

## Evidence for a *D*-Mechanism in the Substitution of Methanol by Pyridyl Ligands in Cobalt(III)(protoporphyrin IX dimethyl ester)(methanollo)(methoxo) Complex in Methanol

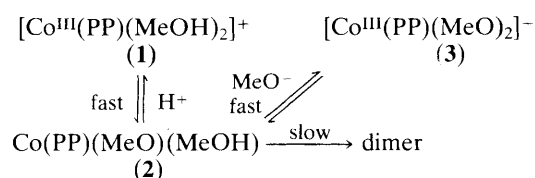
Zdravko Dokuzović, Dušanka Pavlović,\* Smiljko Ašperger,\* and Ivo Murati

Department of Chemistry, Faculty of Pharmacy and Biochemistry, University of Zagreb, Zagreb, Croatia, Yugoslavia

The substitution of MeOH in Co<sup>III</sup>(protoporphyrin IX dimethyl ester)(MeO)(MeOH) by pyridine (py), 4Me-py, or 4CN-py in methanol is a *D*-type process with a limiting rate of 57.8 s<sup>-1</sup> for all three ligands at 25 °C; the subsequent substitution of MeO<sup>-</sup> proceeds via the complex conjugate acid, also in a dissociative manner.

The distinction between *D* and *I<sub>d</sub>* mechanisms in polar co-ordinating solvents is difficult. The most thoroughly investigated substitutions in this respect are the displacements of H<sub>2</sub>O by L in [Fe(CN)<sub>5</sub>(H<sub>2</sub>O)]<sup>3-</sup>, but the mechanism is still a matter for debate.<sup>1,2</sup> For several years substitution of X by L in Co<sup>III</sup>(CN)<sub>5</sub>X was considered to be via a *D*-mechanism, but recently an *I<sub>d</sub>* mechanism was proposed<sup>3</sup> for various ligands L. The replacement of MeOH by L in Co<sup>III</sup>(PP)(MeO)(MeOH) (2) in methanol (PP = protoporphyrin IX dimethyl ester) is one of the rare cases involving the *D*-mechanism. Our arguments that the replacement of MeOH in (2) by pyridyl ligands in methanol follows a *D*-mechanism (*S<sub>N</sub>1*, limiting mechanism) are the same as those put forward by Haim and Wilmarth<sup>4</sup> for replacement of H<sub>2</sub>O in [Co(CN)<sub>5</sub>(OH<sub>2</sub>)]<sup>2-</sup> by N<sub>3</sub><sup>-</sup> in water. They observed a tendency toward rate saturation when plotting *k*<sub>obs.</sub> vs. azide concentration. Recently their results were revised,<sup>5</sup> and a linear dependence for *k*<sub>obs.</sub> vs. azide concentration was established. Therefore, it could not be determined whether a *D* or *I<sub>d</sub>* mechanism is operating. Our results prove the existence of the penta-co-ordinated Co<sup>III</sup>(PP)(MeO) intermediate in methanol, showing that a *D*-mechanism operates for substitution into (2).

When dissolved in methanol, Co<sup>III</sup>(PP)Cl (dark purple crystals) releases its chloride immediately and Co<sup>III</sup>(PP) reacts



Scheme 1

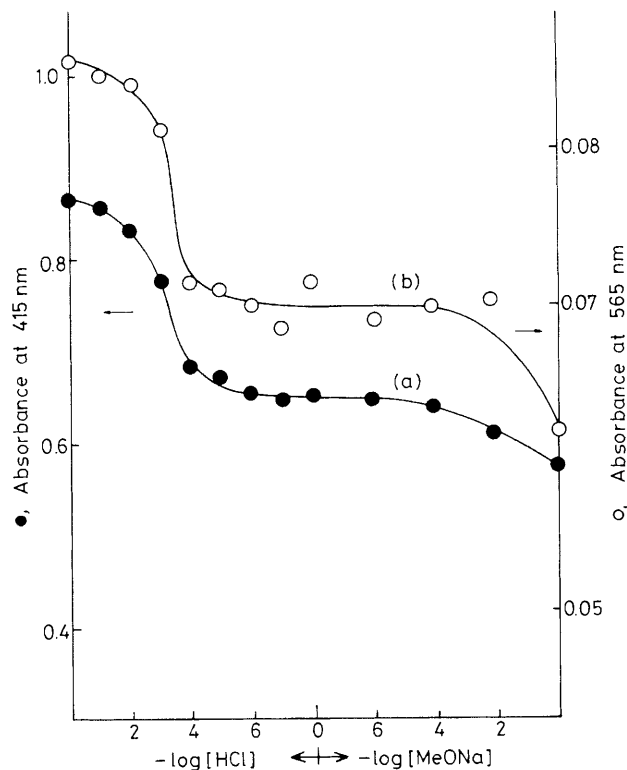


Figure 1. Spectrophotometric titration of Co<sup>III</sup>(PP)(MeOH)(MeO), (2), in methanol with methanolic solutions of HCl, to yield [Co<sup>III</sup>(PP)(MeOH)<sub>2</sub>]<sup>+</sup>, (1), and with MeONa, respectively, to yield [Co<sup>III</sup>(PP)(MeO)<sub>2</sub>]<sup>-</sup>, (3). Total concentration of Co<sup>III</sup>(PP) was kept constant during titration (1 × 10<sup>-5</sup> mol dm<sup>-3</sup>). (a), λ 415 nm; (b), λ 565 nm. Measurements were made immediately after each addition of acid or base. Temperature 25 °C.

**Table 1.** Rates of substitution of MeOH ( $k^I_{\text{obs.}}$ ) and MeO<sup>-</sup> ( $k^{II}_{\text{obs.}}$ ) in (2) with py, 4CN-py, and 4Me-py in methanol<sup>a</sup> (all rate constants in s<sup>-1</sup>).

$10^4 [L]^b$ /mol dm <sup>-3</sup>	Entering ligand (L)					
	4CN-py		py		4Me-py	
	$k^I_{\text{obs.}}$	$k^{II}_{\text{obs.}}$	$k^I_{\text{obs.}}$	$k^{II}_{\text{obs.}}$	$k^I_{\text{obs.}}$	$k^{II}_{\text{obs.}}$
1	3.47	0.043	2.89	0.018	1.0	0.015
	0.15	0.003	0.15	0.002	0.05	0.0015
	5	4	5	5	5	5
5	6.93	0.050	3.85	0.048	3.85	0.048
	0.35	0.003	0.2	0.003	0.2	0.003
	4	5	4	5	5	3
10	17.3	0.11	8.6	0.12	6.93	0.12
	0.8	0.006	0.4	0.008	0.3	0.008
	4	3	3	3	5	5
20	34.7	0.16	18.2	0.20	10.7	0.20
	1.6	0.009	0.7	0.012	0.6	0.015
	5	4	3	4	4	5
30			30.0			
			1.5			
			5			
40	53.3	0.32	38.5			
	3	0.016	2			
	3	5	5			
50		0.35	46.2	0.36	27.7	0.39
		0.02	3	0.02	1.8	0.025
		3	4	3	3	4
60	57.8					
	4					
	4					
80	57.8		57.8			
	3.0		3.0			
	6		5			
100		0.70	57.8	0.81	49.3	0.77
		0.05	3.2	0.06	3	0.05
		4	4	4	4	3
500		2.89		2.89	57.8	2.67
		0.2		0.2	4	0.25
		4		4	4	4
1000		6.03		5.78	57.8	5.77
		0.4		0.3	4	0.4
		4		5	5	4

<sup>a</sup> Concentration of (2)  $5 \times 10^{-6}$  mol dm<sup>-3</sup>; kinetics were followed by stopped-flow technique at 430 nm; temperature  $25 \pm 0.05$  °C. <sup>b</sup> For each concentration of L: first line, mean first order reaction rate constant; second line, standard error of mean; third line, number of kinetic runs. Italic figures represent limiting rates.

with the solvent. † The composition of the equilibrium mixture depends on the acidity of the solution. The species were characterised by their absorption spectra. Spectrophotometric titrations of the substrate with acid and base suggested the existence of the equilibria in Scheme 1. The titration was carried out with solutions of HCl and sodium methoxide in methanol. Curves (a) and (b), Figure 1, correspond to changes in absorbance that occur at 415 (Soret peak) and 565 nm ( $\alpha$ -peak) respectively on addition of acid or base to a freshly prepared solution of (2). It is reasonable to assume that the absorbances corresponding to the plateaus of the titration curves (a) and (b) relate to (2) and the higher absorbances in strongly acidic solutions relate to (1). The low absorptions in strongly basic solution relate to (3). Analogous observations were reported by Ashley *et al.*<sup>7,8</sup> in an aqueous solution of *meso*-tetrakis(*p*-sulphonatophenyl)porphyrinatodiaquacobaltate(III). All equilibria in Scheme 1 are rapidly established (proton transfer reactions). In acidic media (0.1–1 mol

dm<sup>-3</sup> HCl), where (1) strongly dominates, the Beer–Lambert law holds up to  $2 \times 10^{-5}$  mol dm<sup>-3</sup> (1) (at  $\lambda_{\text{max}}$  415 nm,  $\epsilon = 93\,000$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup> at 25 °C). ‡

The kinetics of the reaction of (2) with the pyridyl ligands (py) were measured by the stopped-flow technique. The Soret peak of the methanol–methoxo complex is at 415 nm ( $\epsilon$  ca.  $6.5 \times 10^4$  mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup> at 25 °C). The kinetics were measured at 430 nm. At this wavelength the kinetics of substitution of the MeOH and MeO<sup>-</sup> ligands can be best followed. The substitutions run consecutively. The difference in rates of the two substitutions is large enough to permit independent determinations of the observed rate constants for each step. The kinetic results are summarized in Table 1. Methanol is replaced first and methoxide second. The replacement of methanol is dissociative in nature, since the limiting rate ( $k^I_{\text{obs.}}$ ) was the same with all three entering ligands (57.8 s<sup>-1</sup>, see Table 1). Moreover, the limiting rates in substitution of the methanol ligand by L in methanol solvent reveal that the

† Starting material for the preparation of Co<sup>III</sup>(PP)Cl was horse blood. The method of McConnel *et al.*<sup>6</sup> was partly modified. The purity of the complex was checked by its absorption spectrum. Full details of the preparation will be reported elsewhere.

‡ After prolonged periods (at least 2 days) slow dimerisation of (2) seems to take place, causing a decrease in absorbance, as expected for dimerisation processes.<sup>9</sup> The dimerisation did not interfere since its rate is ca. 1000 times lower than the rates of substitution.

substitution is of the  $D$ -type. If this dissociative substitution were of the  $I_d$  type, a saturation rate would not be observed. The observed rate constant ( $k_{\text{obs}}^1$ ) is equal to  $k_1 k_2 [L] / \{k_{-1} [\text{MeOH}] + k_2 [L]\}$ , where  $k_1$  and  $k_{-1}$  are the rate constants of dissociation of methanol ligand and its reverse, respectively, and  $k_2$  is the rate constant of the reaction of the intermediate  $\text{Co}^{\text{III}}(\text{PP})(\text{MeO})$  with  $L$ . The replacement of methanol ligand in methanol solvent usually gives a linear dependence of  $k_{\text{obs}}$  on  $[L]$ . The fact that limiting rates are obtained reveals that  $k_2$  is much larger than  $k_{-1}$ , which is reasonable. Indeed, on plotting  $1/k_{\text{obs}}^1$  vs.  $1/[L]$  a linear dependence was obtained (slope  $k_{-1}[\text{MeOH}]/k_1 k_2$ , intercept  $1/k_1$ ). This enabled determination of the competition ratios  $k_2/k_{-1}$ . They are 6 800, 3 700, and 2 800 for the entering ligands 4CN-py, py, and 4Me-py, respectively. Large values for the competition ratios would be expected because the pyridyl ligands are more reactive than methanol. However, the order of pyridyl ligand reactivity is somewhat puzzling. Although it might be expected that the most basic pyridyl ligand would react at the fastest rate, the opposite occurs. It appears that methoxide in the  $\text{Co}^{\text{III}}(\text{PP})(\text{MeO})$  intermediate strongly increases the electron density at the *trans* axial position which favours the entry of the less basic pyridyl ligand. The extent of metal to ligand  $\pi$ -bonding is considered to be small in  $\text{M}^{3+}$  complexes. The 'soft' character of the cobalt porphyrin complex may make  $\pi$  back-bonding a more important interaction than might otherwise be the case with an  $\text{M}^{3+}$ -ligand bond.<sup>10</sup> This back-bonding stabilises the transition state. It might be expected that the back-bonding would be the largest with 4CN-py.

The rate of replacement of MeOH by py in  $\text{Co}^{\text{III}}(\text{PP})(\text{MeO})(\text{MeOH})$  was also measured at constant basicity. This was achieved by addition of crude pyridine hydrochloride to methanolic solutions of pyridine keeping the ratio  $[\text{py}]/[\text{pyH}^+] = 1$ . The same limiting rate,  $57.8 \text{ s}^{-1}$ , was obtained with py entering ligand, in unbuffered and in buffered solutions.

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## References

- 1 S. Ašperger, in 'Advances in Solution Chemistry,' Plenum Press, New York, 1981, p. 105.
- 2 C. H. Langford, *Inorg. Chem.*, 1979, **18**, 3288; D. Pavlović, D. Šutić, and S. Ašperger, *J. Chem. Soc., Dalton Trans.*, 1976, 2406; I. Murati, D. Pavlović, A. Šustra, and S. Ašperger, *ibid.*, 1978, 500; R. Juretić, D. Pavlović, and S. Ašperger, *ibid.*, 1979, 2029; A. L. Coelho, H. E. Toma, and J. M. Malin, *Inorg. Chem.*, 1983, **22**, 2703.
- 3 M. H. M. Abou-El-Wafe and M. G. Burnett, *J. Chem. Soc., Chem. Commun.*, 1983, 833.
- 4 A. Haim and W. K. Wilmarth, *Inorg. Chem.*, 1962, **1**, 573.
- 5 A. Haim, *Inorg. Chem.*, 1982, **21**, 2887.
- 6 R. J. McConnel, B. G. Overell, V. Petrow, and B. Sturgeon, *J. Pharm. Pharmacol.*, 1953, **5**, 179.
- 7 K. R. Ashley and J. G. Leipoldt, *Inorg. Chem.*, 1981, **20**, 2326.
- 8 K. R. Ashley and S. Au-Young, *Inorg. Chem.*, 1976, **15**, 1937.
- 9 P. Jones, K. Prudhoe, and S. B. Brown, *J. Chem. Soc., Dalton Trans.*, 1974, 911.
- 10 R. F. Pasternack, M. A. Cobb, and N. Sutin, *Inorg. Chem.*, 1975, **14**, 866.