

DOCTORAL THESIS

Synthesis, crystal structures and spectroscopic properties of mono- and bi-metallic Schiff-base complexes ; Synthesis of polydentate and macrocyclic phosphine ligands, and their reactivities towards transition and lanthanide metal ions

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**Synthesis, Crystal Structures and Spectroscopic Properties of Mono-
and Bi-metallic Schiff-base Complexes.**

**Synthesis of Polydentate and Macrocyclic Phosphine Ligands, and
Their Reactivities towards Transition and Lanthanide Metal Ions**

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Abstract

Four functionally substituted salicylaldehydes 3-(2'-pyridyl)-5-*tert*-butyl-2-hydroxybenzaldehyde (**L**¹), 3-(3'-pyridyl)-5-*tert*-butyl-2-hydroxybenzaldehyde (**L**²), 3-(4'-pyridyl)-5-*tert*-butyl-2-hydroxybenzaldehyde (**L**³) and 3-(3'-quinolyl)-5-*tert*-butyl-2-hydroxybenzaldehyde (**L**⁴) were prepared by Stille cross-coupling reaction, of which **L**², **L**³ and **L**⁴ were firstly synthesized and characterized. A series of main group element and transition metals Schiff-base complexes based on the above substituted salicylaldehydes have been prepared by template method, and spectroscopically characterized. X-Ray crystal structure analyses revealed diversities in coordination patterns of the complexes. Results also showed that central metals, ligands, counter ions, even the solvents play roles in directing the pathways of reactions and the structures of resulting complexes. Crystal structures of **L**³, **L**⁴, intermediate in Stille cross-coupling reaction **II-1**, transition metal and main group metal Schiff-base complexes **II-2** to **II-9**, phenoxy copper complex **II-10** and methylated salt of **L**¹ have been determined by X-ray crystallography.

A new class of lanthanide complexes with tripodal Schiff-base ligands have been synthesized and spectroscopically characterized. Differences of bulkiness and delocalization of the substituents found influence on the physical properties of the complexes. Crystal structures of **III-2** to **III-5**, **III-7** to **III-11**, and **III-16** have been

determined by X-ray crystallography.

Mono-metallic and hetero-bimetallic complexes with tetradentate Schiff-base ligand were prepared and characterized. Complexes **IV-2** and **IV-5** have been structurally characterized by X-ray crystallography. Study showed that in **IV-5**, two of the three NO_3^- anions were coordinated to lanthanide ion as a bidentate ligand, while the third NO_3^- was coordinated to the transition metal as monodentate ligand.

Phosphorus-containing polydentate or macrocyclic ligands have drawn much attention due to the ease of modification of the affinities of the ligands to metals. Starting with **V-1**, we have synthesized and characterized a series of bidentate phosphonates (**V-2**, **V-3** and **V-4**), tetradentate phosphonates (**V-7**, **V-8** and **V-9**) and their lanthanide complexes (**V-10**, **V-11**, **V-12**, **V-13** and **V-14**).

A novel chloro-bridged polynuclear complex **V-15** has been prepared. The result of structural study indicated that all the phenyl substituents at phosphorus atoms were arranged *cis* to each other.

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