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On the Mechanism of the Metal Exchange in Natural Cadmium Porphyrins

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Abstract—The kinetics of the exchange of the Cd^{2+} ions in the complexes with the natural protogroup porphyrins (protoporphyrin, mesoporphyrin, deuteroporphyrin, and hematoporphyrin) for the Zn^{2+} ions is studied. The stoichiometric ratios of components in the reaction of cadmium exchange for zinc in acetonitrile and DMSO are established. The results obtained are compared with the previously published data for the reaction with the Co^{2+} ions. The activation mechanism of the metal exchange reaction is considered, depending on the effect of the nature of substituents in porphyrin, *d*-metal ions, and a solvent.

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Previously [1, 2], we studied the metal exchange kinetics, using the reactions of cadmium mesoporphyrin and protoporphyrin with Co(II) and Zn(II) chlorides in acetonitrile and DMSO, and the changes in the metalloporphyrin spectra during this process. The metal exchange reaction can be written as follows:

$$CdP + MCl_2(Solv)_{n-2} \longrightarrow CdCl_2(Solv)_{n-2} + MP, \quad (1)$$

where CdP and MP are metalloporphyrins, $MCl_2(Solv)_{n-2}$ are the solvation complexes of metal chlorides [3].

It is known [4] that in centimolar solutions of acetic acid in ethanol, CdChl (Chl is the chlorophyll-ligand) dissociates readily with Cd^{2+} elimination. The rate of the Cd complex dissociation increases rapidly with the increasing CH_3COOH concentration. This is explained by an increase in the concentration of solvated proton $C_2H_5OH_2^+$ and by the growth in the chemical activity of the CH_3COOH molecules, which lose their solvation shell as the molar fraction of C_2H_5OH is decreased in a binary solution. We assume that the dissociation of cadmium porphyrins in ethanol–acetic acid mixture occurs in two routs:

$$CdP + 2C_2H_5OH_2^+ \longrightarrow [Cd(C_2H_5OH)_2]^{2+} + H_2P, \quad (2)$$

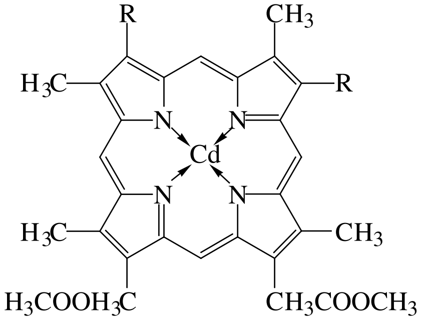
and

$$CdP + 2CH_3COOH \longrightarrow Cd(CH_3COO)_2 + H_2P. \quad (3)$$

Cadmium porphyrins are known not to undergo solvolytic dissociation [1]. The $CH_3COOH_2^+$ concentration is negligible and, hence, the CdP dissociation cannot follow the other route. The above factors of CdP dissociation in solutions should be taken into consideration, when the other sources of solvated protons can appear in reaction (1). In experiments performed in [1, 2], use was made of aprotic solvents and therefore protons did not participate in exchange reaction (1). It has been shown also that reaction (1) of cadmium exchange for zinc and cobalt is a two-stage bimolecular reaction, which is described by the kinetic equation of the second-order reaction:

$$-dc_{CdP}/dt = k_v[CdP][MCl_2]. \quad (4)$$

The bimolecular (true) rate constant ($\boldsymbol{k_v}$) depends not only on the nature of a solvent and metal salt, but also on the metal salt concentration.



CdDP: R = H — cadmium deuteroporphyrin;
CdGP: R = $CH(OCH_3)CH_3$ — cadmium hematoporphyrin;
CdMP: R = C_2H_5 — cadmium mesoporphyrin;
CdPP: R = CH=CH_2 — cadmium protoporphyrin.

In this work, the rates of reaction (1) of cadmium exchange in its complexes with proto-, meso-, hemato-, and deuteroporphyrins for zinc are measured in acetonitrile and DMSO and the kinetic parameters—k_v, E, and $\Delta S^{\#}$ of this reaction are calculated.

EXPERIMENTAL

The porphyrin-ligands and their complexes were prepared by a known procedure [5]. Pure grade acetonitrile was distilled twice over P_2O_5; chemically pure grade DMSO was distilled under reduced pressure. The kinetic measurements were performed on Specord M40 and SF-26 spectrophotometers in the temperature interval 298–318 K at $ZnCl_2$ concentration $(2.09–3.92) \times 10^{-2}$ mol/l. The reaction rate was determined from the change in the optical density of CdGP and CdDP solutions in the electronic absorption spectra at the operating wavelengths $\lambda = 554$ and 550 nm, respectively. The procedure used for calculation of the CdP current concentration and of the kinetic parameters was described in [2]. The changes in the electronic absorption spectra of a CdDP solution in DMSO during metal exchange reaction are shown in Figs. 1, 2; the kinetic data are given in Tables 1, 2.

RESULTS AND DISCUSSION

The metal exchange reaction (1) in the coordination center of metalloporphyrins is the most complex reaction of all the known reaction types [6]. This reaction involves all types of interactions, except for redox (transfer of lone electrons) and acid-base (transfer of protons) interactions. According to classification [6], reaction (1) is the association–dissociation complex formation reaction. In this case, the elementary chemical event consists of simultaneously occurring dissociation of one complex and the formation of the other complex. The above classification is based on the fact that the principal objects of the chemical event are the

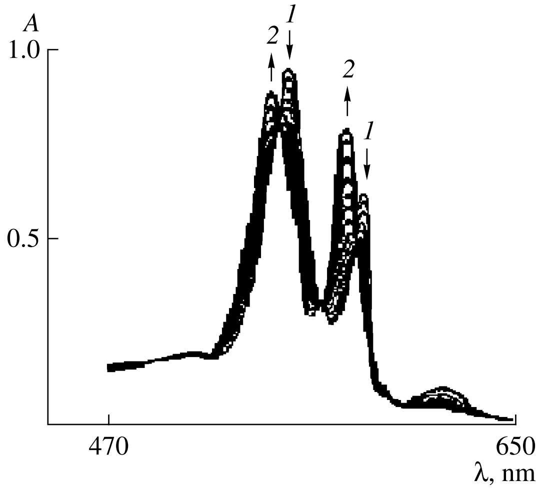


Fig. 1. The changes in the electronic absorption spectra of CdDP solution in reaction with $ZnCl_2$ in DMSO at $c^0_{\mathrm{CdDP}} = 4.6 \times 10^{-5}$, $c^0_{\mathrm{ZnCl_2}} = 7.83 \times 10^{-2}$ mol/l: (*1*) at the initial moment, (*2*) in 120 min.

Table 1. The kinetic parameters of metal exchange reaction (1) between Cd(II) complexes with porphyrins of protoporphyrin group and chlorides of Co(II) [1, 2] and Zn(II) in acetonitrile

Cd porphyrinate	$c_{\mathrm{salt}} \times 10^4$, mol/l	T, K	k_v^{298} of reaction (1), l mol^{-1} s^{-1}	Activation energy E, kJ/mol	Activation entropy $\Delta S^{\#}$, J/(mol K)*
CdMP	$CoCl_2$	298	0.84	30	–210
	1.73	308	1.28		
		318	1.78		
	$CoCl_2$	298	0.35	27	–214
	3.24	308	0.53		
		318	0.71		
CdPP	$CoCl_2$	298	13.0	31	–228
	0.245	308	20.1		
		318	28.3		
	$CoCl_2$	298	13.6	31	–222
	0.460	308	21.3		
		318	30.1		
	$ZnCl_2$	298	0.048	31	–227
	6.13	308	0.071		
		318	0.104		
	$ZnCl_2$	298	0.047	29	–224
	11.50	308	0.070		
		318	0.099		

* The activation energy and entropy were determined to within 8 kJ/mol and 16 J/(mol K), respectively.

Table 2. The kinetic parameters of metal exchange reaction (1) between Cd(II) complexes with porphyrins of protoporphyrin group and Zn(II) chloride in DMSO

Cd porphyrinate	$c_{\text{salt}} \times 10^4$, mol/l	T, K	k_v^{298} of reaction (1), l mol^{-1} s^{-1}	Activation energy E, kJ/mol	Activation entropy $\Delta S^{\#}$, J/(mol K)*
CdMP	$ZnCl_2$	298	0.45	55	–135
	1.17	308	1.00		
		318	1.86		
	$ZnCl_2$	298	0.48	56	–130
	2.19	308	0.91		
		318	1.97		
CdPP	$ZnCl_2$	298	0.71	59	–142
	209	308	1.36		
		318	3.15		
	$ZnCl_2$	298	0.74	52	–137
	392	308	1.40		
		318	2.77		
CdGP	$ZnCl_2$	298	0.015	29	–173
	209	308	0.022		
		318	0.035		
	$ZnCl_2$	298	0.014	30	–173
	261	308	0.022		
		318	0.035		
	$ZnCl_2$	298	0.015	26	–173
	339	308	0.027		
		318	0.035		
	$ZnCl_2$	298	0.015	28	–173
	392	308	0.023		
		318	0.036		
CdDP	$ZnCl_2$	298	0.015	66	–95
	209	308	0.035		
		318	0.081		
	$ZnCl_2$	298	0.016	66	–93
	261	308	0.035		
		318	0.084		
	$ZnCl_2$	298	0.017	67	–90
	339	308	0.038		
		318	0.091		
	$ZnCl_2$	298	0.016	70	–90
	392	308	0.038		
		318	0.092		

* The activation energy and entropy were determined to within 8 kJ/mol and 16 J/(mol K), respectively.

metal cations, in particular, their salts. If the principal object of reaction (1) is taken to be the porphyrin ligand and the ligands in the inner coordination sphere of the *d*-metal salt, then reaction (1) will be the ligand exchange reaction.

In accordance with the classical concepts [7], both approaches described above lead to substitution reactions, unlike the addition and destruction reactions. It is most reasonable to use the above considerations in order to establish the mechanism of reaction (1). The first conclusions on the mechanism were made in [1, 2, 8, 9] and the reactions of metal exchange between Mg and Cd porphyrin complexes and bivalent metal chlorides were shown to be two-stage bimolecular reactions. At the first bimolecular stage, the intermediate binuclear complex (intermediate) is formed:

$$\mathrm{CdP} + \mathrm{MX}_2(Solv)_{n-2} \rightleftarrows (Solv)_m\mathrm{CdP}\cdot\mathrm{MX}_2(Solv)_{n-4}. \quad (5)$$

The intermediate can form immediately after the solutions are poured together and can be easily identified by the spectral method. However, this stage can be also retarded.

At the second slow monomolecular stage, the intermediate undergoes dissociation:

$$\begin{aligned}&(Solv)_m\mathrm{CdP}\cdot\mathrm{MX}_2(Solv)_{n-4}\\ &\rightleftarrows [\mathrm{X}_2\mathrm{Cd}^{2+}\cdots\mathrm{P}^{2-}\cdots\mathrm{M}^{2+}(Solv)_m]^{\#} \qquad (6)\\ &\longrightarrow \mathrm{CdX}_2(Solv)_m + \mathrm{MP}(Solv)_{n-4}.\end{aligned}$$

This stage is accompanied by the change in the absorption band intensities in the electronic absorption spectra with time (Fig. 1, 2).

The situation may happen, when the energetic and kinetic conditions for entering of a new metal (M') into the complex and removal of an old metal (M) from the complex are the same. In the Cd complexes under study, the above situation was not observed. However, the concentrations of components (metalloporphyrin–metal salt–solvent) can be chosen in such a way, that the above conditions will be realized. In this case, the exchange reaction will be bimolecular, but will proceed in one stage though a single transition state (6). We did not observe such cases in our experiments so far.

In a series of reactions (5) and (6) with porphyrins of protoporphyrin group (blood group), of particular interest are the reactions with the alkyl substituents in 2,4-positions of porphyrin. The functional substitution in a series hydrogen atom ⟶ ethyl ⟶ vinyl ⟶ 1-methoxyethyl affects both the rates of the reactions of metalloporophyrin formation

$$\mathrm{H}_2\mathrm{P} + \mathrm{MX}_2(Solv)_{n-2} \xrightarrow{k_V^{\mathrm{form}}} 2\mathrm{HX} + \mathrm{MP} + (n-2)Solv, \quad (7)$$

which in the most cases are chemically irreversible reactions, and on the rates of solvatoprotolytic dissociation reactions

$$\mathrm{MP} + 2\mathrm{H}^+(Solv) \xrightarrow{2\mathrm{X}^-} \mathrm{H}_2\mathrm{P} + \mathrm{MX}_2(Solv)_{n-2}, \quad (8)$$

which are also irreversible.

The effect of substituents, both of σ-electron-donors (C_2H_5) and π-electron-donors ($CH{=}CH_2$) should manifest in the strength of the porphyrin N–M bonds and hence, in the rate of formation (7) and dissociation (8) of Cd and Zn porophyrins. The rates of CdP and ZnP formation are almost identical [10]; the rates of their dissociation reactions differ greatly. The cadmium complex with a natural chlorophyll-ligand (CdChl) dissociates at a rate of 2×10^{-4} and 4×10^{-3} s^{-1} l mol^{-1} in solutions of a 0.04 M and a 0.10 M acetic acid in ethanol, respectively (at 25°C); according to the extrapolation data, ZnChl does not almost dissociate under these conditions ($k = 4 \times 10^{-9}$ s^{-1} l mol^{-1} at 25°C). It thus follows that the ZnChl complex strength determined by the stability constant is 10^6 times as high as that of the CdChl complex [11].

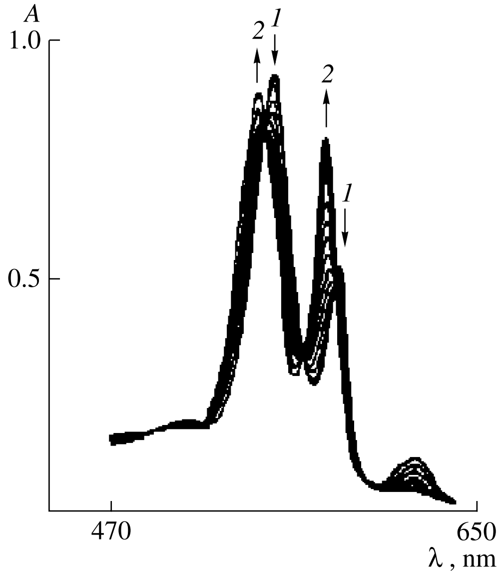
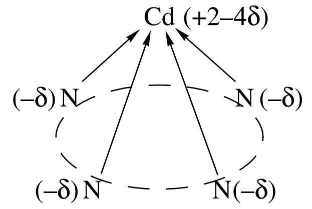


Fig. 2. The change in the electronic absorption spectra of CdGP in reaction with $ZnCl_2$ in acetonitrile at c^0_{CdDP} = 4.6×10^{-5}, $c^0_{\mathrm{ZnCl_2}}$ = 7.83×10^{-2} mol/l: (*1*) at the initial moment, (*2*) in 100 min.

The thermodynamic and kinetic parameters of the CdChl dissociation were estimated in [11]. The energy of cleavage of the Cd–N bonds is compensated due to the energy of Cd^{2+} solvation and protonation of two N atoms of the P^{2-} anion in the transition state. The Cd–Chl bond has the ionic nature.



The conclusions made in [11] apply to the Cd and Zn complexes with the protogroup porphyrins and, hence, to the exchange reaction (1). As follows from [10, 11], the exchange of Cd^{2+} for Zn^{2+} is energetically advantageous. A considerable negative charge on the CdP N atoms involved in coordination favors the attack of $\mathrm{Zn(X)_2}(Solv)_{n-2}$ solvation complex and the formation of the intermediate by reaction (5) at a high rate, provided that the energy of the Zn–N bond will compensate the energy of elimination of two DMSO molecules from its solvation salt. Such conditions are realized due to the occurrence of zinc salts in two coordination forms (tetrahedral and octahedral) and due to the equilibrium

$$Zn(X)_2(Solv)_4 \rightleftharpoons Zn(X)_2(Solv)_2 + 2Solv. \qquad (9)$$

The rate of the intermediate formation is expected to depend only slightly on the nature of the protogroup porphyrin, since the transition state has low energy and is mainly determined by rearrangement of the solvation salt structure. System (5) should further overcome a higher energy barrier. At this stage, the CdP dissociation, which depends on the nature of the functional groups [10], occurs simultaneously with the formation of ZnP, which also depends on the nature of porphyrin [12].

Based on the data available for the reactions of formation and dissociation of Cd and Zn porphyrins and the properties of solvation complexes of these metals with DMSO [3], one can tentatively predict subsequent transformations of the intermadiate into complexes. The removal of Cd as solvation salt or pure solvate $Cd(DMSO)_6^{2+}$ is energetically disadvantageous (the replacement of Cd–N by Cd–O requires some energy) and is kinetically hampered, since the DMSO attack of the Cd–N bond is required under sterically unfavorable conditions. The above removal is favorable at the highest vibronic level at the moment when Cd(II) is at maximum distance from the porphyrin plane [13]. Solvate of Zn(II) reacting with cadmium porphyrin should preliminarily dissociate at the Zn–X bonds (in this work, $X = Cl^-$), which is rather difficult in DMSO, since the latter readily solvates Zn^{2+}, but poorly solvates anions, particularly Cl^- and another halide ions. Therefore, the removal of both Cl^- and some DMSO from the inner sphere of Zn^{2+} is difficult. However, the energy spent on the above kinetically hindered processes is compensated by the energy of formation of stable ZnP complex.

The data in Table 1, 2 show that the rate constants of formation of Zn porphyrins from CdP are low and under standard conditions, they are equal to 0.46 (CdMP) and 0.73 (CdPP) $l\ mol^{-1}\ s^{-1}$, while for hemato- and deuteroporphyrins, the rate constants are $0.015\ l\ mol^{-1}\ s^{-1}$ on the average. As follows from Table 2, the value of k_v^{298} does not depend on the salt concentration, which means that it is exactly the form of a salt, whose concentration remains unchanged under the experimental conditions, that enters the reaction. It is important that in the exchange reraciton (1), the $CH(OCH_3)CH_3$ group in hematoporphyrin is equivalent in the electron-donor properties to the H atom, i.e., is electroneutral, whereas the ethyl group of mesopoephyrin and the vinyl group of protoporphyrin show the electron-donor properties only (+*I*- and +*C*-electron effects), which favor the metal exchange in DMSO. The results of Cd exchange for Co (Table 1) were discussed in [1, 2].

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