MASTER'S THESIS

Synthesis and characterization of meso- and β-substituted porphyrins and their complexes, reactivities of lanthanide porphyrinate complexes

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Synthesis and Characterization of *meso*- and β-substituted Porphyrins and their Complexes. Reactivities of Lanthanide Porphyrinate Complexes

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Abstract

We have synthesized and characterized a *meso*-contained 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)dipyrrolmethane with *p*-cyanobenzenaldehyde gave six cyano-porphyrins. Their zinc and lanthanide complexes were prepared. The structures of triCH3, CN-TPP-Zn(**I-13**) and *trans*-diCH3,diCN-TPP-Zn(**I-15**) were confirmed by X-ray diffraction.

Utilizing $Tm[N(TMS)_2]_3 \cdot xLiCl(THF)_3$ as precuresors, 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_2MeTPP and $H_2[CH(CH_3)_2]TPP$ were used, to give dinuclear thulium porphyrinate complexes $[Tm(MeTPP)(\mu\text{-}OH)(\mu\text{-}H_2O)]_2$ (**I-18**) and $\{Tm[CH(CH_3)_2]TPP(\mu\text{-}OH)(H_2O)\}_2$ (**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 spectrocopically. However, complexes were rather unstable, demetallation took place during the crystallization process. However, lanthanide β-mono and disubstituted porphyrins can be formed and are more stable than lanthanide β-tetrasubstituted bulky porphyrin complexes.

Interaction of cationic lanthanide monoporphyrinate complexes $[Ln(Por)(H_2O)_3]Cl$ (Ln=Yb, Er, Tm) with anionic tripodal ligand NaL_{OEt} gave neutral *3d-4f* bimetallic lanthanide monoporphyrinate complexes $[Ln(Por)L_{OEt}]$; $[Er(triMeOTPP)LO_{Et}]$ (**III-1**), $[Er(MeOTPP)L_{OEt}]$ (**III-2**); $[Er(TPP)L_{OEt}]$ (**III-3**); $[Yb(MeTPP)L_{OEt}]$ (**III-4**); $[Tm(MeTPP)L_{OEt}]$ (**III-5**) and $[Yb(MeOTPP)L_{OEt}]$ (**III-6**), respectively. Structures of **III-1** and **III-3** were confirmed by X-ray crystallography.

Interaction of cationic ytterbium complexes $[Yb(Por)]^+$ with 4,4$^{\cap}$-dipyridine, Zn-Shiff base and potassium tris(3,5-dimethyl-1-pyrazolyl)borohydride give unexpected dinuclear $[Yb^{III}(MeOTPP)(\mu\text{-}Cl)]_2(THF)$ (**III-7**); $[Yb^{III}(MeOTPP)(\mu\text{-}OH)(H_2O)]_2$ (**III-8**) and $[Yb^{III}(MeTPP)(\mu\text{-}OH)]_2(\mu\text{-}THF)$ (**III-9**), respectively. Structures of **III-7** to **III-9** were determined by X-ray crystallography.

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