ported here gave no evidence of birefringence; but the test for nonbirefringence which we used does not rule out a net orientation perpendicular to the film surface. We think such an orientation is unlikely, but should it be present in our films, a quantitative comparison of the cited calculations with these data would not be appropriate. Nevertheless, insofar as such an orientation is small, a qualitative comparison is still allowed.

References and Notes

(1) This work was supported by the National Science Foundation through Grant GB-40426.
(2) Author to whom correspondence should be addressed.
(3) M. A. Young and E. S. Pysh, *Macromolecules*, **6**, 790 (1973).
(4) W. C. Johnson, Jr., and I. Tinoco, Jr., *J. Am. Chem. Soc.*, **94**, 4389 (1972).
(5) F. A. Bovey and F. P. Hood, *Biopolymers*, **5**, 325 (1967).
(6) S. N. Timasheff, H. Susi, R. Townend, L. Stevens, M. J. Gorbunoff, and T. F. Kumosinski, "Conformation of Biopolymers", G. N. Ramachandran, Ed., Academic Press, New York, N.Y., 1967.
(7) R. Mandel and G. Holzwarth, *Biopolymers*, **12**, 665 (1973).
(8) E. S. Pysh, *J. Mol. Biol.*, **23**, 587 (1967).
(9) E. S. Pysh, *J. Chem. Phys.*, **52**, 4723 (1970).
(10) V. Madison and J. Schellman, *Biopolymers*, **11**, 1041 (1972).
(11) L. Tterlikkis, F. M. Loxsom, and W. Rhodes, *Biopolymers*, **12**, 675 (1973).
(12) M. A. Young, Ph.D. Thesis, Brown University, Providence, R.I., 1974.
(13) D. E. Eastman and J. J. Donelon, *Rev. Sci. Instrum.*, **41**, 1648 (1971).
(14) J. L. Bensing and E. S. Pysh, *Chem. Phys. Lett.*, **4**, 120 (1969).
(15) R. K. Momii and D. W. Urry, *Macromolecules*, **1**, 373 (1968).
(16) J. Brahms, J. Pilet, H. Damany, and V. Chandrasekharan, *Proc. Nat. Acad. Sci. U.S.A.*, **60**, 1130 (1968).
(17) J. P. Carver, E. Schecter, and E. R. Blout, *J. Am. Chem. Soc.*, **88**, 2550, 2562 (1966).
(18) W. Traub and U. Shmueli, "Aspects of Protein Structure", G. N. Ramachandran, Ed., Academic Press, New York, N.Y., 1963.
(19) E. W. Ronish and S. Krimm, *Biopolymers*, **13**, 1635 (1974).
(20) E. S. Pysh, *Biopolymers*, **13**, 1563 (1974).

Proton Nuclear Magnetic Resonance Studies of High-Spin Manganese(III) Complexes with Synthetic Porphyrins

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Abstract: The proton NMR spectra of a series of manganese complexes with the synthetic prophyrins, tetraarylporphyrin, octaethylporphyrin, and tetra-*n*-propylporphyrin have been analyzed and assigned. Some discrepancies between the assignments of natural and synthetic porphyrin complexes are noted. The isotropic shifts are shown to be predominantly contact in origin, reflecting extensive porphyrin-to-metal π bonding. This spin transfer mechanism is consistent with the decrease in the extent of spin transfer with increasing π donor properties of the axial halogen. The mechanism of spin transfer appears unaffected upon addition of nitrogenous bases. The bonding in the Mn(III) complexes is compared with that of both high-spin and low-spin ferric porphyrins.

During the past 5 years it has become abundantly clear that NMR spectroscopy in paramagnetic proteins,[2a] particularly hemoproteins,[2b] can provide a wealth of information on the electronic, magnetic, and stereochemical properties of the active site. In view of the complexity of the hemoproteins,[2] parallel advances have been made in analyzing the proton NMR spectra of simple model porphyrin complexes.[3-9] The use of such model compounds has been shown[2b-9] to facilitate the elucidation and interpretation of the spectral properties of the active site in hemoproteins under conditions which permit some latitude in the variation of the parameters of interest.

Although the bulk of the recent interest in model compounds has focused on the iron porphyrins[2b-9] due to their occurrence as the prosthetic group in myoglobins, hemoglobins, and cytochromes,[2a] the demonstrated activity of cobalt-hemoglobin[10] has led to similar interest in the NMR spectra of cobalt(II) porphyrin complexes.[11,12] Proton NMR studies of the high-spin,[3,9] HS, and low-spin,[4-8] LS, ferric and LS cobalt(II)[11,12] complexes have permitted the characterization of the metal porphyrin, M-P, π bonding, the magnetic properties of the metal, as well as certain dynamic and thermodynamic properties of axial ligation. Comparison between complexes of natural[3,4,12] and synthetic[5-9,11] porphyrin ligands has indicated that the bonding, magnetic, and dynamic properties of interest are very similar and that the complexes of synthetic ligands may serve as useful models for some properties of hemoproteins. Furthermore, the high symmetry and structural variety available in synthetic porphyrins has been shown to yield less ambiguous assignments as well as interpretations of the coupling constants in terms of M-P π bonding.

Unambiguous evidence for a biological role for manganese porphyrins is lacking at this time. However, the possible role[13a] of manganese-chlorophyll-type complexes in photosynthesis has been suggested, and recent work indicates the existence of manganese porphyrin in erythrocytes.[13b] Furthermore, both myoglobin, Mb, and hemoglobin, Hb, can be reconstituted[13a] with manganese protoporphyrin IX. Although MnMb and MnHb are inactive with respect to reversible oxygenation, hybrid hemoglobins containing both manganese and iron have been demonstrated[14] recently to serve as valuable models for probing the nature of the cooperatively effect.[15] The possibility of detecting[14] hyperfine shifted resonance due to the Mn(III) in such hemoproteins suggests that an elucidation of the origin of the isotropic shifts in model Mn(III) prophyrin complexes may be useful for interpreting the protein spectra. In addition, a comparison[13a] of the M-P bonding in Mn(III) and Fe(III) complexes may shed some light on the unique role played by iron in these proteins.

Mn(III) porphyrins constitute[13a] a class of well characterized complexes which have been the center of recent attention[16-20] due to unusual optical properties which have been interpreted[21] as reflecting significant M-P π bonding. The complexes[13a] are always HS, with $S = 2$, occurring as both five-coordinate,[19] PMn(III)X, and six-coordinate species[20] (presumably PMn(III)X(B)) (X = halide or

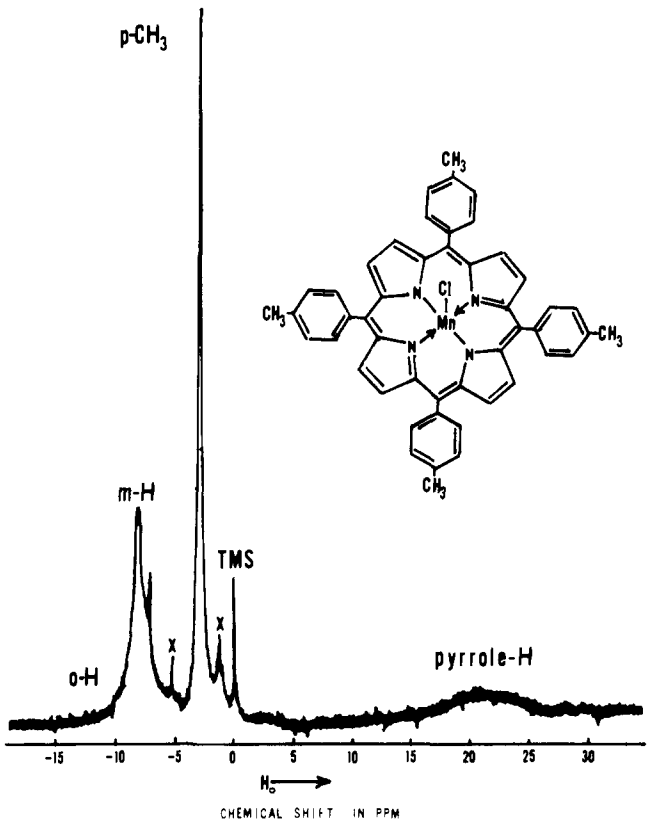

Figure 1. Proton NMR trace of p-CH_3-TPPMnCl in $CDCl_3$ solution.

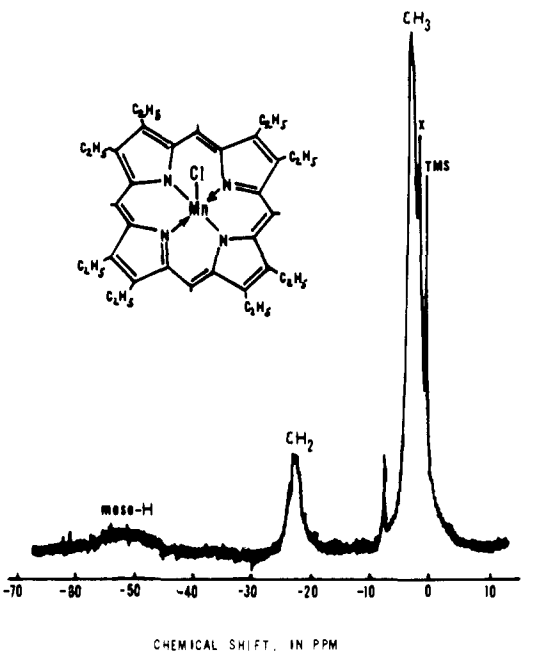

Figure 2. Proton NMR trace of OEPMnCl in $CDCl_3$ solution.

pseudo-halide, B = base). The structures for both cases have been characterized[19,20] by X-ray crystallography. The five-coordinate complex of tetraphenylporphyrin, TPPMnCl, which is obtained from noncoordinating solvents, contains a regular TPP geometry, with the Mn raised 0.27 Å above the mean porphyrin plane.[19]

The proton NMR spectra for the Mn(III) complexes with natural porphyrins have been reported.[18] However, the complexity of the spectra due to the low symmetry yielded some ambiguous assignments,[18] and the lack of a suitable variety of probes prevented a detailed characterization of the M-P π bonding. In view of the demonstrated[6-8] similarity of the isotropic shifts and π bonding in ferric porphyrins of natural and synthetic origin, we have extended our proton NMR investigations to a series of five-coordinate Mn(III) complexes with synthetic porphyrins. We had previously demonstrated[17] that such porphyrins exhibited well-resolved resonances whose line widths yielded useful data on the magnitude and sign of the zero-field splittings,[16] ZFS. The synthetic porphyrins of choice are the tolylporphyrins,[22a] X-CH_3-TPPMnX, (X = F, Cl, Br, I, N_3), which have proved to be useful probes of the magnetic anisotropy,[7,11] and octaethylporphyrin,[22b] OEPMnCl, and *meso*-tetra-*n*-propylporphyrin,[22c] T-*n*-prPMnCl, which possess protons as well as methylene groups at both meso and pyrrole positions, and thereby reflect[23] the nature of the π orbital containing the delocalized metal spin density.

Experimental Section

The series of complexes p-CH_3-TPPMnCl used in this study are the same as those reported[17] previously. OEPMnCl and T-*n*-prPMnCl were prepared according to the method of Adler et al.[24] The structures of OEPMnCl and T-*n*-prPMnCl were confirmed by their proton NMR spectra.

Solutions of the porphyrin complexes were prepared by dissolving a 10-15 mg sample of 0.3 ml dry chloroform-*d* and adding 0.1% TMS as reference. The proton NMR spectra were recorded on a Varian HR-100 spectrometer operating at 100 MHz, modified to operate with variable frequency modulation, and with an ambient probe temperature at 35°. Audio side bands were used for peak calibration, and TMS served as an internal reference. For variable temperature studies, the probe temperature was monitored with a Varian V-4343 Variable Temperature Control Unit which was precalibrated with methanol and ethylene glycol. Diluting $CDCl_3$ samples of TPPMnCl and p-CH_3-TPPMnCl by a factor of 3 did not significantly affect the chemical shifts, indicating that aggregation is relatively unimportant. The ^1H NMR spectra for the diamagnetic ligands and nickel(II) porphyrin complexes were obtained on a Jeolco C-60H spectrometer operating at 60 MHz. All shifts are reported in parts per million.

Results and Discussion

Assignments of NMR spectra. The proton NMR trace of p-CH_3-TPPMnCl in $CDCl_3$ is shown in Figure 1. The assignment of peaks is arrived at on the basis of methyl substitution and line widths. The o-H peak is not resolved, although a broad resonance at ~−8 ppm from TMS is noted at high power levels which probably arises from the broad o-H signal. The T-*n*-prPMnCl peaks are assigned on the basis of intensities and by analogy to TPPMnCl. For OEPMnCl, whose proton NMR trace is given in Figure 2, the broadest peak ~50 ppm downfield from TMS arises from meso-H; the upfield peak belongs to CH_3, and the peak in the middle is due to pyrr-α-CH_2, based primarily on relative intensities and line widths. No peak upfield of TMS is observed contrary to earlier reports[18] on the related natural porphyrins. The isotopic shifts for all assigned resonances, referenced against the analogous diamagnetic Ni(II) complex,[25] are listed in Table I.

We note that our assignment of the meso-H to a downfield resonance differs from that reported by Janson, Boucher, and Katz.[18] Although the different resonance positions could arise due to the possibility that the natural porphyrin complexes are six-coordinate,[13a,20] analysis of the line width suggests that this is not the cause of the discrepancy. In OEPMnCl, the meso-H peak is broader than the pyrr-α-CH_2 by a factor of 5-8, which is similar to the ratio observed for the same HS Fe(III) complex,[6,26] and reflects their relative r^{-6} values.[17] The upfield peaks assigned to meso-H in the etioporphyrin I complex of Mn(III), however, were found[18] to be comparable in line width to the

Table I. Observed Isotropic Shifts for Mn(III) Porphyrins[a]

		Phenyl protons			
	pyrr-H	o-H[b]	m-H	p-H	CH_3
TPPMnCl	+30.3		−0.4	+0.4	
o-CH_3-TPPMnCl	+29.0		−0.5	+0.7	+0.4
m-CH_3-TPPMnCl	+30.0		−0.5	+0.6	+0.22
p-CH_3-TPPMnCl	+30.2		−0.6		−0.29
		Propyl protons			
		α-CH_2	β-CH_2	γ-CH_3	
T-n-pr-PMnCl	+29.3	−4.7	+0.5	~0	
		Ethyl protons			
		α-CH_2	β-CH_3	meso-H	
OEPMnCl		−18.2	−0.7	−41.4	

[a] Shifts in ppm, at 35°, in $CDCl_3$ solution, referenced against Ni(II) complex or free ligand (T-n-prP). [b] The o-H peak is not clearly resolved, but appears to occur as a very broad resonance near $CDCl_3$, its diamagnetic position.

α-CH_2 peaks, which is inconsistent with the demonstrated dominance of dipolar relaxation.[17] The downfield meso-H resonances in the natural porphyrin[18] complexes were not resolved probably due to their excessive width and the low symmetry.

Origin of the Shifts. There is no a priori knowledge of the magnetic anisotropy of the Mn(III) in these complexes, although ESR data on other Mn(III) chelates[27] suggest that g tensor anisotropy should be small. Dipolar shifts[28] due to zero-field splittings, for which a T^{-2} dependence[26] is predicted, are not expected to be significant since D for Mn(III) porphyrin is much smaller[16,17] than for the ferric analogs. The temperature dependence of the pyrr-H peak in p-CH_3-TPPMnCl was determined over the range −20 to +75°. Excessive line broadening prevented measurements at lower temperatures. The isotropic shift yielded a straight line as a function of T^{-1}, although the relatively narrow temperature range and broad peaks do not exclude the possibility of significant curvature. Though the isotropic shift vs. T^{-1} yielded a straight line, the intercept at $T^{-1} = 0$ was 12.7 ppm downfield from the position in the Ni(II) complex. Similar nonzero intercepts were observed[7] for LS Fe(III), and probably arise from the second-order Zeeman interaction.[28]

The absence of significant contribution from the dipolar interaction[28] to the observed shift for any position can be demonstrated by considering the meso-aryl substituent shifts. Previous work has shown[7,11] that a dipolar interaction produces a shift ratio of 10.0:4.6:4.1:3.0 for the o-H:m-H:p-H:p-CH_3 peaks. The observed shifts in Table I do not reflect this attenuation of shift of the same sign, but rather exhibit alternation of sign around the phenyl ring, as expected[23] for contact shifts. In particular, the comparable shift magnitudes but opposite signs for the protons and methyl group at both the meta and para positions argue[23] strongly for negligible dipolar shifts. The semiquantitative agreements of the aryl shifts with those expected for H spin density indicate an upper limit of a 0.1 ppm dipolar shift at o-H. Using published relative geometric factors, the maximum dipolar contributions to the meso-H and pyrr-H shifts are 0.3 and 0.2 ppm, respectively. These contributions are completely insignificant for meso-H shift and are too small to account for the variation in pyrr-H shifts with X (vide infra). Since ESR data for the analogous LS ferric porphyrins[7,29] have indicated that magnetic anisotropy is not very sensitive to the porphyrin substituent, we assume here that the contact mechanism dominates in both OEPMnCl and T-n-prPMnCl.

Table II. Observed Isotropic Shifts of p-CH_3-TPPMnX as a Function of X[a]

X	Pyrr-H	m-H	p-CH_3
F	+28.2	−0.5	−0.28
N_3	+29.6	−0.8	−0.28
Cl	+30.2	−0.6	−0.29
Br	+31.6	−0.7	−0.39
I	+34.7	−0.8	−0.43

[a] Shifts in ppm, at 35°, referenced against diamagnetic Ni(II) porphyrin.

Nature of the M-P π Bonding. The alternating signs of the contact shift for pyrr-H (+30 ppm) and pyrr-α-CH_2 (−18 ppm) clearly reflect predominately π spin density[7,23] in the pyrrole rings. At the bridging positions, the downfield meso-H shift (−41 ppm) and meso-α-CH_2 shift (−5 ppm) suggest primarily σ unpaired spin density[7,23] at the methine carbon. (The minor π spin density on the meso-aryl substituent can arise from σ-π nonorthogonality.) Two ligand π MO's of the correct symmetry[30] (e) have energies suitable for extensive M-P π bonding, e_3, a filled MO, and e_4*, a vacant MO. The latter MO, e_4*, concentrates the delocalized spin at the methine positions, while the former MO, e_3, places the unpaired π spin density in the pyrrole fragment. The present Mn(III) contact shift pattern is therefore consistent with a predominance of P → M π charge transfer[7] as the delocalization mechanism.

Effect of Axial Ligand. The values for the isotropic shifts for p-CH_3-TPPMnX as a function of X = F, Cl, Br, I, and N_3 are listed in Table II. The pyrr-H shifts increase upfield in the order F < N_3 < Cl < Br < I. A similar trend in line width with X was observed[17] previously. A parallel trend of increasing downfield shifts is observed for m-H and p-CH_3. This increase of shift magnitudes in opposite direction for the pyrr-H and phenyl substituent shifts requires that the changes in shifts arise from the contact interaction, since the predicted dipolar shift[7,11] directions are the same for all positions.

This increase in the pyrr-H contact shift must therefore reflect an increase in P → Mn π change transfer. It seems reasonable to assume that changes in Mn-P π bonding result from changes in Mn-X π bonding. In terms of π bonding, X can only act as a donor, in the order F > Cl > Br > I. Hence the change in pyrr-H contact shift reflects the competition between X and P as donors; as the π donor strength of X decreases, the extent of P → Mn π charge transfer increases.

Effect of Added Bases. The proton NMR spectrum of p-CH_3-TPPMnCl was also recorded upon addition of pyridine-d_5 and N-methylimidazole. The porphyrin shifts changed similarly with the amount of either ligand, asymptotically reaching the values of isotropic shifts: pyrr-H = +35 ppm, m-H = +0.5 ppm, and p-CH_3 = 0.3 ppm. At least a tenfold excess of ligand was added to reach the 35 ppm pyrr-H shift. Attempts to determine the nature of the species in solution using optical spectroscopy and the NMR shift proved inconclusive. The absence of clear isosbestic points indicated the presence of several species.[31] Since the shift pattern in the six-coordinate complex with either one or two bases is very similar to that of the five-coordinated species, no further attempt was made to identify the species in solution.[31] The slight upfield bias noted for all resonances in the presence of base suggests the possibility of a small dipolar contribution to the shifts. The changes, however, are so small so as to indicate that the contact shift pattern, and hence the nature of the M-P π bonding in HS Mn(III) porphyrin, does not depend significantly on the coordination number.[13]

Table III. Comparison of Contact Shift Patterns in High-Spin Mn(III), High-Spin Fe(III), and Low-Spin Fe(III) Porphyrins

	HS Mn(III)[b]	HS Fe(III)[c]	LS Fe(III)[d]
Pyrr-H[e]	+30	−61	+20
Pyrr-α-CH_2[f]	−18	−32	−5
Meso-H[f]	−41	+80	−2
Meso-α-CH_2[g]	−5	−50	−5
S	2	$^5/_2$	$^1/_2$
Configuration	$(d_{xy}^{\pi},d_{yz}^{\pi})^2(d_{xy})^1(d_{z^2}^{\sigma})^1$	$(d_{yz}^{\pi}d_{xz}^{\pi})^2(d_{z^2})^1(d_{z^2}^{\sigma})^1$-$(d_{x^2y^2}^{\sigma})^1$	$(d_{xz}^{\pi}d_{yz}^{\pi})^5$
M–P π bonding	P → M	M → P	P → M

[a] In ppm at 35°. [b] This work. [c] Reference 6. [d] Reference 7. [e] Data from TPP complex. [f] Data from OEP complex. [g] Data from T-*n*-prP complex.

Comparison with Ferric Porphyrins. The contact shift pattern for these Mn(III) porphyrins is similar to that previously reported for the LS Fe(III) complexes, in that both reflect π spin density only on the pyrrole. The meso σ spin density is more important for the Mn(III) compounds, presumably because Mn(III) has an unpaired spin in the σ-bonding d orbitals. It is interesting to note that the analogous HS Fe(III) complexes exhibited[6] contact shifts reflecting primarily Fe → P π*charge transfer. The contact shifts and resultant interpretations in terms of M–P π bonding in HS Mn(III) and LS and HS Fe(III) are summarized in Table III.

For the HS ferric system PFeX, where Fe → P π* charge transfer was shown[6,26] to dominate, the net isotropic shift was found to be very insensitive to X. However, since the dipolar shifts due to the ZFS term[16] increase in the order Cl < Br < I, the contact shift, and hence the extent of Fe → P π* charge transfer, decreases[6,26] in the order Cl > Br > I. Therefore, for ferric species, the increase in halogen π donor strength facilitated Fe → P π bonding, in contrast to the present Mn(III) complexes. The contrasting dependence of delocalized H spin density can be traced directly to the different modes of M–P π charge transfer.

The reduced importance of M → P π* bonding in HS Mn(III) relative to HS Fe(III) is somewhat surprising since the higher energies of the Mn(III) d orbitals relative to those of Fe(III) in a series of isostructural complexes should favor this mechanism[32] for Mn(III). The configurations[13] for Mn(III), $(d_{xz},d_{yz})^2(d_{xy})^1(d_{z^2})^1$, place spins in each of the appropriate e type π bonding d orbitals, as does Fe(III), $(d_{xz},d_{yz})^2(d_{xy})^1(d_{z^2})^1(d_{x^2y^2})^1$, so that the different delocalization mechanisms cannot be rationalized by the unavailability[33] of suitable spins in one or another case. The greater importance of σ spin delocalization in the Fe(III) species can be traced to the presence of an unpaired spin in $d_{x^2y^2}$, which is missing in Mn(III).

One plausible explanation of this unexpected difference in M–P π bonding between the HS Mn(III) and Fe(III) may be in the difference in structure of their porphyrin complexes. For the presumed isostructural TPPMCl complexes, X-ray studies have revealed that the iron[34] suffers a significantly larger out-of-plane displacement (~0.38 Å), than does the manganese[19] (0.27 Å). In $TPPMnN_3(CH_3OH)$,[20] the out-of-plane displacement is only ~0.08 Å. Hence the contact shifts for Mn(III) porphyrin appear to be relatively insensitive to the coordination number and out-of-plane displacement, contrary to the case for Fe(III). Proton NMR data of natural porphyrin complexes have suggested[3b,6] that the M–P π bonding in six-coordinate HS Fe(III) differs significantly from that in the five-coordinate species, with the Fe → P π* charge transfer apparently suppressed in the former geometry. Hence the difference in M–P π bonding between Mn(III) and Fe(III) may reflect more the particular stereochemistry (large out-of-plane displacement) for Fe(III) forced on the metal ion by the macrocyclic tetrapyrrole than the inherent bonding tendencies of the metal ions which might be expected to manifest themselves in less constrained ligand systems.

This reduced tendency of five-coordinate Mn(III), relative to Fe(III), to act as a π acid in TPPMX may, in part, account for the failure of Mn(II) to reversibly bind molecular oxygen.[13a]

Comparison of the proton NMR spectra of the Mn(III) species with natural[18] and synthetic porphyrins suggests, as was found to be the case in both HS[6,26] and LS[7] Fe(III), that the synthetic porphyrin complexes may serve as useful models for elucidating structural and electronic properties of the natural hemes as well as of Mn(III) substituted hemoproteins. For the two correctly assigned functional groups in common, pyrr-α-CH_2 and pyrr-β-CH_3, the observed shifts in the natural and synthetic porphyrin complexes were the same.

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References and Notes

(1) (a) University of California, Fellow of the Alfred P. Sloan Foundation; (b) California State University.
(2) (a) W. D. Phillips, "NMR of Paramagnetic Molecules: Principles and Application", G. N. La Mar, W. D. Horrocks, Jr., and R. H. Holm, Ed., Academic Press, New York, N.Y., 1973, Chapter 11; (b) K. Wüthrich, *Struct. Bonding (Berlin)*, **8**, 9 (1970).
(3) (a) W. S. Caughey and L. F. Johnson, *Chem. Commun.*, 1362 (1969); (b) R. J. Kurland, R. G. Little, D. G. Davis, and C. Ho, *Biochemistry*, **10**, 2237 (1971); (c) H. A. Degnani and D. Fiat, *J. Am. Chem. Soc.*, **93**, 4281 (1971); (d) H. A. O. Hill and K. G. Morallee, *ibid.*, **94**, 731 (1972).
(4) (a) K. Wüthrich, R. G. Shulman, B. J. Wyluda, and W. S. Caughey, *Proc. Natl. Acad. Sci. U.S.*, **62**, 636 (1969); (b) R. G. Shulman, K. Wüthrich, T. Yamane, G. Antonini, and M. Brunori, *ibid.*, **63**, 6231 (1969).
(5) K. Wüthrich and R. Baumann, *Helv. Chim. Acta*, **56**, 585 (1973).
(6) F. A. Walker and G. N. La Mar, *Ann. N.Y. Acad. Sci.*, **206**, 328 (1973).
(7) G. N. La Mar and F. A. Walker, *J. Am. Chem. Soc.*, **95**, 1782 (1973).
(8) G. N. La Mar and F. A. Walker, *J. Am. Chem. Soc.*, **94**, 8607 (1972).
(9) G. N. La Mar, *J. Am. Chem. Soc.*, **95**, 1662 (1973).
(10) B. M. Hoffman and D. H. Petering, *Proc. Natl. Acad. Sci. U.S.*, **67**, 637 (1970).
(11) G. N. La Mar and F. A. Walker, *J. Am. Chem. Soc.*, **95**, 1790 (1973).
(12) C. D. Barry, H. A. O. Hill, B. E. Mann, P. J. Sadler, and J. P. Williams, *J. Am. Chem. Soc.*, **95**, 4545 (1973), and references therein.
(13) (a) L. J. Boucher, *Coord. Chem. Rev.*, 7, 289 (1972); (b) R. G. Hancock and K. Fritze, *Bioinorg. Chem.*, **3**, 77 (1973).
(14) B. M. Hoffman, private communication.
(15) E. Antonini and M. Brunori, "Hemoglobin and Myoglobin in their Reactions with Ligands", American Elsevier, New York, N.Y., 1971, Chapter 7.
(16) G. C. Brackett, P. L. Richards, and W. S. Caughey, *J. Chem. Phys.*, **54**, 4383 (1971).
(17) G. N. La Mar and F. A. Walker, *J. Am. Chem. Soc.*, **95**, 6950 (1973).
(18) T. R. Janson, L. J. Boucher, and J. J. Katz, *Inorg. Chem.*, **12**, 940 (1973).
(19) B. M. Chen and A. Tulinsky, private communication to F. A. Walker. The fact that standard deviations are ~0.013 Å indicates that the Mn(III) out-

of-plane distance of 0.27 Å is definitely less that the 0.38 Å value in the analogous Fe(III) complex.
(20) V. W. Day, B. R. Stults, E. L. Tasset, R. O. Day, and R. S. Marianelli, *J. Am. Chem. Soc.*, **96**, 2650 (1974).
(21) L. J. Boucher, *J. Am. Chem. Soc.*, **90**, 6640 (1968).
(22) (a) A. D. Adler, F. R. Longo, J. F. Finarreli, J. Goldmacher, J. Assour, and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967); (b) H. W. Whitlock and R. Hanauer, *ibid.*, **33**, 2169 (1968); (c) A. D. Adler, unpublished work.
(23) Reference 2a, Chapter 3.
(24) A. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).
(25) For T-*n*-prPMnCl, the free ligand was used as reference.
(26) G. N. La Mar, G. R. Eaton, R. H. Holm, and F. A. Walker, *J. Am. Chem. Soc.*, **95**, 63 (1973).
(27) R. M. Golding, E. Sinn, and W. C. Tennant, *J. Chem. Phys.*, **56**, 5296 (1972).
(28) J. P. Jesson, ref 2a, Chapter 1.
(29) J. Peisach, W. E. Blumberg, and A. Adler, *Ann. N.Y. Acad. Sci.*, **206**, 310 (1973).
(30) H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, **18**, 1174 (1950).
(31) More detailed studies of the optical spectra in the presence of nitrogenous bases are in progress (F. A. Walker, C. G. Kreis, and M. W. Lo, to be published).
(32) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965).
(33) G. N. La Mar, *Inorg. Chem.*, **10**, 2633 (1971).
(34) J. L. Hoard, G. H. Cohen, and M. D. Glick, *J. Am. Chem. Soc.*, **89**, 1992 (1967).

Substituent Effects in Noncoplanar π Systems. *ms*-Porphins

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Abstract: Visible and near ultraviolet absorption spectra of substituted *ms*-tetraphenylporphins, *ms*-tetraalkylporphins, and their acid dications show increasing bathochromic shifts relative to *ms*-tetraphenylporphin itself with increasing electron-donating power of the substituents. Simultaneous increases in the transition dipole ratios of the Q(0–0) and Q(0–1) band visible transitions and in the basicity of the pyrrole nitrogens are also observed in these same series. Changes of the largest magnitude are seen for the acid dications. Composite Hammett σ plots including both inductive and resonant terms correlate best for a predominantly resonant contribution. This indicates that resonance interactions may be strongly significant even for those instances where other physical data suggest that the phenyl and porphin π systems are very noncoplanar.

Because of its structural features, the *ms*-tetraphenylporphin molecule is a good model system for the study of substituent effects transmitted via composite π systems. Previous work by the present authors[2a] and others[2b] suggested that despite the noncoplanar configuration of the phenyl and porphin planes,[3-5] resonance-type substituent effects are predominant. Since these observations are in variance with some well-accepted notions on the requirements for resonance-type interactions, it appeared worthwhile to undertake further investigations on the effects of substituents on some features of the chemistry of *ms*-tetrasubstituted porphins. In the present work we investigated the effects of structural variation on the absorption spectra and basicity of meso-tetrasubstituted porphins and the possible implications thereof on the nature of the interactions of peripheral substituents with the porphin ring system.

Experimental Section

The porphyrins were prepared and characterized by previously described methods.[6,7] Approximately 2.0×10^{-5} *M* solutions were prepared in DMF (Baker Spectroquality with 1% H_2O). Changing from "dry" DMF to that containing 4% H_2O produced no detectable effect on the spectra. Beer's law was obeyed in the concentration range 10^{-4} to 10^{-6} *M* indicating that aggregation effects on the absorption spectra under these conditions can be excluded. Fluorescence excitation spectroscopy of the solvents checked that no fluorescing impurities were present.

Acid dication solutions of about 6.7×10^{-6} *M* were prepared with 1.6 *M* $HClO_4$ including 3.9 *M* H_2O in DMF. No detectable absorption due to the free bases could be observed at this acidity and further additions of acid did not cause any further detectable changes in the absorption spectra.

Visible and near ultraviolet absorption spectra were recorded on a Cary Model 14 spectrophotometer. Titrations with 70% aqueous $HClO_4$, at 25°, were carried out on the DMF solutions in the 3 ml cuvette directly. Emission spectra were obtained on a Hitachi Perkin-Elmer Fluorescence Spectrophotometer Model MPF-2A.

Results

Absorption spectra of the para-substituted *ms*-tetraphenylporphins, of two ortho-substituted *ms*-tetraphenylporphins, and of some *ms*-tetraalkylporphins are summarized in Table I.

As the electron-donating character of the substituent increases, the typical "etio" type spectrum as seen in T(*p*-CN)PP, with ($\epsilon_I < \epsilon_{II} < \epsilon_{III} \leq \epsilon_{IV}$), gradually changes into a new type ($\epsilon_{II} < \epsilon_I < \epsilon_{III} \leq \epsilon_{IV}$) as seen, in T(*p*-OH)PP, at the other extreme.[17]

In particular, the following gradual spectral changes are observed with increasing electron-donating power of the para substituents: (a) all peaks shift to the red, and (b) the ratios of the transition dipoles of the Q(0-0) (I and III peaks) to the Q(0-1) (II and IV peaks) bands,[18] correspondingly, increase markedly. This is mainly due to changes in the oscillator strengths of the 0-0 transitions, varying by about 100% between the two extreme members of the series, while the oscillator strengths of the 0-1 transitions only vary by about 20%.

Substituent effects on the spectra of the acid dications of the para-substituted compounds are parallel in all cases to the effects in the corresponding free bases (cf. Table II), with frequency shifts up to four times larger than in the free base spectra.

If direct steric interaction between substituents and the porphin ring, as, e.g., in T(*o*-CH_3)PP or T(*o*-OC_2H_5)PP, is present, the peaks shift to the blue, and the oscillator strength ratios f_I/f_{II} and f_{III}/f_{IV} decrease. This effect of ortho substituents has been previously noted by other workers.[8]

Substituent induced changes in the absorption spectra of the tetraphenylporphins in several other solvents such as toluene, benzene, and $CHCl_3$ were similar in sign and magnitude to those measured in the *N,N*-dimethylformamide