ISSN 1070-3632, Russian Journal of General Chemistry, 2018, Vol. 88, No. 12, pp. 2559–2563. © Pleiades Publishing, Ltd., 2018. Original Russian Text © N.V. Chizhova, A.V. Shinkarenko, N.Zh. Mamardashvili, 2018, published in Zhurnal Obshchei Khimii, 2018, Vol. 88, No. 12, pp. 2044–2048.

N. V. Chizhova^a*, A. V. Shinkarenko^b, and N. Zh. Mamardashvili^a

^a Krestov Institute of Solutions Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia *e-mail: nvc@isc-ras.ru

^b Ivanovo State University of Chemistry and Technology, Ivanovo, Russia

Received May 24, 2018 Revised May 24, 2018 Accepted May 28, 2018

Abstract—Coordination reactions of 5,10,15,20-tetraphenylporphyrin, 2-bromo-5,10,15,20-tetraphenylporphyrin, 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin, 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin and metal-exchange reactions of their cadmium complexes with tin(II) chloride in dimethylformamide are described. Optimum conditions for the synthesis of Sn(IV) tetraphenylporphyrinates have been elaborated. The obtained substances have been identified by electron absorption spectroscopy, ¹H NMR spectroscopy, and mass-spectroscopy.

Keywords: tetraphenylporphyrins, complexes with Cd(II) and Sn(IV), reaction of complex formation, metal exchange reactions

DOI: 10.1134/S1070363218120162

The interest in synthesis and investigation of porphine complexes with metals of variable valency has been arisen due to their possible application in catalysis and biomedicine [1]. Previously $Sn(IV)Cl_2$ tetraphenylporphyrinate [2] has been synthesized by mixing porphine 1 with $SnCl_2$ in refluxing pyridine and acetic acid. Column chromatography on alumina has resulted in anion exchange of chloride anions with hydroxyl ones. Tin complexes with benzene-substituted phthalocyanine have been synthesized by refluxing of the free bases with tin(II) chloride in 1-chloronaph-thalene during 1.5 h [3].

Aiming to develop efficient procedure of synthesis of tin *ms*- β -substituted porphyrinates, we herein present the approaches to prepare the following substances via coordination reactions: 5,10,15,20 – tetraphenylporphyrin **1**, 2-bromo-5,10,15,20-tetraphenylporphyrin **2**, 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin **3**, and 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin **4** and metal exchange of their cadmium complexes **5–8** with tin(II) chloride in DMF (Scheme 1).

It was shown that the reaction of tetraphenylporphyrin with tin chloride (molar ratio 1 : 10) in DMF under reflux proceeded up to conversion of 25% within an hour [Eq. (1)]. The synthesis of $Sn(OH)_2 5,10,15,20$ tetraphenylphorphyrinate **9** required refluxing of a solution of porphine **1** in DMF with excess of tin chloride during 5–6 h.

$$H_2P + MX_2(Solv)_{n-2} \stackrel{\rightarrow}{\leftarrow} (Solv)_m MP + 2HX + (n-2-m)Solv,$$
(1)

where H_2P is a porphyrin, $MX_2(Solv)_{n-2}$ is a solvated metal salt, Solv is the solvent, MP is the metal porphyrinate.

Sn(IV)(OH)₂ 2-bromo-5,10,15,20-tetraphenylphorphyrinate **10** was obtained via the interaction of the bromine-substituted porphyrine **2** with SnCl₂ (molar ratio 1 : 10) in DMF (reflux) within 20 min. Sn(IV)(OH)₂ 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylphorphyrinate **11** was synthesized under similar conditions via refluxing of a mixture of tetrabromotertraphenylporphyrin and SnCl₂ in DMF during 5 min. Duration of the synthesis of Sn(IV)(OH)₂ 2,3,7,8,12,13,17,18octabromo-5,10,15,20-tetraphenylporphyrinate **12** in boiling DMF was reduced to 2 min (molar ratio **4** : SnCl₂ = 1 : 3). Electron absorption spectrum of the obtained substance in DMF contained the bands with c

Scheme 1.



 $R^{1} = R^{2} = R^{3} = H (1); R^{1} = Br, R^{2} = R^{3} = H (2); R^{1} = R^{2} = Br, R^{3} = H (3); R^{1} = R^{2} = R^{3} = Br (4); R^{1} = R^{2} = R^{3} = H, M = Cd(II) (5); R^{1} = Br, R^{2} = R^{3} = H, M = Cd(II) (6), R^{1} = R^{2} = Br, R^{3} = H, M = Cd(II) (7); R^{1} = R^{2} = R^{3} = Br, M = Cd(II) (8); R^{1} = R^{2} = R^{3} = H, M = Cd(II) (7); R^{1} = R^{2} = R^{3} = Br, M = Cd(II) (8); R^{1} = R^{2} = R^{3} = H, M = Sn(IV)(OH)_{2} (9); R^{1} = Br, R^{2} = R^{3} = H, M = Sn(IV)(OH)_{2} (10); R^{1} = R^{2} = Br, R^{3} = H, M = Sn(IV)(OH)_{2} (11); R^{1} = R^{2} = R^{3} = Br, M = Sn(IV)(OH)_{2} (12).$

 $\lambda_{\text{max}} = 671, 617, \text{ and } 476 \text{ nm}, \text{ while the signals of the starting porphyrin 4 with } \lambda_{\text{max}} = 783, 662, 481, \text{ and } 371 \text{ nm disappeared (Tables 1 and 2). Hence, the duration of the synthesis of the corresponding tin porphyrinate was significantly reduced in the case of monobrominated derivative 2 as compared to the parent tetraphenylporphyrin. That was probably due the electronic effects of the substituents as well as the change of the geometry of the molecule of porphyrine 2 compared to that of compound 1 (better accordance of the reactive site N₄H₂ to the size of the SnCl₂(Solv)_{$ *n*-2}) complex.

The porphyrines reactivity towards the coordination with $SnCl_2$ in DMF was increased with the increase in the number of bromine atoms in the macrocycle. That

fact could be explained by the strengthening of coordination interaction of the solvato complex cation $[MX_2(Solv)_{n-2}]$ with porphyrin in transition state [4] due to an increase in the electron density at the tertiary nitrogen atoms in the macrocycle (+*C*-effect of bromine atoms).

According to the reference data [5–8], the use of transmetalation of labile porphyrine complexes [9] to synthesize these with doubly and triply charged metals leads to significant decrease in the reaction duration and increase in the products yield.

The transmetalation reaction can be generalized as follows:

Compound		Deferences			
	band I	band II	bands III, IV	Soret band	References
1	647 (3.84)	591 (3.96)	549 (4.08), 514 (4.40)	417 (5.61)	
2	648 (3.67)	593 (3.70)	552 (3.72), 517 (4.27)	421 (5.55),	[10]
	648 (3.79)	593 (3.81)	551 (3.78), 518 (4.33)	421 (5.58)	
3	685 (4.02)	612 (3.58)	533 (4.30)	436 (5.52)	[11]
	683 (4.06)	612 (3.70)	533 (4.31)	436 (5.46)	
4	743 (3.87)	626 (4.12)	569 (3.96)	469 (5.29)	[15]
				369 (4.48)	
	741 (3.85)	625 (4.11)	569 (3.95)	469 (5.29)	
				369 (4.48)	

Table 1. Parameters of electron absorption spectra tetraphenylporphyrins 1-4 in CH₂Cl₂

Complex	Solvent	λ , nm (log ε)			
	Solvent	band I	band II	Soret band	
5	ДМФА	623 (3.88)	580 (3.85)	438 (5.27), 417 (4.61)	
6	ДМФА	626 (4.16)	584 (4.15)	442 (5.42), 419 (4.68)	
7	ДМФА	641(4.12)	593 (4.12)	449 (5.23), 420 (4.66)	
8	ДМФА	732 (4.14)	661 (4.04)	491 (4.86), 460 (4.41)	
9	CHCl ₃	599 (4.13)	560 (4.32)	425 (5.66), 404 (4.60)	
10	CHCl ₃	601 (4.09)	563 (4.28)	429 (5.52), 408 (4.58)	
11	CHCl ₃	607 (4.05)	569 (4.32)	437 (5.50), 416 (4.81)	
12	CHCl ₃	660 (4.26)	610 (4.29)	469 (5.26)	

Table 2. Parameters of electron absorption spectra of Cd(II) µ Sn(IV) tetraphenylporphyrinates 5–12

$$MP + M'X_n(Solv)_{m-n} \stackrel{\rightarrow}{\leftarrow} M'P + MX_n(Solv)_{m-n}, \qquad (2)$$

where MP and M'P are metal porphyrinates, $MX_n(Solv)_{m-n}$ and $M'X_n(Solv)_{m-n}$ are the metals solvato complexes.

It was shown, that $Sn(IV)(OH)_2$ 5,10,15,20-tetraphenylporphyrinate **9** and 2-bromo-5,10,15,20-tetraphenylporphyrinate **10** could be synthesized within 10– 15 min via the reaction of the corresponding Cd(II) porphyrinates **6** and **7** with tin chloride (molar ratio 1 : 3) in DMF at room temperature. The tetrabrominesubstituted tin porphyrinate **11** was synthesized via heating the mixture of complex **7** and tin chloride (molar ratio 1 : 5) in DMF to boiling. Synthesis of tin octabromotetraphenylporphyrinate **12** under the same conditions required boiling of complex **8** with SnCl₂ in DMF during 3 min.

Higher reactivity of cadmium porphyrinates towards tin(II) chloride in DMF in comparison with the complex formation could be explained by the fact that the transannular NH bonds are not broken in the former process. The reactivity of Cd(II) tetraphenylporphyrinates was reduced with the increase in the number of bromine atoms in the macrocycle. Probably, that fact was due to conjugation of π -electron density of bromine atom with the delocalized π -electron cloud of the tetrapyrrole macrocycle.

Characteristics of electron absorption spectra of cadmium and tin porphyrinates are given in Table 2. As with porphyrinates of doubly and triply charged metals, the increase in the number of the substituting bromine atoms in tin porphyrinates **10–12** led to bathochromic shift of the spectral bands in comparison with the non-substituted complex **9**. Hypsochromic shift of the absorption bands of Sn(IV) porphyrinates

compared to the cadmium complexes was due to the presence of strong π -dative interaction of the $d\pi$ - $eg(\pi^*)$ -type between the metal ion and the porphyrin macrocycle.

¹H NMR spectrum of $Sn(IV)(OH)_2$ tetraphenylporphyrinate contained the signals of pyrrole and phenyl rings at 9.20, 8.32, and 7.83 ppm. The signals of the hydroxyl protons were found in the strong field region, at -7.44 ppm. ¹H NMR spectrum of the octabromoporphyrinate Sn(IV) **12** did not contain any signals of pyrrole rings. The signals of phenyl rings of compound **12** were shifted upfield in comparison with the non-substituted compound **9**.

Mass spectrum of tin(IV) tetraphenylporphyrinate showed the signals with m/z 732.2 and 749.2, assignable to molecular ions appeared via dissociation of the Sn–OH bonds. The signal with m/z 767.2 corresponded to the Sn(IV)P(OH)₂ structure. Mass spectra of tin(IV) porphyrinates **10–12** contained the signals with m/z 845.3, 1083.3, and 1399.2, corresponding to Sn(IV)(OH)₂P.

In summary, β -bromo-substituted tetraphenylporphyrins and their Cd(II) complexes were synthesized. Coordination reaction of the tetraphenylporphyrins and the metal exchange of their cadmium complexes with tin(II) chloride in DMF was studied. It was shown that the use of transmetalation approach significantly reduced the reaction duration and increased the product yield compared to the direct complex formation route. Sn(IV) tetraphenylporphyrinates were synthesized and identified.

EXPERIMENTAL

5,10,15,20-Tetraphenylporphine (Porphychem), DMF, chloroform ("chemically pure"), and aluminum oxide

(Merck) were used as received. Tin(II) chloride ("chemically pure") was annealed at 135°C during 2 h and dried over CaCl₂. 2-Bromo-5,10,15,20-tetraphenylporphyrin and 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin were synthesized via the procedures adopted from [10–12]. 2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetraphenylporphyrin was obtained as described in [13]. Cd(II) tetraphenylporphyrinates were synthesized as described elsewhere [14] using cadmium acetate instead of cadmium chloride. The complex formation and metal exchange reactions were monitored by means of spectrophotometry.

Electron absorption spectra were recorded using a Cary-100 (Varian) spectrophotometer. Mass spectra were recorded using a Shimadzu Biotech Axima Confidence MALDI TOF mass spectrometer (matrix – dihydroxybenzoic acid). ¹H NMR spectra (500 MHz, CDCl₃) were recorded with a Bruker AV III-500 spectrometer (internal reference – TMS).

Sn(IV)(OH)₂ 5,10,15,20-tetraphenylporphyrinate (9). A solution of 0.02 g (0.0276 mmol) of complex 5 in 10 mL of DMF was mixed with 0.0157 g (0.0827 mmol) of SnCl₂. The reaction mixture was kept at room temperature during 10 min; then the mixture was poured into water and NaCl was added. The precipitate was filtered off, washed with water, dried, and purified by column chromatography on alumina (eluent—chloroform–ethanol, 5 : 1). Yield 0.016 g (0.0210 mmol, 77%). ¹H NMR spectrum, δ , ppm: 9.20 s (8H, pyrrole), 8.32 d (8H, Ph^o, J = 7.7 Hz), 7.83–7.81 m (12H, Ph^{m,p}), –7.44 s (2H, OH). Mass spectrum, m/z (I_{rel} , %): 732.2 (36) [M - 20H]⁺ (calculated for C₄₄H₂₈N₄Sn: 731.4).

Sn(IV)(OH)₂ 2-bromo-5,10,15,20-tetraphenylporphyrinate (10). *a*. A mixture of 0.02 g (0.0288 mmol) of porphyrin 2 and 0.055 g (0.288 mmol) of SnCl₂ in 10 mL of DMF was refluxed during 20 min; then the mixture was cooled and poured into water. NaCl was added, the precipitate was filtered off, washed with water, dried, and purified by column chromatography on alumina (eluent—chloroform). Yield 0.015 g (0.0178 mmol, 63%). ¹H NMR spectrum, δ , ppm: 9.072–9.06 m (2H, pyrrole), 9.04 s (1H, pyrrole), 9.03– 9.00 m (2H, pyrrole), 8.98–8.93 m (2H, pyrrole), 8.31– 8.25 m (6H, Ph^o), 8.18–8.15 m (2H, Ph^o), 7.83–7.77 m (12H, Ph^{m,p}), -7.02 s (2H, OH). Mass spectrum, m/z (I_{rel} , %): 845.3 (98) [M]⁺ [calculated for C₄₄H₂₇N₄BrSn(OH)₂: 844.4]. *b*. The target product was synthesized similarly to compounds **9** from 0.02 g (0.0248 mmol) of complex **6** and 0.014 g (0.0745 mmol) of $SnCl_2$ in 10 mL of DMF, the reaction duration being 15 min. Yield: 0.016 g (0.0190 mmol, 75%).

Sn(IV)(OH)₂ 2,3,12,13-tetrabromo-5,10,15,20tetraphenylporphyrinate (11). *a*. A mixture of 0.02 g (0.0215 mmol) of porphyrin 3 and 0.041 g (0.215 mmol) of SnCl₂ in 10 mL of DMF was refluxed for 5 min and then treated as described above. Yield 0.016 g (0.0148 mmol, 70%). ¹H NMR spectrum, δ, ppm: 8.99 s (4H, pyrrole), 8.19 d (8H, Ph^o, J = 7.7 Hz), 7.80–7.77 m (12H, Ph^{m,p}). Mass spectrum, m/z (I_{rel} , %): 1065.3 (49) [M -OH]⁺ [calculated for C₄₄H₂₄N₄Br₄Sn (OH): 1064.1].

b. 0.0182 g (0.0961 mmol) of SnCl₂ was added to a solution of 0.02 g (0.0192 mmol) of complex 7 in 10 mL of DMF. The reaction mixture was heated to boiling, cooled, and treated as was described above. Yield 0.017 g (0.0157 mmol, 80%).

Sn(IV)(OH)₂ 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrinate (12). *a*. 0.0092 g (0.0483 mmol) of SnCl₂ was added to a solution of 0.02 g (0.0161 mmol) porphyrin **4** in 10 mL of DMF. The reaction mixture was refluxed during 2 min, cooled, and treated as described above. The product was purified by chromatography on alumina (eluent – dichloromethane). Yield 0.015 g (0.011 mmol, 75%). ¹H NMR spectrum, δ, ppm: 8.22 d (8H, Ph^o, *J* = 7.7 Hz), 7.82–7.78 m (12H, Ph^{m,p}). Mass spectrum, m/z (I_{rel} , %): 1399.2 (79) [M]⁺ [calculated for C₄₄H₂₀N₄Br₈Sn(OH)₂: 1396.7].

b. 0.014 g (0.0735 mmol) of SnCl₂ was added to a solution of 0.02 g (0.0147 mmol) of complex **8** in 10 mL of DMF. The reaction mixture was refluxed during 3 min, cooled, and treated as described above. Yield 0.015 g (0.011 mmol, 75%).

ACKNOWLEDGMENTS

This study was financially supported by the Russian Foundation for Basic Research (project no. 18-03-00048_a) and performed using the equipment of the Upper Volga Regional Center for Physico-Chemical Studies.

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

REFERENCES

- Porfiriny: spektroskopiya, elektrokhimiya, primenenie (Porphyrins: Spectroscopy, Electrochemistry, Application), Enikolopyan, N.S., Ed., Moscow: Nauka, 1987.
- Arnold, D.P. and Blok, J., Coord. Chem. Rev., 2004, vol. 48, p. 299. doi 10.1016/j.ccr.2004.01.004
- Slodek, A., Schnurpfeil, G., and Wohrli, D., J. Porph. Phthalocyan., 2011, vol. 21, p. 811. doi 10.1142/ S1088424617500833
- 4. Berezin, B.D., *Koordinatsionnye soedineniya porfirinov i ftalotsianina* (Coordination Compounds of Porphyrins and Phthalocyanine), Moscow: Nauka, 1978.
- Zvezdina, S.V., Mal'tseva, O.V., Chizhova, N.V., and Mamardashvili, N.Zh., *Macroheterocycles*, 2014, vol. 7, no. 3, p. 276. doi 10.6060/mhc140492m
- Mal'tseva, O.V., Chizhova, N.V., Kumeev, R.S., and Mamardashvili, N.Zh., *Macroheterocycl.*, 2017, vol. 10, no. 1, p. 68. doi 10.6060/mhc160541c
- Chizhova, N.V., Mal'tseva, O.V., Zav'yalov, A.V., and Mamardashvili, N.Zh., *Russ. J. Inorg. Chem.*, 2017, vol. 62, no. 5, p. 683. doi 10.1134/S0036023617050072

- Zvezdina, S.V., Chizhova, N.V., and Mamardashvili, N.Zh., *Russ. J. Inorg. Chem.*, 2017, vol. 62, no. 4, p. 517. doi 10.1134/S0036023617040222
- 9. Hembrait, P., Usp. Khim., 1977, vol. 46, no. 7, p. 1207.
- Lembo, A., Tagliatesta, P., and Guldi, D.M., J. Phys. Chem. (A), 2006, vol. 110, no. 40, p. 11424. doi 10.1021/jp062735h
- Atkinson, S.T., Brady, S.P., James, J.P., and Nolan, K.B., *Pure Appl. Chem.*, 1995, vol. 67, no. 7, p. 1109. doi 10.1351/pac199567071109
- Kumar, P.K., Bhyrappa, P., and Varghese, B., *Tetrahedron Lett.*, 2003, vol. 44, p. 4849. doi 10.1016/ S004039(03)01143-2
- Chizhova, N.V., Ivanova, Yu.B., and Mamardashvili, N.Zh., Macroheterotsycly, 2018, vol. 11, no. 1, p. 85. doi 10.6060/mhc171265c
- Maltseva, O.V., Zvezdina S.V., Chizhova, N.V., and Mamardashvili, N.Zh., *Russ. J. Gen. Chem.*, 2016, vol. 86, no. 1, p. 102. doi 10.1134/S1070363216010187
- 15. Bhyrappa, P. and Krishnan, V., *Inorg. Chem.*, 1991, vol. 30, p. 239. doi 1021/ic00002a018