Metallation of tetratolylporphyrin by Cu²⁺ catalysed by LiClO₄

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Abstract – The kinetic study of tetratolylporphyrin metallation by copper II ions in the presence of lithium salts was undertaken in an aprotic solvent. A catalytic effect of Li⁺ has been observed leading to a great enhancement ($\times 500$ at 30 °C) in the rate of incorporation of Cu²⁺. *To cite this article: R. Faure et al., C. R. Chimie 5 (2002) 529–532* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

porphyrin / metallation / kinetic / copper II / lithium

Résumé – L'étude de la cinétique de métallation de la tétratolylporphyrine par les ions cuivre II en présence de sels de lithium a été entreprise dans un solvant aprotique. Un effet catalytique de Li⁺ a été observé, avec pour conséquence une augmentation importante ($\times 500$ à 30 °C) du taux d'incorporation de Cu²⁺. *Pour citer cet article : R. Faure et al., C. R. Chimie 5 (2002) 529–532* © 2002 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

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1. Introduction

Numerous papers have been devoted to the study of metal insertion into porphyrins [1] and the mechanism of this reaction has been the subject of a lot of controversial debate [2–5]. The rate of metal insertion into planar porphyrins is very much slower than into open chain ligands; this is because planar porphyrins must largely deform in order to accept the incoming metal ions. Thus, some distorted porphyrins have been synthesised by introducing a methyl group on the pyrrole nitrogen [6, 7]. In this case, the incorporation rate of metal ions is greatly enhanced. Similarly, when β pyrrolic positions are occupied by voluminous substituents like bromine atoms or phenyl groups [8, 9], the porphyrin ring is subjected to some distortion and may adopt a saddle shape. In this latter case, it was demonstrated that such a β substituted porphyrin can form a stable complex with lithium ions, contrary to planar porphyrins that cannot form stable dilithium salts [10, 11]. However, these lithium complexes could very easily lead to divalent cationic porphyrin, but no kinetic studies of this reaction have been reported yet [9, 12].

On the other hand, it was recently demonstrated [13, 14] that the deformation of the planar mesoporphyrin IX induced by an antibody increased the rate of incorporation of Zn²⁺ ions. Thus, it was anticipated that, if the lithium ions were to accommodate with a distorted porphyrin, they would be able to play the role of the antibody and form a transient intermediate that could enhance the rate of metallation of a planar porphyrin by a divalent cation.

For the purpose of this study, we chose to examine the kinetics of metallation of the planar tetratolylporphyrin by copper ions in an aprotic solvent, in the presence of a soluble lithium salt such as LiClO₄.

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2. Experimental

2.1. Reagents and solvents

Dichloromethane (Prolabo) was distilled twice on calcium hydride. Tetratolylporphyrin (H$_2$TTP) was purified by preparative TLC (silica) using dichloromethane as eluent. Copper acetyl acetonate (Aldrich) was used as received. LiClO$_4$ (Acros) was used as received.

2.2. Measurements

The reactions were monitored on a Hewlett Packard 845LA diode array UV–visible spectrophotometer with a thermostated cell compartment maintained within ±0.1 °C. The reactions were run under pseudo-first-order kinetic conditions at 30 °C, with the metal ion at a large excess over the free-base porphyrin concentration.

The formation of metalloporphyrin was carried out in 1 cm quartz cells by mixing a porphyrin solution and a metal ion solution pre-equilibrated at the reaction temperature. Then the absorbances at 516 nm were automatically recorded at 10 s intervals over a period of 600 s.

Pseudo-first-order plots showed good linearities and conditional first order rate constants were obtained from the slopes of such straight lines.

3. Results and discussion

3.1. Kinetics of metal ion incorporation into H$_2$TTP

The kinetics of the reaction of H$_2$TTP with copper II acetyl acetonate in CH$_2$Cl$_2$ at 30 °C was studied.

The rate for the formation of metalled porphyrin is of first order with respect to porphyrin.

$$d[CuTTP]/dt = -d[H_2TTP]/dt = k_a [H_2TTP_t] \quad (1)$$

where k_a is the apparent first order rate constant involving the metal concentration and (H$_2$TTP$_t$) is the actual porphyrin concentration, which is proportional to $(A - A_\infty)$ values. So, the plot of $\ln(A - A_\infty)$ versus t gives a straight line with a slope giving k_a.

It is known [15, 16] that in non-polar solvents like CH$_2$Cl$_2$, copper acetyl acetonate undergoes dimerisation and that the concentration of the available monomer, which is the only reactant species, is given by:

$$[Cu(acac)_2]_m$$

$$= \{-1 + (1 + 8 K_1 [Cu(acac)_2]_0)\}^{1/2}/4 K_1 \quad (2)$$

where [Cu(acac)$_2$]$_m$ is the monomer concentration, [Cu(acac)$_2$]$_0$ is the analytic concentration, and $K_1 = 2130$ mol^{-1} L.

When plotted against [Cu(acac)$_2$]$_m$, the values of k_a give a straight line ($R^2 = 0.945$) (Fig. 1) of slope k_i. Then the general kinetics of the metallation in CH$_2$Cl$_2$ is:

$$-d[H_2TTP]/dt = k_i [H_2TTP] [Cu(acac)_2]_m \quad (3)$$

with $k_i = 4.3$ s^{-1} mol^{-1} L.

3.2. Kinetics of metal ion incorporation in the presence of lithium perchlorate

Before studying the effect of lithium salt on the kinetics of metallation, we tested that this salt did not affect the spectrum of H$_2$TTP for the Q bands considered in the absorbance measurements. So, in a first
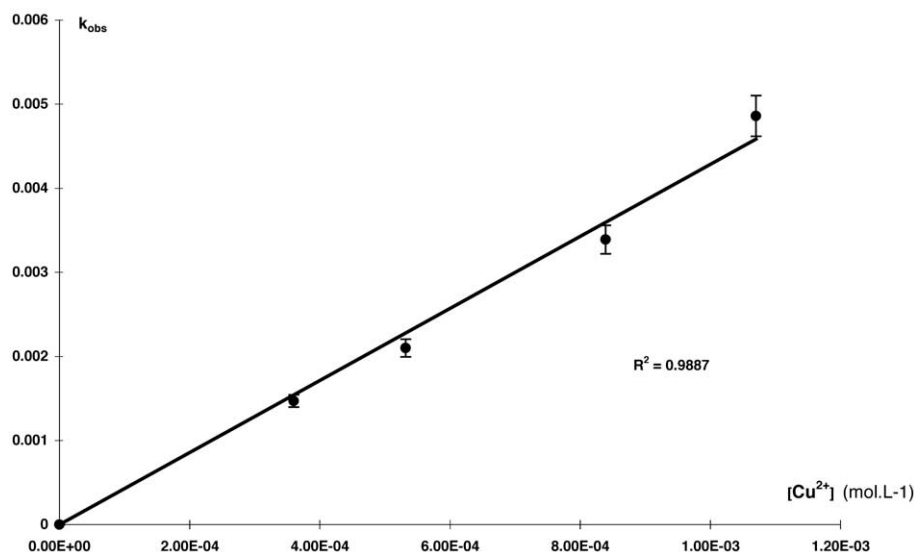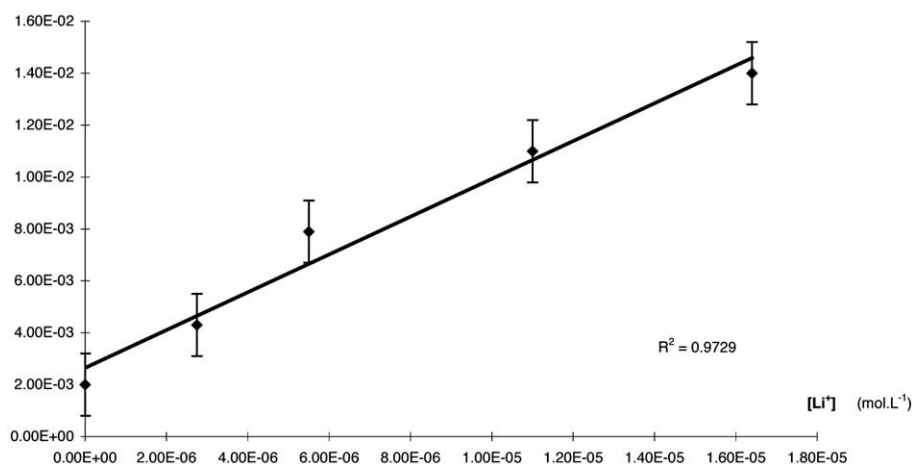

Fig. 1. TTP in CH$_2$Cl$_2$ without Li$^+$.

Fig. 2. $K_{obs} = f(Li^+)$.

series of experiments we studied the rate of metallation at constant $[Cu(acac)_2]_m = 3.8 \times 10^{-4}$ mol L^{-1} for different lithium concentrations.

At a constant concentration of $[Cu(acac)_2]_m$, k_a increased linearly ($R^2 = 0.973$) with Li$^+$ concentration (Fig. 2).

If we assume that lithium (Li) and porphyrin (P) species are in fast equilibrium with the complex (PLi):
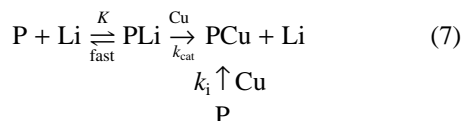
$$P + Li \rightleftharpoons PLi \quad (4)$$

This complex is then subjected to metallation by [Cu^{2+}] with a catalytic constant k_{cat}:

$$PLi + Cu \xrightarrow{K_{cat}} Pcu + Li \quad (5)$$
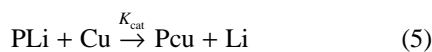
If we include to this mechanism the non-catalytic step:

$$P + Cu \rightarrow PCu \quad (6)$$

we can write the general kinetics reaction:

$$P + Li \underset{fast}{\overset{K}{\rightleftharpoons}} PLi \overset{Cu}{\underset{k_{cat}}{\rightarrow}} PCu + Li \quad (7)$$
$$k_i \uparrow Cu$$
$$P$$

The general kinetics equation will be:

$$v = k_i [P][Cu]\{1 + (k_{cat}[Li])/(1 + k_i[Cu])\} \quad (8)$$

If [Cu] is considered to be constant, the pseudo-first-order constant k_{obs} will be:

$$k_{obs} = k_i[Cu] + k_{cat}[Li][Cu]/(1 + k_i[Cu]) \quad (9)$$

where $k_i[Cu] = 2 \times 10^{-3}$ L s^{-1} is k_{obs} without [Li].

k_{obs} is linear when plotted again [Li] (Fig. 2). The slope of this straight line gives k_{cat}:

$$k_{cat} = slope(1 + k_i[Cu])/[Cu] \quad (10)$$

i.e.:

$$k_{cat} = 1.89 \times 10^6 \text{ s}^{-1} \text{ mol}^{-1} \text{ L} \quad (11)$$

In a second series of experiments, kinetics were conducted at various concentrations of Cu in CH$_2$Cl$_2$ saturated with LiClO$_4$ ($C = 1.22 \times 10^{-3}$ mol L^{-1}). In this case, k_{obs} plotted against [Cu] (Fig. 3) gives a straight line ($R^2 = 0.950$) of equation:

$$k_{obs} = ki[Cu] + \{Const[Cu]/(1 + k_i[Cu])\} \quad (12)$$

$$k_{obs} = 4.3[Cu] + (1.89 \times 10^6) \times (1.22 \times 10^{-3})[Cu]$$

$$k_{obs} = 2300[Cu]$$

This curve shows that in these conditions the reaction is very fast and cannot be performed at high concentrations of [Cu]: in the presence of lithium, the value of k_{obs} is 535 fold that without catalyst.

In summary, we have found that, in aprotic media, metallation of the free-base form of tetratolylporphyrin can be enhanced in presence of Li salts. Such behaviour confirms the effect of the distortion of the macrocycle on the kinetics of metallation. Besides the fundamental interest, we have established a new method for fast metallation of porphyrins. Metal studies on the incorporation of other metals are under investigation in our laboratory.
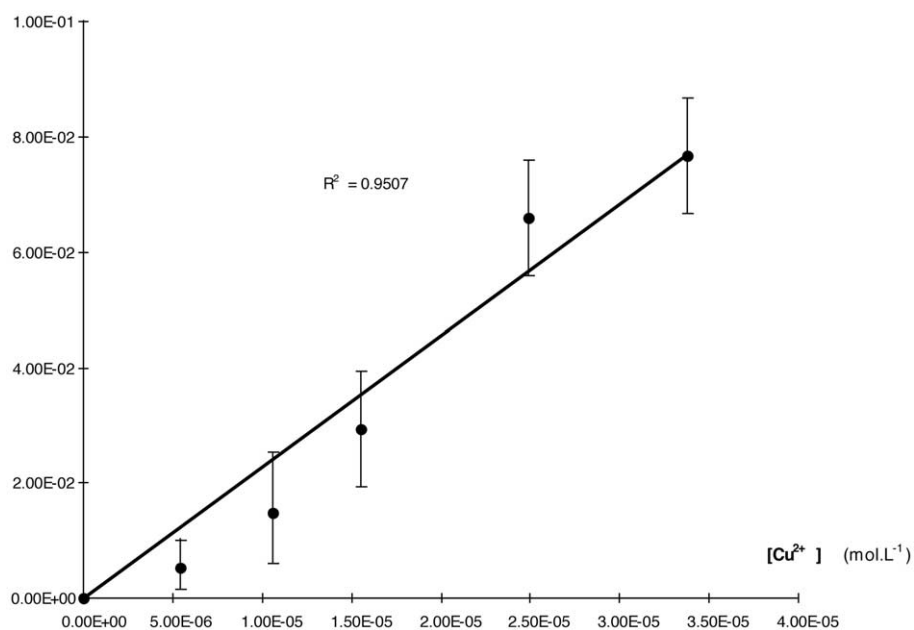
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Fig. 3. TTP in a saturated CH_2Cl_2 solution of Li^+.

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