligated state, even relative to that of the 1,2-dimethylimidazole adduct of mesoheme (178 vs. 194 cm^{-1}). Thus, the Fe–Im bond appears to be substantially weakened by the steric strain introduced by the 2-methyl group in the chelated heme (vida supra). For the CO adduct of **3** the Fe–CO frequency is increased as expected for hindered imidazoles,[36] although by no more than in the 1,2-Me_2Im adduct of mesoheme dimethyl ester. Thus, the enhanced CO dissociation rate is not associated with any weakening in the Fe–CO bond (it is actually somewhat stronger than in the other chelated heme adducts). We suggest that the force responsible for the enhanced off-rate is stored in an expansion of the porphyrin ring, as implied by the lowered ν_3 frequency (1494 vs. 1500 cm^{-1}), brought about by the enhanced steric strain generated by formation of the low-spin CO adduct. Release of the CO would relieve this augmented steric strain.

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Redox Chemistry for the Mononuclear Tris(picolinato)-, Tris(acetylacetonato)-, and Tris(8-quinolinato)manganese(III) Complexes: Reaction Mimics for the Water-Oxidation Cofactor in Photosystem II

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The water-oxidation process ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$; $E°'$(pH 7) = +0.82 V vs. NHE) of green plant photosynthesis apparently makes use of a multinuclear manganese catalytic center. With the goal to model this process in terms of the requisite redox thermodynamics, ligand stability, and biologically relevant donor groups, a series of manganese(III) complexes ($Mn^{III}L_3$; L = 8-quinolinate, acetylacetonate, picolinate, 2,6-pyridinedicarboxylic acid) have been synthesized. The oxidation–reduction processes for each of these complexes have been characterized in aprotic media by cyclic voltammetry, UV–visible spectroscopy, and magnetic measurements. In the case of the picolinate and acetylacetonate complexes, electrochemical oxidation yields a transiently stable $Mn^{IV}L_3^+$ species that rapidly oxidizes H_2O_2 and OH^-. The redox thermodynamics for the Mn(III)/Mn(IV) and Mn(III)/Mn(II) couples for this group of $Mn^{III}L_3$ complexes and their hydrolytic derivatives are discussed in relation to the water-oxidation process of photosystem II.

Manganese is believed to be an essential electron-transfer agent in the charge accumulation center of the water-oxidizing system of photosystem II (PS II) in green plants.[1-4] Its probable role is as a template to bring the oxygen atoms of two water molecules into close proximity to form an O–O bond. In the chloroplasts of green plants there is a loosely bound pool of manganese that acts as a multicentered catalyst for the oxidation of water to dioxygen. However, the number of manganese ions, their oxidation states, and their structural environments are not known.

Flash-photolysis techniques[5-8] produce reactive intermediates of the oxygen evolution center of the chloroplasts (photosystem II). NMR relaxation experiments indicate that during the cyclic process photooxidation of Mn(II) to Mn(III) occurs and that the resting dark-adapted state involves a mixed oxidation state multinuclear manganese complex. In 1970 a four-state mechanism for the photosystem II oxygen-evolution reaction was proposed.[9]

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