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Metal Exchange Reaction of Cd(II) 5,10,15,20-Tetra(4-chlorophenyl)porphyrinate with Copper and Zinc Chlorides in DMSO

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Abstract—The metal exchange reactions of Cd(II) 5,10,15,20-tetra(4-chlorophenyl)porphyrinate with $CuCl_2$ and $ZnCl_2$ in DMSO were studied by the spectrophotometric method. The kinetic parameters of the metal exchange reactions were determined. A possible reaction mechanism was proposed. Zinc(II) and copper(II) 5,10,15,20-tetra-(4-chlorophenyl)porphyrinates were synthesized by the complex formation reactions of zinc(II) and copper(II) acetates with 5,10,15,20-tetra(4-chlorophenyl)porphyrin and by metal exchange of its cadmium complex with $ZnCl_2$ and $CuCl_2$ in dimethylformamide. The resulting compounds were identified by electronic absorption and ^{1}H NMR spectroscopy and mass spectrometry methods.

Keywords: Cd(II), Zn(II), Cu(II) 5,10,15,20-tetra(4-chlorophenyl)porphyrinates, complexation, metal exchange reaction, spectral characteristics

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The metal exchange reaction is one of the complex associative-dissociative chemical reactions of the exchange by metal ions or ligands, which proceeds according to Eq. (1).

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

Here MP and M′P – are metalporphyrins, $M'X_n(Solv)_{m-n}$ and $MX_n(Solv)_{m-n}$ are metal solvatocomplexes.

For the first time, metal exchange reactions were carried out by the Linstead research group [1]. The widespread use of the exchange of some metals for other metals in the composition of porphyrins is described in the monograph [2]. An important condition for metal exchange is the presence of significant effective negative charges on the coordinating nitrogen atoms in the complex (δ^-) and positive charges (δ^+) on the atom of the outgoing metal ion. They may appear due to out-of-plane vibrations of the metal ion in the complex, which are favored by a disruption of the flat structure of the ligand and a decrease in its aromaticity.

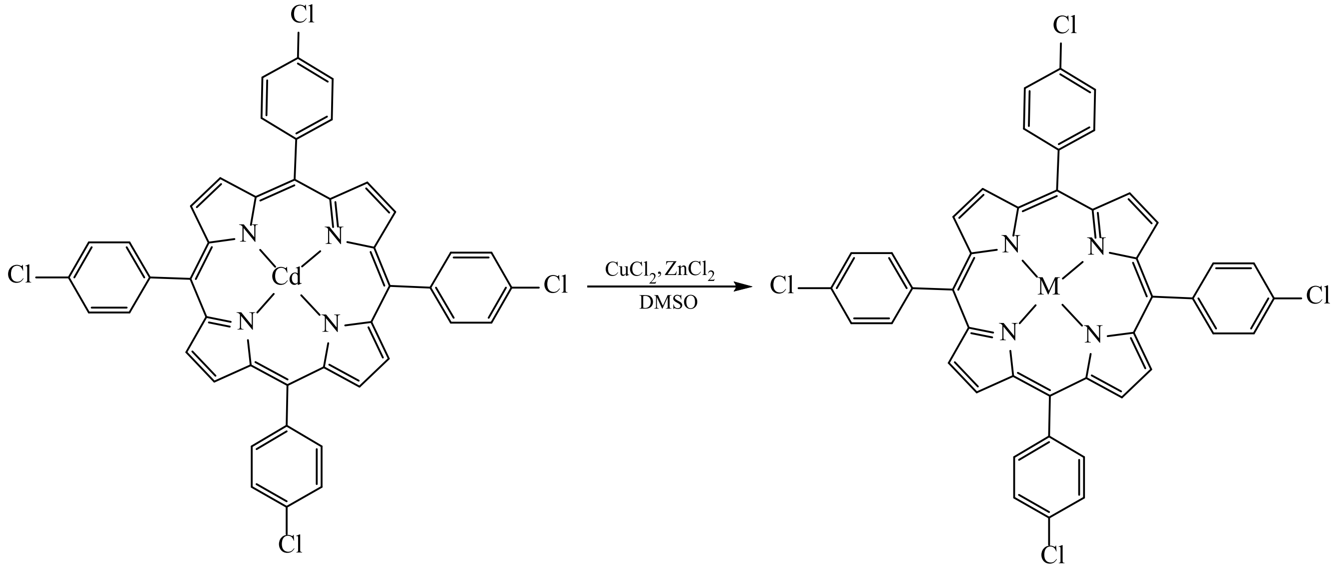
Possible mechanisms of double metal exchange in metalloporphyrins in organic solvents were discussed in [3–5]. The nature of the solvent defines the strength of the salt solvate, thus metal exchange reactions of cadmium porphyrinates in DMF are faster than in DMSO [6, 7]. As the solvating capacity of the solvent increases, the strength of the solvate shell of the salt usually increases, preventing metal exchange.

In order to identify the regularities of the metal exchange reaction, we have studied the remetallization of Cd(II) 5,10,15,20-tetra(4-chlorophenyl)porphyrinate [$CdP(PhCl)_4$] with $CuCl_2$ and $ZnCl_2$ in DMSO (Scheme 1).

Cadmium(II) 5,10,15,20-tetra(4-chlorophenyl) porphyrinate was obtained by heating a dimethylformamide solution of 5,10,15,20-tetra(4-chlorophenyl)porphyrin to the boiling point with cadmium(II) acetate (mole ratio 1 : 10). The EAS of $(PhCl)_4$ in DMF contains bands with maxima of 417, 439, 577, and 622 nm. In the ^{1}H NMR spectrum of $CdP(PhCl)_4$ in C_6D_6, the signal of protons of pyrrole rings at 8.90 ppm, and also of *ortho*- and *meta*-protons of phenyl groups at 7.96 and 7.46 ppm, respectively, were recorded. In the mass spectrum of labile cadmium porphyrinate, along with the peak *m/z* 862.1 corresponding to the molecular ion $CdP(PhCl)_4$, there is a peak of porphyrin *m/z* 753.3.

Cadmium porphyrins are mainly ionic, kinetically unstable complexes [8], and their remetallization reactions with Zn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} salts occur with the

Scheme 1.



M = Zn(II), Cu(II).

formation of stronger compounds [9]. The changes in EAS during the $CdP(PhCl)_4$ metal exchange reaction with $ZnCl_2$ in DMSO are shown in Fig. 1, and the experimental data obtained are shown in Tables 1 and 2.

We found that the reaction order with respect to the salt for the $CdP(PhCl)_4$ metal exchange with $CuCl_2$ and $ZnCl_2$ in DMSO, defined as the slope ratio of the rectilinear dependence $\log k_{ef} = f(\lg c_{CuCl_2})$ and $\log k_{ef} = f(\lg c_{ZnCl_2})$, is equal to one. The rate of $CdP(PhCl)_4$ metal exchange with $CuCl_2$ and $ZnCl_2$ in DMSO is described by first-order Eq. (2) for the cadmium complex, as evidenced by the rectilinear dependence of $\lg[c^0_{CdP(PhCl)_4}/c_{CdP(PhCl)_4}]$ on the reaction time τ.

$$-dc_{CdP(PhCl)_4}/d\tau = k_v[CdP(PhCl)_4][MCl_2]. \qquad (2)$$

Information about a possible mechanism of the stoichiometric metal exchange reaction in macrocyclic and porphyrin complexes is presented in [2, 9]. It is assumed that there are two mechanisms of exchange—associative and dissociative.

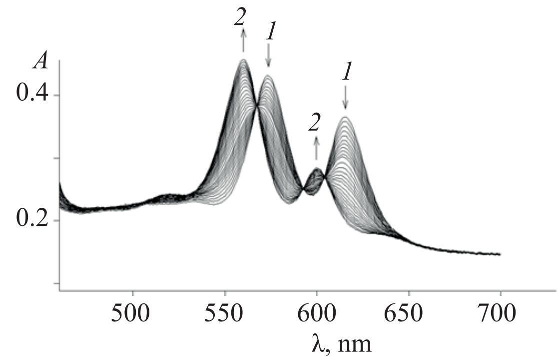


Fig. 1. The change in EAS in the course of metal exchange of $CdP(PhCl)_4$ with $ZnCl_2$ in DMSO, $c_{CdP(PhCl)_4} = 2.0\times10^{-5}$ M (*1*) at the initial time and (*2*) after 80 min at 328 K.

Apparently, the reactions of $CdP(PhCl)_4$ metal exchange with $ZnCl_2$ and $CuCl_2$ in DMSO proceed by a bimolecular associative mechanism [3, 10, 11]. In the first bimolecular stage (3), an intermediate binuclear complex (intermediate) is formed. It can be formed immediately after the solutions are poured together and then it is easily determined spectrally, or this stage is inhibited. In the second slow monomolecular stage (4), the intermediate dissociates to form final exchange products.

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

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

Stage (4) is observed in the EAS as a change in the intensity of absorption bands (Fig. 1). In a strongly coordinating DMSO medium, the intermediate is not fixed spectrally.

During the experiment, the influence of the salt solvate nature on the metal exchange rate was established. Comparison of effective rate constants of the $CdP(PhCl)_4$ metal exchange with $ZnCl_2$ and $CuCl_2$ in DMSO shows that the metal exchange with $CuCl_2$ is 43 times faster than with $ZnCl_2$.

The rate of metal exchange is determined to a greater extent by the stability of the exchange complex itself than

Table 1. Rates of the Cd^{2+} exchange for Cu^{2+} in the complex $CdP(PhCl)_4$ in DMSO [$c_{CdP(PhCl)_4} = 2.0\times10^{-5}$ M]

$c_{CuCl_2}\times10^3$, M	T, K	$k_{ef}\times10^2$, s^{-1}	k_v, L mol^{-1} s^{-1}	E_a, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
2.00	303	3.20±0.01	16.0	65±9	–87±36
	298	2.50±0.01	12.5		
	293	1.50±0.01	7.5		
	288	0.85±0.01	4.3		
1.73	303	3.15±0.01	18.2	72±6	–35±20
	298	2.21±0.01	12.8		
	293	1.40±0.01	8.1		
	288	0.71±0.01	4.1		
1.33	303	2.97±0.01	22.3	73±8	–50±29
	298	1.67±0.01	12.6		
	293	1.08±0.01	8.1		
	288	0.65±0.01	4.9		
1.07	303	2.29±0.01	21.4	74±5	–50±28
	298	1.51±0.01	14.1		
	293	0.89±0.01	8.3		
	288	0.50±0.01	4.6		

Table 2. Rates of the Cd^{2+} exchange for Zn^{2+} in the complex $CdP(PhCl)_4$ in DMSO [$c_{CdP(PhCl)_4} = 2.0\times10^{-5}$ M]

$c_{ZnCl_2}\times10^3$, M	T, K	$k_{ef}\times10^2$, s^{-1}	k_v, L mol^{-1} s^{-1}	E_a, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
2.00	328	9.87±0.01	0.49	14±5	–266±20
	318	8.22±0.01	0.41		
	298	5.88±0.01	0.29		
1.73	328	8.96±0.01	0.52	15±5	–266±20
	318	7.5±0.01	0.43		
	298	5.23±0.01	0.30		
1.33	328	7.01±0.01	0.530.45	14±6	–271±19
	318	5.96±0.01			
	298	4.21±0.01	0.32		
1.07	328	5.91±0.01	0.55	16±7	–266±21
	318	4.95±0.01	0.46		
	298	3.21±0.01	0.30		

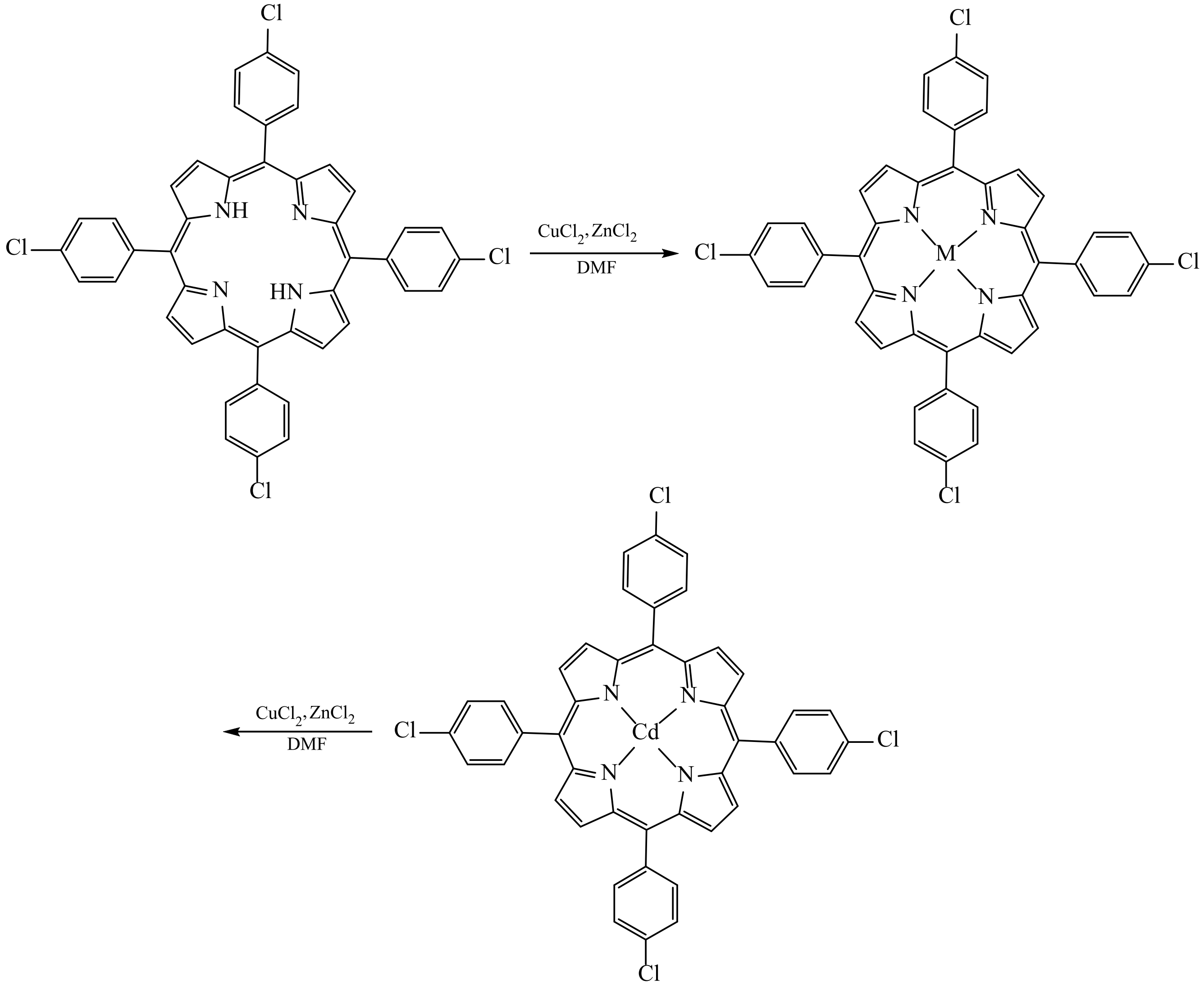
by the coordinating ability of the ligand. This, and also the greater reactivity of complexes in the metal exchange reactions compared to the reactivity of porphyrins in the complex formation reactions, points to the associative path of metal exchange in cadmium porphyrin complexes.

Comparison of effective metal exchange rate constants for Cd(II) octa(4-bromophenyl)porphyrinate $CdP(PhBr)_8$ with $CuCl_2$ and $ZnCl_2$ [7] and for $CdP(PhCl)_4$ metal exchange with the same salts in DMSO shows that the $CuCl_2$ metal exchange with $CdP(PhCl)_4$ in DMSO proceeds ~130 times faster than with $CdP(PhBr)_8$, and the $ZnCl_2$ metal exchange with $CdP(PhCl)_4$ proceeds in DMSO ~300 times faster than with $CdP(PhBr)_8$. This is due to the fact that Cl^- ions are stronger electron-acceptors than Br^- ions.

Complexes of Zn(II) and Cu(II) with tetra(4-chlorophenyl)porphyrin were synthesized in a dimethylformamide medium using complex formation and metal exchange reactions (Scheme 2).

Metal exchange of $CdP(PhCl)_4$ with copper chloride (mole ratio 1 : 10) in DMF occurs almost instantly at room temperature. When $CdP(PhCl)_4$ and copper(II) chloride are dissolved in DMF, the color of the solution changes from emerald green to red-brown. The EAS of the sample dissolved in DMF contains bands with λ_{max} = 415, 539, 579 nm, whereas the bands of the original complex at λ_{max} = 439, 577, 622 nm disappear. Under similar conditions the metal exchange of $CdP(PhCl)_4$ with zinc(II) chloride proceeds for 10 min. The color of the dimethylformamide solution of the reaction mixture turns purple. The EAS of the zinc complex in DMF contains bands with λ_{max} = 405, 426, 559, 598 nm. The complexation of $H_2P(PhCl)_4$ with zinc and copper acetates (mole ratio 1 : 10) in boiling

Scheme 2.



M = Zn(II), Cu(II).

DMF passes for 60 and 20 s, respectively. A significant decrease in the metal exchange temperature of labile cadmium porphyrinate compared to the complexation temperature can be explained by the absence of the need to break the N–H bonds of the macrocycle.

When passing from the cadmium complex to the zinc and copper complexes, a hypsochromic shift is observed in EAS in accordance with spectral strength criterion [12], characterized by strengthening M←N σ-bond (for all systems), and M→N π-back bonds (for copper). The mass spectra of zinc and copper porphyrinates show *m/z* peaks 815.5 and 813.3 corresponding to the molecular ions of the synthesized compounds. In the ^{1}H NMR spectrum of the chloro–substituted zinc complex in $CDCl_3$, the signals of pyrrole rings appear at 8.95 ppm, and the signals of phenyl protons H^o and H^m—at 8.01 and 7.85 ppm, respectively.

Thus, the metal exchange reactions of Cd(II) 5,10,15,20-tetra(4–chlorophenyl)porphyrinate with $CuCl_2$ and $ZnCl_2$ in DMSO were studied by spectrophotometric method, and Zn(II) and Cu(II) 5,10,15,20-tetra(4-chlorophenyl)-porphyrinates were obtained. It was shown that the metal exchange reaction proceeds under milder conditions compared to complex formation.

EXPERIMENTAL

Electronic absorption spectra were recorded on a Cary-100 spectrophotometer (Varian). ^{1}H NMR spectra

(500 MHz, CDCl3) were taken on a Bruker AV III-500 device (internal standard-TMS). Mass spectra were recorded on a Maldi Tof Shimadzu Biotech Axima Confidence mass spectrometer (matrix—dihydroxybenzoic acid).

5,10,15,20-Tetra-(4-chlorophenyl)porphyrin of company "Porphychem," chemically-pure grade dimethylformamide, chloroform, dichloromethane, and cadmium acetate, aluminum oxide and DMSO of "Merck" company were used in the work. $CaCl_2$ and $ZnCl_2$ were calcined for 4 h at 200°C. Cd(II) 5,10,15,20-tetra(4-chlorophenyl)porphyrin was synthesized by the Adler method [13].

Cd(II) 5,10,15,20-tetra(4-chlorophenyl)porphyrinate. A mixture of 0.03 g (0.0399 mmol) of tetra(4-chlorophenyl)porphyrin and 0.092 g (0.399 mmol) of $Cd(OAc)_2$ in 20 mL of DMF was heated to the boiling point. The reaction mixture was cooled and poured into water. The precipitate was filtered, washed with water, dried, and re-precipitated from hexane. Yield 0.031 g (0.0355 mmol, 94%). EAS (DMF), λ, nm (log ε): 417 (4.62), 439 (5.47), 577 (4.12), 622 (4.06). ^1H NMR spectrum (C_6D_6), δ, ppm: 8.90 s (8H, pyrrole), 7.96 d ($8H^o$, J = 7.7 Hz), 7.46 d ($8H^m$, J = 7.6 Hz). Mass spectrum, m/z ($I_{rel.}$, %): 862.1. (22) $[M]^+$ (calculated for $C_{44}H_{24}CdCl_4N_4$: 862.9).

Zn(II) 5,10,15,20-tetra(4-chlorophenyl)porphyrinate. *a*. A mixture of 0.02 g (0.0266 mmol) of tetra(4-chlorophenyl)porphyrin and 0.049 g (0.266 mmol) of $Zn(OAc)_2$ in 15 mL DMF was boiled for 1 min, then cooled, water was added, and the product was salted out. The precipitate was filtered, washed with water, dried, and chromatographed on aluminum oxide, the eluent-chloroform. Yield 0.018 g (0.0221 mmol, 83%). EAS (DMF), λ, nm (log ε): 405 (4.75), 426 (5.64), 559 (4.42), 598 (4.09). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 8.95 s (8H, pyrrole), 8.01 d ($8H^o$, J = 7.7 Hz), 7.85 d ($8H^m$, J = 7.6 Hz). Mass spectrum, m/z ($I_{rel.}$, %): 815.5 (97) $[M]^+$ (calculated for $C_{44}H_{24}Cl_4N_4Zn$: 815.9).

b. A mixture of 0.02 g (0.0232 mol) $CdP(PhCl)_4$ and 0.032 g (0.232 mol) of $ZnCl_2$ in 12 mL DMF was kept for 20 min at room temperature and processed as in method *a*. Yield 0.017 g (0.0208 mmol, 88%).

Cu(II) 5,10,15,20-tetra(4-chlorophenyl)porphyrinate. *a*. A mixture of 0.02 g (0.0266 mmol) of tetra(4-chlorophenyl)porphyrin and 0.048 g (0.266 mmol) of $Cu(OAc)_2$ in 15 mL of DMF was boiled for 20 s, then cooled, water was added, and the product was salted out. The precipitate was filtered, washed with water, dried, and chromatographed on aluminum oxides, the eluent—chloroform. Yield 0.018 g (0.0221 mmol, 85%). EAS (DMF), λ, nm (log ε): 395 (4.58), 415 (5.54), 539 (4.33), 579 (3.72). Mass-spectrum, m/z (I_{rel}, %): 813.3 (98) $[M]^+$ (calculated for $C_{44}H_{24}Cl_4CuN_4$: 814.1).

b. A mixture of 0.02 g (0.0232 mol) of $CdP(PhCl)_4$ and 0.031 g (0.232 mol) of $CuCl_2$ in 12 mL of DMF was kept for 5 min at room temperature and processed as in method *a*. Yield 0.017 g (0.0209 mmol, 90%).

The metal exchange reactions of complexes of tetrapyrrole compounds with *d*-metal salts was studied by chemical kinetics and spectroscopy methods. Experimental procedure and processing of experimental data are presented in [14].

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

1. Barrett, P.A., Frye, D.A., and Linstead, R.P., *J. Chem. Soc*., 1938, p. 1157. https://doi.org/10.1039/JR9380001157
2. Hambright, P., *Porphyrin Handbook*, Smith, K., Kadish, K., and Guillard R., Eds., New York: Academic Press, 2000, vol. 3.
3. Berezin, B.D., Zvezdina, S.V., and Berezin, M.B., *Russ. J. Gen. Chem*., 2013, vol. 83, no. 7, p. 410. https://doi.org/10.1134/S1070363213070189
4. Berezin, M.B., Zvezdin, S.V., and Berezin, B.D., *Russ. J. Coord. Chem*., 2007, vol. 33, no. 7, p. 488. https://doi.org/10.1134/S1070328407070032
5. Zvezdina, S.V., Berezin, M.B., and Berezin, B.D., *Russ. J. Coord. Chem*., 2010, vol. 36, no. 12, p. 913. https://doi.org/10.1134/S1070328410120080
6. Zvezdina, S.V., Chizhova, N.V., and Mamardashvili, N.Zh., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 10, p. 989. https://doi.org/10.1134/S1070363214100211
7. Zvezdina, S.V., Chizhova, N.V., and Mamardashvili, N.Z., *Russ. J. Phys. Chem. (A)*, 2017, vol. 91, no. 3, p. 437. https://doi.org/10.1134/S0036024417030335

8. Berezin, B.D., *Koordinatsionnye soedineniya porfirinov i ftalotsianina* (Coordination Compounds of Porphyrins and Phthalocyanine), Moscow: Nauka, 1978.
9. Yatsimirskii, K.B and Lampeka, Ya.D., *Fizikokhimiya kompleksov metallov s makrotsiklicheskimi ligandami* (Physicochemistry of Metal Complexes with Macrocyclic Ligands), Kiev: Naukova Dumka, 1985.
10. Berezin, B.D., Shukhto, O.V., and Berezin, D.B., *Russ. J. Inorg. Chem*., 2002, vol. 47, no. 8, p. 187.
11. Berezin, B.D., Rumyantseva, S.V., and Berezin, M.B., *Russ. J. Coord. Chem*., 2004, vol. 30, no. 4, p. 291. https://doi.org/10.1023/B:RUCO.0000022806.85114.93
12. Berezin, B.D. and Enikolopyan, N.S., *Metalloporfiriny* (Metalloporphyrins), Moscow: Nauka, 1988.
13. Adler, A.D., Longo, F.R., Kampas, F., and Kim, J., *J. Inorg. Nucl. Chem*., 1970, vol. 32, no. 7, p. 2443. https://doi.org/10.1016/0022-1902(70)805 35-8
14. Zvezdina, S.V., Kozgova, E.V., Berezin, M.B., and Berezin, B.D., *Russ. J. Inorg. Chem*., 2007, vol. 52, no. 9, p. 1430. https://doi.org/10.1134/S0036023607090197