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Transmetalation of (Octaphenyltetraazaporphyrinato)magnesium(II) with Manganese(II) Chloride in Dimethylformamide

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Abstract—The reaction of (octaphenyltetraazaporphyrinato)magnesium(II) with manganese(II) chloride in dimethylformamide gave (chloro)(octaphenyltetraazaporphyrinato)manganese(III). Reactions of the latter with nitrogen-containing bases were studied. The kinetic parameters of the transmetalation of (octaphenyltetraazaporphyrinato)magnesium(II) with $MnCl_2$ in dimethylformamide at 323, 333, and 343 K were determined, and a probable reaction mechanism was proposed.

Keywords: transmetalation, synthesis, (octaphenyltetraazaporphyrinato)magnesium(II)

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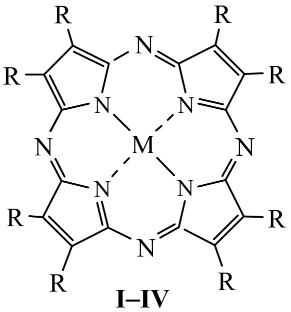
Interest in the synthesis and properties of porphyrazine complexes with transition metal cations is determined by their practical and theoretical importance. These complexes are used as efficient sensors, redox catalysts, photochromic materials, and biologically active substances [1].

Klyueva et al. [2] previously synthesized (chloro)(octaphenyltetraazaporphyrinato)manganese(III) (**II**) by reaction of octaphenyltetraazaporphyrin (**I**) with $MnCl_2$ in boiling dimethylformamide. (Acetoxo)(octaphenyltetraazaporphyrinato)manganese(III) (**III**) was obtained earlier [3] by fusion of diphenylmaleonitrile with anhydrous manganese acetate at 270°C (20 min). Transmetalation [4] is widely used to prepare difficultly accessible *meso*- and β-substituted porphyrinates [5, 6]. This procedure does not include demetalation of labile porphyrinate [Mg(II), Cd(II)], which improves the yield (Scheme 1).

Scheme 1.



I–IV

R = Ph; **I**, M = 2H; **II**, M = MnCl; **III**, M = Mn(OAc); **IV**, M = Mg.

In the present work we examined by spectrophotometry the transmetalation of (octaphenyltetraazaporphyrinato)magnesium(II) (**IV**) with $MnCl_2$ in dimethylformamide. According to published data [7, 8], the complexation of porphyrins and tetraazaporphyrins with MnX_2 ($X = Cl^-$, AcO^-) is usually accompanied by instantaneous oxidation of Mn(II) in the porphyrin complex to Mn(III). As a rule, compounds of the general formula (X)Mn(III)P are formed, where P is a porphyrin or azaporphyrin dianion, and X is an anionic ligand. Absorption bands in the electronic spectra of (X)Mn(III)P are displaced toward longer wavelengths relative to those in the spectra of Mn(II)P, and an additional charge transfer band appears, which provides information on the degree of oxidation of the complex cation [2].

Our results showed that the transmetalation of magnesium complex **IV** with $MnCl_2$ in DMF at room

Table 1. Electronic absorption spectra of compounds **I–VI**

Comp. no.	Solvent	λ_{max}, nm (log ε)			
		I	*II*	*III*	Soret
I	DMF	662 (4.46)	600 (4.35)		368 (4.57)
II	$CHCl_3$	666 (4.77)	615 sh	478 (4.54)	415 (4.66)
III	$CHCl_3$	666 (4.62)	612 sh	476 (4.10)	414 (4.55)
III[a]	$CHCl_3$	665 (4.66)	613 sh	475 (4.12)	414 (4.56)
IV[a]	$CHCl_3$	639 (4.91)	595 (4.30)		379 (4.86)
IV[b]	DMF	634 (1.96)	580 (0.45)		377 (1.69)
V[b]	DMF	639 (2.46)	580 (0.95)		389 (2.67)
VI[b]	Pyridine	627 (0.575)	575 (0.220)		322 (2.27)

[a] Data of [2, 8]. [b] Relative intensities are given.

temperature (molar reactant ratio 1 : 100 to 1 : 10) takes 10 days and yields (chloro)(octaphenylporphyrinato) manganese(III) (**II**). The electronic absorption spectrum of a sample withdrawn from the reaction mixture and dissolved in chloroform contains bands with their maxima at λ 666, 615, 478, and 415 nm. When the reaction mixture was heated to the boiling point, complex **II** was formed almost instantaneously (Table 1). Like (chloro)(tetrabenzoporphyrinato)manganese(III) [6], compound **II** can be reduced to (octaphenyltetraazaporphyrinato)manganese(II) (**V**) by shaking its solution in DMF with addition of potassium hydroxide (0.1 g of KOH per 3 mL of the solution) in a hermetically closed cell. The Mn(III)→Mn(II) reduction process at room temperature was accompanied by the following changes in the electronic absorption spectrum during ~10 min (Fig. 1). The charge transfer band (λ_{max} 480 nm) decreases in intensity, and two new bands appear with their maxima at λ 567 and 647 nm; the latter correspond to the intermediate revealed in [9]. A compound with λ_{max} 639 nm is then formed, and its absorption intensity exceeds that of initial complex **II** by a factor of ~1.3. The Soret band almost does not change its position, but its intensity increases by a factor of ~1.7. As in the reduction of (chloro)(tetrabenzoporphyrinato)manganese(III) [6], we presumed formation of. As the reaction progresses, the bands corresponding to Mn(II)P decrease in intensity, and this complex decomposes completely in ~24 h. The most probable reason for the decomposition of labile (tetraazaporphyrinato)manganese(II) is ligand exchange of P^{2-} for hydroxide ions [6].

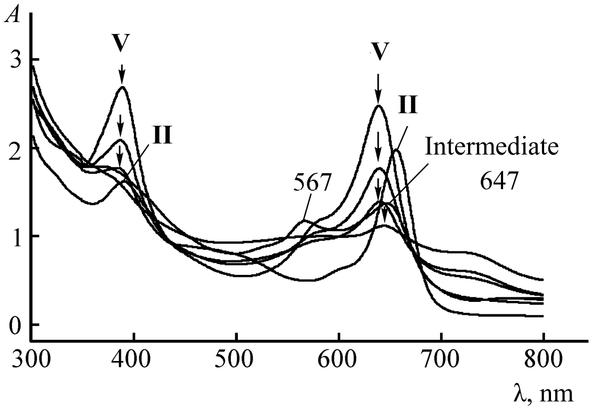


Fig. 1. Variation of the electronic absorption spectrum in the course of reduction of complex **II** in DMF in the presence of KOH.

Dolotova et al. [10] studied manganese complexes with phthalocyanine (MnPc) and found that axial coordination of pyridine with formation of Mn(II) Pc·Py and Mn(II)Pc·2Py initiates intramolecular electron transfer which leads assumingly to radical cation and radical anion species $Pc^{+}\cdot Mn(I)\cdot n Py$ and $Pc^{-}Mn(III)$. Generation of radical cation is favored by the presence of electron-donating substituents in the macrocycle. The electronic absorption spectrum of **II**, as well as of **III** [9], in going to pyridine does not change in ~24 h at room temperature (λ_{max} 661, 610, 478, 398 nm). After 5 days, the charge transfer band (λ_{max} 478 nm) disappears from the spectrum of **II** in pyridine, a new band appears with λ_{max} 575 nm, and band *I* and Soret band shift blue by 3 and 10 nm, respectively. Prolonged keeping of complex **II** in

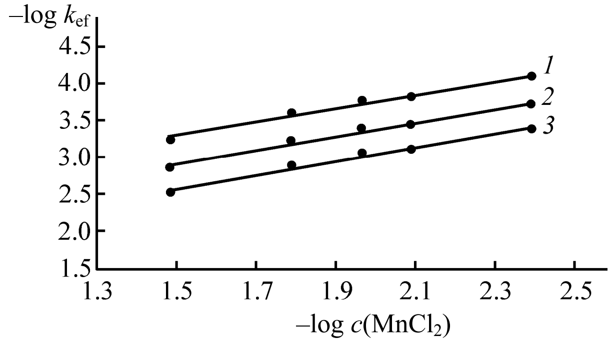


Fig. 2. Plot of log k_{ef} vs. log $c(MnCl_2)$ for the transmetalation of complex **IV** with $MnCl_2$ in DMF at (*1*) 323, (*2*) 333, and (*3*) 343 K.

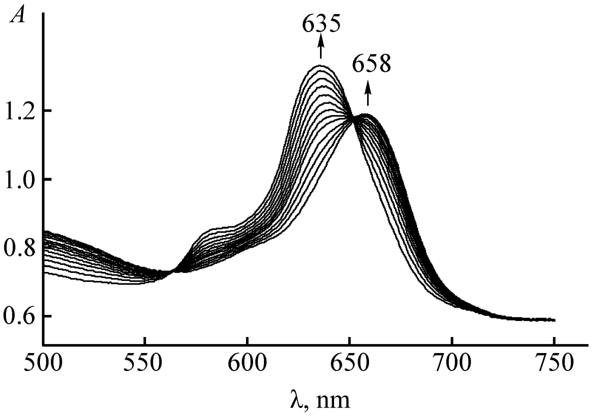


Fig. 3. Variation of the electronic absorption spectrum in the course of transmetalation of complex **IV** with $MnCl_2$ in DMF; $c_{IV} = 1.50 \times 10^{-5}$ M, $c(MnCl_2) = 1.62 \times 10^{-2}$ M, 343 K.

pyridine (~30 days) at room temperature gives a compound with λ_{max} 627, 575, and 322 nm, which is likely to be the complex $Mn(I)P^{+\cdot} \cdot nPy$ (**VI**). Addition of acetic acid to that compound in pyridine instantly yields (AcO)Mn(III)P. When several drops of dibutylamine were added to a freshly prepared solution of compound **II** in pyridine, a compound absorbing at λ_{max} 647, 575, and 372 nm was formed, as in the dissolution of complex **III** in piperidine [11]. A compound having an analogous electronic absorption spectrum was obtained by complexation of octaphenyltetraazaporphyrin with $Mn(OAc)_2$ in pyridine [9]. It was presumed [9] that the Mn(II) complex and the corresponding radical cation exist simultaneously in strongly reducing media (piperidine, pyridine).

In order to elucidate a probable mechanism of the transmetalation process we examined the kinetics of the reaction of complex **IV** with $MnCl_2$ in dimethylformamide at 323, 333, and 343 K. In the general form, the transmetalation equation can be written as follows:

$$MP + M'X_n(Solv)_{m-n} \rightarrow M'P + MX_n(Solv)_{m-n}. \qquad (1)$$

Here, MP and M′P are metalloporphyrins, and $M'X_n(Solv)_{m-n}$ are metal solvation complexes.

We found that the rate of metal exchange depends on the salt concentration. The order of the reaction with respect to $MnCl_2$ was estimated at unity [as the slope of the linear dependence $\log k_{ef}$–$\log c(MnCl_2)$; Fig. 2]. Taking into account 100-fold excess of $MnCl_2$ relative to magnesium complex **IV**, the kinetics of transmetalation reaction (1) may be described by pseudofirst-order equation (2).

$$-\partial c_{IV}/\partial\tau = k_v c_{IV} c(MnCl_2). \qquad (2)$$

Our spectral and kinetic data (Fig. 3, Table 2) for the transmetalation of magnesium complex **IV** with $MnCl_2$ in DMF in combination with those reported in [12, 13] allowed us to presume that the reactions follows associative mechanism. The first bimolecular step (3) gives intermediate dinuclear complex.

$$\begin{aligned}&(Solv)_mMP + M'X_2(Solv)_{n-2}\\ &\rightleftarrows (Solv)_mMP\cdot M'X_2(Solv)_{n-4} + 2Solv.\end{aligned} \qquad (3)$$

This complex can be formed immediately after mixing of the reactants (in this case, it could be readily detected by spectral methods) or this step may be slow. In the second slow unimolecular step (4) dissociation of the intermediate yields final products.

$$\begin{aligned}&(Solv)_mMP\cdot M'X_2(Solv)_{n-4}\\ &\rightleftarrows [(Solv)_mM \cdots P \cdots M'X_2(Solv)_{n-4}]^{\neq} \rightarrow MX_2(Solv)_m\\ &+ M'P(Solv)_{n-4}.\end{aligned} \qquad (4)$$

Step (4) is accompanied by change of the intensity of absorption bands in the electronic spectra (Fig. 3).

Klyueva et al. [9] studied the complexation of ligand **I** with $MnCl_2$ in DMF and showed (Table 3) that the rate of this reaction does not depend on the concentration of $MnCl_2$ provided that the latter is taken in 40–200-fold excess, i.e., the reaction follows unimolecular mechanism [8]. The formation of covalently bonded complex is preceded by fast coordination of the metal salt to one *meso*-nitrogen with formation of ammine complex. This complex is converted into complex **V** in the rate-determining step, and complex **V** is rapidly oxidized to (Cl)Mn(III)P. The effect of the anion in the manganese salt on the rate of complex

Table 2. Kinetic parameters of the transmetalation of magnesium complex **IV** with $MnCl_2$ in DMF ($c_{IV} = 1.5 \times 10^{-5}$ M)

$c(MnCl_2) \times 10^3$, M	T, K	$k_{ef} \times 10^4$, s^{-1}	$k_v \times 10$, L mol^{-1} s^{-1}	E_a, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
4.05	298[a]	0.07±0.002	0.02	77±3	–47±9
	323	0.84±0.03	0.21		
	333	1.93±0.06	0.48		
	343	4.45±0.19	1.10		
8.10	298[a]	0.12±0.004	0.02	77±3	–47±9
	323	1.45±0.05	0.18		
	333	3.50±0.08	0.43		
	343	7.57±0.19	0.93		
10.8	298[a]	0.14±0.004	0.01	79±3	–45±10
	323	1.78±0.07	0.17		
	333	4.01±0.06	0.37		
	343	9.37±0.37	0.87		
16.2	298[a]	0.19±0.006	0.01	81±3	–37±9
	323	2.32±0.06	0.14		
	333	5.92±0.21	0.37		
	343	13.62±0.44	0.84		
32.4	298[a]	0.469±0.02	0.01	80±3	–40±9
	323	5.62±0.12	0.17		
	333	13.70±0.10	0.42		
	343	31.62±1.22	0.98		

[a] Calculated by the Arrhenius equation.

formation was also examined [9]. The complexing ability of manganese acetate toward tetraazaporphyrins was found to considerably exceed that of chlorides. It was also found that octaphenyltetraazaporphyrin **I** does not form complex with $MnCl_2$ in pyridine.

The rate constants for the transmetalation of complex **IV** with $MnCl_2$ are approximately 19 times lower than the rate constants for the complex formation of ligand **I** with the same salt in DMF. However, it is advisable to synthesize manganese complexes via transmetalation since this procedure does not require demetalation of the initial complex and thus ensures higher yield of the final product.

Table 3. Kinetic parameters of the complex formation of octaphenyltetraazaporphyrin **I** with manganese(II) chloride in DMF [$c_I = 1.07 \times 10^{-5}$ M, $c(MnCl_2) = 2.06 \times 10^{-3}$ M)

T, K	$k_{ef} \times 10^3$, s^{-1}	E, kJ/mol	$-\Delta S^{\neq}$, J mol^{-1} K^{-1}
298	0.14±0.01	156±23	217±51
303	0.44±0.04		
308	1.09±0.04		

EXPERIMENTAL

(Octaphenyltetraazaporphyrinato)magnesium(II) (**IV**) was synthesized according to Linstead [14]. The solvents and manganese(II) chloride were purified as described in [15, 16]. The progress of the transmetalation of complex **IV** with $MnCl_2$ and $Mn(OAc)_2$ in DMF was monitored by spectrophotometry. For this purpose, samples of equal volumes were withdrawn from the reaction mixtures at definite time intervals and dissolved in some amount of DMF, and electronic spectrum of the solution was recorded. The electronic absorption spectra were recorded at 298 K on a Varian Cary 100 spectrophotometer. The elemental compositions were determined on a Flash EA 1112 analyzer. The IR spectra were measured in KBr on a Nicolet Avatar 360-FT-IR-ESP spectrometer. Silufol plates were used for analytical thin-layer chromatography.

(Chloro)(2,3,7,8,12,13,17,18-octaphenyl-5,10,15,20-tetraazaporphyrinato)manganese(III) (II). A solution of 0.1 g of complex **IV** and 0.13 g of $MnCl_2$ (molar ratio 1:10) in 20 mL of DMF was heated to the boiling point, cooled, and filtered. The filtrate was poured into water, and the precipitate was filtered off, washed with water, dried, and purified by chromatography on neutral alumina using chloroform as eluent. Yield 0.09 g (0.089 mmol, 84%), R_f 0.77 ($CHCl_3$–CCl_4, 1:1). IR spectrum, ν, cm^{-1}: 3415 s, 2921 s, 2850 s (C–N); 1142 s, 1015 m, 983 s [δ(C–H)]; 744 s, 694 s [γ(C–H)]; 1627 w, 1587 m, 1561 w, 1432 w, 1359 w (C–N, C=C); 1005 s, 745 m, 610 m (pyrrole), 535 m, 467 m (Mn–N). Electronic absorption spectrum (DMF), λ_{max}, nm (logε): 389 (4.38), 494 (4.11), 600 (4.02), 656 (4.47). Found, %: C 76.08; H 4.07; N 11.01. $C_{64}H_{40}Cl\cdot N_8Mn$. Calculated, %: C 76.00; H 3.99; N 11.08.

Kinetic measurements. A spectrophotometric cell maintained at a constant temperature was charged with a solution of complex **IV** and $MnCl_2$ with known concentrations. The optical density of the solution at λ λ 635 nm (**IV**) was measured at definite time intervals. The measurements were performed in the temperature range from 323 to 343 K. The initial concentration of complex **IV** was 1.5×10^{-5} M, and the concentration of $MnCl_2$ was $c(MnCl_2) = (4.05–32.40)\times10^{-3}$ M.

The current concentration of complex **IV** was calculated by Eq. (5).

$$c = c_0\,(A_\tau - A_\infty)/(A_0 - A_\infty). \quad (5)$$

Here, A_0, A_τ, and A_∞ are the optical densities of reaction solution at the initial moment, moment τ, and by the end of the process; c_0 and c are the initial and current concentrations of complex **IV**, respectively.

The effective rate constants k_{ef} were calculated by Eq. (6).

$$-\partial c_{\mathbf{IV}}/\partial\tau = k_{ef}\,c_{\mathbf{IV}}. \quad (6)$$

The energy of activation E_a was calculated by the Arrhenius equation (7).

$$E_a = 19.1[T_1T_2/(T_2 - T_1)]\log(K_2/K_1). \quad (7)$$

Here, K_1 and K_2 are the true rate constants $K_v = k_{ef}/c_{salt}$. The change of the entropy of activation $\Delta S^{\neq}$ was calculated in terms of the ansolute reaction rate theory [17] using Eq. (8).

$$\Delta S^{\neq} = 8.314\ln K_v^{298} + (E_a/298)253.22. \quad (8)$$

The relative error in the determination of k_{ef} was 1–6%, and in the determination of E_a and $\Delta S^{\neq}$, no higher than 15%.

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