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# Formation, photophysics and photochemistry of thallium(III) 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin: New supports of typical sitting-atop features

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## Abstract

In aqueous solutions of thallium(III) and 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin a kinetically labile metalloporphyrin of composition 1:1 ($Tl^{III}P^{3-}$) is formed in a moderately fast bimolecular reaction ($k = 270\,M^{-1}\,s^{-1}$). The formation constant of this sitting-atop (SAT) complex is rather high ($K' = 9.5 \times 10^6\,M^{-1}$ at pH 6), due to the not too large size (compared to the core of the ligand) and the three-fold positive charge of Tl(III). The strong coordinative bond is manifested in the large shifts of the emission and absorption bands of the porphyrin. The directions of these shifts characteristically depend on the structure of the metalloporphyrin, making the identification of the sitting-atop type unambiguous. Compared to the corresponding values of the free-base porphyrin, the dramatically diminished fluorescence quantum efficiency of $Tl^{III}P^{3-}$ ($Q_{fl} = 0.00079$ versus 0.075) can be accounted for by the heavy-atom effect and the distortion to saddle shape. Both Soret- and Q-band irradiations of the $Tl^{III}P^{3-}$ complex lead to the degradation of the porphyrin with quantum yields of $(1–3) \times 10^{-5}$ magnitude in both aerated and argon-saturated solutions. The primary photochemical step in this process is ligand-to-metal-charge-transfer reaction followed by the detachment of the reduced metal center. The latter step is favoured by the out-of-plane position of the metal in the case of SAT complexes. Subsequent to the demetallation, an irreversible ring-opening of the oxidized porphyrin takes place. The results on the photolysis of the $Tl^{III}P^{3-}$ complex confirm that the overall reaction is a four-electron process. Reversible dissociation of the $Tl^{III}P^{3-}$ complex also occurs upon irradiation.

*Keywords:* Water-soluble porphyrin; Sitting-atop complex; Thallium(III) ion; Photochemistry; Photodissociation; Charge transfer

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## 1. Introduction

Porphyrin complexes constitute one of the most important groups of compounds in biochemistry, due to their central role in photosynthesis, oxygen transport and biological redox processes [1–5]. Within this group special properties characterize the so-called sitting-atop (SAT) metalloporphyrins [6–8]. Such a structure is formed each time during the incorporation of the metal center, when in the intermediate state the two pyrrolic protons remain yet on the porphyrin [6]. We designate this intermediate complexes as i-SAT. If the ionic radius of the metal center is too large, so that it is not able to fit coplanar into the core of the ligand even after the deprotonation, it is located above the porphyrin plane [7,8], distorting it. The symmetry of this structure ($C_2$, $C_4$ or $C_s$) is lower than that of the free-base porphyrin ($D_{2h}$) and a regular, coplanar metalloporphyrin ($D_{4h}$) as well. In these finally formed, stable SAT complexes (designated as s-SAT) the metal center fits into the core of the porphyrin ligand to an extent enough to push out the two protons from the diagonally situated pyrrolic nitrogens [9,10]. Thus, protons cannot play any role in the structural distortion of an s-SAT complex. The shorter-lived i-SAT complexes containing both metal ion and pyrrolic protons are formed during the preparation of normal metalloporphyrins too [6,11]. Notably, i-SAT complexes were not detected so far in aqueous systems because of their very short life-time [11]. In the cases of i-SAT metalloporphyrins, mostly with metal center of smaller size, the splitting of both the N–H and the N–M bond can occur because the latter one is rather weak as a consequence of the insufficient overlap between the electron orbitals of the metal ion and the neighbouring nitrogen atoms. This can be one of the reasons of the hindered formation of normal (coplanar) metalloporphyrins. However, metal

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ions of larger size (forming s-SAT complexes), as softer Pearson acids, can bind more strongly to all four pyrrolic nitrogens of softer basicity. Thus, larger metal ions such as $Hg^{2+}$, $Cd^{2+}$ or $Pb^{2+}$ can catalyse the formation of normal metalloporphyrins via coordination to the ligand. Then the distorted structure of the porphyrin increases the accessibility of one, diagonally situated pyrrol–nitrogen pair from the other side of the ligand plane [12–17]. Moreover, the out-of-plane position promotes the formation of bi- and tri-nuclear sandwich complexes [18–21]. Due to this special coordination and kinetic lability, the photoinduced porphyrin ligand to metal charge transfer (LMCT) becomes more efficient for s-SAT metalloporphyrins, establishing their utilization in photocatalytic cycles [22,23].

Among the complexes of metal ions with a radius exceeding the critical 80 pm value, mercury(II) [13,15,24], thallium(I, III) [9,10,25,26] and lead(II) [8,27] porphyrins have been thoroughly studied as the most typical examples of the s-SAT metalloporphyrins. The out-of-plane position of these metal ions has been proved with X-ray analyses. The effects of such a structure can also be studied by other analytical methods. NMR spectroscopy proved to be an efficient method for thallium with 1/2 nucleon spin, mainly because its ions with +3 charge form 1:1 porphyrin complexes ($Tl^{III}$Porphyrin) [9,10], while the composition of metalloporphyrins with its metal ions of a single positive charge is 2:1 ($Tl_2{}^{I}$Porphyrin) [25,26]. Nevertheless, the possibilities offered by their special photochemical behavior due to the SAT coordination have not been recognized yet, and their formation kinetics and equilibrium have been scarcely investigated.

The aim of our work, in the frame of a systematic investigation of the photophysics and photochemistry of water-soluble, stable sitting-atop (s-SAT) metalloporphyrins, was to study the formation and photoinduced behavior of thallium(III) 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin.

## 2. Experimental

### 2.1. Reagents and solutions

For preparation of solutions, analytical grade reagents (tetrasodium 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin ($Na_4(H_2TPPS)\cdot 12H_2O$), Sigma–Aldrich), $Tl^{III}(ClO_4)_3\cdot 3H_2O$ and NaCl were dissolved in deionized, double-distilled water purified with Millipore Milli-Q system. Oxygen-free experiments were carried out by bubbling argon through the reaction solution for 45 min prior to the irradiation. The solutions containing metalloporphyrin were prepared well (at least 1 day) before the photophysical and photochemical experiments so that the complex equilibration was ensured. The actual concentrations of the stock solutions prepared were checked spectrophotometrically, using the molar absorptions of the reagents at characteristic wavelengths; $\varepsilon(413\,\text{nm}) = 4.66 \times 10^5\,\text{M}^{-1}\,\text{cm}^{-1}$ for $H_2TPPS^{4-}$ (abbreviated as $H_2P^{4-}$) [24]. $\varepsilon(246\,\text{nm}) = 15850\,\text{M}^{-1}\,\text{cm}^{-1}$ for tetrachlorothallate(III) complexes in 1 M NaCl solution. This rather high chloride concentration hinders the hydrolysis of the thallium(III) ion and keeps the ionic strength at 1 M. The pH of the solutions was adjusted to pH ≈ 6, using KOH.

### 2.2. Instruments and procedures

Absorption spectra were measured on a GBC 911/A UV–vis and on a Specord S100 diode array spectrometer. Emission and excitation spectra were recorded on a Perkin-Elmer LS50B spectrofluorimeter. Rhodamine-B and $Ru(bpy)_3Cl_2$ were used as references for correction of the detector sensitivity and for determination of the fluorescence quantum yields [28,29]. For continuous irradiations an AMKO LTI photolysis equipment (containing a 200-W Xe–Hg-lamp and a monochromator) was applied. Light intensity was determined by ferrioxalate actinometry and frequently checked by a thermopile. Quartz cuvettes of 1 and 5 cm pathlength were utilized as reaction vessels. During the irradiations the reaction mixtures were continuously homogenized by magnetic stirring. The spectral change was continuously followed by using fiber optics coupled with the diode array spectrometer controlled by a PC. All measurements were carried out at room temperature. The experimental results were processed and evaluated by MS Excel programs on PCs.

## 3. Results and discussion

### 3.1. Absorption spectra and equilibrium

In order to avoid strong hydrolysis, thallium(III) ions had to be converted into water-soluble complexes. Chloride ions proved to be appropriate ligands for this purpose; at relatively high concentration (1 M) they form mainly tetrachlorothallate(III) complexes. Moreover, 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin anion is able to displace chloride ions from the coordinative sphere of Tl(III) with $[Xe]4f^{14}5d^{10}$ electron configuration, leading to a porphyrin complex with 1:1 composition as proved later. Probably only one chloride ligand can remain on the metal center in axial position, while on the other side of the distorted metalloporhpyrin can weekly coordinate nothing but a water molecule [9] (Fig. 1).

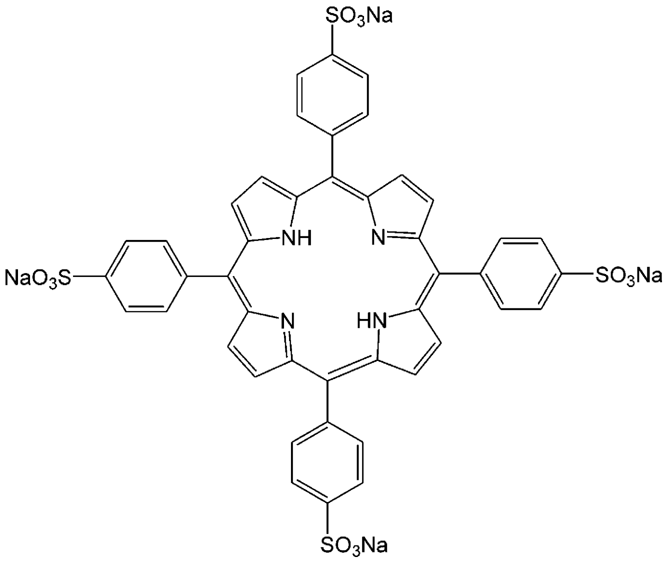


Fig. 1. The structure of water-soluble 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin.

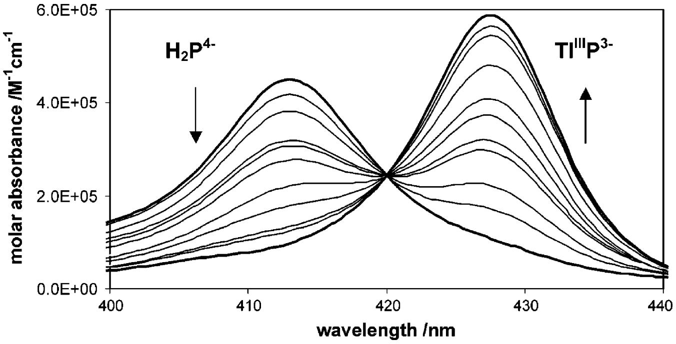


Fig. 2. Spectrophotometric titration of $3.0 \times 10^{-7}$ M $H_2P^{4-}$ with thallium(III) in the concentration range (0–9.0) × $10^{-7}$ M. The bold line peaking at higher wavelengths represents the calculated spectrum of $Tl^{III}P^{3-}$.

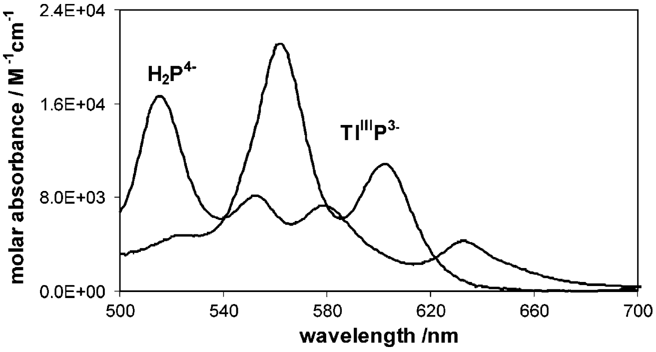


Fig. 3. The Q-bands of the $Tl^{III}P^{3-}$ complex compared to those of the free-base porphyrin.

For study of kinetically labile complexes mostly ligand excess is used. In the case of metalloporphyrins, however, generally metal ions are applied in excess, especially for spectrophotometric measurements, partly because of the extremely high molar absorbances (at the Soret-bands) of the porphyrins.

Deviating from the normal (coplanar) metalloporphyrins, the formation of kinetically labile SAT complexes is an equilibrial process. It can be followed spectrophotometrically because the absorption and emission bands assigned to ligand-centered electron transitions undergo considerable shift and intensity change upon binding metal ions.

As a consequence of the coordination of thallium(III) ion, a bathochrome shift of the Soret-band (350–500 nm, Fig. 2) and hypsochrome shift of the longest-wavelength Q-band (in the region of 500–700 nm, Fig. 3) can be observed.

Moreover, in the latter region the thallium(III) porphyrin displays only two intense absorption bands, while the corresponding spectrum of the free-base porphyrin shows four peaks because of the effect of hydrogens situated diagonally on pyrrolic nitrogens. The molar absorbances of both the Soret- and the Q-bands of the metalloporphyrin are higher than the corresponding values for the free-base porphyrin (Table 1). According to our earlier observations [30–33], this type of spectral properties is unambiguously characteristic for SAT complexes, confirming the expectations based on the size of Tl(III).

At $10^{-6}$ M porphyrin concentration addition of stoichiometric amount of thallium(III) proved to be enough for quantitative formation of the metalloporphyrin, i.e., for the total conversion of the free-base porphyrin to the s-SAT complex. This phenomenon confirmed the 1:1 composition and indicated a rather high formation constant. Thus, determination of the equilibrium constant can be realized at least one order of magnitude lower porphyrin concentration:

$$[\mathrm{Tl^{III}Cl_4}]^- + \mathrm{H_2P^{4-}} \xleftrightarrow{K} [\mathrm{(Cl)Tl^{III}P}]^{4-} + 2\mathrm{H^+} + 3\mathrm{Cl^-} \qquad (1)$$

$$K' = \frac{\mathrm{K}}{[\mathrm{H^+}]^2[\mathrm{Cl^-}]^3} = \frac{[\mathrm{Tl^{III}P}]}{[\mathrm{Tl^{3+}}][\mathrm{H_2P}]} \qquad (2)$$

$$\phi_1 = \frac{[\mathrm{Tl^{III}P}]}{[\mathrm{H_2P}] + [\mathrm{Tl^{III}P}]} = \frac{K'[\mathrm{Tl^{3+}}]}{1 + K'[\mathrm{Tl^{3+}}]} \qquad (3)$$

$$\varepsilon_\lambda = \phi_0 \varepsilon_{\mathrm{H_2P},\lambda} + \phi_1 \varepsilon_{\mathrm{Tl^{III}P},\lambda} = \frac{\varepsilon_{\mathrm{H_2P},\lambda} + K'[\mathrm{Tl^{3+}}]\varepsilon_{\mathrm{Tl^{III}P},\lambda}}{1 + K'[\mathrm{Tl^{3+}}]} \qquad (4)$$

where $K'$ is the apparent stability constant, $[\mathrm{H_2P}]$, $[\mathrm{Tl^{3+}}]$, and $[\mathrm{Tl^{III}P}]$ are the actual concentrations of the free-base porphyrin, the free thallium(III) (as chloro complexes), and the thallium(III) porphyrin, respectively; $\phi_0$ and $\phi_1$ are the partial molar fractions of the different porphyrin forms {0 = free-base, 1 = complex}, $\varepsilon_{i,\lambda}$ is the corresponding molar absorbance at λ wavelength.

Eq. (4) expresses the average molar absorbance of the porphyrin species (free-base and complexed). During the evaluation of the average molar absorbance versus $[\mathrm{Tl^{3+}}]$ data, an iterative least-square procedure (based on Eq. (4)) was used to find the best fitting values of $K'$ and $\varepsilon(\mathrm{Tl^{III}P}, \lambda)$ parameters. Due to the significant band shifts, as a consequence of the strong coordination bond, absorbances in the range of both Soret- and Q-bands were used for such an evaluation giving $K' = (9.5 \pm 0.8) \times 10^6\ \mathrm{M^{-1}}$.

### 3.2. Formation kinetics

The overall reaction for the formation of the thallium(III) porphyrin proved to be of second-order kinetics, i.e., first order for each reagent species (Eq. (5)):

$$k_+ t = \frac{1}{c_{\mathrm{Tl^{3+}}} - c_{\mathrm{H_2P}}} \ln \frac{c_{\mathrm{H_2P}}(c_{\mathrm{Tl^{3+}}} - [\mathrm{Tl^{III}P}])}{c_{\mathrm{Tl^{3+}}}(c_{\mathrm{H_2P}} - [\mathrm{Tl^{III}P}])} \qquad (5)$$

Table 1
Characteristic absorption data of $H_2P^{4-}$ and $Tl^{III}P^{3-}$

| | $H_2P^{4-}$ | | $Tl^{III}P^{3-}$ |
|---|---|---|---|
| Soret-band λ in nm (ε in $M^{-1}$ $cm^{-1}$) | 413 ($4.66 \times 10^5$) | | 428 ($5.73 \times 10^5$) |
| $Q(1,0)$ transition λ in nm (ε in $M^{-1}$ $cm^{-1}$) | $Q_y$: 516 (16700) | $Q_x$: 579 (7290) | 562 (21100) |
| $Q(0,0)$ transition λ in nm (ε in $M^{-1}$ $cm^{-1}$) | $Q_y$: 553 (8150) | $Q_x$: 633 (4250) | 603 (10800) |

Table 2
Characteristic emission data of free-base and thallium(III) porphyrins

| | $H_2P^{4-}$ | | $Tl^{III}P^{3-}$ | |
|---|---|---|---|---|
| $S_1$-fluorescence λ in nm | 647 | 703 | 611 | 663 |
| Quantum yield | 0.0753[a] (0.0624[a] from $Q_y$, 0.0562[b] from Soret) | | $7.94 \times 10^{-4}$ ($2.24 \times 10^{-4}$ from Soret) | |
| $\phi_{IC}$ (to $Q_x$) | 0.828 (from $Q_y$), 0.746 (from Soret) | | 0.282 (from Soret) | |
| Stokes-shift ($cm^{-1}$) | 342 | | 217 | |
| $S_2$-fluorescence λ (nm) | 474 | | 482 | |
| Stokes-shift ($cm^{-1}$) | 3116 | | 2618 | |

[a] Rhodamine-B was used as a reference for determination of the fluorescence quantum yield at Q-band excitations [28].

[b] $Ru(bpy)_3Cl_2$ was used as a reference at Soret-band excitations [29].

$$k_{-}t = \ln\frac{[Tl^{III}P]_0}{[Tl^{III}P]} \tag{6}$$

$$K' = \frac{k_+}{k_-} = \frac{(270 \pm 20)\,M^{-1}\,s^{-1}}{(2.8 \pm 0.3) \times 10^{-5}\,s^{-1}} \tag{7}$$

Notably, subsequent to the encounter of the reagent species, after the formation of the intermediate SAT complex, detachments of the protons from the porphyrin and those of the chloro ligands from the chlorothallate(III) complexes take place, but these processes must be faster than the previous step (i.e., the formation of the i-SAT complex), especially in aqueous solution [11]. Nevertheless, the rate constant for the formation of the thallium(III) porphyrin ($k_+ = 270 \pm 20\,M^{-1}\,s^{-1}$) is therefore lower than that observed for the formation of the corresponding mercury(II) porphyrin ($790 \pm 60\,M^{-1}\,s^{-1}$) [34], because in the previous case the porphyrin reagent must truly displace the monodentate chloro ligands from the coordinative sphere of the thallium(III) ion. Hence, the saturation character, which is typical for equilibrial reactions, i.e., the sigmoidal shape of the partial molar fraction versus time curve can be hardly observed in this case (Fig. 4).

This is also a consequence of the rather low rate constant for the dissociation of thallium(III) porphyrin (Eq. (6), $k_- = (2.8 \pm 0.3) \times 10^{-5}\,s^{-1}$), which was determined by a dilution method. This value of $k_-$ was measured in neutral solution containing 1 M chloride. Notably, under these circumstances, the attack of chloride or rather hydrogen ions cannot play any role in the dissociation of the porphyrin complex. Consequently, the apparent stability constant ($K'$) can be simply expressed as the ratio of the rate constants for the forward and backward reactions (Eq. (7)).

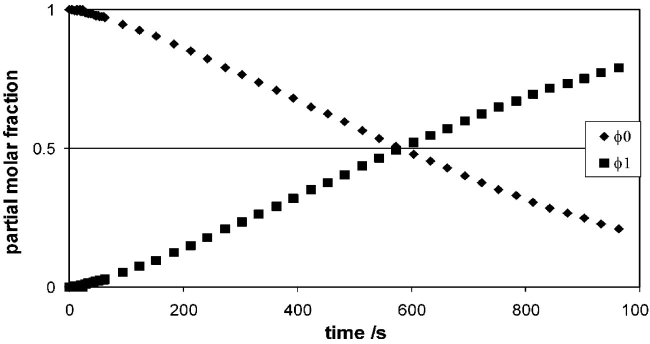


Fig. 4. Formation kinetics of thallium(III) porphyrin (■) at $1.7 \times 10^{-6}$ M free-base porphyrin (◆) and $5.0 \times 10^{-6}$ M thallium(III) ion initial concentrations.

### 3.3. Emission spectra

The first singlet excited state ($S_1$ from $Q_x$ absorption) of free-base porphyrin produces relatively intense fluorescence (the quantum yield of which is 0.08 [35]), but this emission can also be realized by excitation to the second ($S_2$ from Soret absorption) or to another first singlet excited state ($S'_1$ from $Q_y$ absorption in the case of free-base porphyrin having two different polarization dipole moments, in the $x$ and $y$ directions, due to the hydrogen atoms on the pyrrolic nitrogens) through internal conversion (Table 2).

The energy of the emitted photons increases, i.e., hypsochrome effect on the fluorescence from $S_1$ state occurs upon coordination of thallium(III) ion (Fig. 5). Moreover, the $S_1(0,0) \rightarrow S_0(1,0)$ transition becomes more effective than $S_1(0,0) \rightarrow S_0(0,0)$, indicating a larger difference in the nuclear geometries of the ground- and excited-states. This is manifested in the Stokes-shift, which provides information about the structural change (e.g., about the extent of the distortion) occuring upon excitation. Thallium(III) 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin displays lower Stokes-shift than the free-base porphyrin does, indicating that the previous species is more distorted in the ground state, i.e., its excitation results in a smaller change in the nuclear geometry.

Notably, the hydrogen atoms in the core of the free-base porphyrin cease the degeneration of the lowest unoccupied molecular orbital (LUMO $e_g \rightarrow Q_x + Q_y$ [36]), resulting in four Q-bands (Fig. 3), while most metalloporphyrins show only two intense bands in the same region, due to the degeneration of the LUMO. This phenomenon may affect the difference between the Stokes-shifts of SAT metalloporphyrins [30,31,33]. Addition-

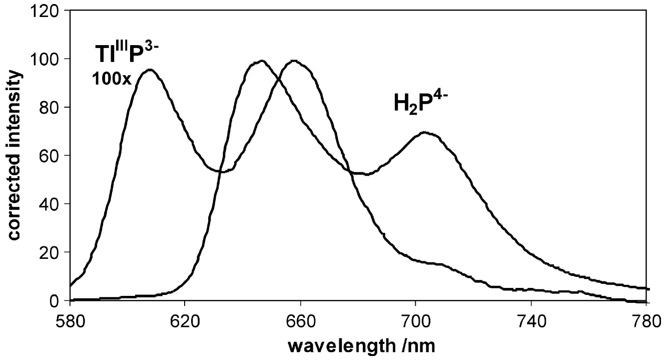


Fig. 5. $S_1$-fluorescence spectrum of the free-base and thallium(III) porphyrins.

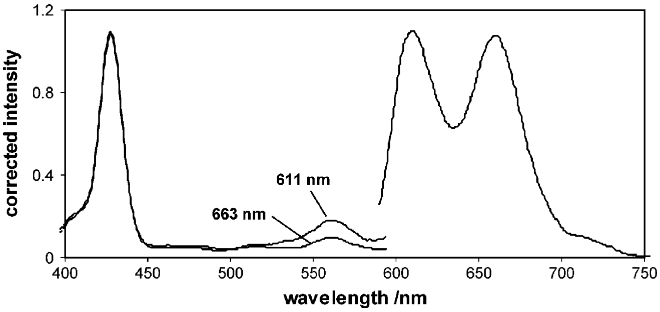


Fig. 6. $S_1$-fluorescence ($\lambda_{ex} = 428$ nm) and excitation ($\lambda_{em} = 611$ and 663 nm) spectra of the thallium(III) porphyrin.

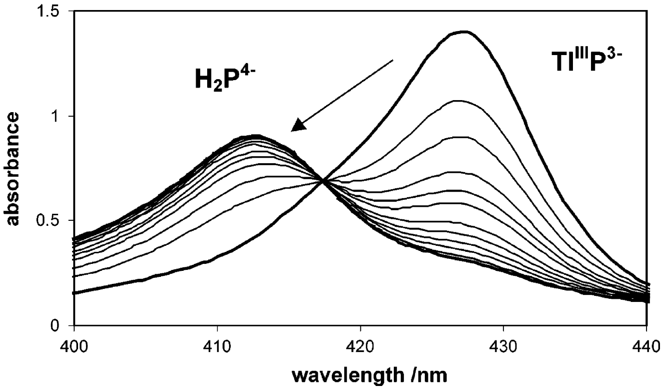


Fig. 7. Sequential spectra from Soret-band photolysis of solution containing $3 \times 10^{-6}$ M porphyrin and thallium(III) ($\ell$=1 cm).

ally, a more significant contribution to these spectral effects may be attributed to different types of ring-distortion: for example mercury(II) 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin ($Hg^{II}P^{4-}$) has a dome-shape [31,33], whereas the corresponding thallium(III) complex must have a more distorted, probably a saddle-shaped, structure, which is manifested in a diminished fluorescence intensity 30 times lower than that displayed by $Hg^{II}P^{4-}$ (0.00079 versus 0.024 [31,33]). The thallium(III) porphyrin has a lower Stokes-shift than the free-base porphyrin (Table 2), while the mercury(II) complex has a larger one (388 $cm^{-1}$ [31]). This indicates that the ground-state structure of the thallium(III) porphyrin is rather similar to the first excited-state saddle-distorted one, while the ground state of the mercury(II) porphyrin has a strongly different dome-shape.

Besides the distortion to saddle-shape induced by the coordinated thallium(III) ion, its heavy-atom effect can also contribute to the two orders of magnitude decrease in the fluorescence intensity of the SAT complex compared to that of the free-base porphyrin. As a result of the previous effects, in the case of the metalloporphyrin, intersystem crossing becomes more efficient than internal conversion and fluorescence (Table 2).

The excitation spectra show (Fig. 6) that two emission bands originate from the same electronically excited state. These are assigned to transitions to different vibronic states of the (electronic) ground state.

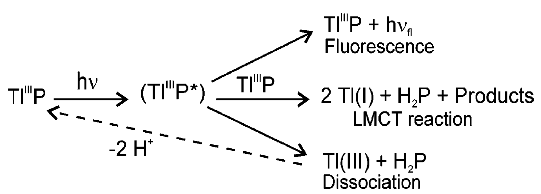
Fluorescence from the second excited singlet state ($S_2$) can be scarcely observed [37]. Nevertheless, this type of emission was also detected for both the Tl(III) complex and the free-base porphyrin. Regarding the $S_2$-fluorescences, the relation between the corresponding Stokes-shifts of these two species is similar to that of the $S_1$-fluorescences (Table 2).

### 3.4. Photochemical activity

According to our observations [30–33], subsequent to the photoinitiated charge transfer from the delocalized π-system of the porphyrin ligand to the metal center (LMCT), a much more efficient back electron transfer from the metal to the ligand (MLCT) takes place at normal (coplanar) metalloporphyrins than at SAT complexes. The out-of-plane position of the metal ion, combined with its decreased positive charge and, thus, increased size, due to its reduction, strongly weakens the coordinative bond. Hence, the detachment of the reduced metal occurs much more probably than in the case of a normal metalloporphyrin. Moreover, the hindered back electron transfer (MLCT) promotes a further oxidation of the ligand, resulting in the cleavage of the porphyrin ring. According to our expectation, Soret-band irradiation of both air-saturated and deoxygenated solutions of thallium(III) 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin leads to the degradation of the complex, confirming its SAT character. Deviating from the SAT metalloporphyrins studied so far, the relatively high stability constant of this Tl(III) complex made us possible to carry out its photolysis in a solution containing porphyrin and thallium(III) at the same concentration ($3 \times 10^{-6}$ M), i.e., in stoichiometric ratio (1:1). Even if no excess of Tl(III) was in this solution, most of the porphyrin ligands (85%) and, thus, the metal ions existed as metalloporphyrin. Upon irradiation of this solution (at the Soret-band) a decrease of the absorption of the complex was observed, accompanied with the gradual increase of another peak (at 413 nm) assigned to the free-base porphyrin (Fig. 7).

On the basis of the absorption changes and the corresponding extinction coefficients, the concentration of the free-base porphyrin released is somewhat higher than half of the complex disappeared. This phenomenon indicates that a photoinduced LMCT step is followed by thermal electron transfers, reducing altogether two Tl(III) ions to Tl(I) on account of the oxidative degradation of one porphyrin (Scheme 1). The products of this reactions are open-chain dioxo-tetrapyrrol derivatives.

Therefore, upon degradation of one macrocyclic ligand, another one is released as free-base porphyrin. This observation provides further evidence for our earlier conclusion drawn by the study of the photochemistry of mercury(II) 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin that four electrons originate from the oxidation of one porphyrin-skeleton in the photolyses of s-SAT metalloporphyrins [31]. These results are in



Scheme 1. Photoinduced reactions of thallium(III) 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin.

Table 3
Photochemical quantum yields for the degradation of the thallium(III) porphyrin ($\Phi \times 10^5$) at different excitation wavelengths in air-saturated and deoxygenated solutions

| | Air-saturated | Argon-saturated |
|---|---|---|
| Soret-band (429 nm) | 2.79 | 1.45 |
| Q-band (562 nm) | 1.49 | 2.68 |

accordance with those observed for the photo-oxygenation of thallium(I) [25] and magnesium(II) *meso*-tetraphenylporphyrin [38], moreover for the chemical oxidation of zinc(II) *meso*-tetraphenylporphyrin [39], giving open-chain benzoylbilitriene (bilinone) by a way of a mechanism involving only one oxygen molecule.

Since the concentration of the ligand released exceeds half of the complex disappeared, photodissociation also occurs (Scheme 1), similarly to the case of mercury(II) porphyrin [31]. While at stoichiometric concentrations of the porphyrin and the thallium(III) ions 35% of the total quantum yield was the efficiency of the photodissociation, no dissociation was observed at fivefold excess of metal ion, i.e., it was entirely depressed through the complex equilibrium.

However, only Soret-band irradiation induces this reversible photodissociation. Excitation in the Q-region results in simply photodegradation, which is valid for all s-SAT metallo-(mono-) porphyrins we studied so far [30–33]. This means that the repulsive potential surface of the state responsible for the dissociation is energetically close to that of the second excited states (Soret-absorption → $S_2$, $T_2$), because the potential surfaces of the first excited states (Q-absorption → $S_1$, $T_1$) do not overlap with the repulsive one. Interestingly, deoxygenation takes opposite effects on the photolyses in these two different absorption regions (Table 3).

These results suggest that this thallium(III) porphyrin in triplet-2 state (formed via intersystem crossing subsequent to Soret-band excitation) can react with dissolved oxygen, which only quenches the triplet-1 state of the complex (formed via Q-excitation followed by ISC). The latter interaction diminishes the efficiency of the LMCT process.

The quantum yields for the photoredox degradation of the thallium(III) porphyrin are one order of magnitude less than those observed in the case of the corresponding thallium(I) complex under similar conditions [30]. These results indicate that the redox potential of the metal center cannot be the determining factor in this process, even if photoinduced LMCT is its initial step. Otherwise, the porphyrin complex of the much more oxidative thallium(III) ion should undergo a more efficient photoinduced degradation. Instead, the size of the metal center plays crucial role in this respect, basically determining the structure and the kinetic lability of the s-SAT metalloporphyrin. The coordination bond between a larger metal ion in out-of-plane position and the porphyrin is much weaker than for a smaller metal center located closer to the core of the porphyrin. This conclusion is supported by the values of the formation equilibrium constants and the ionic radii. The equilibrium constant for the complex of the thallium(III) ion of 95 pm radius is $9.5 \times 10^6\ \mathrm{M}^{-1}$, while $\beta = 3.5 \times 10^3\ \mathrm{M}^{-2}$ in the case of thallium(I) of 147 pm radius [30]. Larger ionic size results in not only lower thermodynamic stability, but higher kinetic lability as well. The latter property is very important for the detachment of the reduced metal subsequent to the LMCT step.

## 4. Conclusion

The thallium(III) 5,10,15,20-tetrakis(4-sulphonato-phenyl) porphyrin as a SAT metalloporphyrin is formed in equilibrial reaction of the metal ion and the free-base porphyrin. This reaction is much faster than the formation of normal (coplanar) complexes. For monitoring the formation of this metalloporphyrin, the shifts of the characteristic bands (compared to those of the free-base porphyrin) in the electronic spectra can be used. The directions of these shifts characteristic for SAT complexes are opposite to those observed in the case of normal metalloporphyrins, both for the Soret- and Q-bands in the absorption spectra and for the emission bands in the $S_1$-fluorescence spectra. The spectral behavior of this thallium(III) porphyrin confirms the general validity of our earlier observations regarding other SAT metalloporphyrins.

The significant decrease in the intensity of $S_1$-fluorescence from the porphyrin upon coordination of thallium(III) is a result of the heavy-atom effect and the distortion to saddle shape as well. Also the out-of-plane position of thallium(III) induces the increase in the photoredox activity of the metalloporphyrin compared to that of the free ligand. In the case of a SAT structure, photodissociation also occurs upon Soret-band excitation.

Consequently, the spectral, equilibrial, kinetic and photochemical features of thallium(III) 5,10,15,20-tetrakis(4-sulphonatophenyl)porphyrin efficiently contribute to our results on the basis of which we are able to more undoubtedly distinguish the SAT metalloporphyrins of distorted structure from the normal (coplanar) complexes. This may be especially important if the size of the metal center is in the transition range (70–90 pm radius). Similar studies with water-soluble cadmium(II) and lead(II) porphyrins are in progress.

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## References

[1] C.K. Mathews, K.E. van Holde, K.G. Ahern, Biochemistry, Addison Wesley Longman, San Francisco, 2000.
[2] R.H. Garrett, C.M. Grisham, Biochemistry, Saunders College Publishing, 1999.
[3] G. Knör, A. Strasser, Inorg. Chem. Commun. 9 (2005) 471.
[4] M.D. Lim, I.M. Lorkovic, P.C. Ford, J. Inorg. Biochem. 99 (2005) 151.
[5] G.G. Martirosyan, A.S. Azizyan, T.S. Kurtikyan, P.C. Ford, Chem. Commun. (2004) 1488.
[6] E.B. Fleischer, J.H. Wang, J. Am. Chem. Soc. 82 (1960) 3498.
[7] H.J. Callot, B. Chevrier, R. Weiss, J. Am. Chem. Soc. 101 (1979) 7729.

[8] K.M. Barkigia, J. Fajer, A.D. Adler, G.J.B. Williams, Inorg. Chem. 19 (1980) 2057.
[9] R.J. Abraham, G.H. Barnett, K.M. Smith, J. Chem. Soc., Perkin I. (1973) 2142.
[10] J.Y. Tung, J.-H. Chen, Inorg. Chem. 39 (2000) 2120.
[11] M. Inamo, N. Kamiya, Y. Inada, M. Nomura, S. Funahashi, Inorg. Chem. 40 (2001) 5636.
[12] M. Tabata, M. Tanaka, J. Chem. Soc., Chem. Commun. (1985) 42.
[13] M. Tabata, W. Miyata, N. Nahar, Inorg. Chem. 34 (1995) 6492.
[14] C. Grant, P. Hambright, J. Am. Chem. Soc. 91 (1969) 4195.
[15] L.R. Robinson, P. Hambright, Inorg. Chem. 31 (1992) 652.
[16] C. Stinson, P. Hambright, J. Am. Chem. Soc. 99 (1977) 2357.
[17] K.M. Barkigia, M.D. Berber, J. Fajer, C.J. Medforth, M.W. Renner, K.M. Smith, J. Am. Chem. Soc. 112 (1990) 8851.
[18] M.F. Hudson, K.M. Smith, J. Chem. Soc., Chem. Commun. (1973) 515.
[19] O. Bilsel, J. Rodriguez, S.N. Milam, P.A. Gorlin, G.S. Girolami, K.S. Suslick, D. Holten, J. Am. Chem. Soc. 114 (1992) 6528.
[20] G. Ricciardi, A. Rosa, E.J. Baerends, S.A.J. van Gisbergen, J. Am. Chem. Soc. 124 (2002) 12334.
[21] X.-J. Liu, J.-K. Feng, A.-M. Ren, X. Zhou, Chem. Phys. Lett. 373 (2003) 197.
[22] H.J. Ledon, M. Bonnet, J. Am. Chem. Soc. 103 (1981) 6209.
[23] M.R. Detty, S.L. Gibson, J. Am. Chem. Soc. 112 (1990) 4086.
[24] M. Tabata, K. Ozutsumi, Bull. Chem. Soc. Jpn. 65 (1992) 1438.
[25] K.M. Smith, J.J. Lai, Tetrahedron Lett. 21 (1980) 433.
[26] K. Heinrich, R.W. Matthews, P.A. Tasker, Inorg. Chem. 16 (1977) 3293.
[27] M.C. Richoux, P. Neta, A. Harriman, J. Chem. Soc., Faraday Trans. 2 82 (1986) 201.
[28] J.N. Demas, G.A. Crosby, J. Phys. Chem. 75 (1971) 8.
[29] J. van Houten, R.J. Watts, J. Am. Chem. Soc. 98 (1976) 4853.
[30] Z. Valicsek, O. Horváth, K.L. Stevenson, Photochem. Photobiol. Sci. 3 (2004) 669.
[31] O. Horváth, Z. Valicsek, A. Vogler, Inorg. Chem. Commun. 7 (2004) 854.
[32] R. Huszánk, O. Horváth, Chem. Commun. 2 (2005) 224.
[33] O. Horváth, R. Huszánk, Z. Valicsek, G. Lendvay, Coord. Chem. Rev. 250 (2006) 1792.
[34] Z. Valicsek, O. Horváth, unpublished work.
[35] K. Kalyanasundaram, M. Neumann-Spallart, J. Phys. Chem. 86 (1982) 5163.
[36] M. Kruk, A. Karotki, M. Drobizhev, V. Kuzmitsky, V. Gael, A. Rebane, J. Lumin. 105 (2003) 45.
[37] J.S. Baskin, H.-Z. Yu, A.H. Zewail, J. Phys. Chem. A 106 (2002) 9837.
[38] K.M. Smith, S.B. Brown, R.F. Troxler, J.J. Lai, Tetrahedron Lett. 21 (1980) 2763.
[39] B. Evans, K.M. Smith, J.A.S. Cavaleiro, J. Chem. Soc., Perkin I (1978) 768.