ABSTRACT

This dissertation comprises a total of seven chapters. **Chapter I** consists of a concise introduction to the design, foundation, and applications of the coordination compounds based on synthetic and commercially available ligands and the applicability of the present work in the recent trends of scientific development.

Chapter II represents the synthesis, X-ray structural analysis, supramolecular architectures, and oxidative coupling of 2-aminophenol of a copper(II) complex, [Cu($\mathbf{L^1}$)](H_2O) (**1**) containing a previously reported Schiff base, $\mathbf{H_2L^1}$ = 2,2'-((1,2-phenylenebis(azanylylidene))bis(methanylylidene))diphenol. The analysis of the crystal structure indicates that the Cu(II) centre adopts a square planar coordination geometry within the $R\bar{3}$ space group. Furthermore, the aqua molecule located nearby actively participates in significant intermolecular hydrogen bonding, resulting in the formation of a water-mediated dimeric unit of the Cu(II) complex. The Hirshfeld surface analysis suggests that C−H···O and O−H···O types of hydrogen bonding, as well as π···π interactions play a crucial role. The catalytic properties of complex **1** were assessed for the oxidative dimerization of 2-aminophenol (2-AP) in methanol, revealing high catalytic efficiency with a k_{cat}/K_M value of 2.14×10^5. Additionally, studies utilizing mass spectrometry confirmed that the catalytic process involves the formation of an enzyme-substrate adduct in the solution phase.

Chapter III represents the synthesis, X-ray structural analysis, Hirshfeld surface analysis, oxidative dimerization of 2-aminophenol and antibacterial activity of a newly designed copper(II)-Schiff base complex, [Cu($\mathbf{L^2}$)$_2$] (**2**), [Schiff base ($\mathbf{HL^2}$) = 2-(2-methoxybenzylideneamino)phenol]. X-ray analysis of complex **2** reveals that the Cu(II) complex forms crystals in a cubic crystal system with the $Ia\bar{3}d$ space group. In its crystalline phase, the Cu(II) centre adopts a unique tetragonal bipyramidal geometry. Complex **2** has been tested for its phenaxozinone synthase activity in acetonitrile, mimicking biological systems, and demonstrated significant catalytic activity with a high turnover number of 536.4 h^{-1}.

Electrochemical analysis of complex **2** showed the appearance of two additional peaks at −0.15 and 0.46 V in the presence of 2-AP. This suggests the formation of $AP^{-}/AP^{\bullet-}$ and $AP^{\bullet-}$/IQ redox couples in the solution. The presence of the iminobenzosemiquinone radical at g = 2.057 was confirmed in the reaction mixture through electron paramagnetic resonance, indicating its role as the driving force for the oxidative dimerization of 2-AP. The ESI-mass spectrum exhibited a peak at m/z 624.81 for complex **2** in the presence of 2-AP, confirming that the catalytic oxidation proceeds through the formation of an enzyme-substrate adduct. Furthermore, complex **2** showed potential antibacterial properties against pathogenic bacterial species such as *Staphylococcus aureus*, *Enterococcus*, and *Klebsiella pneumonia*. Scanning electron microscope studies provided evidence that the antibacterial activity is attributed to the destruction of the bacterial cell membrane.

Chapter IV represents the synthesis, crystal structure, supramolecular architecture, 4-methylcatechol oxidation, and bactericidal activity of an interesting zinc(II)-Schiff base complex, $[Zn(\mathbf{L^2})_2Cl_2]$ (**3**), [Schiff base (**HL^2**) = 2-(2-methoxybenzylideneamino)phenol]. The analysis of the crystal structure of complex **3** indicates that the zinc centre is present in a distorted tetrahedral arrangement. The Schiff base molecule adopts three donor centres, but it becomes protonated and exists as a zwitterionic form, acting as a monodentate coordinator towards zinc. Complex **3** has been studied for its ability to catalyse the biomimetic oxidation of 4-methylcatechol (4-MC) in methanol, and it demonstrates high efficacy with a good turnover number of 1.45×10^3 h^{-1}. Various techniques such as electrochemical studies and electron paramagnetic resonance analysis have been employed to investigate the behaviour of complex **3** in the presence of 4-MC. The results confirm that the catalytic reaction proceeds through enzyme-substrate binding, and the generation of radicals during the catalytic process drives the oxidation of 4-MC. Additionally, an antibacterial study has been conducted against several clinical pathogens including *Bacillus sp*, *Enterococcus*, and *E. coli*. To assess the antimicrobial properties of complex **3**, scanning electron microscope and EDX analysis were performed on the pathogens treated with a low dosage of the complex. The results reveal the destruction of the bacterial cell membrane in the selected zone of inhibition area, with a zinc occurrence of 1.44%. This finding holds significant promise for the development of future antibacterial agents.

Chapter V represents the synthesis and crystal structure of a palladium(II) complex [(κ^4-{1,2-C_6H_4(N=CH−$C_6H_4O)_2$}Pd] (**4**) supported by a dianionic salen ligand [1,2-C_6H_4(N=CH−$C_6H_4O)_2]^{2-}$ (**H_2L^1**) was synthesized and used as a molecular pre-catalyst in the hydroboration of aldehydes and ketones. Complex **4** was evaluated as an effective catalyst in the hydroboration of aldehydes and ketones using pinacolborane (HBpin). This process yielded boronate esters in exceptional yields at room temperature without the need for solvents. Furthermore, complex **4** demonstrated its competence as a catalyst in the reductive amination of aldehydes with HBpin and primary amines. This reaction occurred under mild and solvent-free conditions, resulting in a high yield (up to 97%) of secondary amines. Both methodologies exhibited remarkable conversion rates, excellent selectivity, and a wide range of applicability, accommodating electron-withdrawing, electron-donating, and heterocyclic substituents. A computational investigation utilizing density functional theory (DFT) elucidated the reaction mechanism behind the complex **4**-catalyzed hydroboration of carbonyl compounds in the presence of HBpin. Additionally, the protocols unveiled the dual functionality of HBpin in facilitating the hydroboration reaction.

Chapter VI represents the design and preparation of metal complex salts of the novel hybrid d-f block type, $[Cu(bpy)_2]_2[Ce(NO_3)_6]_2$ (**5**), $[Cu(phen)_2(NO_3)]_2[Ce(NO_3)_6](HNO_3)$ (**6**), $[Zn(bpy)_2(NO_3)][ClO_4]$ (**7**), and $[Zn(phen)_2(NO_3)]_2$ $[Ce(NO_3)_6]$ (**8**); [bpy = 2,2'-bipyridine; phen = 1,10-phenanthroline]. X-ray analysis of the structures of **5** and **6** reveals that the copper(II) centres in the cationic complex units have highly distorted tetrahedral and rare bicapped square pyramidal coordination geometries, respectively. Similarly, **7** and **8** exhibits rare bicapped square pyramidal geometry for their zinc(II) ions, while **5**, **6**, and **8** contain cerium(IV) ions arranged in a dodecahedral geometry. Studying the supramolecular interactions, it is observed that intermolecular O···H and O···π short contacts contribute to binding the complex units in **5**. In contrast, complex salt **6** demonstrates predominantly π···π interactions, along with O···H and O···π short contacts, which facilitate binding among the complex units. To investigate the charge-transport phenomenon, we utilized complex salts (**5**-**8**) to construct Schottky devices. The carrier mobilities (μ) for salts **5**-**8** were determined as 1.76×10^{-6}, 9.02×10^{-6}, 1.86×10^{-8}, and 4.31×10^{-8} m^2 V^{-1} s^{-1}, respectively, with corresponding transit times (τ) of 439, 85, 4.17×10^3, and 1.79×10^3 ns. These results indicate that complex salt **6** exhibits the highest transport properties among all the complex salts. Analysing the charge-transport

properties from a crystal engineering perspective, the superior performance of **6** can be attributed to its predominant π···π interactions. Overall, the synthesis of these novel complex salts, along with their physicochemical properties and charge-transport applications, holds significant promise for the development of new crystalline materials with intelligent functionalities.

Chapter VII outlines an overview of the progress made thus far and identifies prospective avenues for future research.