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Unusual catalytic effect of halide anions in the protolytic dissociation of indium(III) octaphenyltetraazaporphyrins

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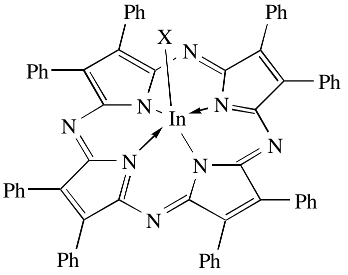
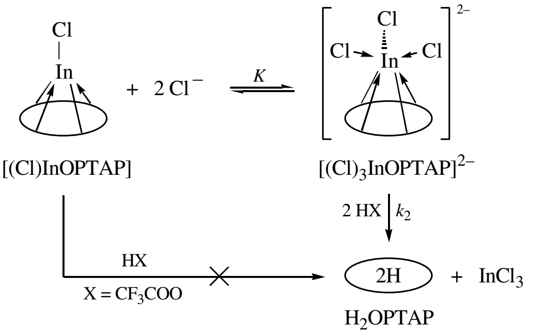
Chloro(octaphenyltetraazaporphyrinato)indium(III) [(Cl)InOPTAP] dissociates easily in slightly acidified dichloromethane solutions (0.001–0.01 M CF_3COOH) after addition of tetraethylammonium chloride; the observed catalytic effect of chloride anions is due to their additional *cis*-coordination to the In atom with formation of the dianionic complex $[(Cl)_3InOPTAP]^{2-}$.

The shielding of the reaction centre $(X)_{n-2}M(N_4)$ in complexes of porphyrins with metal ions in high oxidation states [M^{III}, M^{IV} and M^{V}] by anionic extra ligands X^- was considered[1,2] as an important factor of their stabilisation in the dissociation in acidic media. We found that the coordination of additional anionic ligands may cause an opposite effect and strongly facilitate the dissociation reaction of indium(III) octaphenyltetraazaporphyrinates [(X)InOPTAP] (X is a halide or another anionic ligand).



[(X)InOPTAP]

Previously, it was found that the In^{III} complexes of *meso*-tetraphenyl-, *meso*-diaza- and *meso*-tetraazaporphyrins are stable in carboxylic acids and can undergo slow dissociation only in conc. H_2SO_4.[2–4] The dissociation stability is decreased in the order [(Cl)InTPP] > [(Cl)InDAPMe$_4$Bu$_4$] > [(Cl)InOPTAP] along with the increasing withdrawal of the In atom from the mean N_4-plane due to contraction of the N_4-coordination cavity upon *meso*-aza substitution.[3] The acidification of a [(Cl)InOPTAP] solution in CH_2Cl_2 with trifluoroacetic acid results in the consecutive protonation of two *meso*-nitrogen atoms,[4,5] but no dissociation occurs even in 100% CF_3COOH. However, we found that the addition of chloride anions (as Et_4NCl) to slightly acidified solutions (< 0.01 M CF_3COOH) containing unprotonated [(Cl)InOPTAP] leads to the very rapid dissociation of the complex with the formation of the metal-free macrocycle H_2OPTAP. The typical UV/VIS spectral changes during the dissociation are shown in Figure 1. The absorption bands of [(Cl)InOPTAP] at 378, 475 and 642 nm disappeared, while new characteristic bands of H_2OPTAP appeared at 595 and 663 nm. Note that the addition of Et_4NCl to non-acidified solutions of [(Cl)InOPTAP] caused alomost no changes in the positions and intensities of absorption bands in the UV/VIS spectra.



Scheme 1

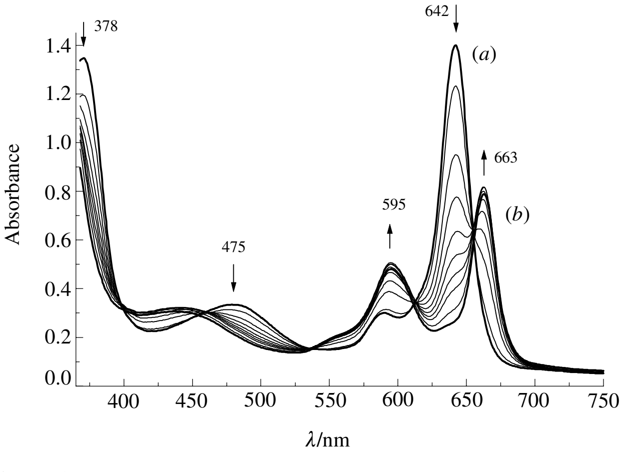


Figure 1 UV/VIS spectra measured after the addition of 0.01 M Et_4NCl to a solution of [(Cl)InOPTAP] in CH_2Cl_2 containing 0.005 M CF_3COOH at 298 K: (*a*) initial spectrum of [(Cl)InOPTAP] in the absence of Et_4NCl, (*b*) final spectrum of H_2OPTAP (recorded 30 min after addition of Et_4NCl).

A spectrophotometric kinetic study demonstrated that dissociation is a first-order reaction with respect to [(Cl)InOPTAP]. The observed rate constants (k_{obs}) were obtained using a pseudo-first-order rate equation (both CF_3COOH and Et_4NCl were taken in a 100 to 1000-fold excess) (Table 1). To elucidate the mechanism of this unusual catalytic effect of chloride anions on the dissociation of [(Cl)InOPTAP], we studied the dependence of kinetic parameters upon the concentrations of CF_3COOH and Et_4NCl.

The linear plot of log k_{obs} *vs.* log [CF_3COOH] [Figure 2(*a*), tan $\alpha = 2.4\pm0.1$] indicates that the dissociation of [(Cl)InOPTAP] has the second order with respect to CF_3COOH, which is typical of metal porphyrin dissociation.[6] Indeed, two acid molecules are required for the rupture of two covalent N–In bonds and the formation of two N–H bonds.

Table 1 The observed rate constants of [(Cl)InOPTAP] dissociation in CF_3COOH–CH_2Cl_2 solutions in the presence of Et_4NCl at 298 K.

$[Et_4NCl]_0 = 0.005$ mol dm^{-3}		$[CF_3COOH]_0 = 0.005$ mol dm^{-3}	
$[CF_3COOH]_0$/ mol dm^{-3}	$k_{obs}/10^{-4}$ s^{-1}	$[Et_4NCl]_0$/ mol dm^{-3}	$k_{obs}/10^{-4}$ s^{-1}
0.001	0.34±0.01	0.0002	0.24±0.01
0.002	3.50±0.01	0.0006	3.50±0.01
0.003	7.02±0.03	0.0010	7.82±0.06
0.004	10.20±0.02	0.0014	14.70±0.02
0.005	23.10±0.03	0.0025	14.60±0.02
0.006	34.40±0.03	0.0050	23.10±0.03
0.008	67.60±0.22	0.0100	12.90±0.03
0.010	110.00±2.86	0.0150	4.81±0.01
		0.0200	5.02±0.01
		0.0250	4.01±0.01

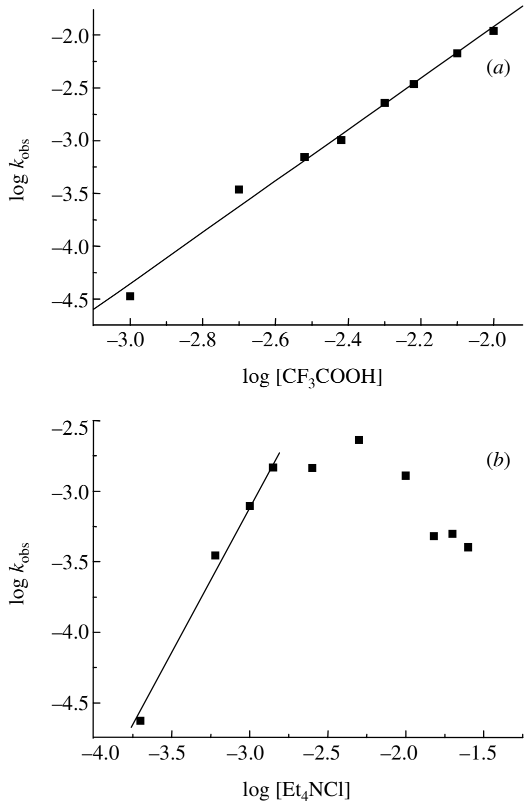


Figure 2 The logarithmic plots of k_{obs} *vs.* (*a*) [CF_3COOH] and (*b*) [Et_4NCl].

The dependence of the observed rate constants k_{obs} on [Et_4NCl] at constant [CF_3COOH] = 0.005 M is more complex (Table 1). With increasing chloride concentration, k_{obs} increased, reached a maximum of 23.1×10^{-4} s^{-1} at [Et_4NCl] = 0.005 M and then decreased to 4.0×10^{-4} s^{-1} at [Et_4NCl] = 0.025 M. The logarithmic plot of k_{obs} *vs.* [Et_4NCl] is shown in Figure 2(*b*). The observed dependence is indicative of a saturation kinetics mechanism, when a reactive intermediate is formed in a rapid reversible reaction. The k_{obs} reached a maximum and then remained constant when the equilibrium was fully shifted to the formation of this reactive intermediate. Evidently, the decrease of k_{obs} at [Et_4NCl] > 0.01 M results from changes in the ionic strength and specific solute–solute interactions with bulky tetraethylammonium cations.

The reaction order with respect to Cl^-, which can be determined from the linear portion of the log k_{obs}–log [Et_4NCl] plot is 2.1±0.2. This allowed us to conclude that two chloride anions are necessary for the formation of an intermediate, which is reactive in the dissociation. Although the coordination number of indium in neutral complexes with porphyrin-type macrocycles is usually five (as in halide complexes) or six (*e.g.*, in complexes with bidentate acetate),[7] additional anionic ligands can be bound at the *cis*-position with the formation of anionic *cis*-complexes. Thus, in phthalocyaninatoindium(III) derivatives, the In atom can be six-coordinated in anionic *cis*-complexes with two fluoride[8] or two cyanate[9] anions (*cis*-[F_2InPc]$^-$ and *cis*-[$(CNO)_2InPc$]$^-$), and has a coordination number of eight in the complex *cis*-[$(NO_2)_2InPc$]$^-$.[10] Due to the large ionic radius of In^{III} (r_{In} = 0.81 Å[11]), *trans*-coordination is not characteristic of its complexes with porphyrins[7] having larger coordination cavities than that of tetraazaporphyrins. The reactive intermediate can be therefore formulated as *cis*-[$(Cl)_3$InOPTAP]$^{2-}$ (Scheme 1). It is not surprising that formation of *cis*-[$(Cl)_3$InOPTAP]$^{2-}$ does not lead to UV/VIS spectral changes. It is known that the UV/VIS spectra of [(X)InOPTAP] with different X (F, Cl, Br, acetate, benzoate, *etc.*) are almost identical, especially, in the visible region.[5,12] Moreover, the coordination centre in σ-bonded tetraazaporphyrin complexes has only slight influence on the energy of the $\pi \rightarrow \pi^*$ transitions.

The kinetic data allowed us to propose the mechanism of [(Cl)InOPTAP] dissociation catalysed by chloride anions (Scheme 1). Neither [(Cl)InOPTAP] nor its *meso*-mono- or *meso*-diprotonated forms [(Cl)InOPTAP]H$^+$ and [(Cl)InOPTAP]H$_2^{2+}$ can undergo dissociation under the action of CF_3COOH. Addition of chloride leads to the formation of the anionic complex *cis*-[$(Cl)_3$InOPTAP]$^{2-}$. Since the withdrawal of the In atom from the mean N_4-plane is increased and the elongated In–N bonds are weakened, this coordination species dissociates easily even in the presence of CF_3COOH in a low concentration.

The application of the Bodenstein approximation to the kinetic equations describing this mechanism allows us to estimate roughly the rate constant of dissociation k_2 as 80±15 s^{-1} M^{-2} and the equilibrium constant of dianionic *cis*-complex formation K = = (7.5±2.0)×10^5 M^{-2}.

Surprisingly, a solution of [(Cl)InOPTAP] in CH_2Cl_2 containing 0.005 M CF_3COOH and 0.005 M Et_4NCl (k_{obs} = 0.00231 s^{-1} at 298 K) is almost 10 times less stable to dissociation than in 96% aqueous H_2SO_4 (k_{obs} = 0.000231 s^{-1} at 298 K),[4] although in the latter case the concentration of H_3O^+, which is one of the most reactive species in the hydroprotolytic dissociation, is very high (~ 4 M). The facts that the dissociation is slow in conc. H_2SO_4 and does not occur in pure CF_3COOH can be well explained. Unlike chloride, hydrosulfate and trifluoroacetate (the only nucleophiles in these media) are weakly coordinating anions, which are less able to *cis*-coordination. The coordination bonds they can form with a metal are much more ionic, and the In atom does not receive any effective negative charge. Moreover, the whole porphyrazine macrocycle is positively charged due to protonation of one or two *meso*-nitrogen atoms in CF_3COOH (> 0.01 M) or in H_2SO_4 solutions. As a result, the attack of the positively charged coordination centre by a proton-donating reagent ($CF_3COOH_2^+$ or H_3O^+) becomes very difficult. Therefore, the double negative charge in the *cis*-complex is another important factor facilitating the rupture of In–N bonds under the action of an acid. Note that the presence of water in the solvent (water has a higher coordination affinity to In^{III} as compared with chloride) retards strongly the dissociation due to the formation of stable neutral aqua complexes.

Fluoride and bromide show similar catalytic effects in the dissociation reaction as is reported here for chloride.

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