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Effect of Octabromo Substitution on the Coordination Properties of Manganese(III) Octaphenyltetraazaporphyrin

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Abstract — Comparative studies of the kinetics of formation of manganese(III) complexes with octaphenyltetraazaporphyrin and its octabromo derivative, of their dissociation and axial ligand exchange were carried out. The effect of octabromo substitution on the coordination properties of the compounds is determined by the –I effect of bromine atoms. The different effects on the kinetic parameters of the reactions [increase in the rate and significant decrease in the activation energy upon complex formation, slowing down of dissociation, and acceleration of acido ligand exchange with nitrido(tetraphenyporphyrin)manganese(V) are caused by the involvement of different reaction centers in the limiting stages (different mechanisms of the processes).

Revealing the dependence of the reactivity of complex compounds on the ligand structure is one of the major problems of coordination chemistry [1]. In the present work we have carried out a comparative study of the kinetics of formation and dissociation of manganese(III) complexes with octaphenyltetraazaporphyrin and its octabromo derivative, as well as the reactions of these complexes with nitrido(tetraphenyporphyrin)manganese(V), resulting in axial ligand exchange. To determine most probable mechanisms of the processes, we measured reaction rates as functions of temperature and initial concentrations of reagents, which allowed full kinetic equations to be found.

The essential distinctions in the positions of band in the electronic absorption spectra of octaphenyltetraazaporphyrin and their complexes with manganese in various oxidation states (Figs. 1–3) make possible studying reactions of such compounds in solutions by the spectrophotometric technique. The reactions of octaphenyltetraazaporphyrin (**I**) or octa(bromo)phenyltetraazaporphyrin (**II**) with manganese(II) acetate or chloride in DMF give rise to corresponding manganese(III) complexes. The spectrum of tetraazaporphyrin **I** or **II**, that contains two strong long-wave bands, passes into a spectrum with one strong band in the region of 670 nm and additional absorption bands at 410 and 470 nm (Fig. 1), which is typical of manganese(III) octaphenyltetraazaporphyrins [2]. The reaction with $Mn(OAc)_2$ proceeds very fast on pouring the solutions together, whereas the use of $MnCl_2$ allows us to record a series of spectral curves relating to different degrees of transformation of the starting compounds and to calculate the rate of formation of complex **III** or **IV** from the change in optical density near strong maxima in the electronic absorption spectrum. The presence of well-defined isosbestic points in the spectra of the reaction mixture in the course of the reaction suggests that the system contains only two colored compounds at each time moment, i.e., as is the case with complexes with classical porphyrins [3], manganese(II) incorporated in a macrocyclic

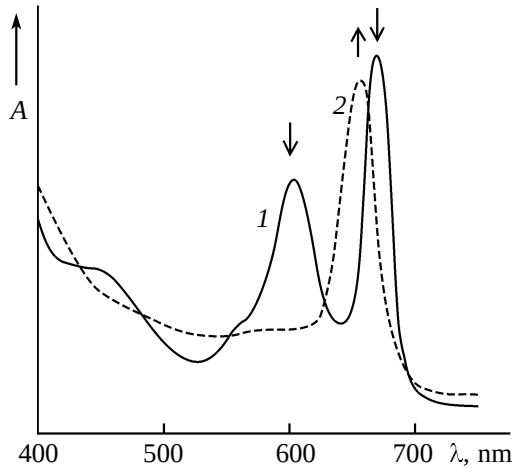

Fig. 1. Electronic absorption spectra of compounds: (*1*) **I** and (*2*) **III** in DMF.

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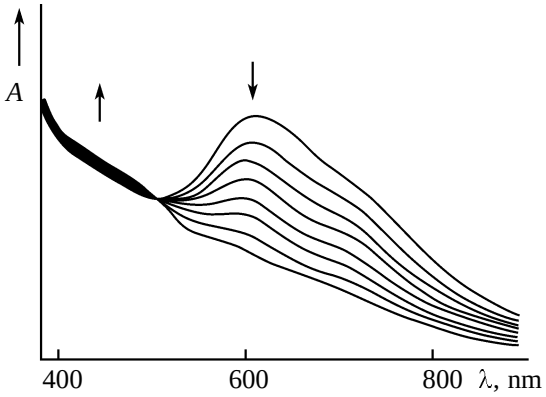


Fig. 2. Change in the electronic absorption spectrum of compound **II** in 18.1 M H_2SO_4 at 318 K.

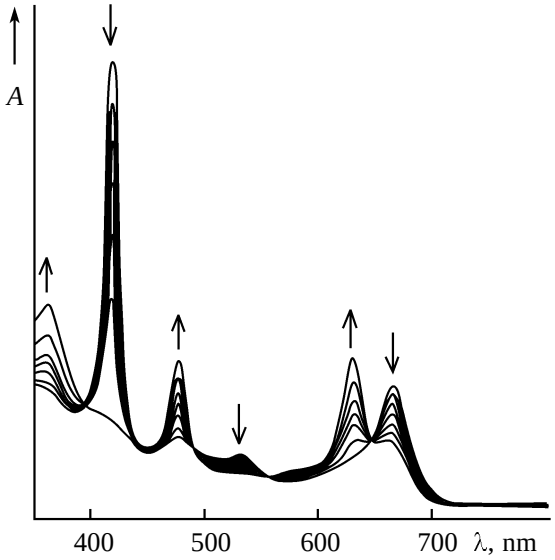


Fig. 3. Change in the electronic absorption spectra during reactions of compounds **IV** (6.56×10^{-6} M) and **V** (6.32×10^{-6} M) in chloroform at 298 K.

complex is immediately oxidized by air oxygen to manganese(III) [scheme (1)].

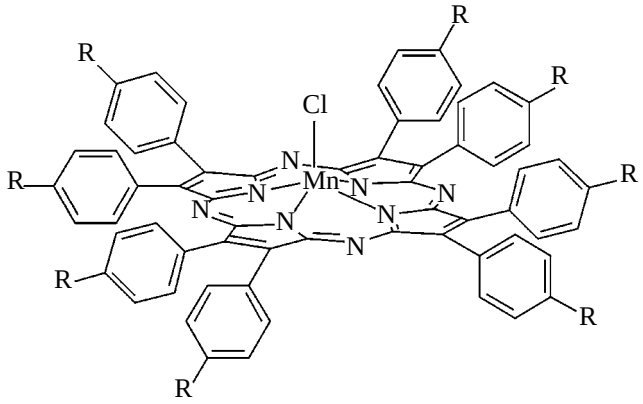
$$H_2P + MnCl_2 \longrightarrow (Cl)Mn^{III}P. \quad (1)$$

Here H_2P is compound **I** or **II**.

The rate of formation of complexes **III** and **IV** in the reactions of compounds **I** and **II** with $MnCl_2$ in DMF under pseudo-first order conditions in azaporphyrin is independent of salt concentration. The kinetic equation takes form (2).

$$-dc_{H_2P}/d\tau = k_{app}^{tr} c_{H_2P}. \quad (2)$$

Here c_{H_2P} is the concentration of octaphenyltetraazaporphyrin **I** or **II**, τ, time, and k_{ap}, apparent rate constant of manganese complex formation.



III, IV

R = H (**III**), Br (**IV**).

The apparent rate constants of the formation of complex **III** by reaction (1) in DMF are $(1.4\pm0.1)\times10^{-3}$, $(4.4\pm0.4)\times10^{-3}$, and $(10.9\pm0.4)\times10^{-3}$ at 298, 303, and 308 K, respectively. At 288 K the reaction proceeds very slowly, and at 318 K it occurs fast, immediately after pouring the solutions together. The apparent activation energy E is 156 ± 15 kJ mol^{-1}, and the activation entropy $\Delta S^{\neq}$ is -217 ± 51 J mol^{-1} K^{-1}. With complex **IV**, the apparent rate constant is $(0.90\pm0.07)\times10^{-3}$, $(1.3\pm0.1)\times10^{-3}$, and $(1.85\pm0.2\times10^{-3}$ at 288, 293, and 298 K, respectively, E 54 ± 4 kJ mol^{-1}, and $\Delta S^{\neq}$ -123 ± 13 J mol^{-1} K^{-1}. The apparent rate constants of formation of complexes **III** and **IV** at 298 K are close to each other, but the activation parameters of the reactions are much different. Kinetic equation (2) agrees with the monomolecular mechanism of coordination of transition metal cations by octaphenyltetraazaporphyrins, offered in [4], according to which formation of a covalent complex is preceded by fast coordination of a metal salt on one of *meso*-nitrogen atoms of azaporphyrin to form an amine complex. In the limiting stage, the amine complex transforms into the metal azaporphyrin. The formation of the amine complex is favored by the high electron-donor power of octaphenyltetraazaporphyrin and by stabilization of the amine complex as a result of interaction of the coordinated solvate with neighboring phenyl rings. The complex formation in this case depends only slightly on the nature of the salt cation, as compared with the formation of complexes of classical porphyrins [4, 5]. The anionic composition of the salt has a much stronger effect. For example, the reaction of porphyrin **I** with manganese(II) acetate in DMF proceeds immediately on pouring the solutions together, whereas the rate of manganese(II) chloride reaction can be measured by

spectrophotometry. The results of the present work point show that the formation of manganese(III) complexes is strongly affected by functional substitution in the octaphenyltetraazaporphyrin ligand. The formation of complex **III** is characterized by a very high activation energy. Octabromo substitution in the macrocyclic ligand reduces the activation energy almost three times, probably, owing to a weaker stabilization of the amine complex. The latter effect is associated with weakened electron-donor power of *meso*-nitrogen atoms in porphyrin **II** as compared to porphyrin **I** and with facilitated ionization of hydrogen atoms in the coordination center of compound **II** (*–I* effect of bromine atoms). It is probable that the *+C* effect of bromine atoms, that also would be expected, does not appear, since phenyl rings deviate from the mean macroring plane, as follows from the MM+-optimized geometry of molecules **I**–**IV**, where the angles between the phenyl and macroring planes are 35°.

Complexes of azaporphyrins with *d* metals are stable in solutions and decompose only under the action of acids [4]. In acidic media, *meso*-nitrogen atoms can interact with proton-donor species [2, 6]. As found by spectrophotometry [2], in strongly acidic solutions, complex **III** is protonated by two meso-nitrogen atoms and dissociates at a measurable rate in concentrated sulfuric acid at room temperature. Dissociation of the complex is accompanied by destruction of the macrocycle. The electronic absorption spectrum of bromine derivative **IV** in concentrated sulfuric acid at 306–328 K changes similarly to the spectrum of its bromine-free analog **III** (Fig. 2). The dissociation rate of complexes **III** and **IV** in 17.4–18.6 M H_2SO_4 is independent of acid concentration. The kinetic equation takes form (3).

$$-dc_{(Cl)MnP}/d\tau = k_{ap}^{dis} c_{(Cl)MnP}. \quad (3)$$

Here $c_{(Cl)MnP}$ is the concentration of complex **III** or **IV**, τ, time, and k_{ap}^{dis}, apparent dissociation rate of the complex.

According to [2], the average k_{ap}^{dis} values for complex **III** are $(1.14 \pm 0.05) \times 10^{-4}$, $(2.9 \pm \pm 0.2) \times 10^{-4}$, and $(7.6 \pm 0.2) \times 10^{-4}$ s^{-1} at 288, 298, and 308 K, respectively. The apparent activation energy E is 70 ± 2 kJ mol^{-1}, and the activation entropy $\Delta S^{\neq}$ is -83.5 ± 6 J mol^{-1} K^{-1}. The k_{ap}^{dis} values for complex **IV** are $(3.1 \pm 0.2) \times 10^{-4}$, $(5.9 \pm 0.4) \times 10^{-4}$, and $(12.6 \pm 0.9) \times 10^{-4}$ at 308, 318, and 328 K. The k_{ap}^{dis} at 298 K extrapolated from the dependence $\log k_{ap}^{dis}$–$1/T$ is $(1.4 \pm 0.1) \times 10^{-4}$ s^{-1}; E and $\Delta S^{\neq}$ are 59 ± 7 kJ mol^{-1} and -128 ± 22 J mol^{-1} K^{-1}, respectively. Thus, octabromo substitution slightly slows down destruction of manganese(III) octaphenyltetraazaporphyrin.

The bromine atoms in phenyl rings of complex **IV** show the *–I* effect. The *+C* effect of brome on Mn–N bonds is prevented by a significant torsion of phenyl rings relative to the macroring plane. Such electronic effects should render the Mn–N bonds in complex **IV** weaker compared to complex **III**. At the same time, owing to the mutual ligand effect, strengthening of the axial Mn–Cl bond in complex **IV** would be expected. The strengthening of the bond between the manganese atom and the axial chlorine atom as a result of the octabromo substitution under consideration is attested by changes in the positions of absorption maxima of complex **IV** compared to complex **III**: the bathochromic shift of the long-wave band from 665 to 668 nm and the opposite shift of the band in the near UV region (from 413 to 411 nm) [7]. A multistage mechanism of dissociation of manganese(III) and manganese(V) complexes with octaphenyltetraazaporphyrin (**I**) in concentrated sulfuric acid has been proposed in [2]. According to this mechanism, the overall reaction rate is determined by the stage of dissociation of the acido complex into the inorganic anion X^{-n} and the octaphenyltetraazaporphyrinmanganese cation. After the slow acido ligand dissociation stage fast dissociation of the complex by Mn–N bonds and destruction of the macroring occur. The enhanced stability of bromine-substituted complex **IV** than unsubstituted complex **III** provides evidence for this mechanism.

Reactions of axial coordination of metal porphyrins are of special importance and in many respects determine properties of macrocyclic complexes [8]. Manganese porphyrins have a unique property: manganese(II) and manganese(III) complexes can enter reactions with nitridomanganese(V) porphyrins, involving complete intermolecular transfer of the nitride nitrogen atom uncomplicated by side reactions [9–11]. The transfer of the nitrogen atom from nitrido-(tetraphenylporphyrin)manganese(V) (**V**) to manganese(III) octaphenyltetraazaporphyrins is irreversible [12, 13], which is caused by stronger π-acceptor properties of the tetraazaporphyrin macroring compared to the porphyrin ring. Changes in the electronic absorption spectra in the course of the reaction of complexes **IV** and **V** [reaction (4)] in chloroform are shown in Fig. 3.

$$(N)Mn^{V}TPP + (Cl)Mn^{V}P \longrightarrow (Cl)Mn^{III}TPP. \quad (4)$$

Here TPP is tetraphenylporphyrin and P, dianion of octaphenyltetraazaporphyrin or of its octabromo derivative.

The rate constants of reaction (4) determined by a second-order kinetic equation (5) are much higher for

bromine-substituted complex **IV** than for complex **III** at practically identical activation characteristics. Thus, the rate constants k of the reaction of complexes **V** and **III** in chloroform are 23 ± 3, 44 ± 5, and 70 ± 6 $mol^{-1}\,l\,s^{-1}$ at 288, 298, and 308 K, respectively, E 41 ± 5 kJ mol^{-1}, and $\Delta S^{\neq}$ -83 ± 18 J $mol^{-1}\,K^{-1}$. For the reaction of complexes **V** and **IV** at the same temperatures, k 151 ± 14, 233 ± 24, and 438 ± 37 $mol^{-1}\,l\,s^{-1}$, E 40 ± 9 kJ mol^{-1}, and $\Delta S^{\neq}$ -74 ± 30 J $mol^{-1}\,K^{-1}$.

The transfer of the nitride nitrogen atom from complex **V** can proceed through formation of a μ-nitrido-bridged intermediate in two ways [11, 12]. Kinetic studies showed that reactions between manganese(III) and manganese(V) complexes of classical porphyrins (tetraphenylporphyrin and octaphenylporphyrin) begin with equilibrium Mn–Cl dissociation to form a cationic manganese(III) complex. Then the highly electrophilic cationic complex reacts with the nitridomanganese(V) complex at the limiting stage [11]. An alternative possibility consists in nucleophilic attack of manganese(III) directly in acido complex **III** or **IV** from the side opposite to the chloride ligand. These mechanisms can be competing, and their relative contribution should depend on reaction conditions. Analysis of the kinetic parameters of the process as a function of the structure of the reagents allows the most probable reaction mechanism to be determined. When reaction (4) follows the first mechanism, the strengthening of the axial Mn–Cl bond due to the $-I$ effect of eight bromine atoms in complex **IV** should decelerate its reaction compared to complex **III**. As the opposite effect is observed experimentally, namely, the reaction rate increases 5–6 times, we should accept that the second mechanism is more probable. The enhanced electrophilicity of manganese(III) in bromine-substituted complex **IV** compared to complex **III** facilitates reaction with the nucleophilic nitride nitrogen atom even in the unionized form of the complex [Eq. (5)].

$$-dc_{(N)Mn^{V}TPP}/d\tau = -dc_{(Cl)Mn^{III}P}/d\tau = kc_{(N)Mn^{V}TPP}c_{(Cl)Mn^{III}P}. \quad (5)$$

Here $c_{(N)Mn^{V}TPP}$ is the concentration of complex **V**, $c_{(Cl)Mn^{III}P}$, concentration of complex **III** or **IV**, and k, rate constant of reaction (4).

Thus, the effect of octabromo substitution in phenyl rings on the coordination properties of octaphenyltetraazaporphyrin and its complex with manganese is determined by the $-I$ effect of bromine atoms. The different effects on the kinetic parameters of the reactions [increase in the rate and significant decrease in the activation energy of complex formation, slowing down of dissociation, and acceleration of acido ligand exchange with complex **V**] are associated with different reaction centers. The $-I$ effect of bromine atoms in phenyl rings attenuates the electrondonor power of *meso*-nitrogen atoms in octa(bromophenyl)tetraazaporphyrin (**II**) compared to octaphenyltetraazaporphyrin (**I**), strengthens the axial Mn–Cl bond, and enhances the electrophilic power of the manganese(III) central atom in bromine derivative **IV** compared to complex **III**. Research into the effect of functional substitution in macrocyclic compounds on their coordination properties provides an important information on reaction mechanisms.

EXPERIMENTAL

The electronic absorption spectra of compounds were recorded on Hitachi U-2000 and SF-26 spectrophotometers.

Compound **I** was synthesized by the procedure in [14]. Compound **II** was prepared by bromination of octaphenyltetraazaporphyrin (**I**) with molecular bromine in trifluoroacetic acid at 293–298 K within 8 days [15]. Complex **III** was obtained by the reaction of compound **I** with $MnCl_2 \cdot 4H_2O$ in boiling DMF. After cooling, the reaction mixture was poured into water, the precipitate was filtered off, dried, and twice purified by column chromatography on alumina, eluent chloroform. Complexes **IV** and **V** were synthesized by the procedures in [16] and [12], respectively. The electronic absorption spectra of compounds **I**–**V** were consistent with published data [12, 14–16].

Manganese(II) acetate was recrystallized from acetic acid and dehydrated by boiling with acetic anhydride within 3 h. Manganese(II) chloride was dried at 493 K to constant weight. DMF was purified by distillation with benzene according to the procedure in [17].

The concentration of H_2SO_4 was determined by titration with an error of less than 0.15%. Solutions of complex **IV** in sulfuric acid were filtered through a Schott filter no. 40 before kinetic measurements. Chloroform (medical grade) was dried with $CaCl_2$ and distilled with a Vigreux column directly before use.

Kinetic measurements were performed by spectrophotometry. The temperature during experiments was maintained with an accuracy of ± 0.1 K. The reaction rate constants were calculated from the changes in the optical density of the solutions near the strongest absorption bands. The apparent rate constants of the formation and dissociation of complexes **III** and **IV** were optimized from $\ln(c_0/c_\tau)$–τ dependences using

the Microsoft Excel program. The rate constants of reaction (4) were calculated as described in [12].

The activation energies were found by least-squares optimization of the linear dependence $\log k$–$1/T$. The activation entropies $\Delta S^{\neq}$ were determined by the basic equation of the transition state theory, transformed to form (6).

$$\Delta S^{\neq} = 19.1\log k_T + E/T - 19.1\log T - 205. \quad (6)$$

The geometries of compounds **I**–**IV** were optimized by the MM+ method. Calculations were terminated at the gradient 0.001 kJ mol^{-1} Å^{-1}.

REFERENCES

1. Kukushkin, Yu.N., *Reaktsionnaya sposobnost' koordinatsionnykh soedinenii* (Reactivity of Coordination Compounds), Leningrad: Khimiya, 1987.
2. Klyueva, M.E., Stuzhin, P.A., and Berezin, B.D., *Koord. Khim.*, 2003, vol. 29, no. 3, p. 201.
3. Boucher, L.J., *Coord. Chem. Rev.*, 1972, vol. 7, no. 1, p. 289.
4. *Porfiriny. Struktura, svoistva, sintez* (Porphirins. Structure, Properties, Synthesis), Enikolopyan, N.S., Ed., Moscow: Nauka, 1985, p. 83.
5. Berezin, B.D. and Enikolopyan, N.S., *Metallporfiriny* (Metal Porphyrins), Moscow: Nauka, 1988.
6. *Phthalocyanines: Properties and Applications*, Leznoff, C.C. and Lever, A.B.P., Eds., New York: VCH, 1996, vol. 4, p. 19.
7. *Inorganic Biochemistry, Eichhorn, G.L.*, Elsevier: Amsterdam, 1975, vol. 2.
8. Berezin, B.D. and Berezin, M.B., *Biologicheski aktivnye veshchestva v rasvorakh. Struktura, termodinamika, reaktsionnaya sposobnost'* (Biologically Active Substances in Solutions. Structure, Thermodynamics, Reactivity), Moscow: Nauka, 2001, p. 254.
9. Woo, L.K. and Goll, J.G., *J. Am. Chem. Soc.*, 1989, vol. 111, no. 10, p. 3755.
10. Woo, L.K., Gzapla, D.J., and Goll, J.G., *Inorg. Chem.*, 1990, vol. 29, no. 20, p. 3915.
11. Woo, L.K., Goll, J.G., Czapla, D.J., and Hays, J.A., *J. Am. Chem. Soc.*, 1991, vol. 113, no. 22, p. 8478.
12. Stuzhin, P.A., Repina, N.V., Klyueva, M.E., and Fedotova, E.V., *Zh. Fiz. Khim.*, 2004, vol. 78, no. 6, p. 1002.
13. Repina, N.V., Klyueva, M.E., Stuzhin, P.A., and Klyuev, M.V., Abstracts of Papers, *XXI Mezhdunarodnaya Chugaevskaya Konferentsiya po Koordinatsionnoi Khimii* (XXI International Chugaev Conferences on Coordination Chemistry), Kiev, 2003, p. 348.
14. Cook, A.H. and Linstead, R.P., *J. Chem. Soc.*, 1937, no. 6, p. 929.
15. Chizhova, N.V., Khelevina, O.G., and Berezin, B.D., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1994, vol. 37, no. 1, p. 20.
16. Chizhova, N.V. and Berezin, B.D., *Zh. Neorg. Khim.*, 2003, vol. 48, no. 9, p. 1495.
17. *Organikum. Organischchemisches Grundpracticum*, Schwentlick, K.M., Ed., Berlin: Wissenschaften, 1976.