Preface

The bond between metal and at least one carbon atom of an organic compound is defined as organometallic chemistry. There is some intense research in this field of chemistry with its innumerable applications. The realistic example of this type of compounds is vitamin B$_{12}$. The first organometallic compound i.e., cacodyl was synthesized in 1760 containing arsenic as metal and the bond is σ bond. Later in 1827 W.C. Zeise synthesized another organometallic compound with metal to carbon π bond i.e., Zeise's salt of platinum metal. Synthesis of diethylzinc by E. Frankland in 1848 and discovery of nickel carbonyl by L. Mond in 1890 has brought immense attention towards metal carbon bonds. Serendipitous discovery of ferrocene by Pauson and Kealy and independently by E.O. Fischer and consequent characterization of its sandwich structure by R.B. Woodward and G. Wilkinson brought new dimensions in organometallic chemistry introducing sandwich compounds. Organometallic complexes found number of applications in catalysis and as reagents notably Grignard reagent using magnesium, Ziegler-Natta catalyst using aluminium, Heck reaction using organo palladium, Noyori catalyst and Grubbs catalyst using ruthenium. There are some potential achievements with this organometallic chemistry which are honoured by Nobel prizes in the 21st century viz., (1) W.S. Knowles, R. Noyori and Karl Barry Sharpless for asymmetric hydrogenation in 2001 (2) Y. Chauvin, R. Grubbs and R. Schrock on alkene metathesis in 2005 and (3) R. F. Heck, E. Negishi, A. Suzuki for palladium catalyzed cross coupling reactions in 2010 which emphasizes the importance of organometallic compounds. The utilization of organometallic complexes is not limited for chemical conversions but also found use in curing diseases. Among the noted examples are Paul Ehrlich’s arsenic based organometallic compound Salvarsan for the treatment of syphilis and titanocene dichloride (Cp$_2$TiCl$_2$), the first non-platinum organometallic complex to undergo clinical trials as a chemotherapy drug. Half-sandwich organometallic complexes possessing good amount of cytotoxicity with their different mechanism of action than the cisplatin in chemical biology. In this thesis, Chapter 1 deals with the general introduction of the arene d$^6$ metal complexes and detailed description of these complexes. A brief explanation of the applications of arene ruthenium, rhodium and iridium complexes in the fields of biology and catalysis. Chapter 2 deals with arene ruthenium {1, 3, 5-tris(di-2-pyridylaminomethyl)benzene} complexes and their synthesis, structural and in vitro functional characterization. Reactions of arene ruthenium precursor with the ligand in 1:2, 1:1 and 3:2 ratio have resulted mono- to tri- nuclear complexes respectively. the complexes are moderate antibacterial with the zone of inhibition value. Mono-nuclear $p$-cymene ruthenium
complex resulted good amount of cytotoxic activity over chosen cancerous cell lines viz., Mouse melanoma (B16F10), Human acute monocytic leukaemia (THP-1), Human prostate (PC-3) and Human ovarian (SK-OV-3). Chapter 3 describes the in vitro antiproliferative activity of multi-nuclear polypyridyl rhodium and iridium complexes against cancer cells and human pathogens. Mono- to multi-nuclear complexes have obtained with the corresponding ratios of metal precursor and ligand. HOMO-LUMO gap resulted di-nuclear complexes are needed less energy to excite an electron in comparison to the other mono- and tri- nuclear complexes. Complexes under study possessed antibacterial activity on one gram-positive and three gram-negative bacterial strains. Tri-nuclear rhodium complex exhibited better cytotoxicity in comparison to the other complexes. Chapter 4 deals with Synthesis, structural studies and antibacterial evaluation of Cp* rhodium and Cp* iridium complexes using dipyridyl ketone based hydrazone ligands. Reaction of rhodium and iridium precursor compounds with ligand L1-L3 in 1:2 and 1:1 metal dimer to ligand ratio has yielded mono-nuclear and di-nuclear complexes respectively. The synthesized complexes are water soluble but di-nuclearization resulted the less solubility. Complexes tested are moderate antibacterial against four bacterial strains viz., S. aureus, B. thuringiensis/K. pneumonia, E. coli and P. aeruginosa. Chapter 5 deals with Synthesis, structural and biological studies of half-sandwich d⁶-metal complexes with pyrimidine-based ligands. Half-sandwich ruthenium, rhodium and iridium complexes were obtained by treatment of the corresponding metal precursors with simple pyrimidine viz., Aminopyrimidine (L1) and Mercaptopyrimidine (L2) ligands. The in vitro antiproliferation and antibacterial activities of the synthesized complexes 1-4 have been explored. Interaction of the complexes 1-4 towards the biomolecule i.e., CT-DNA has elucidated. The rhodium complexes exhibited low energy gap in comparison to the iridium complexes. Such a low gap is well correlation with the antibacterial activity of the complexes. The complexes 1-4 have exhibited better antibacterial activity on E. coli bacterium in comparison to the other chosen bacterial strains. The mercaptopyrimidine complexes possessed good amount of cytotoxicity than the aminopyrimidine complexes. Complexes 3 and 4 exhibited highest activity on MIA PaCa-2 (human pancreatic cancer) cell lines than the HT-29 (human colorectal cancer) and BE (human colorectal cancer) cell lines. Biophysical studies suggested that the complexes are in non-covalent interaction with the CT-DNA. Chapter 6 deals with Synthesis and biological studies of ruthenium, rhodium and iridium metal complexes with pyrazole-based ligands displaying unpredicted bonding modes. Half-sandwich ruthenium, rhodium and iridium complexes (1-12) bearing pyrazole derived ligands L1 and L2 were synthesized and characterized. Variation in the heterocyclic ring resulted atypical bonding modes i.e., mono-dentate or bridge fashion
bonding to the metal centre. HOMO-LUMO gap for the complexes 1-6 suggested that bis-
substituted complexes need less energy for the electronic transition. Complexes 1-6 studied for
their antibacterial and CT-DNA interaction. Complexes under investigation are selective
towards the gram-negative E. coli bacterium with the zone of inhibition value. Biophysical
studies suggest that complexes are in phosphate backbone interaction with the CT-DNA.

Chapter 7 deals with Half-sandwich d⁶ metal complexes with bis(pyridine
carboxamide)benzene ligand: Synthesis and spectral analysis. Reaction between metal
precursor and ligand yielded mono- and di- nuclear complexes with the 1:2 and 1:1 ratios
respectively. Surprisingly, heavier congener i.e., iridium di-nuclear complex exhibited different
orientation of crystallisation with respect to its analogues.

Precisely, in this thesis work, we have synthesized, characterized and studied various
structural features of the arene d⁶ metal complexes with various nitrogen donor ligands and
carried out the preliminary biological activity of some complexes.