The Effect of Chemical Modification of the Macrocycle on the Complex Formation between Porphyrins and Metal Salts in Organic Solvents

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Abstract—The complex formation of β -octaethylporphyrin, β -octaethyl-*meso*-monophenylporphyrin, β -octaethyl*meso*-tetraphenylporphyrin, *meso*-diphenylporphyrin, *meso*-triphenylporphyrin, and *meso*-tetraphenylporphyrin with Zn(II), Cu(II), Co(II), and Mn(II) acetates and chlorides in dimethylformamide, dimethylsulfoxide, pyridine, acetic acid, and a chloroform–methanol 1 : 1 mixture has been studied by means of spectrophotometry. The observed regulations are in line with the concept of chemical reactivity of the N–H bonds in porphyrins of different complexity.

Keywords: porphyrin, complex formation, reaction rate, reactivity, spectrophotometry

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Understanding the relationship between nonplanarity of the porphyrins (H_2P) macrocycle and reactivity of the N–H bonds in their coordination site is a topical issue. The NH-activation, an example of stepwise change in the properties owing to conformational rearrangements, is an important model in the study of the in vivo processes involving porphyrins.

Porphyrins can form complexes with practically any metal [1]. This is due to the formation of four equivalent $N \rightarrow M$ σ -bonds: due to filling of unoccupied s-, p-, and d-orbitals of the corresponding symmetry, the cation can form either direct $(M \rightarrow N)$ or reverse (M \leftarrow N) dative π -bonds with the ligand [2]. Mechanism of coordination of conventional porphyrins with metal cations has been elucidated in the studies of kinetics of the process [1, 2]. In detail, when the porphyrin molecule and the metal cation start to interact, two neighbor M-Solv bonds are weakened, the Solv-M-Solv bond angle is increased, and the bonds are extended. Affected by the metal cation field, two protons of the porphyrin macrocycle leave the molecule plane and are located to the same side of the plane (Scheme 1). This increases the polarity of the N-H bond and strengthens the binding of the proton with the solvent molecule. Further approaching of the

reactants is accompanied by ongoing deformation of two neighbor M-Solv bonds due to the force field of the porphyrin: these solvent molecules are no longer bound to the cation and are expelled from its inner coordination sphere, replaced by two tertiary nitrogen atoms of the porphyrin. The formed donor-acceptor M-N σ-bond is weak but partially compensate the energy loss due to removal of two solvent molecules. At this stage, the interaction follows one of the two possible pathways. If the M-Solv bond as well as the formed H⁺...Solv and X⁻...Solv bonds are not sufficiently strong (in a low-polar solvent: HOAc, CHCl₃, etc.), activation energy of removal of two solvent molecules is low, and the rest of the coordination sphere of the salt is not involved. Other M-Solv and M-X bonds are practically not changed, and the reaction can stop at the stage of the formation of a mixed complex (intermediate) [5].

If the solvent is strongly bound to the cation, and the solvation of the N–H···Solv and M–X···Solv bonds is significant (in a polar coordinating solvent), removal of the two solvent molecules is restricted. Its activation energy is high, and the process can occur only in the proximity of the peak in the potential barrier, when the other M–Solv, M–X, and N–H are



Scheme 1.



strongly deformed and extended. This system is transformed in a strong inner-complex compound (metal porphyrinate) through the transition state via a single elementary bimolecular stage [5].

The major factors determining the complex forming properties of porphyrins include:

- low polarity of the N-H bond (acidic properties of the porphyrin): the reaction mechanism implies that



1, H_2OEtP : $R^1 = R^4 = R^7 = R^{10} = H$, $R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{11} = R^{12} = Et$; **2**, $H_2OEtPPh$: $R^1 = Ph$, $R^4 = R^7 = R^{10} = H$, $R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{11} = R^{12} = Et$; **3**, $H_2OEtP(Ph)_4$: $R^1 = R^4 = R^7 = R^{10} = Ph$, $R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{11} = R^{12} = Et$; **4**, $H_2P(Ph)_2$: $R^1 = R^7 = Ph$, $R^4 = R^{10} = H$, $R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{11} = R^{12} = H$; **5**, $H_2P(Ph)_3$: $R^1 = R^4 = R^7 = Ph$, $R^{10} = Ph$, $R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{11} = R^{12} = H$; **6**, $H_2P(Ph)_4$: $R^1 = R^4 = R^7 = R^7 = R^1 = R^{12} = H$; **7** = R^{10} = Ph, $R^2 = R^3 = R^5 = R^6 = R^8 = R^9 = R^{11} = R^{12} = H$; **6**, $H_2P(Ph)_4$: $R^1 = R^4 = R^7 = R^1 = R^1$

dissociation of the N–H bonds is usually the ratelimiting step of the complex formation [2, 5];

- aromaticity (rigidity) of the porphyrin macrocycle; macrocyclic effect [6–8], effect of atom-electron shielding of the reactive sites hindering the approach of the reactants and decreasing the reactivity;

- strength of the solvation sphere of the reacting salt, determined by the nature of the organic solvent and increasing with the growth of the solvent polarity (ϵ) and donor number (DN) [9];

- the solvent nature: the solvent actively participates in the formation of the transition state and its solvation. Moreover, the solvent polarity triggers the reaction pathway to formation of either intermediate of metal porphyrinate [1, 2, 5].

To elucidate the mechanisms of the porphyrins interaction with metal salts and to estimate the effect of aromaticity of the π -system of the macrocycle on the type of the porphyrins interaction with metal salts and solvents differing in polarity, we studied the steric and electronic effects of *meso*-phenyl substituents in the molecule of porphyrin and octaethylporphyrin (Scheme 2).

Octaethylporphyrins $H_2OEtPPh 2$ and $H_2OEtP(Ph)_4$ 3 are typical octaalkyltetraarylporphyrins; such compounds are among most interesting substituted porphyrins, structural hybrids of $H_2P(Ph)_4$ 6 and $H_2OEtP 1$.



Fig. 1. Spectral changes (a), $\log [c^0(H_2P)/c(H_2P) = f(\tau) \text{ plot (b)}$, and kinetic curve of absorbance at 501 nm (c) during the complex formation of porphyrin 2 with $Zn(OAc)_2$ in DMF ($c_{porph} = 2.5 \times 10^{-5} \text{ mol/L}$, $c_{salt} = 2.5 \times 10^{-3} \text{ mol/L}$).

We studied the complex formation of porphyrins **1–3** with Zn(II), Cu(II), Co(II), and Mn(II) acetates in DMF by means of spectrophotometry. Overall stoichiometric reaction equation of formation of a metal porphyrinate (MP) from free porphyrin H_2P and salt of doubly-charged cation MX_2 in organic solvent medium is as follows (1).

$$H_2P + [MX_2(Solv)_{n-2}] \rightarrow MP + 2HX + (n-2)Solv.$$
(1)

At low concentration of the salt, reaction (1) strictly follows the second-order rate equation (2) with the first order with respect to the porphyrin and the salt; this equation was used to calculate the reaction rate constant.

$$dCH_2P/dt = -k_v[CH_2P][CMX_2].$$
 (2)

The obtained effective reaction rate constants and activation energies are collected in Tables 1 and 2. Processing of the spectral data to study the metal porphyrin formation is exemplified in Fig. 1.

The data in Table 1 show that the *meso*-phenyl substitution in the H₂OEtP **1** molecule (enhancing the nonplanarity of the macrocycle **3**) resulted in the acceleration of the complex formation with metal acetates in DMF, following the Mn(II) < Co(II) <

Zn(II) < Cu(II) series. The introduction of a single phenyl group in the H₂OEtP molecule accelerated the reaction with $Zn(OAc)_2$ by 6 times; in the case of the reaction with $Cu(OAc)_2$, the reaction was accelerated by 9 times. The change in the activation parameters of reaction (1) showed that non-symmetrical *meso*substitution favored the complex formation. That was likely due to the activation of the N–H bond of the coordination site owing to the substitution.

Analysis of the reference data on the structure and reactivity of di-, tri-, and tetraphenylporphyrins revealed the significant gap in the studies of coordination and solvation properties of those compounds. Therefore, we studied the kinetics of the complex formation between compounds **4–6** and Mn(II), Co(II), Zn(II), and Cu(II) chlorides and acetates in DMF. The experimental data collected in Table 2 revealed that the complex formation of porphyrins **1–6** with the metal acetates was accelerated in the Mn(II) < Co(II) < Zn(II) < Cu(II) series. The reaction rate was significantly affected by the solvent nature (its donoracceptor properties and polarity).

The complex formation of dodecasubstituted H_2P and their less substituted analogs with *d*-metal salts

Salt	Т, К	$k_{\rm eff} \times 10^4, {\rm s}^{-1}$	$k_{\rm v}^{298}$, L mol ⁻¹ s ⁻¹	$E_{\rm a},{\rm kJ/mol}$	ΔS^{\neq} , J mol ⁻¹ K ⁻¹		
$H_2OEtP(1)$							
Mn(OAc) ₂	358	Reaction does not occur					
Co(OAc) ₂	358	Reaction does not occur					
Zn(OAc) ₂	308	0.859	0.469 ^a	54.3	-86		
	318	1.905					
	328	3.144					
Cu(OAc) ₂	298	2.196	0.879	121.3	152		
	308	4.913					
	318	12.001					
	l	H ₂ OEtP	$PPh_1(2)$		l		
Mn(OAc) ₂	358	Reaction does not occur					
$Co(OAc)_2$	358	Reaction does not occur					
Zn(OAc) ₂	298	7.314	2.926	47.0	-87		
	308	15.905					
	318	24.276					
Cu(OAc) ₂	298	16.866	7.971	58.4	-40		
	308	36.447					
	318	74.280					
	I	H ₂ OEtP($(Ph)_4$ (3)		I		
Mn(OAc) ₂	358	Reaction does not occur					
Co(OAc) ₂	338	2.368	0.241 ^a	66.8	-56		
	348	4.491					
	358	8.921					
Zn(OAc) ₂	288	9.106	14.010	96.5	92		
	293	14.440					
	298	35.018					
Cu(OAc) ₂	298	Reaction occurs instantaneously					

Table 1. Kinetic parameters of octaethylporphyrins 1–3 coordination with metal salts in DMF ($c_{\text{porph}} = 2.5 \times 10^{-5} \text{ mol/L}$, $c_{\text{salt}} = 2.5 \times 10^{-3} \text{ mol/L}$)

[10–12] has revealed that the successive *meso*-substitution in the $H_2(\beta-Et)_8P$ molecules (enhancing the nonplanarity of the macrocycle [13, 14]) accelerated the complex formation with Zn(II) in electron-donor solvents (DMF, pyridine, and acetonitrile) and decelerated in proton-donor ones (HOAc) [10, 13, 15–17].

We observed significant difference in the kinetic parameters of reaction (1) between porphyrin 2 and

 $Zn(OAc)_2$ depending on the medium (Table 3). The complex formation was decelerated in electron-donor solvents (DMF, pyridine, and DMSO) but accelerated in proton-donor ones (HOAc and 1 : 1 CHCl₃– CH₃OH). That could be explained by the concept of reactivity of the N–H bonds of the H₂P molecules [18]. The macrocycle of phenylporphyrins is practically planar, and the access of solvent molecules to the nitrogen atoms (–N= and –NH) is restricted. Moreover,

Salt	<i>Т</i> , К	$k_{\rm eff} \times 10^4$, s ⁻¹	$k_{\rm v}^{298}$, L mol ⁻¹ s ⁻¹	<i>E</i> _a , kJ/mol	ΔS^{\notin} , J mol ⁻¹ K ⁻¹		
		H ₂ H	$P(Ph)_2(4)$		_ I		
Zn(OAc) ₂	358	Reaction does not occur					
$ZnCl_2$	338	1.095	0.070^{a}	112.9	75		
	348	6.106					
	358	10.551					
Cu(OAc) ₂	338	9.636	1.319 ^a	56.4	-59		
	348	21.065					
	358	37.015					
CuCl ₂	288	8.421	6.532	47.2	-79		
	293	12.061					
	298	16.329					
Co(OAc) ₂	353	6.858	0.208 ^a	73.7	-36		
	358	10.432					
	363	13.700					
CoCl ₂	353	0.845	0.005^{a}	178.9	244		
	358	2.280					
	363	4.543					
Mn(OAc) ₂	358		Reaction does	not occur	I.		
MnCl ₂	358	Reaction does not occur					
		H ₂ H	$P(Ph)_{3}(5)$				
Zn(OAc) ₂			Reaction is very slov	V			
ZnCl ₂	338	1.290	0.089 ^a	104.2	50		
	348	5.796					
	358	10.398					
Cu(OAc) ₂	298	5.861	2.340	54.8	-62		
	308	11.020					
	318	23.440					
CuCl ₂	288	5.584	4.963	56.9	-49		
	293	8.600					
	298	12.408					
Co(OAc) ₂	353	12.330	0.240^{a}	77.4	-21		
	358	18.999					
	363	25.530					
CoCl ₂	353	0.863	0.046	95.8	9		
	358	1.472					
	363	2.124					
$Mn(OAc)_2$	358		Reaction does	not occur	I		
MnCl	358		Reaction does	not occur			

Table 2. Kinetic parameters of coordination of phenylporphyrins **4–6** with metal chlorides and acetates in DMF ($c_{\text{porph}} = 2.5 \times 10^{-5} \text{ mol/L}, c_{\text{salt}} = 2.5 \times 10^{-3} \text{ mol/L}$)

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Salt	Т, К	$k_{\rm eff} \times 10^4, {\rm s}^{-1}$	$k_{\rm v}^{298}$, L mol ⁻¹ s ⁻¹	$E_{\rm a}$, kJ/mol	ΔS^{\neq} , J mol ⁻¹ K ⁻¹		
$H_2P(Ph)_4$ (6)							
Zn(OAc) ₂		Reaction is very slow					
ZnCl ₂	338	1.169	0.081 ^a	107.9	61		
	348	7.130					
	358	10.240					
Cu(OAc) ₂	298	7.043	2.997	62.2	-35		
	308	14.111					
	318	33.978					
CuCl ₂	288	4.910	3.965	50.1	-74		
	293	7.160					
	298	9.913					
$Co(OAc)_2$	353	18.059	0.340 ^a	71.5	-34		
	358	27.284					
	363	35.359					
$Co(OAc)_2$	353	18.059	0.340 ^a	71.5	-34		
	358	27.284					
	363	35.359					
CoCl ₂	353	1.584	0.083	83.8	-19		
	358	2.264					
	363	3.475					
Mn(OAc) ₂	558		Reaction doe	es not occur	1		
MnCl ₂	558		Reaction doe	es not occur			

 Table 2. (Contd.)

^a Calculated using Arrhenius equation.

the N–H bonds are weakly polarized. Both factors practically exclude the interaction of the NH groups with molecules of electron-donor solvent, and the reaction can hardly occur. Due to the low basicity and structural reasons, the HOAc molecule only weakly interacts with the -N= tertiary atoms of the porphyrin molecule via the acid-base mechanism. The formed Hassociate likely exhibit low degree of the proton transfer, since it is not observed in the electronic absorption spectra. The protons of the associate act as acceptors of electron density, due to interrelation of acid-base sites of the porphyrins of the common aromatic π -system of the macrocycle. The considered mechanism is only operative for predominantly planar porphyrins with moderate rigidity of the macrocycle.

According to the obtained kinetic data, the $CHCl_3$ - CH_3OH (1 : 1) system was the best for the complex formation involving compound **2**. Acceleration of reaction (1) in the proton-donor medium in comparison with the electron-donor solvent was primarily due to the entropy factor, the activation energy being almost unchanged (Table 3). Figures 2–5 display the spectral changes during the complex formation of porphyrin **4** with $Zn(OAc)_2$ in different organic solvents.

Analysis of own and reference data showed that the solvent nature marginally affected the general view of



Fig. 2. Spectral changes during complex formation of compound 2 with $Zn(OAc)_2$ in DMSO ($c_{porph} = 2.5 \times 10^{-5} \text{ mol/L}$, $c_{salt} = 2.5 \times 10^{-3} \text{ mol/L}$).

the absorption spectrum, except for acetic acid: in the latter case, the complex formation was preceded by the protonation. The increase in the reactivity of H_2OEtP in the complex formation reaction with the *meso*-substitution of the molecule was due to the simultaneous effects of the macrocycle polarization and distortion. The minor distortion of the H_2P molecule planarity by the *meso*-phenyl groups was confirmed by the kinetic data. Inhibiting action of phenylporphyrins and its acceleration by a proton-donor solvent was revealed; that directly confirmed that the considered compounds were porphyrins with conventional properties.



Fig. 3. Spectral changes during complex formation of compound 2 with $Zn(OAc)_2$ in pyridine ($c_{porph} = 2.5 \times 10^{-5} \text{ mol/L}$, $c_{salt} = 2.5 \times 10^{-3} \text{ mol/L}$).

EXPERIMENTAL

Porphyrins **1–6** (Aldrich, 97%), organic solvents (Merck, 99%), and inorganic salts (Acros, 99%) were used as received.

The complex formation was studied by recording electronic absorption spectra of the solutions using a Cary 300 spectrophotometer (Varian). To do so, solutions of the studied porphyrin $(2.5 \times 10^{-5} \text{ mol/L})$ and the salt $(2.5 \times 10^{-3} \text{ mol/L})$ in an organic solvent were put in the cell maintained at constant temperature (±0.1°C), and the absorbance at the wavelength corresponding to the maximum in the spectrum of the

Table 3. Kinetic parameter 10^{-5} mol/L, $c_{salt} = 2.5 \times 10^{-3}$	ers of porphyrin mol/L)	2 coordination	n with	zinc acetate	in vario	ous organic solvents	$S DMF (c_{por})$	_{ph} = 2	5×
		4	1	200	1 1		,	1	1

Solvent	Т, К	$k_{\rm eff} \times 10^4$, s ⁻¹	$k_{\rm v}^{298}$, L mol ⁻¹ s ⁻¹	$E_{\rm a}$, kJ/mol	ΔS^{\neq} , J mol ⁻¹ K ⁻¹		
DMF	358	Reaction does not occur					
DMSO	353	1.260	0.127 ^a	64.6	-76		
	358	1.763					
	363	2.311					
Pyridine	338	2.780	0.538 ^a	32.1	-154		
	348	3.918					
	358	5.272					
HOAc	288	6.792	5.483	50.1	-71		
	293	10.092					
	298	13.708					
CHCl ₃ -CH ₃ OH (1 : 1)	288	31.054	28.540	59.0	-49		
	293	57.879					
	298	71.341					



Fig. 4. Spectral changes during complex formation of compound 2 with $Zn(OAc)_2$ in HOAc ($c_{porph} = 2.5 \times 10^{-5} \text{ mol/L}$, $c_{salt} = 2.5 \times 10^{-3} \text{ mol/L}$).

formed metal porphyrinate was monitored. Kinetic studies of the complex formation were performed over 288–363 K range.

Current concentration of the starting porphyrin was calculated using Eq. (3).

$$c = c_0 (A_{\infty} - A_{\tau}) / (A_{\infty} - A_0).$$
(3)

In Eq. (3), A_0 , A_{τ} , and A_{∞} are absorbances of the solution at times zero, τ , and after the reaction is complete; c_0 is the starting porphyrin concentration.

Effective reaction rate constant $k_{\text{eff}} = k_v \cdot c_{\text{соль}}, k_v$ being the true rate constant) was calculated from the pseudo first-order kinetic equation (4).

$$k_{\rm eff} = (1/\tau) \ln (c_0/c).$$
 (4)

Activation energy (E_a , kJ/mol) of the reactions was calculated from the temperature dependence of the complex formation rate constant using the Arrhenius equation (5). The activation entropy (ΔS^{\neq} , J mol⁻¹ K⁻¹) was calculated using Eq. (6).

$$E_{\rm a} = 2.3R \frac{T_1 T_2}{T_2 - T_1} \log \frac{k_{\rm v}(T_2)}{k_{\rm v}(T_1)},\tag{5}$$

$$k_{\rm v} = \frac{\frac{\alpha kT}{n} \exp(\frac{\Delta H - T\Delta S}{RT}).$$
 (6)

Since the activation enthalpy $\Delta H = E_a - RT$, assuming that the transmission coefficient was equal to unity $\alpha = 1$, Eq. (7) was obtained.



Fig. 5. Spectral changes during complex formation of compound 2 with $Zn(OAc)_2$ in $CHCl_3$ - CH_3OH (1 : 1) $(c_{porph} = 2.5 \times 10^{-5} \text{ mol/L}, c_{salt} = 2.5 \times 10^{-3} \text{ mol/L}).$

$$\Delta S^{\neq} = 2.3R \log k_{\rm v}^{298} + E_{\rm a}/T - 253.27. \tag{7}$$

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REFERENCES

- Uspekhi khimii porfirinov (Advances in the Chemistry of Porphyrins), Golubchikov, O.A., Ed., St. Petersburg: NII Khimii S.-Peterburg. Gos. Univ., 1997, vol. 1, p. 94.
- 2. Berezin, B.D., Coordination Compounds of Porphyrins and Phthalocyanines, New York; Toronto: Wiley, 1981.
- Askarov, K.A., Berezin, B.D., Evstigneeva, R.P., Nikolopyan, N.S., Kirillova, G.V., Koifman, O.I., Mironov, A.F., Ponomarev, G.V., Semeikin, A.S., and Khelevina, O.G., *Porfiriny: struktura, svoistva, sintez* (Porphyrins: Structure, Properties, Synthesis), Moscow: Nauka, 1985.
- Berezin, B.D. and Enikolopyan, N.S., *Metalloporfiriny* (Metalloporphyrins), Moscow: Nauka, 1988.
- Berezin, B.D., Teor. Eksp. Khim., 1973, vol. 9, no. 4, p. 500.
- Problemy khimii rastvorov (Problems in the Chemistry of Solutions), Kutepov, A.M., Ed., Moscow: Nauka, 2001, p. 326.
- 7. Berezin, B.D., Berezin, M.B., and Berezin, D.B., *Ros. Khim. Zh.*, 1997, vol. 41, no. 3, p. 105.
- Nguyen, N.T., Dehaen, W., Mamardashvili, G., Gruzdev, M., and Mamardashvili, N., *Supramolecular Chem.*, 2013, vol. 25, no. 3, p. 180. doi 10.1080/ 10610278.2012.741687; Borovkov, V.V., Mamardashvili, N.Zh., and Inoue, Y., *Russ. Chem. Rev.*, 2006, vol. 75, no. 8, p. 737. doi 10.1070/ RC2006v075n08ABEH003630

- Berezin, B.D. and Golubchikov, O.A., Koordinatsionnaya khimiya sol'vatokompleksov solei perekhodnykh metallov (Coordination Chemistry of Solvate Complexes of Transition Metal Salts), Moscow: Nauka, 1992.
- Dudkina, N.S., Shatunov, P.A., Kuvshinova, E.M., Semeikin, A.S., Pukhovskaya, C.G., and Golubchikov, O.A., *Zh. Obshch. Khim.*, 1998, vol. 68, no. 12, p. 2042.
- Takeda, J., Ohya, T., and Sato, M., *Inorg. Chem.*, 1992, vol. 31, no. 13, p. 2877. doi 10.1021/ic00039a038
- 12. Berezin, D.B., Bazlova, I.Yu., Malkova, O.V., and Andrianov, V.G., *Russ. J. Coord. Chem.*, 2000, vol. 26, no. 4, p. 295.
- Senge, M.O., Porphyrin Handbook. Highly Substituted Porphyrins, New York: Academic Press, 2000, vol. 1, ch. 6, p. 239.

- 14. Medforth, C.J., *Porphyrin Handbook. NMR Spectroscopy of Diamagnetic Porphyrins*, New York: Academic Press, 2000, vol. 5, ch. 35, p. 1.
- Uspekhi khimii porfirinov (Advances in the Chemistry of Porphyrins), Golubchikov, O.A., Ed., St. Petersburg: NII Khimii S.-Peterburg. Gos. Univ., 2004, vol. 4, p. 268; Golubchikov, O.A., Kuvshinova, E.M., and Pukhovskaya, S.G., *Russ. Chem. Rev.*, 2005, vol. 74, no. 3, p. 249. doi 10.1070/RC2005v074n03ABEH000925
- 16. Berezin, D.B. and Toldina, O.V., *Russ. J. Inorg. Chem.*, 2002, vol. 47, no. 12, p. 1910.
- Berezin, B.D., Karmanova, T.V., Gromova, T.V., and Semeikin, A.S., *Russ. J. Coord. Chem.*, 2002, vol. 28, no. 12, p. 834. doi 10.1023/A:1021626127175
- 18. Berezin, D.B., Toldina, O.V., and Kumeev, R.S., *Russ. J. Phys. Chem. (A)*, 2004, vol. 78, no. 8, p. 1250.