

## DOCTORAL THESIS

### Synthesis, structure and characterization of long distance electrostatic force and hydrogen bond supramolecular polymers synthesis, structure and characterization of bis[2,4-di(pyridyl)-1,3,5-triazapenta-dienato] metal complexes

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**Synthesis, Structure and Characterization of Long Distance  
Electrostatic Force and Hydrogen Bond Supramolecular Polymers**

**Synthesis, Structure and Characterization of  
*Bis*[2,4-*di*(pyridyl)-1,3,5-triazapenta-dienato] Metal Complexes**

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## Abstract

Seven organic charge-assisted hydrogen bond supramolecular polymers, aryl-amidinium diphenylphosphinate, had been synthesized by the oxidative cleavage of N-P bond with silver(I) cation. Their identities were established by elemental analysis, ESI-HRMS,  $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{13}\text{C}$ -NMR and IR spectra. These data were consistent with the structure ascertained by X-ray crystallography. The construction of network of these compounds was studied. The amidinium cations and diphenylphosphinate anions are linked together by long distance electrostatic force and strengthened by hydrogen bonds to form various one-, two- or three-dimensional network. However, if *para*-dicyanoarene was used as starting materials and hydrogen peroxide as the oxidizing agent, the compounds of *para*-aryl-di(N-diphenylphosphinato) amidine were produced instead of the polymeric structure like compounds 1-6.

The fluorescence property of compound 1 had been studied and compared with benzamidine hydrochloride and sodium diphenylphosphinate. The solid-state fluorescence properties of compounds 2-7 were also studied. Due to the strong inter and intra molecular electrostatic and hydrogen bond interaction of compounds 1-7, the unusual excitation and emission appeared in their fluorescence spectra.

Four inorganic/organic charge-assisted hydrogen bond supramolecular polymers and tetrabenzamidinecopper(II) iodide had been synthesized by the addition reaction of  $\alpha$ -H free nitriles. Their identities were established by elemental analysis, MS-FAB and IR. These data were consistent with the structure obtained by X-ray crystallography. The construction of the network of these compounds was studied. Ni(II) and Pt(II) coordination cations are square planar and act as H-bond donor unit leading to the formation of infinite network. Due to the strong interactions between cations and

anions, the supramolecular polymer exhibited the unusual physical property. An unexpected addition reaction of tetrabenzamidinenickel(II) chloride with potassium thiocyanate producing the *bis*[2-phenyl-4-mercapto-1,3,5-triazapenta-dienato] nickel(II) was described.

Nine *bis*[2,4-*di*(pyridyl)-1,3,5-triazapenta-dienato] metal complexes had been synthesized via the interaction of metal halides with lithium amidinate, generated *in situ* from the reaction of cyanopyridine with LiN(SiMe<sub>3</sub>)<sub>2</sub>. The molecular structures of five of them were ascertained by single crystal X-ray analysis. The ESI-HRMS, IR, <sup>1</sup>H-NMR spectra of these complexes were measured. The reaction of lithium benzamidinate with 3-cyanopyridine or 4-cyanopyridine followed by the addition of palladium ion produced the *bis*[2-phenyl-4-(*n*-pyridyl)-1,3,5-triazapenta-dienato] palladium(II) (*n*=3 or 4). The geometry of these metal complexes is square planar with two ligands coordinated to the metal center forming the very stable six-membered ring molecule. The 1,3,5-triazapenta-dienato ligands are difficult to combine with other metals under the same reaction condition and procedures. The nickel, palladium and platinum should play an important template role in the syntheses of these complexes.

The various nucleophilic addition reactions of benzonitrile and cyanopyridine were studied and a plausible mechanism for the formation of the two kinds of compounds was proposed. Experimental results suggest that the palladium may have special affinity for the formation of 1,3,5-triazapenta-dienato palladium complexes. In other words, palladium may be specially suited to stabilize the six membered ring formed by the palladium and the 1,3,5-triazapentadienyl ligand.

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