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Double Metal–Ligand Exchange in Solvate Complex–Metal Porphyrin Systems

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Abstract—The kinetics and mechanism of one of the most complicated chemical reactions of coordination compounds, where two different porphyrin complexes exchange central metal ions and the corresponding ligands, were considered using a number of metal porphyrins as substrates.

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Double metal–ligand exchange reactions constitute a poorly explored class of chemical reactions which have long been used for the synthesis of difficultly accessible coordination compounds. In the beginning of the XXIst century we were the first to initiate studies on the kinetics and mechanism of such reactions in organic solvents with a view to develop new methods of synthesis of practically important metal porphyrins and phthalocyanines [1–8].

Metal exchange reactions (1), as they were called in a simplified manner in the second half of the past century [9, 10], may be regarded as a specific type of chemical reactions, which is not covered by modern classification [11–13].

$$M^1L^1 + M^2L^2 \rightarrow M^1L^2 + M^2L^1. \qquad (1)$$

If ligands L^1 and L^2 that exchange cations M^1 and M^2 are simple molecules or anionic ligands, including chelating ones (amino acids, complexones, etc.), these metal exchange reactions attract interest only from the theoretical viewpoint [13]. Their practical importance strongly increases when one of the reacting coordination compounds (M^1L^1 or M^2L^2) is a metal complex with a natural porphyrin ligand, e.g., protoporphyrin and its structural analogs (hemato-, deutero-, and mesoporphyrins) called *blood group porphyrins*, as well as pyrro- and rhodoporphyrins **I** resulting from chemical modification of chlorophyll.

Of particular importance are bioligands such as chlorophyll (pheophytin) and its structural analogs. The roles of chlorophyll (**II**) and metal exchange therein (Mg^{2+} for other metals) are great. Double metal–ligand exchange with natural porphyrins is typical of animal and plant biosystems [14–16], and these reactions are important for the regulation of biological processes under extreme conditions [17–23].

Metal–Ligand Exchange as a Method of Successful Synthesis of Complicated Coordination Compounds with Macrocycles

The first systematic application of the double metal–ligand exchange was to synthesize metal complexes with phthalocyanine (**III**), especially difficultly accessible complexes with such metals as Be, Cd, Mn, Pb, Hg, Ag, and many other [23, 24]. For this purpose, a solution of readily accessible pure lithium phthalocyanine (Li_2Pc) in anhydrous ethanol or acetone was mixed with an alcoholic solution of anhydrous metal salt ($CdCl_2$, $ZnCl_2$, $MnCl_2$, $PbCl_2$, $CoCl_2$, $AgNO_3$, etc.); highly pure MPc complex instantaneously separated from the mixture. Only the corresponding ligand H_2Pc was obtained from salts capable of undergoing strong solvolysis ($AlCl_3$, $SnCl_2$, $ThCl_4$, $BiCl_3$, etc.). In DMF and other aprotic solvents Li_2Pc with $AsCl_3$ and $TiCl_3$ in boiling quinoline forms the complexes (Cl)AsPc, Ti(Cl)Pc. Likewise, the complexes GaPc, Cl_2MnPc, Cl_2GePc, CrPc, ClRuPc, ClIrPc, ClRhPc, Cl_2OsPc, and (X)LaPc were

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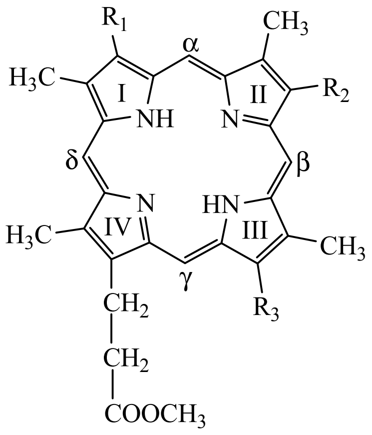
† Deceased.



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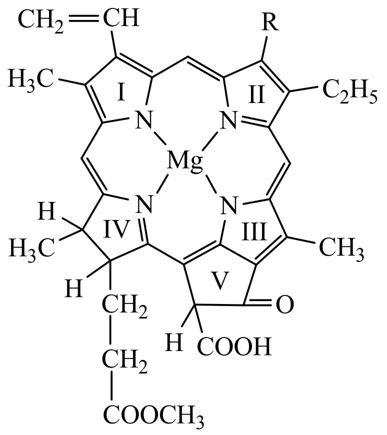
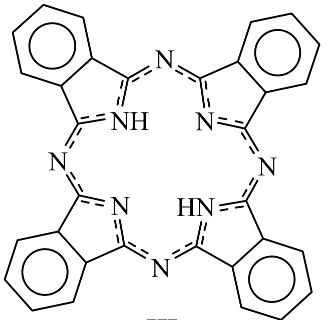


II

I, protoporphyrin (H_2PP), $R^1 = R^2 = CH_2{=}CH$, $R^3 = MeOC(O)(CH_2)_2$ (**a**); mesoporphyrin (H_2MP), $R^1 = R^2 = Et$, $R^3 = MeOC(O)(CH_2)_2$ (**b**); hematoporphyrin (H_2HP), $R^1 = R^2 = MeCH(OMe)$, $R^3 = MeOC(O)(CH_2)_2$ (**c**); deuteroporphyrin (H_2DP), $R^1 = R^2 = H$, $R^3 = MeOC(O)(CH_2)_2$ (**d**); pyrroporphyrin (H_2PyrP), $R^1 = R^2 = Et$, $R^3 = H$ (**e**); rhodoporphyrin (H_2RodP), $R^1 = R^2 = Et$, $R^3 = MeOC(O)$ (**f**); **II**, chlorophyll (MgChl), R = Me (**a**), CHO (**b**); **III**, phthalocyanine (H_2Pc) [23] (NH-localized structure).



III

synthesized. Using Li_2Pc, complexes of a number of metals in unusually low oxidation state were obtained, in particular $Li_2[Cu^0Pc]$, $Li[Mn^{2+}Pc]$, $Li_2[Mn^{1+}Pc]$, $Li[Fe^{1+}Pc]$, $Li[Co^{1+}Pc]$, and $Li[Ni^{1+}Pc]$ [23, 24]. Naturally, the problem of studying the reaction mechanism was not raised by the authors at that time. Wide application of metal exchange within porphyrin complexes was demonstrated in [10]. However, double-decker cerium complexes $Ce(P)_2$ were synthesized from lithium salts in trichlorobenzene. As shown in [10], addition of a small amount of a Cd^{2+} or Hg^{2+} compound to a solution of porphyrin and a *d*-metal salt (Co^{2+}, Ni^{2+}, Cu^{2+}, etc.) strongly accelerates formation of *d*-metal porphyrin complexes. It was presumed that the reaction involves formation of bimetallic intermediate $[M^1–P–M^2]$; however, we believe it to be hardly probable. Undoubtedly, the initial step is fast formation of metalloporphyrins CdP and HgP [reaction (2)], which is followed by double metal exchange [reaction (3)] with Co, Ni, Cu, or other bivalent metal salt.

$$H_2P + CdX_2(HgX_2) \rightarrow 2HX + CdP(HgP), \qquad (2)$$

$$CdR + MX_2(Solv)_{n-2} \leftrightarrow MP + CdX_2(Solv)_{n-2}, \qquad (3)$$

$$HgP + MX_2(Solv)_{n-2} \leftrightarrow MP + HgX_2(Solv)_{n-2.} \qquad (3')$$

The reactions noted in [10] are complex double metal exchange reactions. Removal of a proton requires a considerable energy and the presence of a proton acceptor; therefore, it is possible only along path (2) and is impossible in intermediate $[M^1–H_2P–M^2]$ which was given by the author for some reason with no protons, i.e., as $[M^1–P–M^2]$.

Berezin and co-workers [3–8] were the first to study the kinetics and activation mechanisms of metal exchange; it was presumed that reactions like (1) are a particular case of dissociation of coordination compounds. As shown in [3], the Mg^{2+} ion in the magnesium complex of tetra(*tert*-butyl)phthalocyanine $MgT(Bu^t)Pc$ can be replaced by Cd^{2+} in acetonitrile (AN) solution [reaction (4)].

$$\begin{gathered} MgT(Bu^t)Pc + [Cd(AN_4)(NO_3)_2] \\ \rightarrow CdT(Bu^t)Pc + [Mg(AN)_4(NO_3)_2]. \end{gathered} \qquad (4)$$

At a $MgT(Bu^t)Pc$ concentration of 10^{-5} M and a $[Cd(NO_3)_2]$ concentration of 9×10^{-2} M, the true rate constant k_v^{298} is $(1.17\pm0.09)\times10^{-2}$ l mol^{-1} s^{-1}, E_a = 51±15 kJ/mol, $\Delta S^{\neq}$ = –120±53 J mol^{-1} K^{-1}. The electronic absorption spectra revealed intermediate $[(NO_3)_2Mg\cdots T(Bu^t)Pc\cdots Cd(AN)_2(NO_3)_2]$ (**IV**) whose formation was complete in 4 min; presumably, it is formed through structurally (but not compositionally) similar transition state. This intermediate is then converted into final products. Metal exchange reaction (4) is bimolecular, and it consists of two steps. Interestingly, $Cd(NO_3)_2$ in acetonitrile reacts with tetra(*tert*-butyl)phthalocyanine with a rate constant k_v^{298} of $(0.82\pm0.05)\times10^{-2}$ l mol^{-1} s^{-1}, E_a = 69±7 kJ/mol, $\Delta S^{\neq}$ = –71±25 J mol^{-1} K^{-1}. These data indicate that removal of two protons in acetonitrile is faster by almost two orders of magnitude than elimination of coordinated Mg^{2+} ion. Two nitrate ions remain in the resulting complex as extra ligands. On the other hand, removal of two NO_3^- ions from the Mg^{2+} coordination sphere in intermediate **IV** is hindered due to the lack of affinity of NO_3^- for acetonitrile.

Double metal exchange reactins have found wide application in the synthesis of difficultly accessible coordination compounds with natural and synthetic porphyrins. For this purpose, more accessible porphyrin and phthalocyanine complexes are used as starting compounds [25–30]. For instance, palladium octaphenyltetraazaporphyrin complex (PdOPhTAP) was synthesized according to a simplified procedure [28] from readily accessible MgOPhTAP and $PdCl_2$ in boiling dimethylformamide; the reaction is analogous to reaction (4).

Cadmium porphyrin complexes that are most accessible among labile complexes are used as starting compounds in the synthesis of chlorophyll and protoporphyrin complexes (as well as of all blood porphyrin complexes) [25, 26, 29]. Cadmium porphyrins are relatively less stable than 3*d*-metal complexes but more stable than those derived from Hg(II) and Pb(II).

Cadmium(II) complexes were successfully used to study the effect of solvation on double metal exchange reaction (3). Metal exchange in Mg complexes with chlorophyll derivatives provides a promising way of synthesis of environmentally safe and stable chlorophyll dyes [25] and *d*-metal complexes with blood porphyrins [4–8].

Modern Views on the Stoichiometry and Activation Mechanism of Double Meta Exchange. Role of Structural and Solvation Factors of Metalloporphyrins and Metallophthalocyanines

Problems concerning possible mechanisms of double metal exchange in metalloporphyrins and metallophthalocyanines in organic solvents were discussed for the first time in [3, 7, 8]. As noted in [7], metal exchange between the porphyrin coordination center and solvated *d*-metal salts is the most complex among all known reactions [11]. Metal exchange involves all kinds of interactions, except for redox (unpaired electron transfer) and acid–base (proton transfer). According to the classification proposed in [11], reaction (5) is an association–dissociation complex formation process.

$$M^1P + M^2X_2(Solv)_{n-2} > M^2P + M^1X_2(Solv)_{n-2}. \quad (5)$$

An elementary chemical reaction includes simultaneous (synchronous) dissociation of one complex and formation of another. Here, not only metal exchange (M^1 and M^2) but also ligand exchange (R^{2-} and Solv) occurs. In keeping with the classical concepts [11], reaction (5) belongs to substitution reactions, in contrast to addition and decomposition of chemical compounds. First conclusions on the stoichiometry of reaction (5) were drawn in [3, 4], where the reaction under study was shown to be two-step and bimolecular. The first step is fast formation of dinuclear intermediate $[(Solv)_mM^1PM^2X_2(Solv)_{n-4}]$ (**V**) which can be detected by spectral methods provided that M^2P is much more stable than M^1P.

In the second, slow unimolecular step intermediate **V** decomposes into final products. This step can be monitored by electronic spectroscopy. Dissociation of Cd(II) and Zn(II) chlorophyll analogs was studied in detail in [31], and thermodynamic and kinetic parameters of these dissociation processes were estimated. It was found that the energy of dissociation of Cd–N bonds in the Cd(II) chlorophyll analog is compensated by the energy of solvation of Cd^{2+} ion. The Cd–N ion is ionic with a small contribution of covalent constituent. The conclusions drawn in [31] are applicable to the exchange of Cd^{2+} for Zn^{2+}; the latter forms ionic–covalent bonds with a stronger covalent character as compared to Cd^{2+}. Therefore, exchange of Cd for Zn in blood porphyrins **I** is energetically favorable. The presence of a high fractional charge on Cd porphyrin favors successful attack by solvate complex $MX_2(Solv)_{n-2}$ (where M = Zn, Co, Ni, Cu)

Table 1. Kinetics of metal exchange of Cd-porphyrins with $ZnCl_2$ in DMSO at 298 K

Cd-Porphyrin ($c = 2.3 \times 10^{-5}$ M)	$[ZnCl_2]$ ($\times 10^4$ M)	k_v^{298}, l mol^{-1} s^{-1}	E_a, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
CdMP	1.17	0.45±0.01	55±3	–135±2
	2.19	0.48±0.03	56±2	–130±3
CdPP	209	0.71±0.03	59±10	–142±13
	392	0.74±0.01	52±3	–137±5
CdGP	209	0.015±0.001	29±8	–173±16
	392	0.015±0.001	28±6	–173±12
CdDP	209	0.015±0.001	66±2	–95±6
	392	0.016±0.001	70±2	–90± 6

Table 2. Kinetics of metal exchange of Cd-porphyrins with $CoCl_2$ in acetonitrile at 298 K

Cd-Porphyrin ($c = 2.3 \times 10^{-5}$ M)	$[CoCl_2]$ ($\times 10^5$ M)	k_v^{298}, l mol^{-1} s^{-1}	E_a, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
CdDP	4.60	12.2±0.9	27±4	–142±12
	2.45	9.8±1.4	24±5	–154±15
CdGP	4.60	2.74±0.05	22±5	–171±15
	2.45	2.69±0.01	25±3	–161±9

and facile formation of intermediate **V** provided that the M–N bond energy compensates energy expenditure for elimination of two solvent molecules from the solvate complex. It is assumed that the rate of formation of intermediate **V** depends on the stability of complexes M^1P and M^2P: it increases in parallel with the strength of complex M^2P and decreases as the strength of M^1P increases [reaction (5)].

Naturally, the strength of solvates $M^2X_2(Solv)_{n-2}$, which depends on the solvent nature and its solvation power with respect to cations and anions, also affects the kinetic and thermodynamic parameters of reaction (5). Thus the rate of formation of intermediate from cadmium complexes of the protoporphyrin group weakly depends on the nature of groups R^1 and R^2 since intermediate **V** has a low energy. It is formed only via reorganization of the solvated salt. The transition from intermediate through high-energy state where dissociation of M^1P (CdP in this case) occurs should be determined by the nature of functional substituents in the porphyrin ligand.

Removal of $[Cd(DMSO)_6]^{2+}$ in reaction (5) with CdP in DMSO is energetically unfavorable, for the replacement of Cd–N bonds by Cd–O requires large energy consumption due to high affinity of Cd^{2+} to nitrogen, and it is kinetically hindered due to attack by DMSO on Cd–N bonds under sterically unfavorable conditions created by the macrocyclic effect of porphyrins [4, 5]. It is most favorable at the highest vibronic level, i.e., when Cd ion is maximally distant from the macroring plane [32].

The results of our kinetic study on the metal exchange between cadmium complexes with meso- (CdMP), proto- (CdPP), hemato- (CdHP), and deuteroporphyrins (CdDP) and $ZnCl_2$ in DMSO are collected in Table 1. It is seen that electronic effects of the C_2H_5 group in the mesoporphyrin cadmium complex and $CH{=}CH_2$ group in the protoporphyrin complex are similar (negative inductive effect *–I* [12]) and that solvation of the transition state (≠) changes considerably in going from the hematoporphyrin complex [R = $CH(OCH_3)CH_3$] to deuteroporphyrin (R = H), the rates of metal exchange being similar. The solvation of the transition state (≠) derived from CdHP strongly increases (the energy of activation decreases), whereas the solvation of CdDP strongly decreases (the energy of activation increases). A kinetic compensation effect is clearly seen [11].

An essentially different pattern is observed in the metal exchange reactions of cadmium complexes of deuteroprophyrin and hematoporphyrin with $CoCl_2$ in acetonitrile [5] (Table 2). Replacement of DMSO as solvent which strongly coordinates cations and weakly coordinates anions by weakly coordinating acetonitrile considerably changes the kinetic parameters of double metal exchange. Despite similar stabilities, zinc and cobalt complexes with blood porphyrins [22] showed appreciably different kinetic parameters of reaction (5), the two-step bimolecular mechanism and secobd-order kinetic equation (6) being retained.

$$-\partial c_{\mathrm{CdP}}/\partial\tau = k_v[\mathrm{CdP}][\mathrm{MX}_2]. \qquad (6)$$

Under high dilution conditions (approaching an ideal solution), metal exchange between Cd^{2+} and Co^{2+} in CdHP and CdDP is faster by factors of 300 and 1000, respectively. No appreciable change of the energy or entropy of activation is observed for CdHP. However, the energy of activation for CdDP increases from 25 to 70 kJ/mol, and the entropy of activation abruptly increases (~60 J mol^{-1} K^{-1}) in keeping with the kinetic compensation effect intrinsic to reactions of metalloporphyrins. It is determined by variations in the solvation of the transition states. Almost all studies on metal exchange in CdP by Zn, Co, Cu [3–8] showed more or less rapid formation of intermediate **V** which then slowly decomposes into final products [reaction (5)].

Therefore, the kinetic parameters of the exchange reaction should depend on the equilibrium constant for the formation of intermediate **V**, which is determined in turn by the structure of the solvated salt and metalloporphyrin, steric hindrances created by the macrocyclic effect of more or less rigid porphyrin macroring, and concomitant electronic coordination effects [33, 34]. Strong solvent effect should necessarily be taken into account. Solvent nature affects not only the rate of formation of intermediates and their stability but also the entire subsequent process of decomposition of intermediates into final products. The formation of intermediate **V** [the first step in reaction (5)] involves removal of two solvent molecules from the coordination sphere of solvated salt [reaction (7)].

$$\begin{aligned}&(\mathrm{Solv})_m\mathrm{M}^1\mathrm{P} + \mathrm{M}^2\mathrm{X}_2(\mathrm{Solv})_{n-2}\\ &– (\mathrm{Solv})_m\mathrm{M}^1\mathrm{P}\cdot\mathrm{M}^2\mathrm{X}_2(\mathrm{Solv})_{n-2} + 2\ \mathrm{Solv}. \qquad (7)\end{aligned}$$

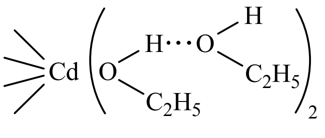
The coordination sphere of the salt in reaction (7) undergoes strong deformation, which also requires some energy. The initial metalloporphyrin molecule can be surrounded by solvate shell (Solv)$_m$ consisting of coordinated solvent molecules as extra ligands (maximum two), which should favor departure of the metal ion from the σ,π-system of the porphyrin macroring ($C_{12}N_4$). The reacting system in the transition state $[(\mathrm{Solv})_m\mathrm{M}^1\cdots\mathrm{P}\cdots\mathrm{M}^2\mathrm{X}_2(\mathrm{Solv})_{n-2}]^{\neq}$ (**VI**) moves toward the potential barrier due to additional solvation and coordination of the anion to the leaving cation (M^{2+}), which compensate rupture of the chemical bonds in MN_4. However, it may be presumed that the largest contribution to the compensation of the energy of activation related to the departing solvated salt $\mathrm{M}^1(\mathrm{X}_2)(\mathrm{Solv})_{n-2}$ is provided by the formation of four stronger chemical bonds in the complex M^2P. In some cases [3] magnesium cation (Mg^{2+}) is replaced by Cd^{2+} despite the former is more strongly bound to porphyrin. The conditions for the exchange of Mg^{2+} in tetrabutylphthalocyanine complex for Cd^{2+} whose complexes with phthalocyanines are less stable by 6–8 orders of magnitude were discussed in [3]. The reaction with cadmium nitrate was carried out in acetonitrile [reaction (8)].

$$\begin{aligned}&\mathrm{MgPc} + [\mathrm{Cd(AN)_4(NO_3)_2}] – [\mathrm{Mg–Pc–Cd(AN)_2\cdots(NO_3^-)_2}]\\ &\rightarrow [\mathrm{Mg(NO_3)_2(AN)_4}] + \mathrm{CdPc}. \qquad (8)\end{aligned}$$

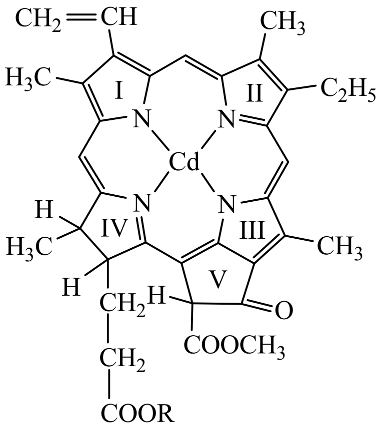
Here, as in the reaction with porphyrins, the reaction is slow and irreversible. The first step is fast and reversible formation of intermediate. The rate constant k_v^{298} is $(1.17\pm0.09)\times10^{-2}$ l mol^{-1} s^{-1}, E_a = 51 kJ/mol, $\Delta S^{\neq}$ = –120 J mol^{-1} K^{-1}. No reaction (8) occurs with stable $Cd(OAc)_2$ in acetonitrile, while replacement of acetonitrile as weak electron donor by DMSO completely suppresses metal exchange.

The role of the rigidity of the macroring in porphyrins and phthalocyanines on metal exchange was noted [3]. According to [35], more rigid macrorings such as tetrabenzoporphyrin (strong macrocyclic effect) still exchange Cd^{2+} in CdTBzP for Zn^{2+}, but the rate of the process is lower by a factor of 250 than that observed for less rigid Cd octaethylporphyrin in DMF at 298 K.

To understand the mechanism of metal exchange in porphyrins and phthalocyanines, which is a complex reaction in its own, detailed analysis of all factors listed above is necessary. Here, the effect of each factor on reaction (5) should be considered in strong interrelation with the others. Let us consider some well studied systems. The kinetics of metal exchange in Cd complexes with natural porphyrins in reaction with $CoCl_2$ in ethanol were studied [8]. Cadmium porphyrins readily coordinate ethanol molecules to form solvate $(C_2H_5OH)_nCdP$ where two ethanol molecules strongly bound to the cadmium ion additionally form the second solvate shell.



As a result, cadmium ion coordinated to porphyrin may deviate from the CdN_4 plane, which ensures shielding of the reaction center from attack by $[CoCl_2\cdot(C_2H_5OH)_4]$ at one side of the porphyrin macroring plane but facilitates attack by the cobalt solvate at the opposite side. The reacting $CoCl_2$ solvate species should lose two ethanol molecules together with their second solvate shell. As substrates, Cd chlorophyll a [CdChl(a)] possessing a long hydrocarbon residue ($C_{20}H_{39}$ in one carboxy group (**VIIa**) and phytol-free Cd pheophorbide a [CdPhe(a)] (**VIIb**) having a $(CH_2)_2COOCH_3$ group in the dehydropyrrole ring were selected.



VII

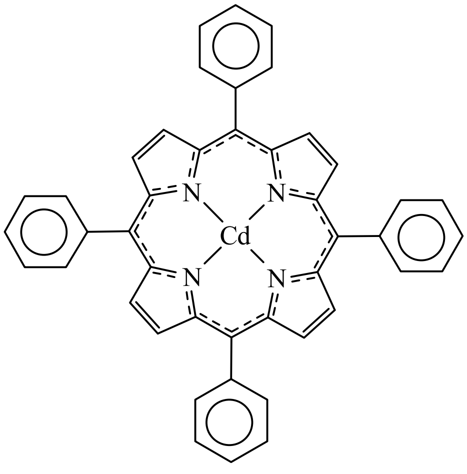
CdChl(a), R = $C_{20}H_{39}$ (**a**); CdPhe(a), R = CH_3 (**b**).

The cadmium–cobalt exchange was a bimolecular reaction following equation (5) through intermediate **V** and transition state **VI**; it conformed to second-order kinetic equation (6). We have found that metal exchange in CdPhe(a) and CdChl(a) for Co in ethanol is much faster than in DMSO. As shown in [8], complex **VII** almost does not exchange cadmium ion for $ZnCl_2$ in ethanol, which indicates an important role of solvation. The phytol residue ($C_{20}H_{39}$; Table 3) strongly shields the reaction center CdN_4 v CdChl(a). Therefore, the rate constant for metal exchange decreases by a factor of more than 6 despite tenfold increase of the $CoCl_2$ concentration. The reaction rate does not depend on the concentration of $CoCl_2$, i.e., an ideal kinetic pattern is observed. The energy and entropy of activation do not depend on the $CoCl_2$ concentration in the range from 1×10^{-3} to 4×10^{-2} M. The transformation of the Cd complex into Co complex can be monitored by electronic absorption spectra where the molar absorption coefficient at the first (long-wave) absorption maximum slightly decreases, and the position of that maximum changes from λ 655 to 644 nm in full agreement with the spectral criterion of the stability of metalloporphyrins [22, 23].

Interesting results were obtained in [29] where the effect of solvent nature (DMSO, DMF, acetonitrile, propan-1-ol, and their mixtures with different compositions) on the exchange of Cd^{2+} ion in complexes with tetraphenylporphyrin (CdTPP) (**VIII**) and tetrabenzoporphyrin (CdTBP) (**IX**) was studied. The macrocyclic ligands in **VIII** and **IX** differ by the rigidity of the main chromophore ($C_{12}N_4$), i.e., by macrocyclic effect; the macroring in **VIII** is relatively flexible, and that in **IX** is moderately rigid. The phenyl groups in the *meso* positions of **VIII** and butadiene fragments attached to pyrrole β,β′-positions in **IX** differ in electronic donor–acceptor properties and shielding effects but are characterized by similar affinities for solvents, i.e., the corresponding solvation effects should be similar.

Table 3. Kinetics of metal exchange of CdPhe(a) and CdChl(a) with $CoCl_2$ in ethanol at 298 K

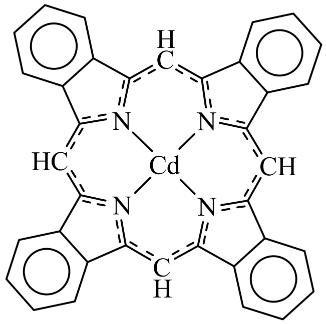
Cd-Porphyrin ($c = 2.3 \times 10^{-5}$ M)	[$CoCl_2$] ($\times 10^3$ M)	k_v^{298}, l mol^{-1} s^{-1}	E_a, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
CdPhe(a)	2.30	0.61±0.04	91±5	–4±18
	1.23	0.59±0.08	91±7	–6±25
CdChl(a)	39.20	0.097±0.007	18±4	–210±16
	20.90	0.096±0.007	18±4	–210±17



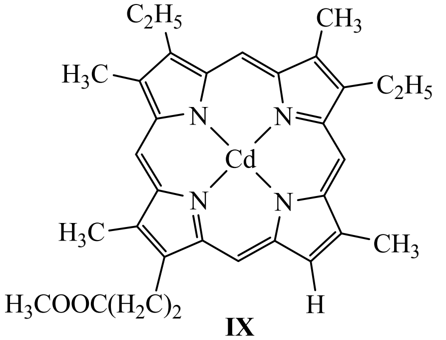
VII

CdTPP

Structures **VII** and **VIII** with delocalized bonds are shown above (for details, see [23, 36, 37]). The $HC_\beta{=}C_\beta H$ fragments in **VII** stabilize the 16-membered macroring via conjugation; therefore, they are incapable of taking up halogens and other active species, in contrast to free pyrrole molecule. The isoindole fragments in **VIII** stabilize the 16-membered chromophore to a much stronger extent than do pyrrole rings since benzene ring is an electron buffer capable of accepting or donating electron density, depending on the reagent. In the complexation with metal ions which cannot form dative π-bonds (forward or back donation) with a d^{10} electron configuration (Zn, Cd, Hg), benzene rings in the isoindole fragments act as



VIII
CdTBP



IX
CdPirP

electron donors thus stabilizing complexes like **VIII** of these and other *d*-metals to a much stronger extent than do pyrrole fragments in **VII**.

The rate of metal exchange in CdTPP and CdTBP with $Zn(OAc)_2(Solv)_n$ in pure solvents is determined mainly by the Gutmann donor numbers: it increases ($1 < 4.6 < 7.5 < 48$ in relative units) as the solvent donor number decreases in the series DMSO > DMF > PrOH > MeCN. It follows that the rate of exchange reaction depends mainly on the strength of the solvate shell of zinc acetate. In this case, other solvent factors are hidden and are not observed. It is sufficient to note that $[Cu(Acac)_2(Solv)_m]$ in benzene ($\varepsilon = 2.28$, $\mu = 0$) does not react with CdTPP at 60°C even when the salt concentration exceeds the concentration of CdTPP by two orders of magnitude. This reflects a very important role of solvent polarity.

The nature of *d*-metal salt solvate is also an important factor. An interesting *trans*-effect of inner-sphere ligands in solvated salt was observed in the reaction of *N*-methyloctaethylporphyrin with copper(II) acetate in binary solvents {DMSO–pyridine, DMF, DMF– pyridine [29]; reaction (9)}. The results are illustrated by Fig. 1.

$$H(N\text{–}CH_3)OEP + [Cu(CN_3COO)_2(Solv^1)_m(Solv)^2_p] > Cu(CH_3COO)(N\text{–}CH_3)OEP + CH_3COOH + m Solv^1 + p Solv^2. \quad (9)$$

The authors of some publications cited in [10, 35] believed that metal exchange in metalloporphyrins and formation of the latter should follow similar relations. It should be emphasized that the study cited in [10] was carried out in water with water-soluble porphyrins. Water is a specific solvent [36–38], so that the conclusions drawn therein cannot be extended to non-aqueous solvents. Unlike H_2TBP, H_2TPP, tetraaza-

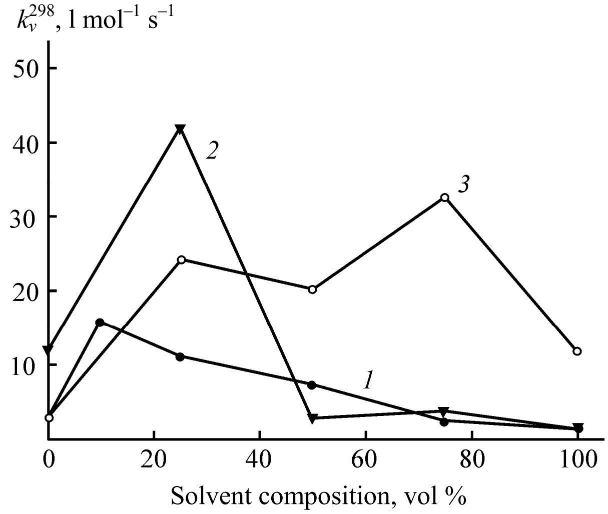


Fig. 1. Plots of the true rate constant k_v^{298} of metal exchange reaction (9) versus composition of binary solvents: (*1*) DMF–pyridine, (*2*) DMSO–pyridine, and (*3*), DMF–DMSO.

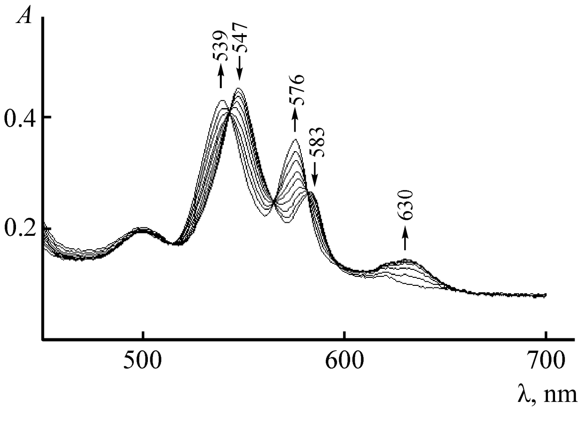


Fig. 2. Variation of the electronic absorption spectrum during the reaction of CdPyrP with $ZnCl_2$ in DMSO at $c_{CdPyrP} = 2.30\times10^{-5}$ M, $c_{ZnCl2} = 2.30\times10^{-3}$ M; temperature 328 K.

porphyrin, and phthalocyanine, reaction (9) with porphyrins having a deformed macroring is relatively fast. Therefore, it should be expected that metal exchange with binary solvate complexes of Cu^{2+} and probably Co^{2+} should be appreciably accelerated due to *trans*-effect. This effect may be exerted only on the rate of formation of intermediate complex in reaction (10) when the process is bimolecular; it involves fast formation of an intermediate which slowly decomposes into final products through a transition state.

$$(X^-)Cd^{2+}(N\text{–}CH_3)OEP + [CuX_2(Solv^1)_2(Solv^2)_2] \underset{\text{fast}}{\overset{-2Solv^2}{\rightleftarrows}} X^- + \underset{\text{intermediate}}{[(X^-)Cd^{2+}(N\text{–}CH_3)OEP...CuX_2(Solv^1)_2]} \quad (10$$

$$\underset{\text{slowly}}{\overset{+Solv^3}{\rightleftarrows}} \underset{\text{transition state}}{[X^-...Cd^{2+}(Solv^3)_nOEP(N\text{–}CH_3)...Cu...(Solv^1)_n...X_2]^{\neq}} \longrightarrow (X)Cu(N\text{–}CH_3)OEP + CdX_2(Solv^3)_{n-2}$$

Analogous pattern [4] was observed by us while studying metal exchange in Cd complex of pyrroporphyrin (**IX**) with zinc(II) chloride in DMSO (Fig. 2, Table 4). Here, the exchange of Cd^{2+} for Zn^{2+} is a bimolecular reaction following equation (5) through intermediate **V** and transition state **VI**; it is described by kinetic equation (6). We have found that metal exchange in CdPyrP with $CoCl_2$ in acetonitrile occurs instantaneously even in the presence of a small excess of the salt.

Thus, double metal–ligand exchange reactions constitute one of the most complicated types of chemical reactions of coordination compounds. In particular, reactions like (10) still have to be studied. Undoubtedly, such reactions do occur, probably in living matter with participation of chlorophyll and complexes with natural porphyrins.

EXPERIMENTAL

Pyrroporphyrin H_2PyrP was synthesized and purified according to the procedure reported in [39]. Complex CdPyrP was prepared and purified as described in [40]. Dimethyl sulfoxide of chemically pure grade was distilled under reduced pressure.

The kinetics of metal exchange reactions were studied by spectrophotometry using a Varian Cary 100 instrument. The optical density of solutions was measured at definite time intervals at a wavelength corresponding to the absorption maximum of CdPyrP (λ_{max} 547 nm). Metal exchange of CdPyrP with $ZnCl_2$ was studied in the temperature range from 318 to 338 K at c_{ZnCl2} ranging from 2.30×10^{-3} to 1.53×10^{-3} M. The current concentration of CdP was calculated by Eq. (11):

$$c = c_0(A_\infty - A_\tau)/(A_\infty - A_0). \qquad (11)$$

Here, A_0, A_τ, and A_∞ are the optical densities of solution at the initial moment, at a time τ, and after reaction completion, and c_0 and c are the initial and current concentrations of the Cd complex, respectively.

The apparent rate constants k_{ap} were calculated by Eq. (12):

$$-\partial c_{CdP}/\partial\tau = k_{ap}c_{CdP}. \qquad (12)$$

The energy of activation E_a was calculated by the Arrhenius equation (13):

Table 4. Kinetics of metal exchange of CdPyrP with $ZnCl_2$ in DMSO ($c_{CdPyrP} = 2.3 \times 10^{-5}$ M)

$[ZnCl_2]$ ($\times 10^3$ M)	T, K	k_v^{298}, l mol^{-1} s^{-1}	E_a, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
2.30	298[a]	0.13	20±2	–64±11
	318	0.22		
	328	0.28		
	338	0.34		
1.99	298[a]	0.14	18±2	–64±11
	318	0.22		
	328	0.28		
	338	0.33		
1.53	298[a]	0.14	19±2	–67±11
	318	0.22		
	328	0.28		
	338	0.35		

[a] Calculated value.

$$E_a = 19.1\frac{T_1 \cdot T_2}{T_2 - T_1}\log\frac{k_2}{k_1}. \quad (13)$$

The entropy of activation $\Delta S^{\neq}$ was calculated by Eq. (14):

$$\Delta S^{\neq} = 8.314 \cdot \ln k^{298} + E_a/298 - 253.22. \quad (14)$$

The experimental data are given in Table 4.

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