Metal Ion Assisted Formation of Metalloporphyrins

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The formation of metalloporphyrins is believed to be extremely slow. A small amount of mercury(II) was found to accelerate the complex formation of manganese(II) with α, β, γ, δ-tetraphenylporphinesulfonate (TPPS). Cadmium(II), lead(II) and zinc(II) also accelerate the formation of Mn–TPPS as mercury(II) does. As evident from Fig. 1 the rate decreases in the following order of metal ions acting as catalysts: Hg > Cd > Pb > Zn. In the complex formation of TPPS catalyzed by a metal ion, the ionic radius of the metal ion appears to be an important factor. The metal ion acting as a catalyst would make favorable the configuration of porphine nucleus for the subsequent attack by incoming metal ion from the back.

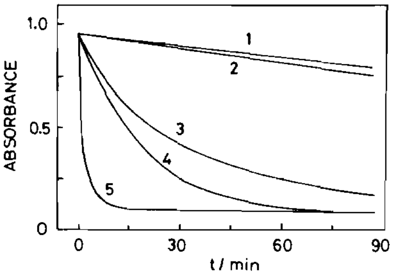

Fig. 1. Catalytic effect of some metal ions (M) on the manganese complexation: $C_M = 4 \times 10^{-7}$ mol dm^{-3}; (1) in the absence of M, (2) Zn, (3) Pb, (4) Cd, (5) Hg; $C_{TPPS} = 1.8 \times 10^{-6}$ mol dm^{-3}; $C_{Mn} = 1.1 \times 10^{-4}$ mol dm^{-3}; pH = 6.9.

The rate law for the Mn–TPPS formation in the presence of mercury(II) is given by

$$d[\text{Mn–TPPS}]/dt = k_0 C_{Hg} C_{Mn} C_{TPPS}$$

where C_X denotes the concentration of X. This rate law defines an activated complex of the composition [Hg–TPPS–Mn].

Mercury(II) also accelerates the complex formation of TPPS with cobalt(II), copper(II) and nickel(II). The same mechanism should apply to these cases.

Effects of Solvents on Glycine, N-Acetyl- and N-Benzoyl-Glycine Coordination Ability toward Zn(II) and Cd(II) Ions

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It is known that cadmium has a chemical behavior very similar to that of zinc, and so the normal process of zinc metabolism can be blocked and distorted by cadmium. There are a number of zinc-dependent enzymes that could be susceptible in *vivo* to cadmium interference.

In this work we have compared the coordination properties of glycine, N-acetyl- and N-benzoyl-glycine toward Zn(II) and Cd(II) ions in aqueous and ethanolic solutions by means of polarographic measurements, to determine the number, type and stability constants of solution complexes.

In aqueous solution only the glycine reacts with the metal ions forming three complexes [ML^+, ML_2, ML_3^- (M = Zn, Cd)] in the 7–9 pH range. The stability constants of Zn(II) complexes are greater than those of the corresponding Cd(II) complexes, according to Irving–Williams sequence [1]. The different coordination ability of the glycine with respect to the other amino acids may be attributed to the fact that the glycine, coordinating through the amino and carboxylate groups, forms stable five-membered chelate rings.

N-acetyl- and N-benzoyl-glycine form four complexes [ML^+, ML_2, ML_3^-, ML_4^{--} (M = Zn, Cd)] in ethanolic solution. The stability constants of Zn(II) complexes are greater than those of Cd(II) complexes.

In ethanolic solution a stability of Zn(II) glycine complexes greater than that of Cd(II) glycine complexes is also found. In fact four complexes exist for Cd(II) also in presence of glycine excess, while Zn(II) forms only two complexes (ZnL^+, ZnL_2), since with a metal glycine ratio greater than 1:2 a solid compound precipitated.

A linear correlation obtained by plotting $E_{1/2}$ and $\ln\beta_4$ (the stability constant of the ML_4^{--} complex) versus σ_p (the substituent constants on the amino group) suggests that, in ethanolic solution, in the metal coordination all the amino acids studied involve the same coordination sites.