

## New Cationic Sandwich-type Intermediate Sitting-atop Complexation between *meso*-Tetraarylporphyrins and Tantalum(V) Chloride: Synthesis, Spectroscopic Characterization and Photoluminescence Study

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Tetrapyrrole compounds are important classes of pigments that have fascinated chemists for many years due to their applications in various disciplines.<sup>1</sup> Sandwich-type complexes of porphyrin dianions with large metal ions such as rare earth, actinide, early transition, and main group metals have been obtained.<sup>2-3</sup> The rare earth sandwich complexes have attracted great attention due to their possible applications in molecular electronics, molecular optronics, and molecular iono-electronics.<sup>4-5</sup> Continuing these encouraging studies for preparation of the sandwich-type complexes, led us to investigate the formation of sitting-atop complexes of tantalum(V) chloride with a number of free base *meso*-tetraarylporphyrins (Figure 1). This work presents the first example for the ionic sandwich-type sitting-atop complexation between free base porphyrins and acceptors. The similarity of results of UV-Vis and (<sup>1</sup>H and <sup>13</sup>C) NMR spectroscopy between the obtained complexes and known SAT complexes of *meso*-tetraarylporphyrins with various acceptors,<sup>6-24</sup> suggested the saddled porphyrin core structures with one tantalum atom bonded to four pyrrolic nitrogens of two porphyrin macrocycles. Tantalum atom had high oxidation number and enough empty d-orbitals for acceptance of four electron pairs of the pyrrolic nitrogen atoms in two porphyrin molecules and formation of complexes with 1:2 (acceptor:donor) mole ratio in contrast known 2:1 or 1:1 (acceptor:donor) complexes.<sup>6-24</sup>

Several evidences confirm that the complexes of free base *meso*-tetraarylporphyrins with tantalum(V) chloride are formed. Changes in the <sup>1</sup>H NMR spectrum of H<sub>2</sub>tpp after mixing of different equivalents of TaCl<sub>5</sub> (0, 0.25, 0.5, 0.75) are presented in Figure 2. The first spectrum (Figure 2a) shows that in the free base H<sub>2</sub>tpp, the N-H protons are upfield and downfield, respectively. The complexation of the *meso*-tetra-

arylporphyrins with TaCl<sub>5</sub> was caused downfield shifts for the proton signals of N-H and aryl rings, and upfield shift for the β-hydrogens. These shifts are because of distortion of the pyrrole rings and decreasing the ring current in the studied complexes.<sup>6-24</sup> TaCl<sub>5</sub> reacts with H<sub>2</sub>tpp for formation of the i-SAT complex with 1:2 (TaCl<sub>5</sub>: H<sub>2</sub>tpp) mole ratio. Figure 2c. Addition of excess amount of TaCl<sub>5</sub> beyond 1:2 (TaCl<sub>5</sub>: H<sub>2</sub>tpp) mole ratio caused no changes in the spectra of the complexes (Figure 2d). Consequently, it is clearly that the reactants have 1:2 (TaCl<sub>5</sub>: porphyrin) mole ratio in the complex. Further, Figure 2b is superimposition of Figure 2a and Figure 2c. The complexation of H<sub>2</sub>(Xp)p with TaCl<sub>5</sub>, similar to known complexation of the *meso*-tetraarylporphyrins with various acceptors was caused

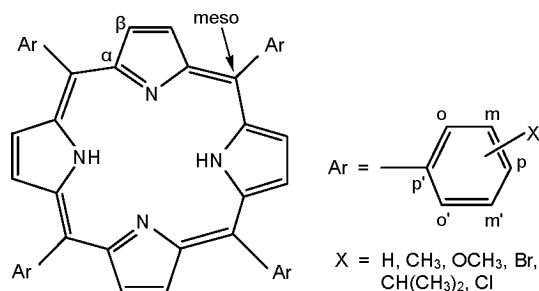


Figure 1. *meso*-Tetraarylporphyrins, H<sub>2</sub>(Xp)p.

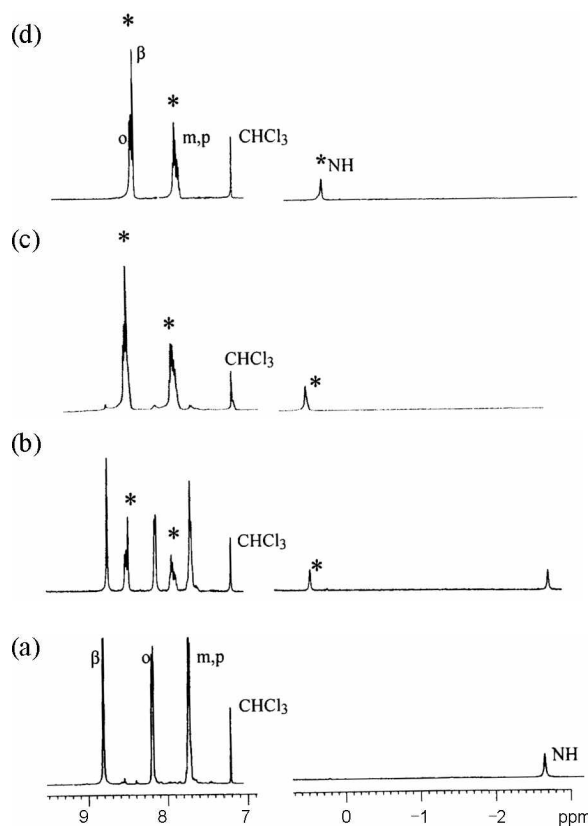
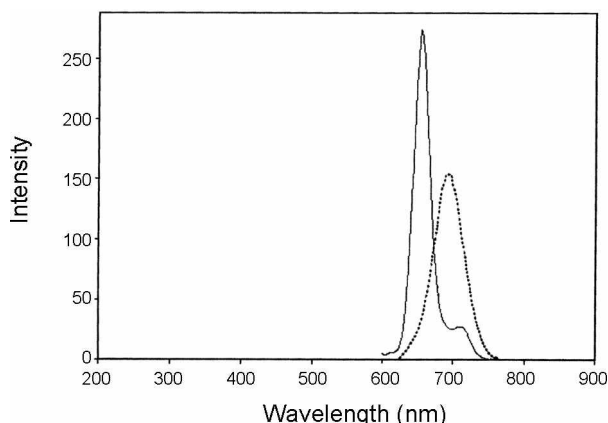


Figure 2. <sup>1</sup>H NMR spectra for the mixing of different equivalents of TaCl<sub>5</sub> (0 (a), 0.25 (b), 0.5 (c), 0.75 (d)) with H<sub>2</sub>tpp are shown. \*The peaks are related to the complex of [(H<sub>2</sub>tpp)<sub>2</sub>TaCl]<sub>4</sub>.

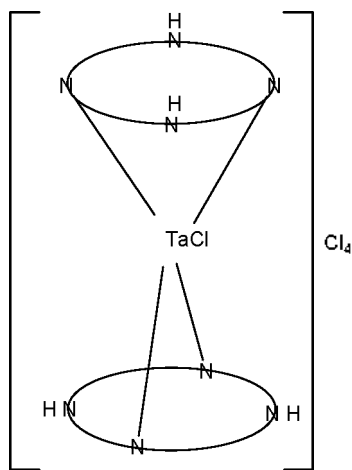
downfield shifts for the proton signals of N-H and aryl rings, and so an upfield shift for the  $\beta$ -hydrogens.<sup>7-19</sup>

The <sup>13</sup>C NMR spectrum of H<sub>2</sub>t(4-CH<sub>3</sub>)p shows six signals in the aromatic region: one broad signal for  $\beta$ -carbons (131.4 ppm) and five sharp signals ( $C_{\beta'}$  = 139.7,  $C_{\alpha\alpha'}$  = 134.9,  $C_{m,m'}$  = 127.8,  $C_{\beta}$  = 137.7 and  $C_{meso}$  = 120.5).<sup>18,19</sup> The  $\alpha$ -carbons peaks at about 145 ppm are too broad and weak to be seen. <sup>13</sup>C NMR spectrum of the complex, [(H<sub>2</sub>t(4-CH<sub>3</sub>)p)<sub>2</sub>TaCl]Cl<sub>4</sub>, had seven signals in the aromatic region: 123.6 ( $C_{meso}$ ), 129.0 ( $C_{\beta}$ ), 130.4 ( $C_{m,m'}$ ), 138.7 ( $C_{\beta'}$ ), 140.1 ( $C_{\alpha\alpha'}$ ), 141.5 ( $C_{\beta}$ ), 147.3 ( $C_{\alpha}$ ). Complexation of H<sub>2</sub>t(4-CH<sub>3</sub>)p with TaCl<sub>5</sub> sharpens the  $\alpha$ -carbon signal. Further, it is caused an upfield shift in  $C_{\beta}$  and  $C_{\beta'}$  signals and a downfield shift in the lines of  $C_{meso}$ ,  $C_{\alpha\alpha'}$ ,  $C_{m,m'}$ ,  $C_{\beta}$ . Complexation of H<sub>2</sub>t(4-CH<sub>3</sub>)p with various acceptors causes the same changes in the respective <sup>13</sup>C NMR spectra.<sup>17-21</sup>

The UV-Vis spectra of *meso*-tetraarylporphyrins have five absorption bands (one Soret (~420 nm) and four Q bands (500 ~ 650 nm)). In the SAT complexes two new absorption bands at 435 ~ 455 nm and 660 ~ 690 nm are revealed. As a result of the SAT complex formation, a bathochromic shift of the Soret-band and Q-bands can be observed. The UV-Vis spectra for titration of TaCl<sub>5</sub> into H<sub>2</sub>tpp (0 : 1, 0.25 : 1, 0.5 : 1, 0.75 : 1)



**Figure 3.** Fluorescence spectra of H<sub>2</sub>t(4-CH(CH<sub>3</sub>)<sub>2</sub>)p (solid line) in chloroform and [(H<sub>2</sub>t(4-CH(CH<sub>3</sub>)<sub>2</sub>)p)<sub>2</sub>TaCl]Cl<sub>4</sub> complex (dashed line) in benzene ( $\lambda_{exc}$  = 391 nm).



**Figure 4.** Two distorted porphyrin macrocycles act as donors to one tantalum center by two pyrrolic nitrogen atoms.

supported 1 : 2 (TaCl<sub>5</sub> : H<sub>2</sub>tpp) mole ratio for the reactants in the complex. The spectrum of the 0.25 : 1 reaction mixture was a superimposition of the H<sub>2</sub>tpp and [(H<sub>2</sub>tpp)<sub>2</sub>TaCl]Cl<sub>4</sub> spectra. An excess of TaCl<sub>5</sub> beyond the 0.5 : 1 (TaCl<sub>5</sub> : H<sub>2</sub>tpp) molar ratios had no measurable effect on the UV-Vis spectrum of the complex. The fluorescence spectrum of [(H<sub>2</sub>tpp)<sub>2</sub>TaCl]Cl<sub>4</sub> (in comparison to the related free base porphyrin, Figure 3) clearly indicates a typical SAT complex with red-shifted. These properties suggest that distorting of the SAT complexes markedly influences their spectral features.

Electrical conductivity measurements of these complexes in methanol solution showed that the complexes were 1 : 4 electrolytes.<sup>25</sup> These results are in accordance with the formulation of [(H<sub>2</sub>t(Xp))<sub>2</sub>TaCl]Cl<sub>4</sub> (Figure 4). In the complexes, the tantalum atom has coordination number of five.

The FT-IR spectra of H<sub>2</sub>t(Xp)p clearly shows a N-H stretching band at around 3320 cm<sup>-1</sup>,<sup>26</sup> which upon the complexation with TaCl<sub>5</sub> have not considerable changes. The FT-IR and <sup>1</sup>H NMR spectral results of the complexes showed that the two pyrrolic protons are remained on the porphyrin. This is in accordance to the proposed structure for the SAT complexes in Figure 4.

The <sup>1</sup>H NMR and UV-Vis spectral data of [(H<sub>2</sub>t(Xp))<sub>2</sub>TaCl]Cl<sub>4</sub> were similar to spectral data of those for the related diprotonated species.<sup>27</sup> The measurement of electrical conductivity of the complexes (in methanol) showed that they were 1:4 electrolyte whereas those diprotonated species (in methanol) were 1:2 electrolytes.<sup>14</sup> Further, the molar absorptivity coefficients of the bands of the complexes were higher than the corresponding values for the free base and the related diprotonated species. The similarity of the spectral data (<sup>1</sup>H NMR and UV-Vis) of [(H<sub>2</sub>t(Xp))<sub>2</sub>TaCl]Cl<sub>4</sub>, H<sub>4</sub>t(Xp)p<sup>2-</sup> and known complexes of porphyrins with various acceptors indicates analogous porphyrin core structures in all of them.

In summary, the sandwich-type complexation of *meso*-tetraarylporphyrins (H<sub>2</sub>t(Xp)p) with tantalum(V) chloride has been investigated. Suitable selection of a tantalum atom with high oxidation number is caused that we could be prepared these complexes as stable form. In the complexes, two porphyrins bonded to a tantalum center through pyrrolic nitrogens and has been produced sandwich-type complexes, [(H<sub>2</sub>t(Xp))<sub>2</sub>TaCl]Cl<sub>4</sub>.

## Experimental Section

To a mixture of H<sub>2</sub>t(Xp)p<sup>2-</sup> (0.5 mmole) and TaCl<sub>5</sub> (0.25 mmole) in a mortar, chloroform (1 ~ 2 mL) was added dropwise with grinding at ambient temperature for 30 minutes, until complexation was complete, which was determined by the disappearance of the Soret band of the porphyrin in the UV-Vis spectrum. The result of elemental analyses for the complex which was dried under vacuum oven for 6 h at 50°C was obtained.

[(H<sub>2</sub>t(4-OCH<sub>3</sub>)p)<sub>2</sub>TaCl]Cl<sub>4</sub>. C<sub>96</sub>H<sub>76</sub>N<sub>8</sub>O<sub>8</sub>TaCl<sub>5</sub> Anal. Calc.: C, 63.1; H, 4.2; N, 6.1%. Found: C, 62.2; H, 4.1; N, 6.0%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.55 (s, 2H, NH), 4.17 (s, 12H, OCH<sub>3</sub>), 8.52-8.54 (d, 8H,  $\alpha$ ,  $\alpha'$ ), 7.53-7.55 (d, 8H, m, m'), 8.49 (s, 8H,  $\beta$ ). IR (KBr):  $\nu_{NH}$  (~3320 cm<sup>-1</sup>). UV-Vis (CHCl<sub>3</sub>): 450.0, 689.8.

[(H<sub>2</sub>t(4-CH<sub>3</sub>)p)<sub>2</sub>TaCl]Cl<sub>4</sub>. C<sub>96</sub>H<sub>76</sub>N<sub>8</sub>TaCl<sub>5</sub> Anal. Calc.: C, 67.8; H, 4.5; N, 6.6%. Found: C, 66.9; H, 4.2; N, 6.4%. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.35 (s, 2H, NH), 2.79 (s, 12H, CH<sub>3</sub>), 8.50-8.52 (d,

8H. o. o'), 7.82-7.84 (d. 8H. m. m'), 8.56 (s. 8H.  $\beta$ ). IR (KBr):  $\nu_{\text{NH}}$  ( $\sim 3320 \text{ cm}^{-1}$ ). UV-Vis ( $\text{CHCl}_3$ ): 449.2, 669.8.

**$[(\text{H}_2\text{t}(\mathbf{4}\text{-CH}(\text{CH}_3)_2\text{p})_2\text{TaCl})_2\text{Cl}_4]$** .  $\text{C}_{112}\text{H}_{108}\text{N}_8\text{TaCl}_5$  Anal. Calc.: C, 69.9; H, 5.6; N, 5.8%. Found: C, 69.1; H, 5.2; N, 5.4%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.36 (s. 2H. NH), 8.541-8.56 (d. 8H. o. o'), 7.87-7.89 (d. 8H. m. m'), 8.58 (s. 8H.  $\beta$ ). IR (KBr):  $\nu_{\text{NH}}$  ( $\sim 3320 \text{ cm}^{-1}$ ). UV-Vis ( $\text{CHCl}_3$ ): 448.3, 671.1.

**$[(\text{H}_2\text{tpp})_2\text{TaCl})_2\text{Cl}_4]$** .  $\text{C}_{88}\text{H}_{60}\text{N}_8\text{TaCl}_5$  Anal. Calc.: C, 66.6; H, 3.8; N, 7.1%. Found: C, 65.6; H, 3.6; N, 7.0%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.29 (s. 2H. NH), 8.64-8.65 (d. 8H. o. o'), 8.04-8.06 (t. 8H. m. m'), 7.97-8.03 (d. 4H. p), 8.62 (s. 8H.  $\beta$ ). IR (KBr):  $\nu_{\text{NH}}$  ( $\sim 3320 \text{ cm}^{-1}$ ). UV-Vis ( $\text{CHCl}_3$ ): 445.8, 660.4.

**$[(\text{H}_2\text{t}(\mathbf{3}\text{-CH}_3\text{p})_2\text{TaCl})_2\text{Cl}_4]$** .  $\text{C}_{96}\text{H}_{76}\text{N}_8\text{TaCl}_5$  Anal. Calc.: C, 67.8; H, 4.5; N, 6.6%. Found: C, 67.1; H, 4.2; N, 6.3%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.25 (s. 2H. NH), 2.83 (s. 12H.  $\text{CH}_3$ ), 8.43 (br. 8H. o. o'), 7.90 (br. 4H. m), 7.78 (br. 4H. p), 8.59 (s. 8H.  $\beta$ ). IR (KBr):  $\nu_{\text{NH}}$  ( $\sim 3320 \text{ cm}^{-1}$ ). UV-Vis ( $\text{CHCl}_3$ ): 446.6, 661.7.

**$[(\text{H}_2\text{t}(\mathbf{3}\text{-OCH}_3\text{p})_2\text{TaCl})_2\text{Cl}_4]$** .  $\text{C}_{96}\text{H}_{76}\text{N}_8\text{O}_8\text{TaCl}_5$  Anal. Calc.: C, 63.1; H, 4.2; N, 6.1%. Found: C, 62.5; H, 3.9; N, 5.9%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.25 (s. 2H. NH), 4.17 (s. 12H.  $\text{OCH}_3$ ), 8.17 (br. 8H. o. o'), 7.90 (br. 4H. m), 7.51-7.53 (br. 4H. p), 8.64 (s. 8H.  $\beta$ ). IR (KBr):  $\nu_{\text{NH}}$  ( $\sim 3320 \text{ cm}^{-1}$ ). UV-Vis ( $\text{CHCl}_3$ ): 450.5, 660.8.

**$[(\text{H}_2\text{t}(\mathbf{4}\text{-Clp})_2\text{TaCl})_2\text{Cl}_4]$** .  $\text{C}_{88}\text{H}_{52}\text{N}_8\text{TaCl}_{13}$  Anal. Calc.: C, 56.7; H, 2.8; N, 6.0%. Found: C, 55.8; H, 2.5; N, 5.7%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.43 (s. 2H. NH), 8.51-8.53 (d. 8H. o. o'), 8.01-8.03 (d. 8H. m. m'), 8.57 (s. 8H.  $\beta$ ). IR (KBr):  $\nu_{\text{NH}}$  ( $\sim 3320 \text{ cm}^{-1}$ ). UV-Vis ( $\text{CHCl}_3$ ): 448.8, 663.4.

**$[(\text{H}_2\text{t}(\mathbf{4}\text{-Brp})_2\text{TaCl})_2\text{Cl}_4]$** .  $\text{C}_{88}\text{H}_{52}\text{N}_8\text{Br}_8\text{TaCl}_5$  Anal. Calc.: C, 47.6; H, 2.3; N, 5.0%. Found: C, 46.8; H, 2.1; N, 4.8%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.42 (s. 2H. NH), 8.44-8.46 (d. 8H. o. o'), 8.17-8.19 (d. 8H. m. m'), 8.58 (s. 8H.  $\beta$ ). IR (KBr):  $\nu_{\text{NH}}$  ( $\sim 3320 \text{ cm}^{-1}$ ). UV-Vis ( $\text{CHCl}_3$ ): 448.3, 664.7.

**$[(\text{H}_2\text{t}(\mathbf{3}\text{-Brp})_2\text{TaCl})_2\text{Cl}_4]$** .  $\text{C}_{88}\text{H}_{52}\text{N}_8\text{Br}_8\text{TaCl}_5$  Anal. Calc.: C, 47.6; H, 2.3; N, 5.0%. Found: C, 46.7; H, 2.1; N, 4.7%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  0.37 (s. 2H. NH), 8.87 (s. 4H. o), 8.54-8.55 (d. 4H. o'), 8.13-8.15 (d. 4H. p), 7.92 (br. 4H. m), 8.63 (s. 8H.  $\beta$ ). IR (KBr):  $\nu_{\text{NH}}$  ( $\sim 3320 \text{ cm}^{-1}$ ). UV-Vis ( $\text{CHCl}_3$ ): 446.6, 657.8.

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