between the lanthanides and aluminum that could offer explanations for their higher enzyme affinity include the possible involvement of the f electrons of the lanthanide ions in binding or the higher ligand exchange rates of the lanthanides (10^7–10^8 s^{-1} for water) as compared to that of aluminum (10 s^{-1} for water).[31] Higher exchange rates would permit the lanthanide complexes to undergo rapid coordination isomerization during binding to the enzyme active site and during the conformational changes that are required throughout a catalytic cycle.

Acknowledgment. This work was supported by a grant from the National Institutes of Health (AG05983). We thank Dr. Joseph Villafranca for providing the sample of glutamine synthetase purified from *E. coli.*

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Synthesis and Proton NMR Studies of the Electronic and Magnetic Properties of Low-Spin Ferric Isocyanide Tetraphenylporphyrin Complexes

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Received August 3, 1988

The preparation and spectral properties of new low-spin ferric isocyanide complexes of tetraphenylporphyrin have been reported. The increase of the CN stretching frequency in IR spectra indicates a higher bond order in the complex than in the free ligand. The proton NMR spectrum of Fe(TPP)(*t*-BuNC)$_2$ClO$_4$ has been analyzed. The hyperfine shifts have been separated into their dipolar and contact contributions. The separated components reflect the very low magnetic anisotropy of the iron, and the unusual orientation of the unpaired spin density when the nitrogen axial ligands are exchanged for isocyanide ligands leads to complete reverse localization.

The relationship between metalloporphyrin stereochemistry and the biochemical functions of hemoproteins has been the subject of extensive investigations. Previous reports from this laboratory have been directed toward systematic examination of new probes of hemoglobins.[1-3] Studies of acyl isocyanide[4] and phosphine[5,6] binding to metalloporphyrins have been of particular interest in exploring the structure of the binding site in natural hemoproteins. We now want to describe the preparation of new low-spin ferric porphyrin isocyanide complexes and their studies by various spectroscopic methods (IR and ^{1}H NMR). A quantitative separation of the dipolar and contact contributions to the hyperfine shifts for Fe(TPP)(*t*-BuNC)$_2$ClO$_4$ shows that isocyanide ligand greatly decreases the magnetic anisotropy of the iron as compared with the effect of the cyanide ligand.[7]

Table I. Isocyanide Stretching Frequencies of FeTPP Complexes[a]

L	free ligand	Fe^{III}TPP(L)$_2$ClO$_4$	Fe^{II}TPP(L)$_2$
t-BuNC	2130	2220	2129[b]
MeNC	2155	2250	2150
Me$_2$C$_6$H$_3$NC	2135	2195	2130

[a] Nujol; cm^{-1}. [b] From ref 11.

Table II. Observed Shifts and Separation of the Isotropic Shift into Contact and Dipolar Contributions in Fe(TPP)(*t*-BuNC)$_2$ClO$_4$ (ppm)

proton type	$\Delta H/H$[a]	$(\Delta H/H)_{\text{iso}}$[b]	$(\Delta H/H)_{\text{dip}}$	$(\Delta H/H)_{\text{con}}$
o-H	0.96	−7.06	0	−7.06
m-H	13.75	6.12		6.12
m-CH$_3$	1.29	−1.22		−1.22
p-H	3.21	−4.42		−4.42
p-CH$_3$	8.95	6.31		6.31
pyrr H	9.73	1.28		1.28
t-BuNC H	−1.87	−1.38		−1.38

[a] Chemical shift at 298 K with Me$_4$Si as internal reference. [b] Isotropic shift with diamagnetic Fe(TPP)(*t*-BuNC)$_2$ complex as reference.

Experimental Section

The following iron porphyrins[8] were prepared by literature methods: Fe(TPP)ClO$_4$,[9] Fe[T(*m*-Me)PP]ClO$_4$,[10] Fe[T(*p*-Me)PP]ClO$_4$,[10] and Fe[T(*o*-Me)PP]ClO$_4$.[10]

tert-Butyl isocyanide, methyl isocyanide, and *o*-dimethylphenyl isocyanide are commercially available (Fluka AG).

Caution! We have not observed detonation of iron porphyrin perchlorates under our conditions, but care is urged.

Fe(TPP)(*t*-BuNC)$_2$ClO$_4$·CH$_2$Cl$_2$. Addition of an excess of *tert*-butyl isocyanide (8 equiv) in toluene (5 mL) to 200 mg (0.26 mM) of Fe(TPP)ClO$_4$ in toluene (60 mL) at 25 °C under argon results in rapid formation of Fe(TPP)(*t*-BuNC)$_2$ClO$_4$. The solution was set aside overnight for crystallization. Fine crystals were collected by filtration and washed with toluene. Recrystallization was achieved by dissolving the product in a minimum amount of CH$_2$Cl$_2$ (10 mL) and adding hexane. The yield of CH$_2$Cl$_2$ solvate was 0.22 g (81%). Anal. Calcd for C$_{56}$H$_{48}$O$_4$N$_6$Cl$_3$Fe: C, 64.48; H, 4.74; N, 8.24. Found: C, 64.54; H, 4.75; N, 8.52. UV-vis ($\lambda_{\max}$, nm (ϵ, mM^{-1} cm^{-1}); toluene): 417 (122), 506 (12), 573 (7.8).

Fe(TPP)(CNR)$_2$ClO$_4$ (R = Me, *o*-(CH$_3$)$_2$C$_6$H$_3$) was prepared similarly. Other Fe(TPP)(CNR)$_2$ClO$_4$ complexes also gave correct analyses. The *tert*-butyl isocyanide derivatives of Fe[T(*m*-Me)PP]ClO$_4$, Fe[T(*p*-Me)PP]ClO$_4$, and Fe[T(*o*-Me)PP]ClO$_4$ were prepared as described above. The products were not recrystallized but were characterized by ^{1}H NMR, IR, and UV-visible spectroscopy. UV-vis ($\lambda_{\max}$, nm; toluene): Fe(TPP)(CN-*o*-(Me)$_2$C$_6$H$_3$)$_2$ClO$_4$, 418, 505, 569; Fe(TPP)(CN-CH$_3$)$_2$ClO$_4$, 418, 507, 572; Fe[T(*m*-Me)PP](*t*-BuNC)$_2$ClO$_4$, 417, 508, 571; Fe[T(*p*-Me)PP](*t*-BuNC)$_2$ClO$_4$, 416, 508, 572.

The synthesis of Fe(TPP)(*t*-BuNC)$_2$ has been previously reported by Jameson and Ibers.[11] Other Fe(P)(CNR)$_2$ compounds were prepared similarly (P = T(*m*-Me)PP and T(*p*-Me)PP). UV-vis ($\lambda_{\max}$, nm; toluene): Fe[T(*m*-Me)PP](*t*-BuNC)$_2$, 433, 538; Fe[T(*p*-Me)PP](*t*-BuNC)$_2$, 434, 537. Electronic spectra were measured with a Jobin Yvon Hitachi spectrophotometer as dichloromethane (or toluene) solutions with small

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(8) Abbreviations used: P, any porphyrin; (TPP)H$_2$, tetraphenylporphyrin; [T(*o*-Me)PP]H$_2$, tetrakis(*o*-methylphenyl)porphyrin; [T(*m*-Me)PP]H$_2$, tetrakis(*m*-methylphenyl)porphyrin; T[(*p*-Me)PP]H$_2$, tetrakis(*p*-methylphenyl)porphyrin; 1-MeIm, 1-methylimidazole; Im, imidazole.

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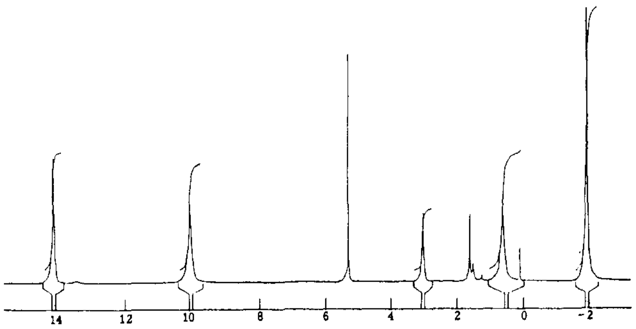

Figure 1. Proton NMR spectrum of Fe(TPP)(*t*-BuNC)$_2$ClO$_4$ in CD_2Cl_2 at 298 K.

amounts of axial ligand to prevent dissociation. IR spectra were recorded on a Unicam SP 1100 infrared spectrophotometer. The ^{1}H NMR spectra were recorded in a pulse Fourier transform mode with a Bruker AM 300 WB spectrometer. Tetramethylsilane was used as the internal reference in CD_2Cl_2. Magnetic susceptibility measurements were performed on a SHE Squid susceptometer operating at 2 kG. The reverse susceptibility curve (experimental curve) was fitted according to the modified Curie–Weiss law ($\chi = \chi_0 + C/(T - \Theta)$; $\chi_0 = -364 \times 10^{-6}$ cgsu, $C = 0.381$, $\Theta = 0.7$, $\mu = 1.73\ \mu_B$).

Results and Discussion

IR Spectroscopy. The IR spectra of the new complexes Fe(TPP)(CNR)$_2$ClO$_4$ are similar to those of Fe(TPP)(py)$_2$ClO$_4$,[9] but they all exhibit a major additional band at 2200 cm^{-1}. The $\bar{\nu}$(C≡N) stretching frequency of CNR is increased upon coordination of the isocyanide to iron(III) porphyrins, increasing from 2130 cm^{-1} for the free ligand to about 2220 cm^{-1} in Fe^{III}(P)(CNR)$_2$ClO$_4$. This increase of the frequency indicates a higher bond order in the complex than in the free ligand.[12] However, with ferrous porphyrin,[4] the isocyanide frequency does not show a significant shift upon complexation to form Fe^{II}(TPP)(*t*-BuNC)$_2$. These results are consistent with the presence of a positive formal charge on the cation in the former case and the observed rise in $\bar{\nu}$(C≡N). The increase of the bond order is attributed to the better donor properties of isocyanides to Fe(III) and to the concomitant decrease in the σ^* population of the CN bond.

^{1}H NMR Spectroscopy. The ^{1}H NMR spectrum of Fe(TPP)(*t*-BuNC)$_2$ClO$_4$ is shown in Figure 1 and the isotropic shifts are listed in Table II. The peaks for the phenyl protons of Fe(TPP)(*t*-BuNC)$_2$ClO$_4$ are assigned completely by methyl substitution on the phenyl group. The splitting for *o*-H and *o*-CH$_3$ in Fe[T(*o*-CH$_3$)PP](*t*-BuNC)$_2$ClO$_4$ results from atropoisomerism and has been similarly observed for related complexes of high-spin iron(III)[13] and low-spin iron(III).[14] For isocyanide axial ligands, measurement of the relative intensities completely determines the assignment.

However, the spectrum in Figure 1 shows unexpected behavior in that the pyrrole proton signal is found in a downfield position at 9.73 ppm. Pyrrole signals in the 70–80 and −15 ppm regions would be apparent for respective high-spin[15] and low-spin species.[16] Evans' magnetic measurements[17] were made for 0.01 M CD_2Cl_2 solutions of Fe(TPP)(*t*-BuNC)ClO$_4$ employing Me$_4$Si as the reference (37 °C). Both the solution magnetic moment ($\mu = 1.73\ \mu_B$) and the solid-state measurement (Figure 2) (μ (37 °C) = 1.80 μ_B) for Fe(TPP)(*t*-BuNC)$_2$ClO$_4$ are compatible with the low-spin state $S = {}^1/_2$.

Variable-temperature spectra of Fe(TPP)(*t*-BuNC)$_2$ClO$_4$ show the expected behavior. A magnetically simple molecule is expected to follow Curie-law behavior in that a plot of δ vs $1/T$ is linear with an intercept equal to the resonance in the analogous diamagnetic complex. Plots of ortho, meta, and para signals of meso-aryl protons are reasonably linear with intercepts respectively at 8.8, 7.3, and 8.6 ppm. Though these values are close to diamagnetic resonances, however, an intercept of ~5 ppm (Figure 3) is to be contrasted with the value of 8.45 ppm for pyrrole in diamagnetic Fe(TPP)(*t*-BuNC)$_2$. We previously observed such a deviation for Fe(TPP)(PMe$_3$)$_2$ClO$_4$, which may also originate in the contact shift.[5]

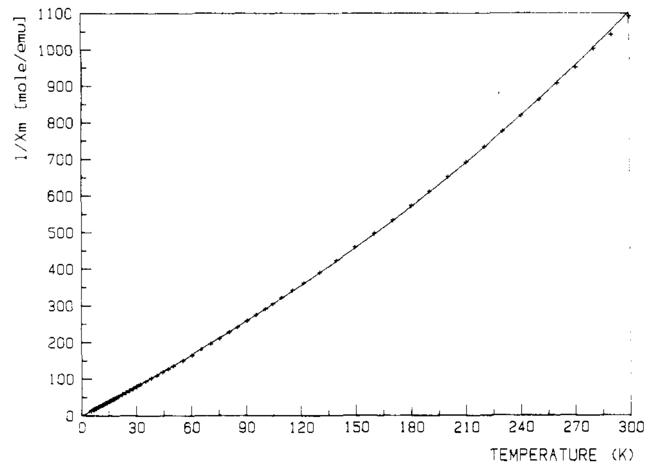

Figure 2. Curie plot for Fe(TPP)(*t*-BuNC)$_2$ClO$_4$.

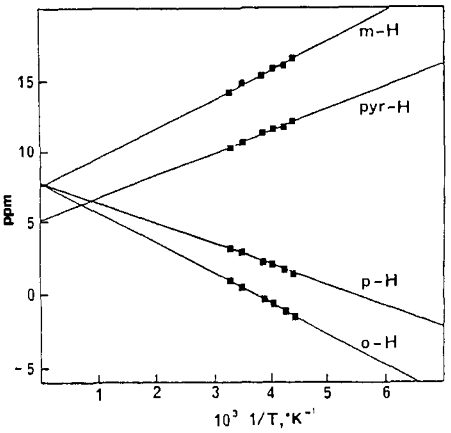

Figure 3. Curie plot for proton resonances for Fe(TPP)(*t*-BuNC)$_2$ClO$_4$ in CD_2Cl_2.

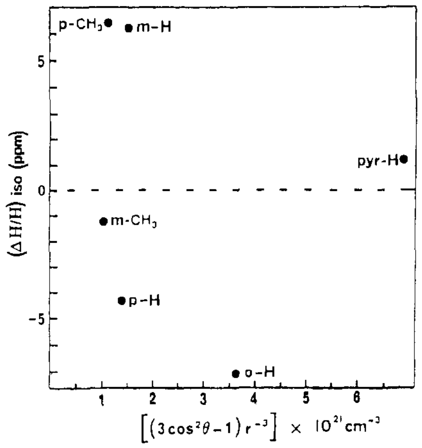

Figure 4. Graph of isotropic shifts at 298 K versus the geometric factor $(3\cos^2\theta - 1)/r^3$ for aryl and pyrrole protons in Fe(TPP)(*t*-BuNC)$_2$ClO$_4$. The deviations of the experimental points from the best-fit straight line through the origin yield $(\Delta H/H)_{\text{con}}$ for each position.

In order to characterize the iron alkyl isocyanide porphyrin electronic structure, analysis of the chemical shift was made according to the method of La Mar.[7] The isotropic shifts $(\Delta H/H)_{\text{iso}}$ were calculated by using Fe(TPP)(*t*-BuNC)$_2$ and related diamagnetic complexes as references. The plot of $(\Delta H/H_{\text{iso}})$

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vs (3 $\cos^2\theta - 1)/r^3$ for all meso-aryl positions for $Fe(TPP)(t\text{-}BuNC)_2ClO_4$ (and methyl substituents) is given in Figure 4. The slope of the best-fit straight line will yield directly the dipolar contribution to all shifts, while the magnitude of the deviation for the individual data points will yield the contact contribution as previously suggested by La Mar.[7] It is clearly observed that (i) the fit of the shifts to the geometric factor is very poor, (ii) the best fit for the points yields a straight line with a slope very close to zero with large deviations of alternating signs (Table II). Thus, here the magnetic anisotropy is negligible.

Hence, the phenyl proton shifts were analyzed in terms of the contact interaction. At the meso position, the contact shifts for the phenyl protons are large and the presence of sign reversal between the proton and the methyl group indicates that a large amount of π spin density is placed on the phenyl carbons. The lowest vacant π molecular orbital (4e π^*) exhibits large meso-carbon spin density for low-spin ferric porphyrins.[18] Hence, the contact shift data are consistent only with dominant spin transfer involving Fe → porphyrin π^* charge transfer. Such a mechanism would be expected if alkyl isocyanides acted as pure donor ligands. The large increase of the frequency ($\bar{\nu}$(CN) ≈ 80 cm^{-1}) indicates that this is the case and there is no significant electron flow toward the π orbitals of the ligands.[12]

The small contact shift for pyrrole protons favors the interpretation that negligible spin density is placed on the pyrrole carbons and accounts for the observed downfield shifts. It is interesting to note that the mechanism of spin transfer appears here to give rise to a conclusion opposite to that observed for low-spin ferric bis(imidazole) complexes of a series of synthetic porphyrins.[14] In this latter case, the phenyl proton shifts of $Fe(TPP)(Im)_2Cl$ were found to be wholly dipolar in origin.

It is noteworthy that the proton NMR data of La Mar et al. have already provided evidence that the magnetic anisotropy is decreased and that the π-contact shifts for the meso position are increased in low-spin dicyano ferric complexes of tetraarylporphyrins as the solvent hydrogen-bonding donor strength increases.[7] Our results are consistent with those reported by these authors since complete protonation of cyanide complexes would lead to isocyanide complexes. In conclusion, the orientation of the unpaired spin density in $S = {}^1/_2$ ferric porphyrin derivatives is strongly influenced by the nature of the axial ligands since exchanging a nitrogen base (imidazole) for isocyanide leads to completely reverse localization.

Acknowledgment. We wish to thank Dr. H. Noel for carrying out the magnetic susceptibility studies.

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Resonance Raman Spectroscopy of Iron(II) Superstructured Porphyrins: Influence of Porphyrin Distortions on CO and O_2 Ligand Dissociation

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Received June 3, 1988

Resonance Raman spectroscopy has been used to probe the effects of a strap strain on the bonding of O_2 and CO of four synthetic Fe(II) [bis(picket)(handle)]tetraphenylporphyrin derivatives complexed with 1-methylimidazole ($Fe^{II}[(Piv)_2C_n](1MeIm)$). The strain is introduced by varying the length of the amide-linked handle from 12 to 8 carbon atoms (n = 12, 10, 9, 8). In the deoxygenated state, minor structural alterations are characterized for the C_8 derivative only at the tetrapyrrole periphery, the phenyl groups, and the Fe–N(axial ligand) bond. Upon CO binding, a gradual increase of the ν(Fe–CO) stretching frequency is found upon handle shortening. The frequency shifts of these modes (4–5 cm^{-1}) upon $^{12}CO \rightarrow {}^{13}CO$ isotope substitution are indicative of a linear Fe–CO grouping, confirming recent X-ray crystallographic data on the C_{12} and C_8 (Ricard, L.; Weiss, R.; Momenteau, M. *J. Chem. Soc., Chem. Commun.* **1986**, 818–820. Fisher, J.; Weiss, R.; Momenteau, M. Unpublished results). The increased frequency of the ν(Fe–CO) mode is interpreted in terms of a shortening of the Fe–CO bond in a linear Fe–CO unit perpendicular to the heme plane when the handle length decreases. Upon O_2 binding, the $\nu(Fe–O_2)$ stretching mode is found nearly insensitive to the handle length (560–563 cm^{-1}). This is the first report for such a low frequency for this mode generally observed in the 568–573-cm^{-1} range for other oxygenated ferroporphyrins and oxyhemoproteins. This frequency lowering is interpreted as corresponding to a deformation of the Fe–O–O angle promoted by an intramolecular H bonding between the bound O_2 and one of the amino groups of the handle. The high-frequency regions of RR spectra of deoxy derivatives show that the core size of five-coordinated complexes is unaffected by the handle shortening. On the other hand, both oxygenated and carbonylated complexes exhibit a gradual frequency increase of the mode ν_4 accompanied by a gradual frequency decrease of the mode ν_2 when the handle is shortened. This effect is attributed to increased deformations of the tetrapyrrole skeleton. Comparisons of the O_2-off rate constants of the four oxygenated complexes with their Fe–ligand bond strengths and porphyrin deformations indicate that porphyrin deformations play a major role in ligand dissociation. Similarly, in the carbon monoxide derivatives, a cancelling effect of the strengthening of the Fe–CO bond by increased porphyrin deformations should explain the near-invariability of the observed CO dissociation rates.

Introduction

The control of affinities for O_2 and CO in hemoproteins may be regulated by both steric and local polar effects provided by distal amino acid residues.[2] Indeed, CO binds to the iron atom of simple Fe(II) porphyrins in a linear structure along the heme normal.[3] In hemoglobins and myoglobins, the steric effects of amino acid side chains constituting the distal side of the heme pocket can modify the linear Fe–CO grouping into a tilted and/or bent conformation.[4] Recently, Kuriyan et al.[5] found two clear

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