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Reactions of Chelate Complexes with Macrocyclic Ligands. Octaphenyltetraazaporphine and Its Derivatives

G. M. Mamardashvili, N. V. Chizhova, and B. D. Berezin

Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia

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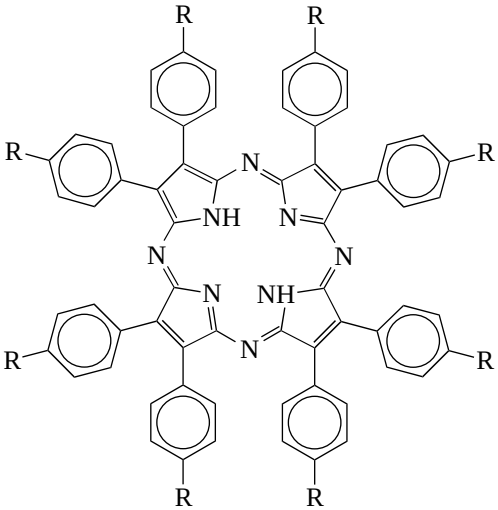
Abstract—Coordination of three azaporphines, namely, octaphenyltetraazaporphine (**I**), octa(4-nitrophenyl)-tetraazaporphine (**II**), and octa(4-bromophenyl)-tetraazaporphine (**III**) with some chelate salts of copper and zinc (hydroxyquinolate (**IV**), α-nitroso-β-naphtholate (**V**), glycinate (**VI**), alaninate (**VII**), valinate (**VIII**), leucinate (**IX**), and glutaminate (**X**)) in DMSO were studied. As in the case with acetates, compound **I** was found to coordinate chelate salts according to the monomolecular mechanism and to give amino complex with the bridging nitrogen atom. Compound **II** reacts with all indicated salts according to the bimolecular mechanism almost instantaneously, except for **VII**. In the same way, reactions of **III** are also instantaneous, even with **VII**. Coordination of **I** with Zn(II) chelate salts proceeds at the rates higher than with acetate.

Studies of coordination between porphyrin macrocycles and chelate salts are complicated by very low rates of coordination of classic porphyrins, for instance, tetraphenylporphine (H_2TPP) [1, 2]. This paper reports the studies of some tetraazaporphyrins, i.e., octaphenyltetraazaporphine (H_2OPTAP) (**I**), octa(4-nitrophenyl)tetraazaporphine (**II**), and octa(4-bromophenyl)tetraazaporphine (**III**). Tetraazaporphyrins are known to enter the complexation reactions in the main solvents, such as pyridine and dimethyl sulfoxide (DMSO), at higher rates than porphyrins proper [3], while the introduction of the electron-accepting bromine atoms or nitro group into the tetraazaporphyrin molecules greatly accelerates the complexation process [4–6].



I: R = H,
II: R = Br,
III: R = NO_2

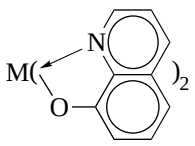
Therefore, the above porphyrins were expected to exhibit high rates of coordination with chelate salts.

EXPERIMENTAL

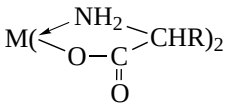
H_2OPTAP and H_2TPP were synthesized and purified according to the known procedures [7, 8]. Compounds **II** and **III** were prepared as described in [9, 10].

The chelate salts, namely, hydroxyquinolates (Ox) (**IV**) and α-nitroso-β-naphtholates (Nft) (**V**) of Cu(II) and Zn(II), glycinate (Gly) (**VI**), alaninate (Ala) (**VII**), valinate (Val) (**VIII**) of Cu(II) were synthesized and identified by the procedures described in [1, 2], while glycinate, valinate, and leucinate (Lei) (**IX**) of Zn(II), according to [11], Cu(II) glutaminate (Glu) (**X**) was prepared by the method reported in [2].

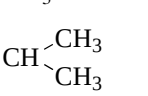
The kinetics of complexation reactions was studied in the same way as in the previous works [1, 2, 4, 5]. The effective rate constant (k_{eff}) was determined with the accuracy of 3–5%.



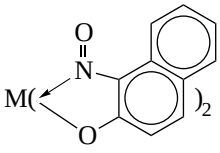
(**IV**)



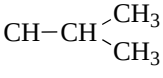
R = H (**VI**)
CH_3 (**VII**)



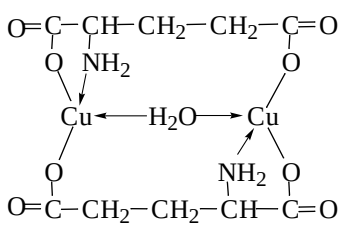
(**VIII**)



(**V**)



(**IX**)



(**X**)

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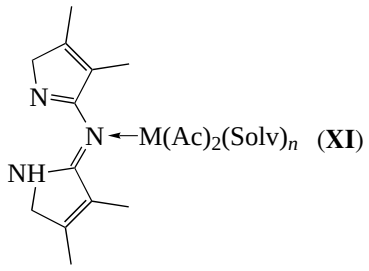
Table 1. Kinetic parameters (k_{eff}) and E_{ac} (activation energy) of complexation reactions of H_2TPP and H_2OPTAP with Cu(II) and Zn(II) salts in DMSO ($c_{salt} = 3 \times 10^{-4}$, $c_{porph} = 1 \times 10^{-5}$ mol/l)

Porphyrin	Salt	$k_{eff} \times 10^4$, s^{-1} (E_{ac}, kJ/mol)		Salt	$k_{eff} \times 10^4$, s^{-1} (E_{ac}, kJ/mol)	
		298 K	363 K		298 K	363 K
H_2TPP	$Cu(Ac)_2$		24.7(43)	$Zn(Ac)_2$		17.0
	$Cu(Ox)_2$ [1]		0.9	$Zn(Ox)_2$ [1]		9.1(56)
	$Cu(Nft)_2$ [1]		3.3(99)	$Zn(Nft)_2$ [1]		6.8(57)
	$Cu(Gly)_2$ [2]		0.52(130)	$Zn(Gly)_2$		very slow reaction
	$Cu(Ala)_2$ [2]		0.018	$Zn(Val)_2$		very slow reaction
	$Cu(Val)_2$ [2]		0.19	$Zn(Lei)_2$		0.39
	$Cu_2[Glu]_2 \cdot H_2O$ [2]		0.30			
H_2OPTAP	$Cu(Ac)_2$	2.6		$Zn(Ac)_2$	0.81	
		5.6 (49) [3]			1.9 (47) [3]	
	$Cu(Ox)_2$	1.2		$Zn(Ox)_2$	1.3	
	$Cu(Nft)_2$	1.8		$Zn(Nft)_2$	2.8	
	$Cu(Gly)_2$	0.44		$Zn(Gly)_2$	4.1	
	$Cu(Ala)_2$	0.047		$Zn(Val)_2$	8.6	
	$Cu(Val)_2$	0.86		$Zn(Lei)_2$	very fast reaction	
	$Cu_2[Glu]_2 \cdot H_2O$ [2]	1.14				

RESULTS AND DISCUSSION

As far as its coordinating properties are concerned, H_2OPTAP occupies a special place among the studied porphyrins. Its reaction with metal acetates has zero order in the metal salt concentration. In order to explain this peculiar phenomenon, the authors of [3] suggested the preliminary coordination of the metal atom to the H_2OPTAP molecule through its *meso*-nitrogen atom according to reaction (1) with the formation of the amino complex $H_2OPTAP \cdot M(Ac)_2$ (**XI**).

$$H_2OPTAP + M(Ac)_2 \underset{\text{quick}}{\rightleftarrows} H_2OPTAP \cdot M(Ac)_2, \quad (1)$$



(**XI**)

Then, at the limiting stage, the metalloporphyrin is produced from the amino complex.

$$H_2OPTAP \cdot M(Ac)_2 \xrightarrow{\text{slow}} MOPTAP + 2HAc. \quad (2)$$

Complexation reactions of H_2OPTAP with chelate salts (**IV**–**X**) are also zero-order reactions in the salts and follow the monomolecular mechanism (Tables 1, 2). Obviously, the metal atom of the salt is preliminarily coordinated to H_2OPTAP through one of its *meso*-nitrogen atoms to give unstable intermediate amino complex **XI**. The electronic absorption spectrum of extremely unstable compound **XI** is similar to that of ligand **I**.

In the case with acetates, the *meso*-nitrogen atom is coordinated by the metal atom of the $M(Ac)_2$ molecule [3]. During complexation with chelate salts, the *meso*-nitrogen atom most likely is coordinated by the monoligand ML^+ moiety, which is produced at the first stage of dissociation of the biligand salt. Otherwise, the complexation reaction of H_2OPTAP with $Cu_2[Glu]_2 \cdot H_2O$ (**X**), for example, would hardly occur.

If the complexation reaction of porphyrin with chelate salt follows the bimolecular mechanism, it is always preceded by dissociation of the biligand salt

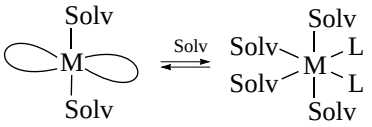
Table 2. Kinetic parameters of complexation of H_2OPTAP (**I**) and its bromine derivative (**III**) with $Cu(Ala)_2$ in DMSO ($c_{porph} = 1 \times 10^{-5}$ mol/l)

Porphyrin	c_{salt}, mol/l	$k_{eff} \times 10^4$, s^{-1} (298 ä)	Reaction order	E_{ac}, kJ/mol
I	0.00009	0.040	~0	105
	0.0003	0.047		
	0.0009	0.049		
III	0.000086	4.9	~0.5	32
	0.000247	8.6		
	0.00200	26		

according to the first stage

$$ML_2(Solv)_n \overset{Solv}{\rightleftharpoons} ML^+(Solv)_{n+1} + L^-, \qquad (3)$$

or by dissociation of the salt without the ligand detachment but with the chelate cleavage:



(4)

Only the "active" particles participate in the complexation reaction:

$$H_2P + ML^+(Solv)_{n+1} \longrightarrow MP + HL + H^+ + (n+1)(Solv). \qquad (5)$$

As the result, the overall complexation reaction

$$H_2P + ML_2(Solv)_n \longrightarrow MP + 2HL + (n+1)(Solv) \qquad (6)$$

significantly depends on the salt stability, i.e., on the shift of equilibria of reactions (3) or (4). In some cases, k_{eff} directly depends on the stability constant K_{st} of the salt.

For H_2OPTAP, the dependence of k_{eff} on the nature of chelate salt is almost similar to that for H_2TPP (established in [2] for a number of chelate salts in DMSO). Althought the coordination of H_2OPTAP is the zero-order reaction in the salt and its rate is almost independent of the salt concentration in the range of 10^{-3}–10^{-4} mol/l, the salt stability is also probably one of the factors that determines the rate of H_2OPTAP complexation with copper salts.

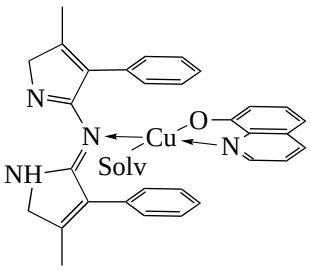
The effect of the salt stability on the overall rate of complexation reaction (as in the case of the bimolecular mechanism) is most likely exhibited at stage (3), which precedes reaction (5). In addition, this effect also can manifest itself at the stage of migration of the metal cation from the *meso*-nitrogen atom to the reaction site of porphyrin H_4N, i.e., in reaction (2). However, this is less probable due to the low stability of complexes **XI**.

Our experimental data showed that the nature of cation, which determines the geometrical structure of the salt, significantly affects the rates of reactions (1) and (2).

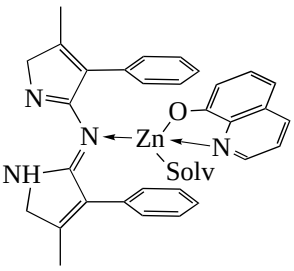
In the case of copper chelate salts with the planar structures, the influence of the salt stability and of structures of the ligands on the reaction rates is less pronounced than in the case of the bimolecular reactions. This is explained by the fact that in the bimolecular reaction (5), the steric hindrances due to the chelate and macrocyclic effect are surmounted directly, whereas in reactions (1) and (2), they are surmounted indirectly.

The amino tetraazaporphyrin complexes with the planar Cu(II) chelate salts can be more stable than those with copper acetate. For instance, the obtained amino complex H_2OPTAP · $Cu(Ox)^+$ (**XII**) can be stabilized by the π–π-interactions between the benzene rings of H_2OPTAP and hydroxyquinolate ion.

Unlike the copper salts, the chelating ligand in the zinc salts with tetrahedral structure does not favor stabilization of the amino complexes H_2OPTAP · $Zn(Ox)^+$ (**XIII**)



(**XII**)



(**XIII**)

(charges in structures **XII** and **XIII** are omitted)

and thus speeds up reaction (2).

Therefore, the rates of H_2OPTAP coordination with all Zn(II) salts under study are higher than with zinc acetate. At the same time, no correlation with the complex stability is observed. The dependences of k_{eff} on the nature of chelate salt for H_2OPTAP and H_2TPP are different.

We believe that the unusually high rates of reactions with Zn(II) amino acid salts can be explained by the fact that in reaction (2), the amino acid residue L^- does not separate from Zn^{2+}, which coordinates porphyrin,

but remains as extra ligand, i.e., it migrates together with Zn^{2+} to the reaction site:

$$H_2OPTAP + Zn(L)^+(Solv)_n \longrightarrow (L)ZnOPTAP + H_2L^+ + n(Solv). \quad (7)$$

When porphyrin coordination occurs according to the common bimolecular mechanism, the ligand detachment from the chelate salt molecule and its further addition to the zinc ion in (L)ZnOPTAP do not affect the rate of reaction (7). One can suggest that if the reaction proceeds through the stage of the amino complex formation, then the possibility of the additional coordination of L by Zn atom in zinc porphyrin accelerates the complexation reaction.

The introduction into the tetraazaporphyrin molecule of the electron-accepting bromine atoms, which make the ionic nature of the N–H bonds more pronounced, significantly accelerates the complexation process. In the pure pyridine, complexation occurs almost instantaneously and therefore, the reaction rates cannot be measured by spectrophotometric kinetic methods [4, 5]. When the electron-accepting substituents (NO_2, Br) are introduced into the phenyl rings of H_2OPTAP, the rate of complexation reaction in chloroform–pyridine mixture increases 10 times [6].

In the case of DMSO, this increase was even more significant. Most of the chelate salts react with compound **II** almost instantaneously. An exception is a weakly coordinating salt $Cu(Ala)_2$, which reacts with **II** at a measurable rate. The introduction of eight bromine atoms into H_2OPTAP increases the rate of its complexation with $Cu(Ala)_2$ almost by two orders of magnitude (Table 2).

It should be noted that unlike **I**, compound **II** is coordinated with $Cu(Ala)_2$ following the bimolecular mechanism. However, as in the case with other copper salts studied by us in [1, 12], the reaction order in the salt is equal to ~0.5. This implies that the solution contains several reactive forms of the salt.

The intermediate amino complex **XI** is likely to form simultaneously due to the donor–acceptor interaction and hydrophobic π–π-interaction of H_2OPTAP with the ligand surrounding of the metal. On the one hand, the introduction of a bromine atom into each phenyl ring increases the electron density on the *meso*-nitrogen atom and thus favors the donor–acceptor interaction, and, on the other hand, it creates the steric hindrances to the cation approaching the *meso*-nitrogen atom. That is why the amino complexes $H_2OPTAP(Br)_8 \cdot M(L)^-$ are not formed in DMSO.

$H_2OPTAP(NO_2)_8$ enter the complexation reaction with all the studied salts (and even with $Cu(Ala)_2$) almost instantaneously. In the absence of the kinetic parameters of reactions with compound **III**, the conclusion about the molecularity of its complexation with chelate salts is difficult.

ACKNOWLEDGMENTS

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