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# Bromo-substituted Mn(II) and Mn(III)-tetraarylporphyrins: Synthesis and properties

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Mono-, tetra- and octa-bromo substituted Mn(II)- and Mn(III)-tetraarylporphyrins were synthesized by reactions of manganese(II) chloride with corresponding porphyrin ligands or their Cd(II)-complexes in DMF. With the use of the metal exchange reaction, the time of the Mn-porphyrins formation is significantly reduced with increase in yield of final products in comparison with the complexation reaction. Mn(III)-tetraarylporphyrins reduce to the Mn(II)-porphyrins in DMF in the presence of NaOH and in pure DMF. The obtained compounds were identified using UV-Vis and <sup>1</sup>H NMR spectroscopy, mass-spectrometry and elemental analysis.

*Keywords:* Bromo-substituted porphyrins; Complexation; Metal-exchange reaction; Mn(II)- and Mn(III)-Tetraarylporphyrins; Spectroscopy

# **1. Introduction**

Manganese is a biometal necessary for life of organisms [1]. A large number of works in this field are conducted at the intersection of chemistry, biology and medicine. The variety of manganese porphyrin especially electronic structure of molecules, their spectral, electrochemical and complex formation properties make it important to study these compounds in terms of the development of theoretical and applied aspects of coordination and bioorganic chemistry. Manganese is essential to perform functions of reproductive, central nervous and endocrine systems. Manganese porphyrins possess the ability to bind free radicals. Mn(III)-porphyrins are usually the most important representative class of metalloporphyrins with catalytic activity in epoxidation of alkenes [2]. The oxidation of sulfides by hydroperite in the presence of the

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Mn(III)-tetra-(4-hydroxyphenyl)porphyrin was studied [3]. According to Miskelly and coworkers [4] and DeFreitas-Silva and coworkers [5], the Mn(III)-5-(3-bromo-4-amino)phenyl-10,15,20-tris-phenyl-2,3,7,8,12,13,17,18-octabromoporphyrin could be used as a biomimetic catalyst of cyclohexane oxidation [5]. Catalytic activity and oxidative stability of a series of pyridyl-substituted manganese porphyrins has been investigated [6].

Electrochemical and electrocatalytic properties of alkyl-substituted porphyrins and their complexes with Mn(III) were investigated [7]. Recently, manganese porphyrins possessing properties of molecular magnetism and capable of nanoporous structures have been prepared and used for the design of new functional materials.

Manganese complexes with tetraphenylporphin were described [8, 9]. Complexes of the Mn(III) with tetrabenzoporphyrin, tetraphenyltetrabenzoporphyrin and octaphenyltetraazaporphyrin were described [10-12]. In present work, the coordination reactions of the 5,10,15,20-tetraphenylporphyrin 1, 2-bromo-5,10,15,20-tetraphenylporphyrin 2, 2,3,12,13tetrabromo-5,10,15,20-tetraphenylporphyrin 3, 5,10,15,20-tetra-(4-bromophenyl)porphyrin 4 and 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin 5 with manganese(II) chloride (MnCl<sub>2</sub>) (eqns. 1 and 2) and the metal exchange reactions of cadmium porphyrin complexes (6-10) (eqns. 3 and 4) with  $MnCl_2$  in DMF were investigated. The metal exchange reaction significantly reduced the time and temperature of the Mn-porphyrins formation in comparison with the complexation reaction. Obtained bromo-substituted Mn(II) and Mn(III)tetraarylporphyrins were identified using UV-Vis and <sup>1</sup>H NMR spectroscopy, mass-spectrometry and elemental analysis.

$$H_2P + MnCl_2 \implies MnP + 2HCl$$
(1)

$$MnP \xrightarrow{O_2, Cl} (Cl)MnP \qquad (2)$$

$$C dP + M n C l_2 \qquad \Longrightarrow \qquad M nP + C dC l_2 \tag{3}$$

$$MnP \xrightarrow{O_2, Cl} (Cl)MnP \qquad (4)$$

# 2. Experimental

#### **2.1.** *Materials and physical measurements*

DMF, CHCl<sub>3</sub>, C<sub>6</sub>H<sub>14</sub>, Cd(OAc)<sub>2</sub>, KOAc, Al<sub>2</sub>O<sub>3</sub> active basic (0.063-0.200 mm) were used without purification; MnCl<sub>2</sub> was annealed at 200 °C for 4 h. Tetraphenylporphyrin 1 and tetra-(4bromophenyl)porphyrin 4 ("Porphychem") were used in the experiment. 2-Bromo-5,10,15,20tetraphenylporphyrin 2 was obtained by an optimized procedure [13]. 2,3,12,13-Tetrabromo-5,10,15,20-tetraphenylporphyrin 3 was synthesized by an optimized procedure [14]. The structure of tetrabromosubstituted porphyrin 3 was proved by X-ray diffraction analysis [14]. 2,3,7,8,12,13,17,18-Octabromotetraphenylporphyrin was synthesized from 5 Cu(II) tetraphenylporphyrin. Cd(II) tetraphenylporphyrins 6-10 were synthesized according to the methods given [15]. Tables S1 and S2 show the characteristics of the UV-Vis spectra of 1-10. The significant difference in UV-vis spectra of basis porphyrin, their Cd-complexes and formed Mn-porphyrins made it possible to use spectrophotometric method for investigating complexation and metal-exchange reactions.

UV-Vis spectra were recorded on a Cary 100 (Varian) spectrophotometer at room temperature. <sup>1</sup>H NMR spectra were recorded on a Bruker AV III-500 spectrometer (internal standard was tetramethylsilane (TMS)). Mass spectra were obtained on a Maldi TOF Shimadzu Biotech Axima Confidence mass spectrometer (matrix – dihydroxybenzoic acid). Elemental analysis was performed on a Flash EA 1112 analyzer.

# 2.2. Synthesis of Cu(II) 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin

To 0.025 g (0.0296 mmol) of copper tetraphenylporphyrin in a mixture of 10 ml of CHCl<sub>3</sub> and 1 ml of DMF was added 0.105 g (0.592 mmol) of NBS and stirred at room temperature for 10 h. The reaction mixture was evaporated to a minimum 10 ml of DMF, H<sub>2</sub>O and NaCl<sub>solid</sub> was added. Dark brown precipitate was filtered off, washed with water and dried, then chromatographed on Al<sub>2</sub>O<sub>3</sub> with CHCl<sub>3</sub>, and precipitated from C<sub>2</sub>H<sub>5</sub>OH. Yield: 68% (0.026 g, 0.0199 mmol). Mass spectrum, m/z (I<sub>rel</sub>,%) 1306.6 (98) [M]<sup>+</sup> was calculated for C<sub>44</sub>H<sub>20</sub>N<sub>4</sub>Br<sub>8</sub>Cu - 1307.5. UV-Vis spectrum in CHCl<sub>3</sub>,  $\lambda$ , nm (log  $\epsilon$ ): 626 sh., 581 (4.33), 467 (5.21), 447 sh.

**2.3.** Synthesis of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin 5 was synthesized according to optimized synthesis procedure [16]. The dark green 5 is formed when

the copper complex in CHCl<sub>3</sub> is treated with mixture of choric and sulfuric acids (4:3) for 2 h at room temperature. Mass spectrum, m/z (Irel,%): 1245.4 (62)  $[M]^+$  was calculated for  $C_{44}H_{22}N_4Br_8$  - 1246.1. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , p.p.m.): 8.22 d. (8H, ortho-C<sub>6</sub>H<sub>5</sub>), 7.79 m. (12H, meta-C<sub>6</sub>H<sub>5</sub> and para-C<sub>6</sub>H<sub>5</sub>), -1.65 s. (2H, NH-protons).

# 2.4. Synthesis of 5,10,15,20-tetraphenylporphyrin chloride Mn(III) (11)

0.02 g (0.0276 mmol) of **6** was dissolved in 40 ml of DMF and 0.07 g (0.552 mmol) of MnCl<sub>2</sub> was added. The reaction mixture was held at room temperature for 30 min, both distilled H<sub>2</sub>O and NaCl<sub>solid</sub> were added to precipitate the product which was filtered off. Finally, dark green precipitate was washed with water, dried and precipitated (powdery) from hexane. Yield: 95% (0.0185 g, 0.0263 mmol). Found %: C 74.98; H 3.97; N 7.88; Cl 4.97. C<sub>44</sub>H<sub>28</sub>N<sub>4</sub>ClMn. Calculated %: C 75.16; H 4.01; N 7.97; Cl 5.04. Mass spectrum, m/z (I<sub>rel</sub>,%): 667.37 (98) [M-Cl]<sup>+</sup> was calculated for C<sub>44</sub>H<sub>28</sub>N<sub>4</sub>Mn - 667.7. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , p.p.m.): 8.30 dr. s. (8H, pyrrole ring), 8.09 br. s. (8H, ortho-C<sub>6</sub>H<sub>5</sub>), 7.75 br. s. (12H, meta-C<sub>6</sub>H<sub>5</sub> and para-C<sub>6</sub>H<sub>5</sub>).

# 2.5. Synthesis of 2-bromo-5,10,15,20-tetraphenylporphyrin chloride Mn(III) (12)

0.02 g (0.0249 mmol) of **7**, 0.06 g (0.498 mmol) of  $MnCl_2$  and 40 ml of DMF was stirred 70 min at room temperature. The dark green precipitate was processed in a similar manner to **11**. Yield: 92% (0.018 g, 0.0230 mmol). Found %: C 67.42; H 3.42; N 10.15.  $C_{44}H_{27}N_4ClBrMn$ . Calculated %: C 67.58; H 3.48; N 10.22. Mass spectrum, m/z ( $I_{rel}$ ,%): 745.22 (95) [M-Cl]<sup>+</sup> was calculated for  $C_{44}H_{27}N_4BrMn$  - 746.6. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , p.p.m.): 8.20, br. s. (7H, pyrrole ring), 8.01 br. s. (8H, ortho- $C_6H_5$ ), 7.55 br. s. (12H, meta- $C_6H_5$  and para- $C_6H_5$ ).

**2.6.** Synthesis of 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin chloride Mn(III) (13) (a) 0.02 g (0.0215 mmol) of 3, 0.054 g (0.430 mmol) of MnCl<sub>2</sub> and 20 ml of DMF was refluxed in a flask for 20 min. After processing, the reaction mixture was dissolved in chloroform, evaporated and precipitated from hexane (dark green precipitate). Yield: 77% (0.017 g, 0.0166 mmol). (b) 0.02 g (0.0192 mmol) of 8, 0.048 g (0.384 mmol) of MnCl<sub>2</sub> and 15 ml of DMF were warmed to a boil and boiled for 25 s (dark green precipitate). Yield: 90% (0.018 g, 0.0173 mmol). They were processed similarly to (a). Found %: C 51.72; H 2.34; N 5.41. C<sub>44</sub>H<sub>24</sub>N<sub>4</sub>ClBr<sub>4</sub>Mn. Calculated %: C 51.88; H 2.38; N 5.50. Mass spectrum, m/z (I<sub>rel</sub>,%): 983.01 (97)  $[M-C1]^+$  was calculated for  $C_{44}H_{24}N_4Br_4Mn$  - 983.3. <sup>1</sup>H NMR (DMSO d<sub>6</sub>,  $\delta$ , p.p.m.): 8.80 br. s. (4H, pyrrole ring), 8.27 br. s. (8H, ortho-C<sub>6</sub>H<sub>5</sub>), 6.75 br. s. (12H, meta-C<sub>6</sub>H<sub>5</sub> and para-C<sub>6</sub>H<sub>5</sub>).

## 2.7. Synthesis of 5,10,15,20-tetra-(4-bromophenyl)porphyrin chloride Mn(III) (17)

(a) 0.02 g (0.0215 mmol) of **4** was dissolved in 10 ml of DMF, 0.054 g (0.430 mmol) of MnCl<sub>2</sub> was added and the reaction mixture was refluxed with stirring for 15 min. Dark green precipitate was obtained and processed in a similar manner to **11**. Yield: 74% (0.016 g, 0.0157 mmol). (b) 0.02 g (0.0192 mmol) of **9**, 0.048 g (0.384 mmol) of MnCl<sub>2</sub> and 10 ml of DMF were heated to a boil and boiled for 20 s. Yield: 89% (0.0175 g, 0.0171 mmol). Found %: C 51.75; H 2.32; N 5.43. C<sub>44</sub>H<sub>24</sub>N<sub>4</sub>ClBr<sub>4</sub>Mn. Calculated %: C 51.88; H 2.38; N 5.50. Mass spectrum m/z (I<sub>rel</sub>,%): 982.68 (75) [M-Cl]<sup>+</sup> was calculated for C<sub>44</sub>H<sub>24</sub>N<sub>4</sub>Br<sub>4</sub>Mn - 983.3. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , p.p.m.): 8.60 br. s. (8H, pyrrole ring), 8.35 br. s. (16H, ortho-C<sub>6</sub>H<sub>5</sub> and meta-C<sub>6</sub>H<sub>5</sub>).

# **2.8.** Synthesis of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin chloride *Mn(III)* (19)

(a) 0.02 g (0.0161 mmol) of **5**, 0.0316 g (0.322 mmol) of potassium acetate, 0.04 g (0.32 mmol) of MnCl<sub>2</sub> and 20 ml of DMF was stirred for 2 min. A dark brown precipitate was obtained. Yield: 75% (0.016 g, 0.0120 mmol). (b) 0.02 g (0.0148 mmol) of **10**, 0.037 g (0.296 mmol) of MnCl<sub>2</sub> and 20 ml of DMF was stirred for 30 s. Yield: 81% (0.016 g, 0.0120 mmol). Found %: C 39.49; H 1.45; N 4.12.  $C_{44}H_{20}N_4ClBr_8Mn$ . Calculated %: C 39.61; H 1.51; N 4.20. Mass spectrum m/z ( $I_{rel}$ ,%): 1298.25 (98) [M-Cl]<sup>+</sup> was calculated for  $C_{44}H_{20}N_4Br_8Mn$  - 1298.8. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ , p.p.m.): 8.05 br. s. (8H, ortho- $C_6H_5$ ), 7.47 m. (12H, meta- $C_6H_5$  and para- $C_6H_5$ ).

# 2.9. Synthesis of tetraphenylporphyrins Mn(II)

Mn(II)-tetraphenylporphyrin **14** is formed by shaking a DMF solution (4 ml) of **11** (0.002 g, 0.00284 mmol) with solid NaOH (0.3 g, 7.5 mmol) in a sealed cell for 1 h. Similar to **14** Mn(II)-porphyrins **15** and **18** were obtained from **12** and **17** in DMF in the presence of NaOH within 10 and 5 min, respectively. Mn(II)-porphyrin **16** is formed by shaking a DMF solution (4 ml) of **13** (0.002 g, 0.00195 mmol) for 30 min. Similar to **16** Mn(II)-porphyrin **20** was obtained from **19** 

within 5 min. Mn(II) porphyrins, when separated from the reaction mixture, are partially or completely oxidized to Mn(III) porphyrins. Table S3 shows the characteristics of the UV-Vis spectra of the Mn(II)-porphyrins.

# 3. Results and discussion

The reaction of formation between porphyrin ligands (H<sub>2</sub>P) and Mn(II)X<sub>2</sub> (X = Cl<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>) in organic solvents is accompanied by formation of Mn(III)-porphyrins [(X)Mn(III)P] [17]. As a rule, the complex formation process cannot be stopped at the stage of the Mn(II)-porphyrin formation. Exceptions are tetraphenylporphyrins with a large number of electron-withdrawing chlorine atoms in the macrocycle [18]. Therefore, investigation of the effect of bromine atoms in the pyrrole and phenyl rings of tetraphenylporphyrins on the ability to form manganese complexes in various degrees of oxidation is needed.

5,10,15,20-Tetraphenylporphyrin chloride Mn(III) **11** and 2-bromo-5,10,15,20tetraphenylporphyrin chloride Mn(III) **12** were synthesized earlier [19] by complexation of corresponding porphyrin ligands with MnCl<sub>2</sub> in boiling DMF within 80 and 65 minutes, respectively. 2,3,12,13-Tetrabromo-5,10,15,20-tetraphenylporphyrin chloride Mn(III) **13** was formed by interaction of porphyrin **3** with MnCl<sub>2</sub> in DMF for 2.5 h.

Manganese(II)-tetraphenylporphyrins (scheme 1) were obtained by using the method described in the works [20,21]. The alkaline dimethylformamide (a solid NaOH in DMF) was taken as the reducing agent. The studies shown that the Mn(II)-tetraphenylporphyrin **14** is formed by shaking of the DMF solution of the compound **11** (C ~  $10^{-4}$ mol/L) with NaOH (C<sub>NaOH</sub> ~  $10^{-1}$  mol/L) in a sealed cell within ~ 1 hour. UV-Vis spectrum of the compound **14** in the system DMF+NaOH has Q bands with  $\lambda_{max}$  617, 576, 533 and Soret band with  $\lambda_{max}$  442 nm (the spectra of "normal type" [22]). These bands arise as a result of electrons transition from higher occupied orbitals of symmetry  $a_{1u}$  and  $a_{2u}$  into the lower vacant orbitals  $e_g$ \*of the porphyrin [23]. The 2-Bromo-5,10,15,20-tetraphenylporphyrin Mn(II) **15** is formed in the corresponding DMF solution of the Mn(III)-porphyrin in the presence of a solid NaOH within ~ 10 min. The compounds **14-15** are oxidized into the Mn(III)-complexes when isolated from the reaction mixture. Chromatography of Mn(III)-porphyrins 14-15 on basic aluminum oxide (eluent-chloroform) results in the formation of a mixture of Mn(II) and Mn(III) complexes.



 $R=R_{1}=R_{2}=R_{3}=H \mathbf{1},$   $R_{1}=Br, R=R_{2}=R_{3}=H \mathbf{2},$   $R_{1}=R_{2}=Br, R=R_{3}=H \mathbf{3},$   $R=Br, R_{1}=R_{2}=R_{3}=H \mathbf{4},$   $R_{1}=R_{2}=R_{3}=Br, R=H \mathbf{5},$ 

R2 R<sub>2</sub>  $M=Cd(II), R=R_1=R_2=R_3=H 6,$ M=Cd(II), R<sub>1</sub>=Br, R=R<sub>2</sub>=R<sub>3</sub>=H 7,  $M=Cd(II), R_1=R_2=Br, R=R_3=H 8,$ M=Cd(II), R=Br,  $R_1=R_2=R_3=H 9$ ,  $M=Cd(II), R_1=R_2=R_3=Br, R=H 10,$  $M = (CI)Mn(III), R = R_1 = R_2 = R_3 = H 11,$  $M = (Cl)Mn(III), R_1 = Br, R = R_2 = R_3 = H 12,$  $M=(Cl)Mn(III), R_1=R_2=Br, R=R_3=H 13,$ M=Mn(II), R=R<sub>1</sub>=R<sub>2</sub>=R<sub>3</sub>=H 14, M=Mn(II), R<sub>1</sub>=Br, R=R<sub>2</sub>=R<sub>3</sub>=H **15**, M=Mn(II), R<sub>1</sub>=R<sub>2</sub>=Br, R=R<sub>3</sub>=H 16,  $M=(Cl)Mn(III), R=Br, R_1=R_2=R_3=H 17,$ M=Mn(II), R=Br, R<sub>1</sub>=R<sub>2</sub>=R<sub>3</sub>=H 18, M=(Cl)Mn(III), R<sub>1</sub>=R<sub>2</sub>=R<sub>3</sub>=Br, R=H **19**, M=Mn(II), R<sub>1</sub>=R<sub>2</sub>=R<sub>3</sub>=Br, R=H **20**.

R



We showed that a mixture of Mn(II)- and Mn(III)-porphyrins is formed upon interaction of porphyrin **3** with  $MnCl_2$  within 20 min [19]. This can be explained by the combined effects of the reaction medium and the electron-withdrawing effect of bromine. Due to residual water, boiling DMF is hydrolyzed [24], which results in the formation of reducing agents such as formate and hydroxide [20, 21, 25] (eqn. 5):

$$CH(O)N(CH_3)_2 + H_2O \rightarrow CH(O)O^- \rightarrow CO + OH^-$$
(5)

When a mixture of manganese tetrabromoporphyrins is dissolved in chloroform, oxidation of Mn(II) to Mn(III) is observed within 10 min. 2,3,12,13-Tetrabromo-5,10,15,20-tetraphenylporphyrin Mn(II) **16** is formed in the corresponding Mn(III)-porphyrin DMF solution within 20-30 min (figure 1). Thus, Mn(III)-porphyrin is formed in the aprotic solvent (CHCl<sub>3</sub>), and in a strongly coordinating solvent of the basic character (DMF), Mn(II)-porphyrin can be obtained.

The studies show that complexation of *para*-bromosubstituted porphyrin **4** with MnCl<sub>2</sub> (molar ratio of reagents of 1:20) in boiling DMF occurs within 15 min with the formation of 5,10,15,20-tetra-(4-bromophenyl)porphyrin chloride Mn(III) **17**. The UV-Vis spectrum of the formed compound in chloroform has bands with  $\lambda_{max}$  at 617, 581 525 477, 416, 402 and 375 nm. While the bands of **1** with  $\lambda_{max}$  at 646, 590, 550, 515 and 418 nm disappear. The synthesized compound **17** and Mn(III)-porphyrins **11-13** possess the hyper-type UV-Vis spectrum [22] with a large number of well-defined bands (figure 2, table S3).

When **17** is dissolved in DMF, full reduction  $Mn(III) \rightarrow Mn(II)$  is not observed. In the UV-Vis spectrum of the DMF solution along with  $\lambda_{max}$  608, 570, 437 and 418 nm, corresponding to the Mn(II)-porphyrin, weak bands characteristic of the Mn(II)-porphyrin are observed (figure 3). Mn(II)-5,10,15,20-tetra-(4-bromophenyl)porphyrin **18** is formed by adding solid alkali (NaOH) to the DMF solution.

When octabromosubstituted porphyrin **5** is refluxed with  $MnCl_2$  in DMF for 30 s, the initial porphyrin is present along with the Mn(II)- and Mn(III)-porphyrins in the reaction mixture. The increase of the reaction time to 5 min or more does not lead to complete conversion of the starting porphyrin into the corresponding manganese complexes. A mixture of octabromosubstituted Mn(II)- and Mn(III)-porphyrins was synthesized in the presence of potassium acetate (molar ratio of H<sub>2</sub>P / KOAc = 1:20). When the mixture of Mn(II)- and Mn(III)-porphyrins is dissolved in chloroform a complete oxidation of the Mn(II)-porphyrins into the Mn(II)-porphyrins [15,10,15,20-tetraphenylporphyrin **19** (figure 4). On the other hand, 2,3,7,8,12,13,17,18-

octabromo-5,10,15,20-tetraphenylporphyrin Mn(II) **20** was formed by dissolving the Mn(II)- and Mn(III)-porphyrins mixture in DMF.

The permetallation method of labile complexes of porphyrins [26] is widely used for the synthesis of various metalloporphyrins. In labile complexes of porphyrins and phthalocyanine, *i.e.* for ionic complexes (Li<sub>2</sub>P, Na<sub>2</sub>P, Li<sub>2</sub>Pc), there is no hindrance for exchange reactions. These reactions for lithium porphyrins (Li<sub>2</sub>P) and lithium phthalocyanines (Li<sub>2</sub>Pc) with p, d and f-metal salts are used in the synthesis of the corresponding MPs and MPCs [27]. Natetraphenylporphyrin (Na<sub>2</sub>TPP) also easily exchanges Na<sup>+</sup> in solutions [28]. Further studies on cation exchange were focused on porphyrin complexes with a significant degree of ionicity of MN bonds. These include the Mg(II), Cd(II), Hg(II), Pb(II) and Zn(II) complexes [27, 29]. It was also noted that metal exchange occurs if more stable complexes are formed during the reaction [30]. Further investigations show the use of the metal exchange method for synthesis of various metalloporphyrins leads to a significant decrease in reaction time and increase in the yield of final products [10-12, 31, 32].

We investigated the metal exchange reaction of **6-10** Cd(II) complexes with MnCl<sub>2</sub> in DMF under conditions comparable to the reaction of the corresponding porphyrin ligands with the metal cations. Mn(III)-porphyrin **11** is formed by interaction of the Cd(II)-tetraphenylporphyrin solution in DMF with MnCl<sub>2</sub> at room temperature for 30 min. There are bands with  $\lambda_{max}$  at 603, 568, 521, 466, 416, 399 and 378 nm in the UV-Vis spectrum of the formed compound (figure 5). The metal exchange reaction of Cd(II)-porphyrin **7** with MnCl<sub>2</sub> in DMF results in formation of mono-bromosubstituted Mn(III)porphyrin **12** under comparable conditions for 70 min.

*Para-* and  $\beta$ -tetrabromosubstituted manganese porphyrins were synthesized at room temperature for 7-8 h. The reaction time is reduced to 20-25 s by refluxing 8 and 9 solutions with MnCl<sub>2</sub> in DMF.

The mixture of Mn(II) and Mn(III)-porphyrins was synthesized by reaction of **10** with manganese chloride (molar ratio 1:20) in boiling DMF for 30 s. In a solution of CHCl<sub>3</sub> the oxidation of Mn(II)  $\rightarrow$  Mn(III) was observed for several hours. When Mn(II) and Mn(III)-porphyrins are dissolved in DMF, 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin Mn(II) **20** is formed.

The synthesized compounds were identified by UV-Vis spectroscopy, <sup>1</sup>H NMR spectroscopy, mass-spectrometry and elemental analysis.

A characteristic feature of the (X)Mn(III) structure is the presence of a strong interaction of manganese with the porphyrin due to the (N $\rightarrow$ Mn) p( $\pi$ )-d( $\pi$ )-interaction, which coincides in direction with the  $\sigma$ -bond. The insertion of the acido-ligands into the internal coordination sphere of Mn(III)-tetraphenylporphyrins changes significantly the geometry of the molecules, which leads to appearance of an additional band ( $\lambda_{max} \sim 478-505$  nm) and increase in the number of bands compared to Mn(II)-complexes (table S3). The Mn(III)-porphyrins are paramagnetic. This leads to the fact that in the <sup>1</sup>H NMR spectra of the Mn(III)-tetraphenylporphyrins, the signals of the pyrrole and phenyl rings are considerably broadened compared to the diamagnetic nitride complexes of the Mn(V)-porphyrins [33].

The signals with a value of m/z 667.3, 746.2, 982.9 982.7 and 1298.2, in the mass spectra of Mn(III)-porphyrins **11-13**, **17** and **18**, correspond to the molecular ions obtained as a result of the M-Cl bond dissociation in corresponding Mn-porphyrins (figures S1-S5, experimental).

# 4. Conclusion

The reactions of the  $\beta$ - and *para*-bromophenyl substituted porphyrins coordination with MnCl<sub>2</sub> and the metal exchange reaction of their cadmium complexes with MnCl<sub>2</sub> were investigated in DMF. Use of the metal exchange reaction significantly reduced the time of manganese porphyrin formation and increased yield of final products in comparison with the reaction of the corresponding porphyrin ligand complexation with Mn(II)-cations.

The metal exchange method of labile Cd-porphyrins made it possible to obtain Mn(III)tetraphenylporphyrin and its monobromo-substituted manganese(III) complex at room temperature. The Mn(III)-tetraphenylporphyrins reduce to Mn(II)-porphyrins in DMF in the presence of NaOH and in pure DMF. With an increase in the number of electron-acceptor bromines (-I eff) in the pyrrole rings of Mn(III)-porphyrins, the reduction of Mn(III)  $\rightarrow$  Mn(II) is enhanced. Bromine atoms in the phenyl rings of the macrocycle exert less influence on the formation of Mn(II)-porphyrins.

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Figure 1. UV-Vis spectra of  $\beta$ -bromosubstituted manganese porphyrins: (a) compound **13** in CHCl<sub>3</sub>, (b) compound **16** in DMF (C<sub>complexes</sub> ~ 1.5×10<sup>-5</sup> mol/L).



Figure 2. UV-Vis spectra in chloroform: (a) the porphyrin 4, (b) 17.



Figure 3. The changes of the UV-Vis spectra of the DMF solution of **17**: (a) at dissolution, (b) after 1.5 h.



Figure 4. The UV-Vis spectra in chloroform: (a) of the mixture of octabromo-substituted manganese porphyrins at dissolution, (b) of the Mn(III) porphyrin **19**.



Figure 5. The UV-Vis spectra in chloroform: (a) of the Cd(II)-tetraphenylporphyrin, (b) of the Mn(III)-tetraphenylporphyrin.

