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Metal Exchange Reactions in Cadmium Complexes with Porphyrins of Various Structures

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Abstract—The reaction kinetics of the metal exchange Cd(II)–Cu(II) and Cd(II)–Zn(II) in the cadmium complexes (CdP) with porphyrin ligands (H_2P) differing by degree of stiffness (tetraphenylporphin, *N*-methyltetraphenylporphin, and tetraphenyltetrabenzoporphin) in the DMSO medium, was studied using spectrophotometric method. The rate of metal exchange reaction depends on the nature of the non-planatrity of H_2P in the structure of CdP complexes, as well as on the additional screening of the reaction center MN_4 by the extra-ligands and substituents. The reduction of the coordinating ability of the anion X^- in the structure of the solvate-salt of incoming metal $M'X_2(Solv)_{n-2}$ in a series: acetylacetonate > acetate > chloride > nitrate favors the metal exchange. In the most studied cases the reaction of CdP proceeds along a combined associative–dissociative mechanism. The order of the metal exchange reaction is found to be depending on temperature indicating a change in the contributions of associative and combined routes. The "pure" associative reaction mechanism in a medium of DMSO was for the first time found for the labile complex CdTPTBP with the saddle-type nonplanar ligand.

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The metal exchange reactions in complexes with macrocyclic ligands (1) belong to a special type of complex coordination interactions [1–3].

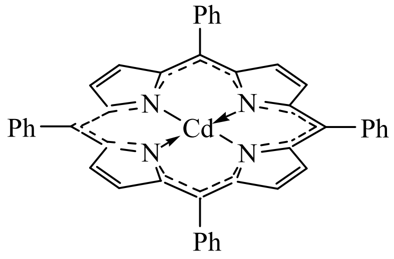
$$ML + M'X_n(Solv)_{m-n} \rightarrow M'L + MX_n(Solv)_{m-n}, \qquad (1)$$

The process of such reactions includes both protonless or solvolytic dissociation of the complex ML into L^{n-} and M^{n+} [4] and the formation by the H_nL ligand of new chemical bonds with the incoming metal ion $(M')^{n+}$. The reactions of metal exchange are widely used in the synthesis and catalysis of reactions of complex formation, to create a fluorescent labels and metal-containing nanoclusters, in preparative and analytical processes [2]. Of particular interest in studying the mechanism of such transformations in order to select the optimal reaction conditions of metal exchange is the case of relatively labile porphyrin complexes [MP, M = Pb(II), Cd(II), Hg(II) and some others], for which the process of solvolytic dissociation is not typical [4, 5].

Among the factors that control the reaction rate and the mechanism of the metal exchange in the porphyrin complexes can be identified the nature of the ligand in the MP composition, the electronic structure and solvation environment of the outgoing $(M)^{n+}$ and the incoming $(M')^{n+}$ cations of salt, the anionic composition (X^-) of the coordination sphere of the solvate-salt $[M'X_n(Solv)_{m-n}]$, and the nature of the solvent (Solv), as well as the presence in the reaction system of active or passive salt background.

This work is aimed at establishing the nature of influence of non-planar structure and other steric features of MP, the influence of the nature of anion in the solvate-salt, as well as the presence of background salt of the outcoming metal, on the reaction of the metal exchange in the medium of a coordinating solvent. For this purpose we studied the kinetics of metal exchange in the cadmium complexes **I–IV** with the ligands differing by the degree of stiffness: tetraphenylporphin, *N*-methyltetraphenylporphin, and tetraphenyltetrabenzoporphin, in the reaction with copper(II) nitrate, chloride, acetate, and acetylacetone, and zinc(II) nitrate and copper(II) acetate in the presence of background salt $Cd(OAc)_2$.

The studies were carried out in DMSO as a medium, over a wide concentration range [c_{salt} = (0.41–3.45)×10^{-3} M] and temperature (291–338 K) intervals. The experimental data are listed in Tables 1 and 2.



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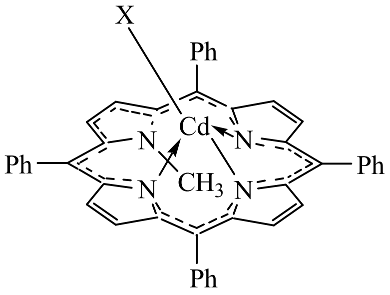

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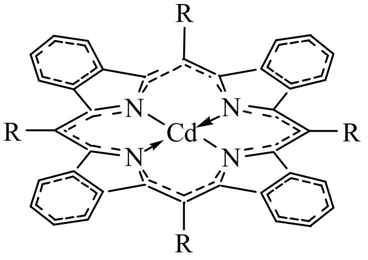

III, IV

R = Ph (**III**); R = H (**IV**).

By the nature of ligands of the cadmium complexes of porphyrins the considered compounds **I–III**, as well as previously studied cadmium tetrabenzoporhin **IV** [6] belong to different structural groups. They are characterized by different degree of non-planatrity of macrocycles, which follows from the results of direct structural [X-ray analysis, the value of ΔC_β or ΔC_{meso} (Å)[1]] and spectral [fluorescent spectroscopy, the values of Stokes shifts of the bands $\Delta\nu^{I}$ (cm^{-1})[2]] measurement, and quantum chemistry data [5, 7]. According to this classification, the porphyrin ligand (H_2TPP) in the composition of compound **I** corresponds to the molecules with a predominantly flat structure (ΔC_β = 0.14–0.23 Å; $\Delta\nu^{I}$ = 146 cm^{-1}), tetrabenzoporhin (H_2TBP) in the case of complex **IV** has a more pronounced aromaticity ($\Delta C_\beta \leq 0.1$ Å; $\Delta\nu^{I}$ 35 cm^{-1}), whereas *N*-methyltetraphenylporphin [H(N–Me)TPP, $\Delta C_\beta \approx$ 0.5 Å; $\Delta\nu^{I}$ 312 cm^{-1}) and tetraphenyltetrabenzoporphin (H_2TPTBP, ΔC_β 0.77 Å; $\Delta\nu^{I}$ 546 cm^{-1}), the ligands of compounds **II** and **III**, respectively, belong to H_2P with strongly non-planar aromatic chromophores. Thus, the degree of stiffness of the macrocyclic ligands in the complexes **I–IV** changes in the series **III** < **II** < **I** < **IV**.

The consideration of the spatial structure of the macrocycles allows good understanding of the data obtained on the reactivity of compounds **I–IV** in the processes of metal exchange. Thus, in the reaction of the porphyrin cadmium complexes with $Zn(NO_3)_2$ ($c_{\text{salt}} = 2.76\times10^{-3}$ M, $c_{\text{CdP}} = 2.76\times10^{-5}$ M) in DMSO medium the rate of metal exchange decreases in the series of compounds: CdTPP {**I**, k_{eff}^{298} ($0.469 \pm 0.027) \times 10^{-3}$ s^{-1}, [6]} > (AcO)Cd(N–Me)TPP [**II**, k_{eff}^{298} $(0.072 \pm 0.007)\times10^{-3}$ s^{-1}, Table 1] > CdTBP (**IV**, very slowly at *T* = 343 K [6]).

In the reaction with $Cu(NO_3)_2$ at 298 K the sequence of the complexes is the following: CdTPP (instantaneous)> CdTBP [k_{eff}^{298} $(1.96\pm0.11)\times10^{-3}$ s^{-1} ($c_{\text{CdTBP}} = 1.43\times10^{-5}$ M and c_{salt} 1.53×10^{-3} M)] > (AcO)Cd(N–Me)TPP {k_{eff}^{298} = $(0.55\pm0.05)\times10^{-3}$ s^{-1} [$c_{\text{(AcO)Cd(N–Me)TPP}} = 2.76\times10^{-5}$ M and $c_{\text{salt}} = 2.76\times10^{-3}$ M]}.

These data suggest that the propensity of metalloporphyrins to the metal replacement reactions decreases with the increasing stiffness of the macrocyclic ligand in the complex, in particular, in going from CdTPP (**I**) to CdTBP (**IV**), due to both structural and electronic factors. With the increasing aromaticity of the H_2P molecule increases the degree of conjugation of π-electrons in it, and thus the effective charges on the coordinating nitrogen atoms in the respective complexes decrease, that adversely affects the rate of the metal exchange.

At the deviation of the H_2P ligand structure in the complex MP from planar the metal exchange should, on the contrary, be facilitated. Indeed, the comparison of the effective rate constants (k_{eff}) of reaction (1) obtained for the system CdP–$Cd(OAc)_2$–$Cu(OAc)_2$ shows that much more nonplanar CdTPTBP (**III**) exchanges the metal 1.5–8.5 times faster than nearly flat CdTPP (**I**) (Table 2).

A different trend is observed in the case of cadmium complex **II** with nonplanar H(N–Me)TPP, whose structure of the coordination center is substantially different from that of compound **I** and other classical metalloporphyrins. Shielding of the metal atom in complex **II** by the methyl group on one side of the conventional macrocycle plane and by the counte-

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[1] Suggested quantities characterize the average deviation of β- and meso-carbon atoms, respectively, of the macrocycle H_2P from the original plane of the molecule.

[2] The value of Stokes shift is defined as a difference between the maxima of the boundary bands in the fluorescence and absorption spectra.

Table 1. Kinetic parameters of the cadmium-porphyrin metal exchange reaction in DMSO, $c_{MP} = 2.76\times10^{-5}$ mol l^{-1}, 298 K

System	λ_{exp}, nm	$c_{salt}\times10^3$, M	$k_{eff}\times10^3$, s^{-1}	k_v, l mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
CdTPP(I)–CuCl$_2$	621	0.41	16.51±0.37	39.87±0.91	58±20	–
		0.69	16.67±0.43	24.16±0.62	54±20	–
		0.96	17.71±0.33	18.33±0.34	58±6	–
		1.24	33.11±2.12	26.65±1.71	47±8	–
		1.38	41.14±0.24	30.02±0.17	48±14	–
CdTPP(I)–Cu(OAc)$_2$	541	1.38	0.53[a]	0.38[a]	58±18	–
		2.07	0.65[a]	0.31[a]	62±12	–
		2.76	0.82[a]	0.29[a]	61±14	–
		3.45	0.91[a]	0.26[a]	64±11	–
CdTPP(I)–Cu(Acac)$_2$	614	1.38	0.12[a]	0.087[a]	42±1	–192±2
		2.07	0.18[a]	0.089[a]	41±3	–183±11
		2.34	0.20[a]	0.088[a]	39±3	–190±10
		2.76	0.25[a]	0.093[a]	45±8	–177±20
(AcO)Cd(N–Me)TPP(II)–Zn(NO$_3$)$_2$	617	1.38	0.019±0.002	0.013±0.001	91±19	–136±20
		2.07	0.059±0.007	0.028±0.003	78±10	–46±17
		2.76	0.072±0.007	0.026±0.002	73±13	–99±20
		3.45	0.18±0.04	0.053±0.012	59±7	–120±20
(AcO)Cd(N–Me)TPP(II)–Cu(NO$_3$)$_2$	610	1.38	0.25±0.03	0.68±0.08		
		2.76	0.55±0.05	0.65±0.059		
		3.45	0.84±0.04	0.75±0.04		

[a] Calculated with Arrhenius equation.

Table 2. Kinetic parameters of reactions of the metal exchange in the system CdP–Cu(OAc)$_2$–Cd(OAc)$_2$–DMSO, $c_{MP} = 2.76\times 10^{-5}$ mol l^{-1}, 298 K

Compound	λ_{exp}, nm	$c_{salt}\times10^3$, M	$k_{eff}\times10^3$, s^{-1}	k_v, l mol^{-1} s^{-1}	E_a, kJ mol^{-1}	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
CdTPTBP(III)	646	0.69	2.80[a]		7±1	–279±5
		1.38	2.30[a]		14±1	–256±5
		2.07	2.39[a]		12±1	–261±1
		2.76	1.90[a]		18±5	–244±18
CdTPP(I)	618	0.69	0.33±0.02	16.71±1.41	74±3	–70±10
		1.38	0.88±0.04	10.50±0.91	49±6	–146±20
		2.07	1.04±0.03	9.49±0.81	45±8	–158±20
		2.76	1.30±0.09	14.86±1.36	41±6	–167±19
		3.45	1.35±0.12	15.35±1.15	43±9	–160±18

[a] Calculated with Arrhenius equation.

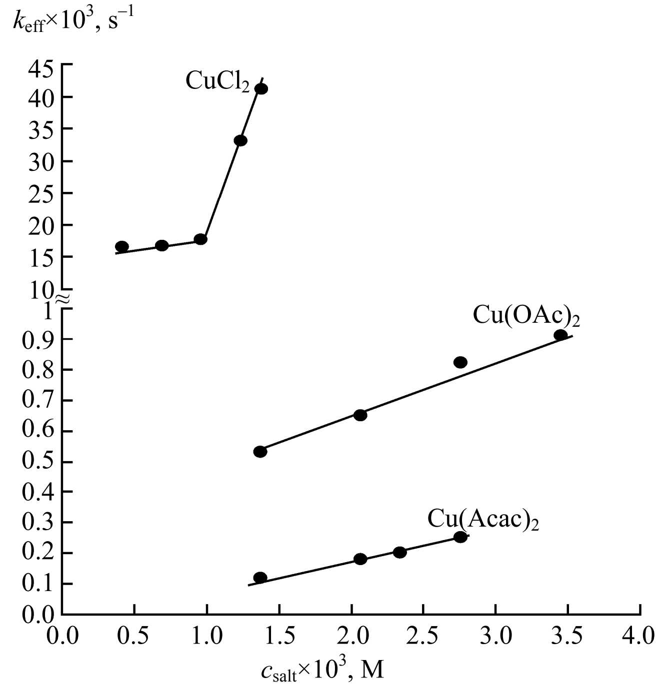


Fig. 1. Concentration dependence of the rate constant of the metal exchange reaction CdTPP **I**–CuX$_2$–DMSO (c_{MP} = 2.76×10^{-5} M) at 298 K on the nature of the anion X$^-$.

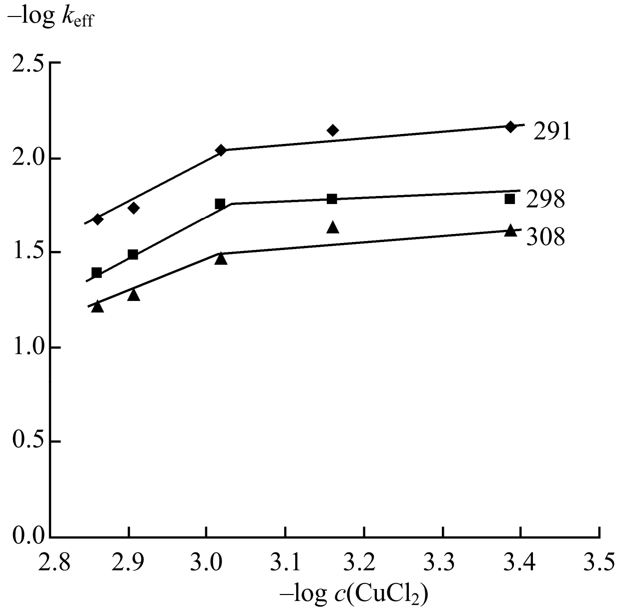


Fig. 2. Logarithmic dependence of the rate constant on concentration for the reaction (1) in the system CdTPP **I**–CuCl$_2$–DMSO at different temperatures.

rion on the other side causes almost 6 times decrease in the rate of the Cd–Zn metal exchange compared to complex **I** with its more flat but not screened reaction center (Table 1) [6]. In the reaction (AcO)Cd(N–Me)·TPP–Cu(NO$_3$)$_2$ the exchange is even more hampered than in the case of stiff CdTBP (**IV**), for which the value of k_{eff} is 4 times higher [5].

Thus, the series with decrease in the rate of metal exchange are defined by both stabilizing influence of macrocyclic effect in the complex MP, its electronic and structural components [4, 5], and by additional shielding of the reaction center MN$_4$ by the substituents (N-substituent, the “lid” in the “covered” porphyrins, etc.) and extra-ligands [e.g., acido-ligand in (AcO)Cd(N–Me)TPP, etc.]. The nonplanar structure of the H$_2$P ligand in the structure of MP facilitates the out-of-plane location of large cations Cd^{2+} and provides significant effective charges on the coordinating nitrogen atoms in the complex (δ$^-$) and positive (δ$^+$) on the outgoing atom of the metal ion that is essential for the effective metal exchange.

The structure of the second participant of reaction (1), namely, the solvate-salt [MX$_n$(Solv)$_{n-2}$], may affect the reaction course no less significantly, and in some cases even can change the exchange mechanism. Therefore, we carried out kinetic measurements (Table 1) of the reaction of complex **I** with copper(II) acetate, acetylacetonate, and chloride in DMSO medium. The study showed that the rate of the metal exchange increases with decrease in the coordination ability of the anion X$^-$ [5, 8] in a series NO$_3^-$ < Cl$^-$< AcO$^-$ < Acac$^-$ due to the weakening of the M–X bond in the solvate-salt that should be destroyed in the reaction (1) (Table 1). In comparable conditions, the metal exchange reaction of complex **I** with Cu(NO$_3$)$_2$ at c_{salt} = 1.38×10^{-3} M proceeds almost instantaneously. Therewith, the Cd–Cu exchange in complex CdTPP (**I**) occurs 80 times faster in the reaction with CuCl$_2$ than with Cu(OAc)$_2$. If, however, as a source of replacement of the metal is taken a copper(II) salt with chelating acetylacetonate ligand, the reaction of the metal exchange proceeds approximately 4.5 times slower compared with Cu(OAc)$_2$ (Fig. 1).

We have discovered an unusual case of changing the order of metal exchange reaction in the system CdTPP **II**–CuCl$_2$ in DMSO medium (Table 1, Fig. 2). The order of the reaction on the copper salt equals zero (n = 0) in the range of concentrations c_{CuCl2} 0–0.001 M and equals two at higher concentrations. The values of the orders are the same in the temperature range 291–308 K. We can assume that the increase in the reaction order is due to the dimerization of the salt in DMSO at its concentration above 1×10^{-3} M.

It was repeatedly noted in literature that the metal exchange in the porphyrin complexes ($MP–M'X_n$) could proceed either faster or slower than the reaction of complexation ($H_2P–M'X_{n-2}$) [2, 9]. However, in most cases the exchange reaction, especially in labile MP, proceeds by 1–3 orders of magnitude faster.

$$H_2P + MX_2(Solv)_{n-2} \rightarrow MP + 2HX + (n-2)Solv. \qquad (2)$$

Reaction of CuTPTBP formation from the ligand and copper acetate proceeds in DMSO only three times slower compared with the metal exchange in the CdTPTBP **III**–$Cu(OAc)_2$–$Cd(OAc)_2$ system (at 298 K, $k^{form} = 0.71\times10^{-3}$ s^{-1}; $k^{exch} = 1.90\times10^{-3}$ s^{-1}), but for complexes with a predominantly planar ligands whose complexation reaction (2) in a medium of electron-donor solvent is greatly inhibited, this difference considerably increases [2].

It is presumable that the driving force of the metal exchange is the gradient of the chemical affinity of the two metals, the outgoing and incoming, to the nitrogen atoms of the coordination cavity N_4. Therefore, as noted in [10], there is some direct relation in the reaction rates of the metal exchange (1) and complex formation (2). For example, H(N–Me)TPP in DMSO reacts with the zinc salt 50 times faster than with the cobalt(II) salt, and CdTPP (**I**) also 50 times faster exchanges the metal by zinc, than by cobalt. However, Hambright et al. [2, 11] mistakenly believe that the rate of the metal exchange in MP (1) increases in direct proportion to the basicity of the ligands in the complexes, and that reaction (1) is affected by the same set of factors as reaction (2). Actually, this approach is applicable only when the compared MPs are of the same structural group and differ only by electronic nature of substituents on the periphery of the molecule. Thus, we obtained a series of the rates of metal exchange in MPs of different structures, for example, in the reactions of MP–$Zn(NO_3)_2$ the sequence CdTBP **IV** < (AcO)Cd(N–Me)TPP **II** < CdTPP **I** is inconsistent with the sequence of the rates of complex formation by the respective ligands [H_2P–$Zn(OAc)_2$–DMSO]: $H_2TPP < H_2TBP <$ H (N–Me)TPP [5], and is inconsistent with the sequence of basicity of the ligands in acetonitrile (H_2P–$HClO_4$–MeCN): $H_2TBP < H_2TPP <$ H(N–Me)TPP [5, 12].

This inconsistency originates from the fact that for some H_2P the main factor determining the rate of reaction of complex formation (1) in the electron-donor DMSO is not the basicity of tertiary nitrogen atoms or strength of the solvate-salt involved in the reaction (1) [13], but the state of NH bonds in the H_2P molecule and the number of these bonds [14]. Thus, tetra-phenylporphin (H_2TPP) is the classic porphyrin with chemically inert localized NH bonds, therefore the rate of reaction (2) in its case in a medium of DMSO is minimal. H_2TBP and H_2TPTBP are nonclassical H_2Ps with partially delocalized NH bonds and therefore more reactive, and H(N–Me)TPP easier enters reaction (2) due to nonplanar molecular structure and the necessity of the dissociation of only one NH bond in the course of the complex formation.

Although in the course of reactions of metal exchange the dissociation of initial complex MP occurs, a direct correlation between the ability of complexes to metal exchange and their stability also does not exist. Thus, in the studied series of compounds the stability against the solvoprotolitic dissociation (MP–HOAc–DMSO) decreases as follows: CdTBP **IV** > CdTPP **I** > (AcO)Cd(N–Me)TPP **II**, namely, with decrease in the planarity of H_2P macrocycle in the MP [4, 5]. In addition, it is known that complexes with a strongly nonplanar ligands $Zn(\beta\text{-}Ph)_8TPP$ and (AcO)Zn(N–Me)TPP, not exchanging metal even in the most favorable conditions [for example, in the system MP–$M'(NO_3)_2$–MeCN] are, nevertheless, by 1–2 orders of magnitude less stable compared with CdTPP (**I**), which readily enters reaction (1). The rate of the metal exchange CdP–$Zn(NO_3)_2$ is significantly lower in the case of compound **IV** compared with moderately flat CdTPP (**I**), although (AcO)·Cd(N–Me)TPP (**II**) is much less flat and less stable toward dissociation compared with CdTPP. Nevertheless, the stability of a complex is a very important factor affecting the rate of metal exchange in it. Thus, in the zinc complexes $Zn(\beta\text{-}Ph)_8TPP$ and (AcO)Zn(N–Me)·TPP that are relatively low stable compared to ZnTBP and ZnTPP the metal exchange was not observed in the temperature range 298–348 K not only in the DMSO medium, but even in MeCN that forms less stable solvates compared with DMSO [6, 13]. Apparently, exchange in these complexes requires more rigid conditions ($T \geq 373$ K), as was observed for the system of ZnTPP–$Zn(OAc)_2$–Py [15].

$$ML_{(MC)} + [M'(solv)_4X_2 \xrightleftharpoons{\text{fast}} [M\text{–}L_{(MC)}\text{–}M']^{2+}X^{2-}$$

$$\xrightarrow{\text{slow}} M'L_{(MC)} + [M'(solv)_4X_2], \qquad (3)$$

$$ML_{(MC)} + n\,solv \rightleftarrows M(solv)_n + L_{(MC)};$$

$$L_{(MC)} + M'X_2(solv)_{n-2} \rightleftarrows M'L_{(MC)} + 2X^- + (n-2)solv. \qquad (4)$$

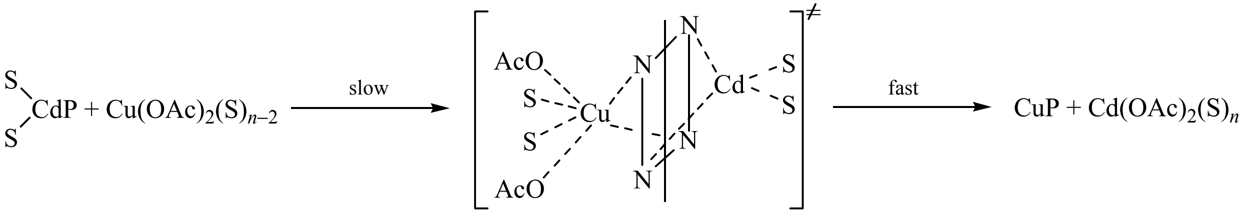
Our results of spectral and kinetic measurements, along with available literature data, allow the consideration of the possible reaction mechanism of metal exchange in more detail. For nonconjugated or weakly conjugated macrocyclic complexes two routes are suggested for the reaction of metal exchange: associative (3) and dissociative (4) [1].

For H_2P, the associative mechanism is more probable, since the high stability of the complexes of porphyrins and their inability to solvolytic dissociation, for example, under the influence of a non-protonogenic solvent, prevents proceeding of reaction (1) by the dissociative mechanism [4].

Our measurements showed [3, 6] that in the case of all kinetically studied complexes the reaction CdP–MX_2 proceeds strictly in accordance with the first order with respect to the parent complex. At the same time, the first order on salt is strictly observed only in the reaction of CdTPP (**I**) with Zn $(NO_3)_2$. The exchange reaction in the systems CdTBP (**IV**)–Cu $(NO_3)_2$ and (AcO)Cd(N–Me)TPP (**II**)–Zn $(NO_3)_2$ is bimolecular, but k_v decreases markedly with the increase in the salt concentration (Table 3) that may be associated with a change in the composition of this solvate-salt. Such concentration dependence of the constants is well known for the reactions of complexation of porphyrins with metal salts [5, 13].

It was suggested above that the rate of the metal exchange is determined largely by the stability of the complex used for the exchange and less by the coordinating ability of the ligand. This fact, together with greater reactivity of the complexes in the metal exchange (1), compared with ligands in complexation reactions (2), points to an associative way of reaction (1) in the case of the cadmium porphyrins complexes. Then, the failure of zinc porphyrins to the metal exchange at the temperatures below 333 K is understandable due to the inability of the complexes to metal exchange in these conditions by the associative mechanism.

At the same time, the absence of an unambiguous correlation of the metal exchange rate with complexation of H_2P or dissociation of MP evidences in favor of the reaction mechanism of mixed or associative–dissociative type (5).



(5)

Table 3. Orders on the incoming metal salt n of reaction (1) in the complexes of cadmium with porphyrins (determined from the equation $\log k_{\mathrm{eff}} = \log k_{\mathrm{v}} + n \log c_{\mathrm{M'}}$)

System	n	Mechanism
CdTPP(I)–$CuCl_2$	At $c < 0.01$ M $n = 0$, at $c > 0.01$ M $n = 2$	Associative Mixed
CdTPP(I)–$Cu(Acac)_2$	0.8	Mixed
CdTPP(I)–$Cu(OAc)_2$	0.4	Mixed
CdTPP(I)–$Cd(OAc)_2$–$Cu(OAc)_2$	(0.4–0.9) increases with increasing T (298–318 K)	Mixed
CdTPTBP(III)–$Cd(OAc)_2$–$Cu(OAc)_2$	0	Associative
CdTPP(I)–$Zn(NO_3)_2$ [3]	1	Mixed
CdTBP(IV)–$Cu(NO_3)_2$ [3]	(0.3–1.0) decreases with increasing T (293–308 K)	Mixed
(AcO)Cd(N–Me)TPP(II)–$Zn(NO_3)_2$	(0.85–0.5) decreases with increasing T (308–333 K)	Mixed
(AcO)Cd(N–Me)TPP(II)–$Cu(NO_3)_2$	1.2	Mixed

We first found the existence of temperature dependence of the order of reaction (1) on the salt-reagent. Thus, the order on the salt in the case of CdTPP (**I**) at the Cd–Zn exchange strictly equal to unity and not invariable with temperature, while at the Cd–Zn and Cd–Cu exchange it varies from 0.85 at 308 K to 0.5 at 333 K for (AcO)Cd(N–Me)TPP (**II**) and from the unity at 293 K to 0.28 at 308 K for CdTBP (**IV**), that is, decreases with increasing temperature (Table 3). A similar situation was observed for the systems CdTPP **I**–Cd(OAc)$_2$–Cu(OAc)$_2$ at the Cd–Cu exchange: The reaction order of the metal exchange with respect to the copper salt varied from 0.4 at 298 K to 0.9 at 318 K. But the order in the case of CdTPP (**I**) at the Cd–Cu exchange in the absence of Cd(OAc)$_2$ remains almost unchanged (~0.4) with temperature.

The temperature dependence of the reaction order of metal exchange on salt is, apparently, evidences in favor of a mixed associative–dissociative reaction path of the metal exchange in cadmium porphyrins in DMSO medium (5) and of reduced contribution of the associative reaction mechanism (2) with increasing temperature in one case and increase in the other (Table 3). The increased contribution of dissociative path of the metal exchange with increasing temperature is logical. Solvolytic dissociation of the majority of cadmium porphyrins is impossible, even at elevated temperatures, however, one cannot exclude that it occurs in the presence of the electrostatic field of the cation of the entering metal. Logical is also the experimental fact that in the case of mixed mechanism (5) in the medium of coordinating DMSO no intermediate compound of the metal exchange reaction is registered in the electron absorption spectra (EAS).

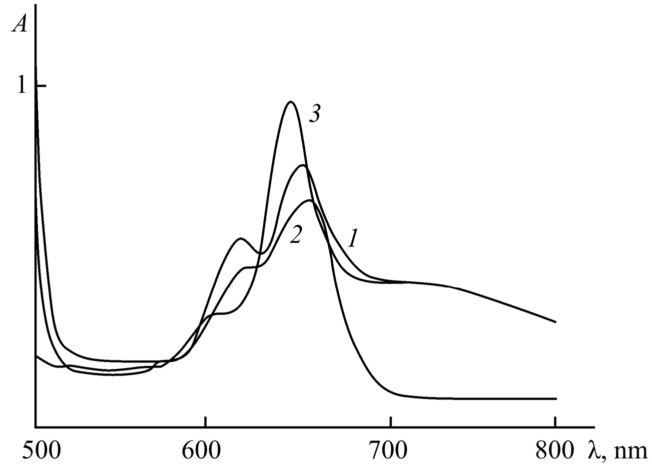


Fig. 3. Changes in the electron absorption spectra in the course of the metal exchange reaction in the system CdTPTBP **III**–Cu(OAc)$_2$–Cd(OAc)$_2$ in DMSO: (*1*) complex CdTPTBP (**III**) (*c* 5.52×10^{-5} M), λmax 653 nm, (*2*) intermediate $[\mathrm{Cd}\cdots\mathrm{TPTBP}\cdots\mathrm{Cu}]^{2+}(\mathrm{OAc}^{-})_2$ (*c* 2.76×10^{-5} M^{1}), λ_{max} 656 nm, (3) complex CuTPTBP, λ_{max} 647 nm.

We first found an example of metal exchange reaction proceeding by “pure” associative mechanism in the system CdTPTBP **III**–Cu(OAc)$_2$–Cd(OAc)$_2$ in the medium of an electron-donor solvent. The very non-planar complex **III** is unstable and collapsed at the attempt to extract it from the reaction mixture with chloroform or other low-polar solvents. Therefore metal exchange in the complex was studied using its solution in DMSO at 10-fold excess of the outgoing metal salts. Fig. 3 shows the change in EAS during the metal exchange reaction CdTPTBP **III**–Cu(OAc)$_2$ in DMSO. After mixing a solutions of the complex CdP, whose EAS in the presence of Cd(OAc)$_2$ contains Q_x band at the wavelength 653 nm, with the solution of Cu(OAc)$_2$ in DMSO immediately formed an intermediate [Eq. (3)], which is accompanied by the red shift of the Q_x band by 3 nm. Then slow decomposition of the intermediate occurs with the formation of the reaction product CuTPTBP, having a Q_x band in the EAS λ_I at 647 nm. Thus, the transformation of CdTPTBP to CuTPTBP leads to a blue shift of the Q_x band in the EAS, which is consistent with the spectral criterion of strength of MP complexes [4, 13].

In the course of calculation of kinetic parameters of the reaction in the system CdTPTBP **III**–Cu(OAc)$_2$–Cd (OAc)$_2$ we found that the reaction rate constant does not depend on the concentration of the entering metal salt [Cu(II)] (Table 2, Fig. 4). The observed zero order with respect to salt in the system, as well as spectral changes during the reaction (Fig. 3) suggest that it proceeds in accordance with the “pure” associative mechanism (3). The reaction course according to scheme (3) in the considered system is favored by the lability of the cadmium complex caused not only by a significant size of the Cd^{2+} ion (r = 0.97 Å), but also by the strongly non-planar structure of the ligand in compound **III**. The N–Cd bonds in the complex are weakly covalent, and on the nitrogen atoms a substantially higher effective negative charge is accumulated favoring the formation of bimetallic intermediates. The probability of the reaction in DMSO along the associative mechanism (3) for such complexes is high even in the presence of the outgoing metal salt.

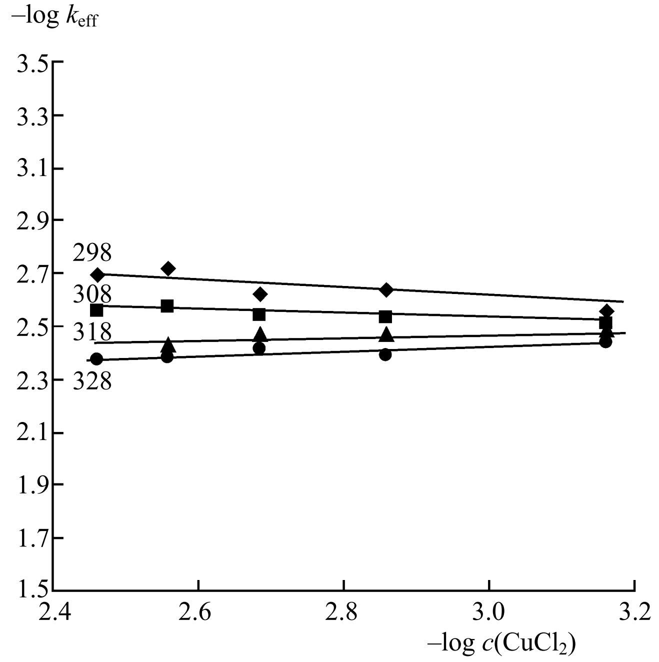


Fig. 4. Logarithmic dependence of the rate constant of reaction (1) in the system CdTPTBP **III**–$Cu(OAc)_2$–$Cd(OAc)_2$–DMSO on the concentration of $Cu(OAc)_2$, tan α ~ 0.

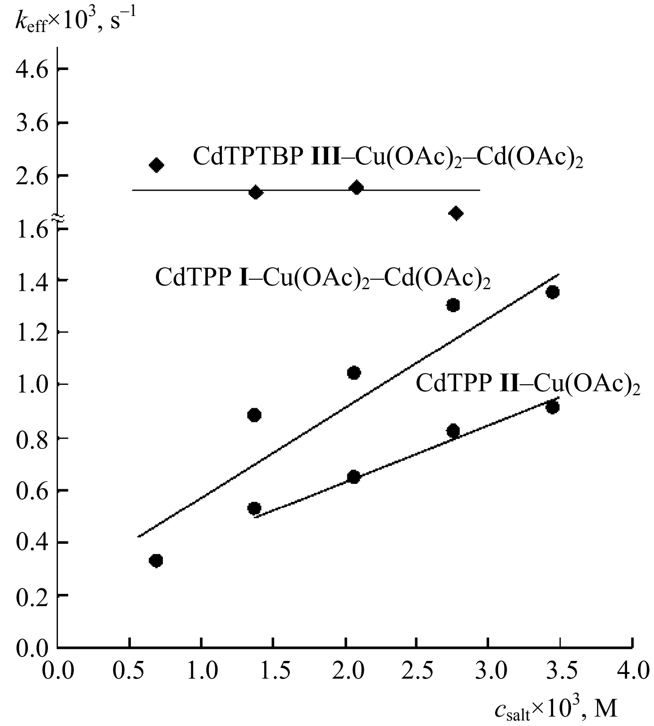


Fig. 5. The dependence of the exchange rate constant [reacyion (1)] for complexes CdTPP (**I**) and CdTPTBP (**III**) (c 2.76×10^{-5} M) in DMSO at 298 K on the concentration of copper acetate in the presence and absence of background salt [$Cd(OAc)_2$].

To determine the nature of the effects of the excess of the salt of the outgoing complex-forming metal on the mechanism and rate of the metal exchange, we studied kinetics of this reaction for CdTPP (**I**) with copper(II) acetate in the presence and in the absence of background salt $Cd(OAc)_2$ in a wide range of concentrations of the reagents. Analysis of experimental data obtained led us to a conclusion that in these systems CdTPP **I**–$Cu(OAc)_2$–$Cd(OAc)_2$ and CdTPP **I**–$Cu(OAc)_2$ the reaction (1) proceeded by a mixed mechanism. The order of magnitude of the metal exchange rate constant was 0.4–0.8 (Table 3, Fig. 5), and intermediates were not fixed in EAS. The presence in solution of cadmium acetate leads to some acceleration of reaction (1) rather than to slowing it, as it would be in the case of it taking the dissociative route. At the molar excess of the reagent salt from 25 to 125 times the metal exchange rate increased 1.5–2.0 times (Table 2), thus the probability of dissociative path (4) of reaction is excluded (1).

Thus, in most cases, the reaction of metal exchange in cadmium(II) porphyrin in a medium of DMSO proceeds along the mixed associative-dissociative mechanism (5), as evidenced by the order of the reaction on the salt in the range $0 < n \leq 1$ and by the absence of spectrally identified intermediates. Extreme cases are hardly probable. Thus, the dissociative mechanism (4) is excluded, since the introduction of excess of the outgoing metal salt does not slow down the reaction (1). “Pure” associative mechanism of the metal exchange (3) is found in the CdP–MX_2–D MSO system in the cases where the complex is of little stability in solution and can exist in the environment of DMSO in the presence of cadmium salts only. The metal exchange can proceed with varied contribution of the associative route (3) to the mixed mechanism (5), which leads to a change in the order of the reaction on the salt of entering metal with the change in temperature.

EXPERIMENTAL

The objects of research **I–III** were prepared by known methods [16, 17]. Purity control was carried out through analysis of EAS, as well as by thin-layer chromotagraphy (sorbent Silica F60, eluent chloroform).

Preparation of solvents was carried out according to standard methods described in [18]. Dimethylsulfoxide of pure grade was kept over calcined BaO and distilled in a vacuum (~1 mm Hg).

Spectrophotometric monitoring of the metal exchange reaction (1) in the complexes **I–III** was performed as follows: a solution of salt in DMSO of a desired concentration was placed in a temperature-controlled cell of a Hitachi U3000 or a SF-46 spectrophotometer, and an equal volume of a temperature-controlled solution of the studied complex in the same solvent was added. Change in the concentration of a complex in time in the course of metal exchange was registered spectrophotometrically as an increase in the optical density of the long-wavelength absorption band of the formed complex.

Reaction (1) was carried out in the presence of 10–100-fold excess of salt, and, therefore corresponded to the pseudo-first order kinetic Eq. (6).

$$-dc_{\mathrm{MP}}/d\tau = k_{\mathrm{eff}}\, c_{\mathrm{MP}};\ k_{\mathrm{eff}} = k_{\mathrm{v}} c_{\mathrm{salt}}. \qquad (6)$$

Calculation of kinetic parameters was carried out according to the equations of formal kinetics, as described in [3].

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