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Metal Ion Promoted Demethylation of *N*-Methyltetraphenylporphinatocopper(II)

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N-Methyltetraphenylporphinatocopper(II) chloride in acetonitrile reacts under mild conditions with di-*n*-butylamine to form the planar tetraphenylporphinatocopper(II) and di-*n*-butylmethylamine. The proposed mechanism involves two paths, one of which invokes solvent as the axial ligand and a second involving the amine as the axial ligand, with fast ligand exchange allowing rapid establishment of the equilibrium between the two forms. The experimental evidence supports the conclusion that the nature of the axial ligand affects this novel facile demethylation of a pyrrolic methyl group. Plots of the observed first-order rate constant as a function of amine concentration give $k_1 = (2.16 \pm 0.05) \times 10^{-2}$ M^{-1} s^{-1}, $K_{eq} = 5.93 \pm 0.75$, and $k_2 = (3.5 \pm 1.0) \times 10^{-3}$ M^{-1} s^{-1} at 45 °C. Plots at 25, 45, and 65 °C give $\Delta H^{\ddagger} = 16.9 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -13.1 \pm 2.9$ eu for the solvent ligand path and $\Delta H^{\ddagger} = 12.8 \pm 4.1$ kcal/mol and $\Delta S^{\ddagger} = -30 \pm 12$ eu for the amine ligand path. The kinetic data for the corresponding reaction with pyridine are consistent with a single-path mechanism. For this reaction $\Delta H^{\ddagger} = 20.4$ kcal/mol and $\Delta S^{\ddagger} = -15.7 \pm 1.1$ eu.

Introduction

During a recent study of the properties of transition metal ion complexes of *N*-methyltetraphenylporphyrin, decomposition of the copper(II) complex in DMF to form tetraphenylporphinatocopper(II) was noticed.[1] Since pyrrolic nitrogen–alkyl carbon bonds are generally difficult to cleave, this reaction was unexpected. A likely cause of *N*-methyl elimination in DMF is the Cu^{2+}-promoted hydrolysis of the solvent to form dimethylamine which then attacks the electrophilic *N*-methyl group. Concomitantly, the Cu^{2+} ion may insert into the plane of the four porphyrin nitrogen atoms and the axial ligand is lost. Using amines less volatile than dimethylamine, with acetonitrile as solvent, it has been found that the reaction rates and activation parameters are quite sensitive to the nature of the nucleophile and to the axial ligand. The reaction involves a novel geometry change for the Cu^{2+} center—from the probable square-pyramidal geometry of the *N*-methylporphyrin to the square-planar geometry of the nonmethylated porphyrin product.

The reaction reported herein may resemble the demethylation of chloro-*N*-methyloctaethylporphinatozinc(II) upon reflux overnight in pyridine, as observed by Hambright.[2] Demethylation of this *N*-methyl complex was demonstrated by the identification of octaethylporphinatozinc(II) as product, but further information about this reaction has not been published.

Experimental Section

Preparation of *N*-Methyltetraphenylporphinatocopper(II) Cation ($CuNCH_3TPP^+$). Stock solutions of $[Cu(H_2O)_6](ClO_4)_2$ (G. F. Smith) and $CuCl_2 \cdot 2H_2O$ (Fisher) were prepared in dried, distilled acetonitrile[3] and analyzed by EDTA titration.[4] *N*-Methyltetraphenylporphine was prepared from tetraphenylporphine[5] and methyl fluorosulfonate (Aldrich) in $CHCl_3$, chromatographed on alumina (Alcoa, baked and 5% hydrated), and crystallized from $CHCl_3$ and 95% EtOH as described previously.[1] The stock solutions were combined volumetrically and followed to completion spectrophotometrically. Evidence concerning the nature of the complex using conductivity and Job's plots has been presented.[1] Stock solutions have been stored for several months at 5 °C without appreciable decomposition.

Product Analysis and Stoichiometry. Tetraphenylporphinatocopper(II) (CuTPP) was determined from its visible absorption spectrum.[6] The very low solubility of CuTPP in CH_3CN (about 10^{-4} M) restricted concentrations of the porphyrin complex which could be employed.

The methylated amine product, di-*n*-butylmethylamine, was identified by carrying out the reaction with a twofold excess of *n*-butylamine relative to $CuNCH_3TPP$. The product mixture was neutralized with aqueous ammonia, extracted into diethyl ether, and analyzed by GC (Carbowax 20M column). The gas chromatogram contained two equal peaks corresponding to the retention times of authentic samples of di-*n*-butylamine and di-*n*-butylmethylamine. The only other peaks were due to ether and CH_3CN.

Methylpyridinium ion was identified by allowing a 100-fold excess of pyridine to react with $CuNCH_3TPP$ until >99% completion. The porphyrin was extracted into $CHCl_3$ and the methylpyridinium ion and pyridine were extracted into water. After neutralization with aqueous ammonia, the water fraction was evaporated, the residue was dissolved in 3.0 ml of H_2O, and its ultraviolet spectrum was recorded. The spectrum matched that of authentic methylpyridinium perchlorate (prepared from methylpyridinium iodide,[7] mp 119 °C, by precipitation with $Pb(ClO_4)_2$ (G. F. Smith)) and was of the correct magnitude to show 1:1 conversion of pyridine to methylpyridinium.

The stoichiometry of the reaction is, therefore, given by

$$CuNCH_3TPP^+ + Nuc \rightarrow CuTPP + CH_3Nuc^+$$

where Nuc represents the nucleophile (either di-*n*-butylamine or pyridine).

Kinetic Measurements. Stock solutions of $CuNCH_3TPP^+$ varied in porphyrin concentration from 10^{-4} to 10^{-3} M and Cu^{2+} concentrations varied from 10^{-4} to 10^{-2} M (generally in excess to allow more rapid formation of $CuNCH_3TPP^+$). Dried, distilled di-*n*-butylamine[3] (Eastman) or Spectro Grade pyridine (Eastman) were in pseudo-first-order excess in the range of 10^2- to 10^4-fold. Reactant solutions and cuvettes were equilibrated to temperature for 0.5 h and the cuvette compartment was regulated to ±0.1 °C. Data were analyzed using the Los Alamos Non-Linear Least Squares Program,[8] with additional subroutines needed to treat the cases in the Results section of this report.

Equipment. The following equipment was used for the indicated purpose: Cary 14 spectrophotometer for visible and ultraviolet absorption spectra, Haake FK-2 for temperature regulation, Varian aerograph, Model 90-P, for GC analysis, the CDC 6400 for data analysis.

Results and Discussion

N-Methyltetraphenylporphyrin in CH_3CN with 1 M di-*n*-butylamine is unchanged after months at 25 °C. Rapid demethylation of *N*-methyltetraphenylporphinatocopper(II), however, occurs under the same conditions.

Data for the reaction of *N*-methyltetraphenylporphinatocopper(II) ($CuNCH_3TPP^+$) in CH_3CN to produce tetraphenylporphinatocopper(II) (CuTPP) and di-*n*-butylmethylamine are summarized in Table I. The following observations concerning the observed pseudo-first-order rate constant are relevant: (1) the reaction is first order in $CuNCH_3TPP^+$, giving an excellent fit (generally a variance of 0.003 OD unit/data point to 5 half-lives), (2) k_{obsd} is independent of $CuNCH_3TPP^+$ concentration under pseudo-first-order conditions (amine in excess), (3) k_{obsd} is independent of excess Cu^{2+} concentration from 10^{-5} to 10^{-2} M, (4) rates of CuTPP formation (540 nm) and $CuNCH_3TPP$ consumption (658 and 570 nm) are identical, giving a good isosbestic plot (Figure 1), (5) preparations using $[Cu(H_2O)_6](ClO_4)$ or $CuCl_2 \cdot 2H_2O$ give the same rates, (6) k_{obsd} is first order in amine at low concentration (up to about 0.01 M), and (7) the rate is *not* first order in amine at higher

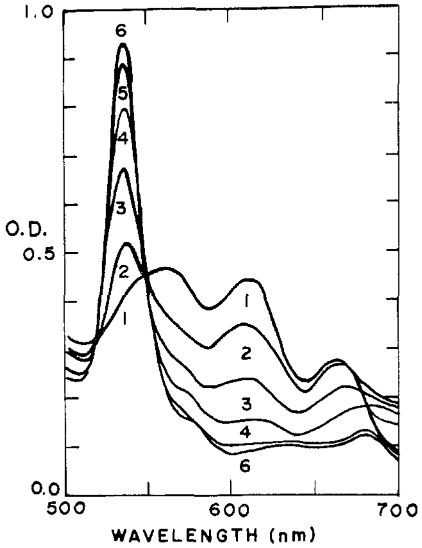

Figure 1. Spectra of the reaction $CuNCH_3TPP^+ + HN(CH_2CH_2CH_2CH_3)_2 \rightarrow CuTPP + HN(CH_3)(CH_2CH_2CH_2CH_3)_2^+$, using 0.114 M amine at 25.0 °C, at various intervals. Number of minutes after addition of di-*n*-butylamine are 0.6 (1), 15.0 (2), 45.0 (3), 90.0 (4), 165.0 (5), and 310.0 (6). Spectra were completed in 1.67 min.

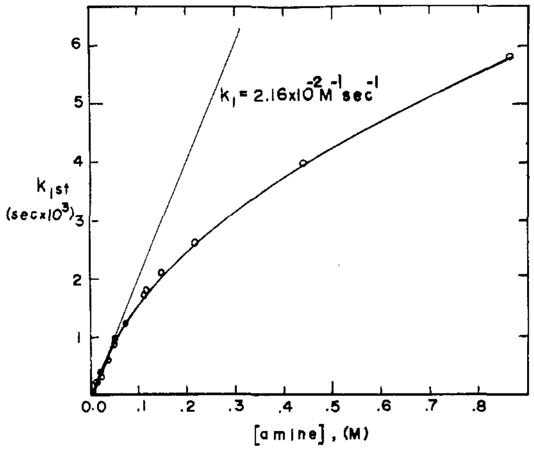

Figure 2. Plot of the observed first-order rate constant ($k_{obsd}{}^{1st}$ in text) as a function of di-*n*-butylamine concentration.

concentration but *does* approach a linear dependence (Figure 2).

In developing a reasonable mechanism consistent with the non-first-order dependence and lower k_{obsd} values at high excess reactant concentrations, a number of possible alternatives are commonly considered. The several explanations considered here include (1) an equilibrium between free Cu^{2+} and porphyrin-bound Cu^{2+} as found in DMF at these concentrations,[1] (2) saturation by amine at high concentrations, (3) the change of dielectric constant of the medium as amine concentrations become appreciable, and (4) a two-path mechanism involving axial coordination of the amine.

The preequilibrium mechanism

$$\begin{array}{l} Cu(HNR_2)_n{}^{2+} + NCH_3TPP \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CuNCH_3TPP^+ + H^+ + nHNR_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad k\downarrow +HNR_2 \\ \qquad\qquad\qquad\qquad\qquad\quad CuTPP + CH_3N(H)R_2{}^+ \end{array}$$

with

$$\frac{d[CuTPP]}{dt} = \frac{kK_{eq}[HNR_2][Cu(HNR_2)_n{}^{2+}]([NCH_3TPP]_0 - [CuTPP])}{K_{eq}[Cu(HNR_2)_n{}^{2+}]/[HNR_2]^n + 1}$$

Table I. First-Order Rate Constants for the Reaction of *N*-Methyltetraphenylporphinatocopper(II) Cation with Di-*n*-butylamine[a]

Temp, °C	[Amine], M	10^3k, sec^{-1}	Temp, °C	[Amine], M	10^3k, sec^{-1}
45	0.0073	0.088 ± 0.001	45	0.868	5.92 ± 0.20
45	0.0182	0.302 ± 0.012	45	1.30	7.24 ± 0.43
45	0.0362	0.630 ± 0.007	25	0.0385	0.112 ± 0.005
45	0.0530	0.808 ± 0.027	25	0.216	0.435 ± 0.003
45	0.0725	1.20 ± 0.020	25	0.453	0.518 ± 0.006
45	0.108	1.36 ± 0.06	25	0.895	0.983 ± 0.016
45	0.112[b]	1.64 ± 0.04	65	0.0362	3.56 ± 0.24
45	0.145	2.11 ± 0.03	65	0.112	6.63 ± 0.06
45	0.216	2.46 ± 0.07	65	0.216	8.58 ± 0.13
45	0.433	3.96 ± 0.04	65	0.441	12.41 ± 0.20
45	0.443[c]	4.05 ± 0.01			

[a] Error limits are the standard deviations of the two to six independent determinations of each rate constant. Internal variance of curve fitting for each determination was (1.0–5.0) × 10^{-3} OD unit/data point. Approximately 50% of the 45 °C determinations involved $CuCl_2 \cdot 2H_2O$, and 50% $[Cu(H_2O)_6](ClO_4)$; 25 and 65 °C determinations were with $[Cu(H_2O)_6](ClO_4)$. Typical determinations involved a (2-5)-fold excess of Cu^{2+}.
[b] Two determinations with $[CuNCH_3TPP^+] = 2.0 \times 10^{-5}$ M and two with $[CuNCH_3TPP^+] = 4.0 \times 10^{-6}$ M. Excess Cu^{2+} concentrations of (18.88, 3.76, 7.52, 15.04, and 30.08) × 10^{-5} M gave k's of (1.58, 1.65, 1.65, 1.65, and 1.64) × 10^{-3}, respectively.
[c] Two determinations with no excess Cu^{2+} and two with $[Cu^{2+}] = 0.046$ M.

could explain a decreasing first-order rate with increasing di-*n*-butylamine concentration if K_{eq} were small. However, this would also require an increasing rate with increased initial copper concentrations. If K_{eq} were large, a rate first order in amine and not decreasing as [amine] increases would be predicted. A large K_{eq} value would be indicated since there is no evidence of free porphyrin in the visible absorption spectrum even at the highest amine concentration (for which k_{obsd} is several times slower than predicted for the first-order k_{obsd} at low amine concentration).

Saturation by amine may be discounted since the onset of non-first-order dependence on amine occurs at quite low amine concentration (0.05 M).

The change of dielectric constant from 38.8 for CH_3CN as the concentration of di-*n*-butylamine (dielectric constant of about 2.5, since that of triethylamine is 2.42) is increased may be ruled out because k_{obsd} is insignificantly affected when the reaction is run at low amine concentration and benzene or dioxane (dielectric constants of 2.27 and 2.21, respectively) is used to change the dielectric constant of the medium.[9]

The following experiments illustrate this point. Reaction of 0.0535 M di-*n*-butylamine (50 µl in a total volume of 13.0 ml) with $CuNCH_3TPP$ at 45 °C results in a pseudo-first-order rate constant of (8.08 ± 0.03) × 10^{-4} s^{-1}. Addition of 750 µl of benzene with the same concentration of amine results in a rate constant of (8.11 ± 0.83) × 10^{-4} s^{-1}. The effect on the dielectric constant of the solution by the addition of 750 µl of benzene is approximately equivalent to an amine concentration of 0.86 M. The rate constant of 0.86 M di-*n*-butylamine is 5.9 × 10^{-3} s^{-1}, using Figure 2. In another experiment, 1.5 ml of dioxane was used with 0.0196 M di-*n*-butylamine at 45 °C, resulting in a pseudo-first-order rate

Scheme I

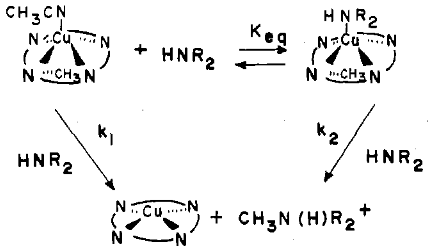

Table II. Best Fit Values for Plots of the Pseudo-First-Order Rate Constant vs. Concentration of Di-*n*-butylamine Used for Determination of Activation Parameters

Temp, °C	k_1, M^{-1} sec^{-1}	k_2, M^{-1} sec^{-1}	K_{eq}
25.0	3.4×10^{-3}	5.8×10^{-4}	8.0
45.0	2.2×10^{-2}	3.5×10^{-3}	6.0
65.0	1.2×10^{-1}	8.8×10^{-3}	3.0

constant of $(3.64 \pm 0.16) \times 10^{-4}$ s^{-1}. The rate for the reaction of 0.0182 M amine without dioxane is $(3.02 \pm 0.12) \times 10^{-4}$ s^{-1}. The concentration of amine necessary to cause a change in dielectric constant similar to addition of 1.5 ml of dioxane is 1.64 M. The rate constant for such a high amine concentration would be about 7.5×10^{-3} s^{-1}.

The most reasonable mechanism appears to be a two-path scheme involving reaction of either solvated CuNCH$_3$TPP$^+$ or HNR$_2$CuNCH$_3$TPP$^+$ with the di-*n*-butylamine to form CuTPP and di-*n*-butylmethylamine. (See Scheme I.)

Studies of the chlorocopper(II) and chlorocobalt(II) *N*-methyltetraphenylporphyrin indicated the presence of one axial ligand.[1] Analysis of data from Table I at 45 °C according to the rate equation derived for the two-path mechanism

$$\frac{\mathrm{d}[\mathrm{CuTPP}]}{\mathrm{d}t} = \left(\frac{k_1 + k_2K_{\mathrm{eq}}[\mathrm{HNR_2}]}{1 + K_{\mathrm{eq}}[\mathrm{HNR_2}]}\right)[\mathrm{HNR_2}][\mathrm{CuNCH_3TPP^+}]$$

was performed by fitting the curve shown in Figure 2. The solid curve in Figure 2 results from values of k_1 of 2.15×10^{-2} M^{-1} s^{-1}, $K_{eq} = 5.93$, and $k_2 = 3.5 \times 10^{-3}$ M^{-1} s^{-1}. Reasonable fits are obtained with uncertainties of $k_1 = (2.6 \pm 0.10) \times 10^{-2}$ M^{-1} s^{-1}, $K_{eq} = 5.93 \pm 0.75$, and $k_2 = 3.5 \pm 1.9$ M^{-1} s^{-1}. Since the concentration of neat CH$_3$CN is 19.2 M, this indicates a perference of Cu^{2+} for di-*n*-butylamine of 10^2, which appears reasonable. If the reaction is concerted, with axial ligand dissociation as well as nucleophilic attack by the amine affecting the activated complex, the path involving a better axial ligand should be slower, as found. The value of k_2 is prone to large uncertainty since it is always associated with K_{eq} in fitting the observed rate, but it is significantly smaller than k_1. Unfortunately, K_{eq} cannot be evaluated independently from kinetic data since the presence of the amine which is involved in the equilibrium necessarily results in the demethylation reaction.

The Eyring activation parameters, derived from curves similar to those of Figure 2 (see Table II) at 25, 45, and 65 °C are $\Delta H^{\ddagger} = 16.9 \pm 1.0$ kcal/mol and $\Delta S^{\ddagger} = -13.1 \pm 2.9$ eu for path 1 and $\Delta H^{\ddagger} = 12.8 \pm 4.1$ kcal/mol and $\Delta S^{\ddagger} = -30 \pm 12$ eu for di-*n*-butylamine as axial ligand (path 2). The much greater magnitude of $\Delta S^{\ddagger}$ in path 2 relative to that in path 1 may indicate a greater steric requirement in the activated complex. The apparent difference in $\Delta H^{\ddagger}$ between path 1 and path 2 of 4 kcal/mol is approximately equal to the ΔH found from the equilibrium data in Table II (5 kcal/mol). This similarity may reflect a correlation between the stability of the porphinatocopper(II) complex and the activation energy for metal insertion. A simple interpretation of these results would be that the energy of the activated complex is insensitive to the identity of the ligand, indicating a large degree of dissociation of the axial ligand in the activated complex.

Table III. Rate Constants for the Reaction of *N*-Methyltetraphenylporphinatocopper(II) Cation with Pyridine

Temp, °C	[py], M	10^5k, M^{-1} sec^{-1}	Temp, °C	[py], M	10^5k, M^{-1} sec^{-1}
45.0	2.43	2.43 ± 0.10	55.0	2.38	6.73 ± 0.13
55.0	0.453	6.48 ± 0.45	65.0	2.36	17.5 ± 0.4
55.0	0.981	6.38 ± 0.37			

Thus, the reaction of CuNCH$_3$TPP$^+$ and di-*n*-butylamine in CH$_3$CN apparently involves concerted dissociation of the axial ligand (CH$_3$CN or amine), attack of the amine to cleave the –CH$_3^+$ group, and insertion of the Cu^{2+} into the plane of the four porphyrin nitrogen atoms. The CuTPP product is planar,[10] and axial ligand association is expected to be insignificant. The change in coordination geometry about the Cu^{2+} center is assumed to be from distorted square-based pyramidal, with three essentially equivalent sp^2 n atoms, one sp^3 n atom (also bound to –CH$_3$), and the axial ligand, to the square geometry of CuTPP. The coordination of copper to all four of the porphyrin nitrogen atoms is supported by the crystallographically determined structure of a closely related copper corrole compound.[11]

Use of diethylamine in place of di-*n*-butylamine gave very similar results. For [di-*n*-butylamine] = 0.0725 M, $k_{\mathrm{obsd}}{}^{1\mathrm{st}}$ (at 45 °C) = $(1.20 \pm 0.02) \times 10^{-3}$ s^{-1}, and for [diethylamine] = 0.0727 M, $k_{\mathrm{obsd}}{}^{1\mathrm{st}} = (8.31 \pm 0.08) \times 10^{-4}$ s^{-1}. Also at 45 °C, when [di-*n*-butylamine] = 0.433 M, $k_{\mathrm{obsd}}{}^{1\mathrm{st}} = (3.96 \pm 0.04) \times 10^{-3}$ s^{-1}, and for [diethylamine] = 0.436 M, $k_{\mathrm{obsd}}{}^{1\mathrm{st}} = (3.42 \pm 0.01) \times 10^{-3}$ s^{-1}. Extrapolation of the di-*n*-butylamine rates to predict the concentration of dimethylamine in the DMF stock solutions which decomposed, allowing formation of CuTPP from CuNCH$_3$TPP$^+$, gives a concentration range of approximately 6.0×10^{-4} to 4.3×10^{-3} M or 0.003–0.022 wt %. Obviously, CuNCH$_3$TPP$^+$ conversion to CuTPP is sensitive to concentration of dialkylamines. The observed rate constant range for the DMF stock solutions at 65 °C is $(0.77–5.2) \times 10^{-4}$ s^{-1}. A $k_{\mathrm{obsd}}{}^{1\mathrm{st}}$ value at 65 °C of 0.2 s^{-1} from the di-*n*-butylamine data was employed in the estimation.

It was of interest to see if a nucleophile which coordinates more poorly with Cu^{2+} than dialkylamines would follow a simple, one-step mechanism. In such a situation, some axial ligation could not be ruled out but could at least be shown to be unimportant in determining the rate of –CH$_3$ cleavage and Cu^{2+} insertion. For this purpose, pyridine was also studied. The slowness of this reaction and necessity of avoiding evaporation loss at elevated temperatures limited the concentration range studied, but the data in Table III are certainly consistent with a simpler mechanism than in the case of the dialkylamines. Eyring activation parameters for the pyridine–CuNCH$_3$TPP$^+$ reactions are $\Delta H^{\ddagger} = 20.4 \pm 0.4$ kcal/mol and $\Delta S^{\ddagger} = -15.7 \pm 1.1$ eu, indicating that the poorer nucleophilicity of pyridine in this reaction is principally evident in an increased activation enthalpy.

Conclusion

The *N*-methyltetraphenylporphyrin complex of Cu^{2+} is susceptible to nucleophilic attack, allowing facile cleavage of a pyrollic nitrogen–methyl carbon bond. The metal ion greatly assists this process since no demethylation of the free porphyrin is evident under similar conditions (concentration of nucleophile, solvent, temperature, etc.) over much longer time scales (months as compared to minutes). The dissociation of the axial ligand appears to be important in the activated complex since good axial ligands, dialkylamines, cause the first-order observed rate constant to decrease at high nucleophile concentrations. Nucleophilic attack is evidently important in the activated complex from the marked dependence of the observed rate on nucleophile concentration. With good axial ligands such as dialkylamines, the mechanism is a competitive two-path process involving concerted loss of axial ligand, nucleophilic attack at the $-CH_3$ group, and assistance by metal ion insertion. At least in the activated complex, then, the metal ion is withdrawing electron density from the $N-CH_3$ bond and the bonding would include metal ion–nitrogen atom coordination.

Poor axial ligands need not involve a second path in which the nucleophile acts as axial ligand as well as nucleophilic reactant. This is apparently the case when pyridine is employed. Cu^{2+} is apparently a better methyl cleavage promoter in *N*-methylporphyrin than Zn^{2+}, since the cleavage using Zn^{2+} in neat pyridine (12.5 M) requires overnight reflux.[2]

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Registry No. $CuNCH_3TPP^+$, 57606-45-8; di-*n*-butylamine, 111-92-2; diethylamine, 109-89-7; pyridine, 110-86-1.

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Reactions of Copper Complexes. I. Reduction of (2,9-Dimethyl-1,10-phenanthroline)copper(II) Complexes by Thiocyanate and Thiourea in Aqueous Perchlorate Media and by Thiourea in Methanol

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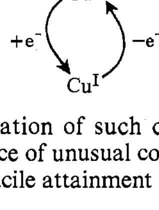
The stoichiometry and kinetics of reduction of dmp–Cu^{II} complexes (dmp = 2,9-dimethyl-1,10-phenanthroline) by SCN^- and thiourea in borate-buffered 0.1 M aqueous sodium perchlorate and by thiourea in methanol at 25.0 °C are reported. The major copper(I) product in all systems was shown to be $Cu(dmp)_2^+$; the measured stoichiometry was consistent with the formation of thiocyanogen and formamidine disulfide, respectively, although these products could not be satisfactorily isolated and characterized. The kinetics of the reactions were followed in a stopped-flow apparatus by monitoring the appearance of $Cu(dmp)_2^+$ in the wavelength range 315–600 nm. All reactions were first order in $[Cu^{II}]$ over the range $(0.5–5.0) \times 10^{-5}$ M and were not affected by variations of the monitoring wavelength, buffer concentration, or the presence of oxygen. The rate law for the reaction with excess SCN^- over the concentration ranges $[dmp]_T = (5.4–18.1) \times 10^{-5}$ M, $[SCN^-] = (1.0–11.3) \times 10^{-2}$ M, and $[H^+] = (0.68–94) \times 10^{-8}$ M is given by $d \ln [Cu^I]/dt = [SCN^-]/(B[H^+] + C)$, where $B = (1.02 \pm 0.02) \times 10^5$ s and $C = (1.40 \pm 0.03) \times 10^{-2}$ M s at 25.0 °C. Three mechanisms are consistent with the data. The first two involve the steady-state intermediacy of $Cu(dmp)_2OHSCN$, which decomposes either to reactants or to primary redox products, while the third mechanism involves the rate-determining reaction of $Cu(dmp)SCNOH$ with SCN^-. This third mechanism is analogous to that proposed for reduction by thiourea in buffered 0.1 M sodium perchlorate, the rate law for which is given by $d \ln [Cu^I]/dt = D[tu]_T^2/(E[dmp][H^+] + F[tu]_T[H^+] + [tu]_T)$, where $D = 74.5 \pm 4.4$ M^{-1} s^{-1}, $E = (2.86 \pm 0.29) \times 10^8$ M^{-1}, and $F = (2.91 \pm 0.29) \times 10^7$ M^{-1} at 25.0 °C over a similar range of concentration conditions. The rate law for reduction by thiourea in methanol is given by $d \ln [Cu^I]/dt = G[dmp][tu]/([dmp] + H[tu] + J[tu]^2)$, where $G = (5.2 \pm 0.6) \times 10^3$ M^{-1} s^{-1}, $H = (6 \pm 2) \times 10^{-2}$, and $J = 1.9 \pm 0.2$ M^{-1} at 25.0 °C. This rate law is consistent with a mechanism involving rate-determining reaction between $Cu(dmp)_2^{2+}$ and tu, with the complexes $Cu(dmp)tu^{2+}$ and $Cu(dmp)(tu)_2^{2+}$ oxidatively stable. It is tentatively concluded that the fastest reactions of the dmp–Cu^{II} system are those which involve the production of $Cu(dmp)_2^+$ as a primary product.

Introduction

Current interest in the reactions of copper complexes reflects the importance of the catalytic properties of copper species in many chemical[2,3] and biochemical[4,5] processes. Many of these processes involve one-electron redox cycles of the kind



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The widespread operation of such catalytic cycles is often ascribed to the existence of unusual coordination environments of the metal or their facile attainment in the catalytic mileu.[3-6]

The mechanistic study of such processes is inevitably complicated by their cyclical nature.[3] An approach to this problem is to cut the catalytic cycle by employing ligand systems which effectively deactivate one of the copper oxidation states. One such system involves the ligand 2,9-dimethyl-1,10-phenanthroline (dmp), which forms the thermodynamically stable[7] and brightly colored[8] $Cu(dmp)_2^+$ moiety. Among the effects of this preferential stabilization is an increase in the reduction potential of the Cu^{II}–Cu^I couple.[2]

In this paper we report on the kinetics and mechanisms of the reduction of dmp–Cu^{II} complexes by thiocyanate and thiourea in aqueous sodium perchlorate at ionic strength 0.1 M. These studies were prompted by implications of the involvement of sulfur-containing ligands in biochemical redox