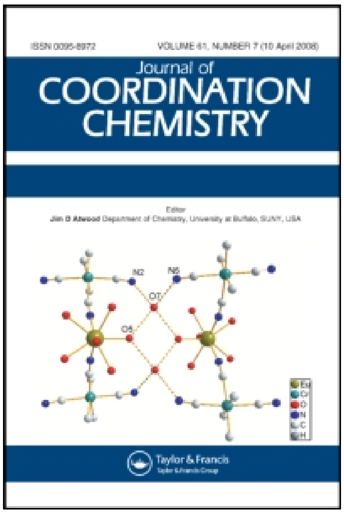

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Thermodynamic studies of sitting-atop (SAT) complexation of uranyl and free base <i>meso</i>-tetraarylporphyrins

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Thermodynamic studies of sitting-atop (SAT) complexation of uranyl and free base *meso*-tetraarylporphyrins

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The interaction of uranyl with *meso*-tetraphenylporphyrin and its para-substituted derivatives ($H_2t(4\text{-}X)pp$, X : H, Br, Cl, $CH(CH_3)_2$, OCH_3, CH_3) in chloroform produced 1 : 1 sitting-atop (SAT) complexes ((uranyl)$H_2t(4\text{-}X)pp$). Formation constants were calculated by computer fitting of complex absorbance *versus* mole ratio data to appropriate equations and found to decrease with temperature increase. Thermodynamic parameters, ΔG^0, ΔH^0 and ΔS^0 were obtained. The formation constants vary with changing of the substituent on the aryl rings of $H_2t(4\text{-}X)pp$ in the following order: (uranyl)$H_2t(4\text{-}OCH_3)pp$ > (uranyl)$H_2t(4\text{-}CH_3)pp$ > (uranyl)$H_2t(4\text{-}CH(CH_3)_2)pp$ > (uranyl)H_2tpp > (uranyl)$H_2t(4\text{-}Br)pp$ > (uranyl)$H_2t(4\text{-}Cl)pp$.

Keywords: Formation constants; Thermodynamics; SAT complex; Porphyrins; Uranyl

1. Introduction

In 1960, Fleischer and Wang first proposed sitting-atop complexes as intermediates of metallation of the protoporphyrin dimethyl ester in chloroform [1]. Two other SAT complexes as intermediates were prepared from hematoporphyrin IX and chloroplatinate(II) in aprotic solvents [2] and from *meso*-tetraphenylporphyrin (H_2tpp) and copper(II) in the presence of triphenylphosphine in microemulsion media [3]. Therefore SAT complexes are metalloporphyrins in which the metal is bonded to fewer than four nitrogen atoms and may be considered as models for the initial steps of the metallation of macrocycles. Tanaka *et al.* [4] have studied the reaction of some divalent metal ions with the free base H_2tpp in DMF, suggesting a pre-equilibrium between metal ions and *meso*-tetraphenylporphyrin and formation of pre-complexes M-H_2tpp prior to metal insertion and proton release. Hambright and Robinson obtained formation constants for Zn(II) SAT complexes with some *meso*-tetraphenylporphyrins in DMF [5]. Funahashi *et al.* detected the SAT complex formed by reaction between Cu^{2+} and *meso*-tetraphenylporphyrin in acetonitrile [6–8]. Recently, thermodynamic parameters for the 1 : 1 or 2 : 1 molecular interactions of various organotin(IV) compounds with *meso*-tetraarylporphyrins that had structures close to SAT complexes were reported [9, 10].

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Complexation of uranyl and ligands containing various donors such as nitrogen, oxygen, and sulfur have been studied extensively [11]. Lomova and Andrianova [12] reported that reaction of H_2tpp with uranyl acetate in phenol produced the double decker U(IV)$(tpp)_2$ and U(III)$(tpp)_3$. In 2001 Sessler *et al.* used an expanded porphyrin to coordinate UO_2^{2+}showing that the macrocycle twisted slightly to accommodate the uranyl while adopting an aromatic structure [13]. The first metal complex from the cyclo[*n*]pyrrole series of expanded porphyrins was formed when cyclo[6]pyrrole was treated with the uranyl cation under aerobic conditions [14].

As compared to low valent uranium cations, the uranyl cation is relatively well studied. However, most work involving this cation has focused on its behavior in aqueous solution [15]. In this work, for the first time we present the SAT complexation of uranyl with H_2tpp and its para-substituted derivatives (figure 1) and the thermodynamic parameters in chloroform. The selection of uranyl as the metal ion (because of the high oxidation state of uranium) and chloroform as solvent caused the SAT complexes to be stable and characterizable by UV-Vis, ^{1}H NMR, and FT-IR techniques.

2. Experimental

Uranyl nitrate hexahydrate, propionic acid, chloroform, benzaldehyde and para-substituted benzaldehyde (bromo, chloro, methyl, isopropyl, and methoxy) were purchased from Merck and used without further purification. Pyrrole obtained from Merck was distilled before use. *Meso*-tetraphenylporphyrin and its para-substituted derivatives were prepared and purified by usual methods [16–18]. Chloroform for UV-Vis measurements was distilled over K_2CO_3 before use.

UV-Vis absorption spectra were obtained by a GBC Cintra 6 UV-Vis spectrophotometer equipped with a Lauda Ecoline RE 206 thermostat. The ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer and the FT-IR spectra carried out in a Magna 550 Nicolet spectrometer using KBr pellets.

In a typical measurement, the solution of *meso*-tetraarylporphyrin (7.5×10^{-6} M) in chloroform was titrated with $UO_2(NO_3)_2 \cdot 6H_2O$ (3×10^{-3} M) and the absorbance of

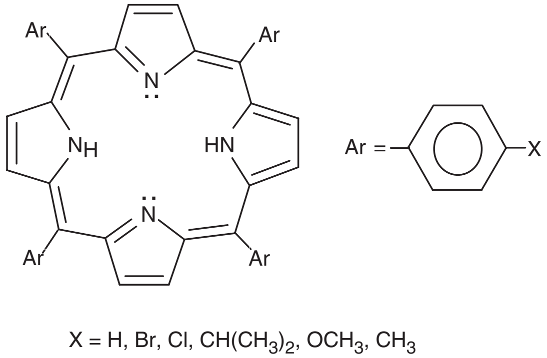

Figure 1. *Meso*-tetraarylporphyrins (H_2t(4-X)pp).

the solution (in λ_{max} of the related SAT complex) *versus* $C_{M/}C_L$ was plotted on the basis of mole ratio method [15]. These photometric titrations were carried out at 5.0, 10.0, 15.0 and 20.0°C.

3. Results and discussion

The UV-Vis spectra for titration of H_2tpp and its para-substituted derivatives with $UO_2(NO_3)_2 \cdot 6H_2O$ in chloroform at 25°C were obtained (figure 2) showing changes to the original peaks of free base *meso*-tetrraarylporphyrins (soret band and Q bands) by interaction of uranyl (table 1). The solution of free base porphyrins changes from purple to green with this interaction; increasing the temperature changes the color to the primary purple of porphyrin solutions.

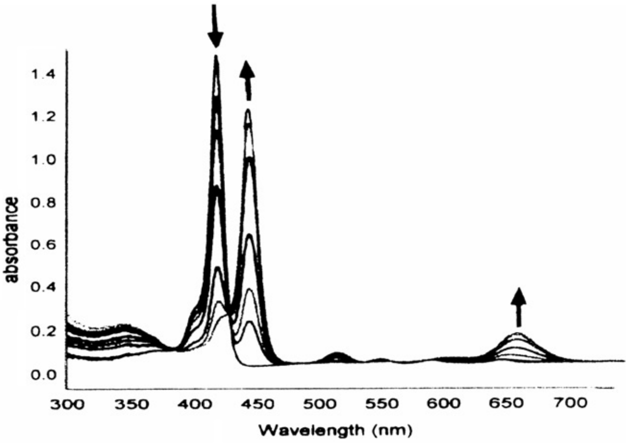

Figure 2. Typical UV-Vis spectra for titration of H_2tpp with $UO_2(NO_3)_2 \cdot 6H_2O$ in chloroform. Bands at 441 and 656 nm are related to the SAT complex with an isosbestic point at 428 nm.

Table 1. UV-Vis peaks λ(nm/$CHCl_3$) of free bases H_2t(4-X)pp and their SAT complexes with uranyl.

Compound	Wavelength (nm)				
H_2tpp	417	514	549	589	646
(uranyl)H_2tpp	441				658
H_2t(4-Br)pp	421	518	555	594	649
(uranyl)H_2t(4-Br)pp	445				659
H_2t(4-Cl)pp	420	512	550	590	646
(uranyl)H_2t(4-Cl)pp	443				661
H_2t(4-$CH(CH_3)_2$)pp	420	519	555	594	650
(uranyl)H_2t(4-$CH(CH_3)_2$)pp	447				669
H_2t(4-OCH_3)pp	419	516	553	591	649
(uranyl)H_2t(4-OCH_3)pp	454				688
H_2t(4-CH_3)pp	419	514	548	591	646
(uranyl)H_2t(4-CH_3)pp	444				669

^{1}H NMR spectra of the 1 : 1 mole ratio for $UO_2(NO_3)_2 \cdot 6H_2O$ and $H_2t(4\text{-}OCH_3)pp$ in $CDCl_3$ (δ −0.25 (2H, NH), δ 4.17 (12H, OCH_3), δ 8.24 (8H, o), δ 7.55 (8H, m), δ 8.55 (8H, β)) showed that two hydrogen atoms remain on nitrogens of the porphyrin. In addition, the N–H and aryl ring signals shift to lower field and the β-hydrogens upfield.

Elimination of soret and Q bands (table 1 and figure 2) in UV-Vis absorption data, thermal instability and the results of ^{1}H NMR spectroscopy indicate uranyl could not drop into the porphyrin cavity, but acted as a σ-electron acceptor and *meso*-tetraarylporphyrins as σ-donors (the bidendate ligands by two pyrrolenine nitrogens). Therefore, we suggest the SAT complex has a structure with a very similar porphyrin core to prior species [19–24]. This conformation induces a distortion in the porphyrin plane enhancing the donor ability of the nitrogen lone pairs by directing them away from the central porphyrin cavity (figure 3). In the IR (400–4000 cm^{-1}) spectra of the free base *meso*-tetraarylporphyrins, an N–H stretching band at 3320 cm^{-1} [25] does not change upon interaction with $UO_2(NO_3)_2 \cdot 6H_2O$. Consequently, there is no intramolecular or intermolecular hydrogen bonding for the N–H of *meso*-tetraarylporphyrins in the SAT complexes.

The non-linear least-squares curve fitting program KINFIT [26], based on Powell's technique [27], was used in formation constants of the resulting complexes. Adjustable parameters are K_f and ε values. The program is based on the iterative adjustment of calculated values of absorbance to observed values by using either the Wentworth matrix technique [28] or the Powell procedure [29, 30].

The data of the photometric titration were best fitted to an ML model (figure 4). Therefore, 1 : 1 SAT complexes (ML) are produced from interactions between uranyl (M) and *meso*-tetraarylporphyrins (L) in solution. The mass balance equation for formation of ML is solved to obtain the equation for free ligand concentration [L]. The resulting equation is

$$K_f[L]^2 + (1 + K_f(C_M - C_L)[L] - C_L = 0 \quad (1)$$

where K_f is the formation constant. The observed absorbance of solution is also given by

$$A_{obs} = \varepsilon_L[L] + \varepsilon_{ML}[ML] \quad (2)$$

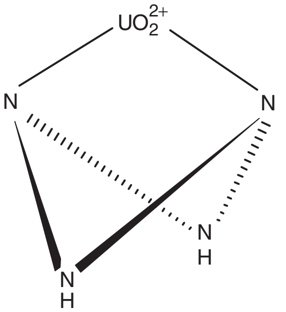

Figure 3. In the scheme only the tetrahedrally tilted pyrrolenine nitrogens of a porphyrin core are shown. Two nitrogen atoms of pyrrolenine on one side of porphyrin plane are electron donors to the uranium.

A_{obs} is the observed absorbance at each titration point and ε values are the molar distinction coefficients. The formation constant can be expressed in terms of the Gibbs free energy change [31, 32]

$$K_f = \exp\left(-\Delta G^0/RT\right) = \exp\left(-\Delta H^0/RT + \Delta S^0/R\right) \tag{3}$$

Values of $\log K_f$ for 1 : 1 SAT complexes at various temperatures are evaluated from computer fitting of the corresponding absorbance-mole ratio data (table 2). The enthalpic and entropic changes of these reactions are calculated by the Van't Hoff plot, equation (4).

$$\log K_f = \left(\frac{-1}{2.303RT}\right)(\Delta H^0 - T\Delta S^0) \tag{4}$$

Plots of $\log K$ *versus* $1000/T$ for the SAT complexes of uranyl with $H_2t(X)pp$ in chloroform were linear; an example is shown in figure 5. The slopes and intercepts

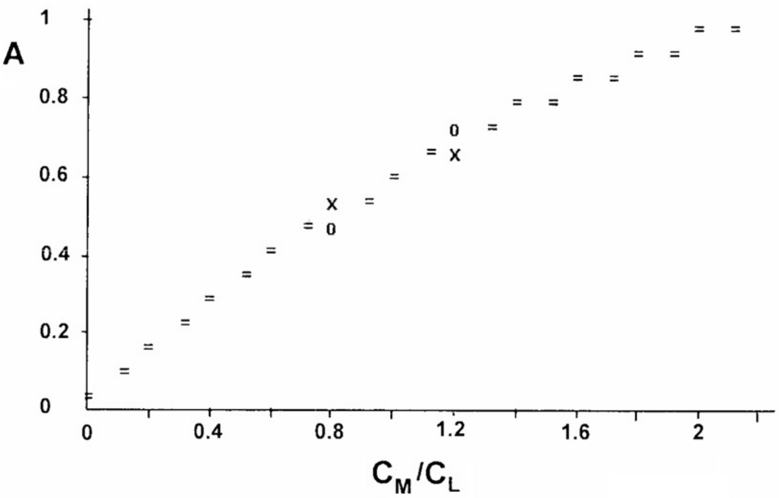

Figure 4. Computer fit of absorbance of $UO_2(NO_3)_2 \cdot 6H_2O/H_2t(4\text{-}Cl)pp$ in chloroform at 443 nm and 15°C as a function of mole ratios. (×) experimental points, (o) calculated points, (=) experimental and calculated points are the same with the resolution of the plot.

Table 2. The logarithm of the formation constants ($\log K$) for the SAT complexes of uranyl with H_2tpp and its para-substituted derivatives in $CHCl_3$.

	Temperature (°C)			
SAT complexes	5	10	15	20
(uranyl)H_2tpp	5.92(±0.01)	5.55(±0.01)	5.32(±0.01)	5.07(±0.01)
(uranyl)H_2t(4-Br)pp	5.63(±0.01)	5.37(±0.01)	5.09(±0.01)	4.83(±0.01)
(uranyl)H_2t(4-Cl)pp	5.49(±0.01)	5.28(±0.01)	5.03(±0.01)	4.80(±0.01)
(uranyl)H_2t(4-CH$(CH_3)_2$)pp	6.22(±0.02)	5.95(±0.01)	5.62(±0.01)	5.35(±0.02)
(uranyl)H_2t(4-OCH_3)pp	6.55(±0.01)	6.16(±0.02)	5.80(±0.03)	5.46(±0.01)
(uranyl)H_2t(4-CH_3)pp	6.10(±0.01)	5.79(±0.01)	5.50(±0.01)	5.21(±0.01)

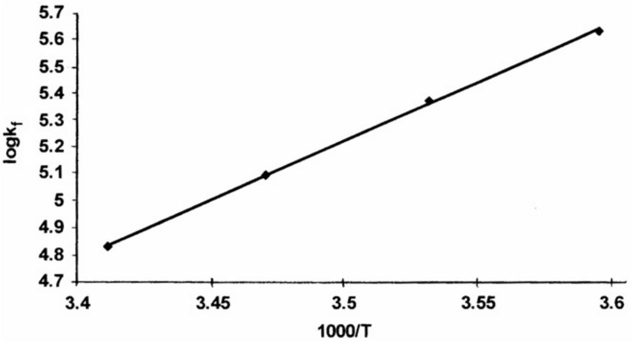

Figure 5. Van't Hoff plot for (uranyl)H_2t(4-Br)pp.

Table 3. The thermodynamic parameters for the SAT complexes from uranyl and free base *meso*-tetraarylporphyrins in chloroform.

SAT complexes	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol K^{-1})	$\Delta G^{0\,a}$ (kJ mol^{-1})
(uranyl)H_2tpp	−86.9(±6.1)	−199.7(±21.3)	−27.4(±0.3)
(uranyl)H_2t(4-Br)pp	−83.65(±1.3)	−192.8(±4.5)	−26.2(±0.1)
(uranyl)H_2t(4-Cl)pp	−72.39(±2.2)	−154.9(±7.8)	−26.2(±0.1)
(uranyl)H_2t(4-$CH(CH_3)_2$)pp	−91.76(±2.9)	−210.6(±10.0)	−29.0(±0.1)
(uranyl)H_2t(4-OCH_3)pp	−113.4(±1.2)	−282.3(±4.3)	−29.2(±0.1)
(uranyl)H_2t(4-CH_3)pp	−92.41(±0.4)	−215.5(±1.5)	−28.2(±0.1)

[a] ΔG^0 at 25°C.

give ΔH^0 and ΔS^0 values (table 3). The free energy values, ΔG^0, are calculated at 25°C.

Temperature variations on SAT complexation (table 2) show that the interactions of $UO_2(NO_3)_2 \cdot 6H_2O$ with *meso*-tetraarylporphyrins are dependent on temperature and the formation constants decrease with increasing temperature.

The data of table 2 show that the values of K_f of the SAT complexes increase from (uranyl)H_2t(4-Cl)pp to (uranyl)H_2t(4-OCH_3)pp at each temperature:

$$\begin{aligned}\text{(uranyl)H}_2\text{t(4-Cl)pp} &< \text{(uranyl)H}_2\text{t(4-Br)pp}\\ &< \text{(uranyl)H}_2\text{tpp} < \text{(uranyl)H}_2\text{t(4-CH}_3\text{)pp}\\ &< \text{(uranyl)H}_2\text{t(4-CH(CH}_3\text{)2)pp}\\ &< \text{(uranyl)H}_2\text{t(4-OCH}_3\text{)pp}\end{aligned}$$

This trend is in accord with better electron donation of the substituent groups on the *meso*-tetraarylporphyrin. Electron-donating substituents (alkyls) increase the formation constant and electron-withdrawing substituents (halogens) decrease it. The methoxy is a π-donor group and the methyl and isopropyl groups are σ-donor, but the isopropyl is a bit stronger. σ-donation is more important than donation. The values of ΔG^0, ΔH^0 and ΔS^0 are negative, indicating strong interactions in these SAT complexes. The negative values of ΔS^0 are related to association of uranyl and the porphyrin.

4. Conclusion

The reaction of uranyl and *meso*-tetraarylporphyrins in chloroform forms (uranyl)H_2t(4-X)pp sitting-atop (SAT) complexes. The formation constants vary on changing substituents on the aryl ring in accord with better electron donation of aryl rings for *meso*-tetraarylporphyrins. The UV-Vis and ^{1}H NMR data for the porphyrin in the SAT complex show a bidentate ligand by two pyrrolenine nitrogens and uranyl is located above or below its plane [20–24].

Acknowledgement

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