



A spectrophotometric and thermodynamic study of the sitting-atop complex formation from reaction between free base meso-tetraarylporphyrins and zirconyl nitrate in chloroform solution

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ABSTRACT

The sitting-atop complexation of meso-tetraarylporphyrins and its para-substituted derivatives ($H_2t(4-X)pp$, X: H, Br, Cl, $CH(CH_3)_2$, OCH_3 , CH_3), as electron donors, with zirconyl, as an electron acceptor, have been investigated spectrophotometrically in chloroform. The mole ratio studies based on physicochemical techniques were employed clearly and revealed the formation of 1:1 sitting-atop complexes which was confirmed by UV–vis, 1H NMR and IR spectroscopic data. The value of the formation constant was estimated for each complex using a nonlinear optimization of the complex absorbance vs. mole ratio data by package KINFIT. The results showed that the stability of these complexes decreases with the temperature enhancement. Thermodynamic parameters, ΔG° , ΔH° and ΔS° , of the SAT complexes have been determined from the temperature dependence of formation constants by Van't Hoff equation. Also, the influence of the substituents of the aryl rings in $H_2t(4-X)pp$ on the stability of the SAT complexes is discussed.

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1. Introduction

Porphyrins have been extensively studied as photosynthetic mimics [1–3], photodynamic therapy agents [4,5], electrocatalysts [6–8] and DNA binding agents [9–11]. These macrocycles form important classes of compounds in biochemistry. Fleischer and Wang introduced the intermediate in the reaction of protoporphyrin IX derivatives with several metal ions in chloroform which was called sitting-atop (SAT) complex [12]. In this intermediate two pyrrolic protons remain yet on the porphyrin. These complexes have been proposed as intermediate in the metallation of porphyrins and may be considered as models for the initial steps of metallation of the macrocycles. In recent years, Funahashi et al. more clearly detected the sitting-atop complexes of some porphyrins with several divalent 3d-block cations in acetonitrile. The very low basicity of acetonitrile causes the pyrrole protons of porphyrin to not be released even after forming the intermediate with metal(II) ion without additional proton acceptors. Therefore, the acid–base property of the solvent is responsible for the stability of the sitting-atop intermediate. They have also been shown that UV–vis absorption spectra of these sitting-atop complexes depend on the number of electrons and the size of the divalent cation [13–16].

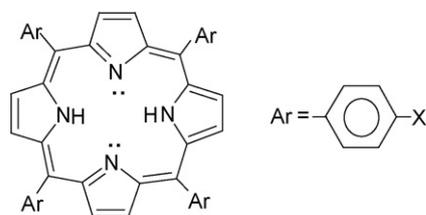
In our previous works, the selection of convenient conditions permitted us to successfully prepare the some sitting-atop complexes as solid. Several spectral signatures including 1H NMR, UV–vis and IR spectroscopies demonstrated out-of-plane deformation of the porphyrin core, which are prevalent in the sitting-atop complexes [17–19].

High-valent metal-oxo complexes have long been intensively studied over the last decades. Classical oxidants, such as CrO_3 and MnO_4^- , are often employed as oxidative catalysts in organic synthetic reactions and there is a clear need in establishing factors governing the reactivities of $M=O$ complexes towards hydride abstraction and oxo-transfer reactions to facilitate the future design of chemo- and regio-selective oxidizing agents. Therefore, in connection with our previous studies carried out on the electron donor–acceptor complexes of meso-tetraarylporphyrins with various acceptors [20–22] and subsequent to the presentation of the thermodynamics of the reactions between meso-tetraarylporphyrins and uranyl [23], here we report on the results of the spectrophotometric and thermodynamic studies concerning the sitting-atop complexation between them and zirconyl as smaller ion in chloroform solution (because of very low basicity of it).

2. Experimental

Benzaldehyde and its para-substituted derivatives were obtained from Merck and were used as received. Pyrrole was pur-

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X = H, Br, Cl, CH(CH₃)₂, OCH₃, CH₃

Fig. 1. *Meso*-tetraarylporphyrins (H₂t(4-X)pp).

chased from Merck and distilled before used. The other solvents that were employed for the synthesis of *meso*-tetraarylporphyrins were obtained from Merck and were used without no purification. *Meso*-tetraphenylporphyrin and its derivatives, Fig. 1, were prepared by the literature methods [24]. ZrO(NO₃)₂·xH₂O (*x* is 32% determined gravimetrically), was commercial product obtained from Fluka and was used as received. Chloroform solvent for UV–vis measurements (Merck) was distilled over K₂CO₃ before use.

All of the electronic absorption spectra and UV–vis measurements were obtained in chloroform on a GBC Cintra 6 spectrophotometer, utilizing a Lauda Ecoline RE 206 thermostat which allowed the temperature to be maintained constant to ±0.05 °C. The cell had an optical path length of 1 cm. The ¹H NMR spectra were recorded on a Bruker 400 MHz spectrometer in CDCl₃. For FT-IR spectra, a Magna 550 Nicolet spectrometer was applied.

Fresh solutions of *meso*-tetraarylporphyrins and ZrO(NO₃)₂·xH₂O were prepared before each series of measurements by dissolving precisely weighed amounts of them in the appropriate volumes of chloroform and methanol, respectively. Addition of zirconyl nitrate solution in titrations was made by a Hamilton microsyringe.

In a typical measurement, the solution of *meso*-tetraarylporphyrin (8 × 10⁻⁶ M) in chloroform was titrated with ZrO(NO₃)₂·xH₂O (8 × 10⁻⁴ M) and the absorbance of the solution (in λ_{max} of the related SAT complex) vs. C_M/C_I were plotted, on the basis of mole ratio method. These photometric titrations carried out at 0.0, 5.0, 10.0 and 15.0 °C.

Table 1

UV–vis results of the various *meso*-tetraarylporphyrins and related sitting-atop complexes with zirconyl.

<i>meso</i> -tetraarylporphyrin sitting-atop complex shifts	λ _{max} (nm)				
	Soret	Q-bands			
H ₂ tpp	416.7	516.8	551.5	592.0	648.0
(zirconyl)H ₂ tpp	441.9				658.3
Δλ	25.2				10.3
H ₂ t(4-Br)pp	418.9	515.3	550.7	589.6	645.9
(zirconyl)H ₂ t(4-Br)pp	445.4				658.3
Δλ	26.5				12.4
H ₂ t(4-Cl)pp	418.2	517.4	551.0	592.1	649.2
(zirconyl)H ₂ t(4-Cl)pp	442.4				655.7
Δλ	24.2				6.5
H ₂ t(4-CH ₃)pp	418.3	518.4	554.0	593.0	649.0
(zirconyl)H ₂ t(4-CH ₃)pp	452.6				686.8
Δλ	34.3				37.8
H ₂ t(4-CH(CH ₃) ₂)pp	418.9	518.0	553.3	592.3	648.6
(zirconyl)H ₂ t(4-CH(CH ₃) ₂)pp	447.1				668.5
Δλ	28.2				21.9
H ₂ t(4-OCH ₃)pp	419.5	520.5	557.1	596.0	653.0
(zirconyl)H ₂ t(4-OCH ₃)pp	452.6				686.8
Δλ	33.1				33.8

Δλ: shifts in the positions of absorption bands of the *meso*-traarylporphyrins upon the sitting-atop complexation.

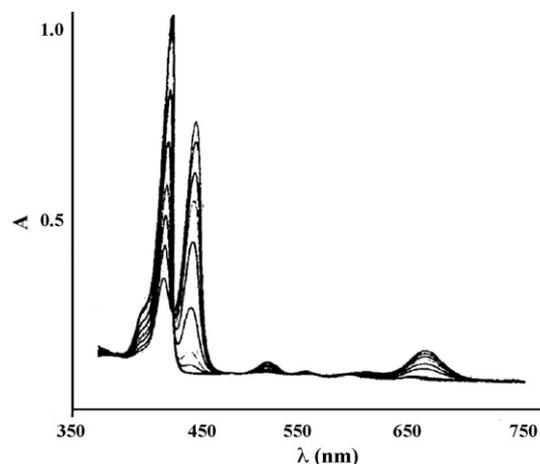


Fig. 2. UV–vis titration of H₂tpp (1.5 × 10⁻⁵) with ZrO(NO₃)₂·xH₂O (1.0 × 10⁻⁵) in chloroform at 25 °C. The isosbestic point appears at 427 nm.

For synthesis of (zirconyl)H₂t(4-CH(CH₃)₂)pp, 0.5 mmol *meso*-tetraarylporphyrin and 0.5 mmol ZrO(NO₃)₂·xH₂O were grinded in a mortar at ambient temperature, with dropwise adding of 1 ml methanol during 30 min. The green product was dried under vacuum at 50 °C.

3. Results and discussion

UV–vis spectra of *meso*-tetraphenylporphyrin and its para-substituted derivatives in chloroform show five original absorption bands (Soret band and Q bands) that upon the titration with ZrO(NO₃)₂·xH₂O are gradually changed to two new bands in upper wavelengths. The purple color of the porphyrin solution on this interaction is converted to green. The results of electronic absorption and titration of H₂tpp (as an instance) have been presented in Table 1 and Fig. 2, respectively.

¹H NMR spectrum of the 1:1 mole ratio solution of ZrO(NO₃)₂·xH₂O and H₂t(4-OCH₃)pp in CDCl₃ (Fig. 3) show five signals for β-pyrrole (one signal), phenyl ring protons (two signals), methoxy groups (one signal) and NH (one signal) which illustrate that two hydrogen atoms are still remained on the nitrogens of the

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