(H–H) = 2.0 Hz; δ(3-H) 7.75; δ(5-H) 6.99. Nmr for uncoordinated pyrazolyl ring: δ(4-H) 6.39, ^3J(H–H) = 2.0 Hz; δ(3-H) 7.63, δ(5-H) 7.45 (these two assignments may be reversed). *Anal.* Calcd for $C_{14}H_{15}BN_8OPt$: C, 32.53; H, 2.92. Found: C, 32.59; H, 2.96.

Acknowledgments. We are grateful to the National Research Council of Canada for financial support of this project and for the award of a scholarship to L. E. M.

Registry No. $Pt(CH_3)[HB(pz)_3](CF_2{=}CF_2)$, 51548-82-4; $Pt(CH_3)[HB(pz)_3](CF_2{=}CH_2)$, 51548-83-5; $Pt(CH_3)[HB(pz)_3](CH{=}CHCOOCO)$, 51607-50-2; $Pt(CH_3)[HB(pz)_3][cis\text{-}(CH_3)O_2CCH{=}CHCO_2(CH_3)]$, 51607-51-3; $Pt(CH_3)[HB(pz)_3][trans\text{-}(C_2H_5)O_2CCH{=}CHCO_2(C_2H_5)]$, 51607-52-4; $Pt(CH_3)[HB(pz)_3](p\text{-}OC_6H_4O)$, 51607-53-5; $Pt(CH_3)[HB(pz)_3][CH_2{=}C{=}C(CH_3)_2]$, 51607-54-6; $Pt(CH_3)[HB(pz)_3][(CH_3)_2C{=}C{=}C(CH_3)_2]$, 51607-55-7; $Pt(CH_3)[HB(pz)_3](trans\text{-}CH_3CH{=}CHCHO)$ (9), 51607-56-8; $Pt(CH_3)[HB(pz)_3](trans\text{-}CH_3CH{=}CHCHO)$ (**10**), 51607-57-9; $Pt(CH_3)[HB(pz)_3][CH_2{=}C(CH_3)CN]$ (7), 51607-58-0; $Pt(CH_3)[HB(pz)_3][CH_2{=}C(CH_3)CN]$ (8), 51607-59-1; $Pt(CH_3)[HB(pz)_3][CH_2{=}C(CF_3)CN]$ (**13a**), 51548-84-6; $Pt(CH_3)[HB(pz)_3][CH_2{=}C(CF_3)CN]$ (**13b**), 51607-60-4; $Pt(CH_3)[HB(pz)_3][CH_2{=}CHCO_2(CH_3)]$ (*cis*-Me, CO_2Me), 51607-61-5; $Pt(CH_3)[HB(pz)_3][CH_2{=}CHCO_2(CH_3)]$ (*cis*-Me, H), 51607-37-5; $Pt(CH_3)[HB(pz)_3][CH_2{=}CH(CN)]$ (*cis*-Me, H), 51540-56-8; $Pt(CH_3)[HB(pz)_3][CH_2{=}CH(CN)]$ (*cis*-Me, CN), 51607-38-6; $Pt(CH_3)[HB(pz)_3](CF_2{=}CFH)$ (**12a**), 51540-57-9; $Pt(CH_3)[HB(pz)_3](CF_2{=}CFH)$ (**12b**), 51607-39-7; $Pt(CH_3)[HB(pz)_3](CH_3CH{=}C{=}CH)$, 51567-33-0; $Pt(CH_3)[HB(pz)_3](CO)$, 51703-30-1; $Pt(CH_3)[B(pz)_4](CO)$, 51567-36-3; $Pt(CH_3)[HB(pz)_3]$, 39395-33-0; $Pt(CH_3)[B(pz)_4]$, 50921-19-2; ^{195}Pt, 14191-88-9.

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Facile Dissociation of a Copper Porphyrin. Chlorocopper(II) *N*-Methyltetraphenylporphine

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All copper complexes of porphyrins studied to date are extremely stable toward dissociation. The complex chloro-*N*-methyltetraphenylporphinecopper(II), however, undergoes dissociation readily on dilution in solutions of dimethylformamide. At a concentration of 3.6×10^{-4} *M*, the copper ion is equally complexed and solvated. The preparation and characterization of *N*-methyltetraphenylporphine is described. The acid dissociation constants of this porphyrin in nitrobenzene are $pK_3 = 5.64$ and $pK_4 = 3.85$ compared to values for tetraphenylporphine of $pK_3 = 4.38$ and $pK_4 = 3.85$. The nature of the complexes in terms of true complex or ion-pair behavior is investigated by conductivity measurements in DMF, by elemental analysis of isolated solids, and by the method of Job's plots. The species are evidently complexes rather than ion pairs, despite the similarity of their visible absorption spectra to monoprotonated *N*-methyltetraphenylporphine.

Introduction

N-Methylporphyrins[1-3] and some metal complexes formed with them[2] have been known for several years. However, little work has been done regarding the nature of bonding of these complexes, their stability constants, and formation kinetics and mechanism. Recently interest has revived in the synthesis of *N*-alkylporphyrins[4,5] and in the metal complexes formed with them.[6,7] Zinc- and copper–chloro complexes of *N*-methylporphyrins were prepared, a zinc ion assisted demethylation of an *N*-methylporphyrin has been observed,[6] and the kinetics of the acid-catalyzed solvolysis of a zinc *N*-methylporphyrin has been described.[7] A comparison has also been made of the incorporation of zinc and cadmium into etioporphyrin III and *N*-methyletioporphyrin III.[8]

The study of metal complexes of *N*-methylporphyrins seems especially important in light of Hambright's recently proposed mechanism for metal ion incorporation into porphyrin molecules.[9] In this mechanism, one species (a metal ion, proton, or *N*-alkyl group) deforms the porphyrin, allowing rapid metal incorporation from the opposite side of the porphyrin. The mono-*N*-methylporphyrin, therefore, may serve as a model for the distorted porphyrin which incorporates the metal ion. (See Figure 1.)

In this study, the mono-*N*-methyl derivative of the widely studied porphyrins α,β,γ,δ-*meso*-tetraphenylporphine has been synthesized and characterized. The copper–chloro and cobalt–chloro complexes have been studied to determine whether they are best described as true complexes or as ion pairs—a feature of metalloporphyrin chemistry which has evoked considerable debate.[10-13] The facile equilibrium of solvated and complexed copper in DMF is described.

Experimental Section

All reagents were at least of reagent grade quality. Perchloric acid was G. F. Smith double-distilled. Dimethylformamide (DMF) was distilled under reduced pressure from benzene, shaken with BaO

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(1) W. K. McEwen, *J. Amer. Chem. Soc.*, 58, 1127 (1936).

(2) W. K. McEwen, *J. Amer. Chem. Soc.*, 68, 711 (1946).

(3) R. C. Ellingston and A. H. Corwin, *J. Amer. Chem. Soc.*, 68, 1112 (1946).

(4) G. R. Dearden and A. H. Jackson, *Chem. Commun.*, 205 (1970).

(5) R. Grigg, A. Sweeney, G. R. Dearden, A. H. Jackson, and J. W. Johnson, *Chem. Commun.*, 1273 (1970).

(6) B. Shears and P. Hambright, *Inorg. Nucl. Chem. Lett.*, 6, 679 (1970).

(7) B. Shears, B. Shah, and P. Hambright, *J. Amer. Chem. Soc.*, 93, 776 (1971).

(8) B. Shah, B. Shears, and P. Hambright, *Inorg. Chem.*, 10, 1828 (1971).

(9) R. Khosopour and P. Hambright, *J. Chem. Soc., Chem. Commun.*, 13 (1972).

(10) E. B. Fleisher and J. H. Wang, *J. Amer. Chem. Soc.*, 82, 3498 (1960).

(11) B. Dempsey, M. B. Lowe, and J. N. Phillips in "Haematin Enzymes," J. E. Falk, R. Lembert, and R. K. Morton, Ed., Pergamon Press, London, 1961.

(12) E. B. Fleisher, E. I. Choi, P. Hambright, and A. Stone, *Inorg. Chem.*, 3, 1284 (1964).

(13) B. F. Burnham and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 92, 1547 (1970).

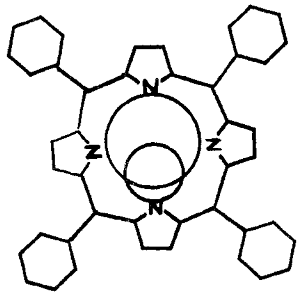

Figure 1. Schematic diagram of *N*-methyltetraphenylporphine (*N*-CH_3TPP); the large circle represents the van der Waals radius of the methyl group (*ca.* 2.0 Å) and the smaller circle that of the hydrogen atom (*ca.* 1.2 Å). The N–N distance in TPP is 4.08 Å [E. B. Fleischer, *Accounts Chem. Res.*, **3**, 105 (1970)]. Note that the phenyl rings are not coplanar with the porphyrin skeleton in TPP but become more planar on distortion of the porphyrin (*ibid*).

periodically for several hours, decanted, redistilled,[14] and stored over molecular sieves in a drybox. It gave a negative test for free amine with 1-fluoro-2,4-dinitrobenzene.[15] Dioxane was distilled under reduced pressure from $LiAlH_4$[15] and stored like the DMF. Acetone was distilled from CaH_2[15] and stored likewise. Anhydrous $CuCl_2$ and $CoCl_2$ were prepared by refluxing the hydrates (J. T. Baker Chemical Co.) with freshly distilled thionyl chloride.[16] They were checked for H_2O by taking infrared spectra using Nujol mulls between salt plates. Tetraphenylporphine (TPP) was prepared and purified by the method of Adler, *et al.*[17] The extinction coefficients agreed well with published values.[18] HCl was generated from concentrated H_2SO_4 and NaCl and passed through a P_2O_5 scrubbing tower.

***N*-Methyltetraphenylporphine.** *N*-Methyltetraphenylporphine (*N*-CH_3TPP) was prepared by three methods.

(1) The first method is metathetical to former preparation of *N*-methylporphyrins.[1-5] Tetraphenylporphine (TPP) and a 100-fold excess of methyl iodide were sealed in a glass tube and heated on a steam bath for 48 hr. The reaction mixture was then dissolved in chloroform, neutralized with 1 *M* NH_4OH, and extracted twice with H_2O. The volume of the reaction mixture was reduced to about 50 ml and chromatographed in 500-mg batches on basic alumina (2 in. × 36 in. column) using chloroform as eluent. The column developed three distinct bands. The first was TPP (rose), the second was *N*-CH_3TPP (green on column, elutes as dichroic violet-green), and the last was further methylated products (green). This method yields 5% *N*-CH_3-TPP and 15–20% further methylated products with about 75% of the TPP recovered as unreacted material.

(2) In the second method, TPP in chloroform (*e.g.*, 1.0 g in 500 ml) was refluxed with a 50-fold excess of methyl iodide for several hours. The work-up was the same as in method 1 and yields were comparable.

(3) The best method involved slow addition (4 hr) of a stoichiometric amount of fluoromethylsulfonate (Aldrich Chemical Co. "magic methyl") (*e.g.*, 0.523 ml in 500 ml) to a dilute solution of TPP in chloroform (*e.g.*, 4.0 g in 1500 ml). The reaction proceeded at room temperature for 2–3 days. The product was isolated as described above and crystallized from chloroform–ethanol (1:1). The products were *N*-methyltetraphenylporphine (30% after crystallization), further methylated products (less than 3%), and unreacted TPP (60%). The TPP was recycled to give a total yield of *N*-CH_3-TPP of about 80%.

The *N*-CH_3TPP is characterized by its distinctive nmr spectrum, which shows a sharp singlet due to the *N*-methyl group at 4.11 ppm upfield from TMS ($CDCl_3$). The striking upfield chemical shift is presumably due to interaction with the very aromatic porphyrin ring system.[4,5,19] The methyl aromatic ratio is 3:28 as expected. The nmr spectra were recorded using a JEOL 100-MHz instrument.

Visible absorption spectra (Cary 14 spectrophotometer) in DMF adhered to Beer's law throughout the range investigated (2.24×10^{-3} to 3.72×10^{-6} *M*), providing evidence for lack of significant association in this concentration range.

Active hydrogen analysis (Huffman Laboratories, Wheat Ridge, Colo.) gave 0.98 active hydrogen per molecule (per cent active hydrogen: calcd, 0.159; found, 0.156). Elemental analysis does not distinguish between TPP (calcd for $C_{44}N_4H_{30}$: C, 86.0; N, 9.12; H, 4.93) and *N*-CH_3TPP (calcd for $C_{45}N_4H_{30}$: C, 86.0; N, 8.92; H, 5.14).

Acid Dissociation Constants. *N*-Methyltetraphenylporphine was titrated spectrophotometrically in matched quartz cuvettes using a Cary 14 spectrophotometer. Titrations were carried out (1) in nitrobenzene (Eastman) using $HClO_4$ in dioxane and (2) in DMF using dry HCl dissolved in DMF. The $HClO_4$ and HCl solutions were standardized by aqueous titration.

Copper–Chloro and Cobalt–Chloro Complexes. Job's plots[20] were made for solutions of $CuCl_2 \cdot 2H_2O$ and $CoCl_2$ in acetone, methanol, and DMF added to solutions of *N*-CH_3TPP in chloroform.

Conductivity measurements were made using a Serfass RC M15 conductance bridge and a Sargent conductance cell with 1-cm^2 electrode faces. The cell was freshly platinized and the cell constant determined as 0.3232. Measurements were made on HCl in DMF and $CuCl_2$ added to *N*-methyltetraphenylporphine in DMF.

Stability Constant of Chloro-*N*-methyltetraphenylporphinecopper(II). Stability constants were determined by adding aliquots of $CuCl_2$ and *N*-CH_3TPP solutions in DMF. For the reaction of unprotonated *N*-CH_3TPP, the DMF was 0.005 *M* in NH_4OH, and for the monoprotonated *N*-methyltetraphenylporphine, it was 0.005 *M* in $HClO_4$. The DMF solutions were prepared by addition of NH_3 (generated from NH_4Cl-$Ca(OH)_2$ and passed through a scrubbing tower of CaO) or concentrated $HClO_4$ to dry DMF and standardized by aqueous titration. Stability constant measurements were also made by diluting a stock solution of $CuCl_2$ and *N*-CH_3TPP in DMF. The solutions were all deaerated with Ar and handled under a CO_2 blanket.

Results

Acidic Dissociation Constants. Since the formation of a metal complex of an *N*-alkylporphyrin involves the release of a proton (eq 1) which could protonate free porphyrin to

$$CuCl_2 + N\text{-}CH_3TPP \rightleftarrows ClCu\text{-}N\text{-}CH_3TPP + H^+ + Cl^- \qquad (1)^{21}$$

give contributions from a second reaction (eq 2), it is neces-

$$H^+ + N\text{-}CH_3TPP \rightleftarrows (N\text{-}CH_3TPPH)^+ + CuCl_2 \rightleftarrows$$
$$ClCu\text{-}N\text{-}CH_3TPP + 2H^+ + Cl^- \qquad (2)$$

sary to know the acid dissociation constants of the *N*-alkylporphyrin before undertaking stability constant studies. To allow comparison with other porphyrins[22] the pK_3 and pK_4 values of *N*-methyltetraphenylporphine were determined in nitrobenzene by titration with $HClO_4$ in dioxane. The pK_3 is defined from $K_3 = [P][H^+]/[PH^+]$ and pK_4 from $K_4 = [PH^+][H^+]/[PH_2^{2+}]$ where P is the free base porphyrin. For TPP, Aronoff[22] found that the K_3 and K_4 values were sufficiently close that isobestic points for the separate processes could not be distinguished. He estimated the values as pK_3 = 4.38 and pK_4 = 3.85. For *N*-methyltetraphenylporphine, however, the values are sufficiently different to give well-defined isosbestics for the first and second protonations (Figures 2 and 3), giving a typical dibasic titration curve. The values in nitrobenzene are pK_3 = 5.64 and pK_4 = 3.85.

Stability Constant. Since DMF dissolves both metal

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(14) A. B. Thomas and E. G. Rochow, *J. Amer. Chem. Soc.*, **79**, 1843 (1957).

(15) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals," Pergamon Press, London, 1966, p 143.

(16) A. P. Pray, *Inorg. Syn.*, **5**, 153 (1957).

(17) A. D. Adler, F. R. Longo, J. E. Finarelli, J. Goldinacher, J. Assou, and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).

(18) G. D. Donough, J. R. Miller, and F. M. Huennekens, *J. Amer. Chem. Soc.*, **73**, 4315 (1951).

(19) W. S. Caughey and P. K. Iber, *J. Org. Chem.*, **28**, 269 (1968).

(20) M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1964, p 282.

(21) At the concentrations used in these experiments (10^{-3}–10^{-6} *M*) HCl acts as a strong electrolyte[14] while $CuCl_2$ exists as a complex mixture of $CuCl^+$, $CuCl_3^-$, and $CuCl_4^{2-}$ ions [H. Hubacek, B. Stancic, and V. Gutman, *Monatsh. Chem.*, **94**, 1118 (1963); L. I. Katzin, *J. Chem. Phys.*, **36**, 3034 (1962)].

(22) S. Aronoff, *J. Phys. Chem.*, **62**, 428 (1958).

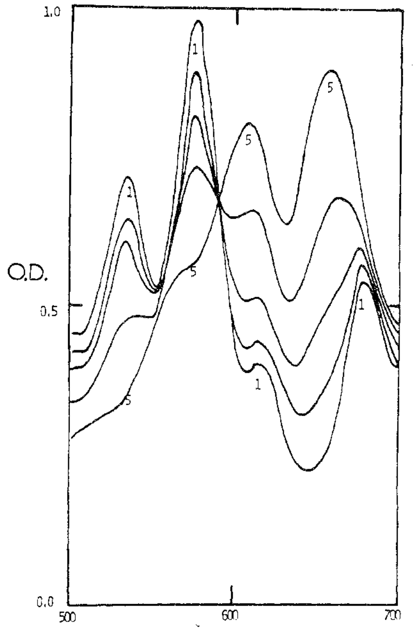

Figure 2. Titration of *N*-methyltetraphenylporphine (1.00 × 10^{-5} *M*) with $HClO_4$ (0.00771 *M* in dioxane; no. 2 and 3, 5-μl aliquots; no. 4 and 5, 10-μl aliquots) to form $(N\text{-}CH_3TPPH)^+$; 100-mm cuvettes containing 29.0 ml of the nitrobenzene solution were used. Spectrum 1 is of *N*-CH_3TPP in nitrobenzene (unchanged by small additions of dioxane only). Spectrum 5, which is found through the plateau region of the titration (Figure 4, H^+ added from 10^{-5} to 10^{-4} *M*) is used as the spectrum of $(N\text{-}CH_3TPPH)^+$ to determine p*K* values.

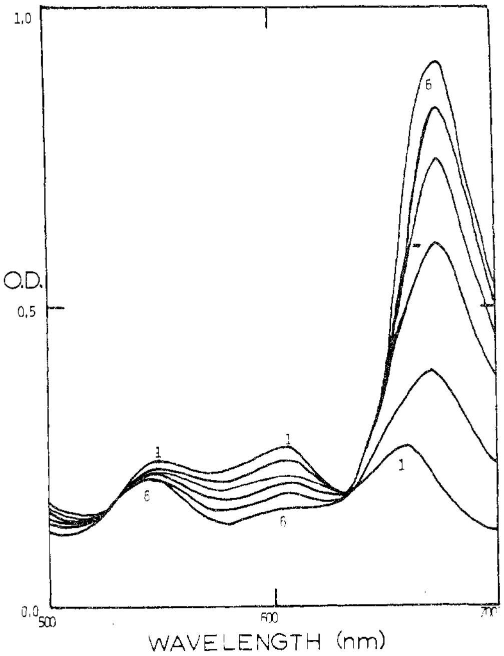

Figure 3. Titration of $(N\text{-}CH_3TPPH)^+$ (2.00 × 10^{-6} *M*) in nitrobenzene with $HClO_4$ (0.00771 *M* in dioxane; no. 1, 250-μl aliquot; no. 2-5, 40-μl aliquots) to form $(N\text{-}CH_3TPPH_2)^{2+}$; 100-mm curvettes containing 29.0 ml of the nitrobenzene solution were used. Spectrum 1, which is found through the plateau region of the titration (Figure 4, H^+ added from 10^{-5} to 10^{-4} *M*), is used as the spectrum of $(N\text{-}CH_3TPPH)^+$. Spectrum 6, which is the limiting spectrum on addition of excess acid, is used as the spectrum of $(N\text{-}CH_3TPPH_2)^{2+}$ to determine p*K* values.

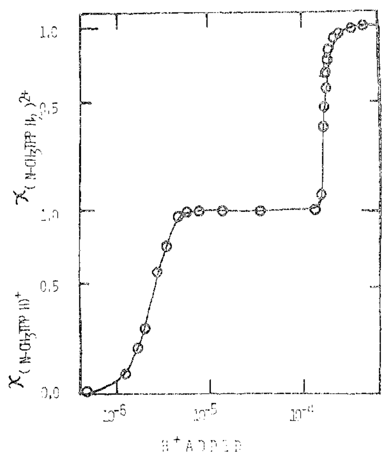

Figure 4. Titration curves for *N*-methyltetraphenylporphine (1.00 × 10^{-5} *M*) in dimethylformamide using HCl (0.1138 *N* in DMF).

salts and porphyrins quite well and has been used successfully in synthesizing a great number of metalloporphyrins,[23] it was chosen as the reaction medium. In taking visible absorption spectra of the copper-chloro complex of *N*-CH_3-TPP, it was apparent that the spectrum was concentration dependent. The complex dissociated readily upon dilution. Prior to a study of the stability constant for the complex in DMF, the basicity of *N*-CH_3TPP in DMF was determined. As in nitrobenzene, the isobestic points were distinguishable for both mono- and diprotonation resulting in the dibasic titration curve shown in Figure 4. In DMF, the pK_3 value is 4.02 and pK_4 is 2.05. The well-defined plateau region allows study of stability constants for the free base plus metal ion, monoprotonated porphyrin plus metal ion, or diprotonated porphyrin plus metal ion by adjusting the hydrogen ion concentration in the DMF.

The stability constant for reaction 3 was studied by main-

$$ClCu\text{-}N\text{-}CH_3TPP + HCl \rightleftharpoons N\text{-}CH_3TPP + CuCl_2 \qquad (3)$$

taining a low concentration of H^+ using NH_4OH. In 0.005 *M* NH_4OH, a plot of log [ClCu-*N*-CH_3TPP] *vs.* log [*N*-CH_3TPP] under conditions of [*N*-CH_3TPP] = [$CuCl_2$] gives a reasonable fit to a line of slope 2 (Figure 5) as predicted from the equilibrium expression

$$K_{eq} = [N\text{-}CH_3TPP][CuCl_2]/[ClCu\text{-}N\text{-}CH_3TPP][HCl] \qquad (4)$$

An isosbestic point is also found for spectra which result from the addition of aliquots of equivalent amounts of *N*-CH_3TPP and $CuCl_2$ to a DMF solution. The dissociation is well behaved when studied either by dilution of the complex or by increasing the concentration of metal and ligand by addition of concentrated aliquots to favor complex formation. The apparent formation and dissociation rates are both rapid.

It was observed during initial experiments of the stability of the copper complex that the isosbestic point began to drift after 1 hr has elapsed. A subsequent reaction was occurring which converted the chloro-*N*-methyltetraphenylporphinecopper into CuTPP. The reaction is quantitative and the CuTPP is identified by its visible absorption spectrum. This reaction and analogous reactions of other transition metals are presently being studied in detail. To avoid the complications arising from the subsequent reaction, measurements were made under argon, with attention to the stability of the isosbestic point.

The stability constant for the dissociation of the copper

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(23) A. D. Adler, F. R. Longo, F. Kampos, and J. Kim, *J. Inorg. Nucl. Chem.*, 32, 2443 (1970).

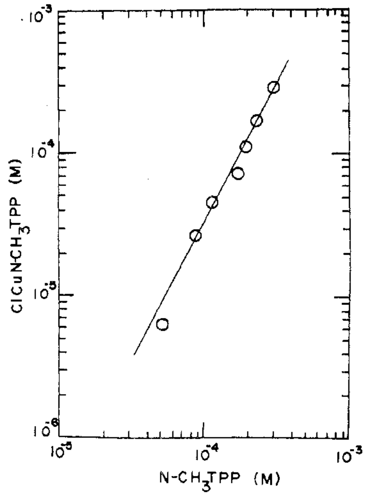

Figure 5. Log-log plot of the concentration of the chlorocopper complex of *N*-methyltetraphenylporphine (ClCu-*N*-CH$_3$TPP) *vs.* the concentration of uncomplexed *N*-CH$_3$TPP for the formation of the complex by addition of CuCl$_2$ in dimethylformamide (DMF) to an equivalent amount of *N*-CH$_3$TPP in DMF. The line is drawn with a slope of 2, not as a least-squares fit.

complex is best defined as a conditional equilibrium constant[24] (*i.e.*, a constant defined only for the stated experimental conditions) due to the difficulty of defining the hydrogen ion concentration in nonaqueous solvents. The value of the conditional stability constant, K_s, was determined for $K_s = [\text{ClCu-}N\text{-CH}_3\text{TPP}]/[N\text{-CH}_3\text{TPP}][\text{Cu}^{2+}]$ for solutions in which the total copper ion concentration was equal to the total porphyrin concentration. In the equation for K_s, $[\text{Cu}^{2+}]$ is the total concentration of all species containing Cu^{2+} other than ClCu-*N*-CH$_3$TPP. The mole fraction of complex was determined by using the ratio of the extinction coefficients at 612 nm (eq 5). Like results

$$X_{\text{complex}} = \frac{\epsilon_{\text{obsd}} - \epsilon_{N\text{-CH}_3\text{TPP}}}{\epsilon_{\text{ClCu-}N\text{-CH}_3\text{TPP}} - \epsilon_{N\text{-CH}_3\text{TPP}}} \tag{5}$$

were obtained using the extinction coefficients at 562 nm. The resulting value for the stability constant using eq 5 is $\text{p}K_s = 3.75 \pm 0.25$.

To determine the dissociation constant for the reaction

$$2\text{H}^+ + \text{Cl}^- + \text{ClCu-}N\text{-CH}_3\text{TPP} \rightleftarrows N\text{-CH}_3\text{TPPH}^+ + \text{CuCl}_2$$

the concentration of hydrogen ion was maintained with a total hydrogen ion concentration of 0.005 *M* using 0.005 *M* HClO$_4$. The stability of the complex in the presence of hydrogen ion was too low to measure by using equal concentrations of copper ion and ligand since the resulting optical density is too large to be measured by the Cary 14 spectrophotometer. In this case, aliquots of a concentrated solution of CuCl$_2$ in DMF (*e.g.*, 0.404 *M*) were added to a solution of *N*-CH$_3$TPP in DMF (*e.g.*, 1.29×10^{-3} *M*). The amount of CuCl$_2$ needed to form the complex in this acidic medium was 300 times that in 0.005 *M* NH$_3$ or $\text{p}K_s \approx 1$. The mole fraction of complex was determined by eq 5 for extinction coefficients at 652 and 604 nm.

The much lower stability in acidic solution is, of course, to be expected since the copper species must approach a positively charged site rather than a neutral one. The corresponding stability of the copper complex of TPP is not directly measurable. Copper can be removed from CuTPP only by rigorous conditions (*e.g.*, concentrated H$_2$SO$_4$).[25] The distorted binding site of *N*-methyltetraphenylporphine increases not only the rate at which metalation occurs with copper but also its ease of dissociation (at least kinetically).

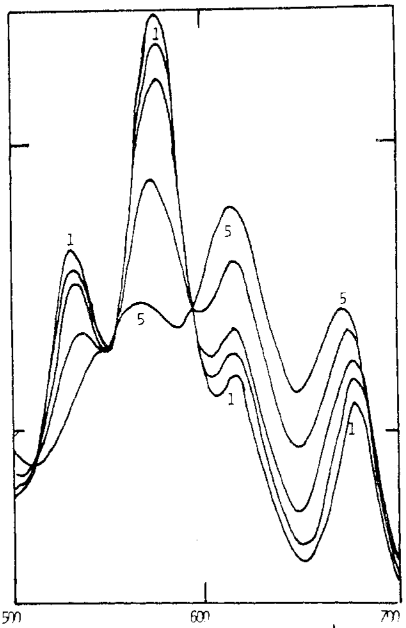

Figure 6. The formation of the chlorocopper complex of *N*-methyltetraphenylporphine by addition of CuCl$_2$ (8.54×10^{-2} *M* in DMF) in small aliquots to a solution of *N*-CH$_3$TPP (1.44×10^{-4} *M* in CHCl$_3$); 10-mm cuvettes were used.

The Nature of the Complex. The 1:1 ratio of copper to *N*-CH$_3$TPP was determined using the method of Job's plot.[20] The formation of only a single complex is apparent from the isosbestic point observed during the titration of the *N*-CH$_3$TPP with relatively concentrated CuCl$_2$ (Figure 6). The result of the determination using a relatively concentrated solution of CuCl$_2$ in chloroform, in which dissociation is not apparent, is shown in Figure 7. Similar results are obtained for CuCl$_2$ in anhydrous acetone, *N*-CH$_3$TPP in chloroform, CoCl$_2$ in DMF added to *N*-CH$_3$TPP in chloroform, etc. The elemental analysis for the cobalt-chloro complex is also consistent with a 1:1 composition ClCoC$_{45}$N$_4$H$_{31}$. *Anal.* Calcd: C, 74.82; N, 7.76; H, 4.33; Cl, 4.91; Co, 8.17. Found: C, 74.68; N, 7.91; H, 4.32; Cl, 4.88, net 8.21. The analysis was performed by Alfred Bernhardt Laboratories, Elbach uber Engelskirchen, West Germany.

The very close resemblance of the spectra of (*N*-CH$_3$TPPH)$^+$ and the products of the reactions of CuCl$_2$ with *N*-CH$_3$TPP in DMF and CoCl$_2$ with *N*-CH$_3$TPP in DMF (Table I) suggests the possibility of the formation of ion pairs rather than true complexes. Such spectral similarities were used by Burnham and Zuckerman to support ion-pair formation for some metal complexes of some porphyrin esters.[13]

To investigate whether the species in solution are true complexes or ion pairs, conductivity measurements were employed. A solution of HCl in DMF was prepared (1.18×10^{-3} *M*) and its conductivity measured, giving a specific conductivity of 30, agreeing with that found by Thomas and Rochow.[14] The conductivity of a DMF solution of *N*-CH$_3$TPP and CuCl$_2$ was then measured (*e.g.*, at 9.57×10^{-3} *M*, $\Lambda = 36$; Thomas and Rochow's[14] value for 1×10^{-2} *M* HCl

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(24) A. Ringbom, *J. Chem. Educ.*, 35, 282 (1958).

(25) W. S. Caughey and A. H. Corwin, *J. Amer. Chem. Soc.*, 77, 1509 (1955).

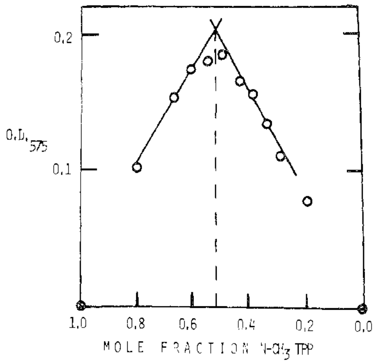

Figure 7. A Job's plot for the complex formed from $CuCl_2$ and *N*-methyltetraphenylporphine, demonstrating 1:1 complex formation.

Table I. Absorption Spectra Maxima and Extinction Coefficients for Some *N*-Methyltetraphenylporphine Species

Compd	λ_{max} (log ϵ)
N-CH_3TPP (DMF)	676 (3.58), 615 (3.60), 573 (4.08), 530 (3.91), 431 (5.35)
(*N*-CH_3TPPH)Cl (DMF)	672 (4.01), 613 (4.02), 573 (3.80)
(*N*-$CH_3TPPH_2)Cl_2$ (DMF)	677 (4.30), 622 (3.87), 572 (3.54)
ClCu-*N*-CH_3TPP ($CHCl_3$)	676 (3.81), 620 (3.88), 573 (3.69)
ClCo-*N*-CH_3TPP ($CHCl_3$)	676 (3.77), 619 (3.93), 573 (3.67)

was $\Lambda = 34$). Reactions of the following types are thought produce a complex (eq 6) or ion pair (eq 7)

$$CuCl_2 + N\text{-}CH_3TPP \rightleftarrows ClCu\text{-}N\text{-}CH_3TPP + H^+ + Cl^- \quad (6)$$

$$CuCl_2 + 2H_2O + N\text{-}CH_3TPP \rightleftarrows [N\text{-}CH_3TPPH]^+ + [CuCl_2(OH)(H_2O)]^- \quad (7)$$

The conductivity measurements favor the formation of a true complex (eq 6) rather than ion-pair formation (*e.g.*, eq 7). If the species present consisted of a significant amount of uncomplexed $CuCl_2$ (as species such as $CuCl_3^-$, $CuCl_4^{2-}$, etc.), the conductivity would be substantially higher.[26] The elemental analysis results for the cobalt complex also support complex formation.

Discussion

The *N*-methylporphyrins are a system of porphyrins with a nonplanar coordination site of pyrrolic nitrogens. The van der Waals radius of the methyl group is too large to occupy the center of the porphyrin ring simultaneously with the pyrrolic hydrogen of the free base (Figure 1). From the large upfield shift of the methyl proton, it is evident that the methyl group is distorted from the center of the porphyrin.[19]

Distortion of the porphyrin coordination site is suggested by Hambright[9] as a reasonable first step in the metalation of porphyrins. The metal should be able to complex an *N*-methylporphyrin more quickly than the undistorted porphyrin since (1) the *N*-methylporphyrins are stronger bases,[3,27] (2) less distortion from the ground-state geometry would be necessary to achieve the transition state for metal complexation,[28] (3) less solvent reorganization is necessary, and (4) less ligand reorganization at the metal center may be necessary.

N-Methyltetraphenylporphine is conveniently prepared by slow addition of fluoromethylsulfonate to dilute solutions of TPP in chloroform. The crystalline product which results from the isolation procedure appears to be stable over several months toward demethylation or photodecomposition. It thus provides a readily available system for the study of metal complexes of distorted porphyrins. The large amount of data available for metal complexes of TPP allows comparisons to be drawn between the distorted and undistorted systems. In *N*-CH_3TPP, the site is already somewhat distorted and the compensation effect should not be as great.

The p*K* values for *N*-CH_3TPP do not differ from one another as much as the values for other methylated porphyrins,[28] and *N*-CH_3TPP is several orders of magnitude less basic than a water-soluble methylated porphyrin (*N*-methyltetra(4-sulfophenyl)porphine).[29] These observations may be explained by the ability of the unsubstituted phenyl rings to delocalize the positive charge of the monocation while it does not greatly affect the basicity of the free base porphyrin. In contrast, the 4-sulfophenyl group greatly affects the basicity, presumably due to its affect on the ground-state electron density of the free nitrogen sites.

Reaction of *N*-CH_3TPP with $CuCl_2$ or $CoCl_2$ in DMF results in 1:1 complexes, as shown by the method of Job's plots, conductivity measurements, and, in the case of Cl-Co-*N*-CH_3TPP, elemental analysis. The copper complex undergoes readily observable dissociation on dilution, unlike the corresponding complex with TPP. Again, this difference is due to the difference in the coordination sites of the two porphyrins. The metal ion is held above the plane of the nitrogen atom in *N*-CH_3TPP and is also bound differently because of the attachment of the methyl group to one of the nitrogen atoms.

The nature of the bonding in these complexes, as well as stabilities of other complexes and the kinetics of their formation, is presently under study.

Further work being undertaken includes a study of the relative stabilities and formation rates of various metal ions with *N*-CH_3TPP and with water-soluble methylated porphyrins, an investigation of the bonding and structure at the coordination site, and the facile demethylation reaction.

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Registry No. *N*-CH_3TPP, 51552-53-5; (*N*-CH_3TPPH)Cl, 51552-54-6; (*N*-$CH_3TPPH_2)Cl_2$, 51552-55-7; ClCu-*N*-CH_3TPP, 51552-51-3; ClCo-*N*-CH_3TPP, 51552-52-4; TPP, 917-23-7; MeI, 74-88-4; fluoromethylsulfonate, 421-20-5.

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(26) C. M. Brown, Dissertation, Drexel University, 1971.

(27) A. Nueberger and J. J. Scott, *Proc. Roy. Soc., Ser. A.*, 213, 307 (1952).

(28) P. Hambright, *Coord. Chem. Rev.*, 6, 247 (1971).

(29) D. K. Lavallee and W. Madonna, unpublished results.