ISSN 1070-3632, Russian Journal of General Chemistry, 2014, Vol. 84, No. 10, pp. 1989–1993. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © S.V. Zvezdina, N.V. Chizhova, N.Zh. Mamardashvili, 2014, published in Zhurnal Obshchei Khimii, 2014, Vol. 84, No. 10, pp. 1712–1716.

Metal Exchange Reaction of Magnesium Octaphenyltetraazaporphyrin with Copper, Cobalt, and Zinc Chlorides in DMSO and DMF

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

Krestov Institute of Solution Chemistry, Russian Academy of Sciences,
ul. Akademicheskaya 1, Ivanovo, 153040 Russia
e-mail: svvr@isc-ras.ru

Received April 10, 2014

Abstract—Metal exchange reaction of (octaphenyltetraazaporphyrinato)magnesium(II) with copper, cobalt, and zinc chlorides in dimethyl sulfoxide and dimethylformamide has been studied by spectrophotometry. Kinetic and thermodynamic parameters of the process have been determined, and a probable reaction mechanism has been proposed. Zinc(II), copper(II), cobalt(II), and cobalt(III) complexes of octaphenyltetraazaporphyrin have been isolated and characterized.

Keywords: Metal exchange reaction, magnesium, zinc, copper, and cobalt octaphenyltetraazaporphyrins.

DOI: 10.1134/S1070363214100211

Porphyrins are unique natural compounds mediating principal biological, photochemical, and enzymatic processes [1]. At present, natural porphyrins and their synthetic analogs are used in many fields of medicine and technology [2]. For instance, chlorins, bacteriochlorins, and purpurins are now used as efficient photosensitizers for photodynamic therapy of cancer [3, 4].

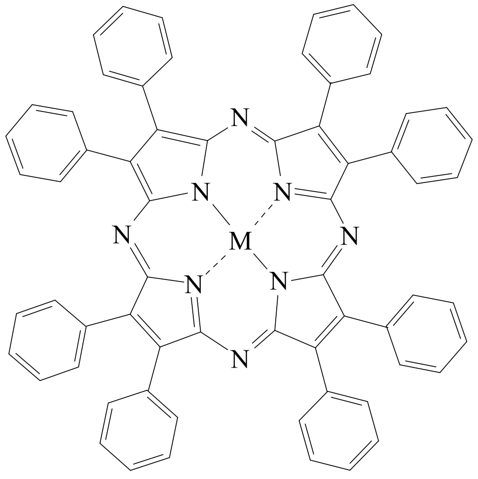
Metal exchange is a reaction typical of metalloporphyrins. In the general case, this reaction can be represented as follows:

$$\mathrm{MP} + \mathrm{M'X}_n(\mathrm{Solv})_{m-n} \rightarrow \mathrm{M'P} + \mathrm{MX}_n(\mathrm{Solv})_{m-n}. \qquad (1)$$

Here, MP and M′P are metalloporphyrins, and $\mathrm{MX}_n(\mathrm{Solv})_{m-n}$ and $\mathrm{M'X}_n(\mathrm{Solv})_{m-n}$ are metal solvate complexes. Metal exchange reactions are widely used in the synthesis of metalloporphyrins [5, 6]; they are advantageous due to the lack of demetalation of the initial complex, which ensures increased yield of the target product.

In the present work we studied by spectrophotometry reactions of (octaphenyltetraazaporphyrinato)magnesium(II) with cobalt(II), copper(II), and zinc(II) chlorides in dimethyl sulfoxide and dimethylformamide. Figure 1 illustrates variation of the electronic absorption spectrum during metal exchange of magnesium octaphenyltetraazaporphyrin (**I**) with $CoCl_2$ in DMSO (Scheme 1). The order of the reaction with respect to the inorganic salt, determined as the slope of the straight line $\log k_{ef} = f(\log c_{salt})$, is equal to unity (Table 1, Fig. 2). In the reaction of magnesium complex **I** with $CuCl_2$ in the same solvent, the order of the reaction with respect to $CuCl_2$ is equal to zero

Scheme 1.



M = Mg(II) (**I**), Zn(II) (**II**), Cu(II) (**III**), Co(II) (**IV**), (Cl)Co(III) (**V**).

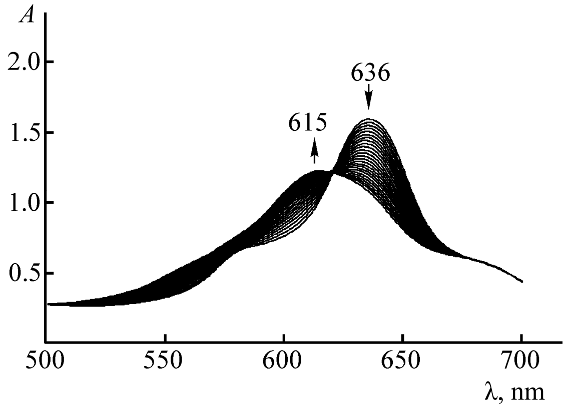


Fig. 1. Variation of the electronic absorption spectrum in the metal exchange reaction of complex **I** with $CoCl_2$ in DMSO; $c_I = 2.5 \times 10^{-5}$ M, $c(CoCl_2) = 2.5 \times 10^{-3}$ M, 358 K.

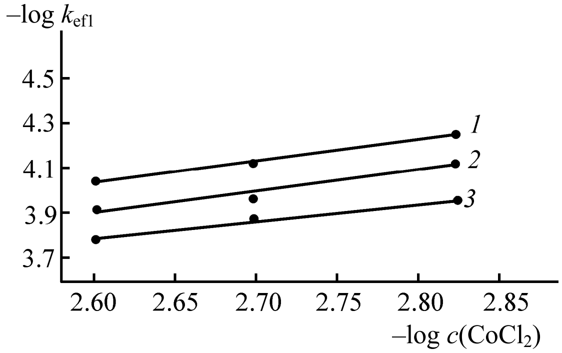


Fig. 2. Plots of log k_{ef1} vs. log $c(CoCl_2)$ for the transmetalation of complex **I** with $CoCl_2$ in DMSO at (*1*) 338, (*2*) 348, and (*3*) 358 K.

(Table 2, Fig. 3). According to our previous data, the rate of the metal exchange reaction of (2,3,7,8,12,13,17,18-octamethyl-5-azaporphyrinato)-cadmium(II) with $CuCl_2$ in DMSO is also independent of the salt concentration [7].

In all cases, the metal-exchange reaction is described by first-order equation in the magnesium complex, as follows from the linear dependence of log (c^0_{MgP}/c_{MgP}) on the reaction time τ (Figs. 4, 5). Then the kinetic equations for the reactions of magnesium complex **I** with $CoCl_2$ and $CuCl_2$ in DMSO are given by

$$-\partial c_{MgP}/\partial\tau = k_v[MgP][CoCl_2]; \quad (2)$$

$$-\partial c_{MgP}/\partial\tau = k_v[MgP]. \quad (3)$$

The reaction of complex **I** with $CoCl_2$ in DMSO follows a bimolecular associative mechanism [8], while the reaction with $CuCl_2$ is likely to conform to a mixed associative–dissociative mechanism [7].

Comparison of the effective rate constants (k_{ef}) for metal exchange of magnesium octaphenyltetraazaporphyrin (**I**) with $CoCl_2$ and $CuCl_2$ in DMSO and DMFA showed that the reaction rates in DMSO are higher than in DMF by factors of 6 for $CoCl_2$ [9] and 3 for $CuCl_2$ ($k^{298}_{ef} = 0.56 \times 10^{-4}$ s^{-1}, $[CuCl_2] = 2.5 \times 10^3$ M). A probable reason is that the dielectric constant of DMSO is higher than that of DMF (45 and 36.71, respectively, at 25°C). As we showed in [9], the reaction of complex **I** with $CoCl_2$ in DMF yields the

Table 1. Kinetic parameters of the reaction of magnesium(II) octaphenyltetraazaporphyrin with $CoCl_2$ in DMSO ($c_{MgP} = 2.5 \times 10^{-5}$ M)

$[CoCl_2] \times 10^3$, 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	2.20[a]	0.88	40±1	–218±4
	338	9.08±0.53	3.63		
	348	12.00±0.42	4.80		
	358	16.35±0.20	6.54		
2.0	298	1.99[a]	0.99	28±7	–249±23
	338	7.53±0.29	3.77		
	348	10.77±0.61	5.39		
	358	13.25±0.60	6.63		
1.5	298	1.08[a]	0.72	34±6	–234±19
	338	5.60±0.15	3.73		
	348	7.51±0.27	5.01		
	358	11.03±0.58	7.35		

[a] Calculated value.

Table 2. Kinetic parameters of the reaction of magnesium(II) octaphenyltetraazaporphyrin with $CuCl_2$ in DMSO ($c_{MgP} = 2.5 \times 10^{-5}$ M)

$[CoCl_2] \times 10^3$, mol/L	T, K	$k_{ef} \times 10^4$, s^{-1}	$k_v \times 104^4$, L mol^{-1} s^{-1}	E_a, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
2.5	298	1.69[a]	1.69	13±7	–282±24
	328	2.68±0.16	2.68		
	338	3.33±0.21	3.33		
	348	3.53±0.04	3.53		
2.0	298	1.68[a]	1.68	12±8	–284±28
	328	2.61±0.15	2.61		
	338	3.27±0.05	3.27		
	348	3.40±0.20	3.40		
1.5	298	1.63[a]	1.63	12±6	–284±19
	328	2.55±0.10	2.55		
	338	3.10±0.07	3.10		
	348	3.32±0.08	3.32		

[a] Calculated value.

corresponding cobalt(II) complex (λ_I 610 nm, λ_{II} 556 nm, λ_{Soret} 349 nm). The reaction of complex **I** with $CoCl_2$ in DMSO afforded a mixture of Co(II) and Co(III) octaphenylporphyrins (λ_I 615 nm). After several days, the Co(II) complex in the reaction mixture was completely oxidized to the Co(III) complex (λ_I 624 nm, λ_{II} 576 nm, λ_{Soret} 379 nm).

The nature of the metal ion affects the rate of metal exchange. The rate of the metal-exchange reaction of magnesium octaphenyltetraazaporphyrin with $CoCl_2$ in DMSO is lower by about an order of magnitude than the rate of metal exchange with $CuCl_2$ (Table 1, 2).

We also tried to examine metal exchange reaction of magnesium octaphenyltetraazaporphyrin (**I**) with $ZnCl_2$ in DMSO. However, the positions of bands in the electronic absorption spectra of the magnesium and zinc complexes in DMSO differed by only ~2 nm; therefore, quantitative study of this reaction was impossible.

The reactions of magnesium(II) octaphenyltetraazaporphyrin with $ZnCl_2$, $CuCl_2$, and $CoCl_2$ in DMF smoothly afforded the corresponding zinc(II), copper(II), and cobalt(II) complexes (molar reactant ratio 1:10, heating under reflux). The oxidation of cobalt(II) octaphenyltetraazaporphyrin to the Co(III) complex takes several days, and it can be accelerated by addition of aqueous HCl to the reaction mixture to deactivate reducing agents present in DMF.

The isolated Zn(II), Cu(II), Co(II), and Co(III) complexes were identified by elemental analyses and electronic absorption, IR, and ^{1}H NMR spectra. Table 3 contains parameters of the electronic spectra of these complexes in comparison with those of the initial magnesium(II) complex. Replacement of the central

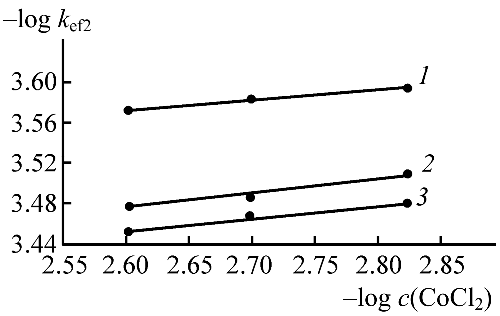


Fig. 3. Plots of log k_{ef2} vs. log$c$ ($CuCl_2$) for the transmetalation of complex **I** with $CuCl_2$ in DMSO at (*1*) 328, (*2*) 338, and (*3*) 348 K.

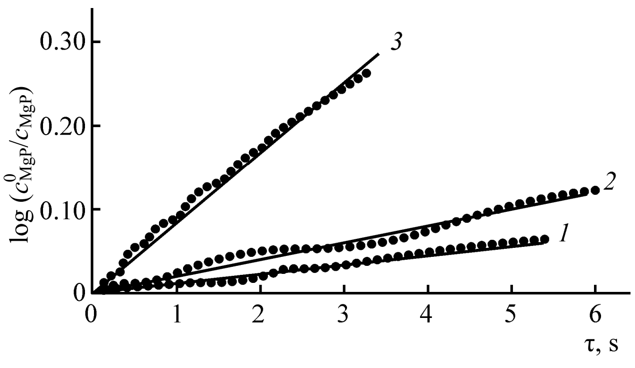


Fig. 4. Kinetic curves for the reaction of magnesium octaphenyltetraazaporphyrin with $CoCl_2$ in DMF at (*1*) 328, (*2*) 338, and (*3*) 348 K; $c(CoCl_2) = 1.5 \times 10^{-3}$ M.

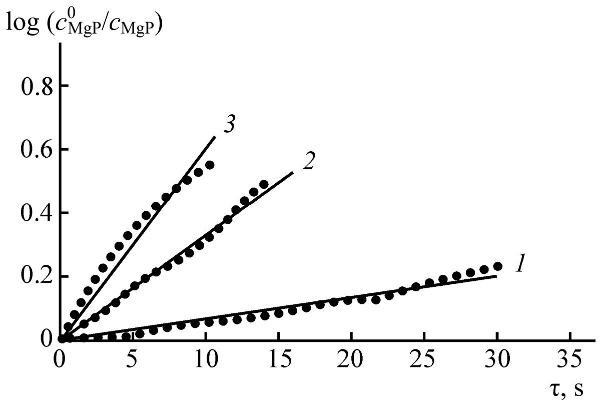


Fig. 5. Kinetic curves for the reaction of magnesium octaphenyltetraazaporphyrin with $CuCl_2$ in DMF at (*1*) 318, (*2*) 328, and (*3*) 338 K; $c(CuCl_2) = 1.5 \times 10^{-3}$ M.

Mg(II) ion by Zn(II), Cu(II), Co(II), and Co(III) leads to a blue shift of absorption maxima, which indicates increased stability of the resulting complexes [1] and reflects strengthening of the N→M dative bond and (for copper and cobalt complexes) of M→N π-back donation. The oxidation of Co(II) to Co(III) is accompanied by a red shift of the absorption maxima.

(Octaphenyltetraazaporphyrinato)cobalt(II) exhibits paramagnetic properties ($3d^7$ configuration) [10]. Therefore, signals from protons in the benzene rings of the Co(II) complex are located in the ^{1}H NMR spectrum in a weaker field relative to the corresponding signals of the Co(III) complex ($3d^6$ configuration).

EXPERIMENTAL

(Octaphenyltetraazaporphyrinato)magnesium(II) was synthesized according to [11]. Cobalt(II), copper(II), and zinc(II) chlorides were calcined for 4 h at 200°C prior to use. Dimethyl sulfoxide and dimethylformamide were commercial products (Merck). Spectrophotometric studies were performed on a Varian Cary 100 spectrophotometer according to the procedure described in [7]. Silufol plates were used for analytical thin-layer chromatography (eluent chloroform–carbon tetrachloride, 1 : 1). The ^{1}H NMR spectra were recorded on a Bruker AV III-500 instrument. The IR spectra were measured on a Thermo Nicolet Avatar 360-FT-IR-ESP spectrometer from samples prepared as KBr pellets. The elemental analyses were obtained on a Flash EA 1112 analyzer.

Table 3. Electronic absorption spectra of complexes **I**–**V** in chloroform

Complex	λ_{max}, nm (log ε)		
	I	*II*	Soret
I	639 (4.91)	595 (4.30)	379 (4.86)
II	636 (5.11)	582 (4.36)	375 (5.05)
III	627 (4.85)	575 (4.28)	362 (4.78)
IV	611 (4.64)	560 (4.23)	341 (4.78)
V	626 (4.73)	572 (4.15)	386 (4.61)

(Octaphenyltetraazaporphyrinato)zinc(II). A mixture of 0.1 g of magnesium octaphenyltetraazaporphyrin (**I**) and 0.16 g $ZnCl_2$ (molar ratio 1 : 10) in 20 mL of DMF was heated to the boiling point. After cooling, the mixture was poured into water, and the precipitate was filtered off, washed with water, dried, and purified by chromatography on alumina using chloroform as eluent. Yield 0.09 g (88%), R_f 0.74. ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 7.87 d (16H, *o*-H, *J* = 7.7 Hz), 7.57 m (24H, *m*-H, *p*-H). Found, %: C 77.82; H 4.12; N 11.25. $C_{64}H_{40}N_8Zn$. Calculated, %: C 77.93; H 4.09; N 11.36.

(Octaphenyltetraazaporphyrinato)copper(II) was synthesized in a similar way from 0.1 g of complex I and 0.14 g of $CuCl_2$. Yield 0.09 g (87%), R_f 0.73. IR spectrum, ν, cm^{-1}: 1143 s, 1017 m, 983 s (δ C–H), 739 s, 687 s (γ C–H), 3044 s, 2908 s, 2840 s (C–H), 1432 w, 1359 w (skeletal vibrations, C=N), 1647 m, 1627 w, 1587 m, 1561 w (skeletal vibrations, C=C), 1064 m, 760 m, 600 m (pyrrole), 594 w, 506 w (Cu–N). Found, %: C 78.02; H 4.19; N 11.21. $C_{64}H_{40}N_8Cu$. Calculated, %: C 78.07; H 4.09; N 11.38.

(Octaphenyltetraazaporphyrinato)cobalt(II) was synthesized in a similar way from 0.1 g of complex **I** and 0.14 g of $CoCl_2$. After cooling, the mixture was transferred onto a Schott filter charged with neutral alumina, and the sorbent was eluted with DMF. The eluate was poured into water, and the precipitate was filtered off, washed with water and methanol, and dried. Yield 0.08 g (0.0817 mmol) (77%), R_f 0.85. IR spectrum, ν, cm^{-1}: 1157 s, 1004 s, 991 s (δC–H), 747 s, 695 s (γC–H), 3048 m, 2925 s, 2852 m (γC–H), 1444 m, 1372 m (skeletal vibrations, C=N), 1647 m, 1630 m, 1587 m, 1561 w (skeletal vibrations, C=C), 1074 w, 747 m, 611 m (pyrrole), 596 w, 507 (γCo–N). ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 14.07 br.s (16H, *o*-H), 9.77 br.s (16H, *m*-H), 9.34 t (8H, *p*-H, *J* = 7.4 Hz). Found,

%: C 78.38; H 4.07; N 11.37. $C_{64}H_{40}CoN_8$. Calculated, %: C 78.48; H 4.12; N 11.44.

(Chloro)(octaphenyltetraazaporphyrinato)cobalt (III) was synthesized in a similar way. After cooling, 4 mL of aqueous HCl was added to the reaction mixture, the mixture was stirred for 15 min, and 50 mL of chloroform and 100 mL of water were added. The organic layer was separated using a separatory funnel and evaporated, and the residue was reprecipitated with hexane. Yield 0.075 g (70%), R_f 0.82. ^{1}H NMR spectrum, δ, ppm ($CDCl_3$): 7.75 d (16H, *o*-H, $J = 7.7$ Hz), 7.60 m (24H, *m*-H, *p*-H). Found, %: C 75.59; H 3.89; N 11.19. $C_{64}H_{40}ClCoN_8$. Calculated, %: C 75.74; H 3.97; N 11.04.

Spectrophotometric and spectral studies were carried out using the equipment of the Shared Use Center, Upper Volga Regional Physicochemical Research Center.

ACKNOWLEDGMENTS

This study was performed under financial support by the Russian Foundation for Basic Research (project nos. 14-03-00009-a, 14-03-00011-a) and by the Chemistry and Materials Science Department of the Russian Academy of Sciences (program no. 6, “Chemistry and Physical Chemistry of Supramolecular Systems and Atom Clusters”).

REFERENCES

1. Berezin, B.D. and Enikolopyan, N.S., *Metalloporfiriny* (Metallopoprhyrins), Moscow: Nauka, 1988.
2. *Porfiriny: spektroskopiya, elektrokhimiya, primenenie* (Porphyrins: Spectroscopy, Electrochemistry, and Application), Enikolopyan, N.S., Ed., Moscow: Nauka, 1987.
3. Brigas, A.F., Costa, A.M., Serra, A.C., and Pires, C., *J. Pharm. Bioallied Sci.*, 2011, vol. 3, no. 2, p. 294. DOI: 10.4103/0975-7406.80770
4. Shan, X.F., Wang, T.Y., Li, S.Y., Yang, L.Y., Fu, L.M., Yang, G.Q., Wang, Z., and Ma, J.S., *J. Photochem. Photobiol. B*, 2006, vol. 82, p. 140. DOI: 10.1016/j.jphotobiol.2005.11.003
5. Chizhova, N.V., Khelevina, O.G., and Berezin, B.D., *Russ. J. Gen. Chem.*, 2003, vol. 73, no. 10, p. 1645. DOI: 10.1023/B:RUGC.0000016039.52090.d2
6. Sheinin, V.B., Chizhova, N.V., and Romanova, A.O., *Russ. J. Gen. Chem.*, 2010, vol. 80, no. 2, p. 351. DOI: 10.1134/S107036321002026X
7. Zvezdina, S.V. and Mamardashvili, N.Zh., *Russ. J. Coord. Chem.*, 2012, vol. 38, no. 5, p. 319. DOI: 10.1134/S1070328412050120
8. Berezin, B.D., Zvezdina, S.V., and Berezin, M.B., *Russ. J. Gen. Chem.*, 2013, vol. 83, no. 7, p. 1410. DOI: 10.1134/S1070363213070189
9. Zvezdina, S.V., Chizhova, N.V., and Mamardasvili, N.Zh., *J. Porphyrins Phthalocyanines*, 2014, vol. 18, nos. 1–2, p. 169. DOI: 10.1142/S1088424613501095
10. Ali, B.B., Belkhiria, M.S., Giorgi, M., and Nasri, H., *Open J. Inorg. Chem.*, 2011, vol. 1, p. 39. DOI: 10.4236/ojic.2011.13006
11. Cook, A.H. and Linstead, R.P., *J. Chem. Soc.*, 1937, p. 929.