ABSTRACT

The preparation, general behaviour and structure of coordination complexes of transition metals with amines has assumed great importance these days due to their pharmacological activities and applications in industry. A survey of literature indicates that an extensive series of investigations have been done on the coordination complexes of copper(II), nickel(II) and cobalt(II), but very little or no systematic work has been done with a view to study the complete shape and configuration of complex molecules and their pharmacological activity.

Hence, it was proposed to prepare several complexes of copper(II), nickel(II) and cobalt(II) with some aliphatic and aromatic amines and diamines to establish their structures and to study their pharmacological activities. A variety of physicochemical methods like conductance, molecular weight, infrared and electronic spectroscopy, magnetic measurements and electron spin and nuclear magnetic resonance spectroscopy have been used for elucidating the structures. Some of these complexes have been subjected to blind pharmacological screening (as their previous pharmacological history is lacking) to evaluate their biological activities and significance.

The results of the above investigation have been
presented in this thesis entitled "Studies on transition metal complexes with substances of biological activity" consisting of five chapters.

The first chapter of the thesis gives some introductory ideas about the coordination compounds and then outlines the existing knowledge about the amine complexes of copper(II), nickel(II) and cobalt(II). The second chapter describes in brief the principles underlying the various physicochemical methods which have been used for the elucidation of structure. The various experimental techniques and the data are presented in the chapter III. The fourth chapter is labelled "Results and Discussion" and gives an account of the structural discussion of the complexes. The last or the 5th chapter contains the experimental details as well as results of the various pharmacological tests.

Interaction of copper(II) selenate and tungstate, nickel(II) tungstate, cobalt(II) tungstate and oxalate with ammonia, methyl, ethyl, n-propyl, iso-propyl, n-butyl, iso-butyl, n-amyl and iso-amylamines, aniline, pyridine, quinoline, ethylene and propylenediamines, 2,2'-dipyridyl and 1,10-phenanthroline yields crystalline complexes which have been characterised on the basis of microanalysis and are assigned the general formulas CuSeO$_4$·$\text{am}$, CuSeO$_4$·$\text{am}$·3H$_2$O, CuSeO$_4$·$\text{dam}$·2H$_2$O, CuSeO$_4$·2$\text{dam}$, CuWO$_4$·$\text{am}$, CuWO$_4$·2$\text{dam}$, NiWO$_4$·3$\text{dam}$, CoWO$_4$·6$\text{am}$, CoWO$_4$·3$\text{dam}$ and Co$_2$Cu$_4$·2$\text{dam}$ where am
stands for ammonia, aliphatic or aromatic amine and dam for any diamine used. The molar conductance and molecular weight measurements on the complexes of copper(II) selenate, copper(II) tungstate, nickel(II) tungstate and cobalt(II) tungstate show that the complexes are electrolytes showing that the selenate and tungstate ions are outside the coordination sphere. The cobalt(II) oxalate complex with propylenediamine is a nonelectrolyte indicating that the oxalate ion besides neutralising the charge is also coordinated to the metal. Hence, the formulae of the complexes should be written as \([\text{Cu(sam)}_4]\text{SeO}_4\), \([\text{Cu(H}_2\text{O})_3\text{(sam)}]\text{SeO}_4\), \([\text{Cu(H}_3\text{O})_2\text{(dam)}]\text{SeO}_4\), \([\text{Cu(dam)}_2]\text{SeO}_4\), \([\text{Cu(sam)}_4]\text{WO}_4\), \([\text{Cu(dam)}_2]\text{WO}_4\), \([\text{Ni(dam)}_3]\text{WO}_4\), \([\text{Co(sam)}_6]\text{WO}_4\), \([\text{Co(dam)}_3]\text{WO}_4\) and \([\text{Co(dam)}_2\text{C}_2\text{O}_4}\).

The infrared spectra of the complexes have been recorded in the range 4000 - 200 cm\(^{-1}\). The shifts observed in the positions of important bands as well as their splittings when compared to the corresponding bands of the free ligands have been taken as evidence of coordination.

The magnetic measurements done on powdered complexes at room temperature have helped in indicating bond hybridisation. The \(\mu\)\text{eff} values for copper(II), nickel(II) and cobalt(II) complexes fall in the usual ranges expected for square planar and octahedral complexes of these metals, respectively.

The electronic spectral bands of the complexes confirm
the geometries assigned to these on the basis of magnetic measurements. The band positions have also been used to calculate the various ligand field parameters, i.e., \( \nu_q \) - the ligand field stabilisation energy, \( B' \) - the Racah parameter, \( \beta \) - the nephelauxetic ratio and \( \lambda' \) - the spin orbit coupling constant.

The electron spin resonance spectra show two resonance signals for copper(II) complexes. The \( g_{ave} \) values give magnetic moments which agree well with the values obtained by using gram susceptibility data. These \( g \) values also suggest a \( d_{x^2-y^2} \) or \( d_{xy} \) ground state location of electron with tetragonal geometry of complex.

The nuclear magnetic resonance spectra of a few complexes of nickel(II) and cobalt(II) have also been obtained. The protons attached to nitrogen give rise to a single absorption peak due to rapid chemical exchange of the amine hydrogens. The fine structure associated with \(-\text{CH}_3\) and \(-\text{CH}_2-\) groups could only be observed in cobalt(II)tungstate-propylenediamine complex; while in other complexes the signals were poorly resolved and broad due to paramagnetism of the complexes.

A few of the prepared complexes have been subjected to pharmacological investigations. The screening has been done for acute toxicity and effects on central nervous and cardiovascular systems. The ALD\(_{50}\) (mice) values are observed between 82-100mg/kg i.p. None of the complexes show any activity on cardiovascular system (cat) but they are stimulants for the central nervous system.