ABSTRACT

The work embodied in this thesis deals with the synthesis and characterization of a number of mononuclear, binuclear to dimeric, homometallic to heterobimetallic and isomeric complexes. Most of them are complexes of Schiff bases synthesized by one-pot method of synthesis. They have been characterized by elemental analysis, TGA/DTA, ESI-MS, FTIR, Raman, UV-visible, NMR and EPR spectroscopic investigations. The electrolytic nature has been established by their molar conductance measurements at room temperature. In case of isomeric complexes, relative energies of optimized geometries have been calculated applying DFT, to support their conformations. Crystal and molecular structure of some of the complexes has been established by single crystal X-ray diffraction. Scanning electron microscopy (SEM) in few cases was done to observe their morphology.

The introductory chapter describes the aims and objectives of the present work and a brief review of the coordination compounds. It explores their structure, chemical and biological applications of Schiff base and dithiocarbamate complexes in general.

In chapter second, a set of Ni(II), Cu(II) and Zn(II) complexes have been synthesized by one pot condensation reaction of 2-hydroxy-4-methoxybenzophenone with 1,3-diaminopropane in presence of metal in 2:1:1 molar ratio. They have been found to be N2O2 type chelates in which Ni(II) and Cu(II) are coordinated through azomethine nitrogen and phenolic oxygen of the ligand. However, in the case of Zn(II) complex two nitrate ions were also found to be coordinated as monodentate ligand. They have been characterized by elemental analysis, conductance
measurement, thermal analysis (TGA/DTA), FT-IR, $^1$H-NMR, EPR spectra, ESI-MS and electronic spectral studies. A single crystal X-ray structure of [Ni(L)] complex was determined. It crystallizes in monoclinic system having unit cell parameters $a=14.015(5)\text{Å}$, $b=13.391(5)\text{Å}$, $c=14.931(5)\text{Å}$ and $\alpha=90.000(5)^\circ$, $\beta=112.237(5)^\circ$, $\gamma=90.000(5)^\circ$ with $P 2_1/c$ space group. The nickel oxygen distances, Ni-O1 (1.828 Å) and Ni-O2 (1.836 Å) are shorter than nickel nitrogen distances Ni-N1 (1.881 Å) and Ni-N2 (1.888 Å). Although the two phenyl rings are identical, one of them is slightly tilted. The molecular packing diagram has shown four formula units per unit cell with no π-π stacking interaction. A square-planar geometry has been confirmed for Ni(II) complex. On the basis of elemental analysis, IR, UV-visible and EPR data a square-planar geometry for Cu(II) and a distorted octahedral geometry for the Zn(II) complex has been proposed. It is apparent from IR absorption bands that NO$_3^-$ coordinates in monodentate fashion in case of Zn(II) complex. The low molar conductivity values of the complexes measured in chloroform and DMSO suggest their non-ionic nature.

The third chapter reports the synthesis of a series of new heterobimetallic transition metal complexes of the type [Cu(pn)$_2$][MCl$_4$] (where M=Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), pn=1,3-diaminopropane). The reaction of [Cu(pn)$_2$]Cl$_2$ with MCl$_2$ leads to the formation of [Cu(pn)$_2$][MCl$_4$]. It is apparent that the chloride ion from [Cu(pn)$_2$]Cl$_2$ has been transferred to MCl$_2$ to maintain equilibrium between the two species. All the compounds are 1:1 electrolyte in DMF. In such complexes, the central metal ion in cationic form explicitly exists in square-planar environment; however, the anionic counterpart maintains its ubiquitous tetrahedral configuration. On the basis of elemental analysis, molar conductance,
TGA, IR, and electronic spectral studies, it is concluded that anionic moiety is electrically stabilized by its cationic counterpart.

Fourth chapter describes the one-pot synthesis of binuclear complexes of Cu(II) with diketones (acetylacetone, benzil and 4,6-diacetylresorcinol), 2-amino pyridine and dithiocarbamate (dtc). The complex 1, [Cu(C_{13}H_{16}N_{4})Cl_{2}] and 4, [Cu_{2}(C_{20}H_{18}N_{4})Cl_{4}] were as expected but 2, [Cu_{2}(C_{20}H_{46}N_{4}S_{8})] and 3, [Cu_{2}(C_{7}H_{5}O_{2})_{4}(C_{12}H_{10}N_{2}O)_{2}] are unprecedented products (Fig. 1). The complex 2 was synthesized by the reaction of 1 with dithiocarbamate, surprisingly the whole organic moiety of 1 was replaced by dtc. On the other hand complex 3 (reported elsewhere) was synthesized by one pot method, refluxing a mixture of Cu(II), benzil and 2-amino pyridine in MeOH for 48h. This complex has also been synthesized by a different route. We have given a mechanism to support the formation of this complex. They have been characterized by elemental and thermal analysis. Spectroscopic investigations include FTIR, Raman, electronic and EPR studies. Their single crystal X-ray have been done to evaluate the molecular structure, inter and intramolecular interactions. Scanning electron microphotographs were taken to reveal the morphology and particle size. IR spectra of dithiocarbamate complexes have shown its symmetrical bidentate mode of coordination. Based on electronic spectra and crystal refinements square-planar geometry for 1 and 4, octahedral for 3 and square pyramidal geometry for complex 2 has been assigned. The crystal structure of 2 reveals its centrosymmetric structure built of [Cu_{2}(Et_{2}dtc)_{4}] unit. The molecule crystallizes in monoclinic system having space group P1 21/c 1. The bridging network formed out of (Cu1–S2–Cu1–S2) in layers, is planar. The four basal sulphur atoms are coplanar.
Fig. 1 Structures of complex 1-4
The copper metal situated at the centre acquires a distorted square pyramidal geometry with four sulphur atoms of its two dithiocarbamate units and fifth (axial) coordination occurs via bridging sulphur atom of third ligand of another unit. Thus the structure of such a molecule is viewed as edge-sharing distorted square pyramid. The equatorial Cu-S bond distance (2.3253Å) is longer than axial Cu-S (2.2957Å) ones. The complex 3 shows a paddle wheel type dimeric structure in which two Cu(II) atoms (Cu–Cu=2.6353Å) are connected by four benzoate ligand and two benzamidopyridine. Each Cu atom in this molecule is octahedrally coordinated with four oxygen atoms of basal benzoate units in equatorial plane, one pyridine nitrogen and another Cu atom. The molecule crystallizes in triclinic system with a space group P-1. The Cu–N bond distances (2.207Å) are longer than Cu–O (1.967Å) while all Cu–O distances are identical. It is concluded that almost constant Cu–O distance (1.967Å) is characteristic of a CuO₄N chromophore. It crystallizes in a triclinic crystal system with P-1 space group. The extended three dimensional network of the molecule has revealed some short intermolecular interactions due to intra- and intermolecular hydrogen bonding (between amide O and H of aromatic rings) and also due to π-π stacking between the aromatic rings.

The final and fifth chapter compiles the synthesis of three isomers of [Cu(pn)₂Cl₂] in solid state by the reaction of Cu(II) with 1,3-diaminopropane under different experimental conditions. They were characterized by elemental analysis, molar conductance, FTIR, TGA, EPR and electronic spectra. Their relative energies were calculated applying Time-Dependent DFT calculations. The molar conductance of 1mM solution of the complexes measured in DMSO falls in 40-44 S cm² mol⁻¹. All the isomers in aqueous medium show similar absorption pattern in the UV-visible region of the spectra. They are nearly identical in solution although in the solid state they exist in three distinct colors. It is known, that six membered ring formed by 1,3-diaminopropane and metal ion possesses great conformational freedom (chair or boat form) with the chair conformation being energetically more stable. The change in the
color of complexes is due to a change in conformations of the 1,3-diaminopropane molecule. The Cu(II) in [Cu(pn)₂Cl₂] lies on an inversion centre and is octahedrally (4+2) coordinated by four N atoms of two 1,3-diaminopropane and two chloride ions displaying three different spatial conformations namely, chair-chair, boat-boat and chair-boat arrangements. The coordination polyhedron of the Cu(II) ion can be described as axially elongated octahedral, with chloride ions at the axial position. The bite angle N-M-N is always found to be smaller than 90°. The Cu-N bond length plays a critical role in the existence of these three isomeric forms in solid state. Axial position in all the cases is occupied by chloride ion. The optimized axial bond lengths of Cu-Cl are longer than Cu-N bond lengths in all complexes. The TGA of the complexes suggest that Cu is left as final residue at 600 °C. The entire data has been supported by DFT calculation.