CHAPTER 1

INTRODUCTION
1.1 INTRODUCTION

The chemistry of chalcone metal complexes represents one of the important fields of chemistry, it has generated intensive scientific studies in the world. In recent years large area of inorganic chemistry is attributed to this study due to its significant properties. This branch of chemistry has gained impetus owing to the large amount of synthetic work and an extensive theoretical treatment for understanding the structure and nature of bonding in coordination compounds. The world knew Chalcones from fifty years ago. Since the twentieth century, the chalcones have been used to form complexes. The synthesis of newer organic chelating agents that can coordinate with transition metal ions has tempted the researchers to synthesize more and more coordinated compounds. In the complexes, the metal ion is present at the center and has the capacity to accept a lone pair of electrons. The negative or neutral species containing one or more unshared pair of electrons and capable to donate such lone pair of electron to the central metal are called as ligand. Sidgwick suggested that the metal ion will continue accepting electron pairs till the total number of electrons in the metal ion and those donated by ligands is equal to that of the next higher noble gas. This total number of electrons is called effective atomic number (EAN) of the metal.

The geometric shapes of the complexes depend on the coordination number of the metal complex, shapes of metal complex of chalcones are tetrahedral, square planar or octahedral. Valence bond theory (VBT), which assumes that all bonds are localized bonds formed between two atoms by the donation of an electron from each atom. According to this theory, the central metal ion makes available equal number of empty orbital to its coordination number. This theory was the suggestion made by Linus Pauling that atomic orbitals mix to form hybrid orbitals, such as the sp, sp², sp³, dsp², and d²sp³ orbitals which give shape to molecule, linear, tetrahe-
The filled ligand orbitals overlap with hybrid orbitals of metal ion and forms coordinate covalent bond. Electronic structure of central metal ion, shapes of complexes, magnetic moments and stereochemistry, explained mainly by this theory, but there is some limitations on this theory, it failed to explain the colour & characteristics of absorption spectra of complex compounds, it does not give proper explanation of Orbital contribution and temperature dependency on magnetic moment of coordination complex, VBT fails to predict any distortion in the shapes of the coordination complexes from regular geometry.

Crystal field theory (CFT) developed by Bethe and Van Vleck is another approach to study the complexes. It describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. CFT qualitatively describes the strength of the metal-ligand bonds. Based on the strength of the metal-ligand bonds, the energy of the system is altered. This may lead to a change in magnetic properties as well as color. IN CFT the interaction of d-orbitals of a central atom with ligands, which are considered as point charges. According to CFT, the attraction between the central metal and ligands in a complex is purely electrostatic. CFT focuses on the interaction of the five (n − 1)d orbitals with ligands arranged in a regular array around a transition-metal ion and splits them into two energy sublevels t_{2g}-triplet and e_{g}-doublet. The ligand field splitting depends on whether the ligands are arranged in an octahedral, tetrahedral, or square planar way around the central ion. The magnitude of the crystal field splitting of the d-orbitals energies may be represented by the symbol Δ. It is used to denote energy difference. The crystal field splitting energy, Δ is frequently measured in terms of a parameter, Dq. The magnitude of 10 Dq or Δ depends upon the nature of ligand and charge on the central metal ion. CFT interprets the magnetic and spectral properties of transition metal complexes quantitatively.

Molecular Orbital Theory this theory can provide quantitative interpretations for all the properties of coordination complexes, (MOT) developed by Van Vleck. The bonding between metal ion and ligand is considered as purely covalent and intermediate. A coordination complex or metal complex involve a central atom or ion.
which called the coordination centre, and a surrounding array of bound molecules or ions, which known as ligands. Many metal-containing compounds, especially those of transition metals, are coordination complexes, then the resulting entity is known as metal complex. N, O and S are common donor atoms presents in ligands. the ligand is attach to a central metal ion by two or more donor atoms to forming a heterocyclic ring structure are called as chelate. The stability of a chelate complex depends on the size of the chelate rings complexes that contain five-membered chelate rings, which have almost no strain, are significantly more stable than complexes with six-membered chelate, the coordination number of metal ion is generally 4 or 6.

Metal complexes formed as a result of a covalent bond between the metal and the donor ions can proceed with or without the replacement of a hydrogen atom from an organic functional group.

Literature survey revealed that many of the organic molecules act as chelating ligands. These organic molecules involves amines, hydrazones, semicarbazones, thiosemicarbazones, carboxylic acids, α, β unsaturated ketones and many of other molecules. α, β unsaturated ketones gives an excellent examples in synthesis of stable metal complexes.

The formation of metal complexes from chalcones, chalcones have been used as ligands. They can act as bidentate, monodentate, or polydentate species towards the metal complexes depend on the number of donor atoms present in the chalcones. The chalcones can form metal chelate when one or more than one donor atoms existing next to to the carbonyl group.

o-hydroxychalcones are the most chalcone ligands widely studied. (Fig.1)
From the oxygen atoms of carbonyl and phenolic group the ligands can make the chelates with metal ions. The different complexes of chalcones with different metal ions due to their good synthetic flexibility can formed from chalcones derivatives. The chalcones derivatives has able to form complexes with Mn(II), Cu(II), Zn(II), Co(II), Ni(II), Ru(III), Rh(III), and Cd(II) by using different metal Salts such as Fluoride sulfate acetate and acetate. 2'-Hydroxychalcones are reported for their varied biological activities like antibacterial, antifungal, anticancer, antitumor, antiviral, antitubercular, antiulcer, antimalarial and antidiabetic agents. Halo hydroxyl acetophenones are the starting materials for the synthesis of 2'-hydroxychalcones, which are of great importance in medicinal chemistry. The biological activities, analytical applications and formation constants of 2'-Hydroxychalcone and its derivatives have been extensively reviewed quite recently.

Transition metal ions bound to organic ligands have been found to possess different activities and find wide applications in analytical, catalytical, biological, medicinal, microbial and insecticidal fields. The diverse applications of metal chelates maybe due to unused coordination sides of complexed ligand systems or due to selective oxidation states of complexed metal ions in coordination sphere. Chalcone is a strong hydroxyl antioxidant, their ability to act as free radical acceptors; the metal complexing properties of these molecules may make some contribution to their total activity. The presence of reactive α, β-unsaturated keto group in chalcones is found to be responsible for their biological activity. The complexes of metallic salts are more potent and less toxic in many cases as compared to the parent drug. These metal complexes are found to be interesting due to their biological applications like antifungal, antibacterial and anti tumor activity. Some chalcones derived from coumarin derivatives, possess significant antimicrobial activity. 2'-Hydroxychalcone complexes and its derivatives have been reported as an anti-HIV agent. Thus it was thought worthwhile to synthesize and characterize various new metal complexes and to evaluate them for antimicrobial activity.

Synthesis, characterization and spectral data (IR, 1H NMR and MASS) of 2'-Hydroxychalcone, N-pyrazolines, N-acetyl-2-pyrazolines and synthesis of Cu(II), Ni(II), Co(II), Fe(II), and Zn(II) complexes of the following selected 2'-hydroxychalcones as ligands are reported in chapter two.
An experimental and spectral techniques carried throughout in the research work are details in chapter three. Thirty compounds of transition metal complexes were synthesised and they were examined for various analytical parameters to establish their chemical composition and physicochemical properties. These metal complexes were further investigated using various instrumental techniques to establish their structural configuration.

Results and discussion of these complexes are present in chapter four. In this chapter analytical, magnetic moment, molar conductivity, UV-visible, IR, $^1$H NMR, ESR, XRD and TGA spectral data of synthesised complexes is tabulated and the respective observed values are interpreted in the light of literature. From these findings it can be concluded that elemental analysis showed stoichiometries of all the metal complexes in 1:2 metal to ligand ratios. The conductivity of all the metal complexes was showed non-electrolytic nature. The IR spectral data indicate the ligands act as mononegative bidentate towards Cu(II), Ni(II), Co(II), Fe(II), Zn(II). The electronic spectral data suggest that all Cu(II) and Zn(II) complexes are square planar and all Ni(II), Fe(II), Co(II) complexes are of octahedral geometry. Magnetic susceptibility measurement indicates paramagnetic behaviour of all complexes except Zn(II) complexes. Thermal analysis studies confirm the existence of coordinated water molecule in Ni(II), Co(II), Fe(II) complexes and absence of coordinated water molecule in Cu(II) and Zn(II) complexes.

The last fifth chapter is devoted to the total account of antibacterial and antifungal study of all the newly synthesised 2'-hydroxychalcones, N-hydro-2-pyrazolines, N-acetyl-2-pyrazolines and metal complexes of Fe(II), Cu(II) and Co(II).

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