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Reaction of Metal Exchange of Cadmium 5,10,15,20-Tetraphenylporphyrinate and Its β-Bromo Derivative with Zinc Acetate in Dimethylformamide

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Abstract—Metal exchange of cadmium 5,10,15,20-tetraphenylporphyrinate (CdTPP) and cadmium 2-bromo-5,10,15,20-tetraphenylporphyrinate (CdTPPBr) with zinc acetate in dimethylformamide was spectrophotometrically examined. The kinetic parameters of the metal exchange reaction were determined. A possible stoichiometric mechanism of the reaction was suggested. The effect of the bromo substituent in β -position of the pyrrole in the cadmium tetraphenylporphyrinate on the metal exchange reaction with Zn(OAc)₂ in DMF was found.

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Interest to the synthesis of metal porphyrins (MP) is associated with the development of modern trends in the chemistry of porphyrins. Metal complexes of porphyrins are studied in chemistry of supramolecular architecture, structures for electron transport, selforganizing systems, biosensors, etc. One of the important reactions, which may include the porphyrin complexes, is the metal exchange. Metal exchange reactions have found wide application in the synthesis of low-accessible complexes of natural and synthetic porphyrins. For this purpose readily available complexes of porphyrins and phthalocyanines [1, 2] are used as starting materials. Thus, the palladium complex with octaphenyltetraazaporphyrin (PdOPhTAP) was synthesized according to the simplified procedure [2] in boiling dimethylformamide starting from MgOPhTAP and PdCl₂. Furthermore, the metal exchange reaction in Mg-complexes of chlorophyll derivatives may be used for the synthesis of the stable ecofriendly dyes of chlorophyll series [3] and to create anti-cyanide drugs [4].

Almost all metal exchange reactions involve the transition metal salts as various solvate complexes [5]. The equation of the metal exchange reaction can be generally presented as follows:

$$CdP + M(OAc)_2(Solv)_{n-2}$$

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

Here CdP and MP are metalloporphyrins, $M(OAc)_2(Solv)_{n-2}$ is solvate complex of metal acetates.

In this work we studied the effect of monobromosubstitution in β -position of the pyrrole of cadmium tetraphenylporphyrinate and the nature of the metal ions on the rate of metal exchange reaction of cadmium 5,10,15,20-tetraphenylporphyrinate (CdTPP) and cadmium 2-bromo-5,10,15,20-tetraphenylporphyrinate (CdTPPBr) with zinc acetate in dimethylformamide.



CdTPP: R = H; CdTPPBr: R = Br.



Fig. 1. Dependence of log ([CdTPP]₀/[CdTPP]) on time of the reaction of CdTPP with Zn(OAc)₂ in DMF at $[Zn(OAc)_2] = 1.5 \times 10^{-3}$ M and T 288 (1), 293 (2), 298 K (3).



Fig. 3. Dependence of log k_{ef} on log $c[Zn(OAc)_2]$ of the reaction of CdTPP with $Zn(OAc)_2$ in DMF at *T* 288 (*1*), 293 (*2*), 298 K (*3*).

The metal exchange reaction (1) corresponds to the complex associative and dissociative type of chemical reactions [6]. In the elementary chemical act occurs simultaneous dissociation of one complex and formation of another. There is not only metal exchange (Cd, and Zn), but also the ligands exchange (P^{2-} and Solv). By classical concepts [6], the reaction (1) belongs to the substitution reactions, in contrast to the addition and decomposition reactions of the chemical compounds.

Experimental data show that the rate of the metal exchange reaction of CdTPP and CdTPPBr with $Zn(OAc)_2$ in DMF is described as the first order reaction with respect to the complex concentration as evidenced by the linear dependence: log ([CdTPP]₀/[CdTPP]) = $f(\tau)$ and log ([CdTPPBr]/[CdTPPBr]) = $f(\tau)$, respectively (Figs. 1, 2). The reaction order with respect to the salt, determined as the slope of the linear dependence log $k_{ef1} = f(\log [Zn(OAc)_2]_0)$ and log $k_{ef2} = f(\log [Zn(OAc)_2]_0)$ in the case of the metal exchange between CdTPP or CdTPPBr with Zn(OAc)₂ in DMF, respectively, is 1 (Figs. 3, 4). Thus, the overall rate of the metal exchange reaction obeys the second-order kinetic Eq. (2).



Fig. 2. Dependence of log ([CdTPPBr]₀/[CdTPPBr]) on time of the reaction of CdTPPBr with Zn(OAc)2 in DMF at $[Zn(OAc)_2] = 1.5 \times 10^{-3}$ M and *T* 288 (*1*), 293 (*2*), 298 K (*3*).



Fig. 4. Dependence of log k_{ef} on log $c[Zn(OAc)_2]$ of the reaction of CdTPPBr with $Zn(OAc)_2$ in DMF at *T* 288 (*1*), 293 (*2*), 298 K (*3*).

$$-dc_{\rm CdP}/d\tau = k_{\rm v}[\rm CdP][M(OAc)_2].$$
 (2)

Our results on the kinetics of the metal exchange reaction of CdTPP and CdTPPBr with $Zn(OAc)_2$ in DMF (Fig. 5, Tables 1, 2) suggest that the reaction (1) proceeds by an associative mechanism [4, 7, 8]. At the first step of this process an intermediate is likely to be rapidly formed [Eq. (3)].

$$CdP + [Zn(Solv)_{n-2}(OAc)_2]$$

$$\xrightarrow{quickly} [Cd-P-Zn(Solv)_{n-4}]^{2+} \cdots 2(OAc)^{-} + 2Solv, \quad (3)$$

$$Solv = DMF.$$

In the second monomolecular rate-limiting step, the intermediate decays slowly to form a more stable complex of Zn^{2+} and cadmium solvate salt [Eq. (4)].

$$[Cd-P-Zn(Solv)_{n-4}]^{2^+\cdots 2}(OAc)^-$$
slowly
$$ZnP + [Cd(OAc)_2(Solv)_{n-2}].$$
(4)

Data from Tables 1 and 2 show that the true rate constants (k_v) of the metal exchange reactions of CdTPP and CdTPPBr with $Zn(OAc)_2$ in DMF do not depend on the salt concentration. Therefore, in the

studied concentration range of the salt the structure of its coordination sphere does not change. This is in good agreement with the literature data [9].

Comparing the effective rate constants of the metal exchange of zinc acetate with CdTPP and CdTPPBr in DMF, we observed the effect of monobromosubstitution in β -position of the pyrrole of CdTPP. The incorporation of one bromine atom in the resulting macrocycle leads to a 5-fold increase in the rate of the metal exchange. This is probably due to a weakening of Cd–N σ-bond owing to the negative inductive effect of the bromine atom. Analysis of the influence of the nature of the metal cation of salt (Cu^{2+} and Zn^{2+}) on the metal exchange reaction of CdTPP and CdTPPBr with copper acetate in DMF shows that the reaction rate $(k_{ef}^{2\%} 8.0 \times 10^{-3} \text{ s}^{-1} \text{ and } k_{ef}^{2\%} 1.4 \times 10^{-2} \text{ s}^{-1}$, respectively) is comparable to the rate of the metal exchange reaction of cadmium porphyrinates with zinc acetate in DMF.

In [10] the dissociation of Cd(II)- and Zn(II)containing chlorophyll analogs were studied in detail. The Cd–N bond is ionic with a small degree of



Fig. 5. Variations in electronic spectra in the course of reaction of CdTPP with $Zn(OAc)_2$ in DMF at [CdTPP] = 2.5×10^{-5} M, [Zn(OAc)_2] = 2.5×10^{-3} M at initial time (1) and after 35 min (2), T 288 K.

covalence, and the energy of Cd–N bonds is compensated by the energy of solvation of Cd²⁺ cation. These findings can be attributed to the metal exchange reaction of Cd²⁺ with Zn²⁺. The low stability of cadmium porphyrinate promotes successful attack of the complex solvates $ZnX_2(Solv)_{n-2}$, which unlike Cd²⁺ form the ionic-covalent bonds of a high covalence with the nitrogen atoms of a coordination center of the tetrapyrrole macrocycle. This contributes to the easy

$c[Zn(OAc)_2] \times 10^3$, M	<i>T</i> , K	$k_{\rm ef} \times 10^2, {\rm s}^{-1}$	$k_{\rm v}$, 1 mol ⁻¹ s ⁻¹	$E_{\rm a}$, kJ mol ⁻¹	ΔS^{\neq} , J mol ⁻¹ K ⁻¹
2.5	288	1.60±0.09	0.64	56±27	-117±89
	293	2.90±0.11	1.16		
	298	3.50±0.09	1.40		
2.0	288	1.40±0.03	0.70	49±27	-138±89
	293	2.40±0.15	1.20		
	298	2.80±0.15	1.40		
1.5	288	1.00±0.06	0.67	55±28	-115±94
	293	1.80±0.04	1.20		
	298	2.20±0.09	1.47		

Table 1. Rate of the metal exchange between Cd^{2+} and Zn^{2+} in CdTPP complex in DMF ($c_{CdTPP} 2.5 \times 10^{-5} \text{ M}$)

Table 2. Rate of the metal exchange between Cd^{2+} and Zn^{2+} in CdTPPBr complex in DMF ($c_{CdTPP} 2.5 \times 10^{-5} \text{ M}$)

$c(\text{ZnAc}_2) \times 10^3$, M	Т, К	$k_{\rm ef} \times 10^2$, s ⁻¹	$k_{\rm v}$, 1 mol ⁻¹ s ⁻¹	$E_{\rm a}$, kJ mol ⁻¹	ΔS^{\neq} , J mol ⁻¹ K ⁻¹
2.5	288	0.88±0.01	3.52	49±8	-123±27
	293	1.32 ± 0.02	5.28		
	298	1.75±0.10	7.00		
2.0	288	0.73±0.03	3.65	43±19	-143±64
	293	1.14 ± 0.03	5.70		
	298	1.35±0.07	6.75		
1.5	288	0.58±0.01	3.87	48±5	-129±18
	293	0.85 ± 0.03	5.67		
	298	$1.14{\pm}0.06$	7.60		

formation of an intermediate in reaction (1), if the formation of the chemical bond M–N compensates the energy consumption for detachment of two solvent molecules from the complex solvate salt.

Thus, the metal exchange reaction of cadmium 5,10,15,20-tetraphenylporphyrinate and cadmium 2bromo-5,10,15,20-tetraphenylporphyrinate with zinc acetate in dimethylformamide was spectrophotometrically studied. The kinetic parameters of the metal exchange reaction were examined. A possible stoichiometric mechanism of the reaction was suggested. The incorporation of one bromine atom into the β position of the pyrrole ring of the macrocycle accelerates the metal exchange reaction with zinc acetate in dimethylformamide about 5 times.

EXPERIMENTAL

Cadmium tetraphenylporphyrinate was synthesized and purified according to the known literature procedure [11]. Cadmium 2-bromo-5,10,15,20-tetraphenylporphyrinate was prepared as described in [11, 12]. The identification was carried out by electron absorption spectra, ¹H NMR, and IR spectra that are fully consistent with those described in the literature. Zinc acetate was recrystallized from glacial acetic acid. DMF (Merck) was used in the experiments.

Spectrophotometric study of the metal exchange reactions was carried out on a Cary 100 Varian spectrophotometer. The experimental procedure and the processing of the experimental data is described in [7]. Measurements were made at a wavelength corresponding to the maximum absorption band of the complexes formed [ZnTPP (λ 558 nm) and ZnTPPBr (λ 562 nm)].

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