Molecular Complexes of Porphyrins: Effect on the Rate of Metalloporphyrin Formation

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Rates of the reaction between $CuCl_2$ or $ZnCl_2$ and protoporphyrin IX dimethyl ester have been measured in *NN*-dimethylformamide (dmf) or in a benzene–dimethylformamide binary solvent in the presence of the nitroarene acceptors 1,3,5-trinitrobenzene and 2,4,7-trinitrofluoren-9-one. The results show that the acceptor–porphyrin molecular complex cannot react with the metal. A mechanism for the formation of metalloporphyrins is evaluated on the basis of these studies.

PORPHYRINS and metalloporphyrins are known to form 1 : 1 molecular complexes with compounds that are electron donors or acceptors.[1-4] While these interactions are not completely understood, it is known that charge-transfer forces contribute to some degree in the stabilisation of the complexes.[1,2] Recent ^1H n.m.r.

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[3] J. G. Heathcote, G. J. Hill, P. Rothwell, and M. A. Slifkin, *Biochem. Biophys. Acta*, 1968, **153**, 13.

[4] D. Mauzerall, *Biochemistry*, 1965, **4**, 1801.

studies[5] on metalloporphyrin molecular complexes have been used in determining the ' structure in solution ' of these complexes with a number of compounds. The structures are consistent with orientations that would facilitate π–π interactions.[6]

The effect of neocuproine (2,9-dimethyl-1,10-phenanthroline) on the rate of formation of iron(II) haematoporphyrin was studied by Kassner and Wang.[7] They found that neocuproine catalysed the metalloporphyrin formation. The catalysis was attributed to the formation of a porphyrin–neocuproine molecular complex and a resulting increase in the entropy of activation for the metal–porphyrin reaction.

We have determined the rates of incorporation of Zn^{II} and Cu^{II} into protoporphyrin IX dimethyl ester (ppdme) in the presence of 2,4,7-trinitrofluoren-9-one (tnf) in *NN*-dimethylformamide (dmf) and in the presence of 1,3,5-trinitrobenzene (tnb) and tnf in benzene–dimethylformamide mixed solvent systems. Our studies show that addition of the nitroarene acceptors to porphyrin solutions causes a decrease in the rate of metalloporphyrin formation, and that the porphyrin bound to the acceptor is incapable of incorporating the metal. The equilibrium constant for the porphyrin–acceptor reaction can be determined from the variation of the observed rates of metallation as a function of the acceptor concentration.

EXPERIMENTAL

Protoporphyrin IX dimethyl ester (ppdme) (' purum ') was obtained from Fluka and used without further purification. 2,4,7-Trinitrofluoren-9-one (tnf) (Fluka) was recrystallised from chloroform, 1,3,5-trinitrobenzene (tnb) (Baker) twice from ethanol–benzene, picric acid (Allied Chemical) from benzene, and triphenylamine (Aldrich) from ethanol–benzene and then from anhydrous diethyl ether. Anhydrous chlorides of Zn^{II} and Cu^{II} were prepared by refluxing the hydrated or moist chloride in thionyl chloride and distilling off the excess of solvent.[8] Standard solutions of the metal chlorides were prepared by dissolving the anhydrous chlorides in dmf and standardising by accepted analytical procedures after diluting an aliquot portion of the dmf solution with deionised distilled water. *NN*-Dimethylformamide (dmf) (Fisher certified reagent) was further purified by stirring overnight over anhydrous magnesium sulphate and distilling under reduced pressure.[9] The purified product was stored in sealed bottles over Linde 4A molecular sieves. Benzene (Baker Spectrophotometric) and chloroform (Baker ' Instra-Analysed ') were not purified further.

Reaction rates were monitored spectrophotometrically on a Cary 14 recording spectrophotometer. A special brass-channelled cell holder was used to thermostat the sample solution at 25 ± 0.1 °C. The appearance of the metalloporphyrin α band was monitored at 572 nm for the copper(II) complex and at 582 nm for the zinc(II) complex.

Infrared spectra were recorded on a Perkin-Elmer 180 instrument which had a resolution better than 1 cm^{-1} at 3 300 cm^{-1}. The instrument had signal-amplification and digital-readout facilities such that the precise position of even the weaker bands could be accurately recorded. A matched pair of solution cells with 1-mm path length and sodium chloride windows was used in the measurement.

THEORY

The following scheme may be considered in order to evaluate the effect of the presence of acceptor A on the rate of incorporation of metal M into the porphyrin H_2P. Protons are excluded from the Scheme for simplicity. Terms in square brackets, [X], refer to the free concentrations and c_X to the analytical concentrations of the species X; k_1 and k_2 are the rate constants for metallation of free and bound porphyrin respectively, and K_1 and K_2 are equilibrium constants for the formation of H_2PA and MPA respectively.

$$\begin{tikzcd} H_2P + A \arrow[r, shift left, "K_1"] \arrow[d, "M"', "k_1"] & H_2PA \arrow[l, shift left] \arrow[d, "M"', "k_2"] \\ MP + A \arrow[r, shift left, "K_2"] & MPA \arrow[l, shift left] \end{tikzcd}$$

SCHEME

Under pseudo-first order conditions when $c_M, c_A \gg c_{H_2P}$, *i.e.* $c_M \sim [M]$ and $c_A \sim [A]$, the overall rate of reaction for the formation of MP + MPA, assumed to be first order in both metal and porphyrin concentrations, will be (1).

$$\text{Rate} = [H_2P](k_1c_M + K_1k_2c_Mc_A) \qquad (1)$$

The total concentration of the unmetallated porphyrin at any instant, $[H_2P]_t$, may be given by $[H_2P]_t = [H_2P] + [H_2PA]$ or $[H_2P] = [H_2P]_t(1 + K_1c_A)^{-1}$. Since the source of all the free and bound metalloporphyrin is the free and bound porphyrin, the rate expression in terms of $[H_2P]_t$ is (2), from whence the observed rate constant may be expressed as (3).

$$\text{Rate} = [H_2P]_t(k_1c_M + K_1k_2c_Mc_A)(1 + K_1c_A)^{-1} \qquad (2)$$

$$k_0 = (k_1c_M + K_1k_2c_Mc_A)(1 + K_1c_A)^{-1} \qquad (3)$$

Expression (3) may be rearranged to a linear form, (4).

$$k_0c_M^{-1}(1 + K_1c_A) = k_1 + K_1k_2c_A \qquad (4)$$

In the case when k_2 is non-zero and K_1 is known, the former may be determined from the gradient of a plot of $Y = k_0c_M^{-1}(1 + K_1c_A)$ against $X = c_A$. If k_2 is zero, expression (4) simplifies to another linear equation (5).

$$c_M(k_0)^{-1} = k_1^{-1} + K_1k_1^{-1}c_A \qquad (5)$$

Independent measures of k_1 and K_1 may be obtained in such a case from the intercept and the gradient of a plot of $c_Mk_0^{-1}$ against c_A.

RESULTS

The porphyrin and independently prepared[10] [Cu^{II}(ppdme)] obeyed Beer's law in benzene and in dmf for the concentration range 10^{-6}—10^{-4} mol dm^{-3}. Molar absorption coefficients could be evaluated with a precision better than

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[5] C. D. Barry, H. A. O. Hill, B. E. Mann, P. J. Sadler, and R. J. P. Williams, *J. Amer. Chem. Soc.*, 1973, **95**, 4545.

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[10] J. E. Falk, ' Porphyrins and Metalloporphyrins,' Elsevier, Amsterdam, 1964.

1%. The rate constants, k_0, were determined from the gradients of the first-order plots of log $(A_\infty - A_t)$ against time; A_∞ is the absorbance of the solution at infinite time and A_t that at time t. Pseudo-first-order conditions were ensured by keeping the concentrations of the metal and acceptor at least 20 times that of the porphyrin. Regression analyses of the rate data showed that the uncertainties in the determined rate constants were of the order of ±10%. Equilibrium constants, K_1, for the ppdme–acceptor interactions were determined spectrophotometrically in the appropriate solvents by the method of Gans and Irving[11] at 505 nm. Spectrophotometric studies showed the absence of any interactions between the metal ions and the acceptors tnf and tnb in the benzene–dimethylformamide mixed solvents and between the metal and tnf in dmf. Solutions of tnf in dmf were stable for at least 24 h if protected from light, while tnb immediately turned red in dmf but was stable in the benzene–dimethylformamide mixed solvent.

The order of the metalloporphyrin formation reaction with respect to the metal, in the presence and in the absence of acceptor, was determined by measuring the rates of the reaction at constant porphyrin and constant porphyrin + acceptor concentrations but varying metal concentrations. In all the experiments in dmf and in the benzene–dimethylformamide mixed solvents, the observed constancy of the second-order rate constant, $k_1 = k_0c_M^{-1}$, showed the reaction to be first order in both $[Cu^{II}]$ and $[Zn^{II}]$. Similar studies showed that k_0 was independent of the porphyrin concentration. A series of parallel straight lines were obtained for the first-order plots obtained from rate measurements at constant metal or constant metal + acceptor concentrations when the porphyrin concentration was varied, indicating that the order of the reaction with respect to the porphyrin concentration is also unity. These results are in agreement with those of Longo *et al.*[12] who also found the order of the reaction to be unity for both the metal and porphyrin concentration in the reaction of many metal chlorides, including $ZnCl_2$ and $CuCl_2$, with *meso*-tetraphenylporphine in dmf. These workers also showed that with this porphyrin the rate of metallation is first order in the concentrations of porphyrin and metal salt for a number of copper salts, thereby offering cirumstantial evidence that the mechanism of the reaction does not depend on the anion of the metal salt. Thus we did not study the fate of the chloride ion.

TABLE 1

Rates of metalloporphyrin formation in the presence and absence of acceptors in dmf and in benzene–dimethylformamide solvents at 25 °C. The rate constants without acceptor are based on a number of measurements. The range of metal salt concentrations were as follows: $CuCl_2$ in dmf, 2.4×10^{-3}—1.0×10^{-1}; $CuCl_2$ in benzene–dimethylformamide (9 : 1), 4.5×10^{-3}—3.0×10^{-2}; $ZnCl_2$ in dmf, 4.7×10^{-2}—4.7×10^{-1}; $ZnCl_2$ in benzene–dimethylformamide (1 : 1), 0.20—0.40 mol dm^{-3}

Metal	Solvent	Acceptor	Concentration of acceptor, 10^2c_A mol dm^{-3}	Rate constant $k_1' = k_0c_M^{-1}$ dm^3 mol^{-1} min^{-1}
Cu^{II}	dmf	tnf	0	2.452 ± 0.057
			0.091_3	1.880
			0.100_9	2.068
			0.182_5	1.539
			0.201_8	1.693
			0.365_0	1.436
			0.405_6	1.274
			0.612_6	0.970
			0.730_0	0.848
			0.816_3	0.800
			1.009_0	0.728
			1.277_5	0.604
			1.412_6	0.507
	C_6H_6–dmf (9 : 1)	tnf	0	24.97 ± 1.11
			0.093_7	20.755
			0.187_5	9.672
			0.375_0	6.013
			0.562_5	4.427
			0.937_5	2.840
			1.312_4	1.878
Cu^{II}	C_6H_6–dmf	tnb	0.497_1	18.61_7
			1.001_7	16.98_9
			1.491_3	13.46_4
			2.485_5	10.13_0
			2.982_6	8.95_5
			3.976_8	7.10_3
Zn^{II}	dmf	tnf	0	$0.114_1 \pm 0.005_4$
			0.099_7	0.093_0
			0.199_5	0.078_5
			0.299_2	0.063_3
			0.398_9	0.053_1
			0.598_3	0.040_1
			0.797_8	0.032_6
*	C_6H_6–dmf (1 : 1)	tnb	0	$0.286_5 \pm 0.005_2$
			0.250_5	0.268_9
			0.500_9	0.263_0
			1.002_0	0.244_0
			1.252_3	0.225_4
			1.503_0	0.223_5
			2.004_0	0.203_7

* At 29.5 °C.

The effect of the addition of tnb and tnf on the rates of the metal–porphyrin reaction was determined by measuring the rates of the reaction at constant porphyrin + metal, but varying acceptor, concentrations. In some cases, only the porphyrin concentration was kept constant while those of the metal and acceptor were varied. The observed rate constants were then normalised by dividing them by the total concentration of the metal: $k_1' = k_0c_M^{-1}$; the primed rate constant, k_1', indicates the presence of the acceptor. Three specific solvents were employed in these determinations. Rates of formation of $[Cu^{II}(ppdme)]$ and $[Zn^{II}(ppdme)]$ were determined in dmf in the presence of tnf, while those for the formation of $[Cu^{II}(ppdme)]$ were determined in the presence of tnf and tnb in benzene–dimethylformamide (9 : 1). The rates of $[Zn^{II}(ppdme)]$ formation in the presence of tnb were determined in benzene–dimethylformamide (1 : 1). The choice of these solvents is discussed later. Table 1 summarises the results obtained from these determinations. It is seen that the addition of acceptor causes a decrease in the rate of metalloporphyrin formation.

In order to rule out any secondary effects that might have

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[11] P. Gans and H. M. N. H. Irving, *J. Inorg. Nuclear Chem.*, 1972, **34**, 1885.

[12] F. R. Longo, E. M. Brown, D. J. Quimby, A. D. Adler, and M. Meot-Ner, *Ann. New York Acad. Sci.*, 1973, **206**, 420.

influenced the rates of metalloporphyrin formation, such as changes in the environment of the metal and porphyrin brought about by the presence of an excess of the organic acceptor molecules, a control experiment was performed. The rates of [Cu^{II}(ppdme)] formation were measured in the presence of varying amounts of triphenylamine in dmf. Triphenylamine was found not to interact with the porphyrin and is not liable to co-ordinate the metal to any appreciable extent. The results showed that, within the limits of experimental error (±10%), there was no change in the rate of the reaction, even in the presence of a 700-fold excess of NPh_3 over the porphyrin.

Spectral scans at various time intervals during the course of the metalloporphyrin formation reaction revealed the presence of isosbestic points, both in the presence and absence of acceptor molecules.

When picric acid was the acceptor, it caused a decrease in the rate of [Cu^{II}(ppdme)] formation in dmf, while an enhancement was observed in the rate of [Zn^{II}(ppdme)] formation. These results were irreproducible, however, and are not considered further.

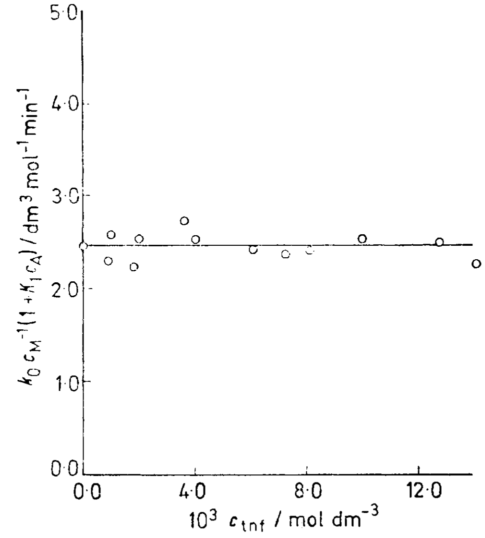

FIGURE 1 Plot of $k_0c_M^{-1}(1 + k_1c_A)$ against c_A [equation (4)] for the formation of [Cu^{II}(ppdme)] in dmf in the presence of tnf at 25 °C. K_1 = 244.5 dm^3 mol^{-1} (Table 2)

DISCUSSION

Plots of $k_0c_M^{-1}(1 + K_1c_A)$ against c_A [equation (4)] for all the five systems listed in Table 1, with values of K_1 directly determined, were linear and parallel to the horizontal axis. Figure 1 shows such a plot for the Cu^{II}–ppdme–tnf system in dmf. While this is indicative of non-metallation of the porphyrin–acceptor complex, *i.e.* of $k_2 = 0$, similar results will be obtained when $k_1 \gg k_2K_1c_A$ and the two cases will be indistinguishable if there is some scatter in the data. However, if the observed rate constants at constant c_M are plotted as a function of the amount of free porphyrin, a straight line with zero intercept should be obtained if $k_2 = 0$. This is seen in Figure 2 for the same system as above, with the amount of free porphyrin calculated from known values of K_1 and c_A. Linear regression analysis of the same data shows that the intercept is not greater than 8×10^{-4} and that k_2 may be taken as effectively equal to zero.

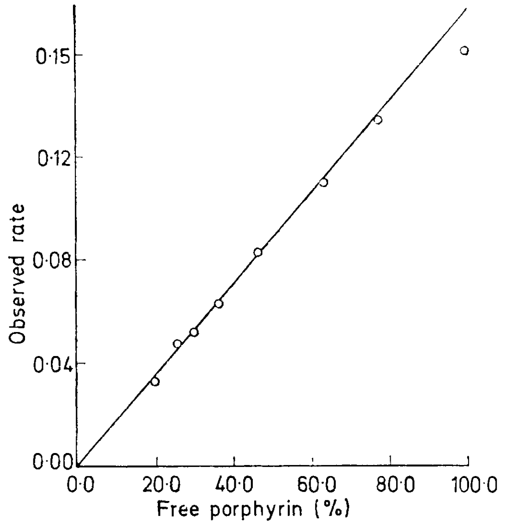

FIGURE 2 The observed constant k_0 as a function of the free porphyrin concentration for Cu^{II}–ppdme–tnf in dmf at 25 °C. Concentrations of free porphyrin were calculated for K_1 = 244.5 dm^3 mol^{-1} at various values of c_A; c_M is constant at 0.0647 mol dm^{-3}

Confirmation of the non-metallation of the bound porphyrin is obtained by a further analysis of the rate data through plots of $c_Mk_0^{-1}$ against c_A [equation (5)]. The plots should be linear and provide independent measures of K_1 and k_1 from the gradients and intercepts. Figure 3 shows such a plot for the same system as in the previous figures, while Table 2 compares the values of k_1 and K_1 obtained from such plots and from direct measurements. The close agreement in these values again confirms the conclusions drawn above with respect to the non-metallation of the porphyrin bound to the

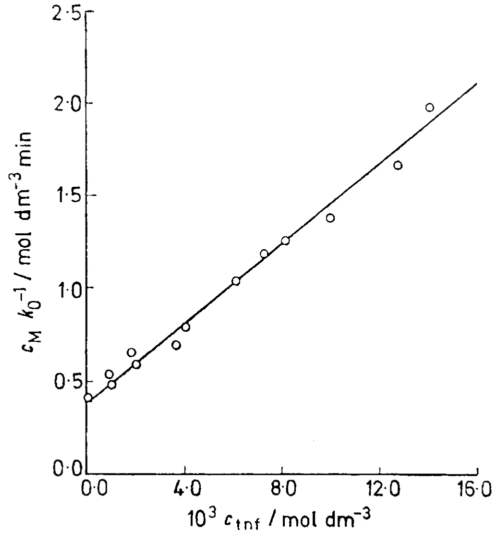

FIGURE 3 Plot of $c_Mk_0^{-1}$ as a function of c_A [equation (5)] for Cu^{II}–ppdme–tnf in dmf at 25 °C. Values of k_1 and K_1 from the gradient and intercept are listed in Table 2

acceptor. The reaction Scheme must be modified by elimination of the right-hand vertical arrow, thereby resembling that proposed by Weaver and Hambright[13] to evaluate the effect of protonating the porphyrin on the rate of metalloporphyrin formation.

TABLE 2

Comparison of the values of k_1 and K_1 determined from plots of $k_0c_M^{-1}$ against c_A [equation (5), Figure 3] with those determined directly. Values in the last row were determined at 29.5 °C. All other measurements were at 25 °C

						From gradient and intercept		From direct measurement	
System	Solvent	Gradient	Standard error of gradient	Standard deviation of Y	Intercept	k_1 / dm³ mol⁻¹ min⁻¹	K_1 / dm³ mol⁻¹	k_1 / dm³ mol⁻¹ min⁻¹	K_1 / dm³ mol⁻¹
Cu^{II}–ppdme–tnf	dmf	106.4	3.5	0.052	0.0368	2.71	260.9	2.45	244.5
	C_6H_6–dmf (9 : 1)	34.28	1.39	0.015	0.035	28.57	856	24.97	795
Cu^{II}–ppdme–tnb	C_6H_6–dmf (9 : 1)	2.498	0.082	0.003	0.0383	26.13	62.4	24.97	56.5
Zn^{II}–ppdme–tnf	dmf	2 525.0	83.5	0.263	8.514	0.1175	288.1	0.1141	244.5
Zn^{II}–ppdme–tnb	C_6H_6–dmf (1 : 1)	69.17	3.44	0.061	3.489	0.2866	19.8	0.2865	22.9

On the basis of these results it seems unlikely that the observed catalytic effect of neocuproine on the rate of the iron(II)–haematoporphyrin reaction is attributable to neocuproine–porphyrin interactions.[7] The effect seems more properly attributable to the co-ordination of Fe^{II} by neocuproine,[14] in view of the reported enhancement of the rate of metalloporphyrin formation in the presence of certain chelating agents.[15] This view is further supported by the work of Schilt[16] who found that co-ordination of Fe^{II} by neocuproine did not preclude further co-ordination of the metal by cyanide ions to form $[Fe(CN)_2(2,9\text{-}Me_2phen)]$ and $[Fe(CN)_4(2,9\text{-}Me_2phen)]^{2-}$ complexes.

The choices of the solvent systems in this study were arrived at partly through practical considerations and partly because variations in the solvent afford a convenient method of varying K_1[17] and k_1.[12] In going from pure dmf to benzene–dimethylformamide (9 : 1), K_1 increases by a factor of *ca.* 3 while k_1 decreases tenfold. The 10% dmf in the latter solvent is necessary to dissolve the metal salt. In the Zn^{II}–ppdme–tnb study a still greater amount of dmf was necessary to prevent $ZnCl_2$ from coming out of solution. The results show, however, that variations in K_1, k_1, and in the solvent do not affect the mode of metalloporphyrin formation in the presence of acceptor molecules and that the modified Scheme is valid even in the mixed solvents.

The formation of a molecular complex is expected to cause a loss of electron density from the porphyrin ring to the acceptor molecule. This will be manifest in a weakening of the N–H bonds and a reduction in basicity of the central nitrogen atoms. Evidence to this effect was observed from measurements of the N–H stretching frequency for the porphyrin molecule dissolved in chloroform with and without the presence of acceptor molecules. The value of $\bar{\nu}$(N–H) decreased from 3 318 ± 1 cm⁻¹ for the unbound porphyrin to 3 308 ± 1 cm⁻¹ in the presence of a 50-fold excess of tnf.* Allen and Caughey[19] observed similar effects on the introduction of electron-withdrawing substituents at the peripheral positions of deuterioporphyrin.

The effect of molecular complex formation by the porphyrin on its rate of metallation can also be considered in terms of the following alternative mechanisms:

Dissociative (S_E1)

$$H_2P \rightleftharpoons P^{2-} + 2H^+$$
$$P^{2-} + M^{2+} \rightleftharpoons MP$$

Associative (S_E2)

$$H_2P + M^{2+} \rightleftharpoons [MH_2P]^{2+} \rightleftharpoons MP + 2H^+$$

For the S_E1 mechanism to apply, it would be expected that $k_2 > 0.5k_1$ since weakening of the N–H bond should promote the dissociative process. (The statistical factor of 0.5 arises because one of the sides for the possible deprotonation of the porphyrin is blocked by the acceptor.) The fact that k_2 was found to be zero rules out this mechanism. In contrast, an associative mechanism implies that $k_2 < 0.5\, k_1$, which is observed. Moreover, the S_E2 mechanism also implies that porphyrin protons will be lost from the side opposite that from which the metal approaches the nucleophilic centres in the porphyrin molecule. But if the opposite side is effectively blocked by an acceptor molecule, metallation is prevented. There is a further implication of this prevention of the loss of porphyrin protons with regard to the formation of any intermediate species in the metal–porphyrin reaction. The associative mechanism may proceed as a single-step concerted process or as a two-step process with the formation of a long-lived intermediate $[MH_2P]$. Fleischer and Wang[20] found spectroscopic evidence for an intermediate 'sitting atop'

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* There are other possible sources for the shift in $\bar{\nu}$(N–H) such as hydrogen bonding between the porphyrin and the acceptor. These types of effects are not liable to be significant, however, because of the negligible differences in the stability of porphyrin- and metalloporphyrin–acceptor complex.[2,18]

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(SAT) complex in metal–ppdme reactions with methanol–chloroform as the solvent. However, in spite of the isolation of such species from solution [21] and the synthesis of complexes resembling it,[22] the SAT phenomenon has been ascribed to secondary effects by some recent workers.[23,24] In considering the metalloporphyrin formation reaction in the presence of acceptor, it follows from the blockage of one side of the porphyrin by the acceptor that a situation exists which may be regarded as ideal for the formation of an SAT type of intermediate. This would especially be so in the 90% benzene solution owing to the presence of an excess of a non-co-ordinating solvent, since loss of solvent co-ordinated to the metal as part of the metalloporphyrin formation process or intermediate formation process will now be easier. This final point is borne out by the slower rate of [Cu^{II}(ppdme)] formation in pure dmf as compared with that in benzene–dimethylformamide (9 : 1). However, no evidence, either spectroscopic or kinetic was found for the presence of any intermediates in the course of our work. It must be concluded, therefore, that the reaction of Zn^{II} and Cu^{II} with ppdme in dmf and in benzene–dimethylformamide mixed solvents proceeds *via* a concerted associative mechanism.

In conclusion it may be noted that the equilibrium constant K_2 for the metalloporphyrin–acceptor interaction [equation (5)] may also be determined through the A_∞ values from the experiments where the rates of metalloporphyrin formation were measured at constant porphyrin + metal, but varying acceptor, concentrations. The determination of K_2 is possible owing to the relatively high thermodynamic stability of the metalloporphyrin. The values of K_2 determined for the copper(II) and zinc(II) complexes of ppdme–tnf in dmf at 25 °C are 193.1 and 181.4 dm^3 mol^{-1} respectively. The magnitude of this constant is thus not very different from the corresponding value of K_1 (244.4 dm^3 mol^{-1}) as has been observed before.[2,19]

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