CHAPTER 1

GENERAL INTRODUCTION AND NATURE OF THE
PRESENT PROBLEM

1.1.A General Introduction

The coordination compounds of cobalt (III) are very large in number, and exhibit substantial variety in both the nature and behaviour. Diversity in cobalt compounds is found as regards the oxidation state, coordination number, molecular structure, lability towards chemical reactions, and in many other aspects of its chemistry. Numerous studies have been directed towards the understanding and application of these important properties of cobalt complexes. The common routes for the study of coordination compounds include synthetic, structural, solution behaviour, spectroscopic, magnetic, kinetic, and thermodynamic aspects.

The cobalt ammines and their analogues with similar donor molecules have been known for many years and have played a principal role in the evolution of the modern concept of coordination chemistry. The historical significance of these substances has been reviewed by Bailor¹ and reasoning involved may be found in Warner's² classic book or the introductory text by Martel and Calvin³. These complexes find use in the fields
such as catalysis in sugar synthesis, developer solution for photosensitive printing plates, luster additives in cadmium electroplating baths, wool-like cellulose textiles, photosensitive compositions for photography, thermal printing head, hair dye preparation, electro recording material. The ammines of Co(III) are also important in biological systems, e.g., vitamin B-12. Ammine complexes and cyano complexes are also useful as homogeneous catalysts in some of the industrial oxidation-reduction processes. Simple ammine complexes of cobalt have provided valuable information for the verification of the theories of bonding. A good account of it is available in many reviews.

1.1. Brief Survey of the Thermal Studies of Cobalt Ammine Complexes

Thermal decomposition of hexammine cobalt (III) chloride was investigated by many workers. Tanaka and Nanjo, on the basis of polarographic and infrared spectroscopic data, concluded that the dissociation reaction is initiated by an electron transfer from either a ligand molecule or an outer sphere to central metal cobalt (III) ion forming less stable cobalt (II) complex. Simmons and Wendlandt proved the mechanism using magnetic susceptibility - TGA technique indicating the formation of an intermediate, \((\text{NH}_4)_2\text{CoCl}_4\). Thus the thermal dissociation of hexammine cobalt (III) chloride involves the following steps:

(i) Electron transfer from a coordinated ammonia to Co(III) ion resulting in the formation of Co(II) species

(ii) formation of a mixture of cobalt (II) chloride and \((\text{NH}_4)_2\text{CoCl}_4\), and
(iii) Dissociation of \((\text{NH}_4)_2\text{CoCl}_4\) to form cobalt (II) chloride and ammonium chloride.

From published work\(^{19-23}\) the thermal dissociation of hexammine cobalt (III) bromide is similar to that of the chloride complex. Same type of a \(\text{Co(III)} \rightarrow \text{Co(II)}\) reduction mechanism takes place.

Thermal dissociation of \([\text{Co(NH}_3)_6]\text{Br}_3\) is more complex\(^{24}\) than halide complexes because of the presence of strong oxidising groups outside the coordination sphere. On heating, the compound dissociates very rapidly due to the reaction of coordinated ammonia ligands and the nitrate ion.

In case of \([\text{Co(NH}_3)_6]_2\text{(SO}_4)_3\cdot2.5\text{H}_2\text{O}\) the DTA curve was somewhat more complex\(^{21}\) than that for chloride, bromide or nitrate complexes. Thermomagnetic curve recorded for sulphate complex by Wendlandt and Smith\(^{23}\) showed that reduction of Co(III) ion began at about 166 °C and was completed at about 345 °C. This temperature range was by far the largest of all the hexammine cobalt (III) complexes studied. Further stoichiometry for thermal dissociation of \([\text{Co(NH}_3)_6]_2\text{(SO}_4)_3\cdot2.5\text{H}_2\text{O}\) was somewhat different from the chloride or bromide complexes.

Only a few investigations are concerned with transition metal ammine complexes containing azide ion either in the coordination or outside it. The stoichiometry of thermal
dissociation of $[\text{Co(NH}_3\text{)}_6]^3^+ (\text{N}_3)_3^-$ and several other azide containing cobalt (III) complexes have been studied in detail by Joyner and Verhock$^{24-26}$. It was found that three types of dissociations were possible$^{24}$ viz. (a) a slow dissociation to Co(II) complex (b) an explosive dissociation (c) a long induction period followed by a rapid, non-explosive dissociation to nitride. Particle size is the most obvious factor affecting these reactions and its effect has been studied by other investigators$^{25,26}$.

Thermal dissociation of $[\text{Co(NH}_3\text{)}_6]^3^+ \text{PO}_4^-$ studied by Viltange$^{19}$ using TGA and DTA indicated that the compound began to lose mass at a little above room temperature giving the anhydrous compound at 157 °C. On further heating the CO$^{27} \text{P}_2\text{O}_7$ was obtained at 500 °C and DTA curve contained two endothermic peaks.

Golovnya and Kokh$^{27}$ recorded the DTA curve for $[\text{Co(NH}_3\text{)}_6][\text{Co(NO}_2\text{)}_4\text{CO}_3]$ and $[\text{Co(NH}_3\text{)}_6][\text{Co(NO}_2\text{)}_2\text{CO}_3\text{]}_2^-$·2H$\text{O}$. Further the TGA curve for dehydration of $[\text{Co(NH}_3\text{)}_6]_2[\text{Be}_4\text{O}(\text{CO}_3)_6]·10\text{H}_2\text{O}$ was recorded by Vinogradov et al$^{28}$. The TGA curve of $[\text{Co(NH}_3\text{)}_6][\text{Fe(CN)}_6]$ has shown$^{19}$ that the compound began to lose weight at 164 °C giving finally, at 270 °C a mixture of 1/3 CO$3\text{O}_4$ + 1/2 Fe$2\text{O}_3$. $[\text{Co(NH}_3\text{)}_6](\text{NO}_2)_3$ decomposes to produce $[\text{Co(NH}_3\text{)}_3(\text{NO}_2)_3]$ over a temperature range 130 to 145 °C.
Halopentammine Co(III) halides have been extensively studied by Wendlandt and Smith. All the halopentammine cobalt (III) halide complexes dissociated by a single step reaction, with the possible exception of \([\text{Co(NH}_3\text{)}_5\text{I}]\text{I}_2\) and \([\text{Co(NH}_3\text{)}_5\text{Br}]\text{I}_2\). The TGA curves for these compounds are thus quite similar to each other. The decreasing thermal stability of these compounds was found to be \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{Cl}_2\) > \([\text{Co(NH}_3\text{)}_5\text{Br}]\text{Cl}_2\) > \([\text{Co(NH}_3\text{)}_5\text{Br}]\text{Br}_2\) > \([\text{Co(NH}_3\text{)}_5\text{I}]\text{Cl}_2\) = \([\text{Co(NH}_3\text{)}_5\text{I}]\text{I}_2\) = \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{I}_2\) > \([\text{Co(NH}_3\text{)}_5\text{I}]\text{Br}_2\). Complexes containing iodide, either in the coordination or outside, were certainly the least stable thermally. This was due to the relative ease of oxidation of the iodide ion to free iodine. From DTA curve thermal stability of these complexes was \(\text{Cl}_2\text{Cl}_2\), > \(\text{Cl}_2\text{Br}_2\) = \(\text{Br}_2\text{Cl}_2\), > \(\text{Br}_2\text{Br}_2\), > \(\text{I}_2\text{Cl}_2\), > \(\text{I}_2\text{I}_2\), > \(\text{I}_2\text{Br}_2\), > \(\text{Br}_2\text{I}_2\), > \(\text{Cl}_2\text{I}_2\). The order is similar to that obtained from TGA curve in vacuo but the dissociation temperatures as would be expected, were higher. EGA peaks matched with all DTA peaks indicating absence of phase transformations.

A series of halopentammine cobalt (III) complexes of general formula \([\text{Co(NH}_3\text{)}_5X]\text{(NO}_3\text{)}_2\) where \(X\) is F, Cl, Br, I and NO₂ were extensively studied by Wendlandt and Smith. In thermal dissociation ammonia was lost followed by further oxidation of coordinated ammonia by nitrate ion giving finally \(\text{Co}_3\text{O}_4\) as a residue in all compounds.
Thermal decomposition studies of monoaquopentammine cobalt (III) complexes were extensively studied by many workers\textsuperscript{32-35} by TGA/DTA methods. Rate of deaquation of several aquopentammine complexes has been determined by Mori\textsuperscript{33} et al and by Wendlandt and Bear\textsuperscript{35} using isothermal methods.

The use of Co(III) ammine complexes as 'thermal indicators' has been studied by Matsui and Nakanishi\textsuperscript{36}. The colour changes were observed visually as the sample temperatures were increased at 1-1.5 °C per min. In the complexes represented by the general formula, \([\text{Co(NH}_3\text{)}_6-n\text{X}_n\text{]}\text{Y}_{3-n}\), the larger the \(n\) the lower the colour change temperatures as the anion or molecule is changed, in order \(\text{NH}_3 > \text{Cl} > \text{NO}_2 > \text{H}_2\text{O} > \text{NO}_3 > \text{Br}\). For a given complex, changing the anion did not noticeably affect the colour change temperature.

The thermal dissociation of cis- and trans-\([\text{Co(NH}_3\text{)}_4\text{N}_3\text{]}\text{N}_3\) was studied by Joyner and Verhock\textsuperscript{37}. These compounds dissociated explosively yielding cobalt, nitrogen, ammonia and hydrogen. A number of Co(III) ammine complexes containing iodate ions either in the coordination or outside have been studied using DTA by Lobanov\textsuperscript{38}. All these complexes decomposed rather violently, as would be expected due to vigorous oxidising nature of iodate ion.

Mori et al\textsuperscript{39} studied the decomposition of
\[ \text{[Co(NH}_3\text{)}_5\text{(H}_2\text{O)}_2 \text{]}_X^3 \text{ where } X = \text{Cl or Br}. \] The reactions for both compounds proceeded slowly at room temperature but increased in rate rapidly at 100 and 150 °C respectively. Wendlandt et al.\(^{40}\) reported the TGA curves for the chloride and bromide complexes, \([\text{Co(NH}_3\text{)}_4\text{(H}_2\text{O)}_2 \text{]}_X^3\), both in air and in nitrogen atmosphere. In air, the bromide complex began to deaquate in the range 85 to 90 °C, at 110 °C it converted into \([\text{Co(NH}_3\text{)}_4\text{H}_2\text{O Br} \text{]}_\text{Br}_2\) and at 170 °C it formed \([\text{Co(NH}_3\text{)}_4\text{Br}_2 \text{]}_\text{Br}\) At 260 to 300 °C which corresponded closely the composition for 1:1 molar mixture CoBr\(_2\cdot\)NH\(_4\)Br, sublimation of NH\(_4\)Br and subsequent oxidation and decomposition of Co(II) bromide to Co\(_3\)O, took place from 325 to 650 °C.

Kido and Watanabe\(^{41}\) studied thermal dissociation of \([\text{Co(NH}_3\text{)}_6 \text{]}_\text{Cl}_2\) by measurement of magnetic susceptibility. The dissociation temperatures were much lower than those previously reported by Biltz\(^{42}\), Naumann\(^{43}\) and Ephraim\(^{44}\). Using modern thermoanalytical techniques, Wendlandt and Smith\(^{45}\) investigated the thermal dissociation of \([\text{Co(NH}_3\text{)}_6 \text{]}_\text{Cl}_2\). The TGA curve indicated that ammonia was evolved in the range 80 to 90 °C. The compound \([\text{Co(NH}_3\text{)}_2 \text{]}_\text{Cl}_2\) was formed at 178-180 °C and at 219-220 °C monoammine was formed, finally giving anhydrous cobalt (II) chloride at 300-302 °C.

Thermal dissociation of \([\text{Co(NH}_3\text{)}_6 \text{]}_\text{Br}_2\) type complexes is very similar to that observed for chloride complexes. Anion
has little effect on dissociation temperature or the type of residue obtained. The TGA curve for \( \text{Co(NH}_3\text{)}_6\text{Br}_2 \) was studied by Wendlandt and Smith\(^{45} \), which indicated the formation of diammine and monoammine compound due to the loss of ammonia. The TGA curve for iodide complex\(^{45} \) showed inflection at 195 °C, which corresponded to \([\text{Co(NH}_3\text{)}_2\text{]}\)\(^2\)I\(^2\). Above this temperature there was no evidence for the formation of either monoammine or anhydrous cobalt (II) iodide, instead, \( \text{Co}_3\text{O}_4 \) was obtained beginning at 315 °C. TGA curve of \([\text{Co(NH}_3\text{)}_6\text{]}\)\(^2\)(\text{NO}_3\text{)}\(_2\) showed that two moles of ammonia per mole of complex were evolved at 125 °C which corresponded to the stoichiometry \([\text{Co(NH}_3\text{)}_4\text{]}\)\(^2\)(\text{NO}_3\text{)}\(_2\), on further heating to 180 °C the compound exploded, leaving a residue \( \text{Co}_3\text{O}_4 \).

TGA curve of \([\text{Co(NH}_3\text{)}_6\text{]}\)\(^2\)\(\text{SO}_4\) contained only one well-defined inflection point at 113 °C corresponding to tetrammine compound finally giving anhydrous cobalt (II) sulphate from 340 °C onwards.

Allan et al\(^{46} \) investigated the thermal properties of Co(II) halide complexes \([\text{CoL}_4\text{]}\)\(_2\), where \( L = \text{pyridine, } \alpha-, \beta- \text{ and } \gamma-\text{picoline, } \text{2,6-lutidine and 5-collidine.} \)

The complexes dissociate by loss of two, one, one third and two-thirds moles of \( L \) per mole of complex giving finally cobalt (II) halide salts. However the iodide complexes dissociated ultimately to yield cobalt (II) iodide and oxide;
which gave Co$_3$O$_4$ with further heating.

By the use of high temperature reflectance spectroscopy, Wendlandt$^{47}$ studied the transition of $\alpha$-Co(py)$_2$Cl$_2$ (octahedral) to $\beta$-Co(py)$_2$Cl$_2$ (tetrahedral). This transition was found to begin at about 100 °C and was completed at about 135 °C. Heat of transition for the above reaction is relatively small. Ocone et al.$^{48}$ also studied the thermal stability of Co(bipy)Cl$_2$, and Co($\varepsilon,\delta$' iminobipyridine)Cl$_2$ by heating the compound under isothermal conditions. Dhar and Basolo$^{49}$ reported TGA curve of Co(bipy)Br$_2$·5H$_2$O. Isothermal heating of the compound gave different results when the compound is prepared by different methods. The TGA/DTA curves of [Co(en)$_3$]C$_2$O$_4$ have been reported by Haschke and Wendlandt$^{50}$. Thermal dissociation reaction, [Co(en)$_3$]C$_2$O$_4$ → Co(en)C$_2$O$_4$ took place in the temperature range from ambient to about 300 °C. The mono(ethylenediamine) complex began to dissociate above 300 °C, slowly at first but more rapidly above 350 °C, giving Co$_3$O$_4$ above 380 °C. The colour changes of several hexamethylenetetrammine complexes of Co(II) salts have been reported by Harmelin and Duval$^{51}$ and Wilke and Opfermann$^{52}$. Most of the colour changes were observed in the temperature range 50 to 150 °C and were found due to the dehydration of the complexes.
1.1.C. Thermogravimetric Method

Methods of thermal analysis are a related group of techniques whereby the dependence of the parameters of any physico-chemical property of a substance on temperature is measured. When the study is based on the observation of weight-change as a function of temperature or time the method is called thermogravimetry (TGA). The study of the measurement of the difference in heat content of a sample with reference to a standard substance, as a function of temperature or time, is the method of differential thermal analysis (DTA). Both TGA and DTA are widely used in chemical analysis, and for obtaining thermodynamic and kinetic data. The kinetics of solid state reactions are elucidated to a large extent using these methods, however, other techniques must be used to complement information on the mechanism of reaction. There are many good reviews available on applications of thermoanalytical methods 53-59. The parameters such as rate constants, energy of activation, order of reaction and frequency factor are derived from these methods.

The present work involves the measurement of the change in weight as a function of temperature and the changes in enthalpy content of the substance (with reference to magnesium oxide) as a function of temperature. Hence, only these methods will be discussed further.
When the kinetic study is based on the observation of the weight change, two approaches are possible: isothermal and dynamic heating methods. The isothermal or static methods are based on the determination of the degree of transformation at constant temperature as a function of time. The static method is still widely in use and many workers in this field largely rely on these techniques. The dynamic method involves the determination of the degree of transformation as a function of time during a linear increase of temperature. During the past twenty years the dynamic methods are becoming increasingly popular because of the following advantages:

(i) it requires small number of experimental data and kinetic parameters could be evaluated from a single thermogravimetric curve for the whole temperature range.

(ii) a small amount of sample is sufficient since the number of experiments involved is much reduced.

(iii) sample to sample uncertainties in static methods are eliminated.

However, it should be noted in applying dynamic methods that the data should be obtained under a precisely known set of experimental conditions, as these affect, to some extent, the kinetic parameters.
The factors affecting the results of TGA experiments could be enumerated into following groups:

(i) Effects arising from the properties of the construction material employed and the general nature of the apparatus:
(a) reactions of the sample with the crucible and of the reaction products with the parts of the apparatus, (b) sublimation and condensation of the reaction products, and (c) shape, size and material of the crucible.

(ii) Effects arising from the instrumental characteristics which include (a) heating rate and heat transfer, (b) rate of recording the curve, (c) the composition of the atmosphere in the reaction chamber (furnace), (d) nature of heating and the effect of buoyancy, (e) sensitivity of the balance and the recording system, and (f) method of temperature measurement.

(iii) Effects arising out of the physical and chemical properties of samples which include (a) amount of sample, (b) particle size, (c) heat of reaction and thermal conductivity of the sample, and (d) nature of sample and type of change taking place.

The following are the factors which affect the DTA experiments and are divided into three groups:

(i) Instrumental characteristics: (a) heat source and temperature regulating system, (b) detecting system for DTA
curves (construction of the calorimeter part itself, material of the block of the detecting systems, geometry of the block, size of the crucible etc.). (c) system of the temperature measurement (kind and size of thermocouple junction its position in the sample and fixing of thermocouple) and (d) system of DTA recording curves (rate and sensitivity of the recording system).

(ii) Experimental conditions which include (a) nature of the sample (size of sample, pretreatment, packing etc.) (b) effect of the atmosphere and the type of contact between the atmosphere and the sample (effect of pressure and composition), and (c) type of heating (rate, linearity and regularity).

(iii) Characteristics of sample and reference. These include (a) physical and chemical properties of the sample and the reference material, and (b) dilution of sample.

1.2 Nature of the Present Problem

In spite of the voluminous work on cobalt ammine complexes, there is still a continuing interest in their studies.

The present work has been undertaken with a specific aspect, the thermal decomposition of Hexammine cobalt (III) halide (chloride, bromide, iodide); hexammine cobalt (III)
oxalate, tetrahydrate and hexammine cobalt (III) trioxalato cobaltate (III), cobalt (II) chloride dihydrate, cobalt (II) bromide dihydrate and cobalt (II) oxalate dihydrate have been studied by TGA/DTA techniques.

The thermal analysis of these compounds in air atmosphere have been investigated until the formation of $\text{Co}_3\text{O}_4$ or $\text{Co}_2\text{O}_3$ as the final product. The intermediates and the final products have been characterized by XRD, SEM, IR, XPS methods. The mechanisms of these decomposition reactions are elucidated using kinetic data supplemented with the above techniques.

A novel attempt has been made in this work in analysing two step decomposition reactions which are commonly known in solution reactions as $A \rightarrow B \rightarrow C$ type reactions. Chemical periodicity in thermal decompositions of hexammine cobalt (III) bromide and cobalt (II) bromide to $\text{Co}_3\text{O}_4$ has been established using precisely controlled experimental conditions.

CHAPTER 2 incorporates experimental techniques and computational methods. In CHAPTER 3, the thermal decomposition of hexammine cobalt (III) chloride (HCC) and cobalt (II) chloride dihydrate has been discussed. CHAPTER 4 deals with the studies on hexammine cobalt (III) bromide (HCBr) and cobalt (II) bromide. This CHAPTER also includes a detailed discussion on oscillatory behaviour of the system,
A brief account of the thermal behaviour of hexammine cobalt (III) iodide (HCI) has been included in CHAPTER 5. CHAPTER 6 contains the description of the thermal behaviour of hexammine cobalt (III) oxalate, tetrahydrate (HCOX), hexammine cobalt (III) trioxalato cobalt (III)(HCTOX) and cobalt oxalate dihydrate. The CHAPTER 7 summarizes the salient features of the present work.
References


43. A. Naumann and J. Rill, Ber., 42, 3792 (1909).
44. F. Ephraim, Ber, 45, 1332 (1912).
55. C.J. Keattch, and D. Dollimore, 'An Introduction to Thermogravimetry', Heyden (1975).