A very useful comparison can now be made between this structure and the structure of bis(imidazole)-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatoiron(III) chloride (Im_2FeTPP^+) recently reported by Hoard.[17] We first note that the in-plane Fe-N distances in the DMG complex are considerably shorter than the value of 1.989 Å observed in Im_2FeTPP^+ and this lends strong support to Hoard's conclusion that the equatorial Fe-N bond lengths in porphyrin complexes are governed by the "resistance of the porphyrin skeleton to undue radial contraction."

Of the two axial Fe-N distances in Im_2FeTPP^+ [1.991 (5) and 1.957 (4) Å] the shorter distance is of interest since in the absence of steric interference between the imidazole hydrogens and the porphyrin ring, this distance can be taken as the one to be expected for Fe(III) bound to an axial imidazole. It is reasonable to suggest that the contraction of the Fe–imidazole bond length by approximately 0.03 Å is directly related to the oxidation state of the iron and as expected the shorter distance is observed for the higher oxidation state.

These results suggest to us that structural studies on DMG complexes of Fe(II) can be very useful in investigating structural problems of iron–porphyrin complexes. One such problem which has drawn considerable attention in the last several years is determining the spatial configuration of the iron atom and the imidazole moiety with respect to the plane of the porphyrin ring. Of particular interest in this respect are complexes in which one of the imidazole rings is replaced by ligands such as CO, NO, N_3^-, and CN^-. These complexes are currently under investigation in our laboratories.

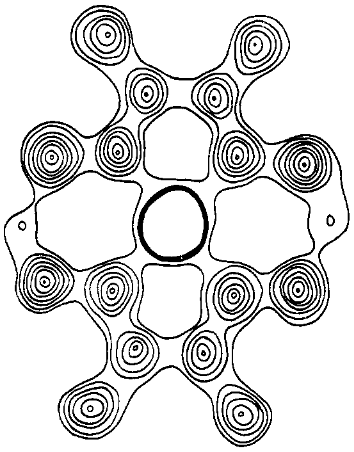

Figure 4. Electron density map through the DMG plane. The lowest contour on the map represents an electron density of 0.2 e/Å and succeeding contours are in increments of 0.5 e/Å. Electron densities greater than 5.0 e/Å are not depicted.

Acknowledgments. We wish to thank Messrs. S. Lipton, B. Spivack, and J. Reed for assistance and the Temple University Chemistry Department for financial support. We also wish to thank the Temple University Computer Center and the Research Corporation for its Equipment Grant.

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[17] R. Countryman, D. M. Collins, and J. L. Hoard, *J. Amer. Chem. Soc.*, 91, 5166 (1969).

Nuclear Magnetic Resonance Spectra of Bis(pyridinato)iron(III)–Protoporphyrin IX Complexes

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Contribution from The Inorganic Chemistry Laboratory, Oxford OX1 3QR, England. *Received October 30, 1970*

Abstract: The ^1H nuclear magnetic resonance spectra of a series of bis(pyridinato)iron(III)-protoporphyrin IX complexes are described. There is a linear relationship between the paramagnetic chemical shifts of the porphyrin protons and the basicity of the coordinated pyridine which is most marked for the peripheral methyl protons. The pseudocontact contribution to the shifts has been estimated and is considered to be appreciable at the meso hydrogens. The main mechanism for spin delocalization at the pyrrole ring carbons is deduced to be charge transfer from a ligand π orbital to the iron. The temperature dependence of the shifts provides evidence for a low-spin-high-spin equilibrium.

The nuclear magnetic resonance (nmr) spectroscopy of paramagnetic metal complexes has proved[3] most useful in revealing details of electronic and molecular structure. In particular it has been possible to derive unequivocal information on electron delocalization. We have previously investigated[4] electron delocalization in diamagnetic complexes but in a number of cases the interpretation of the results was complicated by possible contributions from electric field and ring current effects. Therefore we sought a series of complexes in which one of the ligands was easily varied and most important that the scalar contribution to the paramagnetic shift was large compared to the dipolar term. Since preliminary investigations of bispyridine

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[3] See, for example, D. R. Eaton in "Physical Methods in Advanced Inorganic Chemistry," H. A. O. Hill and P. Day, Ed., Interscience, New York, N. Y., 1968.

[4] H. A. O. Hill and K. G. Moralle, *J. Chem. Soc. A*, 554 (1969); H. A. O. Hill, K. G. Moralle, and G. Pellizer, *ibid.*, 2096 (1969); R. E. Collis and H. A. O. Hill, unpublished work.

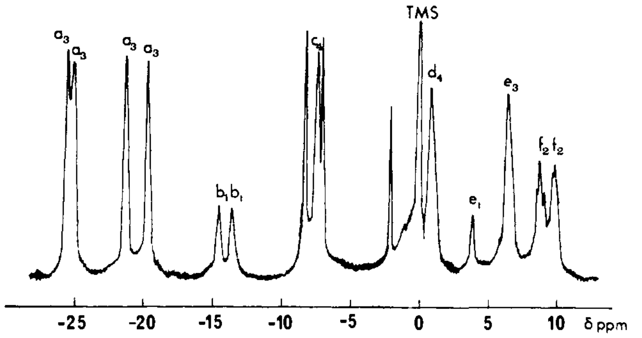

Figure 1. Nmr spectrum of hemin + pyridine-d_5 in $CDCl_3$ at 209°K.

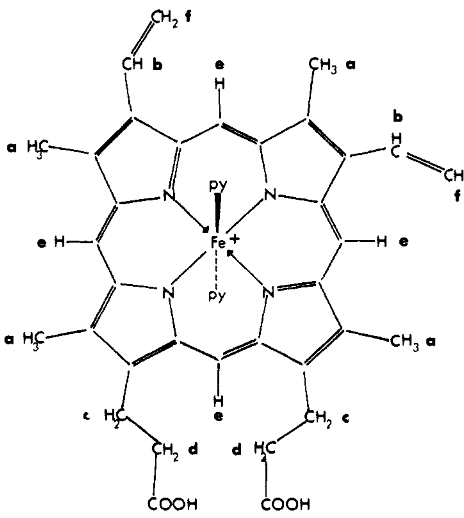

Figure 2. Structure of the hemin–pyridine complex with assignment nomenclature.

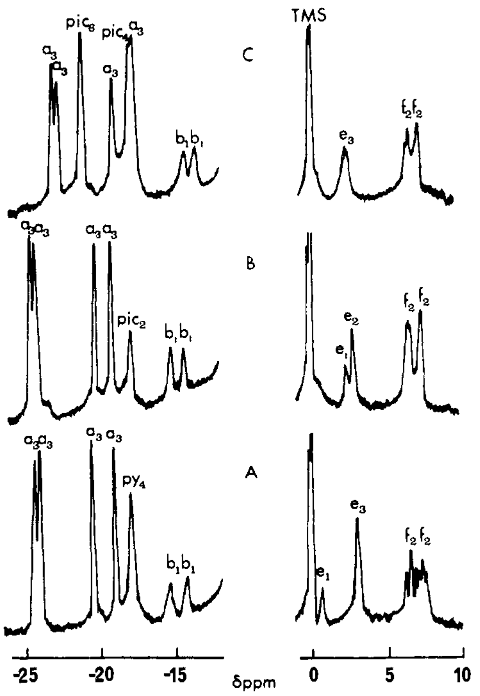

Figure 3. Nmr spectra of hemin + (A) pyridine, (B) 3-methylpyridine, and (C) 4-methylpyridine in $CDCl_3$ at 238°K.

complexes of cobalt(III)–mesoporphyrin had shown that substituents in the pyridine had a small effect on the chemical shifts of the porphyrin protons and Wüthrich, *et al.*, had shown[5] that the nmr spectra of low-spin cyanoiron(III)–porphyrin complexes showed large contact shifts, it seemed reasonable to combine these two approaches in an investigation[6] of bispyridineiron(III) porphyrins.

Experimental Section

Materials. Hemin (iron(III) protoporphyrin IX chloride), pyridine (AR), 4-aminopyridine, and 3- and 4-methylpyridines were supplied by BDH Ltd., 3,4-dimethylpyridine, 3-aminopyridine, and 4-acetylpyridine by Koch-Light Laboratories Ltd., and 3-chloropyridine and 3- and 4-cyanopyridine by Aldrich Chemical Co. The deuterated solvents and pyridine-d_5 were supplied by CIBA (ARL) Ltd.

Solutions of the complexes were prepared by dissolution of hemin in 40% (w/v) solutions of the various pyridines in $CDCl_3$ and CD_3OD.

Nmr spectra were measured at 60 MHz using a JEOL C-60HL high-resolution spectrometer. The spectra were calibrated using kHz side-band modulation. The temperature of the sample was varied using a JEOL JES VT3 temperature controller, calibrated using the nmr spectrum of methanol[7] and controlled to ±1°. Tetramethylsilane was used as an internal reference and chemical shifts, δ, are quoted in parts per million relative to TMS; negative values indicate low-field shifts.

Results

Assignment of Nmr Spectra. The nmr spectrum between -30 and $+15$ ppm of hemin in chloroform-d_1 containing a large excess of pyridine-d_5 is shown in Figure 1. The assignments are indicated in Figure 2 and are based on integrated intensities and comparison with those given for cyanoiron(III) protoporphyrin IX dimethyl ester.[6] As all other protons on carbon atoms bound directly to the porphyrin ring are shifted to the low-field side of their positions in diamagnetic complexes, we further assign the low-field peak c to the β-CH_2 protons and hence, peak d to the α-CH_2 protons of these side chains.

When undeuterated pyridine is used, one additional peak is present at -20 ppm as shown in Figure 3A. This peak corresponds to four protons per porphyrin but in the spectrum of the 3-methylpyridine complex to only two protons (Figure 3B) while in that of the 4-methylpyridine complex again integrates to four protons. This peak is therefore assigned to the hydrogens in the 3 position of the complexed base, two molecules of pyridine being bound to the iron. The peak has an intensity corresponding to four protons for all 4-substituted pyridine complexes but only two protons for all 3-substituted pyridines.

An additional low-field peak, corresponding to six protons, is present in the spectra of the 4-methylpyridine (Figure 3C) and the 3,4-dimethylpyridine (Figure 4) complexes. As no such peak is observed in the spectrum of the 3-methylpyridine complex, it is assigned to the 4-methyl groups of *two* complexed pyridine molecules. Since no peaks were observed outside the normal diamagnetic region that could be assigned to the 2 and 4 protons or the 3-CH_3 protons of the complexed base, they are presumably masked by the

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(5) K. Wüthrich, R. G. Shulman, B. J. Wyluda, and W. S. Caughey, *Proc. Nat. Acad. Sci. U. S.*, **62**, 636 (1969).

(6) For a preliminary communication of part of this work, see H. A. O. Hill and K. G. Morallee, *Chem. Commun.* 266 (1970).

(7) (a) Varian Associates Manual, Palo Alto, Calif.; (b) A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968).

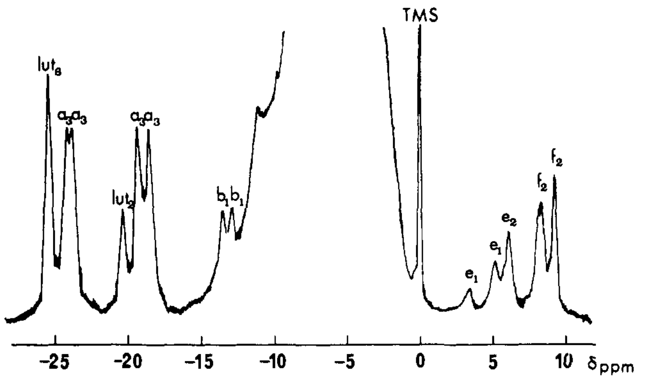

Figure 4. Nmr spectrum of hemin + 3,4-dimethylpyridine in $CDCl_3$ at 212°K.

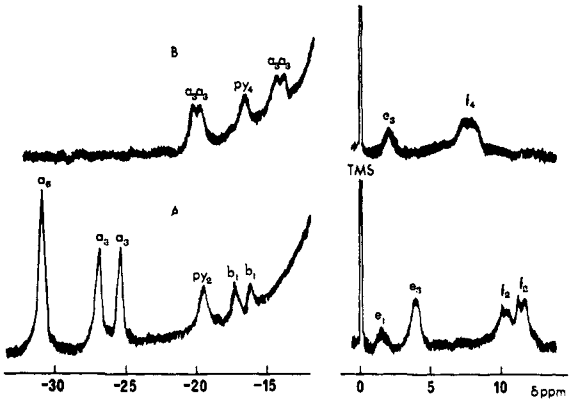

Figure 5. Nmr spectra of hemin + (A) 3-chloropyridine and (B) 4-aminopyridine in CD_3OD at 209°K.

resonances of the uncomplexed ligand. The equivalence of the porphyrin meso protons (e) was affected by the presence in the pyridine of a 3-methyl group, changing from 3:1 to 2:1:1 as shown in Figures 3B and 4.

The effect of substituents on the pyridine is clearly seen in Figure 5, the chemical shifts being much smaller in the bis-4-aminopyridine complex than in the bis-3-chloropyridine complex.

Temperature Dependence of the Nmr Spectra. All spectra were recorded at temperatures between 293 and 200°K and the temperature dependence of the chemical shifts on the spectra of the bispyridine-d_5, bis-4-acetylpyridine, and bis-3-chloropyridine complexes in CD_3OD are shown in Figures 6–9. There is a linear dependence on T^{-1} only at low temperatures. This departure from linearity of the $\Delta\ V^s\ T^{-1}$ relationship is shown for all complexes but at different temperatures.

The linewidths of all resonances depend on both temperature and the substituted pyridine. In XC_5H_4N, with X = 4-CH_3CO-, 4H(D), 3- or 4-CH_3, and 3- or 4-NH_2, the lines were sharp ($\Delta\nu_{1/2} \approx 10$ Hz) in the temperature range 250–190°K; for X = Cl and 3- or 4-CN the resonances were too broad to be observed at all temperatures above 230 and 220°K, respectively. For X = 4-H and 4-CH_3CO, the resonances broadened on raising the temperature from 270 to 290°; no such broadening was observed for bases of higher pK_a. In all cases appreciable broadening occurred below 190°K so that the resonances became unobservable at *ca.* 180°K although the solutions were still mobile.

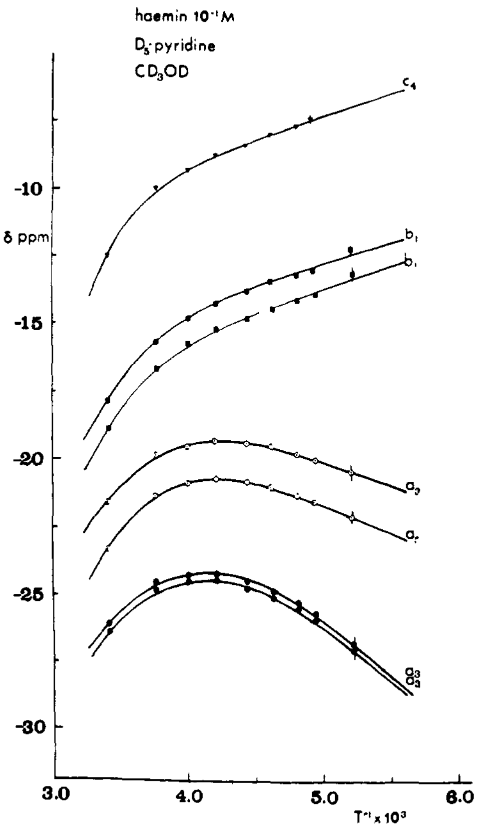

Figure 6. Temperature dependence of the proton chemical shifts (δ) of $[(d_5\text{-py})_2Fe^{III}PROTO]Cl$ in CD_3OD showing low-field peaks.

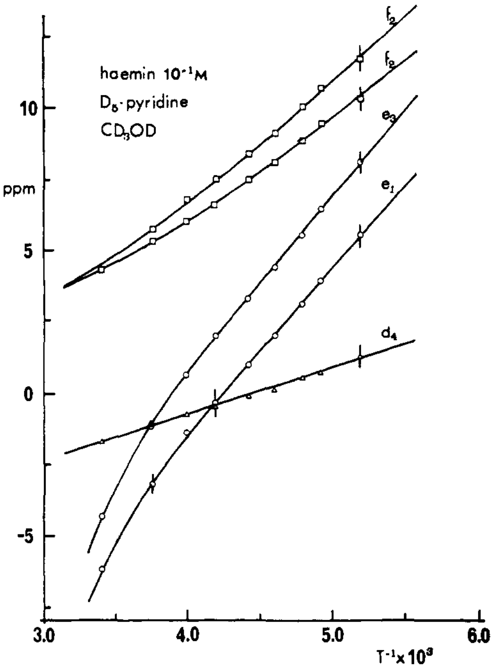

Figure 7. Temperature dependence of the proton chemical shifts (δ) of $[(d_5\text{-py})_2Fe^{III}\ PROTO]Cl$ in CD_3OD showing high-field peaks.

Discussion

General Features. The results show conclusively that at low temperatures the investigated species in solution is a bispyridinatoiron(III)–protoporphyrin IX complex, $[(X\text{-py})_2Fe^{III}PROTO]^+Cl^-$, where X-py = a substituted pyridine and PROTO = protoporphyrin IX dianion. At

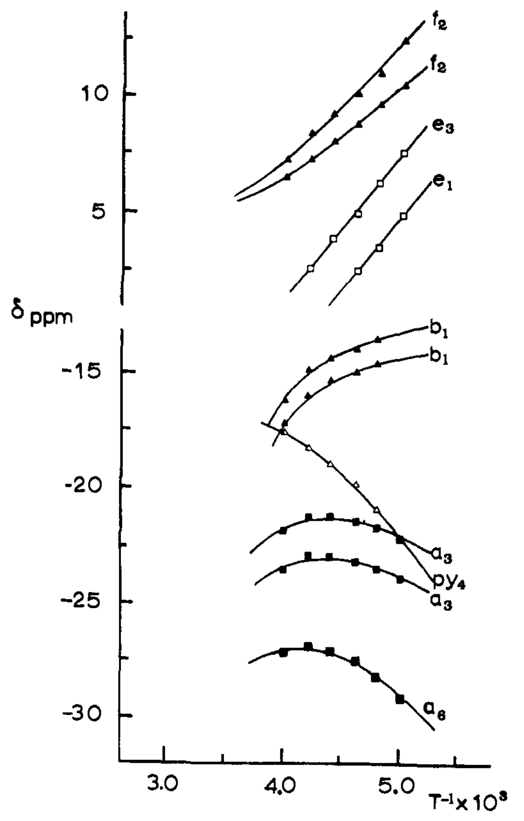

Figure 8. Temperature dependence of the proton chemical shifts (δ) of [(4-CH_3COpy)$_2$Fe^{III}PROTO]Cl in CD_3OD.

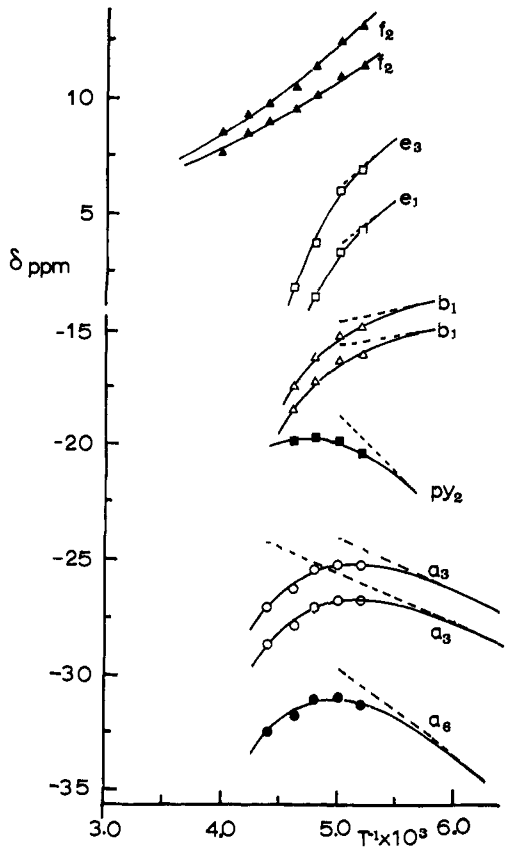

Figure 9. Temperature dependence of the proton chemical shifts (δ) of [(3-Clpy)$_2$Fe^{III}PROTO]Cl in CD_3OD.

higher temperatures, *ca.* 290°K, it was not possible to observe resonances due to the coordinated pyridines and hence impossible to confirm from the nmr spectra that the bispyridine complex is the predominant species in solution.[8] The exchange rate of free and complexed pyridine at and below 260°K must be much smaller than the frequency shift differences between the protons in the two environments [$<5 \times 10^{-2}$ sec^{-2}] as separate resonances are observed for free and complexed pyridines.

The observation of sharp spectral lines in most of the spectra at 200°K indicates that the complexes are low spin [$S = {}^1/_2$], much broader lines being expected for high-spin complexes[9] due to the longer electron spin lattice relaxation time T_{1e}. The chemical shifts vary linearly with T^{-1} at low T.

Origin of the Shifts. Both contact and pseudocontact interactions[2] can contribute to the shifts. There is often some difficulty in estimating the relative size of these contributions, particularly when detailed information on the electronic ground state is absent. Equations 1 and 2 have been derived[10,11] and describe the contact and pseudocontact terms, respectively, though the limitations of these equations have recently been discussed.[12]

$$\left[\frac{\Delta H}{H_0}\right]_i = \Delta_i^{c} = \frac{-2\pi a_i \beta S(S+1)\mathrm{f}(g)}{\gamma_{\mathrm{H}} 3kT} \qquad (1)$$

$$\left[\frac{\Delta H}{H_0}\right]_i = \Delta_i^{d} = \frac{-\beta^2 S(S+1)}{3kT}\,\frac{3\cos^2\chi - 1}{r^3}\,\mathrm{f}'(g) \qquad (2)$$

In eq 1 a_i is the hyperfine coupling constant for nucleus i (sec^{-1}), β the Bohr magneton, S the electron spin, γ_{H} the proton gyromagnetic ratio, k the Boltzmann constant, and f(g) some function of the electronic g values. For a molecule with axial symmetry where the g tensor is characterized by two principle values $g_{\parallel}$ and $g_{\perp}$ and $T_{1e} \ll \tau_c$, where τ_c is the correlation time for tumbling and a_i is approximately isotropic, f(g) is approximately equal to ${}^1/_3(g_{\parallel} + 2g_{\perp})$. In eq 2 r is the distance between nucleus i and the unpaired electron (considered as localized on the transition metal ion), χ is the angle between the vector r and the tetragonal axis of the complex, and $\mathrm{f}'(g) = (3g_{\parallel} + 4g_{\perp})\cdot(g_{\parallel} - g_{\perp})/15$ and $(g_{\parallel} + g_{\perp})(g_{\parallel} - g_{\perp})/3$ for $\tau_c^{-1} \gg |g_{\parallel} - g_{\perp}|\beta H_0 \hbar^{-1}$ and $\tau_c^{-1} \ll |g_{\parallel} - g_{\perp}|\beta H_0 \hbar^{-1}$, respectively.

Extrapolation of the linear portions of the temperature dependence curves to $T^{-1} \rightarrow 0$ should bring the resonances close to the values observed in diamagnetic complexes. The chemical shifts[13] of the protons in PROTO dimethyl ester in $CDCl_3$ are given in Table I. The diamagnetic values for a bis(pyridinato)metalloporphyrin are not expected to differ from these by more than 0.5 ppm. Most of the resonances do not, however, extrapolate to the diamagnetic values; for ex-

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[8] Recent experiments (H. A. O. Hill, C. Wernham, J. Weightman, and R. J. P. Williams, unpublished results) show that the complex, X-py-Fe^{III}PROTO Cl, is present in solution giving rise to broad resonances from −40 to − 50 ppm.

[9] W. S. Caughey and L. F. Johnson, *Chem. Commun.*, 1362 (1969); R. J. Kurland, D. G. Davis, and C. Ho, *J. Amer. Chem. Soc.*, **90**, 2701 (1968).

[10] H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, **28**, 107 (1958).

[11] J. P. Jesson, *ibid.*, **47**, 579 (1967).

[12] R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970).

[13] W. S. Caughey and W. S. Koski, *Biochemistry*, **1**, 923 (1962).

Table I. Diamagnetic Porphyrin Shifts Relative to TMS

Protons	Shift, ppm	Protons	Shift, ppm
Ring CH_3 (a)	−3.5	α-CH_2 (d)	−3.0
Vinyl CH (b)	−6.5	Meso H (e)	−9.5
β-CH_2 (c)	−4.0	Vinyl CH_2 (f)	−6.0

Table II. Hyperfine Shifts[a] of PROTO Protons in [$(X\text{-py})_2Fe^{III}$PROTO]Cl Complexes in CD_3OD at 200°K

		Protons									
								Meso H's			
X	pK_a[b]	$(CH_3)_4$				(Vinyl CH)$_2$		(1)	(3)	(Vinyl CH_2)$_2$	
4-NH_2	9.12	-17.2_5	−16.8	−11.2	-10.6_5				18.1	14.7_5	
3,4-$(CH_3)_2$	6.48	−22.4	−22.2	−16.6	−16.1	−5.6	−5.0	14.9_5	16.8 (1) 17.8 (2)	16.3	17.5
3-NH_2	6.04	-21.7_5	-21.1_5	−16.1	−14.1			14.9	17.6	15.5_5	16.6_5
4-CH_3	6.02	-21.7_5		−17.1	−15.9	−5.8	−4.9		17.1_5	16.2	17.2_5
3-CH_3	5.63	−23.0	-22.8_5	−18.1	−17.0	-6.5_5	−5.6	14.5_5	16.7 (1) 17.2 (2)	16.2	17.5
H	5.17	−22.7	-22.4_5	−18.3	-16.7_5	-7.4_5	−6.5	13.8	16.2	15.6	17.0
4-CH_3CO	3.51	−25.7		−20.5	−18.8	-7.9_5	-6.8_5	14.3	16.9_5	16.5	18.1
3-Cl[c]	2.84	−26.2		−22.2	−20.9	−9.0	−8.1	13.1	15.7	16.9	18.3
4-CN[d]	1.91	−26.4		−22.7	−21.1						

[a] Ppm from the diamagnetic values. [b] p$K_a$of the substituted pyridine: K. Scholfield in "Hetero-Aromatic Nitrogen Compounds—Pyrroles and Pyridines," Butterworths, 1967, Table 5.10. [c] Accurate to 0.2 ppm. [d] Accurate to 0.3 ppm (all other shifts accurate to 0.1 ppm).

Table III. Hyperfine Shifts[a] of PROTO Protons in [$(X\text{-py})_2Fe^{III}$PROTO]Cl Complexes in $CDCl_3$ at 200°K

		Protons									
								Meso H's			
X	pK_a[b]	$(CH_3)_4$				(Vinyl CH)$_2$		(1)	(3)	(Vinyl CH_2)$_2$	
3,4-$(CH_3)_2$	6.48	−21.2	−21.0	−16.3	−15.6	-6.5_5	−5.9	13.7	16.4 (1) 17.3 (2)	15.4_5	16.5
3-NH_2	6.04	-21.2_5	-21.0_5	-15.9_5	−15.5	−5.9	−5.6		17.2_5	14.8	15.7
4-CH_3	6.02	−21.3	−21.0	−17.0	-15.4_5	-7.3_5	−6.4	14.0	16.3_5	14.8	15.7
3-CH_3	5.63	-22.3_5	-22.1_5	-17.7_5	-16.7_5	−7.7	−6.7	14.5	16.4 (1) 17.1 (2)	15.3_5	16.3
H	5.17	−22.5	-22.1_5	−18.2	−16.5	-7.8_5	-6.9_5	14.4_5	17.0_5	15.3	16.5_5
4-CH_3CO[c]	3.51	−25.7	−25.1	−20.8	−19.2			14.3	16.9_5	16.5	18.1
3-Cl[d]	2.84	−24.8		−21.8	−21.0			12.0	14.9	16.0	16.9
4-CN[e]	1.91	−29.0		−23.7	−21.4				16.5	16.2	17.1
3-CN[e]	1.36	−28.1		−25.6	−25.0					17.2	

[a] Ppm from the diamagnetic values. [b] pK_a of the substituted pyridine. [c] Accurate to 0.2 ppm. [d] Accurate to 0.3 ppm. [e] Accurate to 0.5 ppm; all other shifts accurate to 0.1 ppm.

ample in Figures 6 and 7, resonances a extrapolate to *ca.* −10, d to −6, e to −20, and f to −8 ppm. The vinyl CH protons (b) even shift away from their diamagnetic values with increasing temperature as do the β-CH_2 protons (c). These results are similar to those obtained by Wüthrich, *et al.*,[6] for the cyanohemes, which were attributed to temperature-dependent changes in conformation. The deviation of the temperature dependence from linearity at higher temperatures is discussed below in terms of the formation of high-spin species. The shifts, Δ (in parts per million from the diamagnetic values in Table I), for protons of the [$(X\text{-py})_2Fe^{III}$PROTO]Cl complexes at 200°K are given in Tables II [in CD_3OD] and III (in $CDCl_3$]. Since the temperature curves of the complexes, with X = 3-Cl, 3- and 4-CN, are nonlinear in the region of 200°K, it was necessary to extrapolate back to 200°K from the linear part of the curve (Figure 9).

A marked dependence of the hyperfine shifts on the nature of the substituent X is observed: the hyperfine shifts are plotted against the pK_a's of the substituted pyridines in Figures 10–13. The lines plotted are the result of a least-squares regression analysis. As the pK_a of the pyridine increases the hyperfine shifts at the ring methyl protons (a) and the vinyl CH (b) and CH_2 (f) protons become less negative but, in comparison, the shift variations of the meso protons are quite small and become less positive with increasing pK_a.

In an attempt to estimate the contribution of the pseudocontact term, the epr spectrum of the bispyridine complex in frozen solution in $CHCl_3$ at 22°K was obtained.[14] It was typical of polycrystalline material with $g_{\parallel} = 3.4$ and $g_{\perp} = 0.58$. Equation 2 was derived assuming $T_{1e} \ll \tau_c$, a condition likely to be fulfilled in this case. It is also likely that $\tau_c^{-1} > |g_{\parallel} - g_{\perp}|\beta H_0 \hbar^{-1}$ as the latter is equal to 4×10^{11} sec^{-1} with $|g_{\parallel} - g_{\perp}| = 2.82$. Thus taking $f'(g) = (3g_{\parallel} + 4g_{\perp}) \cdot (g_{\parallel} - g_{\perp})/15$, $\chi = 90°$, and the distances of the ring methyl protons and the meso protons from the iron as 6.4 and 4.5 Å, respectively,[15] the following pseudocontact shifts at 200°K are predicted: methyl protons +7 ppm, meso protons +20 ppm. These values are much larger than those estimated for the cyanohemes by Wüthrich, *et al.*[6]

Comparison of the estimates with the experimental values of the hyperfine shifts in Tables II and III suggests that pseudocontact effects cannot be neglected and may constitute the major contribution to the observed shift for the meso protons. Indeed a depen-

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(14) Kindly measured for us by Dr. R. C. Bray.

(15) J. L. Hoard, M. J. Hamon, T. A. Hamon, and W. S. Caughey, *J. Amer. Chem. Soc.*, 87, 2312 (1965).

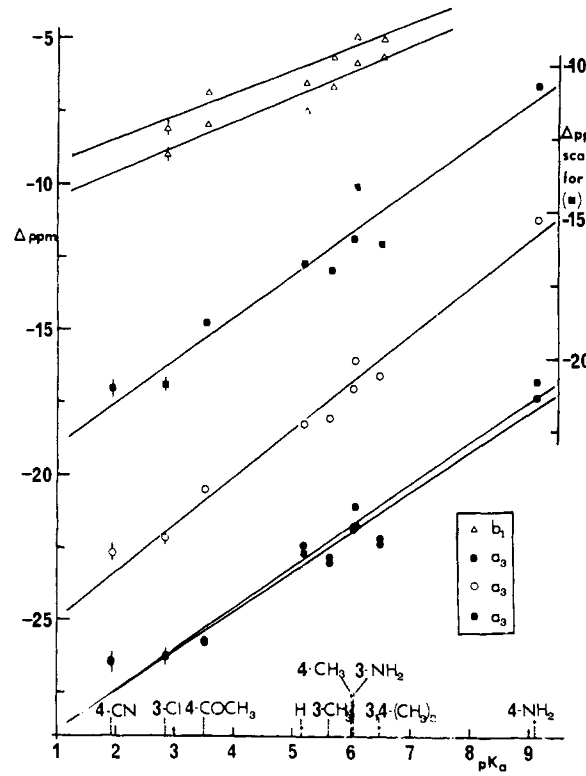

Figure 10. Plot of Δ, the hyperfine shifts in CD$_3$OD, *vs.* pK_a's of pyridines showing low-field peaks.

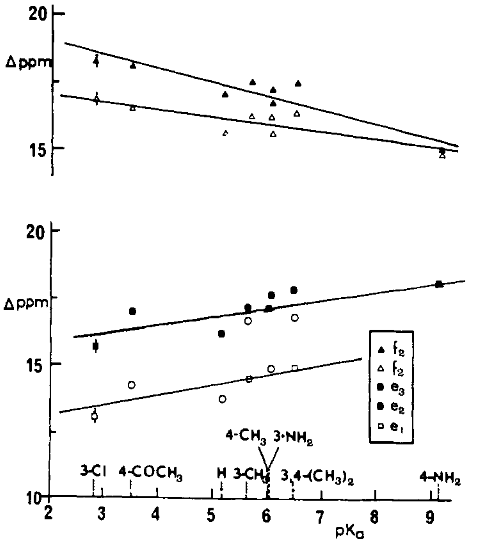

Figure 11. Plot of Δ, the hyperfine shifts in CD$_3$OD, *vs.* pK_a's of pyridines showing high-field peaks.

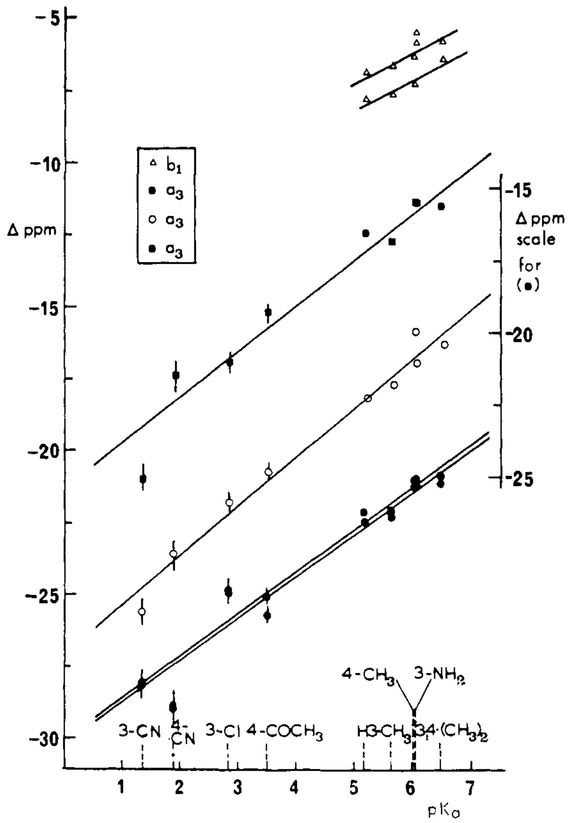

Figure 12. Plot of Δ, the hyperfine shifts in CDCl$_3$, *vs.* pK_a's of pyridines showing low-field peaks.

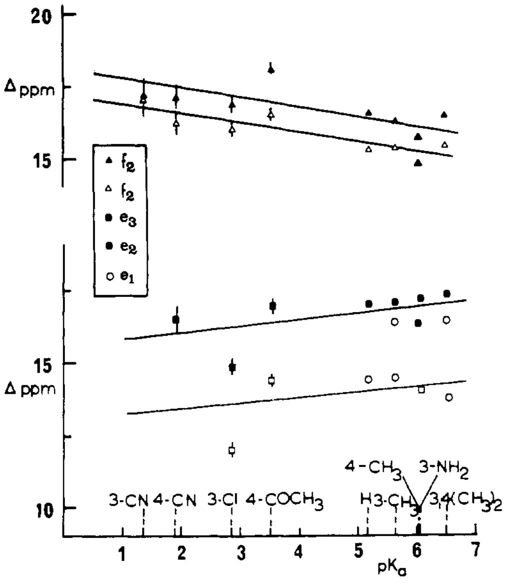

Figure 13. Plot of Δ, the hyperfine shifts in CDCl$_3$, *vs.* pK_a's of pyridines showing high-field peaks.

dence of the g values on the coordinated pyridine of the same order as that observed[16] for some [(X-py)Fe^{III}-PROTO]SR complexes could account for the slight dependence of the hyperfine shift of the meso protons on the substituted pyridine. If the pseudocontact term is the only contribution to the shift for the meso protons, then an equivalent variation in pseudocontact contribution to the hyperfine shift for the ring methyl protons could not account for the large dependence on the substituted pyridine. Therefore, for the protons on the periphery of the porphyrin, we assumed that the nature of the substituent in the coordinated pyridine affects the hyperfine shift *via* the contact effect.

A simple description[17,18] of the orbital energies is given in Figure 14. The ^{2}E ground state $(b_{2g})^2(e_g)^3$ places the unpaired electron in either the d_{xz} or d_{yz}

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[16] H. A. O. Hill, K. G. Morallee, and A. Röder, "Proceedings of the Magnetic Resonance Conference, Cagliari, Sardinia," C. Franconi, Ed., Gordon and Breach, New York, N. Y., in press.

[17] M. Zerner, M. Gouterman, and M. Kobayashi, *Theor. Chim. Acta*, 6, 363 (1966).

[18] H. C. Longuet-Higgins, C. W. Rector, and J. R. Platt, *J. Chem. Phys.*, 18, 1174 (1950).

Table IV. Hyperfine Interaction Data for Some $[(X\text{-py})_2Fe^{III}PROTO]Cl$ Complexes in CD_3OD at 200°K

Parameter	X	Ring methyl protons			
Δ_i^c (ppm)	4-NH_2	−24.25	−23.8	−18.2	−17.65
	H	−29.7	−29.45	−25.3	−23.75
	4-CN	−33.4		−29.7	−28.1
a_i (10^6 sec^{-1})	4-NH_2	8.1	7.95	6.05	5.9
	H	9.9	9.8	8.45	7.9
	4-CN	11.15		9.9	9.35
ρ^π_c (% of one unpaired electron)	4-NH_2	2.05	2.0	1.5	1.45
	H	2.5	2.45	2.1	1.95
	4-CN	2.8		2.5	2.35

orbitals. The spin can be delocalized *via* interaction between metal, e_g and filled porphyrin $3e_g$ (which can be restated as "ligand to metal change transfer"), or by interaction of the metal, e_g with $4e_g$ of the porphyrin (metal-to-ligand change transfer). (The symmetry labels for the D_{4h} point group are used although the real symmetry is lower.) Both types of interaction would lead to positive spin density in the porphyrin π orbitals. The results described in this paper suggest that the main interaction involved in spin delocalization is metal–e_g with $3e_g$ for two reasons. Simple Hückel molecular orbital calculations[18] predict nodes at the methene bridge carbons in porphyrin $3e_g$ and high electron densities at the pyrrole ring carbons, whereas $4e_g$ has high electron density at the methene carbon atoms, much lower at the pyrrole ring carbons. Although the contribution to the real electron density at the methene from the $3e_g$ orbital will not be zero, it will probably be low. Therefore the methene positions will be relatively insensitive to changes in spin density in $3e_g$. As the axial ligands become more basic the positive charge on the iron will decrease and ligand-to-metal charge transfer will be less favored. In other words, interaction between metal e_g and porphyrin $3e_g$ will decrease and, concomitantly, spin density in the porphyrin ring will decrease.

It is possible to calculate the π-electron spin densities at the porphyrin carbons by using McConnell's equation

$$a = \rho^\pi{}_c Q_{CH_3} \tag{3}$$

If the above description applies then $\rho^\pi{}_c$, the spin density at the methane position, is zero. The value of Q in the above equation is known not to be constant for methyl groups joined to an aromatic ring due to hyperconfiguration.[19] If $\rho^\pi{}_c$ remained constant, Q_{CH_3} would have to decrease by a factor of *ca.* 1.5 to explain the hyperfine constants shown in Table IV which were calculated from eq 1 with $f(g) = 1.52$ and $\Delta_i^c = \Delta_i - 7.0$ ppm.

Although this is in the direction expected by analogy with the results for the positive and negative ions of 9-methyl- and 9,10-dimethylanthracene,[19] it is unreasonably large as the Q_{CH_3} values in the anthracene cations were only about this factor greater than those in the anions, and in this case the energy of the orbital containing the unpaired electron varied by $\sim$4 eV. Any contribution to the pK_a dependence of the hyperfine coupling constants from variations in Q_{CH_3} is expected, therefore, to be small, the major contribution arising from changes in spin density at the ring carbon atoms.

Taking Q_{CH_3} as 4×10^7 sec^{-1} [estimated from the chemical shifts of the methyl protons in cyanoiron(III) deuteroporphyrin IX dimethyl ester[6] assuming that the spin densities at the ring carbons, $C_\beta CH_3$, are comparable to those found for $C_\beta H$ after allowing for pseudocontact shifts of +3 and +4.5 (at 25°) at the two types of protons, respectively], the unpaired spin densities at the porphyrin ring carbon atoms were calculated and are given in Table IV. From these values, the spin density on the porphyrin in the bis-4-cyanopyridine complex is nearly double that in the bis-4-aminopyridine complex. If this analysis of the origin of the paramagnetic shift is correct, it suggests that the positive charge on the iron is decreased substantially in the latter complex. Indeed the linear correlation between the observed paramagnetic shift and the basicity of the pyridine implies that basicity is a good guide to the electron donor properties of pyridines to metal ions at least toward iron(III).

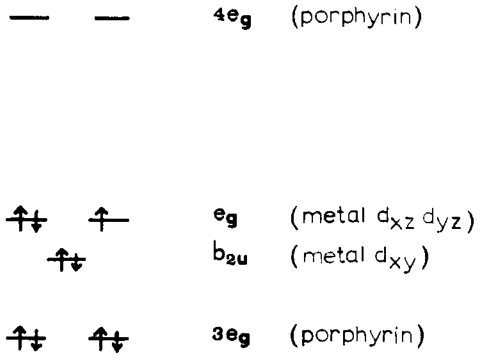

Figure 14. Top-filled and lowest empty π orbitals of iron(III)–porphyrin complexes.

Spin Equilibrium. Inspection of the $\Delta\ V^s\ T^{-1}$ plots, examples of which are shown in Figures 6–9, shows that in nearly all cases the curves become[20] nonlinear as the temperature rises above *ca.* 200°K. The deviations from linearity are most marked for ring methyl protons (a), where the slopes at the curves become zero at a particular temperature, T_c, and thereafter are positive up to room temperature. The values of T_c observed are markedly dependent on the nature of the substituent, a general decrease being observed with decreasing pK_a of the base, and are also slightly solvent dependent being lower (except for 4CNpy complex) in the more polar solvent. A dependence of the resonance line widths has been noted also. The broadening of lines below 190°K is attributed to an increase in

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(19) J. R. Bolton, A. Carrington, and A. D. McLachlan, *Mol. Phys.*, **5**, 31 (1962).

(20) This nonlinearity is also observed even in the absence of X-pyFe^{III}PROTO Cl.

T_{1e} in the low-spin complex but the broadening near room temperature cannot be explained in this way. The latter broadening begins at about $T = T_c$ and increases so that lines are no longer observable at $T = T_c + 30\,(\pm 10)°K$.

These observations are consistent with the formation of a high-spin complex as the temperature increases, with the rate of exchange between the two spin states being very much greater than the frequency shift difference of the protons in the two environments so that a single resonance is observed for each set of protons. As expected, the greater the basicity of the pyridine ligand, the more the low-spin form is favored. Recent investigations[21] of the temperature dependence of the magnetic susceptibilities and absorption spectra of the complexes in solution support these conclusions and suggest that the high-spin form is possibly the intermediate $S = {}^3/_2$ state and not the expected $S = {}^5/_2$ state. A detailed analysis of the temperature dependence of all three properties will be published shortly.

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(21) H. A. O. Hill, C. M. Wernham, and R. J. P. Williams, unpublished observations.

Organometallic Electrochemistry. XVII.[1] Electric Charge Distribution in Organometallic Compounds, Tetrahedral Derivatives of $Co(CO)_3(NO)$ and $Fe(CO)_2(NO)_2$

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Abstract: The investigation of electric charge distribution in transition metal carbonyl and nitrosyl molecules has been extended to a remarkable series of cobalt and iron compounds of the general formulas $CoL_2(CO)(NO)$ and $FeL_2(NO)_2$, where L_2 = 2,2′-bipyridyl, *o*-phenanthroline, and di-2-pyridyl ketone. Coupling electrochemical and spectroscopic tools four distinct charge states of the tetrahedral geometry were examined: dianion (2−), radical anion (1−), neutral (0), and radical cation (1+). Mössbauer magnetic resonance and infrared studies on these systems have led to considerable insight as to the nature and mechanism of molecular charge distribution. Spin density and charge density are not directly related in this series, in comparison to polycyclic aromatic systems.

The preceding papers[1,3,4] in this series dealt with the nature of electron charge and spin distribution in trigonal-bipyramidal, octahedral, and linear organometallic species. The present study probes the mechanism and nature of electron distribution in a tetrahedral series of cobalt and iron molecules of the general formulas $CoL_2(CO)(NO)$ and $FeL_2(NO)_2$ where L_2 = 2,2′-bipyridyl, *o*-phenanthroline, and di-2-pyridyl ketone. Aside from the obvious interest in the extension of these studies to the tetrahedral geometry, there were a number of attractive aspects leading to the initiation of the present investigation. The first of these involves the unusual span of charged species that may be derived from a single neutral precursor molecule. In several cases four distinct charge states may be generated in stable bulk quantities. The (di-2-pyridyl ketone)iron dinitrosyl molecule, for example, has served as the neutral precursor to stable radical anions, dianions, and radical cations. With the subsequent application of Mössbauer, infrared, electron spin resonance, nuclear magnetic resonance and uv-vis[5] techniques to all the species generated, by chemical or electrochemical action, a considerable degree of information as to the electronic structure of these molecules may be derived. As was emphasized in the preceding investigations, this general method of attack offers one the ability of keeping the ligand, metal atom, and to a first approximation, the geometry fixed, while varying the electric charge density. Thus one may avoid the serious risks encountered in chemical alteration of the molecules being considered.

Another important aspect prompting the present inquiry relates to the presence of the nitrosyl moieties in these molecules. The presence of the NO group offers one the opportunity to probe the spin density residing on the nitrosyl groups in these systems. This is in contrast to the octahedral and trigonal-bipyramidal cases where, except for the bidentate organic ligand, only carbonyl ligands having low abundances of magnetic nuclei were present.

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(1) For the previous paper in this series, see R. E. Dessy, J. C. Charkoudian, T. P. Abeles, and A. L. Rheingold, *J. Amer. Chem. Soc.*, **92**, 3947 (1970).

(2) American Chemical Society–Petroleum Research Fund Fellow, 1969–1970.

(3) R. E. Dessy and L. Wieczorek, *J. Amer. Chem. Soc.*, **91**, 4963 (1969).

(4) R. E. Dessy, M. Kleiner, and S. C. Cohen, *ibid.*, **91**, 6800 (1969).

(5) Uv-vis experiments on these systems and, in fact, the other systems investigated by Dessy and coworkers have been performed, and a quantitative treatment of these molecules based on those results is forthcoming.