

## MASTER'S THESIS

### Synthesis and characterization of meso- and $\beta$ -substituted porphyrins and their complexes, reactivities of lanthanide porphyrinate complexes

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**Synthesis and Characterization of *meso*- and  $\beta$ -substituted  
Porphyrins and their Complexes. Reactivities of Lanthanide  
Porphyrinate Complexes**

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## Abstract

We have synthesized and characterized a *meso*-containing long carbon-chain ester group porphyrin (TEBPP)(I-1), and prepared their transition metal (Zn, Ni, Cu) complexes (I-2, I-3 and I-4). The structures of I-3 and I-4 were determined by X-ray crystallography. We have attempted to synthesize Lanthanide TEBPP complexes. Results show that only Yb metal ion can be co-ordinated with porphyrin (TEBPP) to form the corresponding porphyrinate complex, however, Y and Er ion can not form porphyrinate complexes.

Condensation of *meso*-(*p*-tolyl)dipyrromethane with *p*-cyanobenzaldehyde gave six cyano-porphyrins. Their zinc and lanthanide complexes were prepared. The structures of triCH<sub>3</sub>, CN-TPP-Zn(I-13) and *trans*-diCH<sub>3</sub>,diCN-TPP-Zn(I-15) were confirmed by X-ray diffraction.

Utilizing Tm[N(TMS)<sub>2</sub>]<sub>3</sub>·xLiCl(THF)<sub>3</sub> as precursors, we have synthesized six thulium porphyrinate complexes (I-18 to I-23). Formation of thulium porphyrinate complexes were supported by FAB-MS and UV/vis spectra. When H<sub>2</sub>MeTPP and H<sub>2</sub>[CH(CH<sub>3</sub>)<sub>2</sub>]TPP were used, to give dinuclear thulium porphyrinate complexes [Tm(MeTPP)(μ-OH)(μ-H<sub>2</sub>O)]<sub>2</sub> (I-18) and {Tm[CH(CH<sub>3</sub>)<sub>2</sub>]TPP(μ-OH)(H<sub>2</sub>O)}<sub>2</sub> (I-22), whose structure were confirmed by X-ray crystallography.

In order to explore the possibility of preparing lanthanide β-substituted bulky porphyrins, we have synthesized and characterized β-mono, di, tetra-substituted bromo and phenyl-porphyrins. Results show that lanthanide β-tetrasubstituted bulky porphyrin

complexes can be formed and observed spectroscopically. However, complexes were rather unstable, demetallation took place during the crystallization process. However, lanthanide  $\beta$ -mono and disubstituted porphyrins can be formed and are more stable than lanthanide  $\beta$ -tetrasubstituted bulky porphyrin complexes.

Interaction of cationic lanthanide monoporphyrinate complexes  $[\text{Ln}(\text{Por})(\text{H}_2\text{O})_3]\text{Cl}$  ( $\text{Ln}=\text{Yb}, \text{Er}, \text{Tm}$ ) with anionic tripodal ligand  $\text{NaL}_{\text{OEt}}$  gave neutral *3d-4f* bimetallic lanthanide monoporphyrinate complexes  $[\text{Ln}(\text{Por})\text{L}_{\text{OEt}}]$ ;  $[\text{Er}(\text{triMeOTPP})\text{LO}_{\text{Et}}]$  (**III-1**),  $[\text{Er}(\text{MeOTPP})\text{L}_{\text{OEt}}]$  (**III-2**);  $[\text{Er}(\text{TPP})\text{L}_{\text{OEt}}]$  (**III-3**);  $[\text{Yb}(\text{MeTPP})\text{L}_{\text{OEt}}]$  (**III-4**);  $[\text{Tm}(\text{MeTPP})\text{L}_{\text{OEt}}]$  (**III-5**) and  $[\text{Yb}(\text{MeOTPP})\text{L}_{\text{OEt}}]$  (**III-6**), respectively. Structures of **III-1** and **III-3** were confirmed by X-ray crystallography.

Interaction of cationic ytterbium complexes  $[\text{Yb}(\text{Por})]^+$  with 4,4'-dipyridine, Zn-Schiff base and potassium tris(3,5-dimethyl-1-pyrazolyl)borohydride give unexpected dinuclear  $[\text{Yb}^{\text{III}}(\text{MeOTPP})(\mu\text{-Cl})_2(\text{THF})]$  (**III-7**);  $[\text{Yb}^{\text{III}}(\text{MeOTPP})(\mu\text{-OH})(\text{H}_2\text{O})_2]$  (**III-8**) and  $[\text{Yb}^{\text{III}}(\text{MeTPP})(\mu\text{-OH})_2(\mu\text{-THF})]$  (**III-9**), respectively. Structures of **III-7** to **III-9** were determined by X-ray crystallography.

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