Monomer–Dimer Equilibration of Water-soluble Porphyrins as a Function of the Co-ordinated Metal Ion

By M. Krishnamurthy,* J. R. Sutter, and P. Hambright

(*Chemistry Department, Howard University, Washington, D.C.* 20001)

Summary Tetrakis-(4-sulphophenyl)porphyrin and its four co-ordinate metal complexes dimerize, while the five- or six-ligated metalloporphyrins are monomers in aqueous, electrolyte-containing solutions.

The study of porphyrins and metalloporphyrins in aqueous and non-aqueous solution is always complicated by the possible presence of dimers or higher aggregates.[1] The nature and kinetics of μ-oxobridge type dimerization as found in ferric porphyrins is fairly well understood,[2] but the factors that promote association involving either metal-free[3] or normal metalloporphyrins,[4,5] where μ-oxo bonding is absent, are not clear. We report a temperature-jump kinetic study on tetrakis-(4-sulphophenyl)porphyrin H_2-(TPPS$_4$), and eleven of its metal complexes in aqueous solution. The results suggest how the characteristics of the metal ion influence metalloporphyrin dimerization.

The equilibrium constant K_D, for the monomer–dimer reaction $2P = P_2$ (k_f, k_r) was calculated[4] from data on the spectrophotometrically observed deviations from Beers' law found upon porphyrin dilution at 20°, $\mu = 0{\cdot}05$ $NaNO_3$, 0·01 M Hepes buffer, pH 7. Using the temperature-jump method, a single concentration dependent relaxation (τ) was observed. Linear plots of τ^{-2} *vs.* the total porphyrin concentration, C_0, in terms of the equation[5]

$$\tau^{-2} = (8k_f^2K_D^{-1})\ [C_0] + k_f^2K_D^{-2}$$

were obtained. Least-squares procedures were used to calculate k_f from the slope, and k_r in terms of the relationship $K_D = (k_f/k_r)$.

TABLE. Dimerization rate and equilibrium results for porphyrins and metalloporphyrins

Complex (T/K)	K_D/M^{-1a}	k_f /M^{-1} s^{-1a}	k_r /s^{-1a}	Ref.[b]
H_2-(TPPS$_4$) (292)	$9{\cdot}6 \times 10^4$	$1{\cdot}3 \times 10^8$	$1{\cdot}4 \times 10^3$	T.P.
CuTPPS$_4$ (292)	$6{\cdot}7 \times 10^4$	$6{\cdot}2 \times 10^7$	$9{\cdot}2 \times 10^2$	T.P.
PdTPPS$_4$ (292)	$2{\cdot}1 \times 10^5$	$7{\cdot}5 \times 10^7$	$3{\cdot}6 \times 10^2$	T.P.
AgTPPS$_4$ (292)	$6{\cdot}9 \times 10^3$	$4{\cdot}8 \times 10^6$	$7{\cdot}0 \times 10^2$	T.P.
H_2-(TPPS$_3$) (298)	$4{\cdot}8 \times 10^4$	$2{\cdot}2 \times 10^8$	$4{\cdot}6 \times 10^3$	4
H_2-(TPPC$_4$) (298)	$4{\cdot}6 \times 10^4$	$6{\cdot}4 \times 10^7$	$1{\cdot}4 \times 10^3$	4
CuTPPC$_4$ (298)	$1{\cdot}7 \times 10^5$	$4{\cdot}5 \times 10^7$	$2{\cdot}7 \times 10^2$	5
NiTPPC$_4$ (298)	$1{\cdot}6 \times 10^5$	$6{\cdot}2 \times 10^7$	$4{\cdot}0 \times 10^2$	5
H_2-(enP) (298)	$4{\cdot}3 \times 10^6$	$2{\cdot}0 \times 10^8$	50	3

[a] Equilibrium and kinetic data, ± 10%. [b] T.P. refers to this paper.

Using these methods, H_2-(TPPS$_4$), and its Cu^{II}, Pd^{II} and Ag^{II} complexes were found to be dimerized, with the parameters shown in the Table. The H_2-(TPPS$_4$) complexes of Zn^{II}. V^{IV}, Cr^{III}, Mn^{III} and Co^{III}, showed no kinetic relaxations or deviations from Beers' law, and are thus monomeric. Fe^{III} below pH 3 and the iron dimer Fe–O–Fe above pH 8 were also monomeric. Ni^{II}TPPS$_4$ had two relaxations on the same time scale as the other dimers at pH = 7, which may be related to both dimerization and axial ligation.[6]

Stability constants[1,7] indicate that Cu, Ag and Pd porphyrin complexes are primarily four-co-ordinate in solution, having weak interactions with axial ligands. The complexes not found to dimerize are at least five-co-ordinate in solvating media, with the metal ion positioned above the porphyrin plane towards an extraplanar ligand. A five co-ordinated metal ion thus appears to be sufficient to inhibit metalloporphyrin dimerization in aqueous, electrolyte-containing solutions, where such axial groups may prohibit the closeness of approach required for dimer stability. The ferric porphyrins form μ-oxo bridged dimers which do not further associate. The other dimeric porphyrins and metalloporphyrins may be held together by π–π interactions between the porphyrin π clouds, stabilized by a media of moderate ionic strength.[4]

In contrast to other reports, neither phenyl groups[8] nor the symmetry of charge[9] about the porphyrin periphery [both H_2-(TPPS$_4$) and H_2-(TPPS$_3$) dimerize] inhibit aggregation. Our results agree with the limited series of (p-CO_2H)-tetraphenyl-porphyrin complexes [H_2-(TPPC$_4$)],[5] where the free base, Cu and Ni form aggregates, while Zn is monomeric. The equilibrium and kinetic parameters for various porphyrin types (Table) are similar. The ion-pair equilibria noted for the positively charged free base and metal complexes of tetrakis-(4-methyl-pyridyl)porphyrin[10] may explain why this porphyrin does not associate,[4,5,11] while the positively charged ethylenediamine derivative of protoporphyrin-IX [H_2-(enP)],[3] which lacks such behaviour, is dimeric.

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