ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2012, Vol. 57, No. 5, pp. 744–750. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © D.B. Berezin, O.V. Shukhto, N.V. Lazareva, 2012, published in Zhurnal Neorganicheskoi Khimii, 2012, Vol. 57, No. 5, pp. 812–819.

PHYSICAL CHEMISTRY OF SOLUTIONS

Kinetic Control of the Transmetalation of Labile Metalloporphyrins in Individual and Mixed Solvents

D. B. Berezin, O. V. Shukhto, and N. V. Lazareva

Research Institute of Chemistry of Macroheterocycles, Ivanovo State University of Chemistry and Technology,
pr. Engel'sa 7, Ivanovo, 153000 Russia

Received October 14, 2010

Abstract—Transmetalation reactions of cadmium complexes of tetraphenylporphine (CdTPP, **I**) and tetrabenzoporphine (CdTBP, **II**) in individual and mixed solvents have been investigated. For individual solvents, provided that the reaction proceeds via the same mechanism, its rate generally increases as the donor number increases in the order DMSO < DMF < PrOH-1 < MeCN (CdTPP–$Zn(OAc)_2$–Solv system). On passing to the CdTPP–$Cu(OAc)_2$–Solv system, the reaction rate order changes to DMSO < PrOH-1 < MeCN < DMF because the transmetalation mechanism changes from mixed to associative, as follows from the reaction order with respect to the salt being zero. The effect of the DMSO–DMF mixed solvent on the transmetalation reaction is limited to changing the reaction rate through alteration of the stability of the $[CuX_2(Solv^1)_{n-m-2}(Solv^2)_m]$ solvated salts. The *trans* effect of the ligands in the solvated salts does not increase the transmetalation rate.

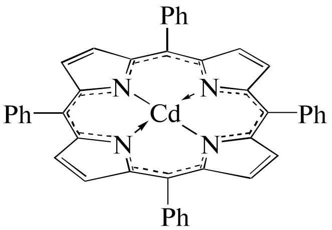
DOI: 10.1134/S003602361205004X

Possessing a wide variety of unique properties, metal complexes of porphyrins (metalloporphyrins, MPs) are promising components for new materials and devices in chemical technology, electronics, and medicine [1, 2]. The transmetalation reaction (1) provides means to obtain MPs that are difficult to synthesize directly via the complexation reaction (2), making use of more readily available labile complexes (M(II) = Cd, Hg, Pb).

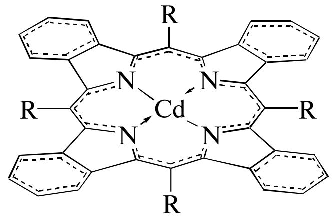
$$\mathrm{MP} + \mathrm{M'X}_n(\mathrm{Solv})_{m-n} \rightarrow \mathrm{M'P} + \mathrm{MX}_n(\mathrm{Solv})_{m-n}, \quad (1)$$

$$\begin{aligned} &\mathrm{H_2P} + \mathrm{MX_2(Solv)}_{n-2} \\ &\xrightarrow{-2\mathrm{Solv}} [\mathrm{H_2P}\cdots\mathrm{MX_2(Solv)}_{n-4}]^{\#} \qquad (2) \\ &\longrightarrow \mathrm{MP} + 2\mathrm{HX} + (n-4)\mathrm{Solv}. \end{aligned}$$

Cadmium complexes of porphyrins, such as compounds **I** and **II**, are among the most readily synthesizable MPs and are convenient objects for investigating the kinetics and mechanism of reaction (1). They are less stable than most MPs and dissociate in acidoprotolytic media (under the action of a molecular acid HX) and solvoprotolytic media (under the action of the solvated proton $H^+_{(Solv)}$) [1, 3, 4]. The comparatively low stability of the cadmium porphyrins is due to the low degree of covalence of their Cd–N coordination σ bonds, whose ionicity is fairly high, and to the large ionic radius of the metal (1.01 Å), which does not match the size of the coordination cavity of the porphyrin ligand (2.01 Å). It is owing to their low stability that the cadmium porphyrins decompose to an H_2P ligand and a metal ion and are very active in other processes involving the dissociation of the complex, including transmetalation [6].



I



II

In order to optimize the conditions for the synthesis of the MP comp-lexes via reaction (1) and gain a deeper insight into the transmetalation mechanism, it is essential to study various factors in the transmetalation reaction. There have been reports on how transmetalation depends on the porphyrin structure in the initial MP [6–9], on the nature of the metal ion being replaced [10, 11], on the nature of the metal ion being introduced [6, 12], and on the nature of the salt anion [9, 13]. Likely mechanisms have been suggested for metal ion exchange in labile MPs [6, 9, 14]. At the

Table 1. Dependence of kinetic parameters of transmetalation in the CdTPP–M(OAc)$_2$ system on the properties of the medium at 298 K ($c_{M(OAc)_2} = 2.76 \times 10^{-4}$ mol/L)

Property	Solvent				
	DMSO	DMF	*n*-PrOH	MeCN	C_6H_6
*DN	29.8	26.6	32.0	14.1	0.1
*AN	19.3	16.0	37.5	18.9	8.2
*ε	46.68	36.7	20.1	36.0	2.3
*μ, D	3.96	3.8	1.6	3.4	0
*V_M	71.3	77.4	75.1	52.9	89.9
*E_R	6.4	19.5	5.7	20.9	~0
Cu(OAc)$_2$					
$k_{app} \times 10^3$, s^{-1}	0.48**	59.66**	2.76 ± 0.70	3.12 ± 0.29	No reaction*****
n_{salt}	~0***	0	~1	–	
E_a, kJ/mol	61 ± 14	32 ± 2	26 ± 3	77 ± 27	
Zn(OAc)$_2$					
$k_{app} \times 10^3$, s^{-1}	0.16 ± 0.01****	0.74**	1.20 ± 0.03	7.60 ± 0.51	No reaction*****
n_{salt}	–	~1	1.4	1.2	
E_a, kJ/mol	–	–	4.0 ± 0.5	52 ± 15	

Notes: * Data from [15, 19].

** Calculated using the Arrhenius equation or an experimental $k_{app} = f(c_{salt})$ function.

*** The order of the reaction decreases with decreasing temperature.

**** $c_{salt} = 2.7 \times 10^{-3}$ mol/L;

***** Reaction with M(Acac)$_2$.

same time, the solvent effect as a significant factor in the reaction rate and mechanism [15] has not been properly investigated at the quantitative level. There have been only comparisons of the Cd/Co and Cd/Zn exchange rates in dimethyl sulfoxide (DMSO) and acetonitrile (MeCN) for blood porphyrins [16].

For this reason, we carried out a spectroscopic and kinetic study of the Cd/Cu and Cd/Zn transmetalation reactions for the cadmium tetraphenylporphine complex (CdTPP, **I**) in *n*-propanol (*n*-PrOH), *N*,*N*-dimethylformamide (DMF), DMSO, and MeCN (Table 1) and the same study of the Cd/Cu transmetalation reaction for CdTPP and cadmium tetrabenzoporphine (CdTBP, **II**) in the DMF–DMSO mixed solvent (Table 2) in wide temperature and concentration ranges.

EXPERIMENTAL

Compounds **I** and **II** were synthesized, purified, and identified using standard procedures [17]. Solvents were pretreated as recommended in [18]. DMSO (pure grade) was held over calcined BaO; DMF (analytical grade), over calcined $MgSO_4$. Both were then vacuum-distilled (bp ≈60 and ≈40°C, respectively). Acetonitrile (reagent grade) was dried by boiling with P_2O_5 and was distilled using a reflux condenser, and the fraction boiling above 80.5°C was collected. *n*-PrOH was boiled with anhydrous K_2CO_3 and was then distilled, and the fraction with bp 97°C was collected. The residual water content of the organic solvents, which was determined by the Fischer method, did not exceed the value specified in [18]. The salts Cu(OAc)$_2$, Zn(OAc)$_2$, and Cu(NO$_3$)$_2$ were recrystallized from the respective acids; Cu(Acac)$_2$, from benzene. The resulting crystals were vacuum-dried at $p \approx$ 133 Pa and T = 80°C. Benzene (C_6H_6, analytical grade) was boiled with P_2O_5 and distilled.

Reaction (1) was monitored spectrophotometrically on a Hitachi U3000 spectrophotometer. A salt solution in the solvent to be examined, with a preset solute concentration, was placed in a temperature-controlled cell. After the preset temperature was established, an equal volume of a thermostated solution of a cadmium complex in the same solvent was added. The time variation of the concentrations of the MP and M'P complexes as a result of transmetalation was monitored as the increase in absorbance for the long-wavelength absorption band of the resulting M'P.

Reaction (1) was conducted in the presence of a 10- to 100-fold excess of a salt to ensure that it obeys the pseudo-first-order rate equation

$$-dc_{MP}/d\tau = k_{app}c_{MP}; \quad k_{app} = k_v c_{salt}. \tag{3}$$

Kinetic parameters were calculated using equations of formal kinetics.

RESULTS AND DISCUSSION

The organic solvents DMSO, DMF, *n*-PrOH, and MeCN are polar coordinating media and have a large dielectric constant of ε = 20–40, a high dipole

Table 2. Kinetic parameters of the transmetalation reaction (1) of complexes **I** and **II** with $Cu(OAc)_2$ and $Cu(NO_3)_2$ in the DMF–DMSO

Porphyrin (c, mol/L)	Salt (λ, nm)	c_{salt}, mol/L	Solvent, DMSO/DMF, vol %	T, K	$k_{app} \times 10^3$, s^{-1}	$k_v \times 10^{-3}$, s^{-1} L mol^{-1}	E_a, kJ/mol	$\Delta S^\#$, J/(mol K)
CdTPP (**I**) (2.76×10^{-5})	$Cu(OAc)_2$ (541)	1.38×10^{-3}	0/100	308	Very rapidly		–	–
			25/75		3.29 ± 0.15	7.74 ± 0.35		
			50/50		2.02 ± 0.18	28.14 ± 2.51		
			75/25		1.79 ± 0.11	15.73 ± 0.98		
			100/0		1.02 ± 0.18	14.21 ± 2.53		
		2.07×10^{-3}	0/100		Very rapidly		–	–
			25/75		3.41 ± 0.16	7.61 ± 0.36		
			50/50		2.38 ± 0.09	28.20 ± 1.07		
			75/25		1.99 ± 0.10	15.30 ± 0.77		
			100/0		1.19 ± 0.20	14.10 ± 2.37		
		2.76×10^{-3}	0/100	298	53.10*		113 ± 19	−95**
			25/75	298	2.60*			
				308	3.59 ± 0.29	7.72 ± 0.62		
				318	9.05 ± 0.09			
				328	52.84 ± 0.13			
			50/50	298	1.90*		69 ± 13	−73**
				308	2.62 ± 0.03	27.66 ± 0.32		
				318	4.76 ± 0.07			
				328	13.47 ± 0.80			
			75/25	298	1.60*		61 ± 4	−102**
				308	2.17 ± 0.03	15.17 ± 0.21		
				318	4.25 ± 0.06			
				328	9.25 ± 0.18			
			100/0	308	1.37 ± 0.02	14.47 ± 0.21	61 ± 14	−107**
				318	3.79 ± 0.04			
				328	5.94 ± 0.16			
		3.45×10^{-3}	0/100	308	Very rapidly		–	–
			25/75		3.69 ± 0.09	38.96 ± 0.19		
			50/50		2.94 ± 0.11	31.04 ± 1.06		
			75/25		2.45 ± 0.08	25.87 ± 0.52		
			100/0		1.46 ± 0.21	15.42 ± 2.03		
CdTBP (**II**) (1.43×10^{-5})	$Cu(OAc)_2$ (630)	1.43×10^{-3}	0/100	298	8.30*		45 ± 2	−158 ± 7
				328	2.86 ± 0.94			
				338	4.88 ± 1.64			
				348	7.55 ± 2.64			
			25/75	298	4.78*		50 ± 13	−147 ± 15
				328	1.62 ± 0.40			
				338	3.45 ± 0.78			
				348	4.73 ± 0.72			
			50/50	298	2.48*		52 ± 11	−147 ± 12
				328	1.04 ± 0.18			
				338	2.19 ± 0.38			
				348	3.15 ± 0.27			
			75/25	298	4.34*		39 ± 2	−184 ± 6
				328	1.45 ± 0.24			
				338	2.15 ± 0.32			
				348	3.34 ± 0.44			
			100/0			Very slowly		
CdTBP (**II**) (1.43×10^{-5})	$Cu(NO_3)_2$ (630)	1.43×10^{-3}	0/100	298	9.78 ± 0.70		–	–
			25/75		2.06 ± 0.47			
			50/50		1.09 ± 0.17			
			75/25		1.79 ± 0.31			
			100/0		2.28 ± 0.18			

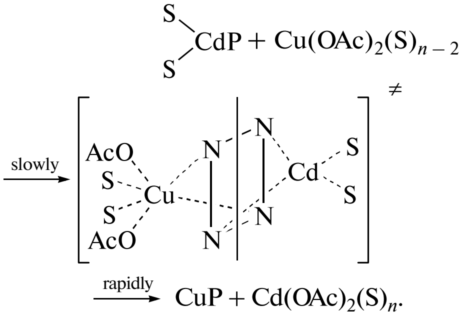
Notes: * Calculated using the Arrhenius equation or an experimental concentration dependence.
** Estimated data.

moment of $\mu = 1.6–4.0$ D, and a large donor number of DN = 14–30 (Table 1) [15]. However, these solvents cannot be assigned to one class of media because they differ in their acid–base, donor–acceptor, and solvation properties. DMSO, DMF, and MeCN are dipolar aprotic (DA) solvents [15], have a high polarity ($\varepsilon > 35$, $\mu \geq 3.5$ D) and a high solvating power toward cations, and are practically indifferent toward anionic species. Owing to their high solvating power, these compounds have a large DN value and a small acceptor number (AN) (Table 1) [15]. The alcohols, including *n*-PrOH, are weakly proton-donating solvents. Possessing moderate polarity characteristics (ε, μ) and a high electron-donating power (DN), they have a large AN exceeding their DN [15].

Because the solvents examined here belong to different classes, we failed to establish a general relationship between the transmetalation rate and the particular properties of the medium. However, for the DA solvents examined, the rate of reaction (1) in the CdTPP–$Zn(OAc)_2$–Solv system typically increases with an increasing DN (Table 1): DMSO < DMF < PrOH-1 < MeCN. The corresponding apparent rate constant (k_{app}) ratios for $c_{salt} = 2.76 \times 10^{-4}$ mol/L are $\leqslant 0.02 : 0.1 : 0.15 : 1$. The rate of the reaction in DMSO is the lowest, although the rate constant for this solvent was measured at a higher salt concentration (Table 1). *n*-Propanol is very different from the other media since it is a protogenic solvent [15].

A coordinating solvent is involved in reaction (1) as a component of the solvation complexes of the entering metal (M') and leaving metal (M), $MX_m(Solv)_{n-m}$ and $M'X_m(Solv)_{n-m}$, thus determining the stability of these complexes [19]. It is believed that the rate of transmetalation in various solvents is determined by the electron-donating power of the medium and, to a lesser extent, by its polarity [5]. For example, in the low-polarity solvent pyridine (Py: $\varepsilon = 12.3$, $\mu = 2.37$ D), which has a high coordinating power (DN = 33.1), the Zn/Cu transmetalation reaction of ZnTPP proceeds very slowly, needs an elevated temperature, and occurs only via a dissociative mechanism [10]. In polar solvents with a less pronounced electron-donating function, the rate of reaction (1) is much higher. The Cd/Zn and Cd/Co transmetalation reactions of blood porphyrins in MeCN ($\varepsilon = 36$, DN = 14.1) are considerably faster than the same reactions in DMSO ($\varepsilon = 46.7$, DN = 29.8) [16]. This is explained by the lower capability of MeCN to form solvation complexes. Pyridine-like solvents, DMF, and DMSO indeed form the most stable complexes, the nitrile solvates are the least stable, and the alcohol complexes occupy an intermediate position; that is, the stability constant K_{st} decreases in the following order: Py (1700 ± 100) < DMF (190 ± 40) < DMSO (37 ± 9) < *n*-BuOH (18 ± 1) < MeCN (4) [19].

We demonstrated in earlier works [9, 12] that most of the transmetalation reactions of cadmium porphyrins in DMSO proceed via a mixed, association–dissociation mechanism (reaction (4)), as is indicated by the fact that the order of the reaction n with respect to the salt is close to unity.



(4)

According to the current views of the transmetalation mechanism [5, 6, 9, 12, 20], a decrease in the coordinating power of the solvent is favorable for the associative pathway of the process because of the increase in the stability of the intermediate of reaction (1). However, *n* is close to unity not only for the strongly coordinating solvent DMF, but also for the CdTPP–$Zn(OAc)_2$–Solv systems in which Solv is a weakly coordinating solvent: for *n*-PrOH and MeCN, *n* is ~1.4 and ~1.2, respectively. Therefore, in all of the solvents, the reaction proceeds via the same mixed mechanism. In all cases, the intermediate, whose formation would imply the associative pathway of reaction (1), did not show itself in the spectrum.

The kinetic study of reaction (1) in the CdTPP–$Cu(OAc)_2$–Solv system demonstrated that the increasing order of reaction rates, DMSO < PrOH-1 < MeCN < DMF, does not correlate with the physicochemical properties of the media (Table 1). While the fact that *n*-PrOH does not fit in with the above kinetic order of media can be explained by this alcohol belonging to protogenic rather than DA solvents [15], DMF, in which the transmetalation reaction proceeds at the highest rate, is a typical DA solvent. Considering the high electron-donating power of DMF, it was expected that transmetalation in this solvent would be much slower than in MeCN, which is the weakest electron donor and has the smallest molar volume ($V_M = 52.9$ versus 71.3, 75.1, and 77.4 for DMSO, *n*-PrOH, and DMF, respectively), the latter factor being favorable for the spatial accessibility of the reaction sites. The transmetalation rate in DMSO was expected to be approximately the same as in DMF. In fact, the transmetalation rates in these solvents, which are very similar in polarity (ε, μ), donor–acceptor properties (DN, AN), and other characteristics in the CdTPP–$Cu(OAc)_2$–Solv system, differ most greatly (by more than 2 orders of magnitude) in the solvent series examined, as follows from the apparent rate constant data (k_{app}, s^{-1}) measured under comparable conditions (Table 1). The apparent rate constant ratios for reaction (1) at $c_{salt} = 2.76 \times 10^{-4}$ mol/L in the solvent series DMSO–PrOH-1–MeCN–DMF is 0.008 : 0.046 : 0.05 : 1.

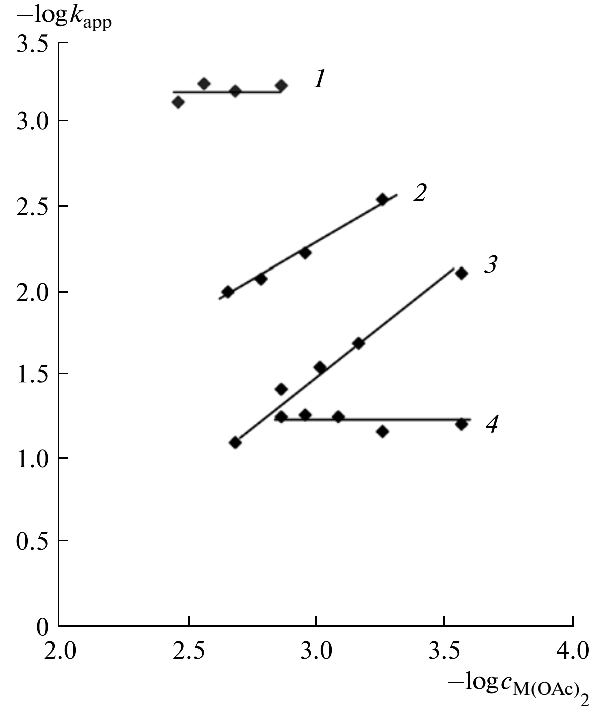


Fig. 1. Graphical determination of the order of the transmetalation reaction in the CdTPP–CuOAc$_2$ system: (*1*) DMSO, tanα = 0; (*2*) PrOH-1, tanα = 1; (*3*) MeCN, tanα = 1.2; (*4*) DMF, tanα = 0; $T = 298$ K. The data for MeCN refer to the CdTPP–ZnOAc$_2$ system.

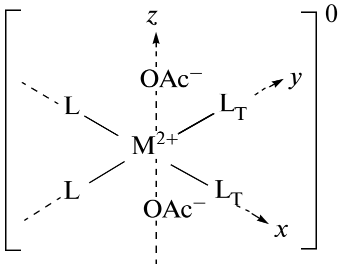


Fig. 2. Structure of the *trans*-active asymmetric salt solvate.

Although the organic solvents examined here, particularly DMF and DMSO, have similar individual parameters characterizing their polarity, structuredness, and acid–base and donor acceptor properties, they may differ in terms of complex multiparametric characteristics [15]. One of these characteristics is so-called reaction field energy E_R [19], which depends on the dielectric constant, dipole moment, and molar volume and takes into account the energy of molecular interaction in the solvent, whose degree decreases with increasing E_R. According to reference data, E_R increases in the following order of solvents: toluene (0.05) < *n*-PrOH (3.6) < Py (5.7) (DMSO (6.4) < DMF (19.5) < MeCN (20.9). Clearly, DMF and MeCN have the largest E_R values, which are well above the same values for DMSO, Py, and particularly toluene. On the whole, this increasing order of E_R is in agreement with the increasing order of reaction rates for CdTPP in the CdTPP–Cu(OAc)$_2$–Solv system, except for *n*-PrOH, which is a proton donor medium. The transmetalation reaction proceeds most rapidly in DMF and MeCN and much less rapidly in DMSO and Py, which are low-E_R media, and it practically does not take place in nonpolar aprotic solvents, such as arenes. Attempts to carry out reaction (1) in the CdTPP–Cu(Acac)$_2$–Solv system in benzene ($\varepsilon = 2.28$, $\mu = 0$) at a 100-fold excess of the salt and $T = 333$ K failed. This is evidence that the polarity of the medium is a significant factor in transmetalation.

However, the key reason why the transmetalation rate order changes on passing from the CdTPP–Cu(OAc)$_2$–Solv system to the CdTPP–Cu(Acac)$_2$–Solv system is that the mechanism of reaction (1) in DMF changes from mixed to associative, as is indicated by the reaction order with respect to the salt becoming zero under these conditions (Fig. 1), as distinct from what is observed for, e.g., propanol (Table 1). In all of the systems examined here, *n* is temperature-independent; that is, the temperature-induced changes exert no effect on the pathway of reaction (1), as distinct from what was observed earlier in DMSO [9].

A specific feature of transmetalation in *n*-PrOH is a very low activation energy both for the Cu(OAc)$_2$ solution (16–29 kJ/mol) and for the Zn(OAc)$_2$ solution (4–12 kJ/mol). This is likely due to the effective solvation of the anionic species by this solvent. The E_a value for the reaction of Cu(OAc)$_2$ in other solvents is markedly larger: 77 kJ/mol for MeCN and 61 kJ/mol for DMSO (Table 1).

Interest in mixed solvents is due to the discovery of new properties of these media. In essence, any mixed solvent (Solv^1-Solv^2) of particular composition is an individual liquid medium with a new set of properties [15]. In addition to changing the coordinating power and polarity of the medium, which determine the composition and stability of the solvation shell of the metal and, accordingly, the reactivity of this shell in reactions (1) and (2) and other coordination reactions, the solvent effect can show itself in polarization of the solvation shells of the reactants. An example of this polarization is the *trans* effect of solvent ligands in mixed solvated salts of *d* metals [5]. The *trans* effect, which means that the π-ligand L_T polarizes the M–L bond that is trans to this ligand [21], weakens this bond many times, thus enhancing the reactivity of the solvate (Fig. 2).

There have been kinetic studies of the complexation reaction (2) of tetraphenyltetrabenzoporphine (H$_2$TPTBP) [5, 22] and *N*-methyl-β-octaethylporphine (H(N-Me)(β-Et)$_8$P) [23] with copper(II) acetate in DMF–DMSO, DMF–Py, and DMSO–Py solvents, which are π-ligands. It was demonstrated [5]

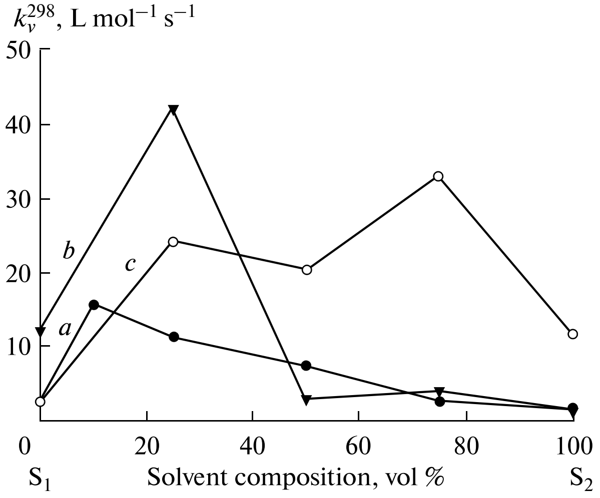


Fig. 3. Rate constant k_v of the complexation reaction between H(N-Me)(β-Et)$_8$P and Cu(OAc)$_2$ as a function of the solvent composition: (*a*) DMF–Py, (*b*) DMSO–Py, and (*c*) DMF–DMSO [23].

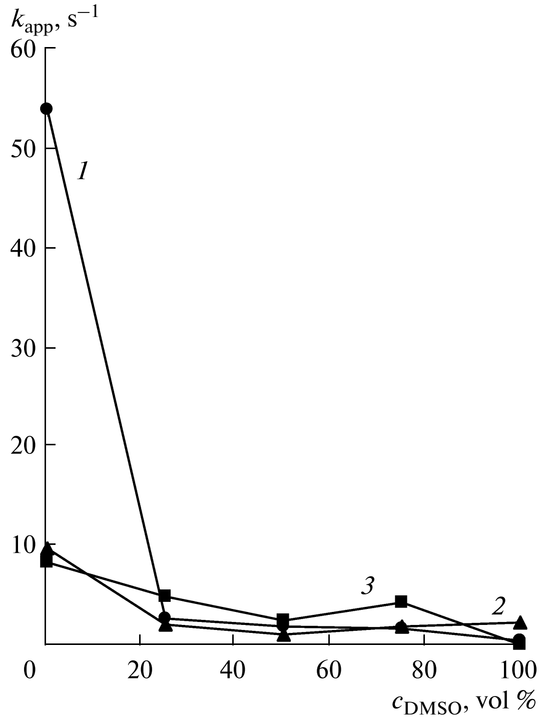


Fig. 4. Apparent rate constant of transmetalation (k_{app}) as a function of the composition of the DMSO–DMF solvent (c_{salt}/c_{CdP} = 100, T = 298 K): (*1*) CdTPP–Cu(OAc)$_2$; (*2*) CdTBP–Cu(NO$_3$)$_2$; and (*3*) CdTBP–Cu(OAc)$_2$.

that, as a consequence of the *trans* effect in the solvated salt, the rate of reaction (2) varies nonlinearly with the solvent composition and the rate constant versus composition curves for the mixed systems show extremums (Fig. 3).

On passing from individual π-coordinating solvents to a mixed one, the largest *trans* effect–induced increase in the rate of reaction (2) is observed in the DMF–DMSO system, which can be as large as two orders of magnitude [5]. It has been claimed in a number of works [6, 11, 24] that the complexation and transmetalation reactions of metalloporphyrins obey the same rules. For example, for both reactions, the true rate constant depends on the salt concentration because of the changes in the structure and stability of the solvated salt [5. 19].

We investigated the transmetalation reaction (1) in the CdTPP(I)–Cu(OAc)$_2$, CdTBP(II)–Cu(OAc)$_2$, and CdTBP(II)–Cu(NO$_3$)$_2$ system in the DMSO–DMF solvent (Table 2). Figure 4 plots the apparent rate constant of transmetalation (k_{app}^{298}) as a function of the DMSO–DMF solvent composition. Clearly, the rate of the reaction in pure DMF under conditions of a threefold excess of the salt over the cadmium porphyrin decreases in the following order (Table 2): CdTPP–Cu(OAc)$_2$ (k_{app}^{298} = 53.10 × 10^{-3} s^{-1}) > CdTBP–Cu(NO$_3$)$_2$ (k_{app}^{298} = 9.78 × 10^{-3} s^{-1}) > CdTBP–Cu(OAc)$_2$ (k_{app}^{298} = 8.30 × 10^{-3} s^{-1})[1]. As was demonstrated in earlier works [9, 11, 13], the transmetalation rate increases with a decreasing rigidity of the macrocycle (CdTBP < CdTPP) and with a decreasing coordinating power of the salt anion (AcO$^-$ < NO$_3^-$).

The character of the nonlinear dependence of k_{app}^{298} on the composition of the mixed solvent is mainly determined by the gradual alteration the structure of the solvated salt CuX$_2$(Solv^1)$_{n-m-2}$(Solv^2)$_m$ caused by the changing composition of the medium. For example, the solvated salt can undergo the following changes: Cu(OAc)$_2$(DMSO)$_4$ → Cu(OAc)$_2$(DMSO)$_3$(DMF) → Cu(OAc)$_2$(DMSO)$_2$(DMF)$_2$, and so on. The transmetalation rate constants for the mixed solvents do not exceed the rate constants for individual DMSO and DMF (Fig. 4); that is, the *trans* effect in the solvated salts does not shows itself in reaction (1), unlike the *trans* effect in reaction (2). This is likely due to the fact that the mechanism of transmetalation is more complicated than the mechanism of complexation involving H$_2$P [1, 5, 9, 14].

Figure 5 shows a typical logarithmic plot of the apparent rate constant of reaction (1) versus the salt concentration for the CdTPP–Cu(OAc)$_2$ system at T = 308 K and different compositions of the DMF–DMSO solvent. The order of the reaction with respect to the copper(II) salt is practically invariable ($n \approx 0.4$) in the solvent composition range from 25 to 100% DMSO, in which the reaction rate changes insignificantly (Fig. 4), and falls to 0.13 and below on passing to the 0–25% DMSO range, in which the react ion rate increases by

---

[1] Calculated by extrapolation.

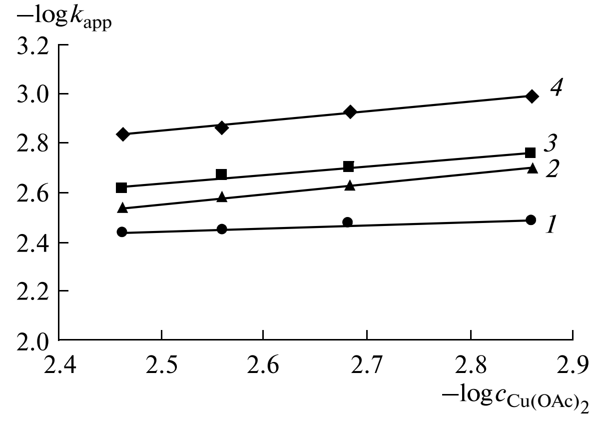


Fig. 5. Graphical determination of the order of the transmetalation reaction in the CdTPP–$Cu(OAc)_2$ system in the DMSO–DMF solvent: DMSO : DMF (vol %) = (*1*) 25 : 75, (*2*) 50 : 50, (*3*) 75 : 25, and (*4*) 100 : 0; $T = 308$ K.

a factor of 20. The decrease in the order of the reaction with respect to the salt on passing from the strongly coordinating solvent DMSO to the less strongly coordinating solvent DMF is due to the increase in the contribution from the associative pathway of transmetalation to the mixed mechanism of reaction (1) [9]. Elucidation of the structural aspects of this effect would provide explanation for the fact that the rate of the transmetalation reaction involving $Cu(OAc)_2$ in DMF is higher than the rate of the same reaction in the other solvents.

Thus, the only effective solvent-based way of controlling the rate of reaction (1) is by selecting a polar medium with a comparatively low coordinating power for processes taking place via the mixed mechanism [5, 9], and a medium with a relatively large reaction field energy (E_R) for the associative mechanism of the reaction.

REFERENCES

1. *Porphyrins: Spectroscopy, Electrochemistry, and Application*, Ed. by N. S. Enikolopyan (Nauka, Moscow, 1987) [in Russian].
2. *The Porphyrin Handbook*, Ed. by K. M. Kadish, K. M. Smith, and R. Guilard (Academic, New York, 2000), Vol. 6.
3. B. D. Berezin and T. N. Lomova, *Dissociation Reactions of Coordination Compounds* (Nauka, Moscow, 2006) [in Russian].
4. D. B. Berezin and O. V. Shukhto, Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. **46** (8), 34 (2003).
5. D. B. Berezin, *Macrocyclic Effect and the Structural Chemistry of Porphyrins* (URSS, Moscow, 2010) [in Russian].
6. P. Hambright, in *The Porphyrin Handbook*, Ed. by K. M. Kadish, K. M. Smith, and R. Guilard (Academic, New York, 2000), Vol. 3, p. 129.
7. D. K. Lavallee, B. A. Kopelove, and O. P. Anderson, J. Am. Chem. Soc. **100** (10), 3025 (1978).
8. S. Cromer, P. Hambright, J. Grodkowski, and P. Neta, J. Porphyrins Phthalocyanines **1**, 45 (1997).
9. D. B. Berezin, O. V. Shukhto, and M. S. Reshetyan, Russ. J. Gen. Chem. **80** (3), 518 (2010).
10. C. Grant and P. Hambright, J. Am. Chem. Soc. **91** (15), 4195 (1969).
11. E. Haye and P. Hambright, Inorg. Chem. **23** (26), 4777 (1984).
12. D. B. Berezin, O. V. Shukhto, M. S. Nikol'skaya, and B. D. Berezin, Russ. J. Coord. Chem. **31** (2), 95 (2005).
13. L. Orzel, M. Wolak, L. Fiedor, et al., in *Abstr. Inorganic Reaction Mechanism Meeting (IRMM-35), Krakow, Poland, 2005*, p. 50.
14. B. D. Berezin, O. V. Shukhto, and D. B. Berezin, Russ. J. Inorg. Chem. **47**, 1187 (2002).
15. Yu. Ya. Fialkov, *Solvent as a Means of Controlling a Chemical Process* (Khimiya, Leningrad, 1990) [in Russian].
16. S. V. Zvezdina, M. B. Berezin, and B. D. Berezin, Russ. J. Inorg. Chem. **51**, 112 (2006).
17. K. A. Askarov, B. D. Berezin, R. P. Evstigneeva, et al., in *Porphyrins: Structure, Properties, and Synthesis*, Ed. by N. S. Enikolopyan (Nauka, Moscow, 1985) [in Russian].
18. A. Gordon and R. Ford, *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References* (Wiley, New York, 1972; Mir, Moscow, 1976).
19. B. D. Berezin and O. A. Golubchikov, *Coordination Chemistry of Solvation Complexes Formed by Transition-Metal Salts* (Nauka, Moscow, 1992) [in Russian].
20. K. B. Yatsimirskii and Ya. D. Lampeka, *Physical Chemistry of Metal Complexes with Macrocyclic Ligands* (Naukova Dumka, Kiev, 1985) [in Russian].
21. Yu. N. Kukushkin, *Chemistry of Coordination Compounds* (Vysshaya Shkola, Moscow, 1985) [in Russian].
22. D. B. Berezin and O. V. Toldina, Russ. J. Coord. Chem. **30** (8), 573 (2004).
23. D. B. Berezin, O. V. Toldina, and B. D. Berezin, Russ. J. Inorg. Chem. **51**, 1728 (2006).
24. J. Reid and P. Hambright, Inorg. Chim. Acta **33,** L135 (1979).