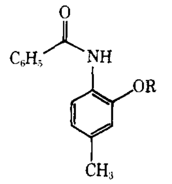
(17) L. Horner and H. Steppan, *Justus Liebigs Ann. Chem.*, **606**, 24 (1957).
(18) (a) B. Robinson, *Chem. Rev.*, **69**, 227 (1969); (b) R. J. Sundberg, "The Chemistry of Indoles", Academic Press, New York, N.Y., 1970; (c) R. K. Brown, *Chem. Heterocycl. Compd.*, **25**, 227 (1972).
(19) For a recent review on the photochemistry of aromatic *N*-oxides see F. Bellamy and J. Streith, *Heterocycles*, **4**, 1391 (1976).
(20) D. S. Breslow, E. Baumgarten, and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1286 (1944).
(21) **7a**, mp 64–65 °C (lit.[22] mp 66 °C); **7b**, mp 80–82 °C, (lit.[22] 82 °C).
(22) P. W. Neber, *Chem. Ber.*, **55**, 826 (1922).
(23) In the absence of pyridine the reaction times are considerably longer (6–24 h) and the yields of rearranged esters are generally lower (33–55%). In the case of malonate **6d**, the major products from the uncatalyzed reaction are i and ii which arise via 1,3 oxygen migration.[17]



i ($R = COCH_2CO_2Et$, 50%)
ii (R = H, 35%)

(24) J. Ficini and C. Barbara, *Tetrahedron Lett.*, 6425 (1966).
(25) Fellowship from The National University of Malaysia, Kuala Lumpur, Malaysia; 1972–1976.

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The Copper-Cadmium *N*-Methyltetraphenylporphyrin Electrophilic Substitution Reaction: Evidence for a Cis Attack

Sir:

The kinetics of the substitution of one metal ion in solution for another coordinated to a porphyrin molecule usually follow a rate law first order in replacing ion and first order in metalloporphyrin, with no evidence for rate retardation by the departing ion.[1] One common interpretation is that the activated complex has the form [M-P-M*], with the entering and leaving metal ions on opposite sides of the porphyrin plane. Such activated complex geometries in solutions are also suggested by solid state crystal structures of several dimetallic mononuclear porphyrins.[2] We report a kinetic study of copper replacing cadmium from the Cd(II) *N*-methyltetraphenylporphin ($Cd\text{-}N\text{-}MeTPP^+$) complex. The *N*-methyl group prohibits the copper from occupying a position on the distal side of the porphyrin plane from the cadmium ion.[3]

The kinetics were run at 25 °C in DMF at an ionic strength of 0.36 using $(Et)_4NBF_4$. Using the mole ratio method, cadmium forms only a 1:1 complex with the *N*-methylporphyrin,[4] even at concentrations of cadmium/porphyrin of 30:1. The $Cu(BF_4)_2/Cd\text{-}N\text{-}MeTPP^+$ reaction, followed spectrophotometrically, went clearly to $Cu\text{-}N\text{-}MeTPP^+$. Isosbestic points were found at 597, 575, and 435 nm, and no evidence for the demethylation[5] of $Cu\text{-}N\text{-}MeTPP^+$ into Cu-TPP was observed during the course of the reaction. Under pseudo-first-order conditions with at least a 20-fold excess of copper to porphyrin, the reaction was first order in porphyrin. As shown in Figure 1, the reaction was also first order in copper, and independent of added cadmium. The second-order rate constant was 25.7 ± 2.2 $M^{-1}\ min^{-1}$.

The lack of rate inhibition by added cadmium tends to rule out a mechanism whereby cadmium first dissociates before copper incorporation. Since the *N*-methyl group sterically blocks one face of the porphyrin toward metal ion coordination, the simplest interpretation is that cadmium and copper are on the same side of the porphyrin plane during the substitution process.

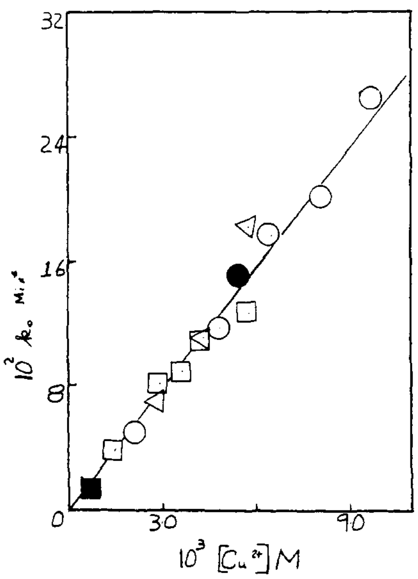
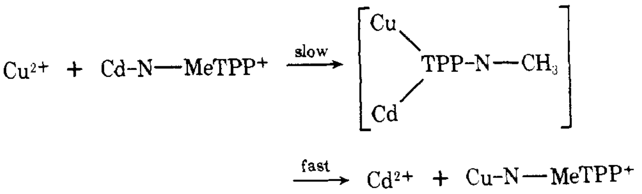


Figure 1. Plot of the observed rate constant k_{obsd} vs. $(Cu^{2+})_0$ for the $Cu^{2+}/Cd\text{-}N\text{-}MeTPP^+$ reaction at 25 °C in DMF at an ionic strength of 0.36 $[(Et)_4BF_4]$. The $Cd(BF_4)_2$ concentrations are: ■ = 7.2×10^{-4} M, ○ = 14.8×10^{-4} M, □ = 35.1×10^{-4} M, ● = 50×10^{-4} M, △ = 1.76×10^{-2} M.



The observations on *N*-methylporphyrins imply that either or both cis and trans geometries may occur during electrophilic substitution reactions of metaloporphyrins themselves.

Preliminary work indicates that, consistent with their basicities, the Cu/Cd-TPP reaction is orders of magnitude faster than that of $Cu/Cd\text{-}N\text{-}MeTPP^+$. In addition, the former reaction is also faster than the $Cu/H_2\text{-}TPP$ process, where N-H bond breaking may be the rate limiting step.

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References and Notes

(1) (a) C. Grant and P. Hambright, *J. Am. Chem. Soc.*, **91**, 4195 (1969); (b) S. Cheung, L. Dixon, F. Fleischer, D. Yeter, and M. Krishnamurthy, *Bioinorg. Chem.*, **2**, 281 (1973); (c) H. Baker, P. Hambright, and L. Ross, *Inorg. Chem.*, **12**, 2200 (1973).
(2) M. Tsutsui and G. Taylor in "Porphyrins and Metalloporphyrins", K. M. Smith, Ed., Elsevier, Amsterdam, 1975, Chapter 7, and references therein.
(3) Molecular steric models (see D. Lavallee and A. Gebala, *Inorg. Chem.*, **13**, 2004 (1974)) indicate that the *N*-methyl side of the porphyrin plane cannot coordinate metal ions. Crystal structures of two chlorocobalt(II)*N*-alkylporphyrins (O. P. Anderson and D. K. Lavallee, *J. Am. Chem. Soc.*, **98**, 4670 (1976), and D. E. Goldberg and K. M. Thomas, *ibid.*, **98**, 913 (1976)) show the metal to be on the opposite face of the porphyrin from the alkyl group. In addition, while tetraphenylporphyrin forms dimetallic mononuclear adducts with mercury(II), only monometallic mononuclear species are obtained with the corresponding *N*-methylporphyrin (H. F. Hudson and K. M. Smith, *Tetrahedron*, **32**, 597 (1976)).
(4) The molar extinction coefficients of $Cd\text{-}N\text{-}MeTPP^+$ under the reaction conditions are 1.24×10^4 at 615 nm, 8.93×10^3 at 650 nm, and 7.26×10^3 at 570 nm.
(5) C. Stinson and P. Hambright, *Inorg. Chem.*, **15**, 3181 (1976).

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