PREFACE

Among the various nitrogen donors ethylenediamine, propylenediamine, diethylenetriamine, triethylenetetramine, 2,2'-dipyridyl, 1,10-phenanthroline, imidazole and 2-methylimidazole have been used to synthesise a variety of coordination compounds possessing inorganic anions. In the present investigation an attempt has been made to present a systematic study on the complexes derived from copper(II), nickel(II) and cobalt(II) with the anions mandelate, malonate and anthranilate, with a view to correlate the structure of these complexes with the symmetry and base strengths of the ligands used.

The results to these investigations which were started in 1989 are presented in this thesis entitled "Studies on copper(II), nickel(II) and cobalt(II) complexes with nitrogen containing ligands" consisting of four chapters.

The first chapter gives an introduction of complexes and the physicochemical methods which have been used for elucidation of structure of the complexes. The second chapter describes an up-to-date survey of literature which were relevant to the present investigation. The third chapter gives the experimental methods used for synthesis of complexes, and complete experimental data. The discussion of experimental data in light of structure assigned to the complexes is given in the chapter four.
In the present investigation twenty seven complexes have been synthesised and studied by elemental analysis, molar conductance, infrared spectrophotometry, electronic spectrophotometry, magnetic susceptibility and thermogravimetric analysis. The general formula assigned for the complexes are:

\[ \text{[CuL}_n\text{]}\text{(C}_8\text{H}_7\text{O}_3\text{)}_2\cdot\text{xH}_2\text{O} \]

where \( n=2 \), when \( L=\text{ethylenediamine, propylenediamine, 2,2'-dipyridyl, 1,10-phenanthroline} \); \( n=4 \) when \( L=\text{imidazole} \); \( x=0 \) or 6.

\[ \text{[Cu(C}_3\text{H}_2\text{O}_4\text{)L]}\cdot\text{xH}_2\text{O} \]

where \( L=\text{ethylenediamine, propylenediamine, diethylenetriamine or triethylenetetramine} \); \( x=0 \) or 1.

and \[ \text{[Cu(C}_7\text{H}_6\text{O}_2\text{N})(\text{C}_3\text{H}_4\text{N}_2\text{)}_2]\text{[C}_7\text{H}_6\text{O}_2\text{N}} \]

\( C_7H_6O_2N = \text{anthranilate anion; } C_3H_4N_2 = \text{imidazole} \)

\[ \text{[M(C}_8\text{H}_7\text{O}_3\text{)}_2\text{L}_n\text{]}\cdot\text{xH}_2\text{O} \]

where \( M=\text{nickel(II), cobalt(II); } L=\text{ethylenediamine, propylenediamine, 2,2'-dipyridyl, 1,10-phenanthroline, } n=1; \) when \( L=\text{imidazole, } n=2; \) and \( x=0, 1, 2. \)

\[ \text{[NiL}_3\text{]}\text{(C}_3\text{H}_2\text{O}_4\text{)}\cdot\text{6H}_2\text{O} \]

\( L=2,2'\text{-dipyridyl, 1,10-phenanthroline} \)

\[ \text{[M(C}_7\text{H}_6\text{O}_2\text{N})(\text{C}_4\text{H}_6\text{N}_2\text{)}\cdot\text{H}_2\text{O}]\cdot\text{xH}_2\text{O} \]

\( C_7H_6O_2N = \text{anthranilate anion, } C_4H_6N_2 = \text{2-methyl imidazole; } x=0, 3 \)
\[ \text{[Co(C}_3\text{H}_2\text{O}_4)\text{L}_2] \cdot x\text{H}_2\text{O}} \]

\[ L = \text{ethylenediamine, propylenediamine, 1,10-phenanthroline,} \]
\[ x = 2 \text{ or } 6. \]

and \[ \text{[Co(C}_4\text{H}_13\text{N}_3)_2(H_2\text{O})_2]\text{[C}_3\text{H}_2\text{O}_4].4\text{H}_2\text{O} \]

\[ \text{C}_4\text{H}_13\text{N}_3 = \text{diethylenetriamine.} \]

The molar conductance values in conductivity water, confirms the proposed formula. The evidence of the coordination of ligands with the metal (II) ion has been obtained from infrared spectra recorded in range 400-4000 cm\(^{-1}\). The comparison of the spectra of free base, with that of the complexes show considerable shifts in position of bands and splitting of some of the bands, which has been taken as indication of coordination.

All the complexes synthesised in the present investigation shows distinct paramagnetic behaviour. In case of copper(II) complexes the magnetic moment observed lie within the range 1.8 - 2.2 B.M. and the electronic transition observed for these complexes in the visible region in range 14.00 - 18.5 kK shows the formation of planar complexes.

In case of nickel(II) complexes the magnetic moment observed lie within range 2.7-3.4 B.M., as expected for outer-orbital octahedral complexes, the geometry proposed for complexes is further supported by electronic spectrum which shows three bands in the ranges. \( \nu_1 = 11.0 - 12.7 \text{ kK} \).
\[ \tilde{\nu}_2 = 14.4 \text{ - } 19.0 \text{ kk} \text{ and } \tilde{\nu}_3 = 26.7 \text{ - } 33.0 \text{ kk, while in case of cobalt(II) complexes the } \mu_{\text{eff}} \text{ value observed lie within the range } 4.2 \text{ - } 4.7, \text{ and electronic transitions observed in range } \tilde{\nu}_2 = 16.2 \text{ - } 21.0 \text{ kk and } \tilde{\nu}_3 = 29.0 \text{ - } 32.5 \text{ kk showing the outer orbital octahedral configuration.} \]

The thermogravimetric studies shows that the lattice water if present is lost upto 110^\circ C followed by the coordinated water from 120-220^\circ C followed by the ligands. The mandelate, malonate and anthranilate were lost after 450^\circ C, with the formation of metal(II) oxide.