

MASTER'S THESIS

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

Hou, Anxin

Date of Award:
2000

[Link to publication](#)

General rights

Copyright and intellectual property rights for the publications made accessible in HKBU Scholars are retained by the authors and/or other copyright owners. In addition to the restrictions prescribed by the Copyright Ordinance of Hong Kong, all users and readers must also observe the following terms of use:

- Users may download and print one copy of any publication from HKBU Scholars for the purpose of private study or research
- Users cannot further distribute the material or use it for any profit-making activity or commercial gain
- To share publications in HKBU Scholars with others, users are welcome to freely distribute the permanent URL assigned to the publication

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

HOU Anxin

A thesis submitted in partial fulfillment of the requirements

For the degree of

Master of Philosophy

November 2000

Hong Kong Baptist University

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)dipyrrolemethane with *p*-cyanobenzaldehyde 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·xLiCl(THF)₃ 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 H₂MeTPP and H₂[CH(CH₃)₂]TPP were used, to give dinuclear thulium porphyrinate complexes [Tm(MeTPP)(μ-OH)(μ-H₂O)]₂ (I-18) and {Tm[CH(CH₃)₂]TPP(μ-OH)(H₂O)}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 spectroscopically. 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 $[\text{Ln}(\text{Por})(\text{H}_2\text{O})_3]\text{Cl}$ ($\text{Ln}=\text{Yb, Er, Tm}$) with anionic tripodal ligand NaL_{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.

Table of Contents

Declaration	i
Abstract	ii
Acknowledgements	iv
Table of Contents	v
List of Schemes	viii
List of Tables	ix
List of Figures	x
Abbreviations and Symbols	xi
Chapter 1	
Synthesis and Characterization of <i>meso</i>-substituted Porphyrins and their Complexes	
1.1 Introduction	1
1.2 Preparation of TEBPP and their complexes	6
1.2.1 Introduction	6
1.2.2 Results and Discussion	8
1.2.2.1 Preparation of 5,10,15,20-tetrakis[4-(ethyl butyrate)-phenoxy] porphyrin (TEBPP) I-1 their transition-metal complexes I-2, I-3, I-4	8
1.2.2.1.1 Preparation of (TEBPP) I-1	9
1.2.2.1.2 Preparation of transition-metal (M=Zn, Ni, Cu) I-2, I-3 I-4 porphyrinate complexes	9

1.2.2.2	Preparation of Lanthanide-TEBPP complexes	14
1.2.3	Experimental Section	14
1.3	Preparation of <i>meso</i> -asymmetric porphyrins and their complexes	17
1.3.1	Results and Discussion	17
1.3.2	Experimental Section	23
1.4	Preparation of the thulium porphyrinate complexes	29
1.4.1	Results and Discussion	29
1.4.2	Experiments	37
1.5	Conclusion	40
	Reference	41

Chapter 2

Synthesis of β -substituted porphyrins and their complexes

2.1	Introduction	43
2.2	Results and Discussion	44
2.3	Experimental Section	48
2.4	Conclusion	53
	Reference	54

Chapter 3

The reactivities of lanthanide porphyrinate complexes

3.1	Introduction	56
-----	--------------	----

3.2	Preparation of neutral <i>3d-4f</i> bimetallic monoporphyrinate complexes [Ln(Por)L_{OEt}]	58
3.2.1	Results and Discussion	58
3.2.2	Experimental Section	68
3.3	Preparation of neutral dinuclear lanthanide porphyrinate complexes	71
3.3.1	Results and Discussion	71
3.3.2	Experimental Section	89
3.4	Conclusion	91
	Reference	92
	Appendix	93
	Curriculum Vitae	140