not necessarily formed at rates proportional to their equilibrium concentrations. Unfortunately, however, the result is inconclusive due to reproducibility problems. These arise from the very low solubility of compound **1** in CD_2Cl_2. The spectra shown in Figure 5, parts a and b, were both measured from supersaturated solutions. Such solutions are exceedingly difficult to deal with on a reproducible basis since spontaneous precipitation occurs on a seemingly random basis. Resolution of this isomerization issue therefore depends upon the development of new experimental approaches.

We note that the existence of a facile process interconverting isomers I and II has significant implications. This process must involve breaking at least two Rh–O bonds and forming at least two new Rh–O bonds. Since the rigidity of the $Nb_2W_4O_{19}^{4-}$ framework precludes a concerted, intramolecular process, the isomerization would have to involve coordinatively unsaturated or solvated rhodium species, possibly of the type j. These species may of course be susceptible to external nucleophilic attack, a possibility currently being investigated.
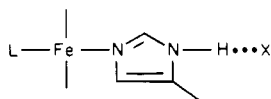
Influence of Hydrogen Bonding on the Properties of Iron Porphyrin Imidazole Complexes. An Internally Hydrogen Bonded Imidazole Ligand

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Abstract: Two new imidazole derivatives have been synthesized, *cis*-methyl urocanate and *trans*-methyl urocanate. The former has been shown by infrared (IR) spectroscopy to contain an N—H···O=C internal hydrogen bond while the latter self-associates by intermolecular hydrogen bonding. The IR properties of these imidazole derivatives have been compared with those of imidazole itself and other imidazole derivatives. A series of complexes of the form $Fe^{III}(TPP)(L)_2SbF_6$, where TPP = tetraphenylporphyrin and L = imidazole or a substituted imidazole, have been synthesized and characterized by visible, electron paramagnetic resonance and IR spectroscopy and cyclic voltammetry in order to evaluate the effects of hydrogen bonding of coordinated imidazole ligands on the properties of iron porphyrin complexes. IR studies demonstrated that imidazole ligands that contain free N–H groups will hydrogen bond to perchlorate ion in solution. Cyclic voltammetric studies of $Fe(TPP)(L)_2SbF_6$ complexes have shown that $E_{1/2}$ of the Fe(III)/Fe(II) couple depends on the pK_a of the ligand and its hydrogen bonding properties. The $E_{1/2}$ values of complexes of imidazoles that form intermolecular hydrogen bonds were shifted to more negative potentials in the presence of excess ligand. By contrast, $E_{1/2}$ values of complexes of cis-methyl urocanate and 1-methyl imidazole were unaffected by excess ligand. The combined evidence of IR and cyclic voltammetry suggests that hydrogen bonding of coordinated imidazoles to uncoordinated imidazoles is of comparable or greater strength than that to o-phenanthroline and that both types of hydrogen bond are stronger than that of coordinated imidazole to an ester carbonyl oxygen.

The coordination of the imidazole ring of a histidyl residue to ferric or ferrous hemes has been reported for a variety of hemoproteins. The functions of these proteins are quite varied, ranging from dioxygen transport proteins, such as hemoglobin and myoglobin, to proteins that catalyze oxidations of substrates, such as horseradish peroxidase, and electron-transfer proteins, such as cytochrome b_5. The observation that histidyl imidazole ligands in hemoproteins are usually hydrogen bonded to another group on the protein has led to the hypothesis that such hydrogen bonding might influence the chemical properties of the heme moiety.[2-19]

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Hydrogen Bonding in Imidazole Complexes

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The object of the study described here was to test this hypothesis using complexes of iron porphyrins with imidazole and imidazole derivatives as ligands.

Studies of the ligand properties of imidazole are complicated by the tendency of that species to self-associate through hydrogen bonding in nonaqueous solution.[20,21] Furthermore, the tendency
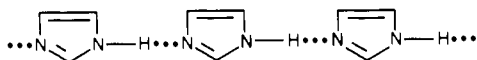
of imidazole to self-associate is increased by metal ion complexation.[22] 1-Methylimidazole may be used to prevent such association, but the replacement of the hydrogen by a methyl group alters the electronic properties of that ligand.

To overcome these problems, we synthesized two isomeric imidazole ligands, *trans*-methyl urocanate (tMU) and *cis*-methyl urocanate (cMU), the methyl ester derivatives of the trans and

cMU

tMU
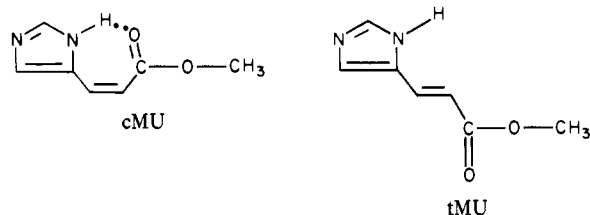
cis isomers of urocanic acid, a naturally occurring histidine metabolite. The ligands were conceived to be electronically similar to each other except for effects due to hydrogen bonding. The trans isomer, tMU, is capable of hydrogen bonding to external acceptors whereas the cis isomer, cMU, is locked into a fixed hydrogen-bonding configuration with the N–H moiety permanently hydrogen bonded to an ester carbonyl oxygen. We carried out our studies of $Fe^{III}(TPP)(L)_2^+$ [23] complexes using SbF_6^- as the counterion. This procedure allowed us to study the bis(imidazole) complex in the absence of any excess ligand and also to study and compare its properties as a function of added excess ligand.[4] By contrast, studies using Cl^- as a counterion are complicated by the requirement for large excesses of imidazole ligands in order to drive reaction 1 to completion.[24]

$$Fe(TPP)(Cl) + 2L \rightleftharpoons Fe(TPP)(L)_2^+ + Cl^- \qquad (1)$$
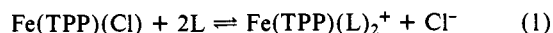
Using the approach described above, we have established that the presence and strength of hydrogen bonds in iron porphyrin imidazole complexes does indeed influence the properties of such complexes. The evidence for such a conclusion is the subject of

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(23) ImH, imidazole; 1MeIm, 1-methylimidazole; 1EtIm, 1-ethylimidazole; 4MeImH, 4-methylimidazole; 4PhImH, 4-phenylimidazole; tMU, *trans*-methyl urocanate; cMU, *cis*-methyl urocanate; 5Cl1MeIm, 5-chloro-1-methylimidazole; BzImH, benzimidazole; Im, imidazolate; TPP, tetraphenylporphyrin; OEP, octaethylporphyrin; PPIX, protoporphyrin IX; L, an imidazole ligand; *o*-phen, *o*-phenanthroline; Et₃N, triethylamine; TBAP, tetrabutylammonium perchlorate; X, counterion; CV, cyclic voltammogram; EPR electron paramagnetic resonance; i_c, cathodic current i_a, anodic current.

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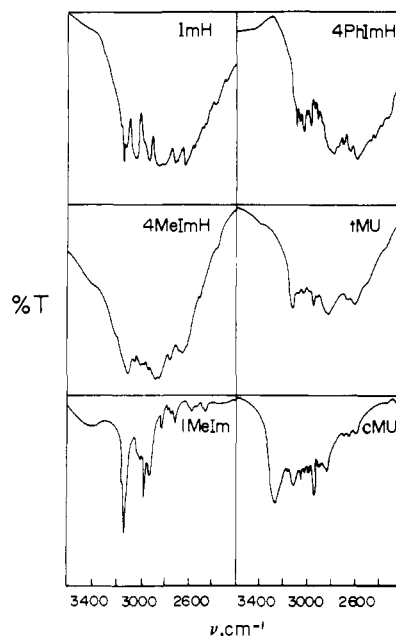
Figure 1. IR spectra of imidazole and derivatives. cMU and 1MeIm were neat liquids; the remainder were solids in KBr.
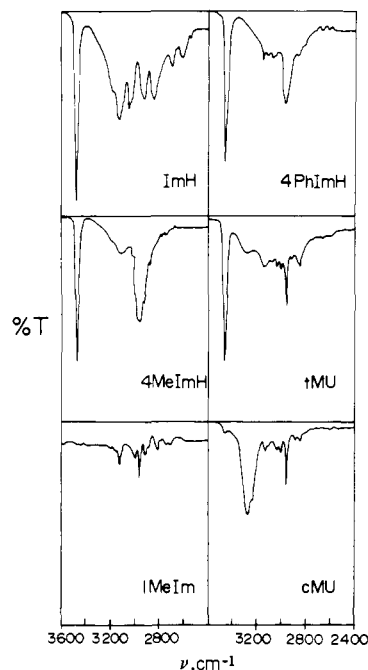
Figure 2. IR spectra of 0.05 M solutions of imidazole and derivatives. For 4MeImH and 4PhImH, the solvent was CH_2Cl_2. For the remainder, the solvent was $CDCl_3$.

this paper.

Results

IR Studies of Imidazole and Derivatives. The IR spectra of imidazole and substituted imidazoles in KBr or neat are illustrated in Figure 1. The spectra of ImH, 4MeImH, 4PhImH, and tMU are characterized by a broad envelope of several bands between 3200 and 2600 cm⁻¹ resulting from the presence of a hydrogen-bonded N–H. The spectrum of cMU also contains a similar envelope of bands in this region as well as a unique band at 3280 cm⁻¹. By contrast, the IR spectrum of 1MeIm reveals no broad envelope of bands in this region and no absorption near 3280 cm⁻¹. The IR spectra of ImH, 4MeImH, 4PhImH, and tMU in solution (Figure 2) are very different from the IR spectra of the solid compounds in KBr. Each spectrum is characterized by the presence of a strong, sharp band between 3470 and 3460 cm⁻¹

Table I. IR Band Positions[a] for Ferric TPP Complexes

	solid[b]				solution[c]	
						ν_{N-H} in presence of
complex	ν_{N-H}	$\nu_{Fe-N(L)}$	ν_{Sb-F}	$\nu_{ligands}$	ν_{N-H}	0.1 M TBAP[d]
Fe(TPP)(ImH)$_2$SbF$_6$	3415, 3370	364	660		3430 (0.12), 3370 (0.06)	3430 (0.04), 3240 (0.15)
Fe(TPP)(4MeImH)$_2$SbF$_6$	3380	367	662		3430 (0.12), 3370 (0.06)	3425 (0.05), 3250 (0.14)
Fe(TPP)(4PhImH)$_2$SbF$_6$	3415	360	662	1595, 1585, 1610		
Fe(TPP)(tMU)$_2$SbF$_6$	3360, 3320	364	662	1645, 1710, 1725	3420 (0.08), 3320 (0.07)	3420 (0.02), 3280 (0.09)
Fe(TPP)(cMU)$_2$SbF$_6$	3200	360	660, 652	1640, 1690	3200 sh (0.08)	3180 sh (0.14)
Fe(TPP)(1MeIm)$_2$SbF$_6$		368	658 sh, 652			

[a] Band positions in cm^{-1}; sh, shoulder. [b] KBr pellets. [c] 3600–3100-cm^{-1} region only; 4 mM solutions in CH$_2$Cl$_2$. [d] TBAP, tetrabutylammonium perchlorate. [e] Numbers in parentheses are absorbances at the specified frequency.

Figure 3. Effects of dilution on the IR spectra of CDCl$_3$ solutions of ImH, tMU, and cMU. The cell path length was increased for each dilution such that the product of the molarity and the path length was constant.

Figure 4. IR spectra of 0.05 M solutions of imidazole and derivatives in CDCl$_3$ in the presence of varying concentrations of o-phen.

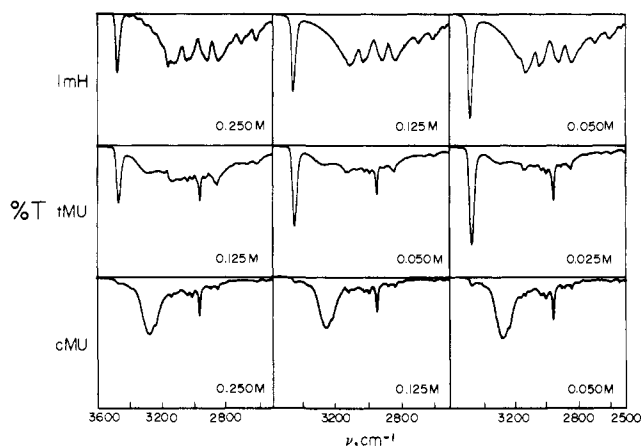due to a non-hydrogen-bonded N–H stretch. By contrast, the solution IR spectra of cMU and 1MeIm are similar to the spectra of the pure liquids. The absence of a non-hydrogen-bonded N–H stretch for cMU is expected if one assumes that this isomer forms an intramolecular hydrogen bond between the N–H and the ester carbonyl oxygen. 1MeIm possesses no N–H bond and an N–H stretch is therefore absent.

The hydrogen-bonding properties of cMU, tMU, and ImH were evaluated by observation of the effects of dilution on the IR spectra[20,21] (Figure 3). The most prominent change upon dilution of ImH or tMU solutions is the dramatic increase in absorbance near 3470 cm^{-1}. A less pronounced decrease in absorbance of the envelope of bands between 3200 and 2600 cm^{-1} is also apparent. By contrast, the spectrum of cMU was virtually unaffected by dilution, and the spectrum of a 0.025 M solution of cMU is remarkably similar to that of neat cMU. The appearance of a relatively weak band near 3470 cm^{-1} upon dilution of cMU we attribute to a small amount of tMU present as an impurity.

The assignment of the band near 3470 cm^{-1} for ImH and tMU to a non-hydrogen-bonded N–H stretch was tested by reaction with o-phenanthroline, o-phen, a hydrogen-bond acceptor. Addition of increments of o-phen, 0–15 equiv, to a 0.05 M ImH solution resulted in a decrease in the absorbance at 3470 cm^{-1} and the appearance of a band near 3180 cm^{-1} (Figure 4). All other bands that appeared as the o-phen concentration was increased were due to o-phen itself. Virtually identical behavior was observed for addition of o-phen to tMU. Conversely, addition of o-phen to a 0.05 M cMU solution led to virtually no changes in the spectra except for the appearance of bands due to o-phen itself.

The experimental results of ligand dilution studies and reaction with o-phen support the premise the cMU forms an intramolecular hydrogen bond involving an N–H bond and a carbonyl oxygen. When the IR spectrum of tMU was recorded in the ester solvent, ethyl acetate, a broad band at 3300 cm^{-1} was observed. This band is apparently characteristic of an imidazole N–H hydrogen bonded to an ester carbonyl and compares well to the 3280 cm^{-1} band
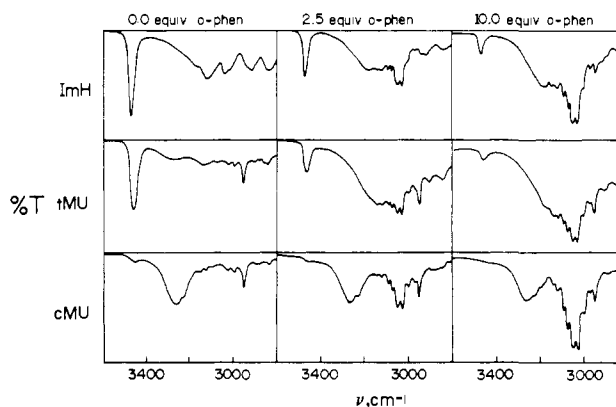
of cMU. Much of the remaining region of the spectrum was obscured by solvent bands and consequently a decrease in absorbance near 3470 cm^{-1} could not be observed.

Properties of Fe(TPP)(L)$_2$SbF$_6$ and Related Complexes. Fe(TPP)(L)$_2$X complexes were readily generated by the reaction of FeTPPX with the imidazole ligands. Complete conversion to the product by reaction with FeTPPCl required a large excess of ligand. By contrast, product formation was complete when 2 equiv of ligand were reacted with Fe(TPP)(SbF$_6$).[4] The visible spectrum of each of these complexes is characterized by four major band maxima. These bands and their average positions are as follows: Soret band, 416 nm; shoulder, 458 nm; β band, 547 nm; α band, shoulder at 578 nm. The above band positions were independent to within 2 nm of the nature of the counterion, X$^-$, and the ligand. In the ultraviolet region, all complexes exhibit a band maximum between 318 and 324 nm. For the complexes with L = 4PhImH, tMU, and cMU, an additional band at 257, 283, and 297 nm, respectively, was observed. This band we assign to a π to π^* transition of the ligand.

The EPR g values of the Fe(TPP)(L)$_2$X complexes were all very similar. All such complexes gave rise to three g values near 2.9, 2.3, and 1.5, characteristic of low-spin ferric porphyrin complexes. By contrast, Fe(TPP)Cl has g values at 6.0 and 2.0, and Fe(TPP)(SbF$_6$) exhibits weak, broad signals at g = 5.8, 4.8, 2.0.[4] As noted above, the formation of Fe(TPP)(L)$_2$X by the reaction of Fe(TPP)Cl required large excesses of ligand. Unreacted Fe(TPP)Cl, where present, could be identified by the presence of a g = 6 signal. The analogous reaction with Fe(TPP)(SbF$_6$) required only 2 equiv of ligand; unreacted Fe(TPP)(SbF$_6$) was not observed as indicated by the absence of signals at g = 5.8 and 4.8. In some cases, however, weak signals at g = 6.0 were observed and may have been due to a small amount of Fe(TPP)Cl or Fe(TPP)F impurity in the reactant solution. Fe(TPP)(L)$_2$SbF$_6$ complexes were easily isolated and recrystallized. EPR spectra of the polycrystalline samples showed no evidence of a high-spin impurity.

Table I summarizes some of the IR band positions of Fe(TPP)(L)$_2$SbF$_6$ complexes in the solid state and in solution. Two features of particular interest are the stretching frequencies of the imidazole N–H and the Fe–N(L) bonds (L = ligand). For

Table II. Half-Wave Potentials of $Fe(TPP)(L)_2SbF_6$ and Related Complexes[a]

complex	pK_a of free ligand	half-wave potential vs. SCE, V				
		$Fe(V)^{[b]}/$ $Fe(IV)^{[b]}$	$Fe(IV)^{[b]}/$ $Fe(III)^{[b]}$	$Fe(III)/$ $Fe(II)$	$Fe(II)/$ $Fe(I)$	$Fe(III)/Fe(II)$ in presence of 0.1 M excess ligand
$Fe(TPP)(ImH)_2SbF_6$	7.11[c]	1.48	1.05	−0.21		−0.25
$Fe(TPP)(4MeImH)_2SbF_6$	7.56[d]	1.47	1.03	−0.23		−0.28
$Fe(TPP)(4PhImH)_2SbF_6$	6.00[e]	1.49	1.06	−0.19		−0.22
$Fe(TPP)(tMU)_2SbF_6$	4.93	1.50	1.10	−0.14		−0.16
$Fe(TPP)(cMU)_2SbF_6$	5.58	1.37	1.12	−0.07		−0.07
$Fe(TPP)(1MeIm)_2SbF_6$	7.33[d]	1.38	1.10	−0.15		−0.15
$Fe(TPP)Cl$		1.42	1.14	−0.30	−1.07	
$Fe(TPP)(SbF_6)$		1.42	1.09	+0.22	irreversible	

[a] 1 mM complex, 0.1 M TBAP in CH_2Cl_2. [b] Formal oxidation states. [c] Reference 22. [d] Grimmett, M. R. In "Advances in Heterocyclic Chemistry"; Katritzky, A. R., Boulton, A. J., Eds.; Academic Press: New York, 1980; Vol. 27, p 241–326. [e] Schofield, K.; Grimmett, M. R.; Keene, B. R. T. "The Azoles"; Cambridge University Press: Cambridge, 1976; p 257–294.

each of these complexes, the magnitude of Fe–N(L) is relatively constant, ranging from 360 to 368 cm^{-1}. Complexes of ImH, 4MeImH, 4PhImH, and tMU exhibited one or two bands between 3500 and 3300 cm^{-1} attributable to N–H stretches of free imidazole N–H's and N–H's hydrogen bonded to SbF_6^-. By contrast, the cMU complex exhibited one broad band at 3200 cm^{-1} due to the stretch of an N–H hydrogen bonded in an intramolecular fashion to an ester carbonyl. For $Fe(TPP)(1MeIm)_2SbF_6$, no bands were observed in the N–H stretching region. The effects on the N–H stretching frequencies of the addition of tetrabutylammonium perchlorate to solutions of the above complexes are also described in Table I. Hydrogen bonding of SbF_6^- and ClO_4^- to the coordinated imidazole ligands is described under Discussion.

Ligand Addition Reactions of Fe(TPP)Cl. Equilibrium constants for the addition of tMU and cMU to Fe(TPP)Cl were determined. Reaction progress was monitored by observing absorbance changes at selected wavelengths of visible spectra as a function of the concentration of added ligand. In all cases, only two absorbing species, $Fe(TPP)Cl$ and $Fe(TPP)(L)_2^+$, were observed. The spectrum of the final product was somewhat sensitive to the concentration of the large excesses of ligand necessary to drive the reaction to completion. Therefore, equilibrium constant values were obtained from analysis of absorbance changes using a method developed by Ketelaar et al.[25] This method requires knowledge of the number of ligands bound but not of the absorbance of the product.

Reaction of 0.01 mM Fe(TPP)Cl in CH_2Cl_2 at 25 °C with cMU or tMU was followed by monitoring absorbance changes at 510 nm, due to the disappearance of reactant, and at 548 nm, due to appearance of product. Isosbestic points were observed at 530 and 618 nm for the cMU reaction and 532 and 610 nm for the tMU reaction. Generally, 10–15 data points were used to evaluate K. Values for the slope and y intercept were obtained from a least-squares fit of the data. The data were judged satisfactory if the correlation factor, R, was 0.9950 or greater. If R was less than 0.9950, the data were discarded. Mean values of K at 25 °C were $(1.2 \pm 0.3) \times 10^4$ M^{-2} for cMU and $(8.6 \pm 0.9) \times 10^3$ M^{-2} for tMU. (Error estimates are based on the range of values obtained for at least three separate experiments.)

Electrochemistry of Fe(TPP)(L)$_2$SbF$_6$ and Related Complexes. The redox properties of various $Fe(TPP)(L)_2SbF_6$ complexes were evaluated by cyclic voltammetry using 1 mM porphyrin solutions in CH_2Cl_2 with 0.1 M TBAP as the supporting electrolyte. Under these conditions, no ligand dissociation from the ferric porphyrin bis(ligand) complex was evident and therefore no excess ligand was added. Visible spectra of the complexes in the presence or absence of TBAP were virtually identical. Scanning over the range +2.0 to −2.0 V resulted in two oxidations and several reductions. Scanning to −2.0 V led also to irreversible behavior. However, scanning from +2.0 to −0.8 V allowed observation of two oxi-

(25) Foster, R. "Organic Charge-Transfer Complexes"; Academic Press: New York, 1969; p 132–133.
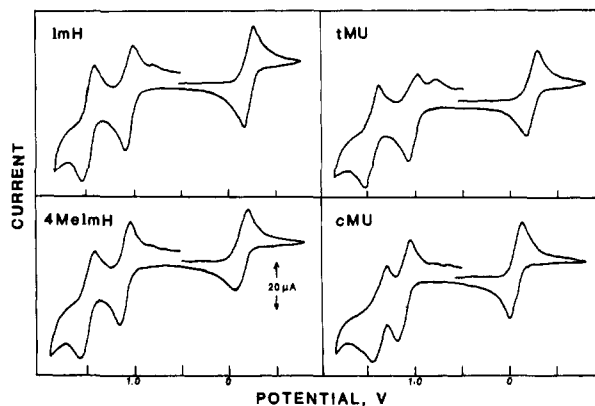
Figure 5. Cyclic voltammograms of $Fe(TPP)(L)_2SbF_6$ complexes, 1 mM porphyrin in CH_2Cl_2, 0.1 M TBAP, +2.0- to −0.6-V scan.
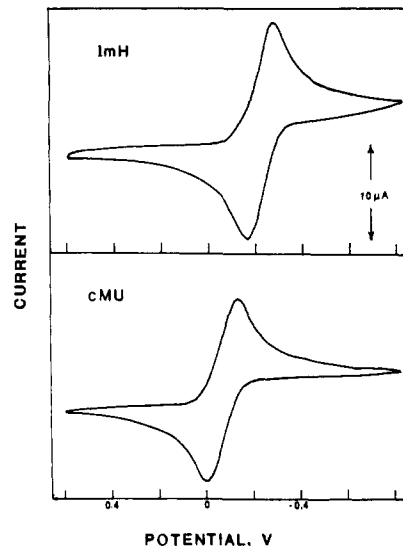
Figure 6. Cyclic voltammograms of $FeTPP(L)_2SbF_6$ complexes, same conditions as Figure 5, +0.6- to −0.8-V scan.

dations and one reduction as illustrated in Figure 5. Also apparent in each such CV was a weaker cathodic peak at +0.8 V of unknown origin. Subsequent scans over this voltage range led to the appearance of weak cathodic and anodic peaks at approximately −0.5 and −0.4 V, respectively.

The primary interest of this study was the half-wave potential of the Fe(III)/Fe(II) couple. A scan of +0.6 to −0.8 V allowed observation of this couple only (Figure 6). Under these conditions, cathodic and anodic peak separations were 90–130 mV when a 50 mV/s scan speed was used. The values of i_c and i_a were invariably equal. Furthermore, no extraneous peaks or changes in the CV with subsequent scans were observed. The CV of

Fe(TPP)Cl, for which the Fe(III)/Fe(II) couple is known to be reversible, resulted in E_{pc}-E_{pa} of 150 mV and i_c equal to i_a. Table II lists the $E_{1/2}$ values for the six different imidazole complexes investigated and those of other porphyrin complexes for comparison.

The effects of excess ligand on the redox properties of Fe(T-PP)(L)$_2$SbF$_6$ complexes were investigated (Table II). In the presence of 0.1 M ligand, porphyrin oxidations were obscured by irreversible oxidation of uncoordinated ligand between +2.0 and +1.4 V. However, scanning between +0.6 and –0.8 V led to observation of the Fe(III)/Fe(II) couple. $E_{1/2}$ values were obtained for 1 mM porphyrin solutions with 0.1 M excess ligand. The addition of excess ligand to the complexes of ImH, 4MeImH, 4PhImH, or tMU resulted in a shift of $E_{1/2}$ values to more negative potentials. The $E_{1/2}$ values of the complexes of 1MeIm and cMU were the same in the presence or absence of excess ligand.

Discussion

Hydrogen Bonding in the Free Ligands. The solid-state IR spectra of imidazoles containing an N–H bond, excluding cMU, are characterized by a broad envelope of bands between 3200 and 2500 cm^{-1} (Figure 1). IR studies of deuterated imidazole itself have confirmed that most of the absorption envelope is due to the presence of extensive hydrogen bonding in the solid state.[26] No absorbances attributable to free, nonhydrogen-bonded N–H stretches are seen for the solids. Assignment of the individual features within the envelope of bands has been difficult.[20,21,26,27] Anderson et al.[21] have tentatively assigned the highest frequency band in this envelope occurring at 3120 cm^{-1} to $\nu_{N-H\cdots N}$ of an imidazole dimer and the lower frequency bands to larger oligomers. The spectra of 4MeImH, 4PhImH, and tMU are similarly characterized by a broad envelope of bands between 3200 and 2500 cm^{-1}, along with additional bands characteristic of methyl or aromatic C–H stretches. Assignment of an individual hydrogen-bonded N–H stretch for these species is also difficult. By analogy with ImH, it is reasonable to assume that $\nu_{N-H\cdots N}$ of tMU occurs at ≤3120 cm^{-1}. 1MeIm, which lacks an N–H bond, exhibits no broad envelope of bands in the 3200–2500-cm^{-1} region, the only bands in this region being those due to C–H stretches.

The IR spectrum of neat cMU (Figure 1) contains a relatively broad absorption envelope between 3200 and 2500 cm^{-1}, within which distinct features at 3120 and 2955 cm^{-1} are assigned to $\nu_{C-H(ring)}$ and $\nu_{C-H(CH_3)}$, respectively. The spectrum of cMU in addition exhibits a unique broad band at 3280 cm^{-1}. The assignment of this band to an intramolecular $\nu_{N-H\cdots O(ester\ carbonyl)}$ is discussed below.

The IR spectra of solutions of imidazole derivatives containing an N–H moiety (excluding cMU) are considerably different from those of the solids (Figures 1 and 2). The principal difference is the appearance of a narrow, intense band in the region 3460–3470 cm^{-1}, assigned to a non-hydrogen-bonded N–H stretch.[20,21] It is interesting to note that the solution spectrum of tMU exhibits an additional relatively broad, weak band at 3280 cm^{-1} not observed with other imidazoles. A comparison with ν_{N-H} of 3300 cm^{-1} obtained for tMU in ethyl acetate suggests that this band is due to the stretch of an N–H hydrogen bonded to an ester carbonyl. By contrast, the solution spectrum of cMU is remarkably similar to that of the pure liquid. Although dissolution apparently results in some loss in intensity of the 3200–2500-cm^{-1} envelope, the band at 3280 cm^{-1} is unaffected. No new bands appear upon dissolution, indicating the absence of a non-hydrogen-bonded N–H and indicating that an intramolecular hydrogen bond is present.

IR dilution studies were used to differentiate inter- and intramolecular hydrogen bonding[20,21,28,29] (Figure 3). In the case

Table III. IR Frequencies for Free and Hydrogen-Bonded ImH, cMU, and tMU

| | ν_{N-H}, cm^{-1} ($\Delta\nu_{N-H}$, cm^{-1})[a] | | | |
	free N–H	N–H···N(Im)	N–H···(o-phen)	N–H···O-(ester carbonyl)
ImH	3470	≤3120 (>350)	3180 (290)	
tMU	3465	≤3120 (>345)	3180 (285)	3300[b] (165)
cMU				3280 (185)[c]

[a] Numbers in parentheses are $\Delta\nu_{N-H}$, the shift from the free N–H frequency to the hydrogen-bonded N–H frequency. [b] tMU in ethyl acetate. [c] Assuming that the free N–H frequency would be the same as that of tMU, 3465 cm^{-1}.

of intermolecular hydrogen bonding, dilution should increase the fraction of non-hydrogen-bonded molecules. Such changes can be detected by the growth in intensity of a non-hydrogen-bonded N–H stretch relative to that of the hydrogen-bonded N–H stretch. The relative intensity of the N–H stretch of an imidazole containing an intramolecular hydrogen bond should be unaffected by dilution.

Solution spectra were obtained by using the very weakly hydrogen-bonding solvent CDCl$_3$. The use of a totally non-hydrogen-bonding solvent was precluded due to the relatively low solubility of various imidazoles in such solvents. Successive dilution of an ImH solution and recording of the IR spectra, using a variable path-length cell under conditions such that the product of the molarity and path length were constant, revealed an increase in the intensity of the band at 3465 cm^{-1} and a decrease of 3200–2500-cm^{-1} envelope.

An analogous dilution study of tMU was confined to a narrower concentration range by its limited solubility in CDCl$_3$ and other non-hydrogen-bonding solvents. Nonetheless, the concentration-dependent spectral changes of tMU were entirely analogous to those of ImH. In particular, dilution resulted in an increase of non-hydrogen-bonded N–H stretch at 3465 cm^{-1} and a proportional decrease of the broad envelope. Furthermore, the band at 3280 cm^{-1} attributed to a carbonyl hydrogen-bonded N–H stretch also decreased in intensity as the solution was diluted.

The results of the dilution studies with ImH, 4MeImH, and tMU support the conclusion that such molecules are hydrogen bonded in an intermolecular fashion and that the fraction of non-hydrogen-bonded molecules increases as the concentration of the solute is decreased. By contrast, the spectrum of cMU is essentially independent of the solute concentration. Relative to the absorbance of the C–H stretching band, the intensity of the 3280-cm^{-1} band is unchanged over the concentration range 0.250–0.0250 M consistent with our conclusion that cMU possesses an intramolecular hydrogen bond.

The presence of non-hydrogen-bonded ImH or tMU in 0.05 M ligand solution was further demonstrated by the IR spectra of such solutions in the presence of added hydrogen-bond acceptors. Recent NMR evidence has shown that o-phen hydrogen bonds to coordinated ImH.[10] For this reason, the IR spectra of various imidazoles were recorded in the presence of various concentrations of o-phen. As can be seen in Figure 4, when the o-phen concentration was increased, the intensity of the 3465-cm^{-1} band decreased and new hydrogen-bonded N–H stretching bands appeared. Although the position of $\nu_{N-H\cdots o-phen}$ is somewhat difficult to estimate due to the presence of bands attributable to o-phen, a relatively broad band at 3180 cm^{-1} increased to intensity as the concentration of o-phen was increased. We tentatively assign this band to the N–H stretch of ImH or tMU hydrogen bonded to o-phen. Addition of o-phen to cMU led to no new bands, except those due to o-phen itself. Furthermore, both the intensity and position of the 3280-cm^{-1} band were essentially unaffected by the presence of o-phen. This result is consistent with the presence of an intramolecular hydrogen bond in cMU.

The observation of the frequencies of the free and the hydrogen-bonded N–H stretches for a series of imidazole derivatives

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allows us to calculate $\Delta\nu_{N-H}$ and thereby to estimate the relative strengths of these hydrogen bonds. Hydrogen-bonding strength has been evaluated by this method for a variety of systems.[28,30-32] For example, calorimetrically obtained values of ΔH and values of $\Delta\nu_{A-H}$ obtained by IR for phenol and pyrazole in the presence of a variety of acceptors are related in a linear fashion.[31,32] Hence a relative value of ΔH for adduct formation can be estimated by measuring values of $\Delta\nu_{A-H}$ spectroscopically.

Values of $\Delta\nu_{N-H}$ have been summarized in Table III. A comparison of such values for ImH···ImH with ImH···*o*-phen suggests that ΔH, and hence the hydrogen bond strength of ImH···ImH, is slightly greater than that for ImH···*o*-phen. An analogous comparison for tMU suggests the following order of increasing hydrogen-bond strength: tMU···O=C << tMU···*o*-phen < tMU···tMU. Such an ordering is consistent with that of pyrrole where $-\Delta H°$ for hydrogen bonding to the N acceptors Et_3N and pyridine was greater than that for hydrogen bonding to the O acceptor ethyl acetate.[32]

These results lead us to several conclusions. It would appear that imidazole and imidazole derivatives with free N–H moieties form hydrogen bonds with other imidazole molecules that are at least of comparable strength to those formed with *o*-phen. It is also clear that both of these types of hydrogen bonds of imidazole N–H to nitrogen are stronger than the hydrogen bond between an imidazole N–H and an ester carboxyl oxygen atom. Thus imidazole complexes in the presence of excess imidazole are likely to be strongly hydrogen bonded. The internally hydrogen-bonded imidazole derivative we have made, cMU, is apparently locked into a relatively *weak* hydrogen bond by steric constraints and the trans isomer, tMU, *in the presence of excess tMU* should be considered to have a *stronger* hydrogen bond. The consequences of these conclusions for the properties of imidazole complexes are discussed in a later section.

Properties of Fe(TPP)(L)₂SbF₆ Complexes. Surprisingly, there is little data concerning the IR spectra of Fe(TPP)(L)₂X complexes in the literature. The results of the present study suggest that this is a valuable source of information. Two spectral regions of particular interest are the Fe–N(ligand) stretching region, 400–300 cm⁻¹, and the N–H stretching region. In the former region, each Fe(TPP)(L)₂SbF₆ complex in the solid state exhibited an IR band between 360 and 368 cm⁻¹. It has been reported that Fe(OEP)(ImH)₂ClO₄ and Fe(OEP)(BzImH)₂ClO₄ exhibit bands at 376.5 and 333 cm⁻¹, respectively, assigned by isotropic substitution to $\nu_{Fe-N(L)}$.[33] Similarly the 1MeIm, 1EtIm, and ImH complexes of Fe(PPIX)(Cl) reportedly exhibit $\nu_{Fe-N(L)}$ of 381, 383, and 384 cm⁻¹, respectively.[34] By analogy, we assign the 360–368-cm⁻¹ band of the TPP complexes to a Fe–N(L) stretch.

In the solid state, Fe(TPP)(L)₂SbF₆ complexes (except L = 1MeIm) exhibited one or two bands in the 3500–3100-cm⁻¹ region attributable to N–H stretches (Table I). Such assignments are supported by the fact that the IR spectrum of Fe(TPP)-(1MeIm)₂SbF₆ is featureless in this region. Fe(TPP)-(4MeImH)₂SbF₆ exhibited a relatively broad band at 3380 cm⁻¹. The broadness of the band and its position suggest that it is due to the stretch of a N–H bond hydrogen bonded to some acceptor moiety. Since SbF₆⁻ is the only potential hydrogen-bond acceptor in the solid, it is reasonable to conclude that N–H is hydrogen bonded to SbF₆⁻. Fe(TPP)(tMU)₂SbF₆ exhibited two relatively broad bands at 3360 and 3320 cm⁻¹, which we likewise assign to hydrogen-bonded N–H stretches. Hydrogen bonding to an ester carbonyl, the only other hydrogen-bond acceptor in the solid, can be excluded since the observed N–H stretch is at a higher energy than that of an uncoordinated imidazole–ester hydrogen bond.

Fe(TPP)(4PhImH)₂SbF₆ exhibited one relatively sharp band at 3415 cm⁻¹. Both the position of this band relative to that of the 4MeImH complex and its sharpness suggest that it is due to a non-hydrogen-bonded N–H stretch. Apparently SbF₆⁻ does not hydrogen bond to coordinated 4PhImH, possibly because of steric interactions between the phenyl substituent and the anion.

Unlike the 4PhImH and 4MeImH complexes, Fe(TPP)-(ImH)₂SbF₆ exhibited two bands in the N–H stretching region: 3370 cm⁻¹, broad; 3415 cm⁻¹, sharp. The 3370-cm⁻¹ band, by comparison with that of coordinated 4MeImH, can be assigned to the stretch of a N–H hydrogen bonded to SbF₆⁻. The position and sharpness of the 3415-cm⁻¹ band and comparison with coordinated 4PhImH suggest that it is due to the stretch of a non-hydrogen-bonded N–H. Evidently the porphyrins are arranged in the solid in such a manner that SbF₆⁻ does not hydrogen bond to two ligands simultaneously and two different N–H stretches are observed.

Fe(TPP)(cMU)₂SbF₆ exhibits one broad band at 3200 cm⁻¹. The crystal structure of this complex clearly shows that the ligand has an intramolecular hydrogen bond between the imidazole N–H and the ester carbonyl.[35] Hence, this IR band can be assigned to the stretch of an N–H bond hydrogen bonded in an intramolecular fashion to a carbonyl.

An investigation of the solution IR properties of Fe(TPP)-(L)₂SbF₆ in CH_2Cl_2 was quite revealing. For the complexes of ImH, 4MeImH, and tMU, two bands were observed in the N–H stretch region; one band between 3435 and 3415 cm⁻¹ and a somewhat broader band at lower energies (see Table I). We assign the former to a non-hydrogen-bonded N–H stretch and the latter to a hydrogen-bonded N–H stretch by comparison with the solid-state spectra. In solution, it is unlikely that SbF₆⁻ could simultaneously hydrogen bond to two adjacent ligands as it apparently does in the solid. It is therefore not surprising to observe two different N–H stretches in solution.

As expected, the solution and solid-state IR spectra of FeTPP(cMU)₂SbF₆ were quite similar. Dissolution of the complex does not lead to the appearance of a band attributable to a non-hydrogen-bonded N–H stretch. This result indicates that the intramolecular hydrogen bond of cMU remains intact in solution.

The assignment of the free and hydrogen-bonded N–H stretches in the iron porphyrin complexes was further supported by the IR spectra of Fe(TPP)(L)₂SbF₆ in the presence of tetrabutyl-ammonium perchlorate, TBAP (Table I). The intent of this portion of our study was to evaluate the interaction between TBAP and coordinated imidazoles and the effects of such interactions on the redox properties of the complexes (see below). For the complexes of ImH, 4MeImH, or tMU, the presence of ClO₄⁻ led to three major spectral changes compared to the complexes in the absence of the anion: (1) a decrease in the absorbance due to the non-hydrogen-bonded N–H stretch, (2) disappearance of the band due to the stretch of N–H hydrogen bonded to SbF₆⁻, and (3) the appearance of new band near 3260 cm⁻¹. The decrease in intensity of the non-hydrogen-bonded N–H stretch suggests that ClO₄⁻ hydrogen bonds to the coordinated ligand thus substantially reducing the fraction of the non-hydrogen-bonded ligand. The band near 3260 cm⁻¹ can be assigned to $\nu_{N-H···OClO_3}$⁻. The observed frequency agrees well with that of Fe(OEP)(ImH)₂ClO₄, 3240 cm⁻¹.[33] The crystal structure of this complex has demonstrated that ImH ligands are hydrogen bonded to ClO₄⁻.[36] Finally, the disappearance of the band at 3370 or 3320 cm⁻¹ ($\nu_{N-H···FSbF_5}$⁻) is consistent with the displacement of SbF₆⁻ by the large excess of ClO₄⁻. By contrast to the results of other imidazole complexes, the IR spectrum of Fe(TPP)(cMU)₂SbF₆ in the presence or absence of ClO₄⁻ were virtually identical. The inability of perchlorate to hydrogen bond to coordinate cMU while it readily hydrogen bonds to the other imidazole derivatives further supports the integrity of the intramolecular hydrogen bond of the ligand in solution.

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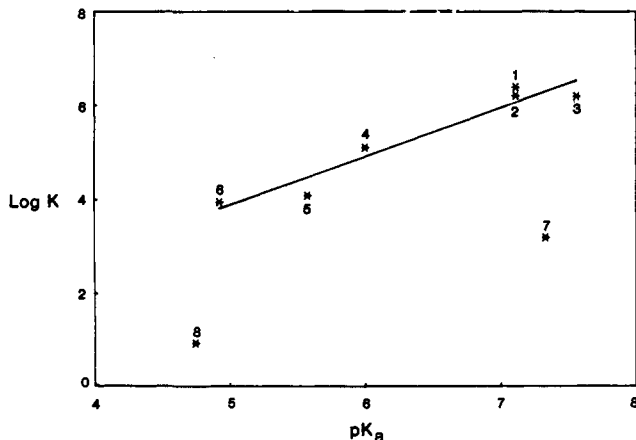
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Table IV. Equilibrium Constants for the Reaction of Imidazole and Derivatives with Fe(TPP)Cl

$$Fe(TPP)Cl + 2L \underset{25\,°C}{\overset{K}{\rightleftharpoons}} Fe(TPP)(L)_2{}^+Cl^-$$

b	L	$pK_a{}^a$	K, M^{-2}	solvent	ref
1	ImH	7.11	2.40×10^6	CH_2Cl_2	c
2	ImH	7.11	1.58×10^6	$CHCl_3$	24
3	4MeImH	7.56	1.00×10^6	$CHCl_3$	24
4	4PhImH	6.00	1.26×10^5	$CHCl_3$	24
5	cMU	5.58^c	1.23×10^4	CH_2Cl_2	c
6	tMU	4.93^c	8.64×10^3	CH_2Cl_2	c
7	1MeIm	7.33	1.50×10^3	$CHCl_3$	24
8	5Cl1MeIm	4.75	8.4	$CHCl_3$	24

^{a} See ref 24 and Table II references for pK_a's other than for cMU and tMU. ^{b} Numbers refer to Figure 7. ^{c} This work.

Figure 8. Plot of $E_{1/2}$ of Fe(III)/Fe(II) couple of $Fe(TPP)L_2SbF_6$ complexes vs. the pK_a of the uncoordinated ligand; ● indicates complex with no excess L; ○ indicates complex with 0.1 M excess L; ◐ indicates complexes with the same $E_{1/2}$ in the presence of 0.1 M excess L or in its absence. A, 4MeImH; B, ImH; C, 4PhImH; D, tMU; E, 1MeIm; F, cMU.

Figure 7. Plot of log K for reaction of imidazole and derivatives with Fe(TPP)Cl vs. pK_a of the ligand. See Table IV for conditions. Numbers refer to ligands, L, in Table IV.

A comparison of the non-hydrogen-bonded ν_{N-H} for coordinated and uncoordinated ligands is also interesting. The non-hydrogen-bonded N–H stretching frequencies for ImH, 4MeImH, and tMU in $CDCl_3$ are 3470, 3465, and 3465 cm^{-1}, respectively. The $Fe(TPP)L_2{}^+$ complexes of these same ligands in CH_2Cl_2 have non-hydrogen-bonded N–H stretches at 3430 cm^{-1} for ImH and 4MeImH and 3420 cm^{-1} for tMU. This 35–45-cm^{-1} shift to lower frequencies upon coordination is consistent with the increased acidity of the ligand due to coordination to a metal.[22,37] The hydrogen-bonded N–H stretch of cMU is also shifted to lower energies upon coordination but in this case $\Delta\nu_{N-H}$ is about twice that observed for other imidazoles (3280 cm^{-1} for free cMU, 3200 cm^{-1} for complexed cMU).

Ligand Addition Reactions of Fe(TPP)Cl. The equilibrium constants for reaction of Fe(TPP)Cl with various imidazole derivatives in CH_2Cl_2 and $CHCl_3$ are summarized in Table IV. The equilibrium constants data in $CHCl_3$ and CH_2Cl_2 suggest that these solvents are very similar and that the data obtained in them may be directly compared. The log K for reaction of Fe(TPP)(Cl) with these imidazole derivatives vs. the pK_a of the ligand is plotted in Figure 7. For the hydrogen-bonded imidazoles, it is clear that the value of K is related to the pK_a of the ligand. Such a relationship has been noted previously.[24] The non-hydrogen-bonded imidazole derivatives 1MeIm and 5Cl1MeIm have binding constants that are significantly depressed from those of the hydrogen-bonding derivatives.[24] It is thus apparent that a relationship between the basicity of various imidazoles with respect to H^+, as reflected by pK_a, and that with respect to iron(III), as reflected by K, only exists for imidazoles of comparable hydrogen-bonding abilities. Determinations of pK_a are carried out in aqueous solution where ImH⋯OH_2 rather than ImH⋯ImH is the predominant mode of hydrogen bonding. Apparently the differences in hy-

drogen-bonding properties of various imidazoles are largely leveled in water solution and the pK_a is primarily dependent on the nature of the substituent groups on the imidazole. Values of K are determined in non-hydrogen-bonding solvents and are apparently influenced more by the nature of hydrogen bonding to coordinated imidazoles than by the nature of the substituent groups on the ligand. Values of the pK_a obtained in non-hydrogen-bonding solvents would reasonably be expected to parallel the basicities of imidazoles with respect to ferric porphyrins.

Electrochemical Studies of $Fe(TPP)(L)_2SbF_6$. The CV's of all $Fe(TPP)(L)_2SbF_6$ complexes in 0.1 M TBAP in CH_2Cl_2 were qualitatively similar to one another (see Figures 5 and 6). Each CV was characterized by two oxidations and several reductions. The reversible oxidations correspond formally to the Fe(V)/Fe(IV) and Fe(IV)/Fe(III) couples, analogous to those observed for Fe(TPP)X. Of the reductions, only the Fe(III)/Fe(II) couple was reversible. Other reductions were apparently irreversible with several overlapping waves and complicated behavior and investigation of these was not pursued further.

For comparative purposes it will be convenient to consider first the complexes of ImH, 4PhImH, 4MeImH, and tMU as group and those of cMU and 1MeIm separately. For the first group, an approximately linear relationship was found between $E_{1/2}$ for the Fe(III)/Fe(II) couple and the ligand pK_a (Table II, Figure 8). As the basicity of the ligand is increased, the ferric state is apparently stabilized relative to the ferrous state and, consequently, a more negative half-wave potential is observed. Kadish and Bottomley[38] have demonstrated that the half-wave potentials of a series of substituted pyridine complexes of $Fe(TPP)(ClO_4)$ in CH_2Cl_2 are likewise dependent on the pK_a of the ligand.

By comparison with the first group of ligands, the half-wave potentials of the complexes of cMU, −0.07 V, and 1MeIm, −0.15 V, seem unreasonably low relative to the pK_a values of the free ligands. The lower than expected $E_{1/2}$ for 1MeIm and cMU complexes can be attributed to the absence of hydrogen bonding beween the imidazole ligand and $ClO_4{}^-$, the supporting electrolyte. Such hydrogen bonding is expected to stabilize preferentially the ferric state and IR studies in the presence of TBAP (see above) clearly indicate that $ClO_4{}^-$ is hydrogen bonded to the complexes of the first group of ligands.

The data described above demonstrate that hydrogen bonding of $ClO_4{}^-$ to coordinated imidazoles influences the Fe(III)/Fe(II) half-wave potential. For this reason, a study of $Fe(TPP)(L)_2SbF_6$ in the presence of excess ligand was undertaken with the expectation that excess ligand would alter the observed half-wave potentials. Electrochemical data were obtained for $Fe(TPP)(L)_2SbF_6$

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complexes in the presence of a 100-fold excess of ligand.[39] Irreversible oxidations of excess ligand precluded observation of all but the half-wave potential of the Fe(III)/Fe(II) couple. In all cases electron transfer was reversible, and one reducible and one reoxidizable species were observed. $E_{1/2}$ values are listed in Table II and graphed in Figure 8. It is evident from these data that the half-wave potential for N–H-containing imidazole complexes is shifted to more negative values by 0.05–0.02 V compared to the complexes in the absence of excess ligand. By contrast, the potentials of the complexes of cMU or 1MeIm in the presence or absence of excess ligands were identical.

That changes in coordination number are not the source of the shift of $E_{1/2}$ is demonstrated by the results for Fe(TPP)(L)$_2$SbF$_6$, L = 1MeIm, cMU. For each ligand, identical $E_{1/2}$ values were obtained in the presence and absence of 100 mM ligand, and only one reducible and one reoxidizable species were observed. Hence, the complexes must exist only as fully ligated species in both the ferric and ferrous states. By analogy, it is reasonable to assume that the shifts in the potentials of other Fe(TPP)(L)$_2$SbF$_6$ complexes in the presence of excess ligand are not due to coordination effects. Likewise, the absence of any shift in $E_{1/2}$ in the presence of excess 1MeIm and cMU indicates that the effect we observe is not due to interactions of excess ligand with the electrode. We conclude that the shift in $E_{1/2}$ for the N–H-containing imidazole complexes in the presence of excess ligand is due to hydrogen bonding of the excess ligand to the coordinated ligand.

Conclusion

Our results indicate that hydrogen bonding of coordinated imidazole can have a substantial effect on the properties of the metal to which it is coordinated. Examination of X-ray structures of several hemoproteins indicates that the histidyl imidazole ligands are frequently hydrogen bonded to carbonyl oxygens from the peptide backbone.[2] This type of hydrogen bonding is likely to be considerably weaker than that of imidazole hydrogen bonded to another imidazole. Caution should therefore be exercised when using results obtained from studies of iron porphyrin complexes in the presence of excess imidazole. In such cases, imidazole is likely to self-associate via relatively strong hydrogen bonds and the properties of the resulting complexes will be different than those of imidazole complexes that are only weakly hydrogen bonded or not hydrogen bonded at all. It is not possible at this point to use our results to make reliable quantitative estimates of the magnitude of these effects in hemoproteins such as hemoglobin, myoglobin, cytochrome c, cytochrome b_5, horseradish peroxidase, etc. Nevertheless, our results do indicate that such effects should in the future be considered in evaluating the properties of metalloproteins containing histidyl imidazole ligands.

Experimental Section

General Procedures. All reactions and distillations, unless stated otherwise, were carried out in an inert atmosphere (Ar or He) by using Schlenkware or a Vacuum Atmosphere's inert-atmosphere chamber.

Materials. Solvents were Burdick and Jackson "Distilled in Glass" grade. Toluene was distilled from Na/benzophenone. CH$_2$Cl$_2$ and ethyl acetate were distilled from CaH$_2$. CDCl$_3$ was distilled from P$_2$O$_5$. ImH, 4MeImH, and 1MeIm were purified as described previously.[4] 4PhImH was recrystallized from hot toluene. The resulting nearly white solid was dried over P$_2$O$_5$ in vacuo. Urocanic acid was dried in vacuo prior to use. o-Phen was vacuum distilled at 120 °C and dried over P$_2$O$_5$ in vacuo for several days. BF$_3$·Et$_2$O was vacuum distilled at 27 °C from a mixture consisting of 100 mL of BF$_3$, 5 mL of anhydrous ethyl ether, and 0.2 g of CaH$_2$. IR grade KBr was dried at 100 °C in vacuo. tMU was synthesized by esterification[40] of urocanic acid. Typically, 20.0 g of urocanic and 55 mL of BF$_3$·Et$_2$O in 360 mL of methanol were refluxed under Ar for 24 h. After cooling to room temperature, 200 mL of 15%

aqueous Na$_2$CO$_3$ was added to the reaction mixture. Following filtration, the product was extracted with anhydrous ethyl ether and then with CH$_2$Cl$_2$. Removal of the solvent under vacuum produced a yellow-white solid. Purification was obtained by recrystallization of the oxalate salt[4] of tMU from acetone/water. The salt was collected by filtration, washed with acetone and then ether, and dried in vacuo. The free base was regenerated by reaction of the oxalate salt with aqueous Na$_2$CO$_3$. Following extraction of tMU with ether and removal of the solvent under vacuum, the solid was recrystallized from hot toluene. The resulting white crystalline solid was washed with cold toluene and dried over P$_2$O$_5$ in vacuo: mp 100–101 °C; UV (CH$_2$Cl$_2$) λ_{max} 285 nm, ϵ 19 000 M^{-1} cm^{-1}.

Synthesis of cMU was carried out by photoisomerization of tMU.[41] Typically, 2.0 g of tMU in 220 mL of methanol was irradiated with 254-nm light in a Rayonnet reactor for 20–24 h. N$_2$ gas was bubbled through the solution during the irradiation. Subsequent removal of the solvent under vacuum produced a yellow oil. An NMR of the oil in C$_6$D$_6$ indicated that it was a mixture of the cMU and tMU. Separation of the isomers utilized the high solubility of cMU in toluene compared to that of tMU. cMU was extracted by stirring the oil with several aliquots of toluene. Following filtration, the solvent was removed under vacuum resulting in an oily liquid. Vacuum distillation at 85 °C resulted in a nearly colorless, viscous liquid, UV (CH$_2$Cl$_2$) λ_{max} 308 μm, ϵ 19 000 M^{-1} cm^{-1}.

Fe(TPP)Cl and Fe(TPP)(SbF$_6$) were synthesized and purified as described previously.[4] Complexes of the form Fe(TPP)(L)$_2$SbF$_6$ where L = ImH, 4MeImH, 4PhImH, 1MeIm, cMU, or tMU were synthesized by the reaction of Fe(TPP)(SbF$_6$) with ligand in toluene. The resulting complex was virtually insoluble in toluene. Typically, 2 equiv of ligand in 10 mL of toluene were added to 20 mL of a 2 mM Fe(TPP)(SbF$_6$) solution. Ligand solutions containing ImH, 4PhImH, and tMU were heated until the ligands dissolved and the solutions were added while hot. After the reaction mixture had stirred for several hours, the solid product was collected by filtration and washed with toluene. The solid was recrystallized by dissolving in CH$_2$Cl$_2$ to give a ~2 mM solution. Addition of an equal volume of toluene and standing at room temperature resulted in a purple crystalline solid. The solid was washed with toluene and dried in vacuo.

Methods. Visible and EPR spectra were recorded as described previously.[4] IR spectra were recorded on a Beckman 4260. Solution IR spectra were recorded using a Beckman Quick-Mount Multicell with KBr windows. The cell path length was adjusted using Teflon-brand spacers of various thicknesses. Spectra were recorded using a reference cell containing the appropriate solvent and having the same path length as the sample cell. Spectra of porphyrin solutions (3–6 mM) were determined in CDCl$_3$ or CH$_2$Cl$_2$ solutions with a cell path length of 1.0 mm.

IR studies of the dilution of ligand solutions were performed in CDCl$_3$. IR spectra were recorded by using a constant molarity times path length product. As the concentration of the ligand solution was decreased, the cell path length was increased proportionally.

CV were recorded with use of a Bioanalytical Systems model CV-1B-120 apparatus and a Houston XY recorder. A three-electrode system was used and consisted of a Pt button working electrode, a Pt wire auxilary electrode, and a saturated calomel reference electrode (SCE). The SCE was separated from the solution under study by means of an electrolyte bridge fitted with a Vycor tip. The electrolyte bridge was filled with the same solvent/electrolyte solution as the sample under study and the SCE was inserted into the bridge.

The electrolytic cell consisted of a 25-mL flask with three 14/20 joints and a three-way stopcock. Prior to use, the cell was thoroughly oven dried, evacuated, and refilled with Ar. Under an Ar purge, the electrodes and the electrolyte bridge with the SCE were inserted into the cell. The solution to be studied was then syringed into the cell and a gentle Ar purge was continued as the CV was recorded. The solvent/electrolyte system was stable over the range +2.0 to –2.0 V. CV's were generally recorded with an initial potential of +0.6 V.

pK_a values were determined at 25.0 ± 0.1 °C by titration of aqueous ligand solutions with aqueous NaOH. Solution pH was determined with a Orion Research Ionalyzer Model 910. The pH electrode was calibrated at pH 4 and 7. Water used in the preparation of all solutions had been boiled and purged with Ar prior to use. Solutions to be studied were 0.1 M in ligand. The ionic strength of these solutions was adjusted to 0.2 M with NaNO$_3$. During the course of the titration, Ar was bubbled through the solution to minimize CO$_2$ contamination. Initially, about 3 μL of concentrated nitric acid was added to the ligand resulting in a pH of less than 3.0. Addition of acid ensured that all ligand was present in its protonated form. Increments of a standardized 0.082 M NaOH solution were added to the ligand solution, and, once the system had stabilized, the pH was recorded. Base additions were continued in this fashion until the pH was 10.0 or greater. The resulting pH vs. titrant

(39) A related electrochemical study of Fe(TPP)L$_2$Cl (L = ImH, 1MeIm) in acetone in the presence of very large amounts of excess ligand has recently been reported. Doeff, M. M.; Sweigart, D. A.; O'Brien, P. *Inorg. Chem.* **1983**, *22*, 851–852.

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volume data was analyzed graphically and the value of the pK_a was taken as the pH at the midpoint between the first and second end points. The estimated errors of reported pK_a values is ± 0.02 pK_a units. Equilibrium constants for the reaction of Fe(TPP)Cl with ligand were determined at 25 °C by optical methods described previously.[4]

Redox Chemistry of Cyclopentadienylcobalt Tetraazabutadienes. Characterization of 19-Electron Anionic Complexes

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Abstract: The results of electrochemical and electronic and EPR spectroscopic studies on a series of novel 19-electron anionic complexes derived from reduction of neutral cyclopentadienylcobalt tetraazabutadienes—CpCo(1,4-R$_2$N$_4$) (R = CH$_3$, C$_6$H$_5$, C$_6$F$_5$, 2,4-F$_2$C$_6$H$_3$, 2,6-Me$_2$C$_6$H$_3$; Cp = η^5-C$_5$H$_5$)—are reported. Investigation of the reduction process by cyclic voltammetry reveals a large dependence of the reduction potential on the nature of R. The reduction potentials are −1.53, −1.01, −0.71, −0.97, and −1.31 V, respectively, vs. the NHE in CH$_3$CN (0.1 M Bu$_4$NBF$_4$). Each anion displays an isotropic EPR spectrum (g = 2.16–2.21) at ambient temperatures characteristic of cobalt-centered radicals (a_{iso} = 50–58 G). The reduction of the neutral complexes has also been followed by electronic absorption spectroscopy, which reveals several isosbestic points in each case. All of the radical anion complexes exhibit a characteristic absorption ca. 1000 nm. Exposure of solutions containing the anion to air or O$_2$ results in essentially quantitative conversion of the anions to the corresponding neutral complexes. Observation of more than one Co-centered radical in the EPR spectrum of CpCo[1,4-(C$_6$H$_5$)$_2$N$_4$]$^-$ is interpreted in terms of the presence of different conformations of the aryl substituents for this compound.

Unsaturated metallacycles containing 1,4-disubstituted tetraazabutadienes[1-13] have attracted interest due to their novel bonding features. Attention has focused on the delocalization of π-electron density in the metallacycles and the role of the metal 3d orbitals in bonding. All of the compounds previously characterized are diamagnetic and obey the 18-electron rule,[14] with the exception of CpNi(1,4-Ar$_2$N$_4$) [Ar = 4-MeC$_6$H$_4$, Cp = η^5-C$_5$H$_5$]. This neutral, 19-electron complex was isolated as a stable intermediate in the synthesis of Ni(1,4-Ar$_2$N$_4$)$_2$ from Ni(Cp)$_2$.[3] We report the results of electrochemical and optical and EPR spectroscopic studies of 19-electron anions derived from the reduction of the neutral compounds, CpCo(1,4-R$_2$N$_4$) (R = CH$_3$,

C$_6$H$_5$, 2,6-Me$_2$C$_6$H$_3$, 2,4-F$_2$C$_6$H$_3$, C$_6$F$_5$). These complexes are the only 19-electron systems containing the cyclopentadienylcobalt moiety for which isotropic room-temperature EPR spectra are known. The chemical and electrochemical stability of the radical anions is also significantly greater than for other (η^5-C$_5$H$_5$)Co derivatives. The results of these experiments are interpreted in the context of SCF–Xα–DV calculations on CpCo(1,4-H$_2$N$_4$) and its anion. The reversible redox activity of these compounds is

unique in the chemistry of metallacyclotetraazabutadienes and affords sensitive spectroscopic probes of the electronic structure of these compounds.

Experimental Section

Electronic absorption spectra were taken of $\sim$1.0 mM solutions of complexes in THF (visible and UV regions) and of 5–10 mM solutions of the complexes in THF in the near-infrared region. The THF employed was freshly distilled from sodium benzophenone ketyl, and all manipulations were carried out under an atmosphere of prepurified nitrogen. The spectra were taken with a Schlenk tube that had been modified with

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