Kinetics of Copper(II) Incorporation in a Porphyrin Using Four Copper Salts

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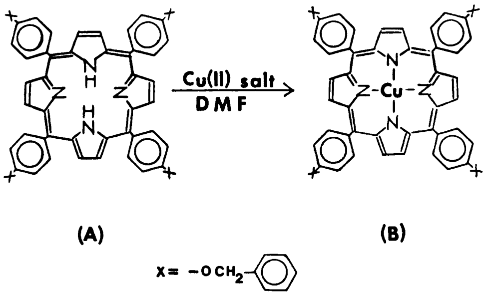
Synopsis. Using excess of acetate, chloride, bromide, and sulfate salts, the kinetics of Cu(II) incorporation in *meso*-tetrakis (4-benzyloxyphenyl) porphyrin, in DMF solution, at different temperatures, have been done. The thermodynamic parameters have been calculated and a mechanism of Cu(II) insertion proposed.

The kinetics of copper(II) incorporation in porphyrins has been reported with nitrate,[1–3] perchlorate,[4,5] acetate,[6,7] sulfate,[8] and chloride[9] salts. Glacial acetic acid,[4,7] aqueous nitric acid,[1–3] acetic acid–water,[4] acetic acid–ethanol,[9] ethanol,[6] and 2.5% dodecyl sulfate[8] were some of the solvents used. No publication has yet appeared showing the effect of different anions attached to the copper(II) on the rate of metallation in a porphyrin under same conditions. We are reporting the kinetic data and a mechanism of copper(II) insertion in *meso*-tetrakis(4-benzyloxyphenyl)porphyrin (A) in DMF solution using the chloride, bromide, sulfate and acetate salts.



Starting with freshly distilled pyrrole and 4-(benzyloxy)benzaldehyde (Aldrich Chemical Company) and following the published procedure,[10] the porphyrin A, was prepared. Analytical sample of A was made by chromatography over silica gel with dichloromethane elution. A pure sample of the copper complex, B, was also made by the literature method.[11] Both A and B gave accurate elemental analysis.[12] Analytical grade copper salts and spectroscopic grade DMF (dried over Molecular Sieve 4A) were used.

The reaction rates were followed in 1.00 cm thermostatted cells (maintained to ±0.1 or better by a Neslab RTE-3 constant temperature circulator) and monitored with a Beckman Model 25 spectrophotometer. A typical kinetic study consisted of measuring the absorbances at 518 and 642 nm[13] over a period of time of a mixture of equal volume of 2.188×10^{-3} mol/dm^3 copper salt and 5.17×10^{-5} mol/dm^3 A at a pre-equilibrated temperature against 1.094×10^{-3} mol/dm^3 copper salt blank.[14] Standard procedure was used to calculate the concentrations of A and B.[15] In DMF solution the rate of copper(II) incorporation is known to be first order with respect to porphyrin as well as metal ion concentration.[9] Since the copper (II) ion concentration has been kept much higher, pseudo-first-order rate constants were obtained from the data of this study. A plot of time (minutes *vs.* ln C_0/C_t, where C_0 and C_t are molar concentrations of A at zero and t minutes respectively, yielded a straight line from which the first-order-rate constants (k) were calculated. (See Table 1)

Activation energy, E_a, was obtained from the slope of a plot $1/T$ (K^{-1}) *versus* log k. Thermodynamic parameters ΔG^*, ΔH^*, and ΔS^* were calculated using standard equations.[16] (see Table 2).

The relative rates of Cu(II) incorporation are found to be sulfate > bromide > chloride > acetate. The activation energy, E_a, and enthalpy of activation, ΔH^*, are highest with acetate and lowest with sulfate; the reverse relationship is observed with free energy of activation, ΔG^*. The entropy of activation decreases in the order, acetate > chloride > bromide sulfate. These data can be rationalized with an assumption that the Cu(II) insertion in DMF proceeds in two steps as follows:

$$\text{Step 1:}\quad \text{4BzO-TPP-H}_2 + \text{Cu(II)} \xrightarrow{k_1} \text{4-B}_2\text{O-TPP-H}_2\cdot\text{Cu(II)(C)}^{17)}$$

$$\text{Step 2:}\quad \text{4BzO-TPP-H}_2\cdot\text{Cu}^{+2} \xrightarrow{k_2} \text{4BzO-TPP-Cu} + 2\text{H}^+$$

The first step is slow formation of an unstable complex C[17] and the second step rapidly forms the product B. The rate K_1 of the slower first step is dependent upon the nature of the anion attached to the Cu(II) or the nature of anion controls the availability of Cu(II). In the solid state copper(II) sulfate pentahydrate has four water molecules and an oxygen atom from each of two sulfate anions octahedrally arranged about the Cu(II) cation.[18] In DMF solution the water ligands may be easily removed, making the Cu(II) easily available to form C. Compared to copper(II) sulfate, the chloride and the bromide have polymeric chain structures formed by planar CuX_4 groups sharing opposite edges. The distances between the chlorine atoms in the chloride are shorter than the bromine atoms in the bromide.[19] It has been postulated that in DMF solution copper(II) chloride is present as

Table 1. Thermodynamic parameters for copper porphyrin formation with different copper salts

	$CuSO_4\cdot5H_2O$	$CuBr_2$	$CuCl_2\cdot2H_2O$	$Cu(OAc)_2$
ΔG^*/kJ mol^{-1}	82.09	82.89	85.35	86.78
ΔH^*/kJ mol^{-1}	56.48	63.14	65.94	81.17
ΔS^*/J mol^{-1} K^{-1}	−87.53	−69.41	−64.06	−18.12
E_a/J	58,915	65,639	68,450	83,730

Table 2. Rate constants for copper porphyrin formation with different copper salts

Copper salt	Temp/°C	k/min^{-1}
$CuSO_4\cdot 5H_2O$	9	0.0054
	16	0.0102
	23	0.0177
	30	0.0318
$CuBr_2$	23	0.0106
	30	0.0199
	37	0.0352
$CuCl_2\cdot 2H_2O$	23	0.0065
	30	0.0125
	37	0.0226
$Cu(OAc)_2$	30	0.0076
	37	0.0146
	45	0.0363

[$CuCl^+.CuCl_3^-$[9]]. If this is accepted, it is reasonable to think that copper(II) bromide in DMF solution should be present as $CuBr^+\cdot CuBr_3^-$. The bromide species will be expected to form the complex C somewhat faster than the chloride species, because in the former the halogens are further apart from each other. Copper (II) acetate in the solid state has a dimeric structure which is expected to remain unchanged in DMF solution.[20] Therefore the Cu(II) from the dimeric acetate will be least favored, compared to sulfate, chloride and bromide, to form the complex C. The thermodynamic data (See Table 2) also suggest that the total gain in entropy due to solvation and subsequent distortion of the ordered structure of the copper salts is more than offset by the loss of entropy due to the formation of the complex C. This is most pronounced with the sulfate and least with acetate. The energy necessary to distort the geometry of the copper salts is greater than the energy released due to the formation of complex C. The difference between these two energies, *i.e.* ΔH^*, is maximum with acetate, and minimum with sulfate (see Table 2).

Two additional experiments have been performed to support the two-step mechanism proposed. The first experiment was to compare the Cu(II) incorporation in TPP–H_2[21] and TPP–D_2[21] in dry DMF solution using anhydrous copper(II) chloride at 23, 30, and 37 °C. The rates observed at these temperatures for both the compounds were identical,[22] supporting that the step 2 is not the rate limiting step.

The second experiment was to measure the Cu^{63}(II)[23] and Cu^{65}(II)[23] insertion in TPP–H_2 at 23, 30, and 37 °C in DMF. The ratio of the rate of Cu^{63}(II) to Cu^{65}(II) insertion found were 1.085(at 23 °C), 1.116 (at 30 °C), and 1.132(at 37 °C). This significant isotope effect supports the step 1 to be the rate limiting step. Our findings and conclusions are further supported by a recent report[24] on the kinetics of copper (II) incorporation into a series "picketfence" type porphyrins, dissolved in a mixture of toluene, 2-propanol, and water. It has been shown that (1) the slow step apparently involves an outersphere association (similar to our complex C) between a reactive intermediate of Cu(II) ion and the porphyrin followed by rapid metal incorporation and (2) the nature of reactive metal intermediate is responsible for the rapid metal incorporation.

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12) Anal. Calcd for $C_{72}H_{54}O_4N_4$ (A): C, 83.24; H, 5.20; N, 5.39%. Found: C, 83.36; H, 5.33; N, 5.26%. Calcd for $C_{72}H_{52}O_4N_4Cu$ (B): C, 78.58; H, 4.73; N, 5.09%; Found: C, 78.64; H, 4.95; N, 5.07%.

13) Spectra in DMF, λ_{nm} ($\varepsilon \times 10^3$) for A: 421(470), 518 (14.3), 520(17.4), 542(5.5), 558(13.5), 600(5.1), 659(7.2). For B: 420(444), 518(4.2), 542(18.7), 584(4.4).

14) The copper salts in DMF solution have negligible absorbances at 518 and 542 nm.

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17) The complex, 4BzO-TPP-$H_2\cdot$Cu(II), is like a "sitting-atop complex" (see "Porphyrins and Metalloporphyrins", First ed., ed by K. M. Smith, Elsevier, Amsterdam (1976), p. 248). It cannot be identified spectrally, perhaps because of its transient nature and its rapid conversion to the stable complex B.

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21) TPP–H_2 is an abbreviation of *meso*-tetraphenylporphyrin. TPP–D_2 is TPP–H_2 in which the two protons on two nitrogens have been exchanged with deuterium. A pure sample of zinc complex of TPP–H_2 was reacted with CF_3COOD and the precipitate obtained was washed with D_2O. The product, TPP–D_2 dried over P_2O_5 at 100 °C showed no trace of N–H stretch near 300 cm^{-1}.

22) The rate constants are 0.0022 min^{-1} (at 23 °C), 0.0047 min^{-1} (at 30 °C), and 0.0091 (at 37 °C).

23) Cu^{63}Cl$_2\cdot 2H_2O$ (99.89% Cu^{63}) and Cu^{65}Cl$_2\cdot 2H_2O$ (99.69% Cu^{65}) were purchased from ICN Chemical and Radioisotope Division, Irvine, California.

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