The present results are not completely consistent with the time dependence previously reported[3] for the magnetic susceptibility of $[Fe(paptH)_2(NO_3)_2$. Although the origin of this discrepancy is not obvious at this moment, the lower accuracy of magnetic measurements with the Gouy method, possible differences between different samples and differences in the rate of cooling for the Mössbauer and magnetic measurements have to be considered.

Obviously, the high-spin → low-spin and low-spin → high-spin transformations will be present in all solid systems showing high-spin, low-spin transitions. Apparent equilibrium behavior will be found where both transformations are reasonably fast. The present system is unique in that the rates are such that, at least in part, a detailed observation of these processes is possible.

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References and Notes

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(2) School of Chemistry, University of New South Wales.
(3) R. N. Sylva and H. A. Goodwin, *Aust. J. Chem.*, **20**, 479 (1967).
(4) E. König, G. Ritter, and H. A. Goodwin, *Chem. Phys. Lett.*, **44**, 100 (1976).
(5) E. König, G. Ritter, H. Spiering, S. Kremer, K. Madeja, and A. Rosenkranz, *J. Chem. Phys.*, **56**, 3139 (1972).
(6) E. König, G. Ritter, B. Braunecker, K. Madeja, H. A. Goodwin, and F. E. Smith, *Ber. Bunsenges. Phys. Chem.*, **76**, 393 (1972).
(7) E. König, G. Ritter, and H. A. Goodwin, *Chem. Phys.*, **1**, 17 (1973).
(8) E. König, G. Ritter, and H. A. Goodwin, *Chem. Phys.*, **5**, 211 (1974).
(9) G. A. Bykov and Pham Zuy Hien, *Zh. Eksp. Teor. Fiz.*, **43**, 909 (1962).
(10) G. Lang, *Nucl. Instrum. Methods*, **24**, 425 (1963).
(11) H. Spiering and H. Vogel, *Hyperfine Interact.*, **3**, 221 (1977).
(12) A. J. Stone, *Nucl. Instrum. Methods*, **107**, 285 (1973).
(13) E. König and G. Ritter, *Solid State Commun.*, **18**, 279 (1976).
(14) E. König, G. Ritter, and B. Kanellakopulos, *J. Phys. C*, **7**, 2681 (1974).
(15) C. P. Slichter and H. G. Drickamer, *J. Chem. Phys.*, **59**, 2142 (1972).
(16) M. Sorai, J. Ensling, K. M. Hasselbach, and P. Gütlich, *Chem. Phys.*, **20**, 197 (1977).
(17) R. Zimmermann and E. König, *J. Phys. Chem. Solids*, **38**, 779 (1977).
(18) E. König and G. Ritter, *Mössbauer Eff. Methodol.*, **9**, 1 (1974).
(19) A. R. Ubbelohde, *Z. Phys. Chem.* (*Frankfurt am Main*), **37**, 183 (1963).
(20) E. König and K. J. Watson, *Chem. Phys. Lett.*, **6**, 457 (1970).
(21) M. A. Hoselton, L. J. Wilson, and R. S. Drago, *J. Am. Chem. Soc.*, **97**, 1722 (1975).
(22) A. R. Ubbelohde, *J. Chim. Phys. Phys.-Chim. Biol.*, **62**, 33 (1966).
(23) E. König, G. Ritter, W. Irler, and B. Kanellakopulos, *J. Phys. C*, **10**, 603 (1977).
(24) B. Kanellakopulos, E. König, G. Ritter, and W. Irler, *J. Phys.* (*Paris*), *Suppl.*, **37**, C6-459 (1976).
(25) E. König, K. Madeja, and K. J. Watson, *J. Am. Chem. Soc.*, **90**, 1146 (1968).

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Solvent and Substituent Effects on the Electron-Transfer Rate Constants of Tetraphenylporphyrins and Their Iron Complexes

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The effect of substituents on the heterogeneous electron-transfer rates of para- and meta-substituted tetraphenylporphyrins and iron tetraphenylporphyrins was investigated by cyclic voltammetry. In all cases electron-donating substituents caused cathodic shifts in the half-wave potential, $E_{1/2}$, and a relationship between $E_{1/2}$ and the Hammett constant σ was found. The heterogeneous rate of electron transfer in dimethyl sulfoxide (Me_2SO) and dimethylacetamide (DMA) showed some relationship with σ, but it appears that solvent effects are more important than previously reported. Metal-free porphyrins were studied in butyronitrile (*n*-PrCN) and when compared with previous studies indicated a higher degree of susceptibility to electron-withdrawing effects for the first ring reduction than for the iron porphyrins.

Introduction

Investigation of the electron-transfer reactions of iron porphyrins is of great interest because of their importance as biological electron-transfer agents.[1] Although iron porphyrins may be oxidized in at least two one-electron steps in aprotic media,[2,3] we shall concentrate here on the three possible one-electron reduction steps[4,5] due to solvent limitations. A number of studies have shown that their reduction potentials and rate of heterogeneous electron transfer depend on solvent medium and axialy coordinated ligands,[6-8] as well as porphyrin basicity. Recently, correlations between chemical and physical properties and porphyrin ring substituents have appeared. Substituent effects on electronic spectra,[10] equilibrium constants for the addition of axial ligands to metalloporphyrins,[11-15] and potentials for porphyrin redox reactions have been studied.[14,16-18]

Previous reports have quantified the effect of substituents on the oxidation and reduction potentials of transition-metal complexes,[14,16] including those of meta- and para-substituted iron porphyrins.[19] Here we wish to extend the work to the heterogeneous electron-transfer rate constants, k_o's, in different solvents and to rate measurements on metal-free porphyrins.

The electrode reactions investigated here include reactions 1–5. P is $(p\text{-x})TPP^{2-}$ or $(m\text{-x})TPP^{2-}$, TPP^{2-} represents tet-

$$[Fe^{III}P]^+ + e^- = [Fe^{II}P]^0 \tag{1}$$

$$[Fe^{II}P]^0 + e^- = [Fe^{I}P]^- \tag{2}$$

$$[Fe^{I}P]^- + e^- = [FeP]^{2-} \tag{3}$$

$$[H_2P]^0 + e^- = [H_2P]^- \tag{4}$$

$$[H_2P]^- + e^- = [H_2P]^{2-} \tag{5}$$

raphenylporphyrin, and x is an electron-withdrawing or -donating group placed in the para or meta positions of the four phenyl rings of TPP^{2-}.

The Hammett free energy equation (eq 6)[20] describes

$$\Delta E_{1/2} = 4\sigma\rho \tag{6}$$

half-wave potential changes with different substituents. Rate constant ratios can also be substituted for $\Delta E_{1/2}$'s,[20] and σ values are taken from ref 20.

Table I. Hammett Reaction Constants (eq 6) for Reactions 1–5 in Several Solvents and Electrolytes and Half-Wave Potentials ($E_{1/2}{}^{H} = E_{1/2}$) for Uncomplexed Tetraphenylporphyrins

Reaction	Me$_2$SO		DMA		n-PrCN	
	$E_{1/2}{}^{H}$	ρ	$E_{1/2}{}^{H}$	ρ	$E_{1/2}{}^{H}$	ρ
1	−0.11[a]	0.025[a]	−0.11[a]	-	0.32	*b*
	−0.06	0.038	−0.06	0.017	-	-
2	−1.14[a]	0.035[a]	−1.08[a]	0.020[a]	−1.06	0.024
	−1.10	0.035	0.98	0.020	-	-
3	−1.61[a]	0.063	−1.66[a]	-	-	-
	−1.59	0.064	−1.63	0.056	−1.72	0.054
4					−1.13	0.063
					−1.15	0.058
5					−1.56	0.060

[a] 0.1 M tetraethylammonium perchlorate (TEAP) (ref 17 and 19). [b] See ref 19.

Experimental Section

The various porphyrins used in this work were prepared as previously indicated[19] by the method of Adler et al.[21] Samples were further purified by chromatography on alumina in chloroform or dichloromethane. Iron was inserted by refluxing the appropriate porphyrin with ferrous chloride in DMA for about 1 h.[22] The reaction mixture was cooled in an ice bath for 15 min, chilled water was added, and the product was filtered off. The filtrate was washed with water, dried in a vacuum oven, and chromatographed on alumina using chloroform or dichloromethane. A small amount of hydrogen chloride gas was bubbled through the Fe(p-x)TPP fraction to destroy any μ-oxo dimers that may have formed. The fraction was taken to dryness under vacuum. The starting compounds for all electrochemical studies were Fe(p-x)TPPCl, Fe(m-x)TPPCl, or comparable metal-free porphyrins.

Dimethyl sulfoxide (Me$_2$SO) was treated with molecular sieves, then distilled at reduced pressure. Samples treated with molecular sieves only gave similar electrochemical backgrounds so the distillation step was eliminated. Dimethylacetamide was purified by vacuum distillation at 10 to 12 mm of mercury. The middle 60% was collected. For this study the supporting electrolyte was tetrabutylammonium perchlorate which was recrystallized from methanol and dried over P_4O_{10} in a vacuum desiccator. Air was removed by passing prepurified nitrogen through the solution for 15 min and passing the gas over the solution during analysis.

Cyclic voltammetric measurements were made with a three-electrode system with a PAR 173 potentiostat (with positive feedback), using a Model 175 universal programmer and a storage oscilloscope. The working electrode was a platinum button (size calibrated with a known ferrocyanide solution for rate measurements), and a platinum wire served as the auxiliary electrode. A commercial saturated calomel electrode (SCE) was used as the reference electrode and placed in contact with the solution with a salt bridge, and a Luggin capillary was placed as close to the working electrode as possible, without generating oscillations, to minimize resistance losses.

Heterogeneous rate constants were measured by observing the peak separation as a function of scan rate[23] for the quasi-reversible reactions measured here, as has proved successful in the past.[8,19,24] A computer program was used to apply statistical analysis to the data and to check other electrochemical functions.

Results and Discussion

Half-wave potentials and reaction constants are shown in Table I for reactions 1–5. The variation of half-wave potentials with supporting electrolyte is such that those for tetraethylammonium perchlorate (TEAP) are almost always a few hundredths of a volt more cathodic than for tetrabutylammonium perchlorate (TBAP). Although this may, at least in part, be due to a determinate experimental error such as liquid-junction potentials, potential variations with supporting electrolyte have been reported[17] and may be due to donor–acceptor properties of the cations.[17] Since these two electrolytes are similar in nature, large differences in potential would not be expected. In any case, the ρ values are of more interest in the study at hand. The ρ values for ring reductions (reactions 3, 4, and 5) are in good agreement with previously reported values (0.061 ± 0.007).[16,19] Positive values for ρ indicate that electron-donating substituents shift a redox reaction to a more cathodic potential.

Values of ρ of 0.061 ± 0.007 have been cited as a clear indication that the electron transfers involve the porphyrin ring and not the central metal.[16] This is borne out in Table I in that ρ for reactions 3, 4, and 5 are similar. Reactions 4 and 5 obviously can have no metal oxidation-state change. Little change in ρ is noticed with solvent change for these reactions.

In contrast, the reaction constants, ρ's, for metal reductions are always smaller (reactions 1 and 2). In Me$_2$SO and DMA there appears to be a slight increase in ρ with the number of "d" electrons, which has been previously shown for metals other than iron.[16] On the other hand, such a trend was not evident for iron porphyrins in n-PrCN.[19] Solvent effects may be important here since n-PrCN has a much smaller "donor number" than DMA and Me$_2$SO.[25] Metal ion charge, spin state, and axial coordination may be important. However, the ρ value for reaction 1 is 0.024 when the metal is complexed with 0.1 M imidazole in DMA. This value is not too different from the value for DMA without imidazole and is of approximately the value expected for a metal reduction. The values of $E_{1/2}$ for solutions containing imidazole are more anodic than without this complexing agent, as expected. Solvent and ligand effects play a larger role in electron-transfer kinetics as opposed to thermodynamic half-wave potentials, which are discussed below.

Heterogeneous Electron-Transfer Rate Constants. A considerable number of electron-transfer rate constants have been measured for metalloporphyrins,[24] especially those of cobalt and iron.[8,19,25,26] These studies showed that if iron(III) was reduced to iron(II) of the same spin state faster rates were found and that a low-spin to low-spin transfer was fastest.[8,24,26] Faster rates were obtained if the axial ligand did not change on reduction.[2,4,8,26,29] The greater the pK_a, the stronger the complex and the faster the rate.[8,27,28] Axial ligands which are not conjugated and thus presumably cannot easily conduct electrons slow the electron-transfer rate noticeably.[27] Likewise, it was noticed that for noncoordinating solvents, in which $[Fe^{III}P]^{+}Cl^{-}$ exists as a five-coordinate complex, electron-transfer rates were slower.[24]

In Table II, heterogeneous rate data are listed for substituted iron tetraphenylporphyrins in Me$_2$SO, DMA, and DMA with the strong axial complexing agent imidazole added. When such tables were constructed for iron tetraphenylporphyrins in butyronitrile,[19] the general trend observed was that electron-withdrawing groups on the phenyl rings of the TPP decreased the rate constant for reductions such as reactions 1, 2, and 3, as well as for oxidations of the various iron tetraphenylporphyrins. Higher rate constants were found for those reactions involving the removal or donation of an electron to the conjugated π-ring system than those in which the electron is added to or removed from the metal.

Although the ρ values of Table I and those of ref 19 are similar, indicating similar effects of substituents on thermodynamic half-wave potentials, the rate constant patterns in Table II are not as simple as the more or less regular increase in rates with decreasing σ values[19] in butyronitrile. For the metal-free porphyrins in butyronitrile (Table III), however, there is the direct relation expected on the basis of the iron porphyrin results,[19] except for the m-F case which remains anomalous even after several repetitions of the measurements. In fact, the large change in rates for reaction 4 indicated an unusually large effect on this first reduction. Quite possibly, maximum conjugation is allowed due to a relatively small dihedral angle for a neutral porphyrin species,[29] which may be more flexible when unconstrained by a central metal or a charge. The rate constant for the reduction of $[Fe^{I}P]^{-}$ is included in Table III as an indication of the fact

Table II. Log Heterogeneous Rate Constants (k_o, cm/s) for Substituted Iron Tetraphenylporphyrins

		Me$_2$SO Reaction			DMA Reaction			DMA–0.1 M imidazole Reaction 1
4σ	Substituent	1	2	3	1	2	3	
2.72	*m*-CN	−2.28	−2.90	−2.88	−3.30	−2.80	−3.44	−2.58
2.64	*p*-CN	−2.42	−2.70	−2.45	−3.15	−2.58	−2.17	−2.02
1.80	*p*-$COOCH_3$	−2.79	−2.99	−2.53	−4.00	−2.92	−2.89	−2.65
1.64	*p*-COOH	−2.18	−1.65		−4.00			−2.49
1.56	*m*-Br	−2.29	−2.68	−2.11	−2.82	−2.29	−1.76	−2.03
1.48	*m*-Cl	−2.35	−2.59	−2.18	−2.72	−2.14	−1.75	−2.09
1.36	*m*-F	−2.34	−2.43	−2.06				
1.20	*m*-$OCH_2C_6H_4$	−2.66	−3.09	−2.55	−3.22	−2.68	−1.96	−2.51
0.92	*p*-Br	−1.84	−2.25	−2.05	−2.98	−2.48	−2.10	−2.20
0.92	*p*-Cl	−2.50	−3.01	−2.02	−3.30	−2.82	−2.25	−2.36
0.24	*p*-F	−2.16	−3.06	−2.20				
0.04	*p*-C_6H_5	−2.17	−2.51	−2.66	−3.40	−2.59		−2.48
0	H	−2.04	−2.51	−2.02	−2.82	−2.60		−1.97
−0.28	*m*-CH_3	−2.09	−2.84	−2.43	−3.05	−2.37		−1.98
−0.68	*p*-CH_3	−1.80	−2.54	−2.42	−2.85	−2.24		−2.07
−0.80	*p*-$C(CH_3)_3$	−2.29	−3.16	−2.62				
−1.08	*p*-OCH_3	−2.24	−2.90	−2.76	−3.15	−2.21		
−1.48	*p*-OH	−2.38	−2.58	−2.04	−3.70	−2.49		−2.26
−1.64	*p*-$OCH_3C_6H_4$	−2.17	−2.89	−2.48	−3.52	−2.98	−2.89	−2.48

Table III. Log Heterogeneous Rate Constants for Metal-Free Tetraphenylporphyrins in Butyronitrile–TEAP

4σ	Substituent	Reaction 4	Reaction 5
2.72	*m*-CN	−3.19	−2.25
1.38	*m*-F	−1.46	−2.23
1.20	*m*-$OCH_2C_6H_4$	−2.10	−2.15
0	H	−1.98 −1.72[a] −2.13[b]	−1.82 −1.84[a]
−0.28	*m*-CH_3	−1.33	−1.87

[a] Me$_2$SO. [b] Rate for ring reduction of $[Fe^IP]^-$.

that metal reduction is slower than ring reduction.

Certain patterns can be found in the data in Table III, despite the fact that there is not a step-by-step decrease in the heterogeneous rate constant as σ values decrease as was found using butyronitrile as the solvent.[19] First, for reaction 1, it may be noticed for the set of the four most electron-donating substituents that the rate constant is faster than expected if one assumes that an overall decreasing trend should exist. This discontinuity was also noticed in butyronitrile, not only for rate constants, but for the plot of $E_{1/2}$ vs. σ.[19] It was suggested that electron-donating groups may change the extent of coordination of $[Fe^{III}P]^+$ or perhaps some slight change in mechanism is involved.

It is of greater interest to compare the logs of the heterogeneous rate constants in different solvents for reaction 1: DMA + imidazole (−1.97), Me$_2$SO (−2.01), *n*-PrCN (−2.51), and DMA (−2.82). This pattern holds for most substituents. As mentioned, we have previously found that the heterogeneous rate constant (k_o) was much slower in DMA than in Me$_2$SO for iron(III) porphyrins.[24] This is due to the fact that the chloride ion remains complexed with the iron in solvents like DMA and *n*-PrCN but not in Me$_2$SO. The second reduction, reaction 2, is on the average faster (except in Me$_2$SO) since no anion is needed to balance the charge. The faster reactions for DMA plus imidazole are explained by the fact that the chloride is removed by the imidazole ligand and, in addition, complexes the iron(II) species, which allows an electron transfer with no change in spin state or in ligand. This explains the generally faster rates found with imidazole as axial ligand.[8,24]

The differences found in Table II are actually not very large but are similar to changes found for other parameters.[12-17] However, the differences are clearly real for different solvents. Some properties of the solvent must be superimposed on the electron-donating effects of the substituents since, although there is a very general trend toward faster rates with electron-donating substituents, a number of exceptions are apparent. Also it must be noted that for Me$_2$SO reaction 2 is generally slower than reactions 1 and 3, while for DMA the reactions are faster in the order 1 > 2 > 3, as found in *n*-PrCN.[19]

The donor numbers[25] of Me$_2$SO and DMA are similar to each other but different from that of *n*-PrCN, which also has a lower dielectric constant. This may explain why substituent effects in *n*-PrCN are directly related to σ. The donating properties of DMA and Me$_2$SO must superimpose themselves on the data, but the effect of *n*-PrCN is much smaller. Me$_2$SO is known not only to remove chloride from $[Fe^{III}P]^+Cl^-$ but also to associate with the porphyrin quite strongly.[24] DMA may have the potential for association but does not remove chloride. Since in Me$_2$SO reaction 2 is slower than reaction 1, Me$_2$SO (but not DMA) must associate rather strongly with $[Fe^{II}P]^0$ as well as with iron(III) porphyrin. When $[Fe^{II}P]^0$ is reduced, solvent rearrangement must be greater in the Me$_2$SO case or tend to decrease electron density on the ring, thus slowing the reaction.[19] Apparently DMA cannot react in the same way and, therefore, reaction 2 is slower in Me$_2$SO to a greater extent than might be expected.

Further comparisons of the k_o's for different reactions can be made. In Me$_2$SO reaction 2 is slower than reaction 1 as mentioned, but reaction 3 is faster than the others for Me$_2$SO and DMA. This may be attributed to the fact that reaction 3 is due to the reduction of the porphyrin ring, rather than the metal.[19] This appears to be a general rule and may be used as one criterion for determining the product of electron transfer. Comparing reactions 2 in DMA and in Me$_2$SO leads to the conclusion that DMA is generally faster, due to the slowness of reaction 2 in Me$_2$SO. This would indicate less solvent interaction in DMA, as the solvent lowers the energy barrier for electron transfer. For reaction 3, the k_o's are similar in DMA and in Me$_2$SO.

It should be pointed out that in DMA it has been found that the more basic the porphyrin the slower the rate.[31] This is attributed to stabilization of the transition state by the solvent. Thus, the mechanism and transition state are important factors. The cases presented here cannot be generalized to all porphyrins in all solvents.

Work with other solvents, which would be desirable if solubility permitted it, might lead to a clearer picture of the mechanism of electron transfer involving metalloporphyrins.

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Registry No. Fe(*m*-CN)TPPCl, 64413-49-6; Fe(*p*-CN)TPPCl, 19570-49-1; Fe(*p*-$COOCH_3$)TPPCl, 64413-48-5; Fe(*p*-COOH)-TPPCl, 55266-17-6; Fe(*m*-Br)TPPCl, 64413-47-4; Fe(*m*-Cl)TPPCl, 64413-46-3; Fe(*m*-F)TPPCl, 64413-45-2; Fe(*m*-$OCH_2C_6H_5$)TPPCl, 64413-44-1; Fe(*p*-Br)TPPCl, 64413-43-0; Fe(*p*-Cl)TPPCl, 36965-70-5; Fe(*p*-F)TPPCl, 60250-86-4; Fe(*p*-C_6H_5)TPPCl, 64413-55-4; FeTPPCl, 16456-81-8; Fe(*m*-CH_3)TPPCl, 52155-49-4; Fe(*p*-CH_3)TPPCl, 19496-18-5; Fe(*p*-$C(CH_3)_3$)TPPCl, 64413-51-0; Fe(*p*-OCH_3)TPPCl, 36995-20-7; Fe(*p*-OH)TPPCl, 64413-57-6; Fe(*p*-$OCM_2C_6H_5$)TPPCl, 64413-56-5; H_2(*m*-CN)TPP, 64397-83-7; H_2(*m*-F)TPP, 50800-86-7; H_2(*m*-$OCH_2C_6H_5$)TPP, 64397-82-6; H_2TPP, 917-23-7; H_2(*m*-CH_3)TPP, 50849-45-1.

References and Notes

(1) D. Dolphin and R. H. Felton, *Acc. Chem. Res.*, 7, 26 (1974).
(2) R. H. Felton, G. C. Owen, D. Dolphin, and J. Fajer, *J. Am. Chem. Soc.*, **93**, 6332 (1971).
(3) A. Wolberg and J. Manassen, *J. Am. Chem. Soc.*, **92**, 2982 (1970).
(4) J. H. Fuhrhop, K. M. Kahish, and D. G. Davis, *J. Am. Chem. Soc.*, **95**, 5140 (1973).
(5) I. A. Cohen, D. Ortfeld, and B. Lichenstein, *J. Am. Chem. Soc.*, **94**, 4522 (1972).
(6) D. Lexa, M. Momenteau, J. Mespeltor, and J. M. Lahoste, *Bioelectrochem. Bioenerg.*, **1**, 108 (1975).
(7) L. A. Constant and D. G. Davis, *Anal. Chem.*, **47**, 2253 (1975).
(8) L. A. Constant and D. G. Davis, *J. Electroanal. Chem. Interfacial Electrochem.*, **74**, 85 (1976).
(9) K. M. Smith, "Porphyrins and Metalloporphyrins," Elsevier, New York, N.Y., 1975.
(10) M. Meot-Nar and A. D. Adler, *J. Am. Chem. Soc.*, **94**, 4763 (1972).
(11) E. W. Baker, C. B. Storn, G. T. McGraw, and A. H. Corwin, *Bioinorg. Chem.*, 3, 49 (1973).
(12) F. A. Walker, E. Hui, and J. M. Walker, *J. Am. Chem. Soc.*, **97**, 2390 (1975).
(13) F. A. Walker, M-W. Lo, and M. T. Ree, *J. Am. Chem. Soc.*, **98**, 5552 (1976).
(14) F. A. Walker, D. Beroiz, and K. M. Kadish, *J. Am. Chem. Soc.*, **98**, 3494 (1976).
(15) G. C. Vogel and B. A. Beckman, *Inorg. Chem.*, **15**, 483 (1976).
(16) K. M. Kadish and M. M. Morrison, *Inorg. Chem.*, **15**, 980 (1976).
(17) K. M. Kadish and M. M. Morrison, *J. Am. Chem. Soc.*, **98**, 3326 (1976); G. Gutzner, K. Danksagmuller, and V. Gutmann, *J. Electroanal. Chem. Interfacial Electrochem.*, **72**, 177 (1976).
(18) H. J. Callot, A. Giraudeau, and M. Gross, *J. Chem. Soc., Perkin Trans. 1*, **11**, 1321 (1975).
(19) K. M. Kadish, M. M. Morrison, L. A. Constant, L. Dickens, and D. G. Davis, *J. Am. Chem. Soc.*, **98**, 8387 (1976).
(20) P. Zuman, "Substituent Effects in Organic Polarography", Plenum Press, New York, N.Y., 1967.
(21) A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and L. Korsalsoff, *J. Org. Chem.*, **32**, 476 (1967).
(22) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).
(23) R. S. Nicholson, *Anal. Chem.*, **37**, 1351 (1965).
(24) K. M. Kadish and D. G. Davis, *Ann. N.Y. Acad. Sci.*, **206**, 495 (1973).
(25) D. T. Sawyer and J. L. Roberts, "Experimental Electrochemistry for Chemists", Wiley, New York, N.Y., 1974, Chapter 4.
(26) B. A. Feinberg, M. Gross, K. M. Kadish, R. S. Marano, S. J. Pace, and J. Jordan, *Bioelectrochem. Bioenerg.*, **1**, 73 (1974).
(27) D. G. Davis and L. M. Bynum, *Bioelectrochem. Bioenerg.*, **2**, 184 (1975).
(28) D. G. Davis and L. Truxillo, *Anal. Chem.*, **47**, 2260 (1975).
(29) S. S. Eaton and G. R. Eaton, *J. Am. Chem. Soc.*, **97**, 3660 (1975).
(30) S. B. Brown and I. R. Lantzke, *Biochem. J.*, **115**, 279 (1969).
(31) K. M. Kadish and G. Larson, *Bioinorg. Chem.*, **1**, 95 (1971).

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Infrared Spectra of *N*-Methyltetraphenylporphyrin Complexes (1600–200 cm^{-1})[1]

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The infrared spectra of chloro-*N*-methyltetraphenylporphinato complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), and Cd(II) as well as *N*-methyltetraphenylporphinatophenylmercury(II) are reported in the region 1600–200 cm^{-1}. Comparisons with infrared spectra of nonmethylated porphyrins in "metal-sensitive" regions near 1000 and 600–200 cm^{-1} indicate that the metal–ligand interactions are more similar among the *N*-CH_3TPP complexes than among corresponding series of nonmethylated porphyrin complexes. Use of the mass effect of *N*-CD_3TPP in comparing the spectra of ClCo-*N*-CH_3TPP, ClCo-*N*-CD_3TPP, and CoTPP allows assignment of peaks in spectra of *N*-CH_3TPP and TPP complexes which have significant C–N components. A comparison of the spectra of BrCo-*N*-CH_3TPP and ClCo-*N*-CH_3TPP allows assignment of metal–halide stretching bands. These bands occur, in cm^{-1}, at 314 (Cl–Mn), 332 (Cl–Fe), 318 (Cl–Co), 257 (Br–Co), 300 (Cl–Ni), 264 (Br–Ni), 313 (Cl–^{64}Zn), 309 (Cl–^{68}Zn), and 292 (Cl–Cd). The softening effect of the porphyrin ligand found for nonmethylated porphyrins (e.g., ν(Cl–Mn) at 271 cm^{-1} for ClMnTPP) is not evident for *N*-CH_3TPP complexes. With the exception of the Cl–Mn stretch, only very small shifts (<1 cm^{-1}) are evident in a comparison of the spectra of Cl^{64}Zn-*N*-CH_3TPP and Cl^{68}Zn-*N*-CH_3TPP. These shifts are smaller than those for ^{64}ZnTPP and ^{68}ZnTPP, indicating greater ionic character of the zinc–porphyrin bonding.

Introduction

In the systematic study of *N*-methylporphyrin complexes,[2–8] we have sought to make comparisons of properties of these species with corresponding nonmethylated porphyrin complexes. Like the nonmethylated porphyrins, *N*-methylporphyrins form complexes with a large variety of metal ions. Unlike the case of planar porphyrins, however, are the (1) tendency for the metal ion to form high-spin rather than low-spin complexes and (2) greater stability of some metal ions (e.g., Co(II) and Mn(II)) to oxidation in the *N*-methylporphyrin complex.[4] *N*-Methylporphyrin complexes may be converted to the corresponding nonmethylated porphyrin complex by a variety of nucleophiles.[3,8,11] This reaction is remarkably sensitive to the metal ion employed.

Structural analysis via x-ray diffraction is being undertaken for several complexes in order to understand the structural similarities and differences between *N*-alkyl and nonalkylated porphyrins.[6,7] Due to the size of these species, and the time and high cost involved in such investigations, however, the number of complexes which can be studied in this way is limited. Hence, infrared spectra are being used for the purpose of structural comparison. The spectra of a number of complexes of *N*-methyltetraphenylporphyrin (*N*-CH_3TPP) are reported herein. This species was chosen because of the

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