

## Activation Volume for the Cobalt(II) Ion Complexation with *N*-Methyltetraphenylporphine. Evidence for a Dissociative Interchange Mechanism

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A positive activation volume ( $8.0 \text{ cm}^3 \text{ mol}^{-1}$ ) for cobalt(II) ion incorporation into *N*-methyltetraphenylporphine in *N,N*-dimethylformamide, obtained by a high-pressure stopped-flow technique, is consistent with a dissociative interchange mechanism.

Although arguments have been put forward to elucidate the detailed pathways by which metal ions become incorporated into porphyrins in solution,<sup>1-4</sup> no clear conclusion has yet been reached. Recently we have used a high-pressure stopped-flow apparatus with spectrophotometric detection which enables us to follow fast reactions in various media at pressures up to  $2000 \text{ kg cm}^{-2}$ .<sup>5</sup> We now report the results of what is to the best of our knowledge the first high-pressure study on the formation of metalloporphyrins, which we undertook in order to clarify the mechanism on the basis of activation volumes.

Rates of reaction for *N*-methyltetraphenylporphine [H(MeTPP)] with cobalt(II) nitrate were investigated spectrophotometrically in *N,N*-dimethylformamide (DMF) at various temperatures and pressures. The reaction studied is given in Scheme 1.

An *X*-ray diffraction study of chloro-*N*-methyltetraphenylporphyrinatocobalt(II) has been reported.<sup>6</sup> H(MeTPP) was prepared according to literature procedures.<sup>7</sup> Extreme care was taken to obtain sample solutions which were as dry as possible. The preparation was carried out just before kinetic measurements were made. The measurements were made under pseudo-first-order conditions with a large excess of cobalt(II) ion relative to porphyrin and with a constant concentration of calcium(II) nitrate  $\{[\text{Ca}(\text{NO}_3)_2] 0.28 \text{ mol kg}^{-1}\}$ . The visible spectra changed during the reaction, with clear isosbestic points at 673, 595, 508, 443, and 395 nm. Pseudo-first-order plots showed good linearity for at least 3 half-lives. The rate is first order with respect to the cobalt(II) ion over a wide range of concentrations ( $3 \times 10^{-4}$ – $7 \times 10^{-2} \text{ mol kg}^{-1}$ ). Thus the rate of cobalt incorporation into H(Me-

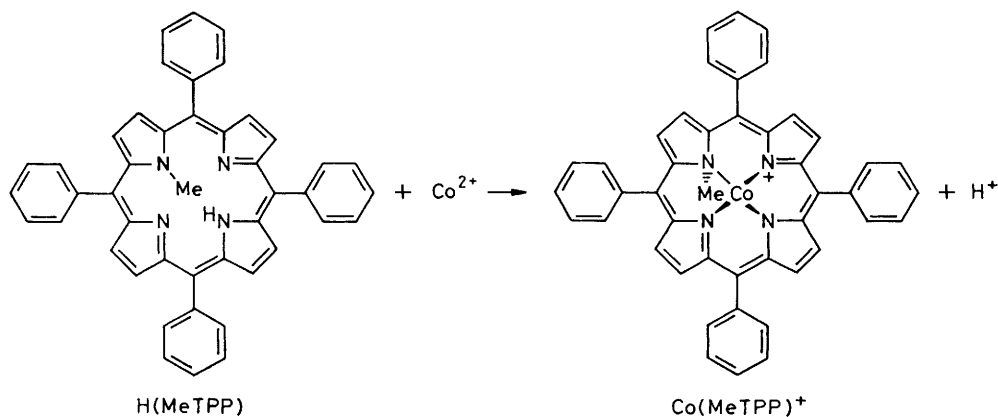
$$d[\text{Co}(\text{MeTPP})^+]/dt = k[\text{H}(\text{MeTPP})][\text{Co}^{2+}] \quad (1)$$

TPP) may be expressed by equation (1); the value of the second-order rate constant,  $k$ , at 298.2 K was determined to be  $0.65 \pm 0.05 \text{ mol}^{-1} \text{ kg s}^{-1}$ . The values of activation enthalpy and entropy ( $\Delta H^\ddagger = 72 \pm 5 \text{ kJ mol}^{-1}$ ,  $\Delta S^\ddagger = -12 \pm 8 \text{ J mol}^{-1} \text{ K}^{-1}$ ) were estimated from the Eyring plot for rate constants at 289.9, 294.9, 298.2, 300.9, and 304.6 K. In Table 1, rate constants at various pressures are summarized. According to the transition-state theory the change in rate constant with pressure is given by equation (2). Since an

$$(\partial \ln k / \partial P)_T = -\Delta V^\ddagger / RT \quad (2)$$

excellent linear relationship is obtained between  $\ln k$  and  $P$ , the activation volume  $\Delta V^\ddagger$  is independent of pressure. The value of  $\Delta V^\ddagger$  was determined to be  $8.0 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ . The rate was not affected by the addition of calcium nitrate ( $0.3$ – $0.005 \text{ mol kg}^{-1}$ ).

The absence of any salt effect is consistent with the porphyrin reactant reacting as a free base. The positive activation volume strongly indicates a dissociative character for the activation process. Recently Merbach *et al.*<sup>8</sup> have reported the activation volume for the solvent exchange of the cobalt(II) ion in DMF:  $6.7 \text{ cm}^3 \text{ mol}^{-1}$  at 296 K and  $9.2 \text{ cm}^3 \text{ mol}^{-1}$  at 253 K. They proposed a dissociative interchange mechanism for the solvent exchange reaction. The activation volume for the formation of the cobalt-porphyrin complex is approximately the same as that for the exchange of DMF at cobalt(II). Rate constants for metal incorporation into H(MeTPP) parallel those for solvent exchange at the metal ions *i.e.*  $\text{Cu}^{II}$



Scheme 1

**Table 1.** Pressure dependence of rate constants for cobalt(II) incorporation into H(MeTPP) in DMF.<sup>a</sup>

$P/\text{kg cm}^{-2}$	$k/\text{mol}^{-1} \text{ kg s}^{-1}$
1 (6) <sup>b</sup>	$0.636 \pm 0.025^c$
250 (6)	$0.595 \pm 0.032$
500 (5)	$0.584 \pm 0.033$
750 (6)	$0.514 \pm 0.026$
1000 (6)	$0.472 \pm 0.021$
1250 (4)	$0.447 \pm 0.010$
1500 (4)	$0.409 \pm 0.033$
1750 (4)	$0.379 \pm 0.006$
2000 (4)	$0.346 \pm 0.010$

<sup>a</sup>  $T = 298.2 \text{ K}$ ,  $[\text{Ca}(\text{NO}_3)_2] = 0.28 \text{ mol kg}^{-1}$ ,  $[\text{Co}(\text{NO}_3)_2] = 0.0404 \text{ mol kg}^{-1}$ ,  $[\text{H(MeTPP)}] \text{ ca. } 5 \times 10^{-6} \text{ mol kg}^{-1}$ . <sup>b</sup> Figures in parentheses indicate the number of data points. <sup>c</sup>  $\pm$  Standard deviations.

$> \text{Zn}^{\text{II}} > \text{Co}^{\text{II}} > \text{Ni}^{\text{II}}$ .<sup>3,9</sup> Thus solvent dissociation from the cobalt(II) ion is an important rate-determining factor in the mechanism. Moreover, the rates for complexation of H(MeTPP) are slower than those for the corresponding solvent exchange,<sup>9</sup> but faster than the rates for complexation of planar tetraphenylporphyrin.<sup>10</sup> These facts point to the deformation of the porphyrin as an important and rapid process occurring

before the rate-determining step.<sup>3</sup> For the deformation of porphyrin the reaction volume may be assumed to be nearly zero.

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## References

- 1 R. F. Pasternack, G. C. Vogel, C. A. Skowronek, R. K. Harris, and J. G. Miller, *Inorg. Chem.*, 1981, **20**, 3763.
- 2 J. Turay and P. Hambright, *Inorg. Chem.*, 1980, **19**, 562.
- 3 M. J. Bain-Ackerman and D. K. Lavalley, *Inorg. Chem.*, 1979, **18**, 3358.
- 4 S. Funahashi, K. Saito, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, 1981, **54**, 2695.
- 5 K. Ishihara, S. Funahashi, and M. Tanaka, *Rev. Sci. Instrum.*, 1982, **53**, No. 8.
- 6 O. P. Anderson and D. K. Lavalley, *J. Am. Chem. Soc.*, 1977, **99**, 1404.
- 7 D. K. Lavalley and A. E. Gebala, *Inorg. Chem.*, 1974, **13**, 2004.
- 8 F. K. Meyer, K. E. Newman, and A. E. Merbach, *Inorg. Chem.*, 1979, **18**, 2142.
- 9 S. Funahashi and R. B. Jordan, *Inorg. Chem.*, 1977, **16**, 1301.
- 10 F. R. Longo, E. M. Brown, D. J. Quimby, A. D. Adler, and M. Meot-Ner, *Ann. N. Y. Acad. Sci.*, 1973, **206**, 420.