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Study of the Metal-Exchange Reaction between Cd(II) Octa(4-bromophenyl)tetraazaporphyrinate and Cobalt Chloride in Organic Solvents

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Abstract—The metal-exchange reaction between Cd(II) octa(4-bromophenyl)tetraazaporphyrinate and cobalt chloride in dimethylformamide and dimethyl sulfoxide was studied by spectrophotometry. Kinetic parameters of the metal-exchange reaction were determined. A possible stoichiometric mechanism of the reaction was proposed. Cobalt(III) octa(4-bromophenyl)tetraazaporphyrinate was synthesized and characterized.

Keywords: metal-exchange reaction, Cd(II) octa(4-bromophenyl)tetraazaporphyrinate, Co(III) octa(4-bromophenyl)tetraazaporphyrinate

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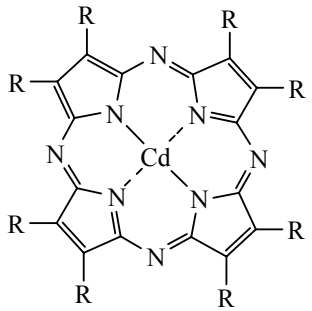
Natural porphyrins and their synthetic analogs have found application in many fields of medicine and technics [1]. A great number of biological systems are known, where metal porphyrins act as triggers of biological processes. Metal exchange is an important reaction of porphyrin complexes [2].

Metal exchange in porphyrin complexes is one of the least studied chemical reactions. According to the commonly accepted classification [3], the metal-exchange reaction (1) is an associative-dissociative chemical reaction.

$$MP + M'X_n(Solv)_{m-n} \rightarrow M'P + MX_n(Solv)_{m-n}. \quad (1)$$

Scheme 1.



I

R = 4-BrC_6H_4.

Here MP and M'P are metal porphyrins and $M'X_n(Solv)_{m-n}$, solvation complexes of the metals.

To gain insight into the regularities of the metal-exchange reaction and its mechanism, we have studied the metal-exchange reaction between Cd(II) octa(4-bromophenyl)tetraazaporphyrinate (**I**) with $CoCl_2$ in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (Scheme 1).

Figure 1 shows changes in the electronic absorption (EA) spectrum over the course of metal exchange of

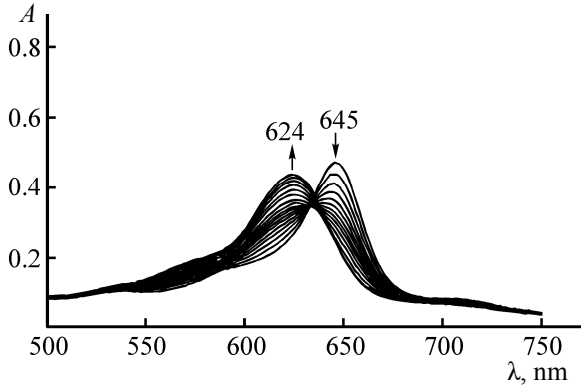


Fig. 1. Changes in the EA spectrum in the course of metal exchange between complex **I** and $CoCl_2$ in DMF at $c_{\mathbf{I}} = 2.5 \times 10^{-5}$ M, $c(CoCl_2) = 2.5 \times 10^{-3}$ M, 298 K.

Table 1. Kinetic parameters of metal exchange between Cd(II) octa(4-bromophenyl)tetraazaporphyrinate and $CoCl_2$ in DMSO[a] ($c_{\mathbf{I}} = 2.5 \times 10^{-5}$ M)

$c(CoCl_2) \times 10^3$, M	T, K	$k_{ef} \times 10^4$, s^{-1}	$k_v \times 10^2$, L mol^{-1} s^{-1}
2.5	298	2.64±0.15	10.56
	308	4.15±0.24	16.60
	318	5.99±0.30	23.96
2.0	298	2.12±0.06	10.60
	308	3.32±0.01	16.60
	318	4.62±0.25	23.10
1.5	298	1.61±0.05	10.73
	308	2.44±0.14	16.27
	318	3.45±0.17	23.00

[a] E_a^{av} = 31±3 kJ/mol, $\Delta S_{av}^{\neq}$ = –220±9 J mol^{-1} K^{-1}.

Table 2. Kinetic parameters of metal exchange between Cd(II) octa(4-bromophenyl)tetraazaporphyrinate and $CoCl_2$ in DMF[a] ($c_{\mathbf{I}} = 2.5 \times 10^{-5}$ M)

$c(CoCl_2) \times 10^3$, M	T, K	$k_{ef} \times 10^3$, s^{-1}	$k_v \times 10^2$, L mol^{-1} s^{-1}
2.5	288	1.59±0.04	0.64
	293	3.10±0.11	1.24
	298	7.29±0.44	2.92
2.0	288	1.41±0.09	0.71
	293	2.54±0.15	1.27
	298	4.89±0.12	2.45
1.5	288	1.02±0.02	0.68
	293	2.03±0.04	1.35
	298	4.29±0.10	2.86

[a] E_a^{av} = 100±9 kJ/mol; $\Delta S_{av}^{\neq}$ = 58±J mol^{-1} K^{-1}.

complex **I** with $CoCl_2$ in DMF. The resulting experimental data are listed in Tables 1 and 2.

It was found that the reaction order in $CoCl_2$ concentration as determined as the slope of the straight-line dependence $\log k_{app} = f(\log c_{salt})$ is 1 both in DMF and in DMSO (Figs. 2 and 3). The rate of metal exchange is first-order in complex **I**, as evidenced by a straight-line dependence of $\log (c_{CdP}^0/c_{CdP})$ on the reaction time τ (Figs. 4 and 5).

It was found that the metal-exchange reaction between complex **I** and $CoCl_2$ in DMF and DMSO occurs by an associative mechanism [4].

The rate of the metal-exchange reaction was found to be solvent-dependent. The reaction in DMSO is about 28 times slower than in DMF. This is associated with the fact that, as a rule, a better solvating solvent enhances the solvation shell of the salt, thereby hindering metal exchange.

Comparison of the apparent rate constants of the metal-exchange reactions of $CoCl_2$ with complex **I** (Table 1) and of $CoCl_2$ with Cd(II) octaphenyltetraazaporphyrinate (**II**) in DMSO (k_{app}^{298} 0.39 × 10^{-4} s^{-1}) revealed an effect of substituents in the phenyl rings. Eight bromine substituents in the macroring accelerate the reaction about 7 times. This is probably associated with the weakening of the σ-Cd–N bond due to the *–I* effect of the bromine atoms. Comparison of the apparent rate constants of the metal-exchange reactions of $CoCl_2$ with complexes **I** (Table 2) and **II** in DMF (k_{app}^{298} 7 × 10^{-3} s^{-1}) revealed no rate effect of bromine substitution.

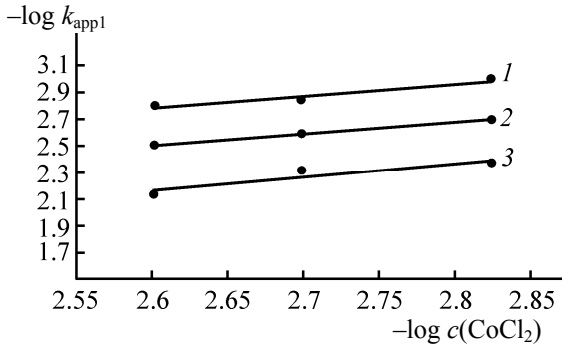


Fig. 2. Dependence of log k_{app1} on log $c(CoCl_2)$ for metal exchange between complex **I** and $CoCl_2$ in DMF at (*1*) 288, (*2*) 293, and (*3*) 298 K.

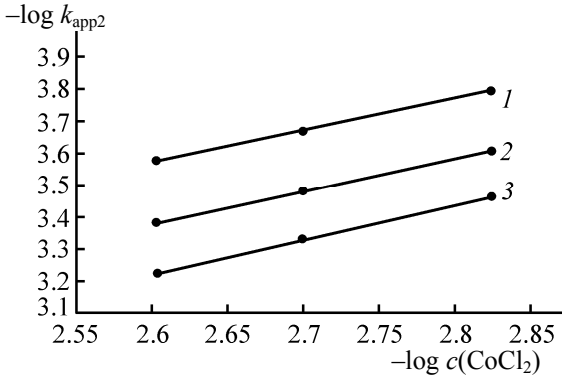


Fig. 3. Dependence of log k_{app2} on log $c(CoCl_2)$ for metal exchange between complex **I** and $CoCl_2$ in DMSO at (*1*) 298, (*2*) 308, and (*3*) 318 K.

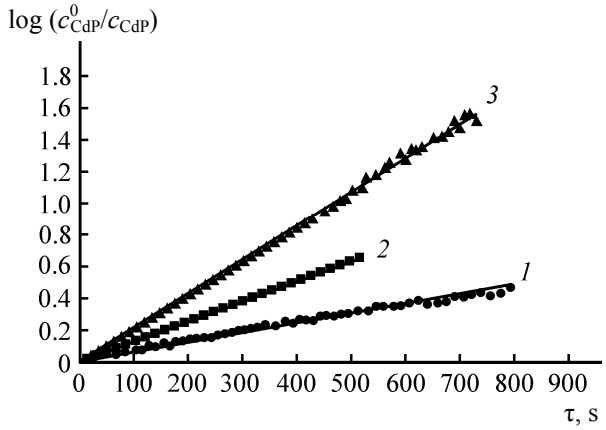


Fig. 4. Dependence of log (c^0_{CdP}/c_{CdP}) on the reaction time of complex **I** with $CoCl_2$ in DMF at (*1*) 288, (*2*) 293, and (*3*) 298 K. $c(CoCl_2) = 2.5 \times 10^{-3}$ M.

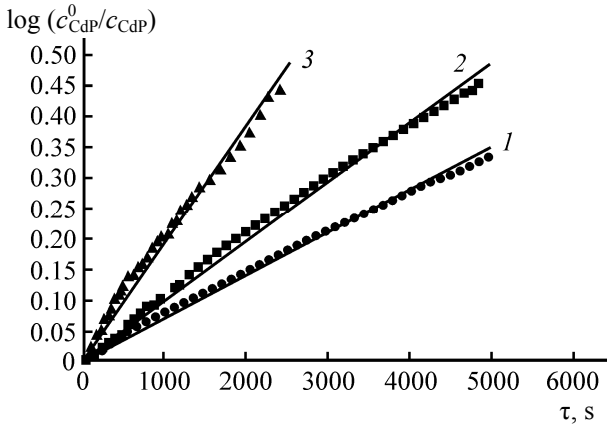


Fig. 5. Dependence of log (c^0_{CdP}/c_{CdP}) on the reaction time of complex I with $CoCl_2$ in DMSO at (*1*) 298, (*2*) 308, and (*3*) 318 K. $c(CoCl_2) = 2.5 \times 10^{-3}$ M.

We compared the rates of metal exchange between complex **I** and $CoCl_2$ and complex formation of the free ligand with the same salt in DMF [5]. The rate of complex formation with $CoCl_2$ is 24 times smaller than the rate of metal exchange in the same conditions.

Thus, metal-exchange reactions are suitable for preparing metal porphyrins that are difficult to prepare by direct synthesis. Probably, one of the main factors controlling the rate of complex formation in DMF is the state of endocyclic N–H bonds in the porphyrin molecules. The absence of the necessity in N–H bond cleavage in the labile cadmium porphyrinate in the metal-exchange reactions drives formation of cobalt porphyrinate.

The complex-forming metal, too, was found to affect the rate of metal exchange. Comparison of the apparent rate constants of the metal-exchange reactions of Cd and Mg octa(4-bromophenyl)tetraazaporphyrinates [5] with $CoCl_2$ in DMF showed that the Cd complex reacts 14.580 times faster than the Mg complex. This difference is explained by the fact that, unlike the covalent Mg complexes, Cd porphyrinates are labile ionic complexes [6].

The metal exchange of complex **I** with $CoCl_2$ in DMF and DMSO gave a mixture of Co(II) and Co(III) porphyrinates ($\lambda_{\mathbf{I}}$ 624 nm in DMF and 618 nm in DMSO). Within a few days, the mixture oxidized to form Co(III) octa(4-bromophenyl)tetraazaporphyrinate (**III**). This complex was isolated and characterized by EA ^{1}H NMR spectroscopy. The oxidation of Co(II) to Co(III) results in a red shift of bands in the EA spectrum ($\Delta\lambda_{\mathbf{I}}$ 18 nm). The ^{1}H NMR spectrum of complex **III** shows porphyrin proton signals in their characteristic region (configuration $3d^6$).

The metal-exchange reactions of complex **I** with $CuCl_2$ and $ZnCl_2$ in DMSO and DMF are very fast already at 288 K. Therefore, measurements at the wavelength of the cadmium complex with these two salts proved impossible.

EXPERIMENTAL

Cobalt(II) chloride was calcined before use at 200°C for 4 h. Dimethyl sulfoxide and DMF were purchased from Merck.

The ^{1}H NMR spectra were recorded on a Bruker AV III-500 instrument.

Mg(II) octa(4-bromophenyl)tetraazaporphyrinate was synthesized by the procedure in [5]. Its treatment with trifluoroacetic acid in chloroform gave **octa(4-bromophenyl)tetraazaporphyrine.** ^{1}H NMR spectrum ($CDCl_3$ + CF_3COOH), δ, ppm: 7.62 d (16H, H^o, Ph, *J* 7.7 Hz), 7.40 d (16H, H^m, Ph, *J* 7.7 Hz).

Cd(II) octa(4-bromophenyl)tetraazaporphyrinate (I). Sodium acetate, 0.05 g, was added to a solution of 0.05 g of octa(4-bromophenyl)tetraazaporphyrine and 0.074 g of $Cd(OAc)_2$ in 10 mL of DMF. The reaction mixture was kept at 20°C for 3 h and then poured into water. The precipitate that formed was filtered off, washed with water, and dried. Yield 0.048 g (90%). EA spectrum ($CHCl_3$), λ, nm (log ε): 382 (4.74), 589 (4.32), 640 (4.80).

Co(III) octa(4-bromophenyl)tetraazaporphyrinate (III). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.85 d and

7.73 d (16H, H^o, Ph, *J* 7.7 Hz), 7.57 d (16H, H^m, Ph, *J* 7.7 Hz). EA spectrum (DMF), λ, nm (log ε): 390 (4.19), 575 (3.84), 631 (4.38).

Kinetic measurements were performed on a Cary 100 Varian spectrophotometer. A solution of complex I and $CoCl_2$ was loaded at a preset temperature into a temperature-controlled cell. The optical density of the solution was measured at regular intervals. The rate of metal exchange was determined from the decrease of the optical density at the absorption maximum of complex I (λ_I 645 nm in DMF and 647 nm in DMSO). The measurements were performed in the temperature ranges 298–318 (DMSO) and 288–298 K (DMF). The salt concentration was 1.5×10^{-3}–2.5×10^{-3} M.

The current concentration of cadmium porphyrinate was calculated by Eq. (2).

$$c = c^0(A_\infty - A_\tau)/(A_\infty - A_0). \quad (2)$$

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

Apparent reaction rate constants (k_{app}) were calculated by Eq. (3).

$$k_{app} = (1/\tau)\ln (c^0/c). \quad (3)$$

The activation energies (E_a) were calculated by the Arrhenius equation (4).

$$E_a = 19.1\frac{T_1T_2}{T_2 - T_1}\log\frac{k_2}{k_1}. \quad (4)$$

Here k_1 and k_2 are the true rate constants $k_v = k_{app}/c_{salt.}$

The changes in the activation entropy ($\Delta S^{\neq}$) were calculated in terms of the theory of absolute reaction rates using Eq. (5) [7].

$$\Delta S^{\neq} = 8.314\ln k_v^{298} + E_a/298 - 253.22. \quad (5)$$

The spectrophotometric and ^1H NMR measurements were performed at the Regional Center for Physical and Chemical Research.

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