observed for the meso-substituted iron(III) porphyrin dimers.

At near neutral pH the pyrrole-substituted derivatives of natural iron(III) porphyrins (hemin *c*, FeDeut, and FeDDS) exhibit magnetic moments only slightly diminished from the expected high-spin value of 5.9 μ_B. However, spectrophotometric[6,8,15] and kinetic[16] studies are consistent with essentially complete dimerization of these compounds under the concentration conditions examined here. FeProt also showed a high magnetic moment[3] under conditions where the spectrophotometric study[15] revealed the compound was dimeric. Although μ-oxo-bridge formation in these pyrrole-substituted iron(III) porphyrin dimers was postulated from the pH dependence of dimer formation,[8,15,16] the nearly high-spin magnetic moments suggest other types of interactions. As was previously discussed for hemin *c*,[6] it appears that pyrrole-substituted iron(III) porphyrins dimerize by formation of a dihydroxo bridge in which antiferromagnetic coupling is not so important[17] or by π-donor–acceptor interactions which require iron(III) hydrolysis to diminish charge and solvation at the iron center to allow porphyrin stacking. However, in high ionic media both FeProt[2,3] and FeDeut (Table I) show diminished magnetic moments consistent with μ-oxo-bridge formation. Apparently changes in the ionic atmosphere can convert these nonantiferromagnetic coupled dimers to μ-oxo-bridged species. FeProt is much more sensitive in this respect than FeDeut. Temperature dependence of hemin *c*, FeDeut, and FeDDS magnetic moments also suggests that at higher temperatures some of the μ-oxo-bridged species may be formed.

Other evidence in the literature supports differences in the type of dimers formed by meso-substituted and pyrrole-substituted iron(III) porphyrins. Rate constants for the dissociation of FeDDS,[8] FeDeut,[16] and metal-free porphyrin dimers[18–20] are approximately three orders of magnitude greater than corresponding rate constants for the FeTPPS$_4$ dimer[4,21] and other known oxo-bridged iron(III) complexes.[1] Increased dimer dissociation rates for pyrrole-substituted iron(III) porphyrins suggest the presence of the expectedly more labile dihydroxo bridges[22] or π-donor–acceptor complexes. Dimerization equilibria for FeTPPS$_4$[4,21] and pyrrole-substituted iron(III) porphyrins[6,8,15,23] also differ in that no predimerization hydrolysis step leading to a hydroxo species is observed for FeTPPS$_4$. Visible–uv spectra may distinguish two types of iron(III) porphyrin dimers since dimerization of hemin *c*[6], FeDeut,[15] and FeProt[15] results in a shift of the near-uv Soret absorption band to shorter wavelengths, whereas dimerization of FeTPPS$_4$[4] and FeTMpyP[14] results in a shift to longer wavelengths. Furthermore, FeTPPS$_4$ dimers were not split by aqueous detergents which are effective for pyrrole-substituted iron(III) porphyrins.[24]

The different solution properties of meso-substituted and pyrrole-substituted iron(III) porphyrins cannot be fully explained at this time. Steric differences must be important, and perhaps meso-substituted porphyrins can be staggered such that aromatic meso groups of interacting porphyrins are parallel, allowing closer approach of porphyrin planes and formation of oxo bridges. It may be that for steric reasons only the edges of pyrrole-substituted porphyrins or selected pyrroles overlap and the iron centers are not properly aligned for bridging. The possible importance of both steric constraints and charge in pyrrole-substituted iron(III) porphyrins is illustrated by the greatly decreased tendency of hemin *c* (with bulky cysteine side chains) and FeDDS (with two negatively charged sulfonate groups) to form oxo bridges in high ionic strength media compared to FeDeut and FeProt.

Registry No. FeTPPS$_4^{3-}$, 60489-11-4; FeTCPP^{3-}, 60489-12-5; FeTMpyP^{5+}, 60489-13-6; FeDeut^{-}, 60489-14-7; FeDDS^{3-}, 60489-98-7; FeProt^{-}, 60489-15-8.

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Spontaneous Demethylation of *N*-Methyltetraphenylporphinatocopper(II) Chloride in Chloroform Producing Methyl Chloride and Tetraphenylporphinatocopper(II)

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While the initial impetus for the study of metal complexes of N-substituted porphyrins was to provide information relative to the corresponding metalloporphyrins,[1] it is now evident that metallo-N-substituted porphyrins have unique properties themselves. Thus rhodium(I)[2] and cobalt(I)[3] *N*-methylporphyrins undergo oxidative addition forming CH$_3$–Rh^{III} and CH$_3$–Co^{III} adducts, and homoporphyrins, having a two-carbon meso bridge,[4] are among the products of Ni^{II}-*N*-CH$_2$CO$_2$EtP (P = porphyrin) reactions. We earlier demonstrated[5] that ZnP is the product of the demethylation of Zn-*N*-MeP in refluxing pyridine and that porphyrin demethylations are promoted by coordinated metal ions. Lavallee[6] has found that *N*-methyltetraphenylporphinatocopper(II) (Cu-*N*-MeTPP$^+$) in the presence of added nucleophiles such as pyridine (or di-*n*-butylamine) produces CuTPP and the methylpyridinium ion (or di-*n*-butylmethylamine). We report another demethylation pathway for Cu-*N*-MeTPP$^+$Cl$^-$, in which the nucleophilic agent is the associated anion itself.

Experimental Section

To prepare Cu-N-MeTPP$^+$Cl$^-$, a fivefold molar excess of CuCl·2H$_2$O was added to H-N-MeTPP in methanol and stirred overnight. The methanol was evaporated and the resulting solid taken up in benzene and filtered. The solution was passed through a dry alumina column and eluted with benzene to remove CuTPP. The copper–chloro complex was eluted with 1% MeOH in C$_6$H$_6$ and the solvent was immediately removed by flash evaporation. The complex was then dried under vacuum at 100 °C. Anal. Calcd for Cu-N-MeTPP$^+$Cl$^-$, C$_{45}$H$_{31}$N$_4$CuCl: C, 74.37; N, 7.71; H, 4.30; Cu, 8.74. Found: C, 74.50; N, 7.54; H, 4.64; Cu, 8.77. Absorption band of Cu-N-MeTPP$^+$Cl$^-$ in CHCl$_3$ (25 °C): 672 nm (log $E_{\max} = 3.60$), 617 nm (3.82), 537 nm (3.80), 452 nm (4.95).

Results and Discussion

When dissolved in CHCl$_3$, Cu-N-MeTPP$^+$Cl$^-$ spontaneously transforms into CuTPP in a first-order fashion. The reaction shows no deviation from first-order kinetics over 3 half-lives and the observed rate was independent of total porphyrin concentration from ca. 10^{-4} to 10^{-6} M. The half-life was 75.0 ± 1.0 min at 25.5 °C; $\Delta H^{\ddagger} = 24.4 \pm 0.5$ kcal/mol and $\Delta S^{\ddagger} = +3.7 \pm 1.0$ eu. Excellent isosbestic points were found as the reaction proceeded and the product CuTPP was identified by the position and intensities of its absorption bands. Acid demetalation of the resulting CuTPP produced H$_2$TPP. The NMR spectra of a distilled fraction of the product solution gave a singlet at 3.1 ppm characteristic of CH$_3$Cl and flushing the solution with nitrogen caused the resonance of the gaseous CH$_3$Cl to disappear. Spectrophotometrically, 1 mol of CuTPP was produced from 1 mol of reactant. The reaction is

$$\text{Cu-}N\text{-MeTPP}^{+}\text{Cl}^{-} \xrightarrow{\text{CHCl}_3} \text{CuTPP} + \text{MeCl}$$

This reaction also occurred in C$_6$H$_6$, CH$_2$Cl$_2$, and CCl$_4$ but was orders of magnitude slower in CH$_3$OH or CH$_3$OH–CHCl$_3$. The methanol presumably solvates the porphyrin and chloride, forming the outer-sphere adduct (Cu-N-MeTPP$^+$)Cl$^-$ which is less reactive than the inner-sphere ion-pair form.

This free base H-N-MeTPP shows no evidence of demethylation after weeks in CHCl$_3$. As another indication of the metal ion specificity of such reactions, Zn-N-MeTPP$^+$Cl$^-$ can be refluxed without change for hours in CHCl$_3$, while the copper adduct decomposes in minutes under similar conditions.

This simple reaction is novel insofar as the spontaneous demethylation of a metallo-N-methylporphyrin in the absence of added nucleophiles has not been reported. The fact that this copper porphyrin type has never heretofore been isolated may be due to its spontaneous decomposition under the usual porphyrin recrystallization conditions and it is noted that this adduct has always been prepared in situ for solution studies.[7] Further work is in progress on the anion, metal, and porphyrin influences in these presumed ion-pair, metal-assisted acid–base reactions.

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Registry No. Cu-N-MeTPP$^+$Cl$^-$, 51552-51-3; CuTPP, 14172-91-9; MeCl, 74-87-3.

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Stereochemistry of Low-Spin Cobalt Porphyrins. 8. α,β,γ,δ-Tetraphenylporphinatocobalt(II)

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There has been considerable recent interest in the stereochemistry of low-spin cobalt porphyrins, and structure determinations for a variety of derivatives have come from our laboratories[1–7] and others.[8–11] Despite this, the molecular stereochemistry of the simplest member of the class, a four-coordinate cobalt(II) porphyrin, has not been determined. We report herein the molecular stereochemistry of one such four-coordinate derivative, as found in tetragonal crystals of α,β,γ,δ-tetraphenylporphinatocobalt(II), to be written as CoTPP. CoTPP crystallizes in the same tetragonal system as that observed for the tetraphenylporphinato derivatives of iron(II),[12] nickel(II),[13] and copper(II);[14] the M(II)–N bond lengths in this sequence are thus subject to the same constraints of crystal packing.

Experimental Section

CoTPP was prepared by the method of Adler et al.[15] Attempts to prepare crystals of CoTPP from a variety of solvents yielded only very fine needles, which were unsatisfactory for diffraction studies. Acceptable crystals were obtained from diethyl ether. CoTPP was placed in a Soxhlet extractor and extracted with diethyl ether for 3 days; well-formed tetragonal-bipyramidal crystals were found in the solvent flask.

Preliminary examination of crystals of CoTPP established that the Laue symmetry and systematic absences were consistent with the choice of two tetragonal space groups,[16] $I4_1md$ and $I\bar{4}2d$. Lattice constants $a = 15.062$ (4) Å and $c = 13.954$ (5) Å (λ 0.71069 Å) came from a least-squares refinement that utilized the setting angles of 29 reflections, each collected at $\pm 2\theta$, given by the automatic centering routine supplied with the Syntex $P\bar{1}$ diffractometer. These constants led to a calculated density of 1.41 g/cm^3 for a cell content of four CoTPP molecules; the experimental density was 1.42 g/cm^3. All measurements were made at the ambient laboratory temperature of 20 ± 1 °C. The crystal used in all measurements was a truncated tetragonal bipyramid with a basal edge of 0.45 mm and a length of 0.23 mm along the unique axis; the unique axis was approximately parallel to the mounting axis.

Diffracted intensities were measured by θ–2θ scanning using graphite-monochromated Mo Kα radiation. The scan range used was 0.8° below Kα_1 to 0.8° above Kα_2. Backgrounds were estimated by profile analysis.[17] Two equivalent forms of data to $(\sin\theta)/\lambda \leq 0.758$ Å^{-1} were measured and averaged. Four standard reflections, measured periodically, showed no trend with time. Variable 2θ scan rates were used as described previously;[3] the slowest was 0.5°/min and the fastest was 6.0°/min. Net intensities were reduced to relative squared amplitudes, $|F_o|^2$, without correction for the absorption of x radiation. The maximum error in any structure amplitude arising from the neglect of absorption was estimated to be ~3%. Reflections having $F_o > 3\sigma(F_o)$ were taken to be observed. A total of 1157 unique data were taken to be observed, 82% of the theoretical number possible within the range of $(\sin\theta)/\lambda$ examined.

The choice of $I\bar{4}2d$ as the probable space group follows that of the isomorphous crystals of FeTPP[12] and CuTPP and PdTPP[14] and was confirmed by all subsequent details of the structure solution and refinement. Initial coordinates for CoTPP were taken from those reported for CuTPP.[14] Full-matrix least-squares refinement,[18] with anisotropic thermal parameters and standard values for the atomic form factors,[19] smoothly coverged. A Fourier difference synthesis gave the approximate positions of all hydrogen atoms in the asymmetric unit of structure; these atoms were then assigned to theoretically calculated positions (C–H = 0.95 Å), with isotropic thermal parameters fixed one unit higher than those of the associated carbon atoms, and their contributions to the calculated structure amplitudes were included in subsequent cycles of refinement. Inclusion of the