A General Mechanism for Metal Ion Incorporation into Porphyrin Molecules

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Summary The mechanism of incorporation of metal ions into porphyrins involves two species, one, a metal ion, proton, or *N*-alkyl group used to deform the porphyrin while a second metal ion enters from the opposite side to form the metalloporphyrin.

A NUMBER of recent studies has dealt with the question of how a metal ion is inserted into a porphyrin molecule. The variety of rate laws obtained have tended to indicate that no one mechanism is applicable to all porphyrin types.[1] We present evidence for a general deformation mechanism which rationalizes both metal ion incorproation reactions, as well as acid catalysed solvolysis and metal ion exchange reactions in porphyrin systems.

The ideas arose from the study of the kinetics of insertion of zinc chloride into mesoporphyrin dimethyl ester at 55° in pyridine containing 11% water. In the absence of added chloride in the form of NaCl or $Et_4N^+Cl^-$, the rate was first order in porphyrin, independent of initial porphyrin concentration (PH_2) over a seven fold range, and *one-half* order in added zinc over a sixteen fold range. The rate was unaffected by $Et_4N^+ClO_4^-$, but with the chloride salt, the rate law shown in equation (1) was obtained.

$$\text{Rate} = \frac{[PH_2][Zn]}{(981 \pm 45)[Cl] + (93{\cdot}9 \pm 4{\cdot}2)[Zn]^{1/2}} \quad (1)$$

Assuming that the zinc is in a tightly bound ion pair form, the mechanism shown in the Scheme can be written.

$$[ZnCl_3(py)]^-[Zn(py)_3Cl]^+ \overset{Q}{\rightleftharpoons} [ZnCl_3(py)]^- + [Zn(py)_3Cl]^+$$

$$[Zn(py)_3Cl]^+ + PH_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Zn(py)_2Cl \cdots PH_2]^+ + (py)$$

$$[Zn(py)_2Cl \cdots PH_2]^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Zn(py)_2 \cdots PH_2]^{2+} + Cl^-$$

$$[Zn(py)_2 \cdots PH_2]^{2+} + [Zn(py)_3Cl]^+ \rightarrow \text{Products}$$

SCHEME

With the steady state treatment, the mechanism predicts that the rate [see equation (2)] is of the same form as that observed.

$$\text{Rate} = \frac{2^{-1}k_1k_2k_3\text{Q}[\text{PH}_2][\text{Zn}]_t}{2^{1/2}\text{Q}^{1/2}(k_{-1}k_3[\text{py}] + k_2k_3)[\text{Zn}]_t^{1/2} + (k_{-1}k_{-2}[\text{py}])[\text{Cl}]_a} \quad (2)$$

The metal ion reacts with the porphyrin by means of a central imino type lone pair occupying a vacant co-ordination position on the metal. (The predissociation of ligands from copper[2] and zinc[3] species in other systems has the same function). A chloride dissociates from the zinc vacating a second position which is filled by the other imino lone pair, making the metal ion two-co-ordinate with respect to the porphyrin. (This species has some stability due to the chelate effect, and has been postulated in acid catalysed solvolysis reactions.[4]). During this time the porphyrin nucleus has deformed, such that the two opposite pyrrole planes are directed upwards to maximize co-ordination with the zinc, whereas the other two pyrroles with the N–H protons point downwards, making the protons more acidic.[5]

A second zinc species approaches the N–H side, and its co-ordinated ligands facilitate N–H dissociation while it incorporates to form the metalloporphyrin. This mechanism explains sitting-atop complexes in aqueous solutions,[6] 1:1 complexes between porphyrins, and cations having spectra similar to monocations, as being the deformed species postulated above. It was previously shown[7] that the sitting-atop metal ion is not the one that forms the metalloporphyrin, in studies showing first order behaviour in lithium and zinc ions. Thus the lithium deforms the porphyrin so that zinc can incorporate from the opposite side.

Most systems show simple first order rate laws in metal ions and porphyrins.[2] This means that the process observed is due to the metal ion deformation, while the second metal ion inserts much more rapidly after the rate determining step. As a proof of this, the kinetics of zinc insertion into etioporphyrin and *N*-methyletioporphyrin showed first order rate laws, with the *N*-methyl reactions 10^5 times faster than etioporphyrin.[8] This could not be explained by statistical or basicity factors. For etioporphyrin the slow step is the deformation. For *N*-methyletioporphyrin, the deformation is accomplished by the bulky *N*-methyl group, and what is observed is the incorporation step, at a rate about 10^4 faster than the deformation. In a similar fashion ions with presumably intact co-ordination shells,[9] protonated,[10] or rearranged porphyrins[11] can be viewed as leading to deformation before metal ion incorporation. All of the electrostatic factors found in porphyrin reactions,[12] and Lewis base catalysis[13] simply facilitate the deformation of the nucleus.

The idea of porphyrin deformation by metal ions, protons or *N*-alkyl groups, leading to subsequent reactions on the opposite side of the porphyrin plane has been used to rationalize acid catalysed solvolysis reactions,[4] and predicts S_E2 character for the second order kinetics[14] observed when one metal ion replaces another co-ordinated in a porphyrin molecule.

The recently synthesised[15] rhenium mesoporphyrin containing two rhenium atoms, presumably on opposite sides of the porphyrin (P) plane, $[(\text{CO})_3\text{RePRe}(\text{CO})_3]$, is a reasonable model for an intermediate in our suggested Scheme.

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