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# Metal Exchange Reaction of Magnesium(II) Octa(4-bromophenyl)tetraazaporphyrinate with Copper and Cobalt Chlorides in Dimethylformamide

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**Abstract**—Metal exchange reaction of magnesium(II) octa(4-bromophenyl)tetraazaporphyrinate with copper and cobalt chlorides in dimethylformamide has been studied by spectrophotometry measurements. Kinetic parameters of the metal exchange reaction have been determined. Possible stoichiometric mechanism of the reaction was proposed.

**Keywords:** metal exchange reaction, magnesium(II), copper(II), cobalt(II) octa(4-bromophenyl)tetraazaporphyrinate, cobalt(III) octa(4-bromophenyl)tetraazaporphyrinate

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Unique properties of natural porphyrin-based compounds (hemoglobin, chlorophyll, vitamin $B_{12}$, etc.) essential for the processes occurring in living organisms depends on both nature of metal atom of coordination center and type of peripheral substituents. Lots of synthetic analogs of these natural compounds have been prepared so far. They are chemically and thermally stable, known for remarkable absorbance (UV, visible, and near IR ranges), redox (many reversible transitions at practically important potentials), and fluorescence properties. With certain combinations of peripheral substituents and metal cation, porphyrins and their analogs form unique stable supramolecular complexes with extraordinary electronic and ionic conductivity, promising for creation of unique materials for various fields of science and engineering [1].

Metal exchange is among the important reactions of porphyrin complexes. Its general scheme is as follows.

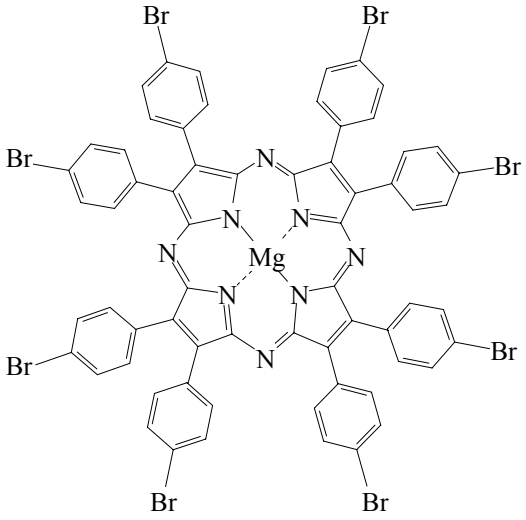
$$MP + M'X_n(Solv)_{m-n} \rightarrow M'P + MX_n(Solv)_{m-n}.$$

Here, MP and M'P are metalloporphyrins; $MX_n(Solv)_{m-n}$ and $M'X_n(Solv)_{m-n}$ are metal solvato complexes.

Extending our earlier research [2] of the effect of tetrapyrrole macrocycle modification on the metal exchange rate, in this work we studied the rate of magnesium octa(4-bromophenyl)tetraazaporphyrinate exchange reaction with $CuCl_2$ and $CoCl_2$ in dimethylformamide (Scheme 1).

Figure 1 illustrates the evolution of electronic absorption spectrum in the course of the exchange reaction with $CuCl_2$. The results revealed formation of more stable copper octa(4-bromophenyl)tetraazaporphyrinate as a result of metal exchange, as confirmed by blue shift of the absorption bands (note the spectral criterion of the complex stability established for porphyrins [3]).

**Scheme 1.**



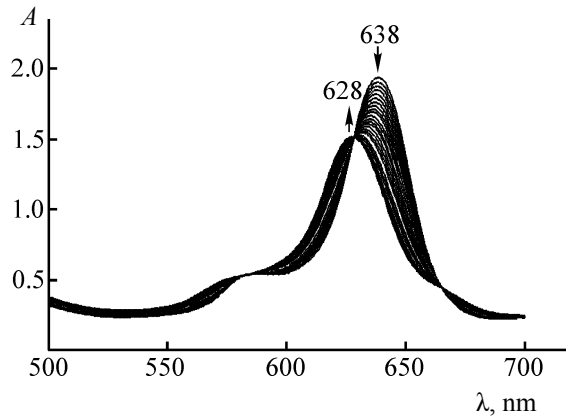



**Fig. 1.** Evolution of electronic absorption spectrum in the course of metal exchange reaction of magnesium octa(4-bromophenyl)tetraazaporphyrinate with $CuCl_2$ in DMF; $c_{MgP} = 2.5 \times 10^{-5}$ mol/L, $c(CuCl_2) = 2.5 \times 10^{-3}$ mol/L, $T$ = 298 K.

Monitoring of the studied metal exchange reactions revealed the first order with respect to salt for both reactions as determined from slope of the linear plots $\log k_{ef} = f(\log c_{salt})$ (Tables 1 and 2; Figs. 2 and 3).

The $\log (c^0_{MgP}/c_{MgP})$ changing linearly with reaction time $\tau$ (Figs. 4 and 5) proved the first order of the reaction rate with respect to the magnesium complex. Therefore, the full kinetic equation for the metal exchange reaction was as follows.

$$-dc_{MgP}/d\tau = k_v[MgP][MCl_2].$$

Basing on the experimental data (Table 1 and 2; Fig. 1) we supposed that the metal exchange reaction of magnesium octa(4-bromophenyl)tetraazaporphyrinate with $CuCl_2$ and $CoCl_2$ in DMF proceeded via the associative mechanism. Likely, the associated intermediate was rapidly formed at the first stage of the reaction; the second rate-determining stage involves dissociation of the intermediate to form more stable copper (or cobalt) porphyrinate and magnesium solvate salt.

Rate of the metal exchange reaction depended on the nature of the metal ion introduced in the reaction with magnesium octa(4-bromophenyl)tetraazaporphyrinate. In particular, the exchange reaction with $CuCl_2$ was 1546 faster than that with $CoCl_2$. That coincided with the published data on rate of formation of octaphenyltetraazaporphyrin complexes with metal acetates in pyridine: Cu > Zn > Cd > > Ni > Co > Mn [4].

Comparison of the effective rate constants of metal exchange reactions of $CuCl_2$ with magnesium octa(4-bromophenyl)tetraazaporphyrinate and octaphenyltetraazaporphyrinate in DMF [5] showed that introduction of eight bromine substituents at the macrocycle led to approximately 5-fold acceleration of the reaction. Similar comparison in the case of the exchange with $CoCl_2$ revealed introduction of the bromine substituents accelerated the reaction by about 44 times. The observed effects were probably due to weakening of the Mg–N σ-bond because of negative inductive effect of bromine atoms.

Noteworthily, cobalt(II) porphyrinate ($\lambda_I$ 612 nm, $\lambda_{II}$ 562 nm, $\lambda_{Soret}$ 348 nm) was formed in the course of the metal-exchange reaction of magnesium octa(4-

**Table 1.** Kinetic parameters of the exchange reaction between magnesium octa(4-bromophenyl)tetraazaporphyrinate with $CuCl_2$ in DMF ($c_{MgP} = 2.5 \times 10^{-5}$ mol/L)

| $c(CuCl_2) \times 10^3$, mol/L | $T$, K | $k_{ef} \times 10^4$, $s^{-1}$ | $k_v$, L $mol^{-1}$ $s^{-1}$ | $E_a$, kJ/mol | $\Delta S^{\neq}$, J $mol^{-1}$ $K^{-1}$ |
|---|---|---|---|---|---|
| 2.5 | 288 | 4.78±0.10 | 0.19 | 38±4 | –185±12 |
| | 298 | 7.73±0.08 | 0.31 | | |
| | 308 | 13.36±0.06 | 0.53 | | |
| 2.0 | 288 | 3.62±0.06 | 0.18 | 38±5 | –186±17 |
| | 298 | 5.78±0.03 | 0.29 | | |
| | 308 | 10.25±0.01 | 0.51 | | |
| 1.5 | 288 | 2.85±0.03 | 0.19 | 36±5 | –197±17 |
| | 298 | 4.40±0.03 | 0.29 | | |
| | 308 | 7.54±0.06 | 0.50 | | |

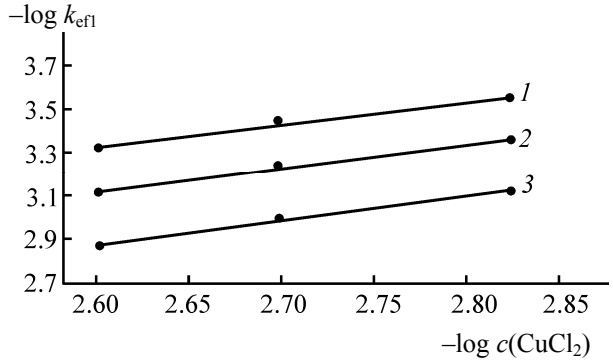



**Fig. 2**. log $k_{ef1}$ as function of log $c(CuCl_2)$ in the case of metal-exchange reaction of magnesium octa(4-bromophenyl)tetraazaporphyrinate with $CuCl_2$ in DMF at $T$, K: (*1*) 288, (*2*) 298, and (*3*) 308.

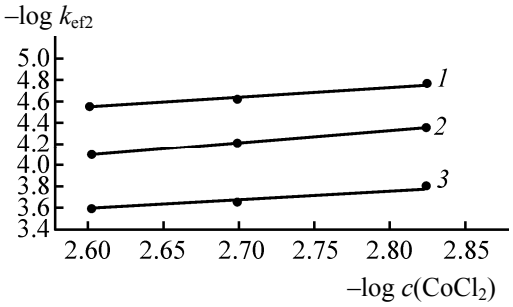



**Fig. 4**. log $(c^0_{MgP}/c_{MgP})$ as function of time in the case of metal exchange reaction of magnesium octa(4-bromophenyl)-tetraazaporphyrinate with $CuCl_2$ in DMF at $c(CuCl_2)$ = $1.5 \times 10^{-3}$ mol/L and $T$, K: (*1*) 288, (*2*) 298, and (*3*) 308.

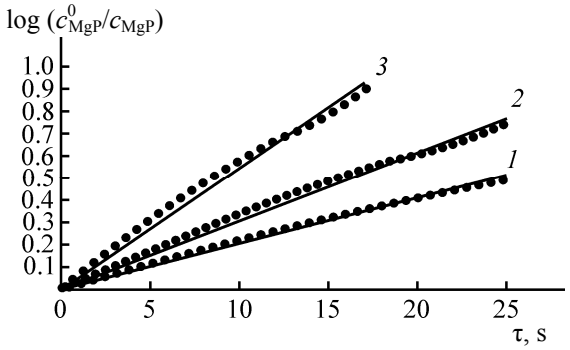



**Fig. 3**. log $k_{ef2}$ as function of log $c(CoCl_2)$ in the case of metal exchange reaction of magnesium octa(4-bromophenyl)tetraazaporphyrinate with $CoCl_2$ in DMF at $T$, K: (*1*) 328, (*2*) 338, and (*3*) 348.

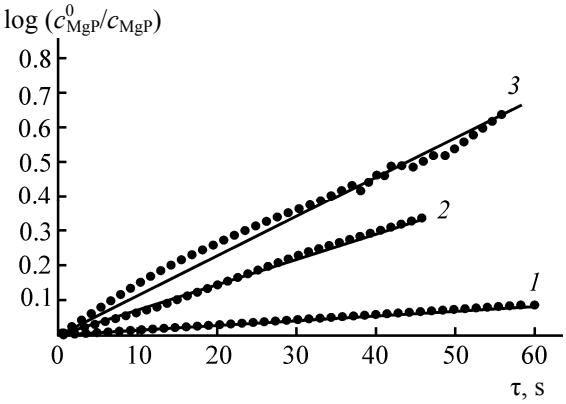



**Fig. 5**. log $(c^0_{MgP}/c_{MgP})$ as function of time in the case of metal exchange reaction of magnesium octa(4-bromophenyl)-tetraazaporphyrinate with $CoCl_2$ in DMF at $c(CoCl_2)$ = $2.5 \times 10^{-3}$ mol/L and $T$, K: (*1*) 328, (*2*) 338, and (*3*) 348.

bromophenyl)tetraazaporphyrinate with $CoCl_2$ in DMF. The product was further oxidized within one day to form the Co(III) complex ($\lambda_I$ 630 nm, $\lambda_{II}$ 572 nm, $\lambda_{Soret}$ 390 nm).

## EXPERIMENTAL

Before the experiments, copper and cobalt chlorides were annealed at 200°C during 4 h. DMF (Merck) was used.

The metal exchange reactions were studied using a Cary 100 Varian spectrophotometer. The data collection and processing were performed as described elsewhere [6]. $^1$H NMR spectrum was recorded using a Bruker AV III-500 spectrometer.

**Magnesium octa(4-bromophenyl)tetraazaporphyrinate**. 5.1 g (0.02 mol) of iodine in 15 mL of methanol was placed into an ice-cooled beaker. A solution of 3.94 g (0.02 mol) of 4-bromophenylacetonitrile in 130 mL of diethyl ether was added to the iodine solution. Next, 0.95 g (0.043 mol) of sodium in 16 mL of methanol was added dropwise to the reaction mixture upon vigorous stirring. The mixture was stirred during 1 h; the precipitate formed was filtered off and washed with water. The filtrate was washed with water, diluted solution of sodium thiosulfate, and again with water. Di(4-bromophenyl)malononitrile formed during the prolonged incubation of the mother liquid was filtered off and dried. Yield 2.5 g (6.44 mmol, 64%).

A mixture of 0.5 g (1.29 mmol) of di(4-bromophenyl)malononitrile and 0.0314 g (1.29 mmol) of metal magnesium was thoroughly ground and placed into an ampoule with a gas outlet tube. The reaction

**Table 2.** Kinetic parameters of the exchange reaction between magnesium octa(4-bromophenyl)tetraazaporphyrinate with $CoCl_2$ in DMF ($c_{MgP}$ $2.5 \times 10^{-5}$ mol/L)

| $c(CuCl_2) \times 10^3$, mol/L | $T$, K | $k_{ef} \times 10^5$, $s^{-1}$ | $k_v \times 10^2$, L $mol^{-1}$ $s^{-1}$ | $E_a$, kJ/mol | $\Delta S^{\neq}$, J $mol^{-1}$ $K^{-1}$ |
|---|---|---|---|---|---|
| 2.5 | 298[a] | 0.05 | 0.02 | 106±11 | –17±37 |
| | 328 | 2.77±0.11 | 1.11 | | |
| | 338 | 7.80±0.42 | 3.12 | | |
| | 348 | 25.88±0.89 | 10.35 | | |
| 2.0 | 298[a] | 0.04 | 0.02 | 106±16 | –18±55 |
| | 328 | 2.38±0.11 | 1.19 | | |
| | 338 | 6.34±0.42 | 3.17 | | |
| | 348 | 22.29±0.14 | 11.15 | | |
| 1.5 | 298[a] | 0.03 | 0.02 | 107±20 | –17±66 |
| | 328 | 1.75±0.10 | 1.17 | | |
| | 338 | 4.54±0.23 | 3.03 | | |
| | 348 | 16.72±1.00 | 11.15 | | |

mixture was heated at 275°C during 15 min. The formed product was dissolved in methylene chloride and twice purified via chromatography on aluminum oxide, eluting first with methylene chloride and then with chloroform. Yield 0.28 g (0.178 mmol, 55%). $^1$H NMR spectrum ($CDCl_3$), δ, ppm: 7.55 d (16H, $H^{ortho}$, $C_6H_4$, *J* 7.7 Hz), 7.35 d (16H, $H^{meta}$, $C_6H_4$, *J* 7.6 Hz). Electronic absorption spectrum (DMF), λ, nm (log ε): 381 (4.89), 586 (4.31), 639 (4.92).

## ACKNOWLEDGMENTS

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