CHAPTER 1

GENERAL INTRODUCTION

A. HISTORICAL INTRODUCTION

B. SURVEY OF THE LITERATURE
A. HISTORICAL INTRODUCTION:

Co-ordination chemistry has been a fascinating branch of chemistry and plays an important role in chemical industry and in life processes of organisms. Haemoglobin and chlorophyll belong to the category of inner complexes. Complex compounds are important in the development of methods of qualitative and quantitative analysis. In industry complex compounds are used in simplifying and improving the methods of mordant dyeing and of tanning, water-softening, colourimetric estimations and decomposition of glass and metal wares.

purification of chemicals\(^\text{10}\). On the basis of the knowledge of complex compounds it has also been possible to develop the electrostatic theory of acids and bases.

Before discussing the subject of co-ordination compounds it is worthwhile to have a clear concept of the word "co-ordination compounds". Although it is very difficult to give a simple universal definition of co-ordination compounds, complex compounds retain their identity in solution and may be defined as "compounds formed between a metal ion and ligands, each capable of existing independently, through electron pair sharing using electrons from the ligands".

B. SURVEY OF THE LITERATURE:

The discovery of co-ordination compounds is usually attributed to Tassart\(^\text{11}\) who isolated orange crystals of CoCl\(_3\cdot6\)NH\(_3\) in 1798. Later on numerous such compounds were isolated in the nineteenth century and various theories were proposed to explain the chemistry and structure of such compounds. Several modifications to these theories were suggested by Gerhardt,\(^\text{12}\) Wurtz,\(^\text{13}\) Rieset,\(^\text{14}\)

\(^\text{10}\) Borsworth; U.S. Patent, \(2: 463, 1949\).
\(^\text{12}\) Gerhardt, Jahresber; Fortschr. Pharm. Tech. Chem. Physik (Liebig), \(2: 335, 1850\).
\(^\text{13}\) Wurtz, Ann. Chim. Phys., \(3: 30, 468, 1850\).
A.W. Hofmann\textsuperscript{15} and Boedecker\textsuperscript{16}. The atmosphere for the development of new theoretical concept again became favourable after the discovery of the theory of ionization suggested by Arrhenius in 1877. These theories were supported by Jørgensen\textsuperscript{17}, Blomstrand\textsuperscript{18}, Graham\textsuperscript{19} and Claus\textsuperscript{20} on observations based on experimental facts.

Primarily, the complex compounds were studied in the Scandinavian countries, and then the study shifted to Werner's laboratories at Zürich towards the end of the nineteenth century, and then to other countries, and most fruitful results were achieved in this branch in twenty years. It is now progressing rapidly which is evident from the fact that with the results obtained, many theories suggested 20 years ago to explain valence problem by several distinguished scientists have now been either discarded or modified. It is hoped that its progress would be more rapid both in the hands of the beginners, as well as scientists of repute.

\begin{footnotesize}
20 Claus, A.; Zentral blatt., 25; 789, 1854.
\end{footnotesize}
Alfred Werner, a Nobel laureate, who postulated the idea of primary and secondary valences in order to solve many complexities and problems of co-ordination compounds, was the pioneer to the second phase of the rapid advance in this field. He suggested that the primary valences may satisfy the charge on the cation and the co-ordination number as well if present in the inner sphere of the complex, while the secondary valences may satisfy the co-ordination number and are those attaching to the co-ordinating group — the term "co-ordination number", signifying the number of atoms, ions or neutral molecules attached to the central metal atom. He further showed that the secondary valences and not the primary valences determine the chemical properties of the complexes.

REVIEW OF THE WORK DONE ON COBALT (II) AND COBALT (III) COMPLEXES:

Numerous complex compounds of cobalt (II) and cobalt (III) have been studied. Since the co-ordination compounds with nitrogen containing ligands represent the most thoroughly studied group of complexes, these are of particular interest, and a review of the findings would be quite appropriate.

COMPLEXES OF COBALT (II):

Structural studies of the co-ordination compounds of bivalent cobalt halides with amines (like ethylamine, urea, thiourea, urethane, acetamide, aniline, tertiary amines) and mixed ligands (like pyridine, ethylenediamine and thiourea); thiocyanate with thiourea; nitrates with pyridine and O-phenanthroline; phthalamide with ethylenediamine; O-phenanthroline, 2-2-bipyridyl; perchlorate or iodide or tetrafluoroborate with O-phenanthroline, 2-picolyamine.

pyridine, \( \gamma \)-picoline and quinoline\(^{36} \) have been made and
classified on the basis of their I.R., visible, u.v., magnetic,
and N.M.R. studies. Complexes of cobalt (II) salts (halides or
perchlorates) with ethylenethioureas,\(^{37} \) 8-hydroxyquinoline\(^{38} \);
oximes,\(^{39} \) cyanide,\(^{40} \) thiourea\(^{41} \) and tri tri (2-pyridyl) amine\(^{42} \);
and mono-2-9 dimethyl-1-10 phenanthroline complexes of bivalent
sulphates\(^{43} \) have also been prepared and studied.

The magnetic, I.R., u.v. and visible absorption spectra of
cobalt (II) complexes with 2,2'-Bipyridine\(^{44} \); Ammonia\(^{45} \); thiourea,\(^{46} \)

\(^{36} \) Brown, D.H.; Nuttal, R.H.; Avoy, J.Mc. and Sharp, D.W.A.;

\(^{37} \) Richard L. Cariou; Smith L. Halt; Inorg. Chem., 2: 849-53,
1963.


\(^{40} \) Ripin, R.; Farcas, A.; Piringer, O.; Z. Anorg. Allgen. Chem.,


\(^{42} \) Whande, R.Mc.; George C. Kulshnan; John C. Drapo; J.


\(^{45} \) George B. Kauffnan; Nobuyuki Sugisaka; Inorg. Syn., 2:

80-81, 1967.
1,2 (2-pyridyl) ethylene 47; 1,1,3,3 tetra methylurea and 1,1,3,3 tetramethyl-2-thiourea, 48 tri-2 pyridylamine 49; 1-Allenyl 3-(pyridyl) thiourea, 50 imidazole and thiazole 51; N-substituted urea 52; N,N,N',N' tetramethyldiamine 53; 2-ethyl pyridine 54; 0-phenanthroline 55 have been obtained and studied. Some complexes of 2,2',6',2'' terp pyridine, 56 1-2 dipyrindyl ethylene 57; 3-aminopropylamine 58; phenylenediamine, 59 2-pyridone 60.

2-Acetylpyridine\textsuperscript{61}; trimethyl amine-N-oxide\textsuperscript{62}; thiourea\textsuperscript{63,64}; 2-aminomethyl pyridine\textsuperscript{65}; dipropylentriamine\textsuperscript{66} have also been reported.

A survey of the literature further shows that cobalt (II) complexes with primary aliphatic amines,\textsuperscript{67} bicyclic tertiary amines, pyridine\textsuperscript{68,69}; amine\textsuperscript{70}; 2-3 and 4-cyanopyridine N-oxide,\textsuperscript{71} primary alkyl amides,\textsuperscript{72} thiourea,\textsuperscript{73} 2-pyrrolidine,\textsuperscript{74} monoethanolamine\textsuperscript{75}; benzenes\textsuperscript{76}; triethanolamine\textsuperscript{77,78} have

\textbf{References:}


\textsuperscript{69} Uhling, Egon; Schaefer Manfred; Z. Chem., \textbf{9}(12): 470, 1968.


\textsuperscript{73} Carfagno, P.P.; Fordham Univ. Brony, N.Y., 125 pp., 1968.


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been reported and characterised on the basis of their analytical, magnetic U.V. and visible, I.R. spectroscopic measurements.

Various physical methods like Magnetic, I.R., U.V. and visible, Reflectance Spectra, N.M.R. have also been used to characterise bivalent cobalt (II) complexes with tetraphenylphosphine imide, \(^79\) urea\(^80,81\), hexamethylphosphoric triamide\(^82,83\), diisopropylamine\(^84\) and some secondary amines\(^85\) (Dimethyl amine, Diethylamine, Dipropyl amine and piperidine).

COMPLEXES OF COBALT (III):

Complexes of trivalent cobalt with ammonia, nitrite and

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nitrates, amines, α-picoline nitramine, ethylene diamine, triethylenetetramine, primary amines, polyamines, linear tetramines, pyridine and Y-picoline, N-methyl-(S) propylene diamine, thiourea, polyamines have been reported and studied using various physical methods. Thin layer chromatography has been used to separate the isomers. Complexes of cobalt (III) halide, nitrite,

thiocyanate, perchlorate with diethylenetriamine, 103
2-picolyamine, 104 ethylenediamine, 105-107 O-phenanthroline 108-111
have also been prepared and studied.

Triamine cobalt (III) complexes of dimethyl glyoxime and
thioura, 112, 113 N-N-N',N' tetrakis (β-aminoethyl) ethylene
diamine (pentene), 114 furil dioxime, 115 glycine, 116 cyclic

quadridentate secondary amine,\textsuperscript{117} 1-3 diaminepropane\textsuperscript{118} and octahedral Co(III) complexes of chloropenta-amine type\textsuperscript{119-24} have been reported and characterised.

Magnetic, U.V., visible and I.R. absorption spectra, and reflectance spectra of co-ordination compounds of trivalent cobalt with 2-4 pentane dionatobis (ethylenediamine),\textsuperscript{125} mixed ethylene-diamine and O-phenanthroline,\textsuperscript{126} mixed compounds (pajndrine, ethylene diamine, pyridine; orthophenanthroline, 2-2-Bipyridine)\textsuperscript{127-29}; ethylene diamine,\textsuperscript{130} triethylene-

\textsuperscript{127} Constanta Gheorghiu; Aviana N. Colaesacu; Analele Univ. Bucuresti; Ser Stiint Nat., 14(11): 143-50, 1965.
tetramine$^{131,132}$ have been obtained and studied.

Stereochemistry, magnetic and electronic spectra, thermal decomposition, of several complexes of trivalent cobalt containing, optically active ligands$^{133-136}$; N-substituted salicylidenamines,$^{137}$ of halides or perchlorates with ethylenediamine,$^{138}$ 1-10, phenanthroline,$^{139}$ 2-2-Bipyridine$^{140}$ have been studied. Some new dimethyl glyoxime complexes of cobalt (III) with benzylamine,$^{141}$ of Iodide,$^{142}$ of pyridine and substituted pyridine,$^{143}$ of quinoline and isoquinoline$^{144}$ have also been reported.

GENERAL METHODS OF PREPARATION OF THE COMPLEXES

AND DATA

1. METHOD USING SHAKING:

A stoichiometric amount of amines was added to 5 g. of cobalt succiniminate, or cobalt perchlorate, or cobalt chromate salts containing 30 ml. of acetone, absolute alcohol or methyl alcohol in a 250 ml. conical flask. The resulting mixture was shaken for 80 hours till homogeneous colour, filtered and washed with 0.2% of amines in absolute alcohol, or acetone repeatedly and finally with ether; dried on calcium chloride and then in a vacuum desiccator over phosphorous pentoxide.

2. METHOD USING REFLUX:

To 5 g. of cobalt succiniminate contained in a 100 ml. round-bottom flask containing 30 ml. acetone, and equipped with a quick fit condenser and calcium chloride tube was added calculated amount of amine and mixture heated under reflux for 72 hours. The product was filtered, washed with acetone repeatedly and finally with ether. The product was dried in a desiccator over calcium chloride and finally in a vacuum desiccator over phosphorus pentoxide.
3. OXIDATION METHOD:

The corresponding cobalt (II) complex was oxidised by hydrogen peroxide till effervescence ceased. A stoichiometric amount of hydrochloric acid or hydriodic acid was added to it, and the solution evaporated to dryness on a steam-bath. The two isomers were separated: by dissolving in absolute alcohol or acetone, recrystallised, dried over calcium chloride, and finally over phosphorus pentoxide in a vacuum desiccator.
EXPERIMENTAL

1. MATERIALS:

All the chemicals used were of A.R. or E. Merck grade, and the apparatus used was of pyrex.

2. COBALT SUCCINIMIDATE:

Cobalt succinimide was obtained by mixing with constant stirring stoichiometric amounts of the solutions in methanol of Potassium succinimide\(^{145}\) and cobalt chloride. The product was filtered and the filtrate evaporated on steam bath and dried over calcium chloride and phosphorus pentoxide.

3. COBALT CHROMATE:

Cobalt chromate was prepared by mixing a calculated amount of cobalt chloride and potassium chromate solution; the product being filtered, washed several times with hot water and dried.

4. COBALT PERCHLORATE:

Cobalt perchlorate\(^{146}\) was prepared by treating cobalt carbonate with perchloric acid and evaporating in a vacuum desiccator over sulphuric acid.

5. **MAGNETIC SUSCEPTIBILITY MEASUREMENTS:**

Magnetic susceptibilities were determined by Guoy's method.

6. **SPECTRAL MEASUREMENTS:**

A Beckmann DU-2-Spectrophotometer was used to record the absorption spectra of the complexes in water (triple distilled) in 275-1000 nm region using 1 cm. quartz cell.

7. **I.R. SPECTRAL MEASUREMENTS:**

The I.R. spectra were recorded in Nujol Mull and as Potassium bromide pellet method at Central Drug Research Institute, Lucknow, U.P.

8. **CONDUCTANCE MEASUREMENTS:**

The conductivity was measured on a Doran (England) conductivity Bridge.

9. **MOLECULAR WEIGHT MEASUREMENTS:**

The molecular weight was determined by cryoscopic method.

10. **ANALYTICAL:**

    Cobalt was estimated as the pyridine complex. \( \text{CO(C}_5\text{H}_5\text{N})_4 \) (CNS)\(_2\), halogen as silver chloride, nitrogen by Kjeldahl's
method, carbon and hydrogen by Liebig's method perchlorate, and chromate as potassium perchlorate and Barium chromate respectively.