Summary

Triphenylphosphine and triphenylarsine complexes of ruthenium(II) and ruthenium(III) have gained considerable interest for the past few decades. These complexes have been used as catalyst in various reactions like hydrogenation, hydroformylation, oxidation, reduction, hydration, isomerisation, decarbonylation and alkylation. Carbonyl compounds of ruthenium complexes were used as important homogeneous catalysts in reactions like carbonylation and oxo reaction. Some of these complexes have been used as starting materials for many ruthenium(II) and ruthenium(III) complexes. The present work described in the thesis concerns with the reactions of ruthenium(II) and ruthenium(III) complexes of tertiary phosphines, arsines and heterocyclic nitrogen bases with ligands containing O,N; N,S; O,N,O and O,N,S donor atoms. The structure of these new compounds have been investigated by using various physico-chemical methods. The in vitro biological activities of some of the complexes have been tested against some pathogenic micro organisms and their activities were compared with activities of some standard antibiotics.

In chapter II, a detailed study on the reactions of ruthenium(III) complexes containing triphenylphosphine or triphenylarsine with tetradeutate Schiff bases have been discussed. The newly prepared complexes have been formulated as [RuX(LL')(EPh3)] (X = Cl or Br; H2LL' = dibasic tetradeutate Schiff base prepared from the reactions of β-diketones with diamines; E = P or As). These complexes have been characterised through elemental analyses, spectral (IR, electronic and EPR)and electrochemical data. An octahedral structure has been tentatively proposed for these complexes. The antibacterial activity of the ligands and their ruthenium(III) complexes has been studied and compared with the standard bacteriocide (Streptomyacin sulfate).
In addition to the above, we focussed our attention on the effect of electron donating groups present in the ligands on the antibacterial activity. Chapter III describes the reactions of \([\text{RuHCl(CO)(PPh}_3]_2(\text{B})]\) (\(\text{B} = \text{PPh}_3\) or py or pip or morph) with various \(\alpha,\beta\)-unsaturated-\(\beta\)-ketoamines. The products of general formula \([\text{RuCl(CO)}(\text{LL'})(\text{PPh}_3)(\text{B})]\) (\(\text{HLL'} = \text{monobasic bidentate ligand; B = PPh}_3\) or pyridine(py) or piperidine(pip) or morpholine (morph)) have been isolated and an octahedral structure has been assigned on the basis of elemental analyses, spectral (IR, electronic, \(^1\text{H}-\) and \(^{31}\text{P}-\) NMR) data. Antibacterial activity was also tested for these complexes against two species of pathogenic bacteria and the results were compared with a standard antibiotic.

The reactions of dibasic tetradentate Schiff base ligands with ruthenium(III) complexes of the type \([\text{RuX}_3(\text{EPH}_3)_3]\) (\(X = \text{Cl}, \text{E} = \text{P}; X = \text{Cl} \text{or Br, E} = \text{As}\)) or \([\text{RxBr}_3(\text{PPh}_3)_2(\text{MeOH})]\)] have been reported in chapter IV. The new complexes obtained are of the type \([\text{RuX(LL')(EPH}_3)]\) (\(X = \text{Cl} \text{or Br}; \text{H}_2\text{LL'} = \text{dibasic tetradentate Schiff base obtained from the reactions of anthranilic acid or 2-amino thiophenol with } \beta\text{-diketones; E = P or As}\). Based on the elemental analyses and spectral (IR, electronic and EPR) data, magnetic moment and electrochemical studies, an octahedral structure has been tentatively proposed for these complexes. The antibacterial activity for some of the ligands and their appropriate ruthenium(III) complexes has also been tested.

The synthesis and characterisation of some stable hexa coordinated ruthenium(III) complexes containing tridentate Schiff bases of general formula \([\text{RuX(LL')(EPH}_3)_2]\) (\(X = \text{Cl \text{or Br; E} = \text{P or As}; LL' = \text{dibasic tridentate Schiff base ligand derived from the condensation of salicylaldehyde or o-hydroxy acetophenone with thiosemicarbazide or semicarbazide}\) have been reported in chapter V. In all these reactions, the Schiff base ligand behaves as a binegative tridentate (\(O,N,S\)- or \(O,N,O\)-) ligand by substituting one triphenylphosphine/arsine
or methanol group and two halide groups from the starting complexes. An octahedral structure has been tentatively proposed for these complexes on the basis of elemental analyses, spectral (IR, electronic and EPR), magnetic moment and electrochemical data. The new complexes have been screened for their biological activity against two pathogenic bacteria (*Salmonella typhi* and *Salmonella aureus*). The antibacterial activity of the ligands and their ruthenium(III) complexes was compared with standard bacteriocide (*Colistin*).

Further, in chapter VI, the reactions of tertiary phosphine and arsine complexes of ruthenium(III) of the type \([\text{RuX}_3(\text{EPh}_3)_3]\) or \([\text{RuBr}_3(\text{PPh}_3)_2(\text{MeOH})]\) with various \(\alpha,\beta\)-unsaturated-\(\beta\)-ketoamines have been reported. The new complexes obtained have been formulated as \([\text{RuX}_2(\text{LL'})(\text{EPh}_3)_2]\) (\(X = \text{Cl or Br; HLL'} = \) monobasic bidentate ligand; \(E=\text{P or As}\)). All these complexes have been characterised by elemental analyses, spectral (IR, electronic and EPR) and electochemical data and an octahedral structure has been tentatively proposed for these complexes. The ligands and ruthenium(III) complexes have been tested *in vitro* to evaluate the antibacterial activity against the *Eenterobacteria feacalis* and *Aeromonas hydrophilla*.

In general, electrochemical studies indicate easier reduction at the metal centre in complexes containing ligands with better electron donating groups. Thus reductions have been observed at lower negative potentials for complexes containing sulphur donor atoms compared to oxygen donor atoms, indicating higher electron donating ability of sulphur atoms. Similarly, the oxidation potentials have been observed at higher positive values for sulphur containing ligands as compared to oxygen containing ligands. Same kind of behaviour of reduction and oxidation has been noted for complexes containing phosphorus and arsenic donor ligands, exemplifying the more electron donating ability of arsenic.
atoms. Besides, the electrochemical data of all the new complexes showed only a single step one electron transfer processes.

As far as the biological activities of the new complexes are concern, the complexes have been found to have more toxic effect than the free ligands. Moreover, it has been observed that the complexes containing tetradeinate ligands are more active than the complexes containing tridentate or bidentate ligands. The activity increases in the order: tetradeinate > tridentate > bidentate. This may be due to the better chelating effect of tetradeinate ligand as compared to tridentate or bidentate ligand. In addition to the above, the complexes containing ligands with sulphur donor atoms showed more activity than the ligands containing oxygen donor atoms. It has also been observed that the ligands containing more electron donating substituents like -CH₃ or -OCH₃ showed an increased activity, demonstrating higher delocalisation in chelation. Above all, the new complexes showed better antibacterial activity as compared to standard antibiotics such as Stereptomycin sulfate and Colistin.