INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
PhD-17 SHORT ABSTRACT OF THESIS

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Thesis Title: Bivalent Ni, Pd, Pt, and Zn Complexes of Some Chemodiverse Ligands: Structure, Biophysical Study, and Catalytic Activity

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SHORT ABSTRACT

The Thesis entitled "**Bivalent Ni, Pd, Pt, and Zn Complexes of Some Chemodiverse Ligands: Structure, Biophysical Study, and Catalytic Activity**" is divided into five chapters.

Chapter 1 provides a comprehensive overview of the recent advancements in the synthesis and applications of divalent Group 10 and zinc complexes, tracing their development from historical discoveries to contemporary progress. It highlights the evolution of palladium-based catalysts in C–C cross-coupling reactions, emerging trends in nickel catalysis, and the biological activities of Pd(II) and Pt(II) complexes. The Chapter also discusses significant progress in carbon dioxide fixation employing zinc(II) complexes as catalysts. Additionally, the general methods, materials, and instrumentation used in experimental works are given in this Chapter.

Chapter 2 deals with synthesis and characterization of a series of mono-, di-, tri-, and tetranuclear Pd(II) complexes along with one Pt(II) analogue using two nitrogen-rich ligands with imidazo[1,5-a]pyridine and imidazolyl-pyridine moieties. the denticity of **L1H** was bis-bidentate or tridentate coordinated through nitrogen atoms with controlled stoichiometry and reaction conditions. The exceptional coordination mode with formation of a seven membered chelate was observed in trinuclear Pd(II) complex (**4**) and a tetranuclear complex was synthesized by reversing the molar

ratio of ligand and $PdCl_2$. Based on X-ray diffraction study and spectroscopic results, the geometry around palladium center was observed to be distorted square planar. The Pd(II) complexes were proved as versatile and potent catalysts in Suzuki cross-coupling, transfer hydrogenation reaction, and alkyne homocoupling under environmentally apposite conditions by taking only 0.1 mol% of tetranuclear Pd(II) complex (**5**) as catalyst. The interaction of all Pd(II) and Pt(II) complexes with calf thymus DNA were examined wherein all displayed intercalative mode of binding and showed high binding affinity with bovine serum albumin (BSA). Further, ADMET calculations and molecular docking study of two bioactive molecules **3s** and **3t** obtained from Suzuki reaction using catalyst **5** were performed towards LTA_4H inhibition.

Chapter 3 outlines the synthetic procedure of a series of Ni(II), Pd(II) and Pt(II) complexes of various ligands bearing benzothiazole hydrazone, chromone fused pyrrole and imidazo[1,5-*a*]pyridine moieties. All the ligands and complexes were characterized thoroughly using various spectroscopic techniques, molecular structures were confirmed by single crystal X-ray diffraction method and computational investigation was also performed to optimize the geometry and calculate energies. The nickel(II) complexes were employed as catalysts in synthesis of imines/diimines via acceptorless dehydrogenative coupling of alcohols and amines/diamine. Among all Ni(II) complexes, **1a** gave maximum yield of 99% in 12 h using only 1.0 mol% catalyst loading offered a cost-effective and sustainable alternative to existed noble metal catalysts. The catalytic activity of Pd(II) complexes was assessed in Heck coupling reaction, effectively produced 1-methylstilbene in ethanol at 90 ºC and 8 hours, surpassing many existing conventional systems relying on DMF or DMSO solvent at high temperature. The pincer Pd(II) complex **2h** was superior catalyst among all, with a yield of 98% using only 1.0 mol% catalyst loading. Furthermore, the versatility of Pd(II) catalysts was tested in cross-dehydrogenative coupling of thiophene-2-carboxaldehyde and formed the product in good yield. The platinum complexes of all ligands were inspected for their interaction with biomolecules such as CT-DNA and BSA and among all Pt(II) complexes, **3e** displayed the highest binding constants with these two biomolecules. Molecular docking study was also carried out to visualize the interaction of **3e** with CT-DNA and BSA, showed high binding free energy and intercalative binding mode with CT-DNA which was in congruence with experimental findings.

Chapter 4 describes the synthesis and characterization of five dinuclear palldium(II) complexes of substituted imidazo[1,5-a]pyridinylpicolinimidamides. Single crystal X-ray analysis revealed that the ligands were coordinated with palladium center through pseudo-pincer type mode and the Pd(II) center possessed distorted square planar geometry while an eight-membered metallic cavity was observed in all complexes. The complexes were employed as highly active catalyst in copper-free Sonogashira coupling and C–P coupling under mild reaction conditions and produced excellent yield using only 0.5 mol% of catalyst loading. High catalytic activity of these complexes was mainly due to cooperativity and synergic effect of two Pd(II) center present in optimum proximity.

Chapter 5 unveils the synthetic methods of fourteen well characterized zinc(II) complexes of nitrogen rich heterocyclic ligands containing imidazo[1,5-*a*]pyridine, triazine, and imidazolylpyridine moieties. Ligands having imidazo[1,5-*a*]pyridine and triazine nucleus were prepared using unified, atom economical one-pot strategy from the reaction of 2-cyanopyridine, corresponding aryl aldehydes and ammonium acetate in a single synthetic pathway. The molecular structure of ligands **L1H**, **L2H**, **L6H**, and **L8H** and all zinc complexes were established by single crystal X-ray diffraction measurements. The disubstituted imidazo[1,5-*a*]pyridine and imidazolylpyridine ligands yielded both mono and trinuclear complexes while the pincer triazine ligands produced only mononuclear complexes. The geometry of tetra coordinated zinc centres in Zn(II) imidazo[1,5-*a*]pyridine and imidazolylpyridine complexes were distorted tetrahedral where their Houser parameter (τ_4) was in the range of 0.8–0.9. A distorted square pyramidal environment was observed in penta-coordinated Zn(II) triazine complexes having Addison parameter (τ_5) 0.044–0.293 while trinuclear imidazolylpyridine complex **14** displayed both distorted tetrahedral and trigonal bipyramidal Zn(II) centres with geometry index 0.88 and 0.76. All fourteen zinc(II) complexes were employed as catalyst in the conversion of carbon dioxide and styrene epoxide into styrene carbonate, yielded excellently in a mild and solvent free condition using balloon pressure CO_2. Using 1.0 mol% catalyst, all mononuclear zinc complexes produced styrene carbonate in comparative yield of 81–94% while trinuclear catalysts yielded 98% using 0.5 mol % catalyst loading.