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Structure of Nonplanar Octabromotetraphenyl Porphyrin and Kinetics of Rapid Metalation Reactions

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Octabromotetraphenylporphyrin adopts a severe saddle-shaped distorted structure owing to the steric crowding of heavy bromine substituents. The rate enhancement of porphyrin metalation reaction is primarily due to the nonplanarity of the ring while the electronic effect diminishes the affinity of the porphyrin towards metal ions.

Structure-activity relationship of metalloporphyrins forms an interesting area of research in view of the ubiquitous nature of metalloporphyrins in biological systems. Structural distortion of porphyrins seems to confer some unusual optical properties, enhanced electrochemical redox reactivity$^{1,2)}$ and increased catalytic efficiency.$^{3)}$ Studies on kinetics of porphyrin metalation reactions have suggested that the deformation of the porphyrins plays an important role in governing the mechanism of such reactions.$^{4)}$ This gains support from the recent studies on metalation reaction of dodecaphenylporphyrin (H_2DPP) by Takeda *et al.*$^{5)}$ and the data on the octabromotetramesityl porphyrin by Robinson and Hambright.$^{6)}$ Here we report the structure of octabromotetraphenylporphyrin and demonstrate that though the electronic effect diminishes the basicity of the porphyrin, the enhanced rates of porphyrin metalation essentially arise from steric features.

The 2, 3, 7, 8, 12, 13, 17, 18 -octabromo-5, 10, 15, 20-tetraphenylporphyrin (H_2OBP) crystallizes with two water and two ethanol molecules in the space group $P\bar{1}$. The structure$^{7)}$ exhibits severe distortion of the porphyrin core (Fig. 1) with adjacent pyrrole rings tilted by 51.6-52.8° and opposite pyrrole moieties are tilted by 77-77.2°. The H_2OBP lacks four-fold rotation symmetry and an expansion of the porphyrin core (radius 2.10Å) is observed. These features are distinct from those observed for the tetramesityl analog$^{8)}$ and regarded to signify severe distortion of the porphinoid skeleton. The heavy bromine substituents are disposed above the pyrrole rings II and III while the bromine atoms of the rings I and IV are positioned below the plane by 0.170 (3)-0.461(4)Å. The phenyl rings are rotated by 29.70(6)-31.4(5)° from the mean plane of the porphyrin as defined by the four nitrogen atoms. The large displacement of the core atoms coupled with the tilting of the individual pyrrole rings lead to the most severe saddle-shaped distortion of the porphyrin. The retainment of this structure in solution is seen from the exhibition of unusual spectral properties of H_2OBP and its metal derivatives.1) These features form an attractive proposition to investigate the kinetics of metal incorporation into H_2OBP.

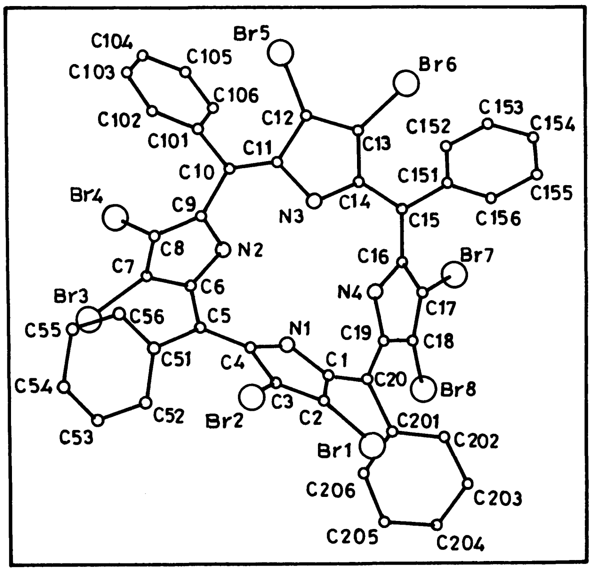

Fig.1. PLUTO diagram of H_2OBP.

The observed rates of metal incorporation reactions9) can be fitted well with the reaction 1 and 2 where the metalation proceeds via a preequilibrium complex.

$$M^{2+} + H_2OBP \overset{K}{\rightleftharpoons} [M^{2+} --- H_2OBP] , \tag{1}$$

$$[M^{2+} --- H_2OBP] \xrightarrow{k_1} MOBP + 2H^+ . \tag{2}$$

The rate expression takes the form

$$k_{obsd} = \frac{k_1 K[M^{2+}]}{1 + K[M^{2+}]} . \tag{3}$$

The data obained are shown in Table 1. The same kinetic scheme holds good if the 'preequilibrium' complex is viewed as 'dead end' then the reaction rate becomes a function of product of porpyrin and metal concentration terms. The present results do not suggest the dependency of rate on the concentration of metal ion as pointed out by Funahashi *et al.*10) A comparison of the rate data obtained for H_2OBP

with those of the unsubstituted meso-tetraphenylporphyrin, (H_2TPP)[11] revealed that the k_{app} values are two to three orders of magnitude greater than those observed for H_2TPP. This rate enhancement cannot be rationalized in terms of basicity, since the bromine substitutents in H_2OBP reduce the values of protonation constants[1] (pK_3 = 2.60 and pK_4 = 1.75). Hence, the permanent distortion of the H_2OBP caused by heavy bromine substituents is an important factor in governing the rates of the metalation reactions. In view of this, the formation of the SAT complex[12] seems an unlikely mechanism for the metal incorporation reaction into H_2OBP. A comparison[13] of the results with those obtained recently for dodecaphenylporphyrin reveals that the rate enhancement in H_2DPP metalation arise from both steric and electronic effects (high basicity) of the porphyrin while in the metalation reactions of H_2OBP, the rate enhancement proceeds only through deformation mechanism. This interesting finding brings forth the importance of steric feature (distortion of the porphyrin) in the kinetics of metalation reactions.

Table 1. Kinetic data for Cobalt (II), Copper (II), and Zinc (II) incorporation into H_2OBP in $CHCl_3$ – CH_3OH (1:1 v/v) mixture at 295 K

Metal	k_1	K	k_{app}
	s^{-1}	$mol^{-1}dm^3$	$mol^{-1}dm^3s^{-1}$
Co(II)	0.32	76.90	24.60
Cu(II)	19.80	70.20	1.39×10^3
Zn(II)	6.5×10^2	3.50	2.30×10^3

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7) Crystal data: $C_{48}H_{38}N_4O_4Br_8$; M = 1372.36. a = 10.460(3); b = 15.486(5); c = 15.476(5); α = 83.47(3), β = 70.29(3); γ = 70.26(3), V = 2221 Å^3; z = 2, D_c = 2.0591 g cm^{-3}; 4098 reflections, final R = 0.095, W_R = 0.099.

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9) The kinetic runs were carried out on a Stopped-flow Spectrometer (SF- 4 series, Hi-Tech Scientific Ltd. England) coupled with Apple II e Computer for data acquisition system. A solvent mixture $CHCl_3$: CH_3OH (1:1 v/v) was employed for the kinetic runs since H_2OBP was not freely soluble in DMF. The decrease in absorbance at 760 nm band of H_2OBP as a function of time was followed for data collection. A constant ionic strength was maintained (0.1 $NaClO_4$) for all the measurements. The k_{obsd} values represent pseudo-unimolecular rates under the condition, $[H_2OBP] \ll$ [metal II acetate]. The rate data are calculated from nonlinear-least-square method. The k_{app} is defined as the product of k_1 and K.

10) S. Funahashi, Y. Yamaguchi, and M. Tanaka, *Bull. Chem. Soc. Jpn.*, **57**, 204 (1984).

11) The H_2TPP metalation was carried out under similar conditions using the same solvent mixture as that employed for H_2OBP. The k_{app} values are compared.

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13) It is assumed that the nature of solvent system though different in the two studies, does not play any significant role in the order of magnitude of the rates owing to severe distortion of the porphyrins imposed by the substituents.

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