

## Kinetic Studies of Zinc(II) Ion Incorporation into Polyvalent Porphyrin, Tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)porphyrin in Dimethylformamide

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### Abstract

Kinetic studies of zinc(II) ion incorporation into polyvalent porphyrin, tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)porphyrin ( $H_2T^tBHPP$ ), which has bulky substituents (tert-butyl groups) in the *meta* position of the *meso*-phenyl groups of the porphyrin ring, in dimethylformamide (DMF) are reported. The rate of zinc ion incorporation, which has been measured spectrophotometrically under pseudo-first-order conditions, is almost the same as or somewhat higher than that of zinc(II) ion into *meso*-tetraphenylporphyrin ( $H_2TPP$ ) which has no substituents in the *meso*-phenyl groups. It is shown that the bulky substituents in the *meta* position of the *meso*-phenyl groups have little effect on the zinc(II) ion incorporation into the porphyrin ring. It has also been shown that the counteranions of the zinc(II) used have a substantial effect on the kinetics of the porphyrin metallation, and the compensation effects have been observed in the seven zinc(II) salts examined. On the basis of zinc concentration dependence and temperature dependence of the rate constants, metallation mechanisms were discussed.

### Introduction

It is well-known that metalloporphyrins are ubiquitous in living organisms and are involved in several biological processes such as oxygen transport (hemoglobin, myoglobin), electron transport (cytochrome *c*), detoxication (catalase, peroxidase, cytochrome P-450) and photosynthesis (chlorophyll). Generally porphyrins are synthesized biologically in a metal-free form and the metal ion is subsequently enzymatically inserted. For an understanding of the metallation mechanism and the possible role of enzymatic catalysis, thorough kinetic studies are required [1].

A number of kinetic studies of metalloporphyrin formation have been reported and several reviews are available [2, 3]. While there are many elegant ways to synthesize metalloporphyrins [4], the mechanisms of metal incorporation reactions are not completely clarified. Recently, Turay and Hambright [5], Pasternack *et al.* [6] and Tanaka *et al.* [7] have proposed mechanisms for the formation of metalloporphyrins. Further, Anzai and Hatano [8] reported that the rate of zinc ion incorporation into the 'picket fence porphyrin' which has the bulky substituents in the *ortho* position of the *meso*-phenyl group in porphyrin is slower than that of *meso*-tetraphenylporphyrin (TPP)<sup>†</sup>. However, there has been no report concerning the effect of the *meta* substituent in porphyrins. Therefore, we synthesized the polyvalent porphyrin, tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)porphyrin ( $H_2T^tBHPP$ ), which has the bulky substituents in the *meta* position of the *meso*-phenyl group. In order to elucidate the effect of the bulky substituent on the rates of metal ion incorporation, the incorporation of many kinds of zinc(II) salts into  $H_2T^tBHPP$  was investigated. We also studied the incorporation of a large number of metal ions into  $H_2T^tBHPP$  in order to compare the rates of the metal incorporation reactions.

In this paper, we describe the results of kinetics of the zinc(II) ion incorporation into  $H_2T^tBHPP$  in dimethylformamide (DMF).

### Experimental

#### Porphyrins

Tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)porphyrin ( $H_2T^tBHPP$ , 1) [9–11] and *meso*-tetraphenylporphyrin ( $H_2TPP$ ) [2, 12] were prepared

<sup>†</sup>Abbreviations used:  $H_2T^tBHPP$ , tetrakis(3,5-di-tert-butyl-4-hydroxyphenyl)porphyrin;  $H_2TPP$ , *meso*-tetraphenylporphyrin; quinone, 5,15-di-(3,5-di-tert-butyl-4-hydroxyphenyl)-10,20-di-(3,5-di-tert-butyl-4-quinomethene)porpho-10,20-dimethene; M, metal ion; P, porphyrin; DME, dimethylformamide;  $Zn(OAc)_2$ , zinc acetate;  $Zn(AA)_2$ , zinc acetylacetonate;  $ZnC_2O_4$ , zinc oxalate.

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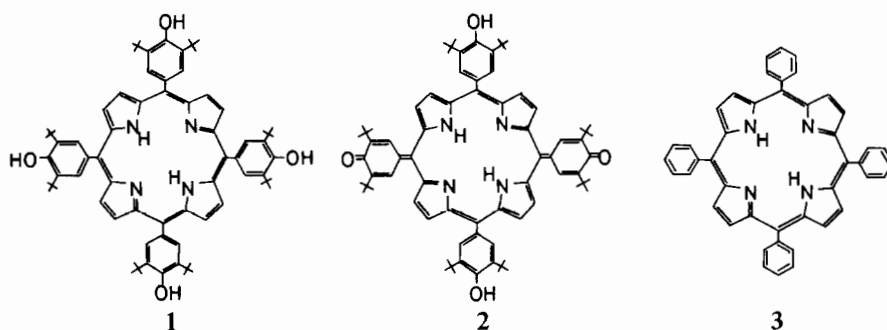


Fig. 1. Structures of porphyrins: 1, tetrakis(3,5-di-*tert*-butyl-4-hydroxyphenyl)porphyrin ( $H_2T^tBHPP$ ); 2, 5,15-di-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10,20-di-(3,5-di-*tert*-butyl-4-quinomethene)porpho-10,20-dimethene(quinone); 3, *meso*-tetraphenylporphyrin (TPP).

and purified by the literature methods. The structures of these porphyrins are shown in Fig. 1, along with the quinone, 5,15-di-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-10,20-di-(3,5-di-*tert*-butyl-4-quinomethene)porpho-10,20-dimethene (2) [10, 13, 14], which is the oxidation product of  $H_2T^tBHPP$  (1).

#### Solvents

The spectrograde *N,N*-dimethylformamide (DMF) was purchased from Wako Pure Chemical Co. Ltd. and stored over freshly activated 4A molecular sieves. Other solvents used were spectrograde or distilled prior to use.

#### Metal Salts

The following zinc(II) salts were used without further purification:  $ZnCl_2$  (Wako),  $ZnF_2$  (Nakarai),  $ZnBr_2$  (Nakarai),  $ZnI_2$  (Merck),  $Zn(NO_3)_2 \cdot 6H_2O$  (Wako),  $Zn(OAc)_2 \cdot 2H_2O$  (Wako),  $Zn(ClO_4)_2 \cdot 2H_2O$  (Alfa),  $Zn(AA)_2$  (Dojin),  $ZnSO_4 \cdot 7H_2O$  (Wako),  $ZnC_2O_4 \cdot 2H_2O$  (Nakarai). Other metal salts used were  $CuCl_2$  (Nakarai),  $CoCl_2$  (Wako),  $MnCl_2$  (Wako),  $MgCl_2 \cdot 6H_2O$  (Wako),  $NiCl_2 \cdot 6H_2O$  (Wako),  $PdCl_2$  (Wako),  $CdCl_2 \cdot 2.5H_2O$  (Wako),  $SnCl_2 \cdot 2H_2O$  (Wako),  $SrCl_2 \cdot 6H_2O$  (Nakarai),  $CaCl_2 \cdot 2H_2O$  (Wako) and  $PbCl_2$  (Wako).

#### Kinetic Measurements

Two spectrophotometers with thermoregulated cuvette holders were employed: a Union Giken SM-401 spectrometer with a Haake thermostat and a Hitachi 228 spectrometer with a Nippon Rikagaku thermoelectric heater/cooler. The kinetic runs were conducted under pseudo-first order conditions with metal salts in large excess. Prior to each run, spectra were taken of reactant solutions to verify concentrations and then, the reactant solutions were allowed to equilibrate at the appropriate temperature for 10 min. The reaction temperature was between 5 and 45 °C. The reaction was started by mixing 2 ml of porphyrin solution ( $\sim 10^{-5}$  M) with 2 ml of metal salt solution ( $\sim 10^{-3}$  M) in a 10 mm capped quartz

cell. No special precautions were taken generally to exclude trace water, because the rate constants did not depend on the concentration of water added externally to the reaction mixtures (data not shown).

#### Results

It is known that the change of the free base porphyrin band I–IV in the region of 500–700 nm has been used to monitor metalloporphyrin formation [15].  $H_2T^tBHPP$  shows absorption bands at 523, 563, 610 and 660 nm, and its zinc complex has absorption peaks at 564 and 606 nm. During the metallation, isosbestic points were observed at 570, 590, 635 and 686 nm. This result indicate that the free base and zinc porphyrins are the major absorbing species. Figure 2 shows the spectral changes during the reaction of  $ZnI_2$  with  $H_2T^tBHPP$  at 35 °C.

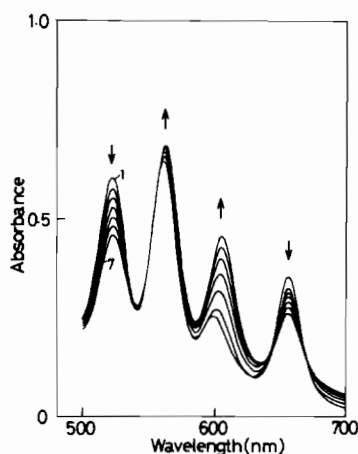


Fig. 2. Spectral changes during the reaction of  $ZnI_2$  with  $H_2T^tBHPP$  in DMF at 35 °C. Spectra were taken at 20-min intervals. Final concentrations:  $Zn(II)$ ,  $4.3 \times 10^{-3}$  M; porphyrin,  $3.6 \times 10^{-5}$  M. The initial spectrum is labelled 1 and the final spectrum is labelled 7.

TABLE 1. Effects of the Counterion on the Rate Constants of Zinc Incorporation<sup>a</sup>

Counterion	$k_{\text{obs}} (\text{min}^{-1}) \times 10^3$	
	H <sub>2</sub> T <sup>4</sup> BHPP	H <sub>2</sub> TPP
OAc <sup>-</sup>	1.96	1.74
NO <sub>3</sub> <sup>-</sup>	1.75	1.94
Cl <sup>-</sup>	1.44	1.51
Br <sup>-</sup>	2.18	0.64
I <sup>-</sup>	4.03	1.79
AA <sup>-</sup>	3.43	1.33
ClO <sub>4</sub> <sup>-</sup>	1.55	1.29

<sup>a</sup>Reaction conditions: temperature, 35 °C; [Zn] =  $4 \times 10^{-3}$  M; [porphyrin] =  $3.6 \times 10^{-5}$  M.

The rate law under pseudo-first order conditions at constant zinc concentration can be written as follows

$$\text{rate} = -d[\text{Porphyrin}]/dt = k_{\text{obs}}[\text{Porphyrin}]$$

where  $k_{\text{obs}}$  is the apparent first-order rate constant and [Porphyrin] is the concentration of H<sub>2</sub>T<sup>4</sup>BHPP. The observed rate constants,  $k_{\text{obs}}$ , for the reaction of H<sub>2</sub>T<sup>4</sup>BHPP with many kinds of zinc(II) salts in DMF are given in Table 1. The rate constants for H<sub>2</sub>TPP are also listed in Table 1. The values for H<sub>2</sub>T<sup>4</sup>BHPP are almost same as or somewhat higher than those for H<sub>2</sub>TPP. The rate constants depend on the Zn(II) salts used. The rate constant is largest in ZnI<sub>2</sub>. It is of interest that a chelate compound, Zn(AA)<sub>2</sub>, has a considerably large value of the rate constant. ZnSO<sub>4</sub> did not show any significant metal incorporation reaction.

Figure 3 shows the zinc concentration dependence of the rate constants for H<sub>2</sub>T<sup>4</sup>BHPP. The rate constants initially increase with the increase of the concentration of zinc salts and saturate at higher concentrations of zinc ion.

The temperature dependence of the rate constant was investigated and the results are given in Table 2.

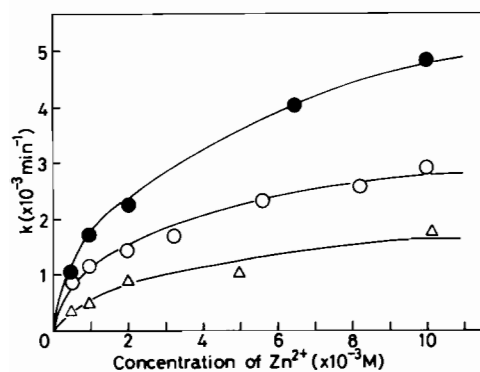


Fig. 3. Dependence of  $k_{\text{obs}}$  on the concentration of representative zinc salts. ○: Zn(OAc)<sub>2</sub>; ●: ZnI<sub>2</sub>; △: ZnCl<sub>2</sub>.

TABLE 2. Activation Parameters for the Zinc Incorporation Reaction in DMF<sup>a</sup>

Zn salts	$E_a^b$	$\Delta G^{*b}$	$\Delta H^{*b}$	$\Delta S^{*c}$
OAc <sup>-</sup>	13.3	24.1	12.7	-37.0
NO <sub>3</sub> <sup>-</sup>	15.0	24.4	14.4	-32.6
Cl <sup>-</sup>	9.9	24.6	9.3	-49.6
Br <sup>-</sup>	10.4	24.3	9.8	-47.1
I <sup>-</sup>	15.5	23.9	14.9	-29.3
AA <sup>-</sup>	18.7	24.0	18.1	-19.2
ClO <sub>4</sub> <sup>-</sup>	12.7	24.5	12.1	-40.4

<sup>a</sup>The concentrations of the zinc salts and porphyrin are  $4 \times 10^{-3}$  M and  $3.6 \times 10^{-5}$  M, respectively. <sup>b</sup>kcal/mol. <sup>c</sup>e.u.

The apparent activation free energy was calculated by the use of the Eyring equation

$$k = \bar{k}T/\bar{h} \exp(-\Delta G^*/RT)$$

where  $\bar{k}$  is the Boltzmann constant and  $\bar{h}$  is Planck's constant.  $\Delta H^*$  and  $\Delta S^*$  were calculated by the use of the equations  $\Delta H^* = E_a - RT$  and  $\Delta G^* = \Delta H^* - T\Delta S^*$ , where  $E_a$  is an apparent activation energy.

There is not much variation in  $\Delta G^*$  for the zinc ion incorporation into H<sub>2</sub>T<sup>4</sup>BHPP (Table 2).

The activation parameters for the reaction of the various zinc ions with H<sub>2</sub>T<sup>4</sup>BHPP in DMF exhibit the compensation effects [16] as shown in Fig. 4 which show that a plot of  $-T\Delta S^*$  versus  $\Delta H^*$  is linear. As shown in Table 2, despite the large difference in the activation energy ( $E_a$ ), free energy ( $\Delta G^*$ ) is constant. This may be caused by the compensation effect between enthalpy ( $\Delta H^*$ ) and entropy ( $\Delta S^*$ ).

When the zinc(II) halides are used for zinc incorporation, the order of the rates of the incorporation is ZnI<sub>2</sub> > ZnBr<sub>2</sub> > ZnCl<sub>2</sub> (Table 3). Also, a plot of the rate constants versus the difference of the electronegativity of Zn(II) halides calculated from the reported values [17] is linear, as shown in

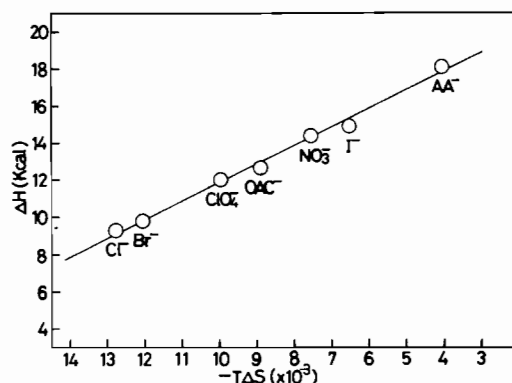


Fig. 4. A plot of  $\Delta H$  vs.  $-T\Delta S$  for the reaction of various zinc(II) salts with H<sub>2</sub>T<sup>4</sup>BHPP in DMF.

TABLE 3. The Rate Constants for Incorporation of Zinc Halides into  $H_2T^tBHPP$  and Differences in their Electronegativities

Halide	$k(\text{min}^{-1}) \times 10^{-3}$	Difference in electronegativity <sup>a</sup>
F	<sup>b</sup>	2.44
Cl	1.44	1.17
Br	2.18	1.08
I	4.03	0.55

<sup>a</sup>Ref. 17. <sup>b</sup> $ZnF_2$  did not dissolve in DMF.

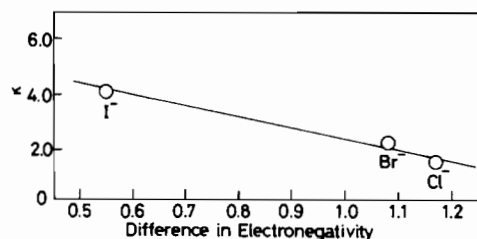


Fig. 5. A plot of the rate constants of zinc halides vs. the difference in their electronegativities.

Fig. 5. That is, the smaller the differences in the electronegativity are, the faster the reaction rates become.

The incorporation of  $Cd(II)Cl_2$  and  $Pd(II)Cl_2$  into  $H_2T^tBHPP$  was very similar to the  $ZnCl_2-H_2T^tBHPP$  reaction (Tables 4 and 5).  $NiCl_2$  was not incorporated below 45 °C. Other non-redox metal ions such as  $Mg(II)$ ,  $Sn(II)$ ,  $Ca(II)$ ,  $Pb(II)$  and  $Sr(II)$  were not incorporated at the highest temperature examined. On the other hand, in the redox active metal ions such as  $Co(II)$ ,  $Cu(II)$  and  $Mn(II)$ , metal incorporation does not occur but the redox reactions between these metal ions and  $H_2T^tBHPP$  may predominantly proceed.

The order of the rates of metal ion incorporation under the same conditions (concentration and temperature) were  $Pd(II) > Zn(II) > Cd(II) > Ni(II) \gg Mg(II)$ ,  $Ca(II)$ ,  $Sr(II)$ ,  $Sn(II)$  and  $Pb(II)$ . As shown

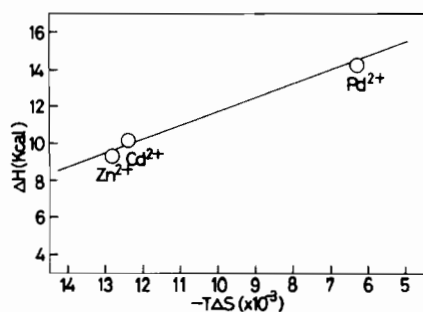


Fig. 6. A plot of  $\Delta H$  vs.  $-T\Delta S$  for the reaction of  $H_2T^tBHPP$  with various metal chlorides in DMF.

TABLE 4. Comparison of Rate Constants for  $Zn(II)$ ,  $Cd(II)$ ,  $Pd(II)$  and  $Ni(II)$  Complexation with  $H_2T^tBHPP$  in DMF<sup>a</sup>

Metal chloride	$k(\text{min}^{-1}) \times 10^{-3}$
$ZnCl_2$	1.44
$CdCl_2$	0.62
$PdCl_2$	18.8
$NiCl_2$	0.23 <sup>b</sup>

<sup>a</sup> $[\text{metal}] = 4 \times 10^{-3}$  M;  $[\text{porphyrin}] = 3.6 \times 10^{-5}$  M; temperature, 35 °C. <sup>b</sup>Does not incorporate below 45 °C in DMF. Temperature, 45 °C.

TABLE 5. Activation Parameters for Metal- $H_2T^tBHPP$  Reactions in DMF<sup>a</sup>

Metal chloride	$E_a^b$	$\Delta G^{*b}$	$\Delta H^{*b}$	$\Delta S^{*c}$
$ZnCl_2$	9.91	24.6	9.29	-49.6
$CdCl_2$	10.8	25.1	10.2	-48.3
$PdCl_2$	14.8	23.0	14.2	-28.5

<sup>a</sup> $[\text{metal ions}] = 4 \times 10^{-3}$  M;  $[\text{porphyrin}] = 3.6 \times 10^{-5}$  M; temperature, 35 °C. <sup>b</sup>kcal/mol. <sup>c</sup>e.u.

in Fig. 6, the reactions exhibit the compensation effects which suggests that the incorporations of various metal ions into  $H_2T^tBHPP$  proceed by similar mechanisms to each other.

## Discussion

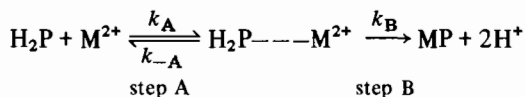
UV-Vis spectral changes during  $Zn^{2+}-H_2T^tBHPP$  reactions gave isosbestic points at the exact positions (570, 590, 635 and 686 nm) where the porphyrin and its zinc derivatives have equal extinction coefficients. The various zinc(II) ions, which have a different counteranion, were easily incorporated into  $H_2T^tBHPP$  in DMF. Rate constant for zinc incorporation is different depending on the counteranion and follows the order  $I^- > AA^- > OAc^- > Br^- > NO_3^- > ClO_4^- > Cl^-$ . The trend for the rate enhancement appears to be correlated with the relative nucleophilicity [18] of the counteranions, except for  $OAc^-$ . Previous studies have suggested that the rate-controlling feature of porphyrin metalation is the nature of the porphyrin itself [18]. More recently, evidence has been presented that the nature of the reactive metal intermediate is, in fact, responsible for rapid metal incorporation [5, 19-21]. Our results support these observations since we have found significant rate enhancement for metalation reactions by  $Zn(II)$  ion when coordinated to nucleophiles, as shown in Table 1.

Prior to discussing the reaction mechanism, the following factors should be considered: the states of metal salt and of porphyrin in the solution [22]. There are no definite data on the state of zinc salts in DMF, although several reports [22] have suggested that complex forms of metal salts exist in solution. Then, we can assume that the concentration of the active zinc species is proportional to the concentration of zinc salts, regardless of what is really the active species. The structure of the porphyrin in DMF must be monomer since the intensity of the visible absorption is proportional linearly with the concentration of the porphyrin. The reactive species of the porphyrin has been claimed to be neutral monomer ( $H_2P$ ) for this kind of the porphyrin in DMF [22].

The apparent incorporation rates and activation parameters for the  $Zn^{2+}/H_2T^tBHPP$  reactions are listed in Tables 1 and 2. The rate constants for  $H_2T^tBHPP$  are almost the same as or somewhat higher than those for  $H_2TPP$ . These results suggest that the bulky substituent, tert-butyl group in the *meta* position, did not affect the zinc ion incorporation, since the bulky substituents, tert-butyl groups, being located far away from the porphyrin ring, do not affect the incorporation of the metal into the porphyrin ring.

The activation energies were determined from the slopes of Arrhenius plots for the  $Zn^{2+}-H_2T^tBHPP$  reactions. These in turn are used to obtain the other activation parameters. The values of  $\Delta G^\ddagger$  are almost constant even when the counterion for zinc(II) was varied. It is notable that the free energy of activation is virtually constant for the seven different zinc(II) salts showing compensation effects. The enthalpies and entropies of activation are much more variable.

The activation parameters for the zinc(II) incorporation in DMF exhibit the compensation effects as shown in Fig. 4. These results suggest that all of the  $Zn^{2+}-H_2T^tBHPP$  reactions proceed via the same mechanism in DMF. This suggestion was confirmed by the zinc concentration dependence of the rate constants (Fig. 3). Anzai and Hatano [8] reported that the metal incorporation reaction consists of two steps: (i) formation of the metal-porphyrin intermediates (step A), and (ii) formation of a stable metalloporphyrin (step B). The mechanism can be written briefly as

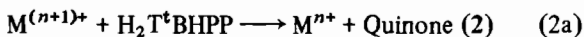
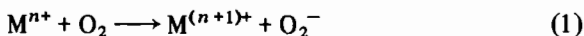


Either step A or step B is rate-limiting. If step A is rate-limiting, the reaction rate should be first-order in metal concentration. If step B is rate-limiting, the reaction rate should depend on the concentration of the intermediate complex,  $H_2P \cdots M^{2+}$ ,

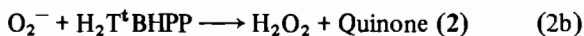
and therefore kinetic expression should not be as simple as in the first case. Since, in all the zinc salts used here,  $k_{obs}$  does not show a first-order dependence on the zinc concentration, step B is important in determining the overall rate ( $k_A > k_B$ ). All of these zinc ion incorporation reactions proceed via the same mechanism. This result is different from that observed in zinc ion incorporation into the 'picket fence porphyrin', in which step B is rate-determining in  $Zn(OAc)_2$ , while step A is suggested to be rate-determining ( $k_B > k_A$ ) in  $Zn(NO_3)_2$  [8].

A linear relationship was observed between the rate constants of the incorporation reactions of zinc(II) halides into  $H_2T^tBHPP$  and the differences in their electronegativities (Fig. 5). Figure 5 shows that the differences in the electronegativities decrease with increase of the reaction rate. This means that the weaker the ionic bonding between the zinc(II) ion and halides becomes, the higher the reaction rate becomes. These results suggest that in the incorporation step zinc(II) ion associates with  $H_2T^tBHPP$  via covalent bonding rather than via ionic bonding. This suggestion is in accordance with the observation that the rate constant in the chelate compound,  $Zn(AA)_2$ , is considerably large.

Finally, the metalation reactions of  $H_2T^tBHPP$  with metal ions other than zinc(II) were considered. Redox-active metal ions such as  $Mn^{2+}$ ,  $Co^{2+}$  and  $Cu^{2+}$  underwent redox reaction with  $H_2T^tBHPP$  to give the quinone (2) [10, 13, 14], rather than metalation reactions. In this case, the following mechanisms are possible: in the reactions of  $Mn^{2+}$  and  $Co^{2+}$  ions with  $H_2T^tBHPP$ , eqns. (1), (2a) or (2b) may occur, while in that of  $Cu^{2+}$  ion with  $H_2T^tBHPP$ , eqn. (2a) should mainly occur.



and/or



In the metalation reactions of the non-redox metal ions such as Cd(II), Ni(II), Mg(II), Pd(II), Ca(II), Sr(II), Sn(II) and Pb(II) with  $H_2T^tBHPP$ , Cd(II) and Pd(II) were easily incorporated into porphyrin as well as Zn(II). However, Ni(II) did not incorporate below 45 °C. Mg(II), Ca(II), Sr(II), Sn(II) and Pb(II) were not incorporated under the experimental conditions examined. The order of the rates of metal ion incorporation under comparable concentration and temperature is  $Pd(II) > Zn(II) > Cd(II) > Ni(II) \gg Mg(II), Ca(II), Sr(II), Sn(II)$  and  $Pb(II)$ .

As shown in Fig. 6, the reactions exhibit the compensation effects which suggest that the various

metals are incorporated into  $H_2T^tBHPP$  by similar mechanisms to that of the zinc(II) case.

### Conclusions

Zinc(II) ions are easily incorporated into polyvalent porphyrin,  $H_2T^tBHPP$ . The bulky substituent, tert-butyl groups in the *meta* position, does not affect these reactions. All of the  $Zn^{2+}$ -porphyrin reactions proceed via the same mechanism in DMF.

Other metal ions such as Cd(II), Pd(II) and Ni(II) can incorporate into  $H_2T^tBHPP$  by the same mechanism as Zn(II), because the incorporation reactions of these metal ions show the compensation effects. Redox-active metals such as Co(II), Mn(II) and Cu(II) gave the redox reaction prior to the metallation reaction.

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