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Preparation and Spectral Properties of β-Bromo-Substituted Mn(III) Tetraphenylporphyrinates

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Abstract—Interaction of 5,10,15,20-tetraphenylporphyrin, 2-bromo-5,10,15,20-tetraphenylporphyrin, and 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin with manganese(II) chloride in dimethylformamide has been studied by means of spectrophotometry. The corresponding chloride acido complexes of manganese(III) has been so prepared and identified. The complexes could be reduced into manganese(II) tetraphenylporphyrinates in the presence of potassium hydroxide in dimethylformamide.

Keywords: β-bromo-substituted tetraphenylporphyrin, complex formation, metal exchange, tetraphenylporphyrinate, manganese, spectral properties

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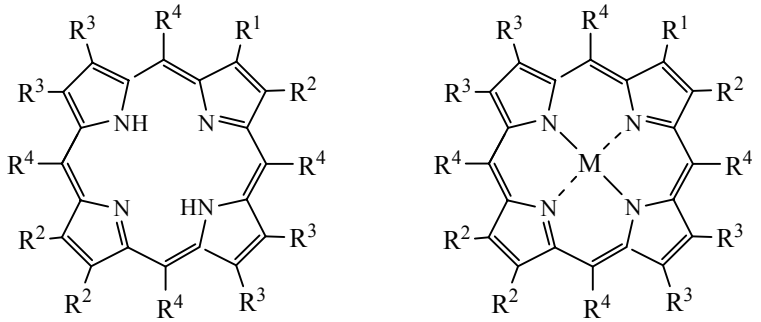
Metal-containing porphyrins are important natural compounds, being components of chloroplasts, hemoglobins, myoglobin, cytochromes, and other biomolecules [1]. Porphyrine complexes with manganese are known for the low redox potential of the central ion E (Mn^{2+}/Mn^{3+}) and therefore act as efficient biocatalysts. Recently, manganese porphyrinates possessing properties of molecular magnetic and capable of forming nanoporous structures have been prepared; these compounds can be used for development of novel materials. Manganese complexes with tetraphenylporphyrin have been described earlier [2–4].

In order to prepare manganese complexes with β-bromo-substituted tetraphenylporphyrins and elucidation of bromine effect on coordination properties of porphyrins, in this work we studied coordination of 5,10,15,20-tetraphenylporphyrin (**I**), 2-bromo-5,10,15,20-tetraphenylporphyrin (**II**), and 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin (**III**) with $MnCl_2$ in

Scheme 1.



I–III **IV–VI**

$R^1 = R^2 = R^3 = H$ (**I, IV**); $R^1 = Br$, $R^2 = R^3 = H$ (**II, V**); $R^1 = R^2 = Br$, $R^3 = H$ (**III, VI**); $R^4 = C_6H_5$, M = (Cl)Mn(III).

Table 1. Electronic absorption spectra of porphyrines **I–III** in CH_2Cl_2 [λ, nm (log ε)]

Comp. no.	Band I	Band II	Bands III, IV, and V	Soret band	Reference
I	647 (3.89)	591 (3.96)	549 (4.08), 514 (4.40)	417 (5.61)	This work
II	648 (3.67)	593 (3.70)	552 (3.72), 517 (4.27)	421 (5.55)	[7]
	648 (3.79)	593 (3.81)	551 (3.78), 518 (4.33)	421 (5.58)	This work
III	685 (4.02)	612 (3.58)	533 (4.30)	436 (5.52)	[8]
	683 (4.06)	612 (3.70)	533 (4.31)	436 (5.46)	This work

Table 2. Electronic absorption spectra of manganese porphyrinates

Complex	Solvent	λ, nm (logε)	Reference
I–Mn(II)	DMSO	607, 569, 530, 437	[2]
I–Mn(II)	DMF + KOH_s	615, 575, 533, 440	
II–Mn(II)	DMF + KOH_s	620, 580, 536, 445	
III–Mn(II)	DMF + KOH_s	635. 590, 455	
IV	$CHCl_3$	616 (3.03), 582 (4.00), 524 (3.81), 478 (4.98), 402 (4.64)	[2]
I–$(N_3)_2$Mn(IV)[a]	CH_2Cl_2	536, 416	[3]
I–(N)Mn(V)[a]	$CHCl_3$	630 sh, 534 (4.54), 418 (5.50)	[4]
IV	$CHCl_3$	615 (3.90), 581 (3.99), 526 (3.89), 478 (4.90), 402 (4.56), 375 (4.62)	
V	$CHCl_3$	619 (3.89), 584 (3.96), 528 (3.84), 480 (4.78), 405 (4.55), 380 (4.60)	
VI	$CHCl_3$	642 (4.04), 600 (4.07), 493 (4.88), 380 (4.77)	

[a] N_3 azide ion; N nitride ion.

boiling dimethylformamide by means of spectrophotometry (Scheme 1).

Since the electronic absorption and ^{1}H NMR spectra of the starting porphyrins and the manganese complexes were significantly different (Tables 1 and 2; figure), those methods could be used to study the complexes formation.

The complex formation of porphyrins with MnX_2 (X = Cl^- or CH_3COO^-) is generally accompanied with instantaneous oxidation of Mn(II) of the porphyrinates into Mn(III) to give the Mn(III)(X)P compounds (P being the porphyrine dianion and X being the acido ligand) [5]. The reaction could not be stopped at the stage of formation of Mn(II) porphyrinates, the exceptions being tetraphenylporphyrins with a few electron-accepting substituents in the macrocycle and phenyl groups [6].

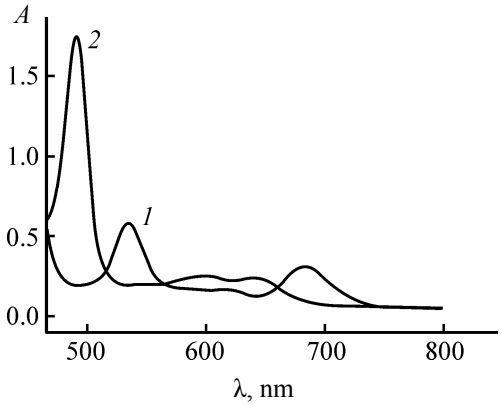
The experiments revealed that the complex formation of porphyrin **I** with $MnCl_2$ (1 : 20 mol/mol) in the boiling DMF occurred within 80 min to yield (Cl)Mn(III) 5,10,15,20-tetraphenylporphyrinate (**IV**):

$$H_2P + MX_2(Solv)_{n-2} \leftrightarrow (Solv)_mMP + 2HX + (n - 2 - m)Solv,$$

with H_2P, porphyrin; $MX_2(Solv)_{n-2}$, the solvated metal salt; Solv, solvent; MP, metalloporphyrin.

The electronic absorption spectrum of the reaction mixture in chloroform contained the bands with maximums at λ_{max} = 617, 582, 524, 477, 402, and 375 nm, the bands of the starting compound **I** with maximums at 647, 591, 549, 514, and 417 nm being vanished.

When a single bromide atom was introduced at β-position of tetraphenylporphyrin (the +*C* effect thus came into play), the corresponding (Cl)Mn(III) 2-bromo-5,10,15,20-tetraphenylporphyrinate (**V**) complex was formed 1.2 times faster as compared to the complex **IV**. The electron-donating substituents increased the electron density at tertiary nitrogen atoms of the macrocycle and thus enhanced the coordination interaction between the cation solvate complex [$MX_2(Solv)_{n-2}$] and the porphyrin in the transition state [9]. However, (Cl)Mn(III) 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrinate (**VI**) complex was formed within 2.5 h in boiling DMF, likely due to sterically restricted coordination of $MnCl_2$ with the tetrabromo derivative **III**.



Electronic absorption spectra of porphyrine **III** (*1*) and complex **VI** (*2*) in chloroform.

In the presence of cadmium(II) chloride (H_2P : $CdCl_2$ = 1 : 10 mol/mol), the manganese complexes were formed faster (within 20 min, the unsubstituted complex **IV**; within 25 min, the monobrominated complex **V**; and within 45 min, the tetrabrominated complex **VI**), following the scheme below:

$$H_2P + CdX_2(Solv)_{n-2} \leftrightarrow (Solv)_mCdP + 2HX + (n - 2 - m)Solv,$$

$$CdP + MX_2(Solv)_{n-2} \rightarrow CdX_2(Solv)_{n-2} + MP.$$

The accelerated complexes formation was due to the absence of the N–H bonds cleavage in the course of the metal exchange reaction involving labile cadmium complex. The observed decrease of Cd(II) tetraphenylporphyrinate reactivity upon introduction of bromine atom at the pyrrole rings was due to the strengthened N→Cd σ-bond [10].

The complexes **IV**–**VI** were characterized by means of elemental analysis as well as electronic absorption and ^{1}H spectroscopy. A special feature of the (X)Mn(III)P structure the strong accepting interaction of the metal atom with the porphyrin ligand due to the direct (N→Mn) p(π)–*d*(π) interaction collinear with the σ-bond. Introduction of the acido ligand at the inner coordination sphere of Mn(III) tetraphenylporphyrinate changed the molecule geometry leading to the appearance of the additional band at λ_{max} 478 nm) and significant red shift of the other bands as compared to the Mn(II) complex (Table 2). Mn(III) tetraphenylporphyrinates were paramagnetic; therefore, the ^{1}H NMR signals of phenyl groups of complexes **IV**–**VI** were broadened and exhibited a downfield shift as compared with the diamagnetic nitride Mn(V) complexes [11].

The prepared compounds, similarly to (Cl)Mn(III) octaphenyltetraazaporphyrinate [12], could be reduced into the corresponding Mn(II) porphyrinates upon shaking of the sealed solution in DMF with KOH during 5–10 min at 20°C. Chromatographic separation of compounds **IV**–**VI** at (alumina, Merck; eluting with chloroform) was accompanied with their partial reduction as well.

EXPERIMENTAL

Electronic absorption spectra were recorded using a Cary-50 spectrophotometer at room temperature. TLC analysis was performed on Silufol plates eluting with chloroform. ^{1}H NMR spectra of the solutions in $CDCl_3$ were recorded using a Bruker AV III-500 instrument. Elemental analysis was performed using a Flash EA 1112 analyzer.

DMF, $CHCl_3$, hexene, tetraphenylporphyrin **I** (Aldrich), and $CdCl_2$ ("chemical pure" grade) were used as received; $MnCl_2$ ("chemical pure" grade) was annealed at 200°C в during 4 h.

2-Bromo-5,10,15,20-tetraphenylporphyrin (II) was prepared via the procedures adopted from [7, 8]. ^{1}H NMR spectrum, δ, ppm: 8.92–8.89 m (2H), 8.86 s (1H), 8.85–8.82 m (2H), 8.79–8.77 m (2H), 8.22 m (6H), 8.11 m (2H), 7.81–7.73 m (12H), –2.82 s (2H).

2,3,12,13-Tetrabromo-5,10,15,20-tetraphenylporphyrin (III) was prepared via the procedures adopted from [7, 8]. ^{1}H NMR spectrum, δ, ppm: 8.72 s (4H), 8.21 d (8H), 7.83 n (12H), –2.80 s (2H).

Complex formation of the porphyrins **I**–**III** with $MnCl_2$ was monitored by means of spectrophotometry (the mixture was periodically sampled; the specimen was dissolved in chloroform and analyzed) and TLC.

5,10,15,20-Tetraphenylporphyrinatochloridomanganese(III) (IV). *a*. A mixture of 0.02 g (0.0325 mol) of compound **I** in 40 mL of DMF and 0.082 g (0.650 mol) of $MnCl_2$ was boiled during 80 min. The mixture was cooled down to ambient, diluted with water, and solid NaCl was added. The precipitate was filtered off, washed with water, and dried. Yield 0.0175 g (0.0249 mmol, 77%), R_f 0.76.

b. A mixture of 0.02 g (0.0325 mmol) of compound **I** and 0.06 g (0.325 mmol) of $CdCl_2$ in 40 mL of DMF was heated to boiling, and then 0.082 g (0.650 mmol) of $MnCl_2$ was added. The mixture was boiled during 20 min and then treated as described in procedure *a*.

Yield 0.018 g (0.0256 mmol, 80%), R_f 0.76. ^{1}H NMR spectrum, δ, ppm: 8.30 br.s (16H, $H^{o,m}$, C_6H_5), 7.75 br.s (4H, H^p, C_6H_5). Found, %: C 74.95; H 3.94; N 7.88. $C_{44}H_{28}ClMnN_4$. Calculated, %: C 75.16; H 4.01; N 7.97.

(Cl)Mn(III) porphyrinates **V** and **VI** were prepared similarly.

2-Bromo-5,10,15,20-tetraphenylporphyrinatochloridomanganese(III) (V). *a*. Prepared from 0.02 g (0.0288 mmol) of compound **II** and 0.072 g (0.576 mmol) of $MnCl_2$; reaction duration 65 min. Yield 0.0176 g (0.0225 mmol, 78%), R_f 0.78.

b. Prepared from 0.02 g (0.0288 mmol) of compound **II**, 0.053 g (0.288 mmol) of $CdCl_2$, and 0.072 g (0.576 mmol) of $MnCl_2$; reaction duration 25 min. Yield 0.018 g (0.0230 mmol, 80%), R_f 0.78. ^{1}H NMR spectrum, δ, ppm: 8.20 br.s (16H, $H^{o,m}$, C_6H_5), 7.55 br.s (4H, H^p, C_6H_5). Found, %: C 67.41; H 3.42; N 10.15. $C_{44}H_{27}BrClMnN_4$. Calculated, %: C 67.58; H 3.48; N 10.22.

2,3,12,13-Tetrabromo-5,10,15,20-tetraphenylporphyrinatochloridomanganese(III) (VI). *a*. Prepared from 0.02 g (0.0215 mmol) of compound **III** and 0.054 g (0.430 mmol) of $MnCl_2$; reaction duration 2.5 h. Yield 0.0166 g (0.0163 mmol, 76%), R_f 0.82.

b. Prepared from 0.02 g (0.0215 mmol) of comound **III**, 0.039 g (0.215 mmol) of $CdCl_2$, and 0.054 g (0.430 mmol) of $MnCl_2$; reaction duration 45 min. Yield 0.017 g (0.0167 mmol, 79%), R_f 0.72. ^{1}H NMR spectrum, δ, ppm: 8.67 br.s (16H, $H^{o,m}$, C_6H_5), 8.05 br.s (4H, H^p, C_6H_5). Found, %: C 51.72; H 2.34; N 5.41. $C_{44}H_{24}N_4ClBr_4Mn$. Calculated, %: C 51.88; H 2.38; N 5.50.

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REFERENCES

1. Rumyantsev, E.V., Antina, E.V., and Chistyakov, Yu.V., *Khimicheskie osnovy zhizni* (The Chemical Basis of Life), Moscow: Khimiya, Koloss, 2007.
2. Valentine, J.S. and Quinn, A.E., *Inorg. Chem. Commun*., 1976, vol. 15, no. 8, p. 1997.
3. Camerzind, M.J., Hollander, F.J., and Hill, C.L., *Inorg. Chem.,* 1983, vol. 22, no. 25, p. 3776.
4. Stuzhin, P.A., Repina, N.V., Klyueva, M.E., and Fedotova, E.V., *Russ. J. Phys. Chem*., 2004, vol. 78, no. 6, p. 864.
5. Boucher, L.J., *Coord. Chem. Rev*., 1972, vol. 7, no. 3, p. 289. DOI: 10.1016/S0010-8545(00)80024-7.
6. Doro, F.G., Lindsay Smith, J.R., Ferreira, A.G., and Assis, M.D., *J. Mol. Catal. (A),* 2000, vol. 164, p. 97. DOI: 10.1016/S1381-1169(00)00352-6.
7. Lembo, A., Tagliatesta, P., and Guldi, D.M., *J. Phys. Chem. (A),* 2006, vol. 110, no. 40, p. 11424. DOI: 10.1021/jp062735h.
8. Kumar, P.K., Bhyrappa, P., and Varghese, B., *Tetrahedron Lett*., 2003, vol. 44, p. 4849. DOI: 10.1016/S004039(03)01143-2.
9. *Koordinatsionnye soedineniya porfirinov i ftalotsianina* (Coordination Compounds of Porphyrin and Phthalocyanine), Moscow: Nauka, 1978.
10. Zvezdina, S.V., Kulikova, O.M., and Mamardashvili, N.Zh., *Russ. J. Gen. Chem*., 2013, vol. 83, no. 11, p. 2103. DOI: 10.1134/S107036213110248.
11. Buchler, J.W., Drecher, C., and Lay, K.L., *Z. Naturforsch. (B),* 1982, vol. 37, p. 1155.
12. Zvezdina, S.V. Chizhova, N.V., and Mamardashvili, N.Zh., *Russ J. Gen. Chem*., 2014, vol. 84, no. 7, p. 1389. DOI: 10.1134/S1070363214070251.