ISSN 1070-3632, Russian Journal of General Chemistry, 2010, Vol. 80, No. 2, pp. 351–356. © Pleiades Publishing, Ltd., 2010.
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Synthesis and Spectral Characteristics of (Tetrabenzoporphyrinato)chloromanganese(III)

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Received January 29, 2009

Abstract—A method is developed of synthesis of (tetrabenzoporphyrinato)chloromanganese(III) from tetrabenzoporphyrinatocadmium(II) (as a donor of the macrocyclic ligand) and the salts, manganese acetate $MnAc_2$ and dichloromanganese $MnCl_2$, in boiling dimethylformamide in the presence of atmosperic oxygen in 80% yield. It is found that under the conditions of the synthesis tetrabenzoporphyrinatomanganese(II) is formed which can be oxidized by the atmospheric oxygen to (tetrabenzoporphyrinato)chloromanganese(III). Absorption spectra in the visible and infrared regions, R_f and the data of elemental analysis characterizing the resulting compound are given.

DOI: 10.1134/S107036321002026X

Metalloporphyrins play an important role in nature. They are a part of the chloroplasts, hemoglobin, myoglobin, cytochromes, and other life-important supermolecules [1]. Porphyrin complexes of iron, manganese, and cobalt created by the nature as a result of biological evolution are characterized by low potential $E_{(M^{2+})/(M^{3+})}$ of the cations recharge, and are biocatalysts and highly effective carriers. Structural modification of the porphin macrocycle allows its adaptation to the specific reaction conditions. Biomimetic approach to finding efficient catalysts for the chemical technology led to the syntheses of metal complexes with phthalocyanine ligands, which are characterized by higher chemical and thermal stability and can, in contrast to metalloporphyrins, work in severe conditions of a process [2]. The phthalocyanines and metallphthalocyanines have been obtained in a high yield and are produced currently on an industrial scale. The phthalocyanine can be considered as a result of deep chemical modification of porphin molecule (Fig. 1) by fusion of pyrrole fragments in conjunction with the replacement of the methine spacers by the aza-bridges. This circumstance causes increased interest in the tetrabenzoporphyrin (H_2TBP) metal complexes, which, along with porphyrazine, represents a transitional structures beween the actual porphyrin (H_2P) and phthalocyanine. The estmation of the constants of acid dissociation (pK_{a1}^{298K}) of porphin (22.35±0.02 [3]), tetrabenzoporphyrin (18.53±0.05 [3]), porphyrazine (11.94±0.18 [4]), and phthalocyanine (10.55 [5]) in DMSO indicates that benzofusion has a strong effect on the compound acidity (–3.82 pK_a units), but it is three times less than the effect of aza-substitution (–10.41 pK_a units), which determines mainly the properties of phthalocyanine.

The basis of all known to-date methods of synthesis of H_2TBP and its metallocomplexes [reaction (1)–(5) are shown in Fig. 2] lies in high temperature cation-template cyclotetramerization (1), consisting in assembling a complex on the metal cation from the precursors, the donors of the methyleneisoindole fragment. The most successful is the classic Linsted's method [6], based on the fusion of 3-carboxymethylenephthalimidine with a metal acetates at 345°C in a nitrogen atmosphere (1). This method allows the preparation of complexes CdTBP and ZnTBP in a yield of about 14.5%. Complexes of other metals can be obtained by the reaction of the respective salts with H_2TBP (3) in universal solvents well dissolving organic and inorganic compounds. In these cases, the demetallation of CdTBP (2) or ZnTBP is preliminary carried out in highly acidic media [7]. At the stage of the demetallation a loss of H_2TBP is about 25%, which decreases the overall yield of the target complex. In the previous paper [8] we showed that stable metalo-

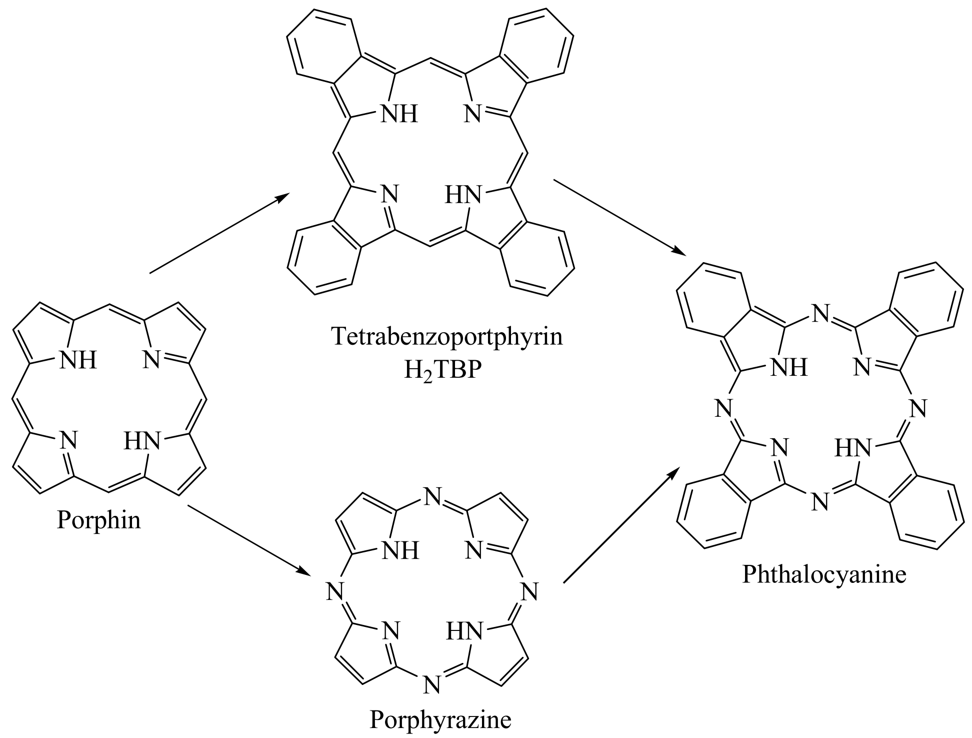

Fig. 1. Porphin and its derivatives.

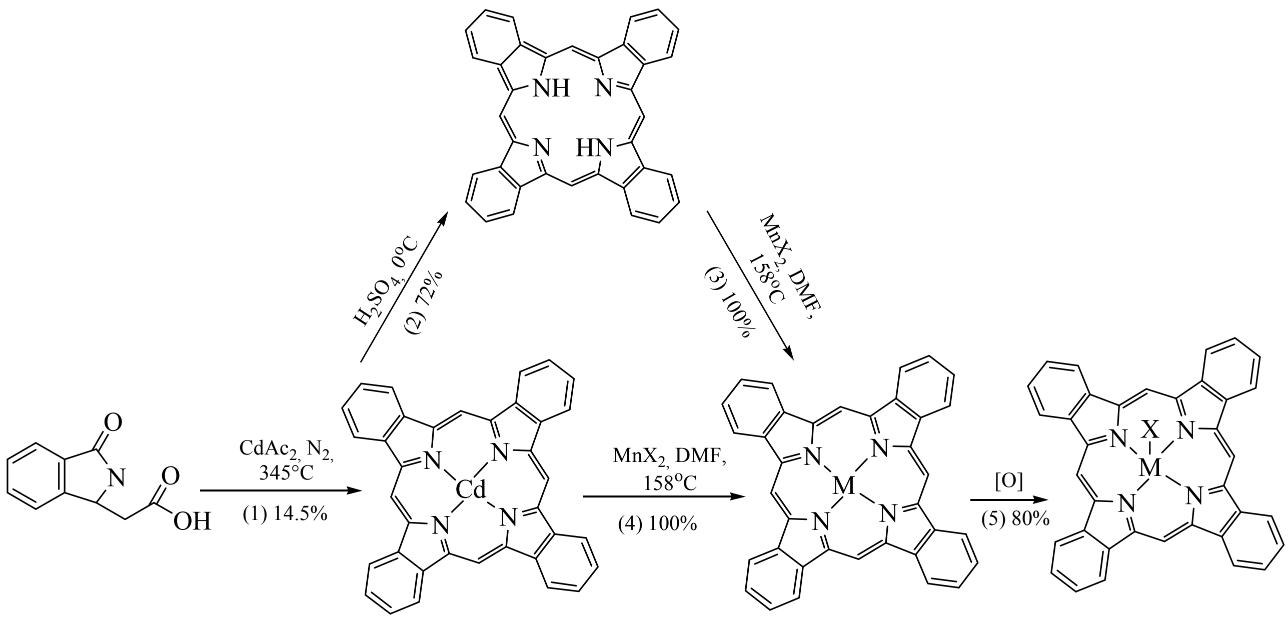

Fig. 2. Scheme of synthesis of XMnTBP. For reactions (1), (2), (3)–(5), and (4)–(5) are indicated yields of pure products, for reactions (3) and (4) the data of spectrophotometric evaluation.

complexes with H_2TBP could be obtained in good yield by using labile complexes CdTBP or ZnTBP as donors of the macrocyclic ligand TBP^{2-} (4) avoiding the stage of demetallation (2). Along the reaction (4) were obtained PdTBP and NiTBP in the yield about 80% per parent CdTBP. In this report, which continues this research, are given the results of the successful synthesis of (tetrabenzoporphyrinato)chloromanganese(III) XMnTBP from CdTBP and salts MnX_2 (X = Ac^- and Cl^-).

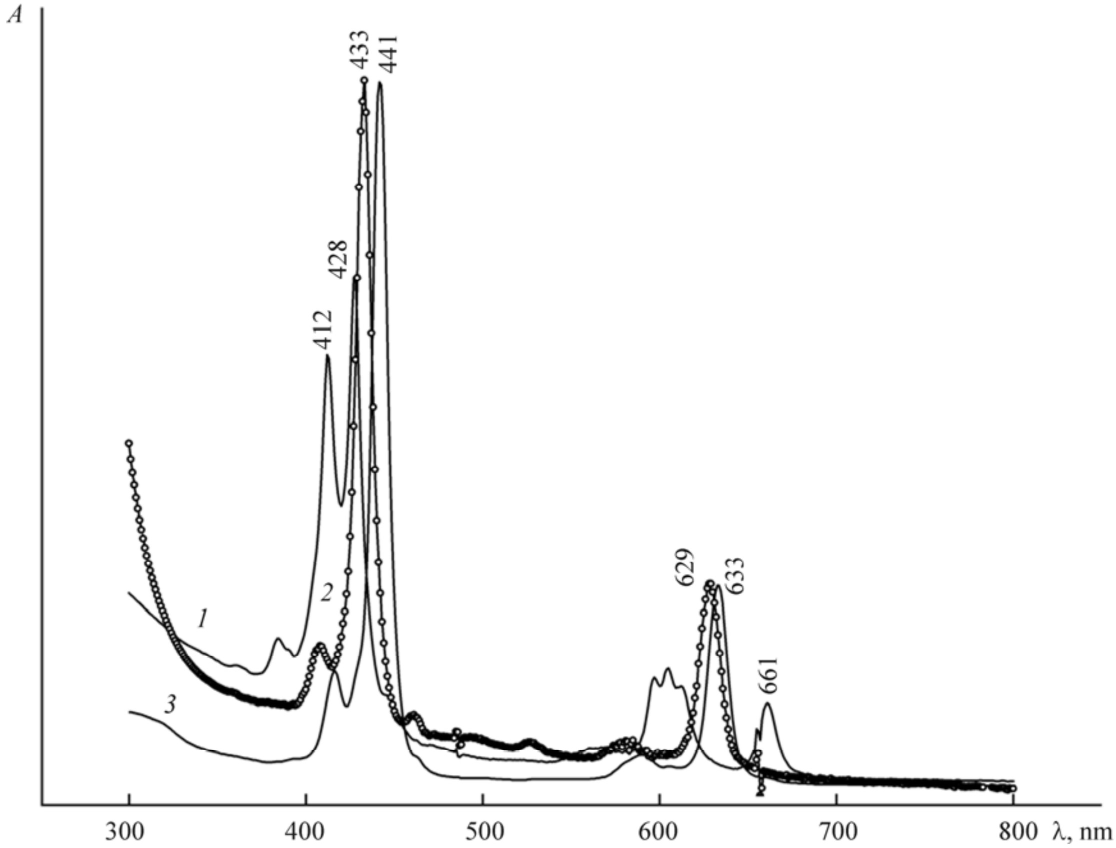

Fig. 3. Electron absorption spectra in dimethylformamide: (*1*) H_2TBP, (*2*) CdTBP, and (*3*) MnTBP.

To compare the efficiency of H_2TBP and CdTBP as donors of the macrocyclic ligand TBP^{2-} the synthesis of XMnTBP was carried out along two parallel schemes, (1), (2), (3), (5) and (1), (4), (5). The process monitoring has been performed by recording electron absorption spectra that are shown in Fig. 3. In boiling DMF the product of reactions (3) and (4) is MnTBP. With ninefold excess of $MnAc_2$ the reaction (3) is completed in 1 h, while the reaction with $MnCl_2$ (3) does not proceed. Reaction (4) proceeds equally well with $MnAc_2$ and $MnCl_2$ and is completely finished already at boiling the reaction mixture with twofold amount of the salt. The molar ratio of CdTBP to MnX_2 is reduced from 1:10 to 1:2 because in this interval the rate of reaction (4) does not depend on the concentration of salt [9]. As already noted, the manganese complexes of simple porphin derivatives are characterized by a low $E_{(M^{3+})/(M^{2+})}$ potential of the complex cation recharge. The magnitude of this potential is largely determined by donor-acceptor properties of tetrapyrrole ligands and can vary within a wide range [2, 10]. Electron-donor substituents (ligands) lead to anodic shift of the recharge potential $E_{(M^{3+})/(M^{2+})}$ and stabilize XMnP, while electron-acceptors lead to the cathodic shift, and stabilize MnP [2, 10]. For this reason, for the manganese complexes with porphyrazine and phthalocyanine ligands is more typical the degree of oxidation II, while for the porphyrin itself, III. According to the published data, the first product of the reaction of salts MnX_2 with simple porphin derivatives is extremely unstable complex MnP, which almost instantly is oxidized by atmospheric oxygen to XMnP [11]. Extra coordination with electron-deficient ligands such as pyridine stabilizes MnP as $(Py)_2$MnP [12]. In the short-wave region of electron spectra of the complexes XMnP there is a unique charge transfer band which allow unambiguous evaluation of the degree of oxidation of the complex cation [2]. We have used all these factors for the identification of the products of synthesis.

As already noted, the product of reactions (3) and (4) in boiling dimethylformamide is MnTBP. This can be explained by a combined effects of the reaction

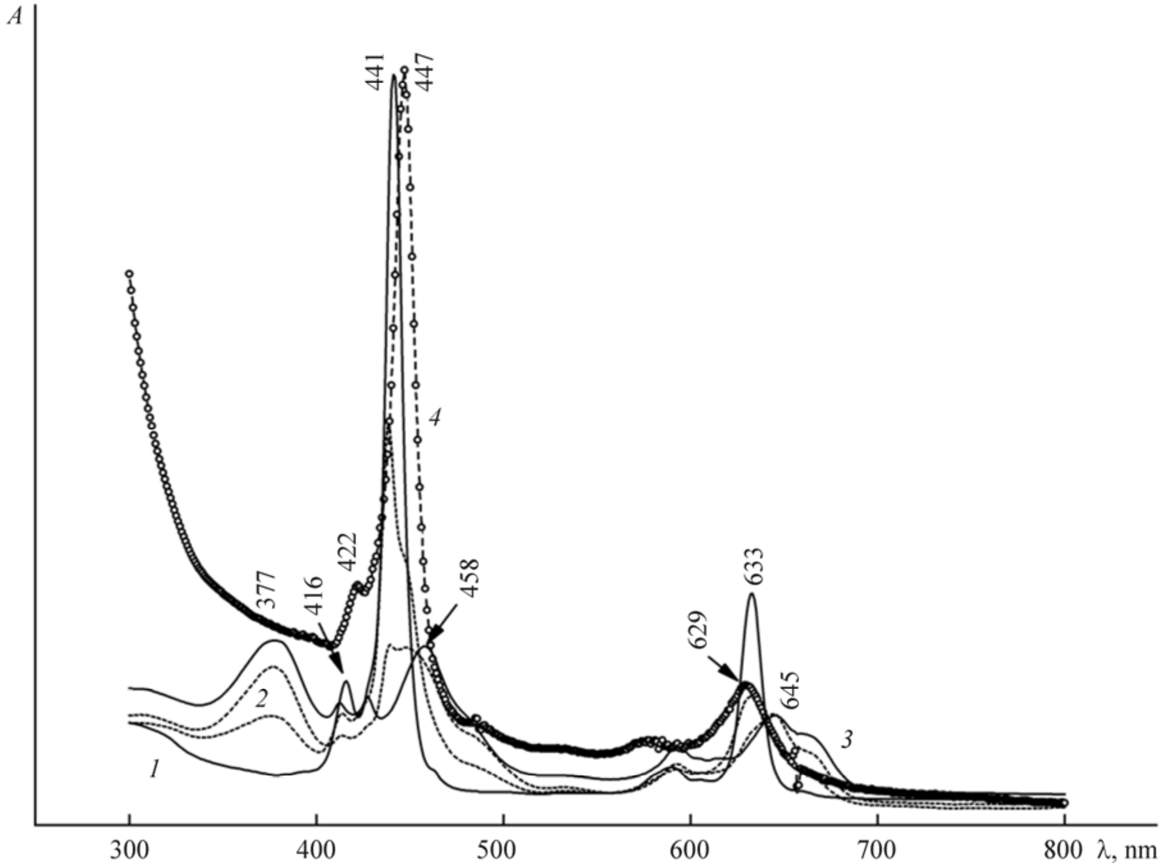

Fig. 4. Electron absorption spectra in dimethylformamide: (*1*) MnTBP, (*2*) a mixture of MnTBP and XMnTBP, (*3*) XMnTBP from acid solution of MnTBP, and (*4*) TBP^{2-}.

medium and the electronic effect of benzofusion. Due to residual water, the boiling dimethylformamide is hydrolyzed [13], which results in the formation of the reducing agents such as hydroxide [14–18] and formate (6).

$$CH(O)N(CH_3)_2 + H_2O \rightarrow CH(O)O^- \rightarrow CO + OH^-. \quad (6)$$

In addition, the hydroxide can also appear as a product of the reaction of the fairly basic DMF with the residual water in the solvent.

At introducing a portion of the reaction mixture (3) or (4) into dimethylformamide, MnTBP reacts with the atmospheric oxygen dissolved theret (5) and is partially oxidized to XMnTBP.

The natural oxidation of the cooled reaction mixture proceeds in a few days. This time is reduced to 1 h at adding acid (in this case, HCl), which deactivates the reducing agents dissolved in DMF. Changes in the electronic spectrum of solution at the oxidation of MnTBP to XMnTBP in acidified DMF are shown in Fig. 4. In contrast to XMnP, the reduced form, MnP, is extremely labile. In acidic media MnP is easily demetallated with the formation of H_2P [19]. For this reason MnTBP is partially decomposed in acidified DMF, as evidenced by the appearance of the absorption maxima of H_2TBP at 412, 428, and 661 nm in the electron absorption spectrum which belong to the formed XMnTBP. In the short-wave region of the electronic spectrum of XMnTBP appears a band with the absorption maximum at 377 nm, which apparently corresponds to the charge transfer band characteristic of the porphyrin complexes of manganese(III) [2]. This band remains unchanged at the action on XMnTBP of a mild oxidant such as PbO_2 [21] in tetrahydrofuran.

XMnTBP within a few minutes is reduced to MnTBP at shaking of its solution in dimethylformamide or dimetilsulfoxide with a pellet off alkali in a sealed cell without access of atmospheric oxygen. Prolonged contact with alkaline solution leads to demetallation of MnTBP, which resulted in transformation of its electron spectrum into a spectrum of free TBP^{2-} [3] (Fig. 4). Despite the fact that MnP complexes are extremely labile and readily undergo metal exchange [20], the TBP^{2-} complexes with the sodium cations were not found in the applied experimental conditions. The most likely cause of the destruction of labile MnTBP is the ligand exchange with replacement of TBP^{2-} by hydroxide ions. The fact that electron spectrum attributed to TBP^{2-} does not correspond to a form of MnTBP or to the product of reduction of the latter, was proved by experiments on the acid ionization of H_2TBP. In addition, acidification of the solution of TBP^{2-} obtained from MnTBP also leads to the formation of H_2TBP (Fig. 3). At dissolving XMnTBP in pyridine are formed consecutively two products, with the electron spectra identical to the spectrum of MnTBP which is characterized by absorption bands at 437, 631, 445, and 631 nm, respectively, that can be assigned to (Py)MnTBP and $(Py)_2$MnTBP. The results of the tests indicate that the properties of MnTBP, XMnTBP, (Py)MnTBP, and $(Py)_2$MnTBP are close to the those of the porphyrin analogs, but MnTBP is more resistant to oxidation by atmospheric oxygen.

EXPERIMENTAL

Tetrabenzoporphyrin (H_2TBP) and tetrabenzoporphyrinatocadmium(II) (CdTBP) are obtained by the Linstead method [6].

Dimethylformamide of “chemically pure” grade was used without additional purification. $MnCl_2$ of chemically pure grade was calcined at 200°C for 4 h. $MnAc_2$ of chemically pure grade was recrystallized from glacial acetic acid of chemically pure grade and dried at 80°C for 1 h.

Monitoring of the reactions (3) and (4) was performed by registering electron absorption spectra by the method of sampling. From the boiling reaction mixture at a specified time intervals were taken samples of equal volume and dissolved in the same amount of dimethylformamide. Electron absorption spectra were recorded at room temperature in a stoppered optical cell on a Cary-100 instrument. IR spectra were recorded on a Specord M-80 instrument from KBr tablets. R_f values were measured on Silufol plates (solvent diethyl ether).

The complex (tetrabenzoporphyrinato)chloromanganese(III) (XMnTBP) was obtained by the methods *a* and *b*.

a. 0.05 g of tetrabenzoporphyrin and 0.17 g of $MnAc_2$ (molar ratio 1:10) were dissolved together in 150 ml of dimethylformamide, the mixture was refluxed for 60 min, then cooled, and left at room temperature for 7 days. Then NaCl was added and the mixture was poured into water, the precipitate formed was filtered off, washed with water, dried, and then subjected to chromatography on aluminum oxide, eluting with a mixture of pyridine–diethyl ether (1:4). Yield 0.042 g (0.07 mmol, 72%), R_f 0.68.

b. 0.05 g of tetrabenzoporphyrinatocadmium(II) and 0.028 g of $MnAc_2$, or 0.02 g of $MnCl_2$ (molar ratio 1:2) were dissolved in 80 ml of dimethylformamide and the mixture was heated to boiling and refluxed for 30 s, then cooled, 2 ml of hydrochloric acid was added to it and the mixture was kept at room temperature for 1 h, and then poured into water. After adding NaCl the precipitate was filtered off, washed with water, dried, and subjected to chromatography on aluminum oxide, eluting with a mixture of pyridine–diethyl ether (1:4). Yield 0.038 g (0.063 mmol, 80%), Found, %: C 72.11, H 3.35, N 9.30. C_{36} $H_{20}ClMnN_4$. Calculated,%: C 72.19, H 3.37, N 9.35. R_f 0.68.

IR spectrum, cm^{-1} : 2954 s, 2923 s, 2854 m, 1626 s, 1599 s, 1462 w, 1432 w, 1362 m, 1249 w, 1157 w, 1121 m, 1099 m, 1645 m, 945 w, 873 w, 757 m, 741 m, 702 w, 501 w, 481 w, 418 w.

Electron absorption spectra of the solution of (Cl) MnTBP, λ, nm (log ε): 377 (4.21), 458 (4.21), 589 (3.73), 645 (4.02).

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