PREFACE
The chemistry of cobalt, nickel and copper is of interest to the scientists in view of a variety of preparative methods and structural types which have been observed with various ligands.

The nature of the anion has been found to be a contributing factor towards stability, colour and many other properties of the complexes and it is surprising that although an extensive series of investigations have been carried out on the simple inorganic salts of these metals, why only very little work has been done where the anion is organic in nature.

Among the various nitrogen donors ligands, pyrazole-5-one, ethylenediamine, propylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, 2,2'-dipyridyl, 1,10-phenanthroline, 2-methylimidazole, benzimidazole, urea, thiourea, phenylthiourea, diphenylthiourea and benzoylthiourea, have been used as ligands for a large number of transition metals. In the past several years, significant growth in the field of such complexes has occurred and in the present investigation, the above mentioned ligands have been complexed with cobalt(II), nickel(II) and copper(II) pyrazoloneate. Additional ligands like 2-methylimidazole, benzimidazole for nickel(II), urea for cobalt(II) and nickel(II), thiourea and diphenylthiourea for cobalt(II) and phenylthiourea and benzoylthiourea have been used as ligands for cobalt(II) and copper(II).
Diethylenetriamine ligand behaves as a bidentate ligand for cobalt(II), nickel(II) and copper(II) pyrazolonate, while triethyleneenetetramine behaves as a tetradoentate ligand for cobalt(II) and nickel(II) but bidentate ligand for copper(II) pyrazolonate and tetracethylenepentamine behaves as a tetradoentate ligand for copper(II) pyrazolonate complexes.

The investigation has been mainly carried out with a view to correlate the structures of the complexes with the symmetry and base strength of the ligands. The results of these investigations which were started in March, 1988 are presented in this thesis entitled "Structural studies on cobalt(II), nickel(II) and copper(II) complexes with nitrogen containing ligands" consisting of four chapters.

The first chapter of the thesis gives some introductory ideas about the coordination complexes and a variety of physicochemical methods like elemental analysis, conductance, infrared, magnetic susceptibility measurements, electronic spectroscopy and thermogravimetric analysis which have been used for elucidating the structures of the complexes.

The second chapter outlines in detail the existing literature on the nitrogen donor ligands complexes of cobalt(II), nickel(II) and copper(II). As a very large number of complexes of these metals are
known, to present a concise account of the so-far reported and related work has been found to be exceeding difficult. However, an attempt has been made to list all the complexes relevant to this work, which have been studied during the years 1940-1990.

Third chapter gives the methods used for the preparation of complexes and also contains complete experimental data collected by the use of above mentioned techniques.

The discussion of the data in the light of the structures assigned to the complexes is given in chapter fourth.

The treatment of 3-methyl-4-nitro-1-(para-nitrophenyl)-pyrazole-5-one in enolic form(L) with cobalt(II), nickel(II) and copper(II) sulphate gives products which are nonelectrolytes and do not give the test of sulphate ion. These are therefore, assigned formula such as [Co or Ni or Cu(L)₂]. These complexes treated with various nitrogen containing ligands (L₁₋L₁₄) results in the isolation of crystalline complexes which have been characterised by their microanalysis and are assigned the general formulae:
[Co(L)₂(L₁)₂]. 3H₂O; [Co(L)₂(L₂)₂]. 4H₂O; [Co(L)₂(L₃)₂]. 4H₂O;  
[Co(L)₂(L₄)₂]. 6H₂O; [Co(L)₂(L₅)₂]. 2H₂O; [Co(L)₂(L₆)₂];  
[Co(L)₂(L₇)₂]. 2H₂O; [Co(L)₂(L₈)₂]. 2H₂O; [Co(L)₂(L₉)₂]. 2H₂O;  
[Co(L)₂(L₁₀)₂]. 3H₂O; [Co(L)₂(L₁₁)₂]. 2H₂O; [Co(L)₂(L₁₂)₂]. 2H₂O.  

[Ni(L)₂(L₁)₂]. 4H₂O; [Ni(L)₂(L₂)₂]. 2H₂O; [Ni(L)₂(L₃)₂];  
[Ni(L)₂(L₄)₂]. 2H₂O; [Ni(L)₂(L₅)₂]. 2H₂O; [Ni(L)₂(L₆)₂]. 4H₂O;  
[Ni(L)₂(L₇)₂]. 6H₂O; [Ni(L)₂(L₈)₂]. 6H₂O; [Ni(L)₂(L₉)₂]. 2H₂O.  

[Cu(L)₂(L₁)₂]₂H₂O; [Cu(L)₂(L₂)₂]. 3H₂O; [Cu(L)₂(L₃)₂]. 2H₂O;  
[Cu(L)₂(L₄)₂]. 3H₂O; [Cu(L)₂(L₅)₂]. 2H₂O; [Cu(L)₂(L₆)₂];  
[Cu(L)₂(L₇)₂]. 6H₂O; [Cu(L)₂(L₈)₂]. 3H₂O; [Cu(L)₂(L₉)₂]. 6H₂O.  

Where:  
L₁ = ethylenediamine  
L₂ = propylenediamine  
L₃ = diethylenetriamine  
L₄ = triethylenetetramine  
L₅ = tetraethylenepentamine  
L₆ = 2,2'-dipyridyl  
L₇ = 1,10-phenanthroline  
L₈ = 2-methylimidazole  
L₉ = benzimidazole  
L₁₀ = urea
\[ L_{11} = \text{thiourea} \]
\[ L_{12} = \text{phenylthiourea} \]
\[ L_{13} = \text{diphenylthiourea} \]
\[ L_{14} = \text{benzoylthiourea} \]

The conductance measurements in water and nitrobenzene indicate that all the complexes are nonelectrolytes.

Further evidence for the coordination of the ligand has been obtained from the infrared spectra which have been recorded in the region 4000 to 600 cm\(^{-1}\). The comparison of the spectra of free ligands and their complexes show shifts as well as splitting in some of the important ligand bands which have been taken to indicate coordination.

Thus the same ligand may be mono, di or tri corresponding to the metal(II) used. The evidence for the different denticities of the ligands has been obtained by infrared spectra.

The magnetic measurements have been made by Gouy's method and all the complexes are found to be paramagnetic, their paramagnetism falling in the usual range of three, two and one unpaired electrons as expected for high spin octahedral complexes of cobalt(II) and nickel(II) and planar complexes of copper(II) respectively.
The electronic spectra have been helpful in confirming the stereocherrmesty of the complexes predicted on the basis of magnetic measurements. A calculation of the various ligand field parameters such as Dq, B and $\beta$ has also been made and values interpreted in a consistent manner. The Dq values show that the ligand field in complexes is of moderate strength, the values of Racah parameter B and nephelauxetic ratio $\beta$ suggest that some covalent bonding is present in complexes.

The thermogravimetric studies show that the lattice water whenever it is present is the first molecule to be lost (60-180°C) and followed by ligands and then pyrazolonate. The formation of the metal oxide occurs around 750°C after which the curve becomes a straight line.