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Metal Exchange Reaction between Magnesium Octaphenyltetraazaporphyrinate and *d*-Metals Salts in Dimethylformamide

S. V. Zvezdina, N. V. Chizhova, and N. Zh. Mamardashvili

G.A. Krestov Institute of Solutions Chemistry, Russian Academy of Sciences,
ul. Akademicheskaya 1, Ivanovo, 153045 Russia
e-mail: svvr@isc-ras.ru

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Abstract—Reaction of metal exchange between magnesium octaphenyltetraazaporphyrinate with copper and cobalt chlorides in dimethylformamide has been studied by spectrophotometry. Parameters of the reactions kinetics have been determined, and their mechanism has been suggested.

Keywords: magnesium octaphenyltetraazaporphyrinate, metal exchange, reaction rate

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Metal exchange (1) involving metal complexes with macrocyclic ligands [MP and M'P being metal porphyrinates, $MX_n(Solv)_{m-n}$ and $M'X_n(Solv)_{m-n}$ representing solvated metal complexes] are classified as a special type of complex coordination interactions [1, 2].

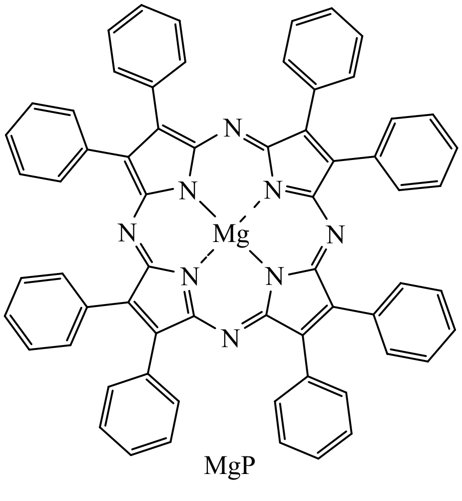
$$MP + M'X_n(Solv)_{m-n} \rightarrow M'P + MX_n(Solv)_{m-n}. \quad (1)$$

Such reactions were reported for the first time as a procedure to obtain metal complexes with phthalocyanine Pc [3, 4]; in particular, starting with Li_2Pc a series of complexes containing metals in the unusually low oxidation states were prepared: $Li_2[Cu^0Pc]$, $Li[Mn^{2+}Pc]$, $Li_2[Mn^{1+}Pc]$, $Li[Fe^{1+}Pc]$, $Li[Co^{1+}Pc]$, and $Li[Ni^{1+}Pc]$. Metal exchange to prepare various water-soluble porphyrins was discussed in [1]; it can serve as a route to otherwise unavailable natural and synthetic porphyrins starting from easier available porphyrins and phthalocyanines [5–10]. For example, palladium complex with octaphenyltetraazaporphyrin was obtained from magnesium octaphenyltetraazaporphyrinate and $PdCl_2$ in DMF under reflux [8].

The systems involving magnesium porphyrazines attract special attention in view of elucidating the mechanism of the metal exchange reactions. Biologically active ligands like pheophytin and similar compounds are of exreme importance. Metal exchange reactions are known to occur in nature [11–13] participating in regulation of biological processes under severe conditions [14–17]. Furthermore, metal exchange in Mg complexes of chlorophyll derivatives may be used to prepare environmentally friendly stable dyes [5] and *d*-metals complexes with blood porphyrins [17–20].

The major factors governing the metal exchange rate and mechanism in the case of porphyrin complexes are the ligand nature in porphyrin structure, electronic structure, and the solvate shell of the outgoing and ingoing cations (M^{n+} and M'^{n+}), anionic

Scheme 1.



MgP

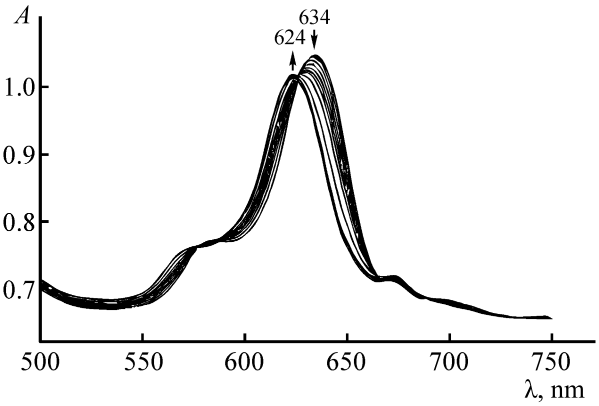


Fig. 1. Electron absorption spectra change in the course of MgP reaction with $CuCl_2$ in DMF, c(MgP) = 2.5×10^{-5} mol/L, $c(CuCl_2)$ = 2.5×10^{-3} mol/L, 328 K.

composition X^- of the solvated sphere of cations $[M'X_n(Solv)_{m-n}]$, and nature of the solvent.

In this work we studied the reaction of magnesium octaphenyltetraazaporphyrinate MgP with $CuCl_2$ and $CoCl_2$ in DMF (Scheme 1).

Figure 1 displays the changes in electron absorption spectra in the course of metal exchange reaction between the MgP complex and $CuCl_2$ in DMF. The data collected in Tables 1 and 2 show that the metal exchange rate depends of the salt concentration. The reaction rate order with respect to the salts as determined by the slope of $\log k_{ef1} = f[\log c(CoCl_2)$ $[(MgP + CoCl_2)$ and $\log k_{ef2} = f[\log c(CuCl_2)]$ $(MgP + CuCl_2)$ was close to unity (Figs. 2 and 3). The reaction rate followed also the first-order kinetics with respect to the MgP complex as seen from linear plots $\log [c^0(MgP)/c(MgP)] = f(\tau)$ (Fig. 4) Hence, the metal exchange reaction was bimolecular and followed the second-order rate equation (2).

$$-dc(MgP)/d\tau = k_v[MgP][MCl_2]. \qquad (2)$$

Taking into account the data collected in this work as well as those reported in the literature details of the metal exchange mechanism could be elucidated. The very first works on the problem showed that reaction (1) was two-stage and bimolecular [17, 21]. In the first (fast) stage, the binuclear intermediate $[(Solv)_mMPM'X_2(Solv)_{n-4}]$ is formed that can be detected in the spectra if M'P complex is more stable than MP.

The exchange reaction rate and other kinetic parameters depend on the equilibrium constant of the intermediate formation that is in turn governed by chemical structure of the reagents, steric hindrance due to the macrocycle rigidity, and the related electronic effects [22, 23]. The solvent nature effect cannot be excluded as well. The solvent nature will determine the rate of intermediates formation and their stability as well as the pathway of the intermediate further decay.

Table 1. Rate of Mg^{2+} exchange with Cu^{2+}; MgP complex in DMF, [c(MgP) 2.5×10^{-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	298	0.56[a]	0.02	69 ± 3	–103 ± 11
	318	3.25 ± 0.13	0.13		
	328	6.95 ± 0.32	0.28		
	338	15.22 ± 0.80	0.61		
2.0	298	0.35[a]	0.02	75 ± 1	–87 ± 4
	318	2.33 ± 0.12	0.12		
	328	5.62 ± 0.12	0.28		
	338	12.55 ± 0.54	0.63		
1.5	298	0.29[a]	0.02	74 ± 1	–88 ± 4
	318	1.92 ± 0.04	0.13		
	328	4.43 ± 0.07	0.30		
	338	10.00 ± 0.02	0.67		

[a] Calculated value.

Table 2. Rate of Mg^{2+} exchange with Co^{2+}; MgP complex in DMF, [c(MgP) 2.5×10^{-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	0.37[a]	0.15	68 ± 15	–130 ± 50
	328	4.70 ± 0.29	1.88		
	338	8.36 ± 0.07	3.34		
	348	19.49 ± 0.11	7.80		
2.0	298	0.30[a]	0.15	66 ± 16	–137 ± 55
	328	3.57 ± 0.22	1.79		
	338	6.13 ± 0.32	3.07		
	348	14.25 ± 0.43	7.13		
1.5	298	0.21[a]	0.14	67 ± 11	–136 ± 36
	328	2.54 ± 0.15	1.69		
	338	4.70 ± 0.17	3.13		
	348	10.47 ± 0.02	6.98		

[a] Calculated value.

In the course of the intermediate formation (3), two solvent molecules are eliminated from the solvated salt coordination sphere.

$$(Solv)_mMP + M'X_2(Solv)_{n-2} \leftrightarrow (Solv)_mMPM'X_2(Solv)_{n-4} + 2Solv. \quad (3)$$

The coordination sphere is therefore highly deformed requiring certain energy expenditure. The initial metal porphyrin can bear extra solvent molecules (up to two) at the metal ion that will favor the metal liberation from the σ,π-system of porphyrin macrocycle.

In the second (slow) monomolecular stage (4), the intermediate decomposes into the final reaction products.

$$(Solv)_mMP{\cdot}M'X_2(Solv)_{n-4} \leftrightarrow [(Solv)_mM{\cdots}P{\cdots}M'X_2(Solv)_{n-4}]^{\neq} \rightarrow MX_2(Solv)_m + M'P(Solv)_{n-4}. \quad (4)$$

To conclude, the metal exchange reaction between MgP complex with $CuCl_2$ or $CoCl_2$ in DMF occurred via the bimolecular mechanism, the interaction with Cu^{2+} being 15 times faster than that with Co^{2+}.

EXPERIMENTAL

The metal exchange reaction rate was studied by means of time-resolved spectrophotometry (the Cary 100 Varian instrument); the experiment details were reported elsewhere [19].

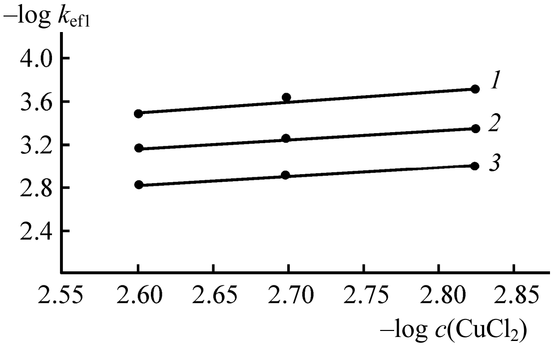


Fig. 2. Rate constant k_{ef1} of MgP metal exchange with $CuCl_2$ in DMF as a function of $CuCl_2$ concentration, at 318 K (*1*), 328 K (*2*), and 338 K (*3*).

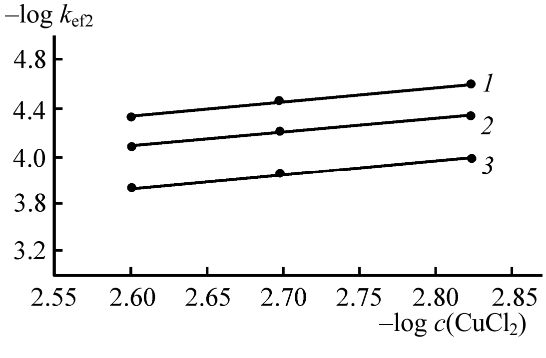


Fig. 3. Rate constant k_{ef2} of MgP metal exchange with $CoCl_2$ in DMF as a function of $CoCl_2$ concentration, at 328 K (*1*), 338 K (*2*), and 348 K (*3*).

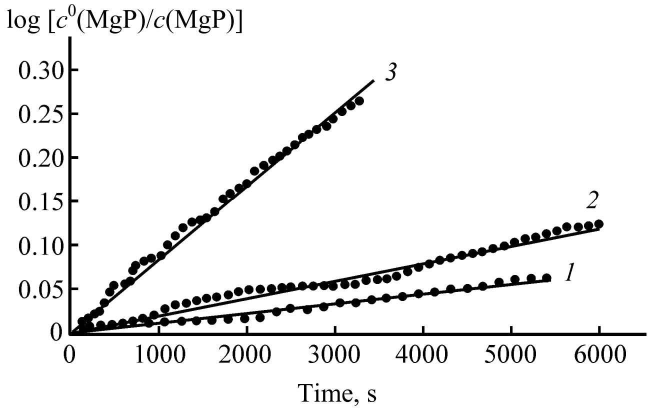


Fig. 4. Kinetics of c(MgP) change in the reaction with $CoCl_2$ in DMF, $c(CuCl_2) = 1.5 \times 10^{-3}$ mol/L; 328 K (*1*), 338 K (*2*), and 348 K (*3*).

Magnesium, cobalt, and copper chlorides were recrystallized from aqueous hydrochloric acid. DMF (Merck) was used as received. Magnesium octaphenyltetraazaporphyrinate was prepared as described elsewhere [24].

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