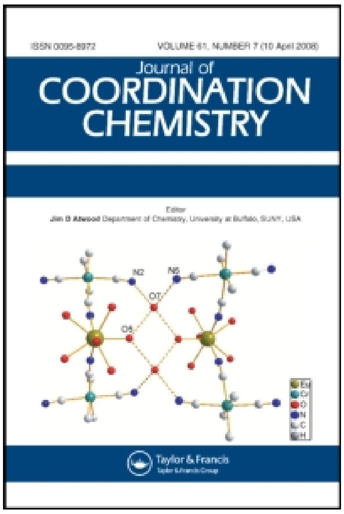

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Thermodynamic studies of sitting-atop complexation between free base meso-tetraarylporphyrins and antimony(III) chloride in chloroform

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Interaction of *para*, *meta* and *ortho*-substituted *meso*-tetraarylporphyrins, ($H_2t(X)pp$, X: OMe, Me, H and Cl) with $SbCl_3$ in chloroform solution afforded 1 : 1 sitting-atop (SAT) complexes ($[(SbCl_3)(H_2t(X)pp)]$). The formation constants were calculated by KINFIT and found to decrease with increasing temperature. The thermodynamic parameters, ΔH°, ΔS° and ΔG°, were obtained. Formation constants of these complexes change with changing substituent (X) on the aryl rings of $H_2t(X)pp$ in the following order: $(SbCl_3)H_2t(4\text{-OMe})pp > (SbCl_3)H_2t(4\text{-Me})pp > (SbCl_3)H_2tpp > (SbCl_3)H_2t(4\text{-Cl})pp > (SbCl_3)H_2t(3\text{-OMe})pp > (SbCl_3)H_2t(3\text{-Me})pp > (SbCl_3)H_2t(2\text{-OMe})pp > (SbCl_3)H_2t(2\text{-Me})pp$.

Keywords: Formation constants; Thermodynamics; SAT complex; Porphyrins; Antimony(III) chloride

1. Introduction

Metalloporphyrin formation is one of the important processes from analytical and bioinorganic points of view. Metalloporphyrins in which the metal is bonded to fewer than four nitrogen atoms are called sitting-atop (SAT) complexes and may be considered as models for the initial steps of metallation of the macrocycle. In 1960, Fleisher and Wang proposed SAT complexes as intermediates of metallation for protoporphyrin dimethyl ester in $CHCl_3$ [1]. Hereafter, SAT complexes as an intermediate were reported, 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]. Funahashi *et al.* detected the SAT complex formed by reaction between Cu^{2+} and *meso*-tetraphenylporphyrin in acetonitrile [4–6]. This first direct detection of the SAT complex $[Cu(H_2tpp)^{2+}]$ was achieved by strategic use of acetonitrile as a solvent with very weak basicity [6]. Recently, it is reported that *meso*-tetraarylporphyrin adducts with diorganotin(IV) dichloride as the acceptor had structures close to SAT complexes [7]. These direct characterizations of SAT complexes led us to investigate antimony(III)

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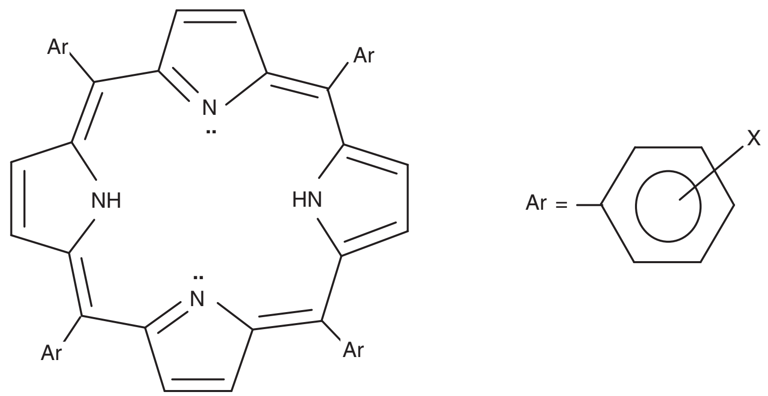

X = H, H_2tpp
X = 4-OMe, H_2t(4-OMe)pp
X = 3-OMe, H_2t(3-OMe)pp
X = 2-OMe, H_2t(2-OMe)pp
X = 4-Me, H_2t(4-Me)pp
X = 3-Me, H_2t(3-Me)pp
X = 2-Me, H_2t(2-Me)pp
X = 4-Cl, H_2t(4-Cl)pp

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

chloride adducts with various *meso*-tetraarylporphyrins, H_2t(X)pp, in non-basic solvents. The suitable selection of electron acceptor and solvent allows preparation of SAT complexes of antimony(III) chloride with *meso*-tetraarylporphyrins. In these adducts *meso*-tetraarylporphyrins are bidentate ligands forming a stable SAT complex. We present formation constants and thermodynamic parameters for the SAT complexation of antimony(III) chloride with a number of free base *para*, *meta* and *ortho*-substituted *meso*-tetraarylporphyrins (figure 1) in chloroform solution.

2. Experimental

Synthesis of porphyrins was carried out with benzaldehyde and *para*, *meta* and *ortho*-substituted benzaldehydes (Merck), distilled pyrrole (Merck), propionic acid and chloroform (Merck). Chloroform for UV-Vis measurements was distilled over K_2CO_3 before use. Antimony(III) chloride was obtained from Merck and used as received.

The UV-Vis absorption spectra were obtained with a GBC Cintra 6 UV-Vis spectrophotometer, equipped with a Lauda Ecoline RE 204 thermostat with a quartz cell of path length 1.0 cm. The absorbances of the solutions were measured at five

Table 1. Mass-balance equations used in the computer program KINFIT for evaluation of spectrophotometric data.

Model	Reactions	Formation constants equations	Mass-balance
I	$M + L \leftrightarrow ML$	$K = [ML]/[M][L]$	$C_M = [M] + [ML]$ $C_L = [L] + [ML]$

temperatures by UV-Vis. The ^{1}H NMR spectra were recorded on a Bruker 500 Ultrashield spectrometer in $CDCl_3$. The residual $CHCl_3$ in the 99.8% atom $CDCl_3$ gives a signal at $\delta = 7.27$ ppm, which was used as a reference. FT-IR spectra were recorded on a Magna 550 Nicolet spectrometer using KBr pellets. *meso*-tetraarylporphyrins and the substituted porphyrins (*para*, *meta* and *ortho*) were prepared and purified by usual methods [8–10] before SAT complexes with $SbCl_3$ in chloroform were prepared.

In this work, solutions of H_2tpp (7×10^{-5} M) and $SbCl_3$ (7×10^{-5} M) are prepared separately. Then on the basis of mole ratio method [11], various solutions of SAT complexes with different C_L/C_M mole ratios were prepared from addition of different amounts of porphyrin solutions to fixed amounts of $SbCl_3$ solution.

The non-linear least-squares curve fitting program KINFIT [12], based on Powell's technique [13], was used to evaluate the formation constants of the resulting complexes. Adjustable parameters are K_f and ε. The program is based on the iterative adjustment of calculated values of absorbance to observed values by using either the Wentworth matrix technique [14] or the Powell procedure [15, 16].

1:1 SAT complexes (ML) result from interactions between *meso*-tetraphenylporphyrin or its derivatives (L) and $SbCl_3$ (M) in solution (table 1). The mass balance equation for formation of ML can be solved to obtain the free ligand concentration [L],

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

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

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

A_{obs} is the observed absorbance at each titration point and ε values are the molar absorptivities. Equilibrium constants can be expressed in terms of the Gibbs free energy change [17, 18]:

$$K_f = \exp(-\Delta G^\circ/RT) = \exp(-\Delta H^\circ/RT + \Delta S^\circ/R), \qquad (3)$$

where ΔH° is the enthalpy change and ΔS° is the entropy change for the reaction.

3. Results and discussion

The UV-Vis absorption spectra for titration of $SbCl_3$ with *meso*-tetraphenylporphyrin and its derivatives are obtained; an example is shown in figure 2 and spectral data are listed in table 2. During the titration, the $SbCl_3$ solution gradually turns green. Interactions of $SbCl_3$ with free base porphyrins led to color change from purple to green.

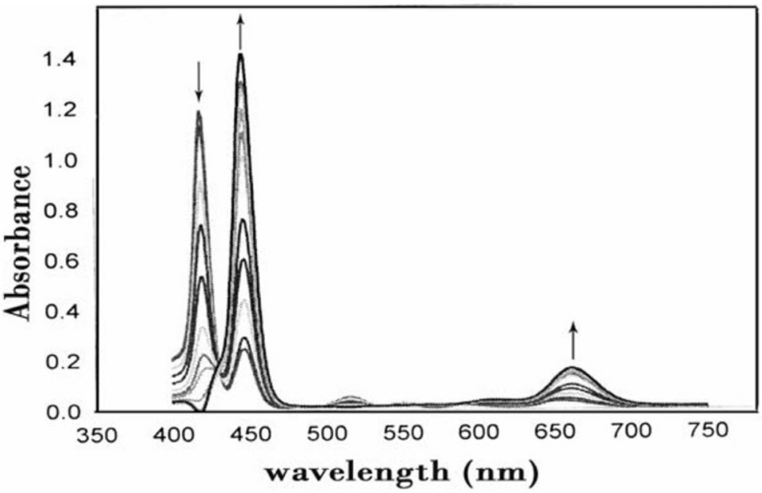

Figure 2. Typical spectra for titration of $SbCl_3$ with $H_2t(3\text{-}Me)pp$ in chloroform. Bands at 445 and 662 nm are related to the SAT complex. There is an isosbestic point at 431 nm.

Table 2. UV-Vis peaks λ ($CHCl_3$/nm) of free bases $H_2t(X)pp$ and their SAT complexes with $SbCl_3$.

Compound	Wavelength (nm)				
H_2tpp	417	514	549	589	646
$(SbCl_3)H_2tpp$	446				660
$H_2t(4\text{-}OMe)pp$	421	518	555	594	649
$(SbCl_3)H_2t(4\text{-}OMe)pp$	453				689
$H_2t(3\text{-}OMe)pp$	420	512	550	590	646
$(SbCl_3)H_2t(3\text{-}OMe)pp$	451				660
$H_2t(2\text{-}OMe)pp$	420	514	548	590	648
$(SbCl_3)H_2t(2\text{-}OMe)pp$	451				654
$H_2t(4\text{-}Me)pp$	419	516	553	591	649
$(SbCl_3)H_2t(4\text{-}Me)pp$	447				671
$H_2t(3\text{-}Me)pp$	419	514	548	591	646
$(SbCl_3)H_2t(3\text{-}Me)pp$	445				663
$H_2t(2\text{-}Me)pp$	415	512	544	588	644
$(SbCl_3)H_2t(2\text{-}Me)pp$	441				653
$H_2t(4\text{-}Cl)pp$	418	514	550	590	646
$(SbCl_3)H_2t(4\text{-}Cl)pp$	448				664

The spectra of a series of solutions containing a constant concentration of $SbCl_3$ and various amounts of the *meso*-tetraarylporphyrins were obtained (mole ratio method) and the continuous variation method (figure 3) was used to determine the stoichiometry [19–21]. Upon addition of porphyrin or its derivatives to the $SbCl_3$ solution, the absorption band becomes more intense and shifts to longer wavelength. On further addition of porphyrin to the $SbCl_3$ solution, the absorption band shifts to longer wavelength and remains almost unchanged at extended ratios>1. These methods confirm formation of 1 : 1 SAT complexes (ML) in solution.

The absorbance-mole ratio data were best fit to the model given in table 1. SAT complexation is accompanied by a relatively strong shift of the absorption bands on porphyrin, towards longer wavelengths and elimination of those bands in

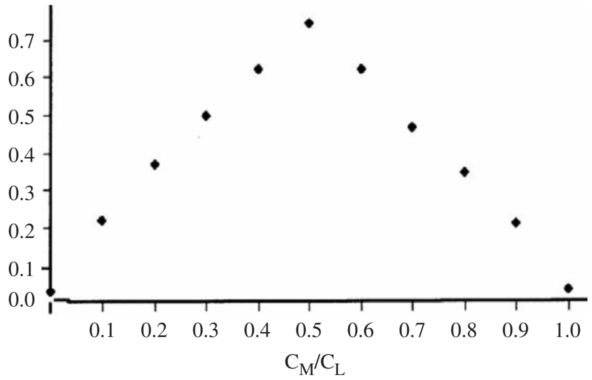

Figure 3. Continuous variation plot for [$(SbCl_3)H_2t(4\text{-}OMe)pp$]; total concentration, 2.8×10^{-5}; $\lambda = 689$ nm.

Table 3. The formation constants K (M^{-1}) for SAT complexes of $H_2t(X)pp$ with $SbCl_3$ in $CHCl_3$ solvent.

		Temperature (°C)				
SAT Complexes		5	10	15	20	25
$(SbCl_3)H_2tpp$	log K	6.99(±0.01)	6.93(±0.02)	6.86(±0.01)	6.79(±0.01)	6.73(±0.01)
$(SbCl_3)H_2t(4\text{-}OMe)pp$	log K	7.15(±0.01)	7.07(±0.01)	6.98(±0.01)	6.88(±0.01)	6.82(±0.01)
$(SbCl_3)H_2t(3\text{-}OMe)pp$	log K	6.87(±0.01)	6.81(±0.01)	6.75(±0.01)	6.70(±0.01)	6.65(±0.01)
$(SbCl_3)H_2t(2\text{-}OMe)pp$	log K	6.54(±0.01)	6.49(±0.01)	6.45(±0.01)	6.40(±0.01)	6.37(±0.02)
$(SbCl_3)H_2t(4\text{-}Me)pp$	log K	7.04(±0.02)	6.97(±0.01)	6.89(±0.01)	6.81(±0.01)	6.74(±0.01)
$(SbCl_3)H_2t(3\text{-}Me)pp$	log K	6.81(±0.01)	6.75(±0.01)	6.70(±0.01)	6.64(±0.01)	6.60(±0.01)
$(SbCl_3)H_2t(2\text{-}Me)pp$	log K	6.12(±0.01)	6.08(±0.01)	6.05(±0.02)	6.01(±0.01)	5.97(±0.01)
$(SbCl_3)H_2t(4\text{-}Cl)pp$	log K	6.95(±0.02)	6.89(±0.01)	6.83(±0.01)	6.77(±0.01)	6.71(±0.01)

product (table 2). Formation constants of the resulting 1 : 1 SAT complexes were measured as a function of temperature and log K values evaluated from the computer fitting of the corresponding absorbance-mole ratio data (table 3). Enthalpic and entropic parameters to these reactions were calculated by Van't Hoff plot (equation 4), obtained from the linear plot of log K *versus* 1/T.

$$\log K_f = (-1/2.303RT)(\Delta H^\circ - T\Delta S^\circ). \tag{4}$$

Plots of log K *vs.* 1000/T for the SAT complexes in chloroform were linear (figure 4). ΔH°, ΔS° and ΔG° values are shown in table 4.

Interactions of $SbCl_3$ with $H_2t(X)pp$ are dependent on temperature (figure 5); table 3 shows that formation constants decrease with increasing temperature.

The data in table 3 show that formation constants of the SAT complexes increase from $H_2t(2\text{-}Me)pp$, $H_2t(2\text{-}OMe)pp$, $H_2t(3\text{-}Me)pp$, $H_2t(3\text{-}OMe)pp$, $H_2t(4\text{-}Cl)pp$, H_2tpp, $H_2t(4\text{-}Me)pp$ to $H_2t(4\text{-}OMe)pp$. At all five temperatures the following order of formation constants is found: $(SbCl_3)H_2t(4\text{-}OMe)pp > (SbCl_3)H_2t(4\text{-}CH_3)pp > (SbCl_3)H_2tpp > (SbCl_3)H_2t(4\text{-}Cl)pp > (SbCl_3)H_2t(3\text{-}OMe)pp > (SbCl_3)H_2t(3\text{-}Me)pp > (SbCl_3)H_2t(2\text{-}OMe)pp > (SbCl_3)H_2t(2\text{-}Me)pp$, in accord with the better electron donation and lower steric effect for the porphyrins. Methoxy is a π-donor group,

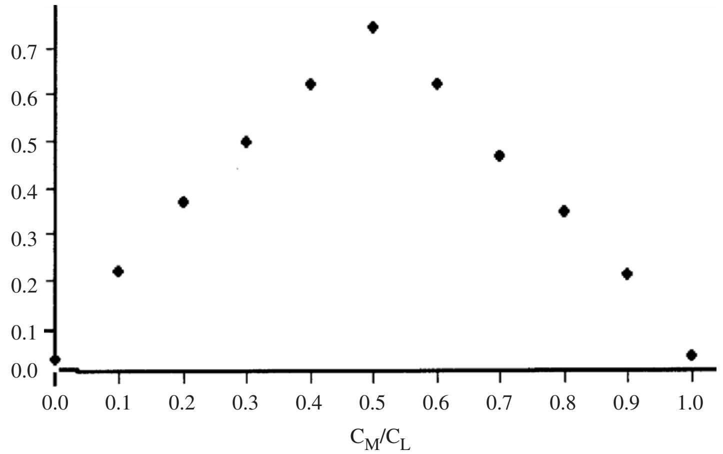

Figure 4. Van't Hoff plot for [$(SbCl_3)H_2t(4\text{-}Me)pp$].

Table 4. The thermodynamic parameters for SAT complexes, $(SbCl_3)H_2t(X)pp$, in $CHCl_3$ solvent.

SAT Complexes	$\Delta H^\circ (kJ\,mol^{-1})$	$\Delta S^\circ (J\,mol^{-1}\,K^{-1})$	$\Delta G^\circ (KJ\,mol^{-1})^a$
$(SbCl_3)H_2tpp$	−21.2(±0.8)	58(±3)	−38(±3)
$(SbCl_3)H_2t(4\text{-}OMe)pp$	−27(±1)	40(±4)	−39(±4)
$(SbCl_3)H_2t(3\text{-}OMe)pp$	−17.7(±0.3)	68(±1)	−38(±1)
$(SbCl_3)H_2t(2\text{-}OMe)pp$	−14.27(±0.03)	74(±2)	−36(±2)
$(SbCl_3)H_2t(4\text{-}Me)pp$	−24.5(±0.8)	47(±3)	−38(±3)
$(SbCl_3)H_2t(3\text{-}Me)pp$	−16.7(±0.2)	70(±1)	−38(±1)
$(SbCl_3)H_2t(2\text{-}Me)pp$	−11.7(±0.4)	75(±1)	−34(±1)
$(SbCl_3)H_2t(4\text{-}Cl)pp$	−19.2(±0.7)	64(±2)	−38(±3)

[a] ΔG° at 25°C

methyl is σ-donor group and π-donation effect is greater than σ-donation. The SAT complexes have negative values of ΔH° and ΔG° (table 4), indicating the strong interactions in the system and favorable adduct formation. The most negative values of ΔH° and ΔG° for [$(SbCl_3)H_2t(X)pp$] indicate the strongest interactions for $(SbCl_3)H_2t(4\text{-}OMe)pp$. These results show that the interactions of [$(SbCl_3)H_2t(X)pp$] toward $SbCl_3$ vary in the order:

$$\begin{aligned}&(SbCl_3)H_2t(4-OMe)pp > (SbCl_3)H_2t(4-Me)pp > (SbCl_3)H_2tpp >\\&(SbCl_3)H_2t(4-Cl)pp > (SbCl_3)H_2t(3-OMe)pp > (SbCl_3)H_2t(3-Me)pp >\\&(SbCl_3)H_2t(2-OMe)pp > (SbCl_3)H_2t(2-Me)pp.\end{aligned}$$

^1H NMR spectrum of the SAT complex between $H_2t(4\text{-}Me)pp$ and $SbCl_3$ (in $CDCl_3$ solvent with 1 : 1 mole ratio) showed two hydrogen atoms remain on nitrogens of the porphyrin, and the porphyrin is bidentate (^1H NMR ($CDCl_3$) for [$(SbCl_3)H_2t(4\text{-}Me)pp$]: δ 0.19 (s, 2H, NH), δ 2.8 (s, 12H, CH_3), δ 8.50–8.52 (d, 8H, o), δ 7.82–7.83 (d, 8H, m), δ 8.57 (s, 8H, β)). Correspondence between ^1H NMR and UV-Vis (447 and 671 nm, table 2) spectral data of the SAT complex, [$(SbCl_3)H_2t(4\text{-}Me)pp$], and complexes of σ- or π-acceptors with *meso*-tetraarylporphyrins [22–25] (where the

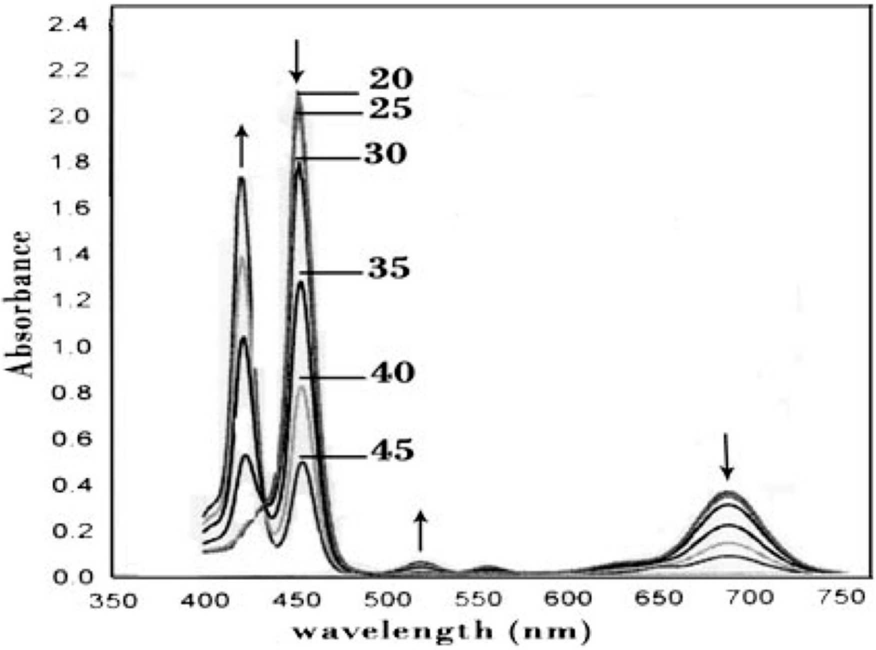

Figure 5. Thermal dissociation spectra of [(SbCl$_3$(H$_2$t(4-OMe)pp] from addition of the porphyrin (7×10^{-5} M) to SbCl$_3$ (7×10^{-5} M) in chloroform in a UV-Vis cell at 20 °C. The composition of the cell remained constant and the temperature was raised stepwise to 45°C.

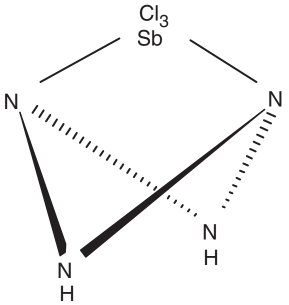

Figure 6. In the scheme only the tetrahedrally tilted pyrrolenine nitrogens of a porphyrin core are shown. Two nitrogen atoms of pyrrolenine in one side of porphyrin plane act as the electron donors to antimony.

porphyrin is coordinated by two pyrrolenine nitrogens) suggests a similar porphyrin core structure in all of those species. This conformation causes the lone pairs of two pyrrolenine nitrogens to locate above or below the mean plane of the porphyrin (figure 6) as the donors to SbCl$_3$. In the IR (400–4000 cm^{-1}) spectra of the free base *meso*-tetraarylporphyrins, an N-H stretching band is observed at 3320 cm^{-1} [26] and does not change upon reaction with SbCl$_3$. This indicates no intramolecular or intermolecular hydrogen bonding exists for N-H of *meso*-tetraarylporphyrins in the SAT complexes (figure 6).

Finally, the formation constant for the porphyrins with ortho-substituents is lower than other complexes, from steric hindrance. The ^{1}H NMR spectrum of o-methyl substituted porphyrins shifts upon complexation with $SbCl_3$, similar to shifts for the SAT complexation of H_2t(4-Me)pp with $SbCl_3$ (upfield for β-hydrogens and downfield for N-H and aryl hydrogens).

(^{1}H NMR ($CDCl_3$) for [($SbCl_3$)H_2t(2-Me)pp]: δ −1.02 (t, 2H, NH), δ 2.09 (s, 12H, CH_3), δ 8.33–8.38 (quart., 4H, o), δ 7.76–7.78 (d, 8H, m), δ 7.83–7.89 (t, 4H, p), δ 8.63-8.68 (t, 8H, β)).

Furthermore, porphyrins with ortho-substituents have four atropisomers. In our work ^{1}H NMR spectral data indicates that four atropisomers of the o-substituted porphyrins bond differently to $SbCl_3$. A triplet for NH and a triplet for β-hydrogens of [($SbCl_3$)H_2t(2-Me)pp] shows that four atropisomers bind differently.

Acknowledgement

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