ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2018, Vol. 63, No. 5, pp. 682–686. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © N.V. Chizhova, O.V. Mal'tseva, R.S. Kumeev, N.Zh. Mamardashvili, 2018, published in Zhurnal Neorganicheskoi Khimii, 2018, Vol. 63, No. 5, pp. 650–654.

Synthesis and Spectral Properties of Ni(II), Pd(II), Pt(II), and Pt(IV) Tetraphenyltetrabenzoporphyrinates

N. V. Chizhova*, O. V. Mal'tseva, R. S. Kumeev, and N. Zh. Mamardashvili
Krestov Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, 153045 Russia
**e-mail: nvc@isc-ras.ru*

Received February 2, 2017

Abstract—Complexation reactions of 5,10,15,20-tetraphenyltetrabenzoporphyrin and transmetallation of its cadmium complex with nickel(II) acetate, Ni(II), Pd(II), and Pt(II) chlorides in dimethylformamide and phenol have been studied. The corresponding Ni(II), Pd(II), and Pt(II) porphyrinates have been synthesized. $Pt^{IV}Br_2$ porphyrinate has been obtained by the treatment of Pt(II) 5,10,15,20-tetraphenyltetrabenzoporphyrinate with bromine in chloroform. The obtained compounds have been characterized by elemental analysis, electronic absorption and ^{1}H NMR spectroscopy and mass spectrometry.

DOI: 10.1134/S0036023618050200

Interest in the synthesis and properties of nickel, palladium, and platinum porphyrin complexes is caused by the possibility of their application as molecular thermometers, sensors, and molecular switches [1–3]. Porphyrin compounds with palladium are used for designing controllable functional materials.

Nickel(II) tetraphenyltetracyclohexenoporphyrinate was obtained in the work [4] by reaction of the corresponding porphyrin with nickel(II) acetate in a refluxing chloroform–methanol–triethylamine mixture. Oxidation of the resultant compound with 2,3-dichloro-5,6-dicyanobenzonitrile (DDQ) in tetrahydrofuran led to Ni(II) 5,10,15,20-tetraphenyltetrabenzoporphyrinate. The synthesis of Pd(II) tetra(4-methoxycarbonylphenyl)tetracyclohexenoporphyrinate required refluxing of the corresponding porphyrin with palladium chloride in benzonitrile for 3–5 min [4]. Pd(II) tetra(4-buthoxycarbonylphenyl)tetrabenzoporphyrinate was prepared in similar manner by the complexation of porphyrin ligand with $PdCl_2$ in refluxing benzonitrile [5]. The yield of metalloporphyrins in the cited works was 85–90%. Palladium(II) 5,10,15,20-tetraphenyltetrabenzoporphyrinate was synthesized by the authors [6] by refluxing porphyrin ligand with palladium(II) acetate in dimethylformamide solution in 12.3% yield.

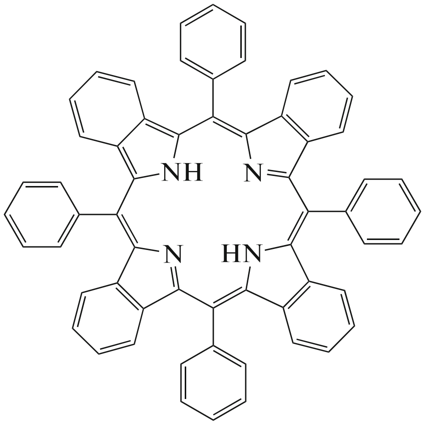
Template cyclotetramerization is often used for preparing labile Cd(II) and Mg(II) porphyrinates [7–9]. In this case, it is expedient to use transmetallation of labile porphyrin complexes to prepare metalloporphyrins [10]. A comparative study of tetrabenzoporphyrin complexation and transmetallation of its cadmium complex with nickel and palladium chloride was carried out in the work [11]. It was shown that reaction time decreases by about an order of magnitude when method [10] is used.

Reaction of tetraphenyltetrabenzoporphyrin and its cadmium complex with copper(II), cobalt(II), and tin(II) chlorides in dimethylformamide (DMF) resulted in preparation of the corresponding Cu(II), Co(II), and Sn(IV) porphyrinates [12].

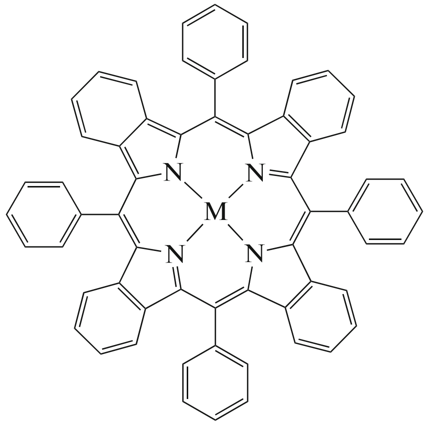
In continuation of works [11, 12], we studied in this work complexation reactions of 5,10,15,20-tetraphenyltetrabenzoporphyrin (**1**) and metal exchange of its cadmium complex (**2**) with nickel(II) acetate, Ni(II), Pd(II), and Pt(II) chlorides in DMF and phenol.

EXPERIMENTAL

^{1}H NMR spectra were recorded on a Bruker AV III-500 spectrometer using TMS as an internal reference. Mass spectra were obtained on a Shimadzu Biotech Axima Confidence Maldi TOF mass spectrometer (with dihydroxybenzoic acid as a matrix). Elemental analysis was performed on a Flash EA 1112 analyzer. DMF, phenol, chloroform, benzene, $Cd(OAc)_2$ of reagent grade, $PdCl_2$, and $PtCl_2$ from Acros were used without additional purification. $NiCl_2$ of reagent grade was calcined at 200°C for 4 h. $Ni(OAc)_2$ of reagent grade was recrystallized from glacial acetic acid and dried at 80°C for 1 h. Aluminum oxide used in the work was from Merck.



(1)



(2)

M = Cd(II) (**2**),
M = Ni(II) (**3**),
M = Pd(II) (**4**),
M = Pt(II) (**5**),
M = Pt(IV) (**6**)

5,10,15,20-Tetraphenyltetrabenzoporphyrin (1) was obtained by procedure reported in [13, 14]. **Cadmium(II) 5,10,15,20-tetraphenyltetrabenzoporphyrinate (2)** was obtained by the complexation of porphyrin **1** with cadmium acetate in dimethylformamide. Synthesis procedure for complex **2** was reported in the work [12].

^{1}H NMR (C_6D_6, δ, ppm): 8.37 (d, 8H, *ortho*-C_6H_5), 7.73 t, (4H, *para*-C_6H_5), 7.63 (d, 8H, *meta*-C_6H_5), 7.16–7.13 (m, 8H, benzene rings in the 3- and 6-positions), 7.10–7.07 (m, 8H, benzene rings in the 4- and 5-positions).

For $C_{60}H_{36}N_4Cd$ anal. calcd. (%): C 77.88; N 6.05; H 3.92.

Found (%): C 77.65; N 6.15; H 3.99.

The course of complexation and metal exchange reactions was monitored by spectrophotometry by sampling. Electronic absorption spectra were recorded on a Cary-100 spectrophotometer at ambient temperature.

Nickel(II) 5,10,15,20-tetraphenyltetrabenzoporphyrinate (3). (a) A mixture of 0.02 g (0.0246 mmol) of porphyrin **1** and 0.044 g (0.246 mmol) of $Ni(OAc)_2$ was dissolved in 4 mL of DMF, heated to reflux, refluxed for 40 s, and cooled, water was added, the resultant precipitate was separated by filtration, washed with water, dried, and chromatographed on aluminum oxide (using chloroform as an eluent). Yield 0.017 g (0.0195 mmol, 79%). (b) A mixture of 0.02 g (0.0216 mmol) of complex **2** and 0.028 g (0.216 mmol) of $NiCl_2$ was dissolved in 4 mL of DMF and heated to reflux for 30 s. The mixture was treated similarly to method (a). Yield 0.017 g (0.0195 mmol, 90%).

^{1}H NMR ($CDCl_3$, δ, ppm): 8.04 (d, 8H, *ortho*-C_6H_5), 7.83 (t, 4H, *para*-C_6H_5), 7.75 (d, 8H, *meta*-C_6H_5), 7.16–7.13 (m, 8H, benzene rings in the 3- and 6-positions), 7.10–7.07 (m, 8H, benzene rings in the 4- and 5-positions). MS (m/z (I_{rel}, %)): 870 (83) $[M]^+$, calcd. for $C_{60}H_{36}N_4Ni$: 871.

Palladium(II) 5,10,15,20-tetraphenyltetrabenzoporphyrinate (4). A mixture of 0.02 g (0.0216 mmol) of complex **2** and 0.038 g (0.216 mmol) of $PdCl_2$ was dissolved in 4 mL of DMF, heated to reflux, and refluxed for 30 s. The mixture was treated similarly to complex **3**. Yield 0.016 g (0.0174 mmol, 80%).

^{1}H NMR ($CDCl_3$, δ, ppm): 8.26 (d, 8H, *ortho*-C_6H_5), 7.92 (t, 4H, *para*-C_6H_5), 7.85 (d, 8H, *meta*-C_6H_5), 7.23–7.20 (m, 8H, benzene rings in the 3- and 6-positions), 7.13–7.09 (m, 8H, benzene rings in the 4- and 5-positions). MS (m/z (I_{rel}, %)): 918 (98) $[M]^+$, calcd. for $C_{60}H_{36}N_4Pd$: 919.

Platinum(II) 5,10,15,20-tetraphenyltetrabenzoporphyrinate (5). A mixture of 0.02 g (0.0216 mmol) of complex **2** and 0.057 g (0.216 mmol) of $PtCl_2$ was dissolved in 6 g of phenol, the mixture was heated to reflux for 1 min, refluxed for 2 min, cooled, DMF and distilled water were added, the resultant precipitate was separated by filtration, washed with water, dried, and chromatographed on aluminum oxide using chloroform as an eluent. Yield 0.0165 g (0.0164 mmol, 75%).

^{1}H NMR ($CDCl_3$, δ, ppm): 8.28 (d, 8H, *ortho*-C_6H_5), 7.92 (t, 4H, *para*-C_6H_5), 7.85 (d, 8H, *meta*-C_6H_5), 7.20–7.16 (m, 8H, benzene rings in the 3- and 6-positions), 7.13–7.09 (m, 8H, benzene rings in the 4- and 5-positions). MS (m/z (I_{rel}, %)): 1007 (48) $[M]^+$, calcd. for $C_{60}H_{36}N_4Pt$ 1008.

Platinum(IV)$(Br)_2$ 5,10,15,20-tetraphenyltetrabenzoporphyrinate (6). Complex 5 (0.02 g, 0.0198 mmol) was dissolved in 10 mL of $CHCl_3$. Twelve drops (0.11 mL) of bromine was dissolved in 5 mL of chloroform, 25 drops of the resultant solution was added to the solution of the complex with stirring. The mixture was kept at ambient temperature for 20 min, water was added, the organic layer was separated, and the solvent was evaporated. Yield 0.019 g (0.0163 mmol, 83%).

^{1}H NMR ($CDCl_3$, δ, ppm): 8.34 (br s, 8H, *ortho*-C_6H_5), 8.05 (br s, 4H, *para*-C_6H_5), 7.88 (br s, 8H, *meta*-C_6H_5), 7.20–7.16 (m, 8H, benzene rings in the 3- and 6-positions), 7.08–7.04 (m, 8H, benzene rings in the 4- and 5-positions).

For $C_{60}H_{36}N_4PtBr_2$ anal. calcd. (%): C, 61.71; N, 4.80; H, 3.11; Br, 13.68.

Found (%): C, 61.63; N, 4.89; H, 3.17; Br, 13.40.

RESULTS AND DISCUSSION

The complexation of porphyrin **1** with $Ni(OAc)_2$ (molar ratio 1 : 10) in DMF proceeds when reaction mixture was heated at reflux for 40 s to give Ni(II) 5,10,15,20-tetraphenyltetrabenzoporphyrinate (**3**):

$$\begin{gathered}H_2P + M(OAc)_2(solv)_n \\ \rightleftarrows (solv)_mMP + 2H(OAc) + (n-m)solv,\end{gathered} \tag{1}$$

where H_2P is porphyrin; $M(OAc)_2(solv)_n$ is metal salt solvated complex; solv is solvent; MP is metalloporphyrin.

Electronic absorption spectra of sample dissolved in DMF exhibits the bands with λ_{max} 642, 591, 446, and 417 nm, while the bands of the initial compound at λ_{max} 695, 636, 592, and 465 nm disappeared (Fig. 1). Under similar conditions, Ni(II) tetrabenzoporphyrinate forms on refluxing dimethylformamide solution of the porphyrin and metal salt for 20 min. When $Ni(OAc)_2$ was replaced by nickel chloride, reaction time increases to 60 min [11]. Formation of Sn(IV) tetraphenyltetrabenzoporphyrinate requires porphyrin ligand to be refluxed with tin chloride in DMF for 2 min [12]. Under comparable conditions, Sn(IV) tetrabenzoporphyrinate was obtained for 3 h [6]. Increase in the reactivity of tetraphenyltetrabenzoporphyrin in reaction (1) as compared with unsubstituted tetrabenzoporphyrin can be explained by the electronic effect of the substituents (+C effect of phenyl substituents). According to literature data [15], increase in electron density on tertiary nitrogen atoms of the macrocycle amplifies the interaction of solvated complex cation $MX_2(Solv)_n$ with porphyrin in transition state. The introduction of four bulky phenyl substituents into *meso* positions of tetrabenzoporphyrin seems to result in considerable change in molecule geometry. It is known [15] that coordination properties of porphyrins are considerably affected by the spatial structure of molecules and the size of N_4H_2 reaction center.

Nickel(II) 5,10,15,20-tetraphenyltetrabenzoporphyrinate readily forms on heating of dimethylformamide solution of complex **2** with $NiCl_2$ (molar ratio 1 : 10) to boiling point:

$$CdP + M(OAc)_2(solv)_n \rightarrow Cd(OAc)_2(solv)_n + MP, \tag{2}$$

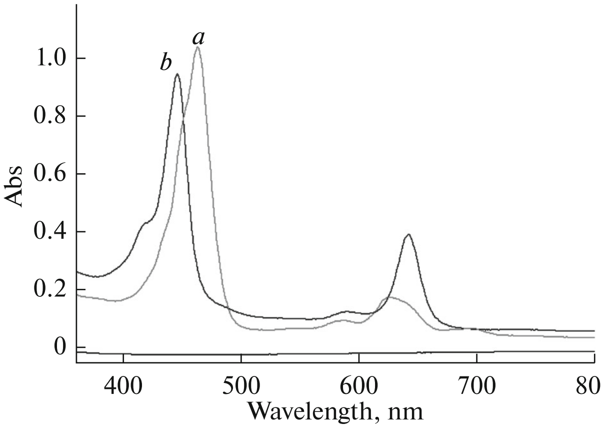


Fig. 1. Electronic absorption spectra in DMF: (*a*) porphyrin **1**, (*b*) Ni(II) complex **3**.

where CdP is cadmium porphyrinate **2**; $MX_2(solv)_n$ is solvato complex of metal salt; solv is solvent; MP is metalloporphyrin.

Electronic absorption spectrum of compound **3** in DMF displays the bands with λ_{max} 642, 591, 446, and 417 nm, and the lack of bands of initial complex 2 with λ_{max} 654, 618, and 481 nm.

Palladium(II) 5,10,15,20-tetraphenyltetrabenzoporphyrinate (**4**) forms in 80% yield when dimethylformamide solution of complex **2** and palladium(II) chloride (molar ratio 1 : 10) was refluxed for 30 s (Fig. 2). The reaction of porphyrin **1** with palladium acetate in DMF leads to compound **4** in much lower yield [6]. Our study showed that the complexation of porphyrin **1** with $PdCl_2$ in refluxing DMF for 5 min proceeds with 25% conversion. Further heating of reaction mixture at reflux leads to the partial destruction of the macrocycle and decrease of yield of the final product.

Reduction of time of metal exchange reaction for labile cadmium complex **2** with nickel and palladium salts as compared with complexation reaction can be explained by the lack of necessity to cleave NH bonds of the macrocycle.

Previously [16], we prepared the corresponding Pt(II) porphyrinates by the reaction of tetraphenylporphyrins substituted at the *meso* and β positions with $PtCl_2$ in refluxing phenol. The reaction of complex **2** with Pt(II) chloride under similar conditions (molar ratio 1 : 10) in refluxing phenol for 2 min leads to formation of Pt(II) 5,10,15,20-tetraphenyltetrabenzoporphyrinate (**5**).

Oxidation of Pt(II) tetraphenylporphyrinate into Pt(IV) complex with Br_2 in chloroform at 0°C for ~2 h was described in the work [17].

We showed that the oxidation of compound **5** with bromine in $CHCl_3$ proceeds over 20 min at ambient temperature to give Pt(IV)Br_2 5,10,15,20-tetraphenyltetrabenzoporphyrinate (**6**). Complex **6** undergoes

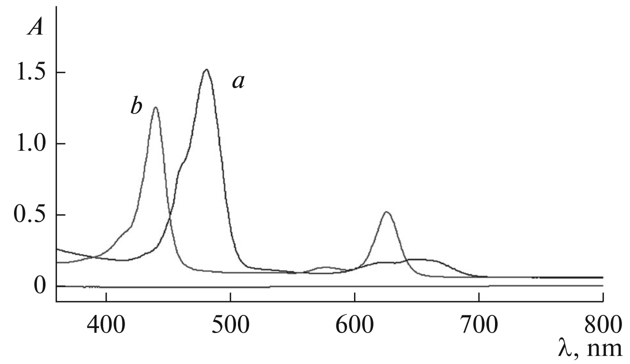


Fig. 2. Electronic absorption spectra in DMF: (*a*) Cd(II) complex **2**, (*b*) Pd(II) complex **4**.

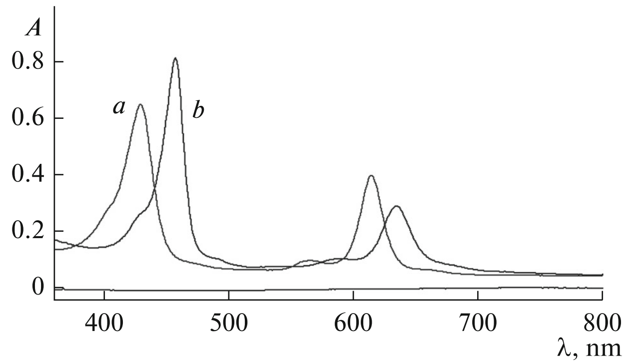


Fig. 3. Electronic absorption spectra in chloroform: (*a*) Pt(II) complex **5**, (*b*) Pt(IV) complex **6**.

partial reduction to Pt(II) porphyrinate **5** when dissolved in DMF and completely transforms into complex **5** one day later.

Table 1 shows electronic absorption spectra of the prepared Cd(II), Ni(II), Pd(II), and Pt(II) porphyrinates in comparison with those described in the literature. A hypsochromic shift of bands in accordance with spectral strength criterion [18], which is characterized by the strengthening of M ← N σ bond (for all complexes) and reverse M → N π bond (for nickel, palladium, and platinum complexes), is observed on passing from Cd(II) to Ni(II), Pd(II), and Pt(II) porphyrinates. The introduction of phenyl substituents in the meso positions of Ni(II), Pd(II), and Pt(II) tetrabenzoporphyrinates leads to the considerable shift of absorption bands to the long-wavelength region as compared with unsubstituted Ni(II) and Pd(II) porphyrinates [11]. Pt(II) → Pt(IV) oxidation also leads to the bathochromic shift of bands in electronic absorption spectra (Fig. 3).

On passing from Ni(II) tetraphenyltetrabenzoporphyrinate to Pd(II) and Pt(II) porphyrinates, ^{1}H NMR spectra in $CDCl_3$ display a downfield shift of *ortho*, *meta*, and *para* phenyl protons. The oxidation of Pt(II) tetraphenyltetrabenzoporphyrinate to Pt(IV) complex leads to signal broadening and downfield shift for *ortho*, *meta*, and *para* protons by 0.06, 0.13, and 0.03 ppm, respectively.

Thus, the reaction of Cd(II) tetraphenyltetrabenzoporphyrinate with $NiCl_2$, $PdCl_2$ in dimethylformamide and $PtCl_2$ in phenol results in the preparation of the corresponding nickel(II), palladium(II), and platinum(II) porphyrinates. Transmetallation method (2) in comparison with complexation approach (1) allows one to shorten reaction time and increase the yield of final products up to 75–90%.

Pt(IV)Br_2 porphyrinate was obtained by the oxidation of Pt(II) tetraphenyltetrabenzoporphyrinate with bromine in chloroform.

The prepared compounds were identified by electronic absorption spectroscopy, ^{1}H NMR, mass spectrometry and elemental analysis.

Table 1. Electronic absorption spectra for Cd(II), Ni(II), Pd(II), Pt(II), and Pt(IV) tetraphenyltetrabenzoporphyrinates, λ, nm (logε)

Compound	Solvent	Band I	Band II	Soret band	Reference
2	DMF	654 (4.20)	618 (4.13)	481 (5.08)	This work
3	CH_2Cl_2	643 (4.73)	591 (4.01)	446 (5.11)	[4]
3	DMF	644 (4.42)		447 (4.84)	[13]
3	DMF	642 (4.47)	591 (3.94)	446 (4.92), 419 (4.42)	This work
4	DMF	628	579	442	[6]
4	DMF	628 (4.44)		442 (4.88)	[13]
4	DMF	626	578	441	[18]
4	DMF	626 (4.46)	578 (3.80)	441 (4.90), 414 (4.27)	This work
5	DMF	613 (4.52)	564 (3.78)	429 (4.75), 402 (4.35)	This work
5	$CHCl_3$	614 (4.53)	565 (3.77)	430 (4.74), 402 (4.34)	This work
6	$CHCl_3$	635 (4.42)	590 (3.82)	458 (4.89), 428 (4.32)	This work

ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation (project no. 14-13-00232) using equipment of the Shared Facility Center "The Upper Volga Regional Center for Physicochemical Research."

REFERENCES

1. *Porphyrins: Spectroscopy, Electrochemistry, and Application*, Ed. by N. S. Enikolopyan (Nauka, Moscow, 1987) [in Russian].
2. M. Engeser, L. Fabbrizzi, M. Licchelli, and D. Sacchi, Chem. Commun. **1191** (1999). doi 10.1039/A901931F
3. J. M. Lupton, Appl. Phys. Lett. **81**, 2478 (2002). doi 10.1063/1.1509115
4. O. S. Finikova, A. V. Cheprakov, I. P. Beletskaya, et al., J. Org. Chem. **69**, 522 (2004). doi 10.1021/jo0350054
5. I. V. Rietveld, E. Kim, and S. A. Vinogradov, Tetrahedron **59**, 3821 (2003).
6. S. A. Vinogradov and D. F. Wilson, J. Chem. Soc., Perkin Trans. **2**, 103 (1995). doi 10.1039/P29950000103
7. R. P. Linstead and P. T. Weiss, J. Chem. Soc. 2975 (1950).
8. A. H. Cook and R. P. Linstead, J. Chem. Soc. 929 (1937).
9. S. V. Zvezdina, O. V. Mal'tseva, N. V. Chizhova, and N. Zh. Mamardashvili, Macroheterocycles **7**, 276 (2014). doi 10.6060/mhc140492m
10. P. Hambright, Usp. Khim. **46**, 1207 (1977).
11. N. V. Chizhova and A. O. Romanova, Russ. J. Inorg. Chem. **52**, 1713 (2007). doi 10.1134/S0036023607110137
12. N. V. Chizhova, O. V. Mal'tseva, A. V. Zav'yalov, and N. Zh. Mamardashvili, Russ. J. Inorg. Chem. **62**, 683 (2017). doi 10.7868/S0044457X17050075
13. N. E. Galanin, E. V. Kudrik, and G. P. Shaposhnikov, RF Patent No. 2215003, Byull. Izobret., No. 30 (2003).
14. N. E. Galanin, Extended Abstract of Doctoral Dissertation in Chemistry (Ivanovo State University of Chemistry and Technology, Ivanovo, 2010).
15. B. D. Berezin, *Coordination Compounds of Porphyrins and Phthalocyanines* (Nauka, Moscow, 1978) [in Russian].
16. N. V. Chizhova, O. M. Kulikova, and N. Zh. Mamardashvili, Russ. J. Gen. Chem. **70**, 2108 (2013). doi 10.1134/S107036321311025X
17. L. M. Mink, J. W. Voce, J. E. Ingersoll, et al., Polyhedron **19**, 1057 (2000). doi 10.1016/S0277-5387(00)00349-1
18. B. D. Berezin and N. S. Enikolopyan, *Metalloporphyrins* (Nauka, Moscow, 1988) [in Russian].
19. A. Y. Lebedev, M. A. Filatov, A. V. Cheprakov, and S. A. Vinogradov, J. Phys. Chem. A **112**, 7723 (2008). doi 10.1021/jp8043626

Translated by I. Kudryavtsev