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Metal Exchange Reaction between Mg(II) and Cd(II) Octa(4-bromophenyl)tetraazaporphyrinates with Manganese(II) Chloride in Dimethylformamide

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Abstract—Reaction of metal exchange of Mg(II) and Cd(II) octa(4-bromophenyl)tetraazaporphyrinates with $MnCl_2$ in dimethylformamide has been studied by means of spectrophotometry. Kinetic parameters of the reaction have been determined; the reaction stoichiometry mechanism has been suggested.

Keywords: metal exchange, octa(4-bromophenyl)tetraazaporphyrinate, magnesium, cadmium, manganese

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Metal complexes with porphyrines have been widely applied in science and technology. In particular, the use of metal porphyrinates in development of catalytic and biologically active systems has determined the increased interest to this class of compounds.

In this work the metal exchange reactions of Mg(II) and Cd(II) octa(4-bromophenyl)tetraazaporphyrinates (**I** and **II**, respectively) with $MnCl_2$ in dimethylformamide were studied by means of spectrophotometry.

The evolution of electronic absorption spectrum of the reaction mixture in the course of the metal exchange between complex **I** and $MnCl_2$ is illustrated in Fig. 1.

The reaction rate order with respect to the salt was determined from the slope of the log k_{eff} = f[log $c(MgCl_2)$ plot; it equaled to unity in the cases of the both complexes **I** and **II**. The plots of log (c^0_{MgP}/c_{MgP}) were linear with time (Figs. 2 and 3); hence, the reaction rate order with respect to the complexes **I** and **II** equaled to unity as well. The overall kinetic equation was as follows:

$$-dc_{MP}/d\tau = k_v[MP][MnCl_2].$$

The experimental data shown in Tables 1 and 2 suggested that the reaction of complexes **I** and **II** with $MnCl_2$ in DMF occurred via the associative mechanism [1].

The true rate constant of the metal exchange reaction involving complex **I** was about 3 times higher than that in the case of the bromine-free magnesium(II) octaphenyltetraazaporphyrinate, other conditions being the same [2]. That was likely due to the Mg–N σ-bond weakening resulting from the negative inductive effect of bromine substituent.

The rate of the metal exchange reactions is known to be sensitive to the nature of metal ion substituting the one of the tetraazaporphyrinate complex. In particular, it was found that the reaction of complex **I** with $MnCl_2$ in DMF was 20 times faster than that with

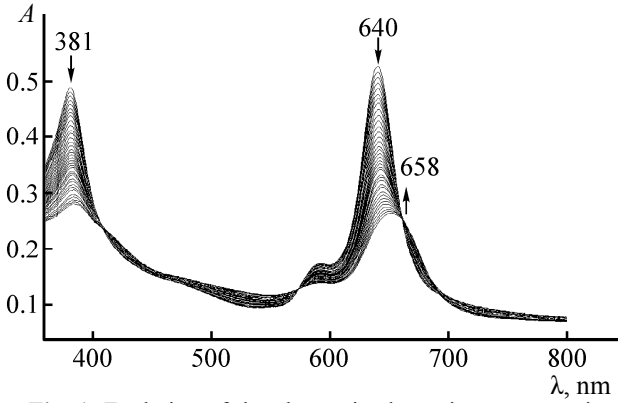

Fig. 1. Evolution of the electronic absorption spectrum in the course of the reaction between complex **I** and $MnCl_2$ in DMF. $c_I = 2.5 \times 10^{-5}$ mol/L, $c(MnCl_2) = 2.5 \times 10^{-3}$ mol/L, T = 348 K.

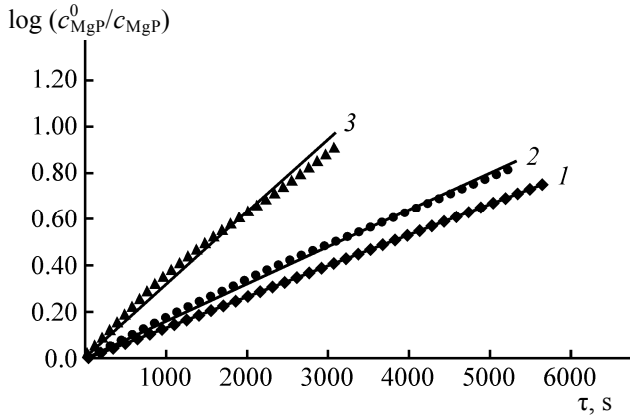

Fig. 2. log (c^0_{MgP}/c_{MgP}) as function of the duration of the reaction between complex **I** and $MnCl_2$ in DMF at $c(MnCl_2) = 2.5 \times 10^{-3}$ mol/L; T = (*1*) 348, (*2*) 353, and (*3*) 358 K.

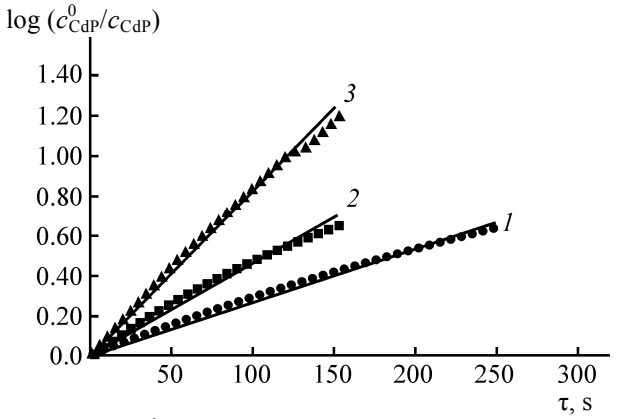

Fig. 3. log (c^0_{CdP}/c_{CdP}) as function of the duration of the reaction between complex **II** and $MnCl_2$ in DMF at $c(MnCl_2) = 2.5 \times 10^{-3}$ mol/L; T = (*1*) 283, (*2*) 288, and (*3*) 293 K.

$CoCl_2$ and 77 times slower than that with $CuCl_2$, other conditions being the same [3].

The nature of the central ion in the porphyrinate complex affected the metal exchange reaction rate as well. In particular, the true rate constant of the reaction of Cd(II) complex **II** with $MgCl_2$ in DMF was about 3650 times higher than that of the similar reaction of Mg(II) complex **I**. That was evidently due to the fact that the Mg(II) complex was the covalently bound one, whereas the Cd(II) complex was a labile ionic compound. The observation was in line with the data on the stability of Mg^{2+}, Zn^{2+}, and Cd^{2+} complexes with the mesoporphyrine in the *tert*-butanol–trichloroacetic acid medium [4].

EXPERIMENTAL

The metal exchange reactions were studied using a Cary 100 Varian spectrophotometer. Procedures of the experiment and the data processing have been earlier described [5].

Table 1. Rates of Mg^{2+} exchange with Mn^{2+} in complex **I** in DMF ($c_{\mathbf{I}} = 2.5 \times 10^{-5}$ mol/L)

$c(MnCl_2) \times 10^3$, mol/L	T, K	$k_{ef} \times 10^4$, s^{-1}	$k_v \times 10^2$, L mol^{-1} s^{-1}
2.5	298	0.10[a]	0.40±0.03
	348	3.07±0.03	12.51±0.23
	353	3.90±0.08	15.94±0.34
	358	5.55±0.26	22.35±0.25
2.0	298	0.08[a]	
	348	2.53±0.03	
	353	3.22±0.06	
	358	4.45±0.23	
1.5	298	0.06[a]	
	348	1.89±0.05	
	353	2.42±0.02	
	358	3.39±0.13	

[a] The calculated value. E_a = 60±11 kJ/mol, $\Delta S^{\neq} = -149 \pm 36$ J mol^{-1} K^{-1}.

Table 2. Rates of Cd^{2+} exchange with Mn^{2+} in complex **II** in DMF ($c_{\mathbf{II}} = 2.5 \times 10^{-5}$ mol/L)

$c(MnCl_2) \times 10^3$, mol/L	T, K	$k_{ef} \times 10^3$, s^{-1}	$k_v \times 10^2$, L mol^{-1} s^{-1}
2.5	283	6.45±0.28	2.54±0.19
	288	11.35±0.58	4.33±0.21
	293	21.12±0.50	7.85±0.60
	298	36.51[a]	13.15±1.45
2.0	283	5.39±0.28	
	288	8.59±0.23	
	293	15.47±0.29	
	298	24.86[a]	
1.5	283	3.52±0.18	
	288	6.23±0.11	
	293	10.92±0.19	
	298	18.61[a]	

[a] The calculated value. E_a = 78±5 kJ/mol, $\Delta S^{\neq} = -24 \pm 18$ J mol^{-1} K^{-1}.

Manganese(II) chloride was calcined at 200°C during 4 h prior to the experiment.

Cadmium octa(4-bromophenyl)tetraazaporphyrinate. 0.05 g of octa(4-bromophenyl)tetraazaporphyrine and 0.074 g of $Cd(OAc)_2$ (the molar ratio of 1 : 10) were diluted in 10 mL of DMF, and 0.05 g of NaOAc was added. The mixture was incubated at 20°C during 3 h and then poured in water. The precipitate was filtered off, washed with water, and dried. Yield 0.048 g (90%). Electronic absorption spectrum ($CHCl_3$), λ, nm (log ε): 382 (4.74), 589 (4.32), 640 (4.80).

Magnesium(II) octa(4-bromophenyl)tetraazaporphyrinate was prepared via cyclization of di(4-bromophenyl)maleindinitrile with magnesium metal [6].

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