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Kinetics and Mechanism of Metal Exchange Between Cadmium Porphyrin Complexes and *d*-Metal Salts in DMF

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Abstract—The metal-exchange reaction between cadmium 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrinate and zinc and copper acetates in DMF was studied. Kinetic Parameters of the metal-exchange reaction were determined. A possible stoichiometric reaction mechanism was proposed.

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The structural diversity of metal porphyrins opens up possibilities for their application in various fields. Metal porphyrins are promising candidates for application in photodynamic therapy of oncological diseases [1, 2], design of high-selectivity catalysts and organic semiconductors [3–5], as well as coloring pigments [6]. Metal exchange is one of the principal reactions of porphyrin complexes. Metal-exchange reactions are widely used for the synthesis of hardly accessible complexes of natural and synthetic porphyrins [7, 8], fluorescence labels, metal nanoclusters, as well as for other preparative and analytical purposes [9].

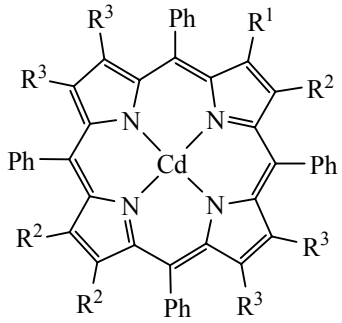
The aim of the present work was to find out how the nature of both the β-substituent in cadmium tetraphenylporphyrines and the metal salt affect the rate of their metal exchange. To this end, we studied the metal-exchange reactions between cadmium 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrinate ($CdTPPBr_8$) and $Cu(OAc)_2$ and $Zn(OAc)_2$ in DMF. The rate constants of these reactions were compared with the rate constants of the metal-exchange reactions of cadmium 2-bromo-5,10,15,20-tetraphenylporphyrinate (CdTPPBr) and cadmium tetraphenylporphyrinate (CdTPP) with the same salts in DMF. A mechanism of the metal-exchange between $CdTPPBr_8$ and $Cu(OAc)_2$ and $Zn(OAc)_2$ in DMF was proposed.

The rate of the exchange reaction and its kinetic parameters depends on the equilibrium constants of intermediate formation, which depends on the chemical structure of the salt solvate and the metal porphyrin, steric hindrances created by the more or less rigid porphyrin ring, and the associated electronic effects of coordination. A strong effect of the solvent is not also excluded. To gain insight into the mechanism of the metal-exchange reaction in porphyrins and phthalocyanines, one has to study in detail all the above-mentioned factors, taking into account their strong interrelationship.

The metal-exchange reaction equation can take the following general form:

$$CdP + M(OAc)_2(Solv)_{n-2} \rightarrow Cd(OAc)_2(Solv)_{n-2} + M. \quad (1)$$

Here CdP and MP are metal prophyrins, $M(OAc)_2 \cdot (Solv)_{n-2}$, salvation complexes of metal acetates, and n, the maximum coordination number of the salt cation.



CdTPP: $R^1 = R^2 = R^3 = H$ (**I**); CdTPPBr: $R^1 = Br$, $R^2 = R^3 = H$ (**II**); $CdTPPBr_4$: $R^1 = R^2 = Br$, $R^3 = H$ (**III**); $CdTPPBr_8$: $R^1 = R^2 = R^3 = Br$ (**IV**).

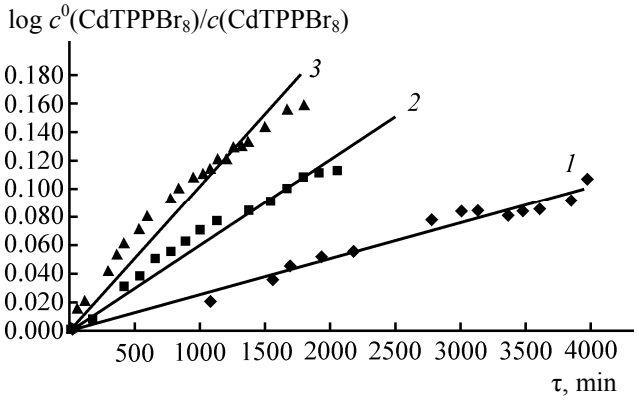


Fig. 1. Dependence of log [c^0(CdTPP)/c(CdTPP)] on the reaction time of CdTPPBr$_8$ with Zn(OAc)$_2$ in DMF at c[Zn(OAc)$_2$] 1.5×10^{-3} M and T (*1*) 298, (*2*) 308, and (*3*) 318 K.

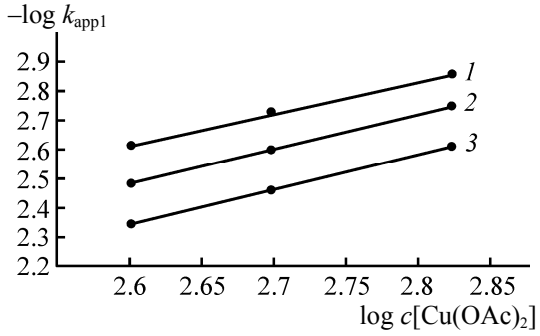


Fig. 2. Dependence of log k_{app1} on log c[Zn(OAc)$_2$] in the metal-exchange reaction of CdTPPBr$_8$ with Cu(OAc)$_2$ in DMF at T (*1*) 288, (*2*) 293, and (*3*) 298 K.

Two stoichiometric mechanisms (associative and dissociative) were suggested in the literature for the metal-exchange reactions in macrocyclic [10] and porphyrin complexes [9, 11].

The metal exchange of CdTPPBr$_8$ with Cu(OAc)$_2$ and Zn(OAc)$_2$ in DMF follows a first-order reaction equation in cadmium porphyrinate concentration. This is evidenced by a straight-line dependence of log c^0(CdTPPBr$_8$)/c(CdTPPBr$_8$) on reaction time τ. Figure 1 shows the log c^0(CdTPPBr$_8$)/c(CdTPPBr$_8$) = f(τ) dependences for the reaction of CdTPPBr$_8$ with Zn(OAc)$_2$ in DMF. The reaction order in salt concentration, determined as the slope of the straight-line dependence of log k_{app1} on log c[Cu(OAc)$_2$] and log k_{app2} on log$c$[Zn(OAc)$_2$], is equal to 1 (Figs. 2, 3). Thus, the kinetic equation of reaction (1) takes the following form.

$$-dc\mathrm{CdP}/d\tau = k_v[\mathrm{CdP}][\mathrm{M(OAc)_2}]. \quad (2)$$

Figure 4 shows the spectral changed in the course of the metal-exchange reaction between CdTPPBr$_8$ and Cu(OAc)$_2$ in DMF.

The resulting kinetic data for the exchange of cadmium for copper and zinc in CdTPPBr$_8$ (Tables 1 and 2) suggest an associative mechanism of reaction (1) in both cases [9, 12]. The first stage is likely to involve intermediate formation.

$$\mathrm{CdP} + [\mathrm{M(Solv)}_{n-2}(\mathrm{OAc})_2] \xrightleftharpoons{\text{fast}} [\mathrm{CdPM(Solv)}_{n-4}]^{2+}\cdots 2(\mathrm{OAc})^- + 2\mathrm{Solv}, \quad (3)$$

Solv = DMF.

The second, monomolecular limiting stage involves slow dissociation of the intermediate to form a stronger metal complex and cadmium salt solvate.

$$[\mathrm{CdPM(Solv)}_{n-4}]^{2+}\cdots 2(\mathrm{OAc})^- \xrightarrow{\text{slowly}} \mathrm{MP} + [\mathrm{Cd(OAc)_2(Solv)}_{n-2}]. \quad (4)$$

Comparison of the apparent rate constants of the metal-exchange reactions between copper and zinc acetates and CdTPP and CdTPPBr in DMF [13–15] shows that the introduction of one bromine substituent into the β-pyrrole position of the macroring accelerates the reaction by about an order of magnitude. This fact is probably explained by a weakening of the Cd–N σ-bond due to the $-I$ effect of the bromine atom. The apparent rate constants of the metal-exchange reactions between CdTPPBr$_8$ and Cu(OAc)$_2$ and Zn(OAc)$_2$ in

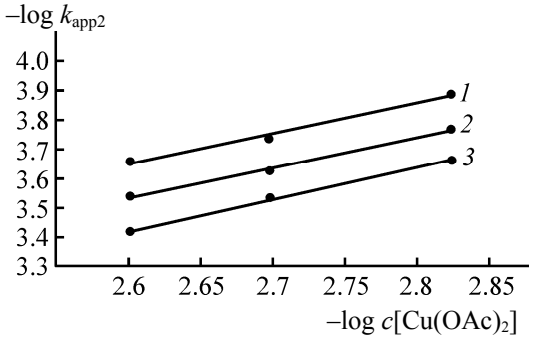


Fig. 3. Dependence of log k_{app2} on log c[Zn(OAc)$_2$] in the metal-exchange reaction of CdTPPBr$_8$ with Cu(OAc)$_2$ in DMF at T (*1*) 298, (*2*) 308, and (*3*) 318 K.

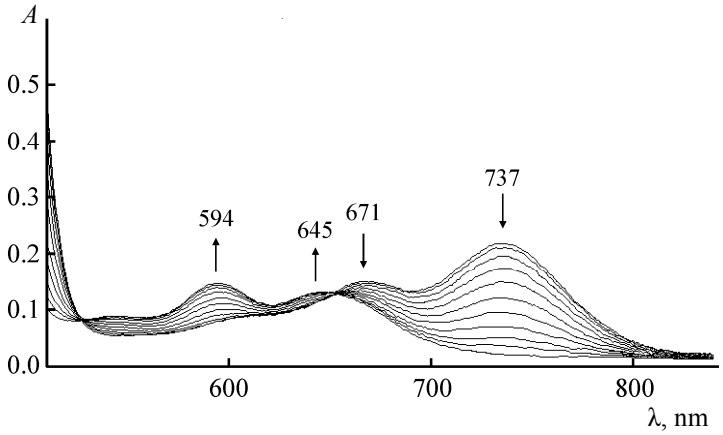


Fig. 4. Change of the electronic absorption spectrum in the course of the metal-exchange reaction of $CdTPPBr_8$ with $Cu(OAc)_2$ in DMF at $c(CdTPPBr_8)$ 2.5×10^{-5} M, $c[Cu(OAc)_2]$ 2.5×10^{-3} M, T 298 K.

Table 1. Exchanges rates of Cd^{2+} for Zn^{2+} in $CdTPPBr_8$ in DMF [$c(CdTPPBr_8)$ 2.5×10^{-5} M]

$c[Zn(OAc)_2]\times10^3$, M	T, K	$k_{app}\times10^4$, s^{-1}	k_v, L mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
2.5	298	2.17±0.12	0.09	22±1	–249±3
	308	2.87±0.18	0.11		
	318	3.80±0.17	0.15		
2.0	298	1.85±0.10	0.09	19±1	–261±3
	308	2.40±0.10	0.12		
	318	3.00±0.15	0.15		
1.5	298	1.30±0.08	0.09	21±1	–258±1
	308	1.70±0.09	0.11		
	318	2.20±0.14	0.15		

Table 2. Exchange rate of Cd^{2+} for Cu^{2+} in $CdTPPBr_8$ in DMF [$c(CdTPPBr_8)$ 2.5×10^{-5} M]

$c[Zn(OAc)_2]\times10^3$, M	T, K	$k_{app}\times10^3$, s^{-1}	k_v, L mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
2.5	288	2.47±0.11	0.99	44±4	–149±13
	293	3.30±0.20	1.32		
	298	4.60±0.29	1.84		
2.0	288	1.85±0.12	0.93	45±3	–150±9
	293	2.50±0.12	1.25		
	298	3.47±0.22	1.74		
1.5	288	1.40±0.08	0.93	41±5	–167±18
	293	1.80±0.08	1.20		
	298	2.47±0.12	1.65		

DMF are lower compared with those for the metal-exchange reactions of CdTPP and CdTPPBr and the same salts. This is probably explained of the conjugation effect of eight bromine atoms in $CdTPPBr_8$. We made an attempt to perform metal exchange between $CdTPPBr_4$ and $Cu(OAc)_2$ and $Zn(OAc)_2$ in DMF and found that under conditions, comparable with those for CdTPP, CdTPPBr, and $CdTPPBr_8$, these reactions reach equilibrium. Therefore, their rate constants could not be measured.

The metal-exchange reaction in porphyrin complexes is strongly affected both by the nature of the outgoing and ingoing metals and the nature of the surrounding solution, specifically, the type of the salt anion ad the solvent. Berezin et al. [16] found that the metal-exchange rate increases as the coordination ability of the anion X^- decreases in the series NO_3^- < Cl^- < < AcO^- < $acac^-$, on account of the weakening of the metal solvate M–X bond which is to be broken reaction (1). Under comparable conditions, the metal-exchange reaction between CdTPP and $Cu(NO_3)_2$ at c_{salt} 1.38×10^{-3} M occurs almost immediately. There-with, the Cd–Cu exchange in CdTPP occurs 80 times faster with $CuCl_2$ than with $Cu(OAc)_2$. With $Cu(acac)_2$ as a source of the substituting metal, the metal-exchange reaction is about 4.5 times slower than with $Cu(OAc)_2$.

Comparison of the data for the metal exchange between CdTPPc and $Cu(OAc)_2$ in DMSO [13] with our data for the metal exchange between CdTPP with the same salt in DMF [15] showed that the latter reaction is 5 times faster. As the solvation power of the solvent increases, the salvation shell of the salt generally tends to get stronger, thereby preventing metal exchange. Therefore, Berezin et al. [16] suggested that reaction (1) is favored by solvents with a moderate electron-donor function.

EXPERIMENTAL

Zinc and copper acetates were recrystallized from glacial acetic acid; DMF was purchased from Merck.

The metal-exchange reaction was studied on a Cary 100 Varian spectrophotometer. The temperature-controlled cell of the spectrophotometer was changed with $CdTPPBr_8$ and salt solutions of known concentrations. Measurements were performed at the absorption maxima of the complexes $ZnTPPBr_8$ (λ 647 nm) and $CuTPPBr_8$ (λ 593 nm), which are formed by the metal-exchanged reactions. The following temperature ranges were used: 288–298 K for the reaction of $CdTPPBr_8$ with $Cu(OAc)_2$ and 298–318 K for the reaction of $CdTPPBr_8$ with $Zn(OAc)_2$. The salt concentrations $c[Cu(OAc)_2]$ and $c[Zn(OAc)_2]$ in both cases were 1.5×10^{-3}–2.5×10^{-3} M.

The current concentration of $CdTPPBr_8$ was calculated by Eq. (5).

$$c = c^0(A_\infty - A_\tau)/(A_\infty - A_0). \quad (5)$$

Here A_0, A_τ , and A_∞ are the optical densities of the solution at the initial time moment, time τ, and after reaction completion and c^0 and c, initial and current $CdTPPBr_8$ concentrations, respectively.

The apparent rate constants k_{app} were calculated by Eq. (6).

$$K_{app} = (1/\tau)\ln (c^0/c). \quad (6)$$

The activation energy E_a were calculated by the Arrhenius equation (7).

$$E_a = 19.1 \frac{T_1T_2}{T_2 - T_1} \log \frac{k_2}{k_1}. \quad (7)$$

The activation entropy $\Delta S^{\neq}$ was calculated by Eq. (8).

$$\Delta S^{\neq} = 8.314\ln k_{298} + E_a/298 - 253.22. \quad (8)$$

The experimental data are presented in Tables 1 and 2.

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