## Ligand Exchange in the Complexone–Porphyrin Macrocycle System in Reactions of Copper(II) Ethylenediaminetetraacetate with Porphyrins and Phthalocyanines

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**Abstract**—Complexation between 5,10,15,20-tetraphenylporphine  $H_2TPP$  and tetra(*tert*-butyl)phthalocyanine  $H_2(t-Bu)_4Pc$  with copper(II) ethylenediaminetetraacetate in DMSO was studied by spectrophotometry. The kinetic parameters of the reaction were calculated and the mechanism of ligand exchange in the complexone–porphyrin macrocycle system was proposed. The reactivities of  $H_2TPP$  and  $H_2(t-Bu)_4Pc$  in reactions with copper ethylenediaminetetraacetate and some other copper chelate complexes were compared.

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Complexonates and complexes with macrocyclic ligands that form several adjoining chelate rings are known to be highly stable due to the polychelating and macrocyclic effects [1–2].

For instance, stable complexes are formed by such complexones as ethylenediaminetetraacetic acid  $H_4EDTA$  and its disodium salt  $Na_2H_2EDTA$  (trilon B) [3]. In complexation between  $H_4EDTA$  and metal ions, four carboxy groups become ionized and the metal ion forms a distorted octahedron surrounding composed of two N atoms and four ionized O atoms



The high stabilities of 3*d* metal ethylenediaminetetraacetates (e.g., the stability constant  $K_{st}$  of Cu(EDTA)<sup>2-</sup> in water is  $7.24 \times 10^{18}$  [4]) by no means imply that the M–N and M–O bonds are strong. The high stabilities of these complexes in solutions are mostly due to high shielding of the metal ion by adjacent atomic groups [5]. Complexes with macrocyclic ligands are generally more stable than complexonates (for metal porphyrins,  $10^{35-40}$  [6]).

Since the  $K_{st}$  values of complexonates and metal porphyrins differ by more than 10 orders of magnitude and complexonates, in contrast to complexes with macrocycles, can undergo sequential opening of the metal chelate rings [7–8], ligand exchange in a complexone– macrocyclic ligand system is theoretically possible. In real systems, this occurs very infrequently because of great steric hindrances due to the large sizes of interacting molecules (complexone and porphyrin). Our studies showed that out of six *d* metal ethylenediaminetetraacetates, only copper complexonate is involved in ligand exchange with porphyrin in DMSO. Cobalt(II), cadmium(II), mercury(II), zinc(II), and nickel(II) ethylenediaminetetraacetates did not react with porphyrins even if they are soluble in DMSO.

We studied complexation between copper(II) ethylenediaminetetraacetate and macrocyclic ligands with two porphyrin macrocycles as examples, namely, 5,10,15,20-tetraphenylporphine H<sub>2</sub>TPP ("porphyrin proper") and tetra(*tert*-butyl)phthalocyanine H<sub>2</sub>(*t*-Bu)<sub>4</sub>Pc (unsubstituted phthalocyanine is virtually insoluble in organic solvents). Although porphyrins and phthalocyanines are related compounds, they behave differently in complexation reactions.

## **EXPERIMENTAL**

The porphyrins  $H_2$ TPP and  $H_2(t-Bu)_4$ Pc





 $H_2(t-Bu)_4Pc$ 

were prepared and purified as described in [9, 10].

Dimethyl sulfoxide was purified according to a standard procedure. The copper salt  $CuH_2(EDTA)$  was synthesized from copper(II) acetate and  $Na_2H_2EDTA$ . The parameters of the electronic absorption spectra of the  $Cu(EDTA)^{2-}$  ion in water and DMSO are given in Table 1.

Kinetic studies of the complexation between porphyrins and Na<sub>2</sub>Cu(EDTA) by spectrophotometry were performed as described in [11–15]. The pseudofirst order of the reaction in porphyrin was confirmed by the linear dependence  $\ln(c_0/c_{\tau}) = f(\tau)$ . The effective rate constants  $k_{\text{eff}}$  were calculated from the changes in the optical density of the solution at the peak wavelengths of metal porphyrin over certain intervals by the equation

$$k_{\rm eff} = \frac{1}{\tau} \ln \frac{c_0}{c_{\tau}} = \frac{1}{\tau} \ln \frac{D_0 - D_{\infty}}{D_{\tau} - D_{\infty}}$$

where  $\tau$  is the current time of the reaction and  $D_0$ ,  $D_{\tau}$ , and  $D_{\infty}$  are the optical densities at the initial, current, and final points, respectively. The error in  $k_{\text{eff}}$  determination was 3%. In all cases, the reaction order in the salt (calculated from the slope of the graph  $\log k_{\text{eff}} =$  $f(\log c_{\text{salt}})$  was close to unity. Activation energies  $E_a$ were calculated by the Arrhenius equation from the temperature dependences of  $k_{\text{eff}}$  obtained in the range from 338 to 363 K for H<sub>2</sub>TPP and from 288 to 313 K for H<sub>2</sub>(*t*-Bu)<sub>4</sub>Pc.

Spectrophotometric measurements were carried out on a Specord M40 spectrophotometer.

## **RESULTS AND DISCUSSION**

The reaction of  $H_2$ TPP with Cu(EDTA)<sup>2–</sup> in DMSO can be generally written as follows:

$$H_{2}TPP + Cu(EDTA)^{2-} + 2H^{+}$$

$$\implies CuTPP + H_{4}EDTA.$$
(1)

Since, according to the calculation, the concentration of free Cu<sup>2+</sup> ions (at  $c_{\text{Cu(EDTA)}^{2-}} = 10^{-4} \text{ mol/l}$ ) does not exceed  $10^{-11}$  mol/l, only complexonate Cu(EDTA)<sup>2-</sup> rather than its dissociation products can act as the kinetically active species in reaction (1).

As noted above, the Cu(EDTA)<sup>2–</sup> ion is highly stable because of shielding of the metal ion by adjacent groups of the complexone, which prevents water,  $H_3O^+$ , etc. from having access to the central atom and from causing dissociation of donor–acceptor chemical bonds.

The electronic state of the Cu<sup>2+</sup> ion in Cu(EDTA)<sup>2–</sup> only slightly depends on the solvent nature, in contrast to many other salts (in particular, acetates), which can also be attributed to this shielding. For instance, when passing from water to DMSO, the absorption band corresponding to the forbidden  $d-d^*$  transition characteristic of most transition metals with the incomplete dlevel experiences a hypsochromic shift by 47 nm in the electronic absorption spectrum of Cu(OAc)<sub>2</sub> (the band intensity increases six times), while the absorption band in the spectrum of Cu(EDTA)<sup>2–</sup> is shifted only by 3.5 nm (its intensity increases 1.4 times). The electronic

**Table 1.** Parameters ( $\lambda$ , nm ( $\epsilon$ )) of the electronic absorption spectra of Cu(OAc)<sub>2</sub> and Cu(EDTA)<sup>2-</sup> in water and DMSO

Solvent	H <sub>2</sub> O	$H_2O: DMSO = 1:1$	DMSO
Cu(OAc) <sub>2</sub>	764.5 (30)	734.1 (47)	717.3 (180)
Cu(EDTA) <sup>2-</sup>	739.6 (112)	734.1 (161)	734.1 (162)

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absorption spectra of  $Cu(EDTA)^{2-}$  in pure DMSO and water-DMSO (1 : 1) are virtually identical (Table 1).

Reaction (1), which has the first order in the salt and the first order in porphyrin, is bimolecular and, like all other complexation reactions of porphyrins, obviously follows self-consistent bimolecular mechanism with associative–dissociative activation of both reagents [6]. Apparently, the stereochemical configuration of copper(II) ethylenediaminetetraacetate is more "favorable" for an interaction with the porphyrin macrocycle than the configurations of other metal complexonates. When  $Cu(EDTA)^{2-}$  and H<sub>2</sub>TPP approach each other, the force field of porphyrin deforms the complexonate by extending two nearest bonds (M–O or M–N). At the same time, two protons of the coordination center of the porphyrin molecule affected by the metal ion field go out of the macrocycle plane so that they are on the one side of it. The N–H bonds become more polarized, also because of solvation by DMSO.

At a certain distance between  $H_2TPP$  and  $Cu(EDTA)^{2-}$  (peak of the potential barrier), two adjacent bonds (M–N or M–O) undergo cleavage resulting in opening of the chelate rings. Two liberated coordination sites are occupied by the tertiary N atoms of porphyrin. Then the reaction system converts into a stable intramolecular chelate complex CuTPP. Reaction (1) can be schematically represented as follows:



CuTPP; Solv stands for the solvent molecule

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Porphyrin (c <sub>por</sub> , mol/l)	$c_{\mathrm{Cu(EDTA)}^{2-}}, \mathrm{mol/l}$	$k_{\rm eff} \times 10^4,  {\rm s}^{-1}$ (353 K)	$k_{\rm eff} \times 10^4,  {\rm s}^{-1}$ (333 K)	$k_{\rm eff} \times 10^4,  {\rm s}^{-1}$ (298 K)	$E_{\rm a}$ , kJ/mol ( $\Delta S$ , J/(mol K))
H <sub>2</sub> TPP	0.00016	0.48	0.33	0.24	11 (-233)
$(8 \times 10^{-6})$	0.00032	0.89	0.70	0.44	
	0.00064	1.56	1.24	0.78	
$H_2(t-Bu)_4Pc$	0.00016	14.4	13.2	10.6	5 (-222)
$(9 \times 10^{-6})$	0.00032	22.8	20.6	16.7	
	0.00064	35.9	32.3	26.2	

**Table 2.** Kinetic parameters of the complexation reactions of  $H_2$ TPP and  $H_2(t-Bu)_4$ Pc with copper(II) ethylenediaminetetraacetate in DMSO

Table 3. Kinetic parameters of the complexation reactions of  $H_2$ TPP and  $H_2(t-Bu)_4$ Pc with copper(II) salts in DMSO [11–14]

Cu(II) complex ( $\dot{O} \approx 3-3.2 \times 10^4 \text{ mol/l}$ )	$k_{\rm eff} \times 10^4,  {\rm s}^{-1},$ (298 K)	$k_{\rm eff} \times 10^4,  {\rm s}^{-1},$ (363 K)	E <sub>a</sub> , kJ/mol	$k_{\rm eff} \times 10^4,  {\rm s}^{-1},$ (298 K)	E <sub>a</sub> , kJ/mol
		H <sub>2</sub> TPP	$H_2(t-Bu)_4Pc$		
Cu(Dz) <sub>2</sub> (dithizonate)	No reaction			1.2 (358 K)	
Cu(Ox) <sub>2</sub> (8-hydroxyquinolate)	0.00064	0.9	110	3.87	
$Cu(Nft)_2$ ( $\alpha$ -nitroso- $\beta$ -naphtholate)	0.0024	3.3	100		
Cu(Gly) <sub>2</sub> (glycinate)	0.00005	0.524	130	8.80	
$[Cu(GlyGly)Cl \cdot H_2O (glycylglycinate)$	0.0069	2.63	85	3.15	32
[Cu(GlyGlyGly)Cl (glycylglycylglycinate)	0.018	6.42	80	3.68	26
CuCl <sub>2</sub>	0.079	9.43	66	2.10	8.3
Cu(OAc) <sub>2</sub>	1.10	24.7	43	36.0	

Apparently, the reaction of Cu(EDTA)<sup>2–</sup> with phthalocyanine occurs analogously. However, since the N–H bonds in dissolved phthalocyanine can be localized [6], the protons are removed more easily from the transition state, which increases the reaction rate of copper complexonate with  $H_2(t-Bu)_4Pc$  as compared to  $H_2TPP$ .

In contrast to complexation between porphyrins and acetates (or various salts with bidentate ligands such as acetyl acetonates, hydroxyquinolates, amino acids, etc.), the rate of reaction (1) is virtually temperature-independent, particularly for  $H_2(t-Bu)_4Pc$  (Table 2). As the result, Cu(EDTA)<sup>2–</sup>, which at high temperatures is superior in reactivity only to amino acid complexes, is more reactive toward porphyrins and phthalocyanines at room temperature than all Cu(II) chelate complexes we studied (Table 3) and even than monodentate adeninates and adenosinates [15].

The low enthalpies of activation of reaction (1) suggest a low energy barrier to be surmounted for conversion of the starting reagents into final products. At the same time, the probability of formation of such transition states is very low because of steric mismatch of the reactive sites in porphyrin and Cu(EDTA)<sup>2–</sup>. This is evident from the high negative entropies of activation for  $H_2TPP$  and  $H_2(t-Bu)_4Pc$  (-233 and -222 J/(mol K), respectively (Table 2)).

Another distinctive feature of reaction (1) is a relatively small difference between the complexation rates of  $H_2TPP$  and  $H_2(t-Bu)_4Pc$  (only 35 times). The reactivities of porphyrins and phthalocyanines in complexation with bidentate ligands usually differ by several orders of magnitude (Table 3, [14]). Phthalocyanines are more reactive in basic solvents such as DMSO or pyridine, while porphyrins are more reactive in protic solvents. Apparently, the small difference between the complexation rates of  $H_2TPP$  and  $H_2(t-Bu)_4Pc$  is also due to the major contribution from the entropy factor, which depends only slightly on the porphyrin nature (i.e., on the state of the N–H bonds of the reactive site).

Thus, ligand exchange in a complexone-macrocycle system is mainly precluded by great steric hindrances arising when such large molecules as complexonates and porphyrin macrocycles approach each other. Such an interaction takes place only in separate cases, e.g., in complexation between porphyrins and copper(II) ethylenediaminetetraacetate, whose stere-ochemical configuration seems to be most favorable for the formation of the transition state  $[H_2TPP \cdot Cu(EDTA)^{2-}]$  among other metal ethylenediaminetetraacetates.

The complexation reactions of porphyrins and phthalocyanines with Cu(EDTA)<sup>2–</sup> in DMSO are characterized by very low enthalpies, high negative entropies, and small differences between the complexation rates of porphyrins and phthalocyanines.

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