CHAPTER I
GENERAL INTRODUCTION

The studies of metal complexes are getting considerable attention in recent decades due to their immense usefulness in various branches of theoretical and applied chemistry. Abundant literature is, therefore, available on the interaction of metal ions with both organic and inorganic ligands. It includes work on the structure, composition, stability and the kinetics of the complexes. For a long time the scope of studies was confined to the determination of the composition of complexes formed and their isolation. However, the pioneering work of Bjerrum\textsuperscript{1} on the stability of complexes in late thirties and early forties opened new vistas of knowledge in the field of metal-organic ligand chemistry. The main thrust of the work published is oriented towards the quantitative aspect of stability of metal complexes.

The proteins, amino acids, amides and pyrimidines form a very important class of ligands containing nitrogen and oxygen atoms in functional groups. The ligands possess biological significance and are also much used in the different methods of chemical analyses. The growing interest in recent years in such fields as bioinorganic and environmental chemistry has inspired a large number of workers to explore the area in much depth. There has, also, been a significant activity in the field of reaction kinetics specially in the area involving interactions
of metal ions. New fast-reaction techniques have removed the upper limit on rates that can be measured, and extension to less familiar central metal atoms as well as labile metal ions\textsuperscript{2-4} have begun in earnest. The conventionally used methods on slower reactions have been of much help to extend the frontiers of knowledge in this field. In biological reactions metal ions play a very important role, since the enzymatic reactions are mostly activated or controlled by metallic cations, which are in the combined state with proteins, amino acids, lipids and related compounds. Thus studies of metal complexes with such ligand are important because they act as a model for complicated proteins\textsuperscript{5}.

Before proceeding further it would be appropriate to discuss as what are complex compounds and how can they be formed. A complex is defined as a species formed by the association of two or more simpler species each capable of independent existence. Complex formation is not confined to association between two ions of opposite charge. A metal cation, a proton or another species having a positive charge may react with an electron donor, whether it is negatively charged, electrically neutral, or even positively charged\textsuperscript{6,7}. The reactions

\[
\begin{align*}
\text{H}^+ + \text{NH}_3 & \rightarrow \text{NH}_4^+ \\
\text{Ag}^+ + \text{NH}_3 & \rightarrow \text{AgNH}_3^+ \\
\text{AgNH}_3^+ + \text{NH}_3 & \rightarrow \text{Ag(NH}_3)_2^+ 
\end{align*}
\]
are typical of complex formation between cations and uncharged or cationic electron donor. Similarly, an anion may combine with an electron acceptor, regardless of its charge. The formation of various iodo complexes of cadmium may be cited as examples

\[
\begin{align*}
\text{I}^- + \text{Cd}^{2+} & \rightarrow \text{CdI}^+ \\
\text{I}^- + \text{CdI}^+ & \rightarrow \text{CdI}_2 \\
\text{I}^- + \text{CdI}_2 & \rightarrow \text{CdI}_3^- \\
\text{I}^- + \text{CdI}_3^- & \rightarrow \text{CdI}_4^{2-}
\end{align*}
\]

Interactions between an electron donor and an acceptor may also occur if both species are uncharged, familiar examples of complexes of this type are that of iodine with benzene and other aromatic systems. Moreover, cations may sometimes act as electron donores to ligands with vacant π-orbitals, e.g., in complexes of Cu(I) and Ag(I) with unsaturated organic molecules. Some confusion has arisen over the use of adjective stable to a complex. The term stability describes the amount of association that occurs in solutions containing two or more component species in equilibrium. The more stable the resultant complex, the greater is the association that will occur under a given set of conditions. The stability of a complex may be described
quantitatively in terms of one of its stability constants. Other workers have sometimes described a complex as stable either (1) if the ligands are replaced only slowly by water or other competing species present in solution, or (2) if the solid complex can be precipitated or crystallized from solution. The first usage refers to the kinetic behaviour of a complex rather than to the equilibrium conditions under which it is formed. Those complexes which undergo substitution reactions at a measurable rate are called as robust or inert.

The area of chemistry concerned here is that of coordination chemistry or complex compounds. The evolution of the coordination chemistry over the years is discussed below.

Progress in any science is seldom equally rapid all along the advancing front, but occurs rather in successive bursts at different points. Coordination chemistry has known to such periods of rapid advance. The first, occurring about the beginning of this century, was the period of classical coordination chemistry, when general principles were established and a solid foundation was laid for later developments. At that time interest and controversy centred on Werner's theory, which stands today as one of the mile-stones in the progress of inorganic chemistry. But X-ray analysis has displaced the counting of isomers as a means of studying stereochemistry and whole new
series of compounds have been obtained, of which even the prototypes were unknown seventy five years ago. The new advance of coordination chemistry during the past few decades has been more, however, than a mere accumulation of new data. It has become apparent that the process of coordination, far from being an academic sideline, is one of the dominant factors determining the chemistry of the elements.

Historically, coordination chemistry is of comparatively recent origin. Coordination compounds were unknown to the Arabian chemists of the Middle Ages and the Alchemists did not come upon them. The earliest recorded coordination compound is probably prussian blue, obtained by artists' colour maker, Diesbach, in Berlin during the first decade of the eighteenth century. Its discovery, like so many important developments in the history of chemistry, was accidental; the blue pigment being obtained as a by-product when animal refuse and soda were heated in an iron pot. Iron, indeed, seems to have played an important part in the accidental advancement of coordination chemistry as it was involved in the discovery of three other types of coordination compounds: the carbonyls in 1891, the phthalocyanins in 1926 and the cyclopentadienyles in 1951.

The beginning of coordination chemistry, however, is usually dated from the discovery of the cobalt-amines by Tassaert
in 1798. Tassaert observed that ammoniacal solutions of cobalt chloride deposited the orange compound CoCl$_3$.6NH$_3$ on standing overnight, and recognized in this a new type of chemical substance, formed by the combination of two already fully saturated compounds, but possessing properties quite different from either.

During the following half-century, increasing numbers of these complex compounds were obtained, not only of cobalt but also of other elements, for instance 'red-prussiate of potash' (potassium ferricyanide) in 1822, Magnus's green salt in 1828 and the nitroprussides in 1849. At this time several theories were proposed to explain the nature of these 'complex' compounds. One of the most favoured was that of Graham in 1837, suggesting that the compounds were ammonium salts in which one of the hydrogen atoms was replaced by a metal atom; though at that time not very helpful to the further understanding of these compounds, this idea has a remarkable affinity with the modern Lewis acid-base approach to the process of coordination.

In 1854, Claus put forward a view not unlike that of Werner 40 years later: he recognized the submergence of the usual properties of the ammonia and the metal in the complex salts, but that the equivalence of the metal was unaffected; he also drew the parallel between the complex salts and the salt
hydrates. Claus's ideas, however, were not generally accepted and in 1858 an event occurred which was to hold back the development of inorganic chemistry for nearly half a century. This was Kekule's demonstration of the tetravalency of carbon and the chain structure of the higher hydrocarbons. Within 10 years Blomstrand had produced his famous chain theory of the structure of complex ammines, the complexes PtCl$_2$.4NH$_3$ and CoCl$_2$.6NH$_3$, for example, being represented as

\[
\begin{align*}
\text{Pt} & \quad \text{NH}_3\cdot\text{NH}_3\cdot\text{Cl} \\
\text{NH}_3\cdot\text{NH}_3\cdot\text{Cl} & \quad \text{Co} \quad \text{NH}_3\cdot\text{NH}_3\cdot\text{NH}_3\cdot\text{Cl} \\
\text{NH}_3\cdot\text{NH}_3\cdot\text{Cl} & \quad \text{and} \quad \text{NH}_3\cdot\text{NH}_3\cdot\text{NH}_3\cdot\text{Cl}
\end{align*}
\]

The unfortunate influence of the contemporary development of organic chemistry is again seen in Wurtz's cyclic structure for the salt hydrates

\[
\begin{align*}
\text{SO}_4\cdot\text{Cu} & \quad \text{OH}_2\cdot\text{OH}_2 \\
\text{OH}_2\cdot\text{OH}_2 & \quad \text{OH}_2
\end{align*}
\]

proposed in 1879. In 1887, however, Arrhenius introduced the conception of ionization and within only a few years inorganic chemistry began to develop again along its rightful course.
In 1891, Werner published the first of his papers on complex compounds, in which he suggested that an atom does not necessarily have a fixed small number of valence bonds, but that its valency might be exerted over the whole surface of the atom and he divided into various units of different strength. This he developed two years later into the well known concept of 'primary' and 'secondary' valencies, which has remained the basis of coordination chemistry ever since.

According to Werner, the 'primary' valencies were those involved in satisfying the chemical equivalence of the atom and the 'secondary' valencies were those by which the 'coordinated' molecules of ammonia were attached, so that in luteocobaltic-chloride, for example, the three primary valencies of the cobalt are used to attach the three chlorine atoms and six secondary valencies are required to retain the six coordinated ammonia molecules. In the roseo salt, \( \text{CoCl}_3\cdot5\text{NH}_3\cdot\text{OH}_2 \), one of the six secondary valencies binds the water molecule. When this salt is heated it loses water, giving the purpureo salt, \( \text{CoCl}_3\cdot5\text{NH}_3 \); Werner's explanation of the precipitation of only two-thirds of the chlorine in this compound by silver nitrate is that one of the chlorine atoms has become attached by a secondary valency, replacing the lost water molecule. It thus appears that although the primary valencies may not all be used, the secondary valencies invariably are. Loss of another molecule of ammonia as in the
praseo salts, CoCl$_3$·NH$_3$, thus leads to only one-third of the chlorine being precipitated by silver nitrate. One of the consequences of Werner's theory (and a test point, since it predicts here a different result from the chain theories) is that the loss of yet another molecule of ammonia from the praseo salt should give a compound, CoCl$_3$·3NH$_3$, from which silver nitrate should not precipitate any of the chlorine. Unfortunately no such compound can be prepared.

From the above evidence it is apparent that one of the differences between primary and secondary valencies is that the primary allow ionization of the bound atoms whereas the latter do not. Although the crucial compound CoCl$_3$·3NH$_3$ could not be made, several series of compounds are known in which three or more molecules of ammonia are replaced by other group, for example, the complete series:

- Co(NO$_2$)$_3$·6NH$_3$
- Co(NO$_2$)$_3$·5NH$_3$
- Co(NO$_2$)$_3$·4NH$_3$
- Co(NO$_2$)$_3$·3NH$_3$
- Co(NH$_2$)$_3$·2NH$_3$·KNO$_2$
- Co(NO$_2$)$_3$·NH$_3$·2KNO$_2$
- Co(NH$_2$)$_3$·3KNO$_2$
- PtCl$_4$·6NH$_3$
- PtCl$_4$·5NH$_3$
- PtCl$_4$·4NH$_3$
- PtCl$_4$·3NH$_3$
- PtCl$_4$·2NH$_3$
- PtCl$_4$·NH$_3$·KCl
- PtCl$_4$·2KCl
Werner investigated many of these series by conductivity method and showed that successive loss of ammonia molecules resulted in the formation of successively fewer ions, the compounds Co(NO$_2$)$_3$·3NH$_3$ and PtCl$_4$·2NH$_3$, for example, being non-electrolytes.

In this way the precipitation by silver nitrate of two-thirds and one-third of the chlorine in CoCl$_3$·5NH$_3$ and CoCl$_3$·4NH$_3$ was shown to correspond with the formation of three and two ions in solution, so that the formulae become

$$[\text{Co(NH}_3)_5\text{Cl}]^{2+} 2\text{Cl}^-$$
$$[\text{Co(NH}_3)_4\text{Cl}_2]^+ \text{Cl}^-$$

the secondary valencies remaining in full use.

Werner evolved the concept of 'coordination complex' and deduced the geometrical structures of many of them. The term 'coordinate' has its origin in the fundamental assumption by Werner$^{20}$ that complex salts result from the capacity of certain atoms to combine with a given maximum number of other atoms or radicals. The number Werner described as the coordination number. A coordination compound is one in which several atoms, groups, or radicals are directly and more or less firmly attached to a central atom. This cluster Werner referred to as the first coordination sphere and in its formal representation he enclosed
the cluster within brackets. Furthermore, depending on the nature of the compound, there may be atoms or radicals less firmly attached to the complex. These exist in the so-called second coordination sphere and are represented outside the brackets. Werner put forward the concept that the secondary valence bonds are directed in space around the central metal ion. The concept of directed valence bonds has been of paramount significance in the field of stereochemistry of the compounds. Werner was awarded the coveted Nobel prize in chemistry for his distinguished work in 1913.

Although Werner's postulate regarding the stereochemistry of complex compounds was vindicated by experiment, widespread dissatisfaction with his ideas of primary and secondary valencies served as a strong deterrent to the general acceptance of his entire theory as late as 1916.²¹

It was not until the development of the electronic theory of valency by Lewis, Kossel, Langmuir, Sidgwick, Fajans, Pauling and others that a self consistent explanation of valence types evolved. The models which were developed for the electronic theory were so successful in resolving the confusion about the ideas of primary and secondary valencies that almost general acceptance of Werner's views soon followed the work of Lewis and his contemporaries.
Modern X-ray diffraction data have now provided unequivocal experimental elucidation for Werner's ideas on stereochemistry. Quantum mechanics has also provided the framework for a more detailed solution of valence problems, although the approach is extremely complex unless many simplifying assumptions are made; as a result, the simple molecular models suggested by Kossel and others are still of fundamental importance in correlating fact and theory.

Since coordination compounds differ greatly in nature and stability, chemists are not completely agreed on a simple definition of the term. According to the theory of Sidgwick and Lowry, a coordinate bond (and hence, a coordination compound) can be formed between any atom or ion which can furnish a pair of electrons (the donor). The donor is non-metallic—it may be part of an ion, like \( \text{Cl}^- \), \( \text{CO}_3^- \) or \( \text{NH}_2\text{CH}_2\text{COO}^- \). Ordinarily, an acceptor requires several donors, which may be alike or different. The resulting complex may be a positive ion, a negative ion, or a neutral molecule.

In general, the small, highly charged cations form the most stable coordinate bonds, and it is often mistakenly supposed that the ability to form complexes is limited to the transition metals. This is far from being so, as is seen from the fact that the beryllium derivative of acetylacetone can be distilled without
decomposition at 270°C. Even the alkali metal ions form complexes as shown by the work of Sidgwick and Brewer.\[^{22,23}\] In short it can be said that stability depends upon many factors and cannot be directly correlated with bond type. Among the many other factors that are important in determining stability are charge on the acceptor atom, nature of the donor atom and of the molecule of which it is a part, chelation, cationic, anionic, or neutral nature of the complex, and the nature of the ion with which it is associated (if the complex is an ion).

The relationship between the donor and acceptor atom is especially interesting. Nearly all of the complexes of the light metals (periodic groups IA, IIA, IIIB, IVB) contain oxygen as the donor atom. It may be furnished in the form of water, hydroxide ion, an oxyanion, an alcohol, ether, ketone, or in a variety of other ways. These light metals seldom coordinate with molecules containing nitrogen, sulfur, carbon or the halogens. Vanadium, at the head of group VB, is a powerful oxygen coordinator, but also shows some ability to form ammines and complex cyanides. Proceeding across the periodic table towards the right from vanadium, we encounter elements which easily coordinate with nitrogen. Thus, chromium forms a large number of ammines, most of which are slowly destroyed in water solution. The ammines of manganese are still less stable, and neither Fe(II) nor Fe(III) ion reacts with ammonia in water solution to give ammines. These
ions coordinate instead with hydroxyl ions generated in the water by the addition of ammonia with cobalt, copper and zinc, however, stable ammines are formed. The ions of these metals retain the ability to coordinate with oxygen in even greater degree than do the ions of the lighter metals, but the tendency to form link with nitrogen is still more pronounced. Starting with vanadium, too, we see an increasing tendency to coordinate with carbon, all the elements from vanadium to zinc form stable cyanides, those from chromium to nickel form carbonyls, and copper at least forms compounds with olefinic substances. The ability of metals in the series to combine with sulfur also increases. Copper, vanadium, chromium and manganese occur in nature in oxide ores, iron both in oxide and sulphide ores, and cobalt, nickel, copper and zinc largely as sulphide ores.

The elements of periodic group IB and IIB form complex cyanides, but only palladium, silver, platinum, rhodium and mercury are known to form compounds with ethylenic double bond. All of them form ammines (the ammines of mercury readily lose protons but the metal-nitrogen bond remains), but platinum and gold form few complexes containing a metal-oxygen bond. The metals of group IIIA, IVA and VA form many complexes in which the donor atom is oxygen, sulphur or a halogen. Compounds in which the donor is carbon or nitrogen are much less common.
Metal chelate also plays a very important role in biochemical processes. If the substance which combines with the metal contains two or more donor groups so that one or more rings are formed, the resulting structure is said to be a chelate compound or metal chelate, and the donor is said to be a chelating agent. Example is the combination of glycinate ion with Cu(II).

\[
\text{Cu(II)-glycinate}
\]

Many organic compounds form stable coordination compounds. Formate and acetate ions form strong bonds, but monocarboxylic acids with longer chains show a rapidly decreasing ability to coordinate. Formate and acetate often bind two metal together, each oxygen of the carboxyl group linking to a different metal atom,
When the carboxyl group is attached to only one metal atom, however, it fills but one position in the coordination sphere. Complexes of the type $[\text{Co(NH}_3\text{)}_5\text{OOCH}_3]^2^{+24}$ and $[\text{Co(NH}_3\text{)}_5\text{OOCCH}_3]^2^{+25}$ are well known and easily prepared.

Among the examples in which the carboxyl group forms a bridge between two metal atoms are the 'basic' beryllium salts, $\text{Be}_4\text{O(OOC.R)}_6$, in which $\text{R}$ represents $\text{CH}_3$, $\text{C}_2\text{H}_5$, etc. Structural studies indicate$^{26-28}$ the presence of a central oxygen surrounded tetrahedrally by four beryllium ions. Each edge of the tetra-

hedron is composed of the grouping $\text{Be}——\text{O}——\text{C}——\text{O}——\text{Be}$. Similar compounds of zinc$^{29}$ and zirconium, $(\text{ZrO})_4\text{O(OOCR)}_6^{30}$, are known.

The oxalate ion forms a large number of coordination compounds, usually acting as bidentate group. The best known are those of the types $[\text{M}^{\text{II}}\text{Ox}_3]^{4-}$, $[\text{M}^{\text{III}}\text{Ox}_3]^{3-}$ and $[\text{M}^{\text{III}}\text{Ox}_2]^{-}$. The oxalate group can share the coordination sphere with ammonia, ethylenediamine, water, or other groups. Oxalatobis(ethylenediammine)cobalt(III) chloride, $[\text{Coen}_2\text{Ox}]\text{Cl}$, is readily obtained by the action of an alkali oxalate upon the dichlorosalt$^{20,31}$; the corresponding chromium salt is prepared by the action of ethylenediamine upon the tris-(oxalato)salt$^{32}$. Hamm and Davis$^{33}$ have studied the formation of these ions by the reaction of $[\text{Cr(H}_2\text{O})_6]^{3+}$ and oxalate ion and Hamm$^{34}$ has followed the rate of isomerization of $[\text{Cr(H}_2\text{O})_2\text{Ox}_2]^{-}$ in water solution. He suggested
that upon collision with the ion, a water molecule knocks one end of an oxalate group away from the chromium and takes its place; on return of the oxalate, either the cis- or trans-isomer may be formed, depending upon which molecule of water is eliminated. A small amount of alkali converts the diaqua compounds to hydroxo aqua compounds, the cis isomer of which is converted upon heating into the tetrakis(oxalato)-μ-diolsalt.

The compounds of the α-amino acids are of great stability and have received extensive study. The cobalt complexes of the α-amino acids, [Co(AA)$_3$], exist in two stereoisomeric forms, both of which are remarkably stable. Elliott$^{35}$ has utilized this stability in the preparation of highly insoluble and stable 'super-complexes' by the reaction of Co(III) hydroxide with

\[
\text{HOOC-CH-}
\begin{array}{c}
\text{(CH$_2$)$_n$} \\
\text{NH$_2$}
\end{array}
\text{-CH-}
\begin{array}{c}
\text{COOH} \\
\text{NH$_2$}
\end{array}
\]

Chromium(III) forms inner complexes which are similar but of less stability, they are slowly decomposed by hot acids, by sodium hydroxide, and to a degree, by boiling water. Keller$^{36}$ has
studied the reactions of a good number of α-amino acids with chromium(III) hydroxide and chromammines in boiling water. In all cases compounds of the formula \([\text{Cr}(\text{AA})_3]\) seem to form, but are quickly hydrolyzed to

\[
\begin{array}{c}
\text{(AA)}_2 \text{Cr} \\
\text{OH} \\
\text{C} \text{r} \\
\text{(AA)}_2 \\
\text{OH}
\end{array}
\]

which, in turn, hydrolyse slowly to

\[
\begin{array}{c}
\text{(AA)}_2 \text{Cr} \\
\text{OH} \\
\text{C} \text{r} \\
\text{OH} \\
\text{(AA)}_2 \\
\text{OH} \\
\text{C} \text{r} \\
\text{(AA)}_2 \\
\text{OH}
\end{array}
\]

and more complex products.

The β-amino acids also form inner complexes with the transition metals, but these are less stable than those of the α-acids. Hearn\textsuperscript{37} has shown that α-amino acids can be distinguished from the β-acids by the fact that the former react with cobalt(III) hydroxide to give coloured complexes, which the latter do not. The \(\text{D-}, \text{L-}\) and α-amino acids do not form chelate rings with metals, so form normal salt\textsuperscript{38,39}. 
Transition metals which have got greater tendency to form the coordination complexes with various organic and inorganic ligands, are defined as those elements which have partly filled d or f shells in any of their commonly occurring oxidation states. In view of this definition majority of all known elements are transition elements which can be subdivided into three main classes: (a) main transition or d-block elements, (b) lanthanide elements, and (c) actinide elements.

These transition elements have certain general common properties:

1. They are all metals.

2. They are practically all hard, strong, high melting, high boiling metals which conduct heat and electricity well. In short, they are 'typical' metals of the sort we meet in ordinary circumstances.

3. They all form alloys with one another and with other metallic elements.

4. Many of them are sufficiently electropositive to dissolve in mineral acids although a few are 'noble', that is, they have such low electrode potentials that they are unaffected by simple acids.
5. With very few exceptions, they exhibit variable valence, and their ions and compounds are coloured in one if not all oxidation states.

6. Because of partially filled shells they form at least some paramagnetic compounds.

In addition to these properties, the peculiar characteristic associated with the transition elements, in general, is their tendency to form coordination compounds with various organic and inorganic ligands. The formation of coordination compounds in abundance is due to their following specialities: (a) The transition metal cations are relatively very small in size and hence have high positive charge density which makes it easy for the transition metal cations to accept the lone pairs of electrons from the ligands, (b) The transition metal cations have vacant (n-1)d orbitals of suitable energy to accept lone pair of electrons, and (c) Transition metals are capable enough of showing a wide range of oxidation states because of the fact that the outer ns electrons are supplemented by the (n-1)d electrons which act as reservoir, for valency purposes.

During the last three decades the studies on the kinetics and mechanism of coordinated compounds started developing on the same lines as those of organic reactions. From the survey of the literature it becomes evident that this field is also well
advanced although not yet at par with organic reaction mechanism. By the use of different techniques, both slow and fast reactions are being studied, but most of the work is still limited to those reactions which are relatively slow and can be investigated by conventional methods. As the complexes of Co(III) and Cr(III) have contributed a lot in the development of the coordination chemistry, they have been, and are of, much interest, so far as their coordination chemistry is concerned. But chromium(III) complexes have been less well studied than the corresponding cobalt(III) systems. Evidence accumulating over three decades has created a considerable degree of interest in the chemistry of chromium due to its biological activity and its nutritional role in plants, animals and human beings. At the same time, its proven use as mordant in dyeing, in tanning of leather, in electroplating etc., makes it one of the most important transition elements. Keeping in view its widespread significance and scope of investigation the work on the coordination chemistry of chromium(III) was undertaken. A brief review of the coordination chemistry of Cr(III) is attempted in the following pages, with special reference to the work on the kinetics and mechanism which is our present field of interest.

COORDINATION CHEMISTRY OF CHROMIUM

Chromium was discovered by Nicolas Louis Vauquelin in 1797 in Siberian red lead, the mineral crocoite, PbCrO₄. In
1798, he isolated the new metal by reduction of CrO$_3$ with charcoal at high temperature. In the same year, he analysed a Peruvian emerald and found that its green colour is due to the new element. Chromium is the most recently recognized biologically essential trace metal. The first conclusive evidence demonstrating a metabolic role of chromium was obtained by Mertz and Schwarz in a series of investigations of which the first report appeared in 1955.$^{41}$

Chromium belongs to periodic group VIB. The members of VIB group, chromium, molybdenum and tungsten, have the following configuration of their outermost electron shells: Cr, $3d^54s^1$; Mo, $4d^55s^1$; W, $5d^46s^2$. As members of the same periodic group these elements have many characteristics in common, differ markedly in certain properties which are dependent on their atomic and ionic radii. With increasing number of electron shells, the trend in properties is such that the chemistry of molybdenum and tungsten (which are quite similar chemically) differs from that of chromium in many respects. Thus, chromium forms many compounds of types unknown or rare in molybdenum and tungsten chemistry (and conversely).

The most common and stable oxidation states of chromium are $+2$, $+3$ and $+6$. The lowest, $-2$, $-1$, 0 and $+1$, are formal oxidation states displayed by chromium in compounds such as carbonyls, nitrosyls and organometallic complexes.
The most stable and important oxidation state of chromium is +3. The aqueous chemistry of Cr(III) is almost entirely the chemistry of coordinate and chelate compounds of which thousands are known. Only a few compounds of Cr(IV) and Cr(VI) have been isolated. Compounds of these oxidation states occur as transient intermediates in reduction of Cr(VI) compounds. Otherwise there is no aqueous chemistry of Cr(IV) and Cr(V) because they rapidly disproportionate to Cr(III) and Cr(VI). All Cr(VI) compounds except CrF₆ are oxo compounds. Compounds of Cr(VI) are quite effective oxidizing agents. Chromium forms several peroxides, which are compounds of Cr(VI), Cr(V) and Cr(IV).

In most aspects Cr(III) complexes resemble with those of Co(III) but the complexes of Cr(III) are inert as the rates of ligand interchange reactions of these complexes are usually slow. The complexes of Cr(III), however, are more susceptible to hydrolysis and formation of polynuclear complexes by olation.

**Types of Chromium(III) Complexes**

Chromium(III) forms a large number of complexes with different types of the ligands (organic and inorganic) since any ion or molecule which is capable of donating a lone pair of electrons (acting as a Lewis base) is potentially capable to combine with the chromium(III) ion in the role of a Lewis base.
Cr(III) complexes may be cationic, anionic or neutral molecules. Although the number of Cr(III) complexes known is very large but they can be classified into small number types:

1. Mononuclear Cr(III) complexes with mono- and bidentate ligands - the types of such complexes described are \([\text{CrA}_6]^{3+}\), \([\text{CrA}_5\text{B}]^{3+}\), \([\text{CrA}_5\text{X}]^{2+}\), \([\text{CrA}_3\text{B}_2\text{X}]^{2+}\), \([\text{CrA}_4\text{X}_2]^+\), \([\text{CrA}_3\text{BX}_2]^+\), \([\text{CrA}_3\text{X}_3]^0\), \([\text{CrA}_2\text{X}_4]^-\), \([\text{CrAX}_5]^{2-}\), \([\text{CrX}_6]^{3-}\).

2. Complexes with polydentate ligands which include ligands such as iminodiacetate (tridentate), methyliminodiacetate (tridentate), triethylenetetrammine (tetradeinate), ethylenediaminetetraacetate (pentadentate), tetraethylenepentammine (pentadentate), 1,3-propanediaminetetraacetate (hexadentate).

3. Bridged Cr(III) complexes - due to the ability of Cr(III) complexes to polymerise, many compounds with one or two Cr atoms per molecule are known where bridging groups are \(\text{nOH}^-\), \(\text{nPO}_4^2-\), \(\text{HCOO}^-\), etc.

**SUBSTITUTION REACTIONS OF CHROMIUM(III)**

In a coordination compound the immediate environment of the central metal atom is described by its coordination number and its coordination state and also by the geometry and relative positions of the ligands. The reaction with coordination compounds may be related to the changes in the oxidation state, the changes
in the coordination shell, or the changes in the coordinated ligands. The changes in the oxidation state or changes in the coordinated ligands have not been investigated systematically in the case of Cr(III) complexes and the bulk of the work is related with changes in the coordination shell. Chromium(III) ions in aqueous solution are always found coordinated with water molecules or with other coordinating species present in the solution. Therefore, the reactions related with the coordination shell are mainly those which are associated with the replacement of one ligand by another. Thus the discussion of the kinetics and mechanism of the reactions of Cr(III) complexes is mainly confined to the ligand substitution reactions. It is, therefore, imperative to give a detailed account of the studies related with the kinetics and mechanism of such reactions in the following pages.

Nature of Substitution Reactions

Reactions involving replacement of one ligand by another, or one metal by another are called substitution reactions. Substitution reactions of inorganic complexes have been receiving intensive experimental investigation and many hundreds of research papers have appeared reporting and interpreting kinetic data.

A generalized equation for ligand substitution reactions may be written as
in which $M$ stands for the central metal atom plus all of the
attached ligands not undergoing substitution and $X$ and $Y$ are
any two ligands. For example, in the reaction

$$[\text{Co(NH}_3\text{)}_5\text{Br}]^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Co(NH}_3\text{)}_5(\text{H}_2\text{O})]^3+ + \text{Br}^- \quad (10)$$

$M = [\text{Co(NH}_3\text{)}_5]^3+$, $X = \text{Br}^-$ and $Y = \text{H}_2\text{O}$. In practice, we may make
the following generalizations concerning equation (9):

(i) The central atom may be a transition or a non-transition
metal, but most studies have involved the former and only a few
of these have been investigated in detail.

(ii) The forward reaction rate may range from very fast ($t_1$ of
$10^{-1}$ to $10^{-7}$ at room temperature) to very slow ($t_1$ of the order
of days or weeks at room temperature).

(iii) Most of the substitution reactions that have been studied
systematically and in detail have been with six coordinated
octahedral complexes of Co(III) and Cr(III), and with four coordi­
nated planar complexes of Pt(II) and Au(III). A few complexes of
a great many other metal ions have been studied over the years but
the bulk of the data exists for the four central species just
mentioned, and this is undoubtedly due to the fact that each of
these central atoms forms a great variety of complexes and is
extremely inert or nonlabile towards substitution.
(iv) Stereochemical changes may or may not occur during a given reaction of the type shown in the equation (9). However, it is important to know this information before reasonable mechanisms can be proposed, not only for the number of steps but for the steric course of the reaction.

(v) When Y is H₂O the reaction is termed an aquation or acid hydrolysis reaction and if Y is OH⁻, the reaction is a base hydrolysis reaction. When Y is any other ligand the reaction is termed an anation reaction. However, if X is an anion then the anation reaction in aqueous acid solution always seems to proceed in at least two steps.

(vi) When X=Y we are dealing with an exchange reaction, and in order to study the rate in this case either X or Y must be labeled, for example X = CN⁻ and Y = ¹⁴CN⁻, or X = Cl⁻ and Y = ³⁶Cl⁻, or X = SC(NH₂)₂ and Y = ³⁵SC(NH₂)₂.

(vii) The factors that may influence reaction rates of complexes, aside from the usual factors such as temperature, catalysts, etc. are:

(a) the nature of the central metal ion
(b) the nature of the leaving ligand
(c) the nature of the entering ligand
(d) the nature of other ligands attached to the central atom
(e) the charge on the complex
(f) the nature of the solvent
(g) the presence of other ligands or metal ions in the solvent.

(viii) For octahedral substitution reactions we may visualise two limiting sequences (or pathways) which may be labeled as follows:

(A) \[ M - X + Y \rightarrow Y - M - X \rightarrow M - Y + X \] (11)

This type may be described as displacement or \( S_N^2(\text{lim}) \) or A mechanism, where \( S_N^2(\text{lim}) \) stands for substitution(S), nucleophilic(N), bimolecular(2) and lim implies for this case the existence, even though transient, of a true seven coordinated intermediate.

(B) \[ M - X \xrightarrow{-X} M \xrightarrow{+Y} M - Y \] (12)

This type of reaction is referred to as either \( S_N^1(\text{lim}) \) or D mechanism, where \( S_N^1(\text{lim}) \) stands for substitution, nucleophilic, monomolecular, and the lim in this case implies the existence of a true, even though transient, five coordinated intermediate.

Another possibility is the four centre mechanism\(^{43}\), in which two acid-base complexes simultaneously exchange groups.

\[ M - X + M' - Y \rightarrow M \xrightarrow{M'} M - Y + M' - X \] (13)
This process does not require the expulsion of the group X or Y into the solution as free ions or molecules. This is possible for those cases in which the X or Y is very unstable as a free particle and the bond M-X or M'-Y is very covalent so that the dissociation into the ions is difficult and the solvent is non-polar or absent.

Classification of Ligand Substitution Mechanisms

The most natural division in mechanistic study is that between stoichiometric and intimate mechanisms. The classical categories of substitution mechanism introduced in organic chemistry by Hughes and Ingold\textsuperscript{44} and later applied to ligand substitution processes were originally based on a feature of stoichiometric mechanism, the molecularity of the rate-determining step of the reaction. A reformulation is possible that distinguishes categories of stoichiometric mechanism from categories of intimate mechanism and provides a natural place for 'cage' reactions. The first task is to anticipate the types of stoichiometric mechanism that will be important in ligand substitutions and to choose designations for these.

Langford and Gray\textsuperscript{45} have described sequences of elementary steps which make up the reaction mechanism as stoichiometric mechanism and proposed that the substitution mechanism may follow three pathways:
(a) **Dissociative path** (D), in which the leaving ligand is lost in the first step, producing an intermediate of reduced coordination number

\[ MX_n \xrightarrow{-X} MX_{n-1} \xleftarrow{+Y} MX_{n-1}Y \]  

(14)

(b) **Associative path** (A), in which the entering ligand adds in the first step, and an intermediate of increased coordination number is produced

\[ MX_n \xleftarrow{+Y} MX_nY \xrightarrow{-X} MX_{n-1}Y \]  

(15)

(c) **Concerted path or interchange** (I), in which the leaving group is moving from the inner to the outer coordination sphere and the entering group is moving from outer to inner. An interchange may occur along a multistep path, since the formation and dissociation of an outer-sphere complex may often be easily separable steps of a reaction, but the defining characteristic of interchange is the absence of an intermediate in which the primary coordination number of the metal is modified.

\[ MX_n \ldots Y \rightarrow MX_{n-1} \ldots X \]  

(16)

\[MX_n \ldots Y\] represent an outer-sphere complex, for example an ion-pair such as \(\text{Co(NH}_3\text{)}_6^{3+} \ldots \text{SO}_4^{2-}\).
In a dissociative activated intimate mechanism the rate of reaction should be insensitive to the nature of the entering group except for small effects arising from 'solvation' interaction while the rate of an associatively activated mechanism should be very sensitive to the nature of entering group. There are many kinetic and stereochemical techniques that can be used to detect the presence of reactive intermediates. Such tests provide means for assigning an A or D label which can only be done when the evidence for the approximate intermediate is forthcoming. The interchange mechanism presents a great problem in the sense that its demonstration is negative, i.e., an I-mechanism is assigned when no evidence can be produced for a reactive intermediate. The interchange process can have either associative or dissociative activation and therefore I\textsubscript{a} and I\textsubscript{d} mechanisms are visualized. The identification of I\textsubscript{a} mechanism is easy due to the synchronous bimolecular process but the I\textsubscript{d} mechanism presents some problem. The D and I\textsubscript{d} processes are best distinguished in terms of the life-time of the intermediate. If it lives long enough to equilibrate with its solution environment it will obey the test characteristic of a D mechanism. On the other hand, if it interacts with environment it has inherited then the mechanism is I\textsubscript{d}.

Since most of the studies on the kinetics and mechanism of octahedral complexes have been described in the light of these
four types (A, I<sub>a</sub>, I<sub>d</sub> and D) of mechanisms, they are summarized as follows.

**Summary of Mechanistic Classification**

There are three categories of stoichiometric mechanisms distinguished operationally by kinetic tests.

(a) **Dissociative** (D), intermediate of reduced coordination number, which may be detected by its selective reactivity.

(b) **Associative** (A), intermediate of increased coordination number, which may be detected by departure of the rate expression from strict second-order kinetics when the reaction is followed in the direction for which the transition state lies after the intermediate.

(c) **Interchange** (I), no kinetically detectable intermediates.

There are two major categories of intimate mechanism that may be distinguished operationally if it can be assumed that a group of reactions with related mechanism can be identified.

(i) **Associative activation** (a), the reaction rate is approximately as sensitive (or more sensitive) to variation of the entering group as to variation of the leaving group.
(ii) **Dissociative activation** (d), the reaction rate is much more sensitive to variation of the leaving group than to variation of the entering group.

D mechanisms must be dissociative. A mechanisms must be associative. Therefore, the following is adopted as the simplest combined notations designating both stoichiometric and intimate mechanisms: A, Iₐ, Iₐ, D.

**Labile and Inert Complexes**

The substitution of one ligand for another in a coordination compound often takes place in a time interval comparable to the time required to mix the reactants. Complexes that undergo such rapid substitution reactions are classified as labile complexes. Compounds that undergo slow substitution reactions (half life >1 min) are called inert complexes. Since labile complexes rapidly reach equilibrium with their environment, the properties of their solutions are independent of the previous history of the solution, whereas the same is not true for inert complexes.

Taube, while reviewing the available data, pointed out a striking correlation between the electronic configuration and rates of reaction of inner orbital (valence bond terminology) octahedral complexes. Inner orbital complexes having one or more
remaining empty inner d orbitals are labile, those with no empty inner d orbitals are inert—even though the d–orbitals may be singly occupied (see Table 1.1). The most striking feature of the table is the sharp distinction between inert and labile complexes of the same metal in different oxidation states.

**Hydrolysis Reactions**

The term aquation has been applied to reactions that involve the replacement of a group by water molecules, whereas hydrolysis has been used to mean the replacement of ligand by a hydroxide ion. Since both involve reactions with water, it would appear more appropriate to describe these as hydrolysis reactions. The aquation reactions can be illustrated by the typical equation

$$\text{MA}_5X^{n+} + H_2O \rightarrow \text{MA}_5H_2O^{(n+1)^+} + X^-$$  \hspace{1cm} (17)

Likewise, the hydrolysis reactions are of the type

$$\text{MA}_5X^{n+} + OH^- \rightarrow \text{MA}_5OH^{n+} + X^-$$  \hspace{1cm} (18)

If the reaction product is an aqua complex (17), the reaction is termed as acid hydrolysis, whereas, if the product is hydroxo complex (18) the reaction is called base hydrolysis.
<table>
<thead>
<tr>
<th>Electronic Configuration</th>
<th>Valence Bond</th>
<th>Molecular Orbital</th>
<th>Central Metal Ions</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>t&lt;sub&gt;2g&lt;/sub&gt;</td>
<td>e&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Labile Complexes</td>
</tr>
<tr>
<td>d&lt;sup&gt;0&lt;/sup&gt;d&lt;sup&gt;0&lt;/sup&gt;d&lt;sup&gt;2&lt;/sup&gt;SP&lt;sup&gt;3&lt;/sup&gt;</td>
<td>000</td>
<td>00</td>
<td>Sc(III), Y(III), rare earths(III), Ti(IV), Zr(IV), Hf(IV), Ce(IV), Th(IV), Nb(V), Ta(V), Mo(VI), W(VI)</td>
</tr>
<tr>
<td>d&lt;sup&gt;1&lt;/sup&gt;d&lt;sup&gt;0&lt;/sup&gt;d&lt;sup&gt;2&lt;/sup&gt;SP&lt;sup&gt;3&lt;/sup&gt;</td>
<td>100</td>
<td>00</td>
<td>Ti(III), V(IV), Mo(V), W(V), Re(VI)</td>
</tr>
<tr>
<td>d&lt;sup&gt;2&lt;/sup&gt;d&lt;sup&gt;1&lt;/sup&gt;d&lt;sup&gt;2&lt;/sup&gt;SP&lt;sup&gt;3&lt;/sup&gt;</td>
<td>110</td>
<td>00</td>
<td>Ti(II), V(III), Nb(III), Ta(III), W(IV), Re(V), Ru(VI),</td>
</tr>
<tr>
<td>d&lt;sup&gt;3&lt;/sup&gt;d&lt;sup&gt;1&lt;/sup&gt;d&lt;sup&gt;2&lt;/sup&gt;SP&lt;sup&gt;3&lt;/sup&gt;</td>
<td>111</td>
<td>00</td>
<td>V(II), Cr(III), Mo(III), W(III), Mn(IV), Re(IV),</td>
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<tr>
<td>d&lt;sup&gt;2&lt;/sup&gt;d&lt;sup&gt;1&lt;/sup&gt;d&lt;sup&gt;2&lt;/sup&gt;SP&lt;sup&gt;3&lt;/sup&gt;</td>
<td>211</td>
<td>00</td>
<td>Cr(CN)&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;4-&lt;/sup&gt;, Mn(CN)&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;3-&lt;/sup&gt;, Re(III), Ru(IV), Os(IV)</td>
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<td>d&lt;sup&gt;2&lt;/sup&gt;d&lt;sup&gt;2&lt;/sup&gt;d&lt;sup&gt;2&lt;/sup&gt;SP&lt;sup&gt;3&lt;/sup&gt;</td>
<td>221</td>
<td>00</td>
<td>Mn(CN)&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;4-&lt;/sup&gt;, Fe(II), Fe(CN)&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;3-&lt;/sup&gt;, Fe(phen)&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;3+&lt;/sup&gt;, Ru(III), Os(III), Ir(IV)</td>
</tr>
<tr>
<td>d&lt;sup&gt;2&lt;/sup&gt;d&lt;sup&gt;2&lt;/sup&gt;d&lt;sup&gt;2&lt;/sup&gt;SP&lt;sup&gt;3&lt;/sup&gt;</td>
<td>222</td>
<td>00</td>
<td>Fe(CN)&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;4-&lt;/sup&gt;, Fe(phen)&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;2+&lt;/sup&gt;, Ru(II), Os(II), Co(III)(except CoF&lt;sub&gt;6&lt;/sub&gt;&lt;sup&gt;3-&lt;/sup&gt;), Rh(III), Ir(III), Pd(IV), Pt(IV)</td>
</tr>
</tbody>
</table>
Chromium salts (chloride, sulfate, nitrate, etc.) are aqua complexes characterized by ions such as $[\text{Cr(H}_2\text{O)}_6]\text{Cr}^{3+}$, $[\text{Cr(H}_2\text{O)}_5\text{Cl}]^{2+}$ and $[\text{Cr(H}_2\text{O)}_4\text{Cl}_2]^+$. In aqueous solution, the replacement of coordinated group by water molecules (aquation) is a common reaction

$$[\text{CrA}_5\text{X}]^{2+} + \text{H}_2\text{O} \rightarrow [\text{CrA}_5\text{H}_2\text{O}]^{3+} + \text{X}^- \quad (19)$$

The extent of aquation depends on several factors including the relative coordinating tendencies of $\text{H}_2\text{O}$ and $\text{X}^-$ and the concentration of $\text{X}^-$. Thus, every aqueous solution of Cr(III) is actually or potentially a solution of aqua complexes.

The substitution reactions illustrated by equation (20)

$$\text{MCl(N}_3\text{)}^{2+} + \text{H}_2\text{O} \rightarrow \text{M(N}_3\text{OH)}^{3+} + \text{Cl}^- \quad (20)$$

are known as aquation or acid hydrolysis reactions because they are normally carried out in acidic solution. In such cases, the rate law can be expressed by equation (21) where $k_{aq}$ is independent of the acidity but slightly dependent on

$$\text{Rate} = k_{aq} [\text{complex}] \quad (21)$$

ionic strength ($\mu$). Exceptions to this occur when the leaving group is a basic ligand, e.g. $\text{NO}_2^-$, $\text{N}_3^-$, $\text{F}^-$, etc., where the rate increases with increasing acidity in a some-times complicated
manner. Indeed it is difficult to systematize this type of reactions because of the wide variety of experimental parameters that can be varied.

In acid hydrolysis reactions the studies made in aqueous solutions give a linear plot for first-order kinetics. The result is to be expected, since the concentration of the reactant and solvent does not change during the reaction. The rate is, therefore, dependent only on the concentration of the complex and is first-order or pseudo-first-order.

Chromium(III) reactions are in general expected to favour the dissociative mode of activation but, surprisingly, kinetic results now available are better accommodated in terms of an associative mechanism. However, the mechanistic interpretation of substitution reactions of complexes of the type \( \text{Cr}(\text{H}_2\text{O})_5^X^{2+} \) is controversial\(^{46,47}\). A recent investigation\(^{48}\) of the aquation reactions of \( \text{Cr}(\text{H}_2\text{O})_5^X^{2+} (X = \text{Br}^-, \text{I}^-, \text{NO}_3^-, \text{SCN}^-) \) in HCl medium reveals that the results are best interpreted in terms of an 'I\(_a\)' mechanism, whereas the conjugate base species \( \text{Cr}(\text{H}_2\text{O})_4(\text{OH})^X^+ \) appear to react via an 'I\(_d\)' path. The 'transition enthalpy'\(^{49}\) of the aquation reaction of \( \text{Cr}(\text{H}_2\text{O})_5^X^{2+} \) varies with the leaving group \( X \), indicating the associative nature of the transition state\(^{50}\).
The rates of aquation of \( \text{Cr}(en)_2X^+ \), \( \text{Cr}(en)(H_2O)_2X^+ \) and \( \text{Cr}(NH_3)_2(H_2O)_2X^+ \) (\( X = \text{halogen} \)) decrease in the sequence \( \text{Br}^->\text{Cl}^- \) and show much greater dependency on the nature of the leaving group than the corresponding Co(III) complexes\(^{51}\). This suggests that the haloammine complexes of Cr(III) probably undergo reaction via an 'I\(_d\)' mechanism. Unlike Co(III), the trans effect sometimes becomes a dominant factor in the aquation reactions of Cr(III).

Spontaneous aquation of trans-[\( \text{Cr}(NH_3)_4(H_2O)I \)]\(^{2+}\) in HCl and HBr gives products which consist of a considerable amount of \( \text{Cr}(NH_3)_4(H_2O)X^{2+} \) (\( X = \text{Cl}^- \) or \( \text{Br}^- \)) in addition to the diaqua species. Since the anation of diaqua species is very slow, the incorporation of halide ions into the coordination sphere can only be accounted for by the trans-labilization of the coordinated water by iodide\(^{52}\). The intimate mechanism for these reaction is almost the same as the rate of the water-exchange process\(^{53}\). Trans-[\( \text{Cr}(NH_3)_4ICl \)]\(^+\) aquates to form trans-[\( \text{Cr}(NH_3)_4(H_2O)Cl \)]\(^{2+}\) which then undergoes further hydrolysis to form a diaqua species. Here one clearly sees that the leaving group effect of iodide surpasses its trans-labilizing power\(^{54}\). The aquation reactions of a series of cis- and trans-(haloaqudtetrammine)chromium(III) complexes have been studied\(^{55}\) and for both the cis- and trans-series the reactivities decrease in the sequence I->Br->Cl in keeping with the strength of the Cr-X bond.
Aquation of trans-[Cr(en)$_2$X$_2$]$^+$ ($X = F^-, Cl^-, Br^-, NCS^-$) also shows the same reactivity pattern$^{56}$. Unlike Co(III) complexes, one frequently encounters in the aquation of Cr(III) complexes in acid media concurrent fission of the metal-to-nitrogen bond of an ammine ligand and the metal-to-leaving group bond. This is, indeed, kinetically a difficult problem. The aquation$^{56}$ of trans-[Cr(en)$_2$F$_2$]$^+$ gives $\sim 98\%$ trans-[Cr(en)(enH)(H$_2$O)F$_2$]$^+$. Monoaquabis(ethylenediammine)(pyridylmethyl)chromium(III) complexes undergo aquation by the release of ethylenediammine to form pentaaquapyridylmethylchromium(III) which then aquates via C-Cr bond cleavage$^{57}$.

It is prudent to discuss at this stage the results of steric effects on the aquation of Cr(III) complexes as this may give some clue to the mechanism of the aquation reaction. The only systematic study in this direction has been done by House and his coworkers$^{58}$ who have looked at the aquation rates of trans-[CrY$_2$X$_2$]$^+$ ($Y = en$, pn and tmd and $X = Cl^-$, Br$^-$). The rate of release of the first halide has been found to be independent of the nature of $Y(10^5 k$ for $X = Cl^-$ has values 7.2, 8.14 and 7.85 units for en, pn and tmd at 35°C in 0.1 mol dm$^{-3}$ HNO$_3$) suggesting an associative mechanism($I_a$) for these reactions. However, a slightly increased value for trans-[Cr(pn)$_2$Cl$_2$]$^+$ as compared to en has been ascribed previously$^{59}$ to the steric effect expected for an $I_d$ mechanism. Some acid hydrolysis rate constants for
Cr(III) complexes are listed in Table 1.2 in comparison with the constants for hydrolysis of the analogous Co(III) complexes. In the base hydrolysis reactions the process of replacement of coordinated ligand by OH\(^-\) may not be direct. These reactions are singled out for special mention because it apparently contradicts the statement that the rate of substitution of an octahedral complex is not markedly sensitive to nature of the entering group. This is not a general reaction but is confined mainly to a range of Co(III) ammine complexes and their Ru(III) analogues. Similar complexes with Cr(III), Rh(III) and Ir(III) sometimes exhibit this reaction but the effect is far less marked.

The rate law takes the form

\[-d[\text{complex}]/dt = k[\text{complex}][\text{OH}^-]\] (22)

and the actual rate of reaction can be very much greater than that associated with the behaviour of the complex in the absence of base, and accelerations upto and beyond a factor of \(10^8\) can be achieved provided the alkali concentration is high enough. An alternative mechanism, while accounting for the extraordinary effect of hydroxide, allows the process to remain essentially dissociative. In it, the hydroxide functions as a base and serves to remove a proton for an ammine ligand. This part of the mechanism is strongly supported by the fact that no complex lacking
TABLE 1.2: Acid hydrolysis rate constants

<table>
<thead>
<tr>
<th>Complex</th>
<th>Cr(III)</th>
<th>Co(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_{\text{acid}} (s^{-1})$</td>
<td>$t (^{\circ} C)$</td>
</tr>
<tr>
<td>$[\text{M(NH}_3]_6^{3+}$</td>
<td>$2.5 \times 10^{-5}$</td>
<td>25</td>
</tr>
<tr>
<td>$[\text{M(NH}_3]_5\text{H}_2\text{O}]^{3+}$</td>
<td>$1.0 \times 10^{-6}$</td>
<td>40</td>
</tr>
<tr>
<td>$[\text{M(NH}_3]_5\text{Cl}]^{2+}$</td>
<td>$1.0 \times 10^{-5}$</td>
<td>25</td>
</tr>
<tr>
<td>$[\text{M(NH}_3]_5\text{Br}]^{2+}$</td>
<td>$5.0 \times 10^{-5}$</td>
<td>25</td>
</tr>
<tr>
<td>$[\text{M(NH}_3]_5\text{I}]^{2+}$</td>
<td>$2.0 \times 10^{-4}$</td>
<td>0</td>
</tr>
<tr>
<td>$[\text{M(NH}_3]_5\text{NCS}]^{2+}$</td>
<td>$1.0 \times 10^{-7}$</td>
<td>25</td>
</tr>
<tr>
<td>$[\text{cis-Men}_2\text{Cl}_2]^+$</td>
<td>$3.3 \times 10^{-4}$</td>
<td>25</td>
</tr>
<tr>
<td>$[\text{trans-Men}_2\text{Cl}_2]^+$</td>
<td>$3.8 \times 10^{-5}$</td>
<td>25</td>
</tr>
<tr>
<td>$[\text{Cr(H}_2\text{O})_5\text{NCS}]^{2+}$</td>
<td>$9.1 \times 10^{-5}$</td>
<td>25</td>
</tr>
</tbody>
</table>
such a proton has yet been found to be markedly sensitive to base hydrolysis. The deprotonated species, called the conjugate base, is dissociatively labile and the overall process can be represented taking cobalt(III) as example

\[ [\text{Co(NH}_3\text{)}_5\text{Cl}]^{2+} + [\text{OH}^-] = [\text{Co(NH}_3\text{)}_5\text{OH}]^{2+} + [\text{Cl}^-] \] (23)

\[ \text{[Co(NH}_3\text{)}_5\text{Cl]}^{2+} + [\text{OH}^-] \xrightleftharpoons[k_1]{k_-1} \text{[Co(NH}_3\text{)}_4\text{NH}_2\text{Cl}]^{+} + \text{H}_2\text{O} \] (24)

\[ \text{[Co(NH}_3\text{)}_4\text{NH}_2\text{Cl}]^{+} \xrightarrow{k_2} \text{[Co(NH}_3\text{)}_4\text{NH}_2\text{]}^{2+} + \text{Cl}^- \] (25)

\[ \text{[Co(NH}_3\text{)}_4\text{NH}_2\text{]}^{2+} + \text{H}_2\text{O} \xrightarrow{\text{fast}} \text{[Co(NH}_3\text{)}_5\text{OH}]^{2+} \] (26)

The mechanism is generally designated as $S_{N1cb}$ (substitution, nucleophilic, unimolecular, conjugate base) although in the Langford-Gray nomenclature it would be $D_{cb}$. The proton transfer reaction (eq. 24) is reversible and generally fast compared to the subsequent dissociation of conjugate base. Under these circumstances it can be represented as an equilibrium with constant $K$. In the chloropentaamminecobalt(III) complex the rate constant for proton exchange could be as much as $10^5$ times greater than that for chloride release. A pre-equilibrium proton transfer leads to specific base catalysis in aqueous solution and this is in accordance with observations in the most cases. For such a pre-equilibrium the full rate expression would become
and would reduce to the experimentally observed form of \( k[OH^-] \ll 1 \). This holds good for nearly all cobalt(III) ammine complexes where \( k \ll 0.1 \) or even 0.01.

The mechanistic role of \( OH^- \) in the base hydrolysis of Cr(III) complexes is thought to be similar to that of the corresponding Co(III) complexes which proceed through \( S_{Nc}cb \) mechanism. It has been realized, however, that the base hydrolysis reactions of Cr(III) complexes are less pronounced presumably because of smaller effects of donor ligands on the dissociative process and the less favourable pK values of the ammine ligands. Jones and Phillips\textsuperscript{62} have proposed an 'I\(_a\)' mechanism for the base hydrolysis of halopentaamminechromium(III) complexes on the basis of their polarographic results. A linear free energy plot has been obtained for the base hydrolysis of \( Cr(NH_3)_5X^{2+} \), where \( X = F^- \), \( Cl^- \), \( Br^- \), \( I^- \) and \( NCS^- \) and the slope of 0.53 suggests that bond making and bond breaking processes are important. Bannerjea and Chatterjee\textsuperscript{63} have reported studies of the base hydrolysis of \( Cr(NH_3)_5SCN^{2+} \) and \( Cr(NH_3)_5ONO^{2+} \) and have suggested a normal \( I_d \) mechanism for the former, and a 'pseudo-substitution' of \( NO_2^- \) by \( OH^- \) without the rupture of the Cr-O bond.
Exchange Reactions

Exchange of a ligand with the coordinated ligand can be followed by the use of isotopic tracers. The inert character of \( \text{Cr(III)} \) complexes is demonstrated by the low rate of exchange of \( H_2^{18}O \) with coordinated water of \( \text{Cr(H}_2\text{O)}^3_6 \). Plane and Taube\(^6\) reported the rate of water exchange in \( \text{Cr(H}_2\text{O)}^3_6 \) in the presence of \( \text{NO}_3^- \), \( \text{ClO}_4^- \) and \( \text{Br}^- \) ions and found that the rate was first order in \( \text{Cr(H}_2\text{O)}^3_6 \) which increased with the concentration of anion and promoting effect was in the order: \( \text{HNO}_3^- > \text{ClO}_4^- > \text{Cl}^- > \text{Br}^- \). With \( \text{Cl}^- \) as the only anion present, the rate of exchange greatly exceeds the rate of formation of the ion \( \text{Cr(H}_2\text{O)}^5\text{Cl}^{2+} \).

Hund and Plane\(^6\) in their studies of the effect of ionic strength on the exchange reaction, found the equation

\[
\text{rate} = k_1[\text{Cr(H}_2\text{O)}^3_6]^{3+}
\]  

The first-order rate constant \((k_1)\) increased slightly with ionic strength and has an average value \(3.45 \times 10^{-6} \text{ s}^{-1}\) at infinite dilution at \(20^\circ\text{C}\) in both nitrate and perchlorate solutions.

Anation Reactions

The general reaction of displacement of coordinated water molecule from the aqua complex by another ligand is often
known as anation. This is the reverse of an acid hydrolysis reaction and may be represented by general equations

\[
M(H_2O)^{+m}_n + X^{-1} \longrightarrow M(H_2O)_{n-1}X^{+(m-1)} + H_2O \tag{29}
\]

\[
M(H_2O)^{+m}_n + X \longrightarrow M(H_2O)_{n-1}X^{+m} + H_2O \tag{30}
\]

Generally the rate of reaction of an aqua ion with a ligand remains almost unaffected by the nature of the ligand and the rates for a given ion are approximately the same as the rates for water exchange for that ion. These facts are presumed to be accounted for a reaction mechanism comprising of two steps 
(1) formation of outer-sphere complex, and (2) elimination of water from aqua ion\textsuperscript{42}.

The replacement of water in a species containing five non-labile ligands such as \([\text{Co(NH}_3)_5\text{H}_2\text{O}]^{3+}\) takes place by the following way

\[
[L_5M(H_2O)] \xrightarrow{k_1} [L_5M] + H_2O \quad \leftarrow \quad [L_5M] + Y \xrightarrow{k_2} [L_5MY] \tag{31}
\]

Since \(Y\) competes with solvent water for the active intermediate \([L_5M]\), the rate of formation of \([L_5MY]\) can be dependent on the concentration of \(Y\). On the other hand, there should be some high
concentration of Y at which the rate of replacement of water no longer depends on the concentration of Y. The rate of formation of $[L_5MY]$ at this concentration should be equal to the rate of formation of $[L_5M]$ and also equal to the rate of exchange of water between $[L_5M(H_2O)]$ and the solvent. Thus the rate of formation of $[L_5M]$ is given by

$$\frac{d[L_5M]}{dt} = k_1[L_5M(H_2O)] - k_{-1}[L_5M][H_2O] - k_2[L_5M][Y]$$  \hspace{1cm} (33)$$

According to the steady-state approximation, the concentration of the very reactive $[L_5M]$ remains small and constant during the reaction (i.e. $d[L_5M]/dt = 0$ at the steady state). Thus,

$$[L_5M] = \frac{k_1[L_5M(H_2O)]}{k_{-1}[H_2O] + k_2[Y]}$$  \hspace{1cm} (34)$$

and

$$\frac{d[L_5MY]}{dt} = \frac{k_1 k_2[L_5M(H_2O)][Y]}{k_{-1}[H_2O] + k_2[Y]}$$  \hspace{1cm} (35)$$

If $k_{-1}[H_2O] \gg k_2[Y]$,

$$\frac{d[L_5MY]}{dt} = \frac{k_1 k_2}{k_{-1}} [L_5M(H_2O)][Y]$$  \hspace{1cm} (36)$$

and a second-order reaction will be observed. On the other hand, if $k_2[Y] \gg k_{-1}[H_2O]$,

$$\frac{d[L_5MY]}{dt} = k_1[L_5M(H_2O)]$$  \hspace{1cm} (37)$$
giving first-order kinetics with the overall first-order constant equal to that for the dissociation of the aqua complex; furthermore, if $Y$ represents a group of reagents, the same limiting rate should apply to all. If $k_2[Y] \sim k_1[H_2O]$, the kinetic behaviour may be complicated, though for very low and very high concentrations of $Y$ the kinetics will approach those for second-order and first-order processes, respectively. However, at the high concentrations of $Y$ necessary to achieve first-order kinetics, ion-pairing becomes important and the second-order ion-pairing mechanism takes over.

Ion-pairing can, however, be avoided by studying substitution of an anion into an anion. For entry of wide range of anions into the complex $[\text{Co(CN)}_5(H_2O)]^{2-}$ a dissociative mechanism has been established. Under these conditions

$$d[\text{Co(CN)}_5Y]/dt = k[\text{Co(CN)}_5(H_2O)]$$  \hspace{1cm} (38)

where

$$k = \frac{k_1k_2[Y]}{k_{-1}[H_2O] + k_2[Y]}$$  \hspace{1cm} (39)

or

$$1/k = \frac{k_{-1}[H_2O]}{k_1k_2[Y]} + \frac{1}{k_1}$$  \hspace{1cm} (40)

Thus values of $k_1$ and $k_{-1}/k_2$ can be obtained from a graph of $1/k$ against $1/[[Y]$ for various concentrations of $Y$. For $[\text{Co(CN)}_5(H_2O)]^{2-}$
was found to be approximately constant at constant ionic strength, and was very nearly the same as the rate constant for the exchange of coordinated water with H$_2^{18}$O. The values of $k_2/k_1$ permit a comparison of the reactivity of all the ligands examined (including water) towards the intermediate [Co(CN)$_5$]$^{2-}$, and the sequence established is OH$^-$ > N$_3^-$ > SCN$^-$ > I$^-$ > NH$_3$ > Br$^-$ > S$_2$O$_3^{2-}$. An analogous mechanism has been established for the reaction

$$[\text{Co(NH}_3)_4(\text{SO}_3)^X] + Y = [\text{Co(NH}_3)_4(\text{SO}_3)^Y] + X$$  \hspace{1cm} (41)

for the X, Y pairs SCN$^-$, NH$_3$; NO$_2^-$, NH$_3$; OH$^-$, NH$_3$; NH$_3$, SCN$^-$; NH$_3$, OH$^-$; NH$_3$, CN$^-$; NH$_3$, NO$_2^-$ and OH$^-$, CN$^-$. Anation reactions have been studied in detail for Co(III) Rh(III), Pt(II) and Cr(III) complexes and their mechanisms have been proposed. The study of entering-group-effects in the substitution of Cr(III) complexes has become more fascinating than that of Co(III) complexes because of the extraordinary stability of Cr(H$_2$O)$_6^{3+}$ and its conjugate base. The work done on the anation of Cr(III) complexes is reviewed here in detail.

Werner$^{66}$ demonstrated that, for potassium dichromate-oxalic acid ratios between 1:1 and 1:9, the product was always potassium dioxalatodiaquachromate(II). Croft$^{67}$ reported the formation of trioxalatochromate(III) ion by the addition of
neutral alkali oxalates to a boiling solution of the dioxalato-
diaquachromate(III). Wyrouboff investigated that treatment of
neutral alkali oxalates with chromium(III) salt solution resulted
in the formation of a 'practically insoluble' chromium oxalate,
indicating that to study the direct reaction of hexaaquachromium
(III) and oxalate ions, dilute solutions would be necessary, so
that precipitation is avoided. Hamm and Davis reported the
formation of dioxalatodiaquachromate(III) ion from hexaaqua-
chromium(III) and oxalate ions. The rates of reaction of the two
species, \([\text{Cr(H}_2\text{O)}_4(\text{C}_2\text{O}_4)]^+\) and \([\text{Cr(H}_2\text{O)}_2(\text{C}_2\text{O}_4)_2]^-\), were determined
polarographically by measuring current at the diffusion plateaus.
The reactions were found to be first-order with respect to the
reacting metal species. The rate of the first step was found to be
inversely proportional and that of the second one as independent of
the hydrogen ion concentration. Both the rates were independent of
oxalate ion concentration. The proposed mechanism is as follows:
Hamm and Perkin\textsuperscript{69} provided the evidence for the existence of malonato complexes of chromium(III) containing one, two and three malonate groups per chromium atoms. The values of activation parameters were calculated and compared with those of oxalate. The comparison between malonate and oxalate for the first and second chelation steps indicated that the slow steps were nearly identical. Later Huchital and Taube\textsuperscript{70} reported the studies on the monodentate form of the malonate–Cr(III) complex. They suggested that the substitution was as slow as it was for exchange of water, particularly because the local concentration of the free carboxalate ion was high and the displacement of water was not greatly assisted by the incoming carboxyl group.

Banerjea and Chatterjee\textsuperscript{71} studied the rate of formation of tetraaquamonomalonatochromium(III) ion from hexaaquachromium(III)
ion and malonic acid in aqueous HClO$_4$ + NaClO$_4$ under conditions in which no significant amount of bis-malonatochromate(III) ion is formed. From the observed dependence of the rate on malonic acid and perchloric acid concentrations (acceleration by malonic acid and retardation by perchloric acid) a mechanism involving the rate-determining reaction of the ion-pair Cr(OH$_2$)$_6^{3+}$·HMal$^-$ (H$_2$Mal = malonic acid) to form the product was proposed. From the comparison of the values of the activation parameters for this complex system with the corresponding literature values for the water exchange of [Cr(H$_2$O)$_6$]$^{3+}$ ion, it was suggested that the ion-pair reacts through $S_{N1}$ process.

Banerjea and Choudhuri$^{72}$, in another study on the kinetics and mechanism of formation of tetraaquamonooxalato-chromium(III) ion from hexaaquachromium(III) ion and oxalic acid, interpreted their experimental results to be consistent with a mechanism involving a rate determining reaction of a weak outer-sphere associated species. The values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ showed that the dissociation of the first Cr(III)–OH$_2$ bond is important in the transition state. In marked contrast with Hamm and coworkers, Banerjea et al. always found a dependence of the reaction rate on ligand concentration.

Kelm and Harris$^{73}$ investigated the anation reaction of cis-bis(oxalato)diaquachromium(III) ion, cis-[Cr(C$_2$O$_4$)$_2$(H$_2$O)$_2$]$^-$. 
with oxalate ion in aqueous solution. The complex ion interacts with either $\text{HC}_2\text{O}_4^-$ or $\text{C}_2\text{O}_4^{2-}$ ion, resulting in the formation of the tris(oxalato)chromium(III) ion. The ligand-water dissociation from the diaqua complex ion, following an outer-sphere associative equilibration of the latter with bioxalate or oxalate ion, was assumed to be the rate determining step. The observed first-order rate constant was given by the equation

$$k_{\text{obs}} = \frac{k_w K_1 [\text{HC}_2\text{O}_4^-]}{1 + K_1 [\text{HC}_2\text{O}_4^-] + K_2 [\text{C}_2\text{O}_4^{2-}] / \{1 + K_2 [\text{C}_2\text{O}_4^{2-}]\}}$$

(42)

where $k_w$ is the rate constant of the water replacement and $K_1$ and $K_2$ are association constants for bioxalate and oxalate, respectively.

Hamm et al. 74 made a significant contribution in the field by studying polarographically the rates of reaction of a series of organic acid anions, such as acetate, glycolate, lactate, phthalate, citrate and tartarate with chromium(III). Based on the similarities in these rates and those previously reported for oxalate and malonate, the following general reaction mechanism was suggested in which the dissociation of a water molecule is proposed to be a slow step.
The rate equation was given as

$$\frac{d[Cr_t]}{dt} = \frac{k_3 K_2 K_1 [B] [Cr_t]}{[H^+] + ([H^+] + K_2) K_1 [B]}$$ (47)
where \([Cr_t]\) designates the concentration of the total polaro-
graphically measurable chromium. A dissociative mechanism was
proposed in all the above studies as the rates were found to be
independent of ligand concentration. As the concentrations of
anions used was high (0.1 mol dm\(^{-3}\)) Basolo and Pearson\(^7\) later
suggested a saturated ion-pairing mechanism which seems to be
more reasonable.

Banerjea and Mohan\(^8\) reported the studies on the kine-
tics and mechanism of formation of cis-diaquabis(oxalato)chromate
(III) from the mono-oxalato complex and oxalate ions. The rate
of the reaction is first-order with respect to the mono-oxalato
complex. The values of \(\Delta H^\ddagger\) and \(\Delta S^\ddagger\) were found to be 23.9
cal mol\(^{-1}\) and 8.6 e.u., respectively. The proposed slow step is
the initial one ended attachment of the incoming oxalate ion, by
substitution of water molecule attached to the chromium(III),
followed by rapid ring closure by the oxalate resulting in the
displacement of another water molecule from an adjacent coordina-
tion site forming the bis-oxalato complex. The observed retarda-
tion by H\(^+\) ion and acceleration by oxalate was explained by this
mechanism quantitatively.

The mechanism of formation of oxalato complexes of
Cr(III) has been investigated in detail by Kelm and coworkers\(^9\).
The rates of successive oxalate additions to Cr(H\(_2\)O)\(^{3+}\) are 4x10\(^{-5}\),
5.3x10\(^{-4}\) and 1.4x10\(^{-4}\) 1mol\(^{-1}\)s\(^{-1}\), respectively. An associative
mechanism has been proposed for these reactions since the formation rates are much faster than the ligand–water exchange process.

The negative volumes of activation obtained for the oxalate anation reactions, as well as for cis–trans isomerisation of \( \text{Cr(H}_2\text{O)\text{C}_2\text{O}_4} \text{)}_2^- \) in water and in mixed solvents further support the 'Ia' mechanism.

Acid catalysed \(^{18}\text{O}\)-exchange of \( \text{Cr(C}_2\text{O}_4\text{(H}_2\text{O)}\text{)}_4^{+} \), \( \text{Cr(C}_2\text{O}_4\text{)}_2\text{(bipy)}^- \), \( \text{Cr(C}_2\text{O}_4\text{)}_2\text{(phen)}_2^- \) and \( \text{Cr(en)}_2\text{(C}_2\text{O}_4\text{)}_2^{+} \) has been studied and, unlike Co(III) and Rh(III) oxalate complexes, the inner and outer oxygens of oxalate undergo exchange with solvent water at kinetically indistinguishable rates. Chelate ring opening or carbonyl–carboxyl O-interchange has been proposed for racemisation reactions of complexes of this type. Cis–

\[ \text{Cr(C}_2\text{O}_4\text{)}_2\text{(H}_2\text{O)}_2^- \]

disproportionates slowly in aqueous solution into \( \text{Cr(C}_2\text{O}_4\text{(H}_2\text{O)}\text{)}_4^{+} \) and \( \text{Cr(C}_2\text{O}_4\text{)}_3^- \) via a dimeric intermediate with an oxalate bridge. The mechanism of the acid catalysed aquation of cis–\( \text{Cr(mal)}_2\text{(H}_2\text{O)}_2^- \) is very similar to that of the corresponding oxalate complex. The mechanism involves a rapid protonation equilibrium followed by a rate-determining attack of water on the protonated species.

Trans–\( \text{Cr(mal)}_2\text{(H}_2\text{O)}_2^- \) has been found to undergo acid-catalysed isomerisation to the cis form, which then decomposes to \( \text{Cr(mal)(H}_2\text{O)}_4^{+} \). Trans–\( \text{Cr(mal)}_2\text{(OH)}_2 \text{)}^{3+} \) isomerises with dissoci-
ation of a water molecule, followed by rearrangement of the penta-coordinated species\(^87\).

The kinetics of the reaction of aquachromium(III) ion with EDTA was first investigated by Hamm\(^88\). He observed that the rate of reaction was independent of the EDTA concentrations. Olson\(^89\) later reported that the reaction mechanism of the above reaction involves reversible formation of an ion-pair followed by rate-determining anation. Yamamoto et al.\(^90\) reported the same results as those of Hamm for the rate dependence on EDTA concentration.

Studies on the complex formation between aquachromium (III) ion and EDTA, catalysed by NaNO\(_2\) or Na\(_2\)SO\(_3\) at 25\(^\circ\)C, ionic strength 0.5M and pH = 3.5-4.8, were further investigated by Ohashi and coworkers\(^91\). When concentration of EDTA or catalyst was in large excess over aquachromium(III) ion, it was noticed that reaction to form Cr(III)-EDTA complex was first-order with respect to the aquachromium(III) ion concentration and the rate increased with increasing concentration of EDTA or catalyst.

Ogino et al.\(^92-96\) studied the equilibrium and kinetics of the reactions

\[
[CrY(H_2O)](n-3)^- + X \xrightarrow{k_f \over k_b} [CrXY](n-2)^- + H_2O
\] (48)
where $X = \text{N}_3^-, \text{OAc}^-, \text{ONO}^-$ and $\text{NCS}^-$ and $Y$ represents

\[
\begin{align*}
\text{ooc-} & \quad \text{CH}_2 \quad \text{COO}^- \\
\text{NCH}_2-\text{CH}_2\text{N} & \\
\text{ooc-} & \quad \text{CH}_2 \quad \text{COO}^- \\
\end{align*}
\]

edda^4-  
(ethylene-diammine-N,N,N',N'-tetraacetate)

\[
\begin{align*}
\text{ooc-} & \quad \text{CH}_2 \quad \text{CH}_2\text{OH} \\
\text{NCH}_2-\text{CH}_2\text{N} & \\
\text{ooc-} & \quad \text{CH}_2 \quad \text{COO}^- \\
\end{align*}
\]

ehdra^3-  
(N-(hydroxyethyl)ethylenediammine-N,N',N'-triacetate)

\[
\begin{align*}
\text{ooc-} & \quad \text{CH}_2 \quad \text{H} \\
\text{NCH}_2-\text{CH}_2\text{N} & \\
\text{coo-} & \quad \text{CH}_2 \quad \text{COO}^- \\
\end{align*}
\]
edtra  
(ethylenediammine-N,N',N'-triacetate)
It was observed that the formation constants of $[\text{CrXY}]^{(n-2)-}$ increase in the following order with the nature of the $X^-$: $\text{Br}^-, \text{Cl}^- < \text{ONO}^- < \text{NCS}^- \sim \text{OAc}^- < \text{N}_3^-$. It appears that the order is not related directly to that of the basicity of the $X^-$. 

The values of anation rate constants, $k_f$, are not so sensitive to the change of nature of $X^-$. The order of reactivities is $[\text{Cr(H}_2\text{O)}_6]^{3+} < [\text{Cr(NH}_3)_5\text{H}_2\text{O}]^{3+} << [\text{Cr(medtra)}(\text{H}_2\text{O})] < [\text{Cr(edtra)}(\text{H}_2\text{O})] < [\text{Cr(hedtra)}(\text{H}_2\text{O})] < [\text{Cr(aedtra)}(\text{H}_2\text{O})]$. 

$n$ is 4 for edta and 3 for hedtra, edtra, medtra and aedtra.
The substitution reactions of chromium(III) complexes reported in this work are very rapid in comparison with both the acidopentaaqua- and acidopentaamminechromium(III) complexes. The results are interpreted on the basis that coordination of $Y^{n-}$ reduces the positive charge of the central chromium(III) ion and leads to loosening of the Cr-OH$_2$ bond. The N-substituted groups in the [Cr(edtra)(H$_2$O)] and [Cr(medtra)(H$_2$O)] complexes have no coordinating ability for the metal ions. The $k_f$ values are much larger than those of the [Cr(edtra)(H$_2$O)] and [Cr(medtra)(H$_2$O)] complexes when the N-substituent groups of $Y^{n-}$ have coordinating ability, such as CH$_2$COOH, CH$_2$CH$_2$OH, CH$_2$CH$_2$OOCCH$_3$ or CH$_2$COO$^-$. On this basis it was suggested that the Cr-OH$_2$ bond rupture is enhanced by the transient coordination of these pendant groups to central chromium(III) ions.

Sykes and his coworkers$^{97}$ studied the equilibration kinetic studies on the rapid complexation of ethylenediammine-N,N,N',N'-tetraacetatoaquachromate(III), Cr(EDTA)H$_2$O$^-$, with chromate(VI), molybdate(VI) and tungstate(VI) using the stopped flow technique at 25°C, in the pH-range 7.3-8.7 and $\mu = 1.0$ moldm$^{-3}$ (LiClO$_4$). Replacement of the coordinated water which is labilized by the free EDTA was observed.

$$Cr(EDTA)H_2O^- + x^{n-} \xrightarrow{k_f \over k_b} Cr(EDTA)x^{(n+1)-} + H_2O$$ (49)
They also carried out the temperature jump and stopped flow studies with $X^{-} = \text{azide}$ at pH $4.3-5.4$ and pH $7.38$, respectively. The hydrogen ion dependence of $k_{f}$ was in all cases given by $k_{1}-k_{2}[H^{+}]$, where $k_{2}$ made $\leq 2.5\%$ contributions with molybdate(VI) and azide and $\leq 10\%$ with chromate(VI) and tungstate(VI). Kinetic equilibrium constants $K_{1}=k_{f}/k_{b}$ were reported to be in conformity with those obtained by spectrophotometric measurements.

The kinetics of the reaction of EDTA with aquachromium(III) ion in mixed solvents of water and methanol/ethanol were reported by Kimura and Shirai. The reaction was found to be first order with respect to the chromium(III) concentration and proceeded only through dissociation of coordinated water molecules out of hexaaquachromium(III) and hydroxypentaaquachromium(III) ions. The rate of the reaction was observed to be independent of EDTA concentrations. The proposed mechanism and the rate law are given below.

\begin{align*}
\text{Cr(H}_2\text{O)}_{6}^{3+} & \xrightarrow{K_{a}} \text{Cr(OH)(H}_2\text{O)}_{5}^{2+} + H^{+} \quad \text{(50)} \\
\text{Cr(H}_2\text{O)}_{6}^{3+} & \xrightarrow{k_{1}} \text{Cr(edta)(H}_2\text{O)}^{-} + 5\text{H}_2\text{O} \quad \text{(51)} \\
\text{Cr(OH)(H}_2\text{O)}_{5}^{2+} & \xrightarrow{k_{2}} \text{Cr(edta)(H}_2\text{O)}^{-} + 4\text{H}_2\text{O} + \text{OH}^{-} \quad \text{(52)}
\end{align*}
The rate law was

\[ k_{\text{obs}} = \frac{k_1 + k_2 K_a/\left[ H^+ \right]}{1 + K_a/\left[ H^+ \right]} \]  \tag{53}  

\(k_1\) and \(k_2\) were independent whereas the value of \(K_a\) was slightly decreased with increasing concentration of alcohols. An important observation that hydroxopentaaquachromium(III) is more labile than hexaaquachromium(III) by a factor of \(10^2\) was made but the most notable observation was the lack of ion-pairing, unlike Olson\textsuperscript{89}.

Kinetics of anation of cis-diaqua(ethylenediammine)(oxalato)chromium(III) complex ion by oxalato species were reported by Kallen et al.\textsuperscript{99}. The observed pseudo-first-order rate constants exhibited a complex hydrogen ion dependence and a mass law retarded first-order dependence on the formal oxalate concentration. The following associative interchange (I\(_a\)) mechanism was proposed

\[
\begin{align*}
   \text{H}_2\text{C}_2\text{O}_4 & \overset{K_1}{\rightleftharpoons} H^+ + \text{HC}_2\text{O}_4^- \\
   \text{HC}_2\text{O}_4^- & \overset{K_2}{\rightleftharpoons} H^+ + \text{C}_2\text{O}_4^{2-} \\
   \text{cis-Cr(Ox)(en)(H}_2\text{O})^+ & \overset{K_{a1}}{\rightleftharpoons} \text{Cr(Ox)(en)(OH)(H}_2\text{O)} + H^+ \\
   \text{cis-Cr(Ox)(en)(H}_2\text{O})^+_2 + \text{HC}_2\text{O}_4^- & \overset{K_B}{\rightleftharpoons} \text{(IP-1)} 
\end{align*}
\]  

\[
\begin{align*}
   \text{H}_2\text{C}_2\text{O}_4 & \overset{K_1}{\rightleftharpoons} H^+ + \text{HC}_2\text{O}_4^- \\
   \text{HC}_2\text{O}_4^- & \overset{K_2}{\rightleftharpoons} H^+ + \text{C}_2\text{O}_4^{2-} \\
   \text{cis-Cr(Ox)(en)(H}_2\text{O})^+ & \overset{K_{a1}}{\rightleftharpoons} \text{Cr(Ox)(en)(OH)(H}_2\text{O)} + H^+ \\
   \text{cis-Cr(Ox)(en)(H}_2\text{O})^+_2 + \text{HC}_2\text{O}_4^- & \overset{K_B}{\rightleftharpoons} \text{(IP-1)} 
\end{align*}
\]  

\[
\begin{align*}
   \text{H}_2\text{C}_2\text{O}_4 & \overset{K_1}{\rightleftharpoons} H^+ + \text{HC}_2\text{O}_4^- \\
   \text{HC}_2\text{O}_4^- & \overset{K_2}{\rightleftharpoons} H^+ + \text{C}_2\text{O}_4^{2-} \\
   \text{cis-Cr(Ox)(en)(H}_2\text{O})^+ & \overset{K_{a1}}{\rightleftharpoons} \text{Cr(Ox)(en)(OH)(H}_2\text{O)} + H^+ \\
   \text{cis-Cr(Ox)(en)(H}_2\text{O})^+_2 + \text{HC}_2\text{O}_4^- & \overset{K_B}{\rightleftharpoons} \text{(IP-1)} 
\end{align*}
\]
cis-Cr(Ox)(en)(H₂O)²⁺ + C₂O₄²⁻ $\xrightarrow{K_C}$ (IP-2)⁻ (58)

(IP-1) $\xleftrightarrow{K_2}$ (IP-2)⁻ + H⁺ (59)

(IP-1) $\xrightarrow{k_1}$ Cr(Ox)₂(en)⁻ + H₃O⁺ + H₂O (60)

(IP-2) $\xrightarrow{k_1}$ Cr(Ox)₂(en)⁻ + 2H₂O (61)

The rate constant derived for Iₐ mechanism was given by the expression

$$k_{obs} = \frac{k_1 K_C[H⁺]([H⁺] + K_1'[C₂O₄²⁻])}{K_2'([H⁺] + K_{al}) + K_C[H⁺] + K_1'[C₂O₄²⁻]}$$ (62)

where $K_2'$ denotes the acid dissociation constant of an associated hydrogen oxalate ion and $K_{al}$ is the first acid dissociation constant of the aqua ligand of the complex ion. A two-step oxalate anation mechanism was suggested for this complex ion and other oxalate complexes of chromium(III). The mechanism was initiated by one ended dissociation and isomerisation of an oxalato-O, O'-ligand to oxalate-O, O bonding mode. Associative interchange of an ion-paired oxalate species for an aqua ligand was proposed to occur in the second step as a direct consequence of ligand isomerisation. The mechanism successfully explained differences in the nature of activation parameters for oxalate anation of oxalato complexes of chromium(III).
An important characteristic of polycarboxylate complexes is that both their rates of formation and dissociation exhibit acid-dependent and acid-independent paths. In this respect the formation of the \( \text{Cr(III)-EDTA} \) complex from \( \text{Cr(H}_2\text{O)}^3\text{+} \) and EDTA, the stepwise protonation of EDTA, and the participation of various Cr(III) hydroxo species in the reaction has been discussed. The results can be explained in terms of a mechanism. Since various acid-base equilibria are involved in these reactions one would expect catalysis by anions like \( \text{CO}_3^{2-} \), \( \text{SO}_3^{2-} \) and \( \text{NO}_2^- \) to be due to their effect on the acid-base equilibria, and a study to this effect has been made by Phatak, Bhat and Shankar.

Bannerjea and Choudhuri have studied the formation of the Cr(III)-EDTA complex by reacting Cr(en)$_3^{3+}$, Cr(Ox)$_3^{3-}$, Cr(acac)$_3$ and Cr(biguanide)$_3^{3+}$ with EDTA. The pH-dependence of these reactions may be attributed to the existence of a pH-controlled chelate-ring opening process which occurs during the reaction. Although such studies with multidentate ligands are undoubtedly important, their kinetics are very difficult to unravel.

The Cr(III)-EDTA complex which has been formulated as Cr(EDTA)(OH)$_2$ undergoes dechelation in highly basic solution to form a quadridentate complex, Cr(EDTA)(OH)$_3$. The rechelation of this quadridentate form to the quinquedentate form has been studied in the pH-range 0-12. It is evident from the rate vs pH
profile that neighbouring group effects are important in this
interconversion process. A markedly faster rate of chelation
than is usual in Cr(III) substitution reactions is believed to
be due to the replacement of H$_2$O by the -COO- group. A high
degree of S$_N$2 character has been proposed for the reaction.$^{107}$

Two schemes A and B were proposed due to the authors' inability to choose anyone, as both gave the same hydrogen ion
dependence in terms of rate constants $k_1$, $k_2$, $k_3$, $k_4$ and $k_5$ and equilibrium constants $K_1$, $K_2$, $K_3$ and $K_4$.

The rate constant derived was

$$k_{\text{obs}} = \frac{k_1[H^+]^4 + k_2K_1[H^+]^3 + k_3K_1K_2[H^+]^2 + k_4K_1K_2K_3[H^+] + k_5K_1K_2K_3K_4}{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4} \quad (63)$$

The two mechanisms (A and B) may be represented as follows:
Mechanism A

\[ \text{Mechanism A} \]

\[ \begin{align*}
\text{CO}_2^+ & \rightarrow \text{CO}_2^- + \text{H}^+ \\
\text{H}_2\text{O} & \rightarrow \text{OH}^- + \text{H}^+ \\
\text{CO}_2^- & \rightarrow \text{CO}_2^- + \text{OH}^- \\
\text{OH}^- & \rightarrow \text{OH}^- + \text{H}^+ \\
\text{CO}_2^- & \rightarrow \text{CO}_2^- + \text{OH}^- \\
\end{align*} \]
Mechanism B

\begin{align*}
\text{CO}_2\text{H} & \quad \text{CO}_2\text{H} \\
\text{N} & \quad \text{H}_2\text{O} \\
\text{K}_1 & \quad \text{K}_2 \\
\text{k}_1 & \quad \text{k}_2 \\
\text{CO}_2^- & \quad \text{OH}_2 \\
\text{N} & \quad \text{H}_2\text{O} \\
\text{K}_3 & \quad \text{K}_4 \\
\text{k}_3 & \quad \text{k}_4 \\
\text{CO}_2^- & \quad \text{OH} \\
\text{N} & \quad \text{OH} \\
\text{k}_5 &
\end{align*}
The anation reaction of the hexaaquachromium(III) ion by thiocyanate ion has been studied by different authors\textsuperscript{61,108,109}. On the basis of observed influence of $[H^+]$ on the reaction rate, it has been suggested that the reaction proceeds via three aqua complexes $\text{Cr}(H_2O)_6^{3+}$, $\text{Cr}(H_2O)_5(OH)^{2+}$, and $\text{Cr}(H_2O)_4(OH)^{+}$. Although the reaction proceeds very slowly at room temperature, the rates for both the forward and reverse reactions during the few tenths of a percent were evaluated. Measurements upon the forward reaction demonstrated the rate law

$$d[\text{CrNCS}^{2+}]/dt = [\text{Cr}^{3+}][\text{SCN}^-] \{k_1+k_2[H^+]+k_3[H^+]^{-2}\} \quad (64)$$

The combination of this with the net reaction equation gave the rate law for the reverse reaction

$$d[\text{SCN}^-]/dt = [\text{CrNCS}^{2+}] \{k_1+k_2[H^+]+k_3[H^+]^{-2}\} \quad (65)$$

This was confirmed by the direct measurements to the extent of a demonstration of first order dependence upon $[\text{CrNCS}^{2+}]$ and the evaluation of $k_{-1}$.

In a study on the effect of ionic strength on the reaction rate of $\text{Cr}(H_2O)_6^{3+}+\text{SCN}^-$, Holba\textsuperscript{110} has successfully interpreted the results on the basis of Moelwyn-Hughes theory\textsuperscript{111}. Ion-pair formation mechanism was already confirmed by the work of Phipps and Plane\textsuperscript{112}.
Baltisberger and King reported the equilibrium and kinetics of chromium(III) and chloride ions in methanol-water mixed solvent. The rate at which methanol replaces water in the first coordination shell of chromium(III) ion was determined and was found to be very similar to the rate of exchange of water between solvent and the first coordination shell of chromium(III) ion in aqueous solution. The rate at which chloride ion dissociates from chromium(III) ion was found to be ca. x10 lower than the replacement of methanol. Baltisberger and coworkers later on reported the thiocyanate anation of hexaaquachromium(III) and pentaaquamethanolchromium(III) ions in water-methanol solvent with 0.308 mole fraction of methanol. The following mechanism was proposed

\[
\begin{align*}
\text{CrO}_6^{3+} + \text{N}^- & \quad \underset{k_1}{\longrightarrow} \quad \text{CrO}_5\text{N}^{2+} + \text{O} \\
\text{CrO}_5\text{M}^{3+} + \text{N}^- & \quad \underset{k_2}{\longrightarrow} \quad \text{CrO}_5\text{N}^{2+} + \text{M} \\
\text{CrO}_5\text{M}^{3+} + \text{N}^- & \quad \underset{k_3}{\longrightarrow} \quad \text{trans-CrO}_4\text{MN}^{2+} + \text{O} \\
\text{CrO}_5\text{M}^{3+} + \text{N}^- & \quad \underset{k_4}{\longrightarrow} \quad \text{cis-CrO}_4\text{MN}^{2+} + \text{O} \\
\text{CrO}_5\text{N}^{2+} + \text{M} & \quad \underset{k_5}{\longrightarrow} \quad \text{trans-CrO}_4\text{MN}^{2+} + \text{O} \\
\text{CrO}_5\text{N}^{2+} + \text{M} & \quad \underset{k_6}{\longrightarrow} \quad \text{trans-CrO}_4\text{MN}^{2+} + \text{O}
\end{align*}
\]
\[
\text{CrO}_5\text{N}^{2+} + M \xrightleftharpoons[k_8]{k_6} \text{cis-CrO}_4\text{MN}^{2+} + \text{O}
\]  

(71)

where \( M = \text{CH}_3\text{OH}, \text{O} = \text{H}_2\text{O}\) and \( \text{N}^- = \text{SCN}^- \) coordinated through nitrogen.

Thusius\textsuperscript{115} has compiled data concerning the rates and activation parameters of the anation reactions of \( \text{Cr(H}_2\text{O})_6^{3+} \) and \( \text{Cr(H}_2\text{O})_5\text{OH}^{2+} \) with various ligands. Table 1.3 illustrates these data. It has been proposed\textsuperscript{116} that the greater span of the anation rate constants for \( \text{Cr(H}_2\text{O})_6^{3+} \) than for \( \text{Cr(H}_2\text{O})_5\text{OH}^{2+} \) is indicative of bond making as an important process in the \( \text{Cr(H}_2\text{O})_6^{3+} \) reactions. However, the activation enthalpies for complex formation with \( \text{Cr(H}_2\text{O})_6^{3+} \) are higher than for formation with \( \text{Cr(H}_2\text{O})_5\text{OH}^{2+} \) and the difference is due to the difference in lability of these two complexes. The isokinetic relationship obtained for \( \text{Cr(H}_2\text{O})_5\text{OH}^{2+} \) shows that the compensating differences in \( \Delta H^f \) and \( \Delta S^f \) largely account for the weak discrimination of hydroxo species towards different nucleophiles.

Attempts have been made to determine the outer-sphere ion-association constant and the rate of formation of inner-sphere complexes from the kinetics of the reaction of the Cr(III) ion with Br\textsuperscript{−} ion in HBr acid solution\textsuperscript{117}. Unfortunately, too many uncertainties in results prohibit any precise determination of the constants.
TABLE 1.3: Rate constants and activation parameters for the reactions of Cr(H₂O)₆³⁺ and Cr(H₂O)₅OH²⁺ with ligands Lⁿ⁻ at 25°C

<table>
<thead>
<tr>
<th>Lⁿ⁻</th>
<th>Cr(H₂O)₆³⁺</th>
<th></th>
<th></th>
<th>Cr(H₂O)₅OH²⁺</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10⁸k</td>
<td>ΔH ≠</td>
<td>ΔS ≠</td>
<td>10⁵k</td>
<td>ΔH ≠</td>
<td>ΔS ≠</td>
</tr>
<tr>
<td></td>
<td>(1mol⁻¹s⁻¹)</td>
<td>(kcal mol⁻¹)</td>
<td>(cal deg⁻¹mol⁻¹)</td>
<td>(1mol⁻¹s⁻¹)</td>
<td>(kcal mol⁻¹)</td>
<td>(cal deg⁻¹mol⁻¹)</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1100</td>
<td>29.1</td>
<td>+10</td>
<td>39</td>
<td>25.5</td>
<td>+11</td>
</tr>
<tr>
<td>HF</td>
<td>56</td>
<td>24.2</td>
<td>-6</td>
<td>29</td>
<td>19.0</td>
<td>-11</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>73</td>
<td>26.1</td>
<td>+1</td>
<td>9.0</td>
<td>20.0</td>
<td>-10</td>
</tr>
<tr>
<td>NCS⁻</td>
<td>180</td>
<td>25.1</td>
<td>+1</td>
<td>4.9</td>
<td>22.8</td>
<td>-1</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>2.9</td>
<td>30.3</td>
<td>+9</td>
<td>2.8</td>
<td>26.0</td>
<td>+8</td>
</tr>
<tr>
<td>Br⁻</td>
<td>0.9</td>
<td>28.9</td>
<td>+2</td>
<td>1.7</td>
<td>22.8</td>
<td>-4</td>
</tr>
<tr>
<td>I⁻</td>
<td>0.08</td>
<td>30.6</td>
<td>+6</td>
<td>0.26</td>
<td>27.0</td>
<td>+11</td>
</tr>
<tr>
<td>SCN⁻</td>
<td>0.4</td>
<td>29.6</td>
<td>+2</td>
<td>0.5</td>
<td>24.5</td>
<td>-1</td>
</tr>
<tr>
<td>HSO₄⁻</td>
<td>13</td>
<td>28.2</td>
<td>+5</td>
<td>627</td>
<td>14.2</td>
<td>-21</td>
</tr>
<tr>
<td>H₂O</td>
<td>250⁺</td>
<td>26.1</td>
<td>-</td>
<td>10</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F⁻</td>
<td>2000</td>
<td>31.0</td>
<td>+24</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H₃PO₂</td>
<td>2900</td>
<td>20.3</td>
<td>-11</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>HgCl⁺</td>
<td>0.13</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Carey, Jones and Swaddle\textsuperscript{118} studied the mechanism of substitution reactions of azidopentaaquachromium(III) complexes and reported an associative interchange (I\textsubscript{a}) type mechanism for acid independent substitution processes in aquachromium(III) complexes, but a conjugate base such as Cr(H\textsubscript{2}O)\textsubscript{4}OH\textsuperscript{+} to react by a dissociative interchange (I\textsubscript{d}) mechanism.

Lo and Watts\textsuperscript{119} studied the anation reactions of hexa-(dimethylsulphoxide)chromium(III) by X\textsuperscript{-} = N\textsubscript{3}\textsuperscript{-} and SCN\textsuperscript{-} in dimethylsulphoxide as a function of concentration, temperature and ionic strength in both condition of X\textsuperscript{-} in excess over Cr(Me\textsubscript{2}SO\textsubscript{5})\textsuperscript{3+} and Cr(Me\textsubscript{2}SO\textsubscript{5})\textsuperscript{3+} in excess over X\textsuperscript{-}, where greater certainty existed concerning the nature of solution species. The reactions were interpreted in terms of I\textsubscript{d} in which anation was probable result of dissociation only when the anion occupied a position in the first solvation sphere of the complex. The proposed mechanism is

\[
\text{Cr(Me}_2\text{SO)}\textsubscript{5}^3+ + \text{X}^\text{-} \overset{K}{\rightleftharpoons} \text{Cr(Me}_2\text{SO)}\textsubscript{5}^3+.\text{X}^\text{-} \quad \text{(ion-pair)} \tag{72}
\]

\[
\text{ion-pair} \overset{k}{\longrightarrow} [\text{Cr(Me}_2\text{SO)}\textsubscript{5}\text{X}]^2+ + \text{Me}_2\text{SO} \tag{73}
\]

On the basis of the above mechanism, the derived rate law is

(a) when the complex is in excess

\[
k_{\text{obs}} = kK[\text{complex}]/(1+K[\text{complex}]) \tag{74}
\]
(b) when the \( X^- \) is in excess there is a possibility of ion-triplet formation

\[
X^- + \text{ion-pair} \xrightleftharpoons{K'} \quad \text{Cr(Me}_2\text{SO)}_6^{3+} \cdot 2X^- \quad \text{(ion-triplet)}
\]

\[
\text{ion-triplet} \xrightarrow{k'} \quad \text{Cr(Me}_2\text{SO)}_5X^{2+} + X^- + \text{Me}_2\text{SO}
\]

The overall mechanism for \([X^-]\) in excess gives

\[
k_{\text{obs}} = \frac{kK[X^-] + k'KK'[X^-]^2}{1 + k[X^-] + k'K'[X^-]^2}
\]

The competitive anation reaction

\[
\text{[Cr(Me}_2\text{SO)}_6]^{3+} + X^- + \text{Cl}^- \quad \xrightarrow{\quad} \quad \text{[CrCl(Me}_2\text{SO)}_5]^{2+} + \text{Me}_2\text{SO}
\]

\[
\text{[Cr(Me}_2\text{SO)}_6]^{3+} + \text{X}^- + \text{Cl}^- \quad \xrightarrow{\quad} \quad \text{[CrX(Me}_2\text{SO)}_5]^{2+} + \text{Me}_2\text{SO}
\]

(where \( X^- = N_3^- \) or SCN\(^-\)) had been studied in \( \text{Me}_2\text{SO} \) at one temperature as a function of the concentration of \( X^- \) and Cl\(^-\). The results were consistent with an \( I_d \) mechanism. The formation of ion-pair and ion-triplet occurs during the course of reaction. The results were found to be consistent with their previous results on the anation of \( \text{Cr(Me}_2\text{SO)}_6^{3+} \) separately by SCN\(^-\), \( N_3^- \) and Cl\(^-\).
Lo and Swaddle\textsuperscript{121} investigated the detailed mechanism for anation, ion-pairing and solvent exchange of chromium(III) with various ligands ($X^-$) in N,N-dimethylformamide. Rate coefficients, enthalpies and entropies of activation were obtained for anation of $\text{Cr(DMF)}^3_6$ in DMF by $\text{Br}^-$, $\text{NCS}^-$ and $\text{ClO}_4^-$, as well as exchange rate data at a single temperature in the presence of $\text{NCS}^-$ and $\text{N}_3^-$. Ion-pair formation quotients were also estimated from the kinetics of one or both reactions for $\text{Br}^-$, $\text{Cl}^-$, $\text{NCS}^-$, $\text{N}_3^-$ and $\text{ClO}_4^-$. They reported that the solvent exchange rates were depressed slightly by ion-pairing and roughly to the same extent for all the above anions. The following interchange model was proposed.

\begin{align}
\text{Cr(DMF)}^3_6 + X^- & \xrightleftharpoons[k_{\text{IP}}]{k_i} \text{Cr(DMF)}^3_6 \cdot X^- \\
\text{Cr(DMF)}^3_6 \cdot X^- & \xrightarrow{k_i} \text{Cr(DMF)}^2_6 X^2+ + \text{DMF} \\
\{\text{Cr(DMF-d}_7^3)^3_6, X^-\} + 6\text{DMF-h}_7 & \xrightarrow{k_2} \text{Cr(DMF-h}_7^3)^3_6 \cdot X^- + 6 \text{DMF-d}_7 \\
\text{Cr(DMF-d}_7^3)^3_6 + 6\text{DMF-h}_7 & \xrightarrow{k_2} \text{Cr(DMF-h}_7^3)^3_6 + 6 \text{DMF-d}_7
\end{align}

According to the interchange mechanism of eqn. (74) and (75), the dependence of rate constant on the concentration of free anion $X^-$, $[X^-]_f$, is given by
\begin{equation}
k_{\text{obs}} = \frac{k_1 K_{\text{IP}} [X^-]_f}{(1 + K_{\text{IP}} [X^-]_f)}
\end{equation}

if the ionic strength is constant.

Kinetics and mechanism of formation and aquation of hypophosphitechromium(III) ion were studied by Espenson and Binau\textsuperscript{122}. Investigations were carried out as a function of \([H^+]\) between 45-65\(^{\circ}\) at unit ionic strength. The net rate of formation of complex was given by equation

\begin{equation}
d[\text{CrH}_2\text{PO}_2^{2+}] / dt = k_f [\text{Cr}^{3+}][\text{H}_3\text{PO}_2] - k_{a\text{q}} [\text{CrH}_2\text{PO}_2^{2+}][H^+]
\end{equation}

Values of rate constant and their thermodynamic activation parameters were evaluated and compared with those of kinetic data for similar complexes. No unequivocal mechanism was suggested.

Bannerjea and Choudhuri\textsuperscript{123} studied the rate of formation of chromium(III)-glycine complexes from \text{Cr(OH}_2)_6^{3+} and glycine by spectrophotometry in weakly acidic media. A probable mechanism involving the formation of an ion-pair, \text{Cr(OH}_2)_6^{3+}.G^- was proposed. The reaction was assigned to have an associative character on the basis of much lower observed values of \(\Delta H^\ddagger\).

Sengupta and Banerjea\textsuperscript{124} carried out the work on the kinetics and mechanism of formation of \([\text{Cr(bigH}_2)(\text{AA})]^{3+}\), from
the reaction of cis-[Cr(bigH)₂(OH₂)₂]³⁺ with 2,2'-dipyridyl or 1,10-phenanthroline. The reaction was observed to be first order with respect to the ligand concentration. Activation parameters were evaluated. They suggested the mechanism involving an outer-sphere association followed by transformation and dissociation of the outer-sphere complex.

Costa et al.¹²⁵ studied the kinetics of the substitution reaction

$$\text{Cr(H₂O)}₆^{3+} + \text{P}_4\text{O}_{12}^{4-} \rightarrow \text{Cr(H₂O)}₅(\text{P}_4\text{O}_{12})^- + \text{H}_2\text{O} \tag{85}$$

and suggested an ion-pair reaction mechanism of $S_N^1$ type. The reaction is first-order, with energy of activation 18.8 kcal/mol and entropy of activation -17.9 e.u.

Stanisava et al.¹²⁶ studied the kinetics and mechanism of complex formation between hexaaquachromium(III) and trimetaphosphate and tetrametaphosphate anions. Observations regarding the effect of ionic strength and temperature on rate were made. They also proposed an ion-pair mechanism of $S_N^1$ type. The reaction was found to be first-order. The activation parameters were evaluated.

De and coworkers reported the anation reactions of hexaaquachromium(III) ion with neutral bidentate donors like 2,2'-dipyridyl¹²⁷, 1,10-phenanthroline¹²⁸ and anionic ligands like
nitrilotriacetic acid$^{129}$, α-picolinic acid$^{130}$, quinolinic acid$^{131}$ and picolinic acid N-oxide$^{132}$. A mechanism involving prior formation of ion-pair, followed by the interchange reaction, was suggested. The observed low $\Delta H^\ddagger$ values in comparison to isotopic water exchange were used as criterion for assigning an associative mechanism to all the substitution reactions. The observed higher pseudo-first-order rate constant for anation of picolinic acid N-oxide than that of picolinic acid was attributed to the higher value of ion-pair equilibrium constant observed for the former.

Recently, kinetics and mechanism for anation of hydroxo-pentaaquachromium(III) by dl-alanine and dl-phenylalanine have been investigated by Niogy and De$^{133,134}$. The pH was so adjusted that only the conjugate base existed in appreciable amounts. The anation rates were found to be higher as compared to water-exchange and other anation processes and therefore an $I_a$ mechanism was suggested.

In a series of papers, Tyagi and Khan$^{135-138}$ have reported the anation reactions of hexaaquachromium(III) with various carboxylic acids, both in aqueous and aqueous-ethanolic media. The rate constants were always found to be dependent on [ligand]. The results were interpreted in terms of an 'I_a' mechanism.
Ali and Murtaza\textsuperscript{139} have recently reported the kinetics of the interaction of hexaaquachromium(III) ion with potassium octacyanomolybdate(IV) using conductance and spectrophotometric data. The reaction was found to be pseudo-first order with respect to $[K_4Mo(CN)_8]$ and inverse first order with $[H_3O^+]$. The rate of the reaction was observed to increase with increase in ionic strength and temperature. On the basis of the results obtained an ion-pair mechanism was proposed and rate law was derived. Activation parameters have also been calculated. Ali and Sharma\textsuperscript{140} have also made a similar study with hexacyanoferrate(II).

Abdullah et al.\textsuperscript{141,142} in their studies on anations of hexaaquachromium(III) with glycine and cysteine have found the rate equation

$$k_{obs} = k + k'[H^+]^{-1}$$ (86)

The most striking result reported by them is that under all the conditions studied the reaction is zero order in [glycine]. This may be due to the involvement of a saturated outer-sphere complex (as concentrations of glycine used, for example, were $>0.1$ mol dm$^{-3}$). The following mechanism was proposed (for the formation of the glycinato complex)
\[ [\text{Cr(H}_2\text{O})_6]^{3+} \xrightarrow{K_\text{OS}} [\text{Cr(H}_2\text{O})_6\cdot\text{glyH}]^{3+} \xrightarrow{k_1} [\text{Cr(H}_2\text{O})_4\text{gly}]^{2+} \]

\[ [\text{Cr(H}_2\text{O})_5(\text{OH})]^{2+} \xrightarrow{K'_\text{OS}} [\text{Cr(H}_2\text{O})_5(\text{OH})\cdot\text{glyH}]^{2+} \xrightarrow{k'_1} [\text{Cr(H}_2\text{O})_3\text{OHgly}]^{+} \]

\( k_1 \) route was suggested to have an associative character whereas \( k'_1 \) route was proposed to have more dissociative nature.

Kabir-ud-Din and coworkers have studied the kinetics of anation of hexaaquachromium(III) ion by glycine\(^{143}\), dl-serine\(^{144}\), dl-valine\(^{145}\), dl-\( \alpha \)-alanine\(^{146}\) and l-asparagine\(^{147}\) in aqueous-acidic medium under pseudo-first order conditions of excess ligand. The dependence of observed rate constants on [ligand] and \([\text{H}^+]\) was found to be compatible with a mechanism which involves ion-pair formation between hexaaquachromium(III) ion and ligand in the zwitterionic form, followed by slow interchange of the bound water and the entering ligand in the ion-pair. The interchange mechanism was always associative type.

NATURE OF RESEARCH WORK DESCRIBED IN THIS THESIS

In going through the literature on the kinetics and mechanism of substitution reactions of chromium(III) complexes and especially the anation reactions it was observed that there is a marked difference in their mechanistic behaviours as, in
some cases, the rates were found to be independent of ligand concentration whereas in other cases an increase was observed with the increase in ligand concentration. Both $D$ and $I_a$ mechanisms were proposed. This difference in mechanisms and reaction paths owing to the difference in the nature of incoming ligand and the difference in the experimental conditions, coupled with the fact that only a limited number of kinetic studies have been carried out on the anation of chromium(III) with amino acids, stimulated us to undertake the present studies on the kinetics of anation of Cr(III), by $\alpha$-amino acids. Furthermore, only in a limited number of studies the workers have considered the lability of both the free metal ion and monohydroxy species (i.e. $\text{Cr}^{3+}$ and $\text{CrOH}^{2+}$).

The chromium(III) chemistry has become more topical from another viewpoint; Mertz$^{41,148}$ has shown that a low-molecular weight chromium(III) complex known as the 'Glucose Tolerance Factor' (GTF) potentiates insulin activity. A complex containing nicotinic acid, glycine, glutamic acid, cysteine and chromium(III) has been isolated from brewer's yeast$^{149}$. This substance of unknown structure shows remarkable in vitro activity, potentiating the action of insulin in glucose oxidation by chromium deficient rat adipose tissue. It has been suggested$^{150}$ that the active ingredient is a nitrogen-coordinated $\text{Cr(III)(nicotinic acid)}_2$$(\text{H}_2\text{O})^+$ complex which is protected from olation by the presence of the amino acids. Recently, however, it has been shown that contrary
to the suggestion of Mertz\textsuperscript{150}, coordination of two nicotinic acid ligands to a chromium ion via the pyridine ring nitrogen atoms does not result in GTF activity. However, coordination of the nicotinic acid ligands via the oxygen atoms of the carboxylate groups does result in a complex which possesses good biological (GTF) activity in the yeast biassay system\textsuperscript{151}. The structure of the biologically active O-coordinated chromium–dinicotinic acid complex was given as

\[
\begin{align*}
\text{Cr(nic)}_2\text{H}_2\text{O}_4^{3+} & \\
\end{align*}
\]

which contains trans arrangement of nitrogen containing functional group. Interest in GTF has stimulated work on chromium(III)–
nicotinic acid complexes and reports on various aspects have appeared\textsuperscript{152-155}. 

We have also begun a systematic study of the reaction of chromium(III) with individual components of the mixture described by Toepfer\textsuperscript{149} as well as other amino acids which include measurements of equilibrium constants, structure determinations and kinetic studies\textsuperscript{143-147,156,157} as not only the composition but other aspects too might be helpful in understanding the nature of the Glucose Tolerance Factor.

The work on the kinetics and mechanisms of anation reactions of chromium(III) with α-amino acids, l-leucine, l-glutamine, sarcosine, dl-tryptophan, l-cysteine, l-phenylalanine and l-hydroxyproline in aqueous and aqueous-alcoholic media are described in this thesis. The studies were carried out by varying the

(1) concentration of chromium(III)
(2) concentration of hydrogen ion
(3) concentration of amino acids
(4) ionic strength
(5) percentage of alcohol (v/v), and
(6) temperature.
The composition of the complexes formed were determined by Job's\textsuperscript{158} method of continuous variations. The kinetic results were analysed for each reaction separately and the mechanisms were proposed.