

# Chapter 1: Introduction

The physical study of mixed ligand complexes having one synthesized ligand attached to metal ion has received a great importance in recent years because of their wide applications in various fields of chemical activity and more particularly because of their presence in biological systems. An antimicrobial is a substance that kills or inhibits the growth of microbes such as bacteria, fungi, or viruses. Antimicrobial drugs either kill microbes (microbicidal) or prevent the growth of microbes (microbistatic). The history of antimicrobials begins with the observations of Pasteur and Joubert, who discovered that one type of bacteria could prevent the growth of another. They did not know at that time that the reason one bacteria failed to grow was that the other bacteria were producing an antibiotic. Technically, antibiotics are only those substances that are produced by one microorganism that kill, or prevent the growth, of another microorganism. Of course, in today's common usage, the term antibiotic is used to refer to almost any drug that cures a bacterial infection. Antimicrobials include not just antibiotics, but synthetically formed compounds as well. The discovery of antimicrobials like penicillin and tetracycline paved the way for better health for millions around the world. Before 1941, the year penicillin was discovered, no true cure for gonorrhoea, or pneumonia existed. Patients with infected wounds often had to have a wounded limb removed, or face death from infection. Now, most of these infections can be easily cured with a short course of antimicrobials.

## 1.1 BONDING THEORIES

Several theories have been advanced to account for the formation and properties of coordination complexes[1-5]. The two extreme view points visualize the metal-ligand both as purely ionic and purely covalent, respectively.

In the former view, due mainly to Kossel [6] and improved further by Magnus, Van Vleck and DeBoer [7] and particularly by Garrick, the positively charged metal ion is forming the centre of coordination is believed to attract and hold the negative ions or the negative end of polar ligand molecules around it, by electrostatic forces.

In 1931, Bohr developed his theory of atomic structure and formulated a scheme for the electron distribution in the atoms of different elements of the periodic table. Lewis, Sidgwick [8-9] proposed that ligands donate electron pair to metal ions and thus form a coordinate link. Pauling extended this approach like the valence bond theory. During the end of the year 1950, crystal field theory was introduced and in 1935 the molecular orbital theory was being developed.

Most widely used theories are as under:

- (i) Valence Bond Theory
- (ii) Crystal Field Theory
- (iii) Molecular Orbital Theory
- (iv) Ligand Field Theory

## 1.2 STABILITY

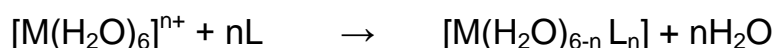
The use of the term stability is without any qualification means that complex is existent under suitable condition and it is possible to store complex for appreciable time.

The use of term stability is general because the coordination compounds are stable in one reagent but dissociate or decompose in presence of another reagent. It is also possible that term stability can be referred as an action of heat or light or compound. The stability of complex is expressed qualitatively in terms of

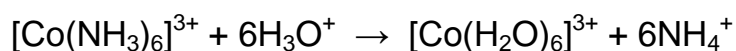
- (i) Thermodynamic stability
- (ii) Kinetic stability

**(i) Thermodynamic stability:**

It is the measure of extent of formation or transformation of complex under given set of condition at equilibrium. Thermodynamic stability depends on the strength of bond between metal ligand. The most of complexes are highly stable but they are dissociated in aqueous solution to some extent. The strength of bond between metal and ligand varies widely. For example the complexes like  $[\text{Co}(\text{SCN})_4]^{2+}$  ion the bond is very weak and on dilution, it breaks immediately and forms another compound.



On the other hand, the complex of  $[\text{Fe}(\text{CN})_6]^{3-}$  the bond is stronger in aqueous solution and in this complex  $\text{Fe}^{3+}$  cannot be detected by any sensitive reagent. So it is indicated that thermodynamic stability deals with metal-ligand bond energy, stability constant and other thermodynamic parameters. In terms of thermodynamic stability, the complexes are referred as stable and unstable. The thermodynamic stability of the species is the measure of extent to which species will be formed or transformed into other species under certain condition when system attained equilibrium. The tetracyano nickelate ion is a good example of thermodynamically stable complex that is kinetically labile. The classic example of the opposite case. i.e. a kinetically inert complex and thermodynamically unstable is the Hexa amine cobalt(III) cation in acid solution. It is expected to decompose:



The tremendous thermodynamic driving force of six basic ammonia molecules combining with six protons results in an equilibrium constant for the above reaction of value  $10^{25}$ . Nevertheless acidification of a solution of Hexamine cobalt(III) results in on immediate change and several days are required (at room temperature) for degradation of the complex despite the favourable thermodynamics. The inertness of the complex results from the absence of a suitable low-energy pathway for the acidolysis reaction. The difference between stability and inertness

can be expressed thermodynamically, a stable complex has large positive free energies of reaction  $\Delta G^0$ . The standard enthalpy change,  $\Delta H^0$  for this reaction is related to the equilibrium constant,  $\beta_n$  by the well thermodynamic equation.

$$\Delta G^0 = -RT \ln \beta$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

For similar complexes of various ions of the same charge of a particular transition series and particular ligand,  $\Delta S^0$  values would not differ substantially and hence a change in  $\Delta H^0$  value be related to change in  $\beta_n$  values. So order of values of  $\Delta H^0$  is also the order of the  $\beta_n$  value.

***(ii) Kinetic stability:***

It is referred to rate or speed at which a complex formation or transformation reaction proceeds at equilibrium. Time factors play an important role in deciding the kinetic stability of the complex. The kinetic stability deals with the rate and mechanism of a chemical reaction. In kinetic stability, hence the complexes are referred as “inert” or “labile”. Tube [10] had used term “Inert” for thermodynamically stable complexes and “labile” for reactive complexes. The exceptions are complexes of some Polydentate ligands like the naturally occurring chlorophyll which is extremely inert to exchange with  $Mg^{2+}$  ion in solution, the extended conjugation helps making the ring rigid [11-12]. The effect of EDTA addition upon homeostatic equilibrium of some trace elements, including copper has been evaluated by some workers in terms of simplified blood plasma model.

### **1.3 VARIOUS FACTORS AFFECTING THE STABILITY OF COORDINATION COMPOUNDS**

Following factors are affecting the stability of coordination compounds

(1) Nature of the Central Metal Ion

(i) Ionic Size

- (ii) Ionic Charge
- (2) Nature of the Ligand
  - (i) Size and Charge
  - (ii) Basic Character
  - (iii) Ligand Concentration
- (3) Chelate Effect
  - (i) Ring Size
  - (ii) Number of Rings
  - (iii) Effect of Substitution
  - (iv) Macrocyclic effect

**[1] Nature of Central Metal Ion:**

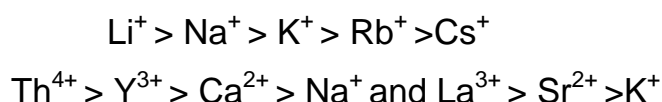
The important characteristics of the metal atom in determining stability of the complexes are given below.

**(i) Ionic Size:**

The stability of coordination compound (complex) decreases with increase in size of metal ion. Zn(II) forms more stable complexes than Cd(II). The size of Zn(II) ion is  $0.74\text{\AA}$  and Cd(II)  $0.97\text{\AA}$ .

**(ii) Ionic Charge:**

The effect of ionic charge of the central metal ion on the stability of coordination compounds may be described by comparing the change in stability in a series of complexes by changing the ionic charge on metal ion. If the charge of the central metal ion is more and the size is small, then the stability of the complex is more. In general, the small and highly charged cation can form more stable coordinate compounds because of most stable coordinate bonds.



**[2] Nature of the Ligand:**

Nature of the ligand or important characteristics of ligand affects to determine the stability of the compounds is explained in the following manner.

**(i) Size and Charge:**

Ligands with less charge and more size are less stable and form less stable coordination compounds. Ligands with higher charge have small size and form more stable compounds.

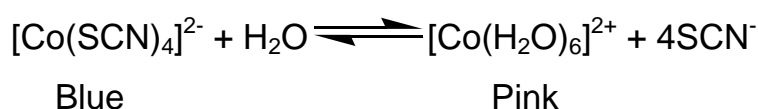
More size  $\longrightarrow$  Less Stable  $\longleftarrow$  Less Charge  
Small size  $\longrightarrow$  More stable  $\longleftarrow$  More Charge

**(ii) Basic Character:**

Calvin and Wilson [13] suggested that the higher basic character or strength of the ligand, higher will be the stability of coordination compounds. It is defined that a strong base or higher basic strength of the ligand means it forms more stable compounds or its donating tendency of electron to central metal ion is higher. e.g. Aromatic diamines form unstable coordination compounds while aliphatic diamines form stable coordination compounds. Ligands like  $\text{NH}_3$ ,  $\text{CN}^-$  etc have more basic character that means they form more stable compounds.

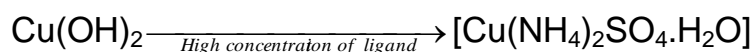
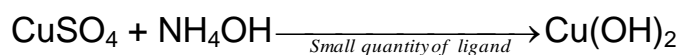
**(iii) Ligand Concentration:**

Some coordination complexes exist in aqueous solution only in presence of higher concentration of coordination group. In some cases aqueous molecules show greater coordinating tendency than the coordinating group which is originally present. e.g. in presence of highly concentrated solution of  $\text{SCN}^-$  (thiocyanate ion), the  $\text{Co}^{2+}$  metal ion forms a stable blue colored coordination complex but on dilution in aqueous medium the blue complex is destroyed and a pink aqua complex  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  is formed and then by further addition of ligand ( $\text{SCN}^-$ ) pink color disappears.



The color change indicates that there is a competition between  $\text{H}_2\text{O}/\text{SCN}^-$  in formation of complex with  $\text{Co}(\text{II})$  ion.

In the synthesis of tetra amine cupric sulphate complex at lower concentration of ammonia forms copper hydroxide, while at higher concentration of ligand form following complex.

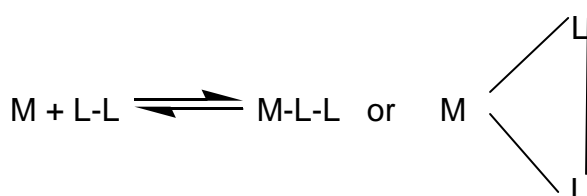


### [3] Chelate Effect:

The process of forming metal chelate by the attachment of multidentate ligand with central metal ion in which ligand act as chelating agent is known as chelation. Chelation is expressed by the following unidentate and bidentate ligand reaction.



$$K = \frac{[\text{ML}_2]}{[\text{M}][\text{L}]^2}$$



$$K = \frac{[\text{M-L-L}]}{[\text{M}][\text{L-L}]}$$

Morgan proposed the term chelate to describe the cyclic structure which arise by multidentate (poly) ligand and a metal ion. The name chelate is derived from the Greek word 'CHELA' means 'CLAW OF LOBSTER OR CRAB'.

Multidentate ligands [14] form more stable coordination compounds than monodentate ligands [15]. In 1937 Dielh [16] gave the comprehensive review of the chelate rings and more recent treatment is given by Martell and Calvin [17] who gave the review of the unusually high stability of metal chelate compounds.

Following factors are of great importance in chelate formation.

#### (i) Ring Size:

The stability of chelate is depending on the size of chelate ring. The stability of coordination complex increases with number of chelate

ring. It is found that 4-membered rings are unstable and rare than 5-membered rings which are common and stable. For chelate (saturated chelate) rings the following is the decreasing order of stability with increasing ring size

Five membered > Six membered > Seven membered

The stability of metal chelates decrease by increasing the chelate size [18-19].

**(ii) Number of Rings:**

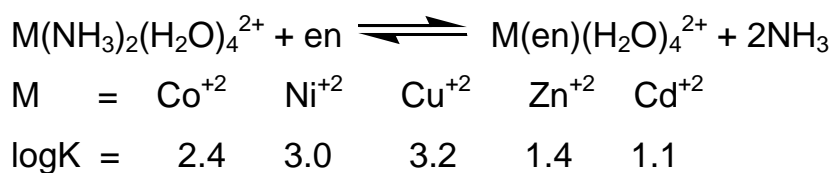
In recent years ligands capable of occupying as many as six coordination positions on a single metal ion have been described. The studies on the formation constants of coordination compounds with these ligands have been reported [20-24]. In general it is observed that the stability of the complex goes up with an increase in the number of groups available for coordination.

Increase in the number of rings increase the stability of compounds [25]. e.g. Value of  $\log K_1$  for Ni complexes with ethylenediamine is 7.9 and with trine is 14.0 and with penten 19.3.  $\log K_1$  for Zn with ethylenediamine is 6.0 and with trine is 12.1 and with penten 16.2.  $\text{Log}\beta_6$  for  $\text{Ni}(\text{NH}_3)_6^{2+}$  is 8.3 at 25°C while the comparable value of  $\log\beta_3$  for  $\text{Ni}(\text{en})_3^{2+}$  is 18.4, although in each of these octahedral complex ions  $\text{Ni}^{2+}$  has six amine nitrogen in the coordination environment. The species  $\text{Ni}(\text{en})_3^{2+}$  having three chelate rings is ca.  $10^{10}$  times as stable as that in which no such ring is formed. The sexadentate ligand ethylenediamine tetraacetate ( $\text{EDTA}^{4-} = \text{y}^{4-}$ ) is well known for its tendency to form unusually stable complexes with a large variety of metal ions including the alkaline earth ions as shown below

Metal ion	$\log \beta_{MY}$ (25°C, I = 0.1M)
$\text{Ca}^{2+}$	10.7
$\text{Cu}^{2+}$	18.8
$\text{Fe}^{3+}$	25.1



This increase in stability with the dentate character of the ligand has been referred to as the chelate effect by Schwarzenbach [26]. This effect is larger for the transition metal ions than the non-transition metal ions as illustrated below by the logK values (at 25°C) for the reaction



**(iii) Effect of Substitution in the Chelating molecules (steric Effect):**

In some cases the clashing of groups on two coordinated ligands will result in distortion of bond angles and a decrease in stability. This is the phenomenon of F-strain, described by Brown [27], as applied to coordination compounds.

As steric effect is decreasing, the stability of a complex is increasing. Due to steric effect in Ni(II) complexes with 2-methyl 8-hydroxy quinoline are less stable than complexes with 8-hydroxy quinoline. Similarly complexes of ethylene diamine are more stable than its tetramethyl derivatives.

**(iv) The Macrocyclic Effect:**

Just as any n-dentate chelating ligand gives more stable complexes than n-unidentate ligands of comparable type, (having identical donor sites), similarly an n-dentate macrocyclic ligand gives even more stable complexes than the similar n-dentate open chain ligand. This is called as macrocyclic effect [28], which results essentially from a very favourable entropy change ( $\Delta S$ ) assisted usually also by a favourable enthalpy ( $\Delta H$ ) change.

## 1.4 DETERMINATION OF STABILITY CONSTANTS OF COMPLEXES IN SOLUTION

The numerous parameters [29], like distribution coefficients, conductance, refractive index, temperature, volume changes, nuclear

magnetic resonance, magnetic moment changes and optical activity are useful in specialized situation for determination of formation constants. Various modern techniques [30-31] are used to determine the stability constant of simple as well as mixed ligand compounds.

## **[I] Methods Based on Study of Heterogeneous Equilibria:**

### ***(i) Solubility Methods:***

If the metal ion forms a relatively insoluble salt, solubility product of which is known and a complex which is rather more soluble, the formation constant of the complex may be determined by measuring the increased solubility of the salt caused by the presence of the ligand. Andrew and Keefer [32] established the existence of complexes of the type of  $[AgAr]^+$  where Ar=Benzene, Naphthalene, Phenanthrene, Toluene etc. and determined their instability constants.

### ***(ii) Distribution Method:***

It involves the study of distribution of the central ion, ligand or complex species between two immiscible solvents like water and some organic solvents ( $CCl_4$ , Benzene etc.).

### ***(iii) Ion-Exchange Method:***

It involves a study of the central ion or ligand between solution and an ion exchange resin. An ion exchange resin is an insoluble solid organic polymer containing positive and negative ions which are positive and negative ions which are insoluble. The total concentration of metal in the resin phase as well as that in the liquid phase can most conveniently be determined if the metal is radioactive. The polarizing effect of central cation Cu(II) and Zn(II) on stability of amino acid complexes was studied by an ion exchange method.

## **[II] Electrometric Techniques:**

These involve a study of the equilibrium between a free metal and its ion in solution. Some of these methods are mentioned below.

### ***(i) Potentiometric Methods [33]:***

The principle of the method is that a solution of known concentration of the base (or acid) to be studied is titrated with a strong acid (or strong base) and the reaction is carried out potentiometrically. The method can be used for studying the protonation equilibria of ligands which in the protonated and non protonated form are sufficiently soluble to form at least  $10^{-3}$ -M solutions and which do not decompose during the titration.

***(ii) Polarographic method [34]:***

The polarographic method is used to determine the stability constant by plotting a polarographic curve in the presence and in the absence of substances producing complex formation. A shift in the half-wave potential of a metal ion in solution in the presence of an added ligand (anion or neutral molecules) is indicative of complex formation.

**[III] Other Methods:**

***(i) Rate Method:***

If a complex is relatively slow to form and also decomposes at measurable rate, it is possible, in favourable situations, to determine the equilibrium constant.

***(ii) Freezing Technique:***

This involves the study of the equilibrium constant of slow complex formation reactions. The use of tracer technique is extremely useful for determining the concentrations of dissociation products of the coordination compound.

***(iii) Biological Method [35]:***

This method is based on study of the effect of an equilibrium concentration of some ion on the function at a definite organ of a living organism. The equilibrium concentration of the ion studied may be determined by the action of this organ in systems with complex formation.

**(iv) Spectrophotometric Method:**

The principle of the method is based on the fact that in a solution at a pH at which both the base and its protonated product are present, the ratio of the two species is determined by spectrophotometry and the protonation constant is calculated by using the basic equation

$$\log K = \log \frac{[HL]}{[L]} + pH$$

**(v) Bjerrum's Method [36]:**

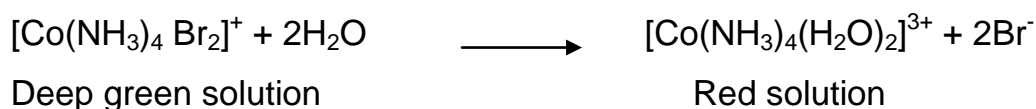
This method can be used in the case of successive complex formation, if the ligand tends to protonate (and the protonation constants are known) and the complex with maximum number of ligands has selective light absorption at the wavelength of choice while determining stability constants, it is also necessary to know the composition of the complex species formed.

**(vi) Isotopic dilution Method:**

If a complex ion is slow to reach equilibrium, it is often possible to apply the method of isotopic dilution to determine the equilibrium concentration of one or more of the species. Most often radioactive isotopes are used.

**(vii) Conductance Measurement Method:**

This method was extensively used by Werner and others to study metal complexes. In the case of a series of complexes of Co(III) and Pt(IV), Werner assigned the correct formulae on the basis of their molar conductance values measured in freshly prepared dilute solutions. In some cases the conductance of the solution increased with time due to a chemical change, e.g.,



The rise in conductance in this case was accompanied by a sharp color change of the solution from deep green to red.

***(viii) Migration in an electrical field (Transference Studies) [37]:***

During the passage of an electric current through an ordinary electrolyte, the metal cations travel to the cathode; but in a medium where it is complexed with a sufficient number of negative ions to give rise to an anionic complex, the metal migrates to the anode. Thus silver nitrate solution treated with an excess of KCN yields  $K[Ag(CN)_2]$  in solution. In this the silver as  $Ag(CN)_2^-$  migrates to the anode during electrolysis.

***(ix) Calorimetric Method [38]:***

This method involves the study the number of complex species formed in solution from the value of the heat effect on mixing of the starting solutions.

***(x) Cryoscopic and Ebullioscopic Method [39]:***

These methods are based on a study of the change in freezing or boiling point of solutions, which is connected with change in the number of species in solution during complex formation.

***(xi) Kinetic Method:***

This method is based on the measurement of the rate of any reaction involving one of the components of the dissociation equilibrium of the complex species in the presence and in the absence of complex forming substances, this method makes it possible to determine experimentally the equilibrium concentration of the central metal ion, ligand or complex.

## **1.5 IMPORTANCE OF TRANSITION METAL COMPOUNDS**

For many decades, organic and inorganic laboratory analysis makes use of a very large number of complexes including chelates. Both, quantitative as well as qualitative analysis required coordination compound which find application in almost all types of analyses like volumetric, gravimetric colorimetric, spot-tests, ion exchange, solvent extraction, masking damasking electro analytical methods etc. A special reference of crown compounds is important. Macrocyclic polyether and

other hetero atom-macrocyclic compounds are important. Macrocyclic polyether and other hetero atom-macrocyclic compounds form important complexes with alkali metals. They find increasing use in solvent extraction, phase transfer catalysis, stabilization of reactive oxidation states and promotion of otherwise improbable reactions [40].

In recent years the inorganic constituents of biological systems have been receiving increasing attention [41]. The importance of biochemistry of essential metallic elements may be illustrated by numerous examples of metal complexes in biological systems. Some of the representatives are (i) The iron complex haemoglobin (ii) Numerous iron containing enzymes having the heme and related iron binding groups such as catalases, peroxidases and cytochromes; the iron containing proteins ferritin, transferrin and hemosiderin (iii) magnesium containing complex chlorophyll present in green plants (iv) The zinc complexes insulin, carbonic anhydrase and the carboxypeptidases (v) The cobalt complex, vitamin B<sub>12</sub>; the copper complexes, ceruloplasmin and plastocyanin and (vi) the molybdenum containing enzymes xanthine oxidase and nitrate reductase.

Reactions in biological systems i.e. in animal and plant metabolism are generally enzymic reactions, which mean that they are initiated by specific enzymes acting as catalysts. An enzyme generally consists of a protein called an apoenzyme as its major constituent and of a non protein which is called the prosthetic group of the enzyme.

Ferredoxins and Rubredoxins [42] are several nonheme iron sulphur proteins that are involved in diverse electron transfer processes such as photosynthesis, hydroxylation of steroid hormones, nitrogen fixation, etc. Several such proteins were isolated and characterized during the 1950's and early 1960's. They are found in many species of plants, animals and microorganisms.

Crystallographic study [43] has shown that the heme group of cytochromes C lies in a crevice in the essentially globular protein, with

an edge of the porphyrin ring located at its surface. Ceruloplasmin is another blue colored copper containing enzyme, which is found in the blood plasma of mammals, birds, reptiles and amphibians. Human ceruloplasmin has a molecular weight of Ca. 130,000 and appears to consist of four peptide chains; the number of copper atoms present is two of Type-I, one of Type-II and three of Type-III [44]. In the body, ingested iron Fe(II) from stomach is absorbed and transported across membranes as Fe(II), but it is transported in plasma and stored in tissues as Fe(III) protein complexes.

Hence, ceruloplasmin is an important factor in the metabolism of iron and has a direct effect on the availability of iron for synthesis of hemoglobin and other essential iron proteins. About 98% of the Copper in normal human blood plasma is present as ceruloplasmin.

Plastocynin [45] (M.W., Ca. 10,500), azurin (M.W., Ca. 16,000) and stellacyanin (M.W., Ca. 16,800) are typical examples of other blue proteins containing one atom of copper per molecule, found in plants and function as one electron transfer agents.



Many complex compounds of gold have been used since early day in the treatment of tuberculosis, syphilis and other diseases and in the treatment of chronic arthritis since 1935 [46]. Metal chelates of EDTA have been used in the treatment of deficiency of Fe, Mn and Zn in plants. Detailed study of Albert et al. [47] have shown that the antibacterial action of 8-hydroxyquinoline is increased many times by iron(III), suggesting that the Fe(III) chelate is the active agent.

The energy of muscular contraction is derived from the transformation of ATP to ADP, resulting from coordination of magnesium of actomyosin with the ATP, facilitating the cleavage of the terminal phosphate group [48-49]. The anti tubercular activity of isonicotinic acid hydrazide is similarly potentiated by copper(II).

The use of the metal complexes and ligands in the fight against disease in general has been discussed. One significant development in the field of biological activity of metal chelates is the observation that metal chelation apparently plays a definite role in the cause and treatment of cancer. There are indications that some metal chelates of ligands, which have anticancer activity, are more carcinostatic than the free ligands [50]. Werner paid attention to the importance of Inorganic compounds in dyeing in 1908. Morgan and his coworkers must be credited for the first chelate study in this field. Some of the ecofriendly dyes are ecofriendly metal complex dyes premetallised metal complexes. Azo dyes are also medically metallised coordinating ligand to the metal ion. Azo dyes, anthraquinone, nitrodiphenylamine dyes are well known as metallised dyes [51]. Colorless, 2,4,5-trihydroxy toluene complexes with Copper(II), Iron(II) and Cobalt(II) to give wool medium brown to black colors are reported [52]. Alizarin forms a Cobalt(III) complex containing two cobalt atoms for each five ammonia molecules [53]. Perlon fast yellow-G is complex of chromium and used for nylon type fiber.

The coordination compounds are widely studied and used as catalysts in different chemical processes.  $[\text{Ti}_2(\text{tartarate})_2(\text{OR})_4]$  are useful catalysts in asymmetric epoxidation of allylic alcohols. The decomposition of  $\text{H}_2\text{O}_2$  is catalysed by many things including iron compounds. Wilkinson catalyst, complexes of  $\text{Pd}^{2+}$  and  $\text{Pt}^{2+}$  are used as hydrogenation catalyst, in Monsanto process,  $[\text{RhI}_2(\text{CO})_2]$  is used as homogeneous catalyst. Commercially water gas-shift reaction is carried out by homogeneous catalyst. The chiral phosphine ligand is referred to as DIPAMP is used for hydrocyanation reaction of butadiene to adiponitrile. For hydroformylation reaction, the use of two carbonyl complexes has got numerous applications, they are  $[\text{Co}(\text{CO})_4\text{C}_4\text{H}_9]$ . Hydrolysed polynuclear complexes of  $\text{Cr}^{3+}$  are of considerable importance in the dyeing and tanning industries.



For extraction of many metals from their ores the chemical process make use of coordination compounds [54]. As reagents, organometallic compounds and coordination compounds have found numerous applications for organic synthesis [55-56]. Special application in the photographic process because of the quantitative complexation of unexposed silver halide by the hypo solution to form water soluble  $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$ . A number of metals, for example, Ag, Cu, and Au etc are generally electroplated using a solution of their complex ions. An another example is the formation of  $\text{Na}[\text{Au}(\text{CN})_2]$  from gold containing rock. The coordination compounds can be used for reducing environmental pollution [57].

## **1.6 MATERIAL INVESTIGATED**

### **1.6.1 Cobalt**

Cobalt is a ferromagnetic metal with a specific gravity of 8.9 (20°C). Pure cobalt is not found in nature, but compounds of cobalt are common. Small amounts of it are found in most rocks, soil, plants, and animals. It has the atomic number 27. The Curie temperature is 1115 °C, and the magnetic moment is 1.6–1.7 Bohr magnetons per atom. In nature, it is frequently associated with nickel, and both are characteristic minor components of meteoric iron. Mammals require small amounts of cobalt which is the basis of vitamin B<sub>12</sub>. Cobalt-60, an artificially produced radioactive isotope of cobalt, is an important radioactive tracer and cancer-treatment agent. Cobalt has a relative permeability two thirds that of iron. Metallic cobalt occurs as two crystallographic structures: hcp and fcc. The ideal transition temperature between hcp and fcc structures is 450 °C, but in practice, the energy difference is so small that random intergrowth of the two is common.[58-60]

## Compounds

Common oxidation states of cobalt include +2 and +3, although compounds with oxidation state +1 are also known. The most common oxidation state for simple compounds is +2. Cobalt(II) salts form the red-pink  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  complex in aqueous solution. Adding excess chloride will change the color from pink to blue, due to the formation of  $[\text{CoCl}_4]^{2-}$ . [61]

## Coordination compounds

As for all metals, molecular compounds of cobalt are classified as coordination complexes, i.e. molecules or ions that contain cobalt linked to several ligands. The ligands determine the oxidation state of the cobalt. For example  $\text{Co}^{+3}$  complexes tend to have amine ligands. Phosphine ligands tend to feature  $\text{Co}^{2+}$  and  $\text{Co}^+$ , an example being tris(triphenylphosphine)cobalt(I) chloride ( $(\text{P}(\text{C}_6\text{H}_5)_3)_3\text{CoCl}$ ). Oxide and fluoride can stabilize  $\text{Co}^{4+}$  derivatives, e.g. caesium hexafluorocobaltate ( $\text{Cs}_2\text{CoF}_6$ ) and potassium percobaltate ( $\text{K}_3\text{CoO}_4$ ). [62]

Alfred Werner, a Nobel-prize winning pioneer in coordination chemistry, worked with compounds of empirical formula  $\text{CoCl}_3(\text{NH}_3)_6$ . One of the isomers determined was cobalt(III) hexammine chloride. This coordination complex, a "typical" Werner-type complex, consists of a central cobalt atom coordinated by six ammine ligands orthogonal to each other, and three chloride counteranions.

Using chelating ethylenediamine ligands in place of ammonia gives tris(ethylenediamine)cobalt(III) chloride ( $[\text{Co}(\text{en})_3]\text{Cl}$ ), which was one of the first coordination complexes that was resolved into optical isomers. The complex exists as both either right- or left-handed forms of a "three-bladed propeller." This complex was first isolated by Werner as yellow-gold needle-like crystals. [63]

## Organometallic compounds

Cobaltocene is a stable cobalt analog to ferrocene. Cobalt carbonyl ( $\text{Co}_2(\text{CO})_8$ ) is a catalyst in carbonylation reactions. Vitamin B<sub>12</sub> (see below) is a rare organometallic compound found in nature.

**Table 1.1: Properties of Cobalt**

General properties						
<b>Name, symbol, number</b>	cobalt, Co, 27					
<b>Element category</b>	transition metal					
<b>Group, period, block</b>	9, 4, d					
<b>Standard atomic weight</b>	58.933195(5) g·mol <sup>-1</sup>					
<b>Electron configuration</b>	[Ar] 4s <sup>2</sup> 3d <sup>7</sup>					
<b>Electrons per shell</b>	2, 8, 15, 2 (Image)					
Physical properties						
<b>Color</b>	metallic gray					
<b>Density (near r.t.)</b>	8.90 g·cm <sup>-3</sup>					
<b>Liquid density at m.p.</b>	7.75 g·cm <sup>-3</sup>					
<b>Melting point</b>	1768 K 1495 °, C2723 °, F					
<b>Boiling point</b>	3200 K 2927 °, C5301 °, F					
<b>Heat of fusion</b>	16.06 kJ·mol <sup>-1</sup>					
<b>Heat of vaporization</b>	377 kJ·mol <sup>-1</sup>					
<b>Specific heat capacity</b>	(25 °C) 24.81 J·mol <sup>-1</sup> ·K <sup>-1</sup>					
Vapor pressure						
<i>P/Pa</i>	1	10	100	1 k	10 k	100 k
at <i>T/K</i>	1790	1960	2165	2423	2755	3198
Atomic properties						
<b>Oxidation states</b>	5, 4, 3, 2, 1, -1 [58]					

	(amphoteric oxide)				
<b>Electronegativity</b>	1.88 (Pauling scale)				
<b>Ionization energies (more)</b>	1st: 760.4 kJ·mol <sup>-1</sup>				
	2nd: 1648 kJ·mol <sup>-1</sup>				
	3rd: 3232 kJ·mol <sup>-1</sup>				
<b>Atomic radius</b>	125 pm				
<b>Covalent radius</b>	126±3 (low spin), 150±7 (high spin) pm				
<b>Miscellanea</b>					
<b>Crystal structure</b>	hexagonal				
<b>Magnetic ordering</b>	ferromagnetic				
<b>Electrical resistivity</b>	(20 °C) 62.4 nΩ·m				
<b>Thermal conductivity</b>	(300 K) 100 W·m <sup>-1</sup> ·K <sup>-1</sup>				
<b>Thermal expansion</b>	(25 °C) 13.0 μm·m <sup>-1</sup> ·K <sup>-1</sup>				
<b>Speed of sound (thin rod)</b>	(20 °C) 4720 m/s				
<b>Young's modulus</b>	209 GPa				
<b>Shear modulus</b>	75 GPa				
<b>Bulk modulus</b>	180 GPa				
<b>Poisson ratio</b>	0.31				
<b>Mohs hardness</b>	5.0				
<b>Vickers hardness</b>	1043 MPa				
<b>Brinell hardness</b>	700 MPa				
<b>CAS registry number</b>	7440-48-4				
<b>Most stable isotopes</b>					
<b>iso</b>	<b>NA</b>	<b>half-life</b>	<b>DM</b>	<b>DE (MeV)</b>	<b>DP</b>
<sup>56</sup> Co	syn	77.27 d	ε	4.566	<sup>56</sup> Fe
<sup>57</sup> Co	syn	271.79 d	ε	0.836	<sup>57</sup> Fe

$^{58}\text{Co}$	syn	70.86 d	$\epsilon$	2.307	$^{58}\text{Fe}$
$^{59}\text{Co}$	100%	$^{59}\text{Co}$ is stable with 32 neutrons			
$^{60}\text{Co}$	syn	5.2714 years	$\beta^-,\gamma,\gamma$	2.824	$^{60}\text{Ni}$

## Applications

Cobalt-based superalloys consume most of the produced cobalt. The temperature stability of these alloys makes them suitable for use in turbine blades for gas turbines and jet aircraft engines, though nickel-based single crystal alloys surpass them in this regard. Cobalt-based alloys are also corrosion and wear-resistant.[64] Special cobalt-chromium-molybdenum alloys are used for prosthetic parts such as hip and knee replacements.[65] Cobalt alloys are also used for dental prosthetics, where they are useful to avoid allergies to nickel.[66] Some high speed steels also use cobalt to increase heat and wear-resistance. The special alloys of aluminium, nickel, cobalt and iron, known as Alnico, and of samarium and cobalt (samarium-cobalt magnet) are used in permanent magnets.[67]. Lithium cobalt oxide ( $\text{LiCoO}_2$ ) is widely used in Lithium ion battery electrodes.[68] Nickel-cadmium (NiCd) and nickel metal hydride (NiMH) batteries also contain significant amounts of cobalt.

Several cobalt compounds are used in chemical reactions as oxidation catalysts. Cobalt acetate is used for the conversion of xylene to terephthalic acid, the precursor to the bulk polymer Polyethylene terephthalate. Typical catalysts are the cobalt carboxylates (known as cobalt soaps). They are also used in paints, varnishes, and inks as "drying agents" through the oxidation of drying oils.[68] The same

carboxylates are used to improve the adhesion of the steel to rubber in steel-belted radial tires.

Cobalt-based catalysts are also important in reactions involving carbon monoxide. Steam reforming, useful in hydrogen production, uses cobalt oxide-base catalysts. Cobalt is also a catalyst in the Fischer-Tropsch process, used in the conversion of carbon monoxide into liquid fuels.[69] The hydroformylation of alkenes often rely on cobalt octacarbonyl as the catalyst,[70] although such processes have been displaced by more efficient iridium- and rhodium-based catalysts, e.g. the Cativa process.

The hydrodesulfurization of petroleum uses a catalyst derived from cobalt and molybdenum. This process helps to rid petroleum of sulfur impurities that interfere with the refining of liquid fuels.[68]

### ***Biological role***

Cobalt is essential to all animals, including humans. It is a key constituent of cobalamin, also known as vitamin B<sub>12</sub>. A deficiency of cobalt leads to pernicious anemia, a lethal disorder. Pernicious anemia is however very rare, because trace amounts of cobalt are available in most diets. The presence of 0.13 to 0.30 mg/kg of cobalt in soils markedly improves the health of grazing animals.

The cobalamin-based proteins use corrin to hold the cobalt. Coenzyme B<sub>12</sub> features a reactive C-Co bond, which participates in its reactions.[71] In humans, B<sub>12</sub> exists with two types alkyl ligand, methyl and adenosyl. MeB<sub>12</sub> promotes methyl (-CH<sub>3</sub>) group transfers. The adenosyl version of B<sub>12</sub> catalyzes rearrangements in which a hydrogen atom is directly transferred between two adjacent atoms with concomitant exchange of the second substituent, X, which may be a carbon atom with substituents, an oxygen atom of an alcohol, or an

amine. Methylmalonyl Coenzyme A mutase (MUT) converts MMI-CoA to Su-CoA, an important step in the extraction of energy from proteins and fats.

Although far less common than other metalloproteins (e.g. those of zinc and iron), cobaltoproteins are known aside from non-B<sub>12</sub>. These proteins include Methionine aminopeptidase 2 and Nitrile hydratase are two examples.[72]

### 1.6.2 Chromium

Chromium is a chemical element which has the symbol **Cr** and atomic number 24, first element in Group 6. It is a steely-gray, lustrous, hard metal that takes a high polish and has a high melting point. It is also odorless, tasteless, and malleable. The name of the element is derived from the Greek word "chrōma" (χρῶμα), meaning color, because many of its compounds are intensely colored. It was discovered by Louis Nicolas Vauquelin in the mineral crocoite (*lead chromate*) in 1797. Crocoite was used as a pigment, and after the discovery that the mineral chromite also contains chromium this latter mineral was used to produce pigments as well.

Chromium was regarded with great interest because of its high corrosion resistance and hardness. A major development was the discovery that steel could be made highly resistant to corrosion and discoloration by adding chromium to form stainless steel. This application, along with chrome plating (electroplating with chromium) are currently the highest-volume uses of the metal. Chromium and ferrochromium are produced from the single commercially viable ore, chromite, by silicothermic or aluminothermic reaction or by roasting and leaching processes. Although trivalent chromium (Cr(III)) is required in trace amounts for sugar and lipid metabolism in humans and its

deficiency may cause a disease called chromium deficiency, hexavalent chromium (Cr(VI)) is toxic and carcinogenic, so that abandoned chromium production sites

## Characteristics

### *Physical properties*

Chromium is remarkable for its magnetic properties: it is the only elemental solid which shows antiferromagnetic ordering at room temperature (and below). Above 38 °C, it transforms into a paramagnetic state.[73]

**Table 1.2: Properties of Chromium**

<b>General properties</b>	
<b>Name, symbol, number</b>	chromium, Cr, 24
<b>Element category</b>	transition metal
<b>Group, period, block</b>	6, 4, d
<b>Standard atomic weight</b>	51.9961(6)g·mol <sup>-1</sup>
<b>Electron configuration</b>	[Ar] 3d <sup>5</sup> 4s <sup>1</sup>
<b>Electrons per shell</b>	2, 8, 13, 1 (Image)
<b>Physical properties</b>	
<b>Phase</b>	solid
<b>Density (near r.t.)</b>	7.19 g·cm <sup>-3</sup>
<b>Liquid density at m.p.</b>	6.3 g·cm <sup>-3</sup>
<b>Melting point</b>	2180 K1907 ° ,C3465 ° ,F
<b>Boiling point</b>	2944 K2671 ° ,C4840 ° ,F
<b>Heat of fusion</b>	21.0 kJ·mol <sup>-1</sup>
<b>Heat of vaporization</b>	339.5 kJ·mol <sup>-1</sup>
<b>Specific heat capacity</b>	(25 °C) 23.35 J·mol <sup>-1</sup> ·K <sup>-1</sup>
<b>Vapor pressure</b>	



<i>P</i> /Pa	1	10	100	1 k	10 k	100 k
at <i>T</i> /K	1656	1807	1991	2223	2530	2942
<b>Atomic properties</b>						
<b>Oxidation states</b>	6, 5, 4, 3, 2, 1, -1, -2 (strongly acidic oxide)					
<b>Electronegativity</b>	1.66 (Pauling scale)					
<b>Ionization energies (more)</b>	1st: 652.9 kJ·mol <sup>-1</sup>					
	2nd: 1590.6 kJ·mol <sup>-1</sup>					
	3rd: 2987 kJ·mol <sup>-1</sup>					
<b>Atomic radius</b>	128 pm					
<b>Covalent radius</b>	139±5 pm					
<b>Miscellanea</b>						
<b>Crystal structure</b>	body-centered cubic					
<b>Magnetic ordering</b>	AFM (rather: SDW[73])					
<b>Electrical resistivity</b>	(20 °C) 125 nΩ·m					
<b>Thermal conductivity</b>	(300 K) 93.9 W·m <sup>-1</sup> ·K <sup>-1</sup>					
<b>Thermal expansion</b>	(25 °C) 4.9 μm·m <sup>-1</sup> ·K <sup>-1</sup>					
<b>Speed of sound (thin rod)</b>	(20 °C) 5940 m/s					
<b>Young's modulus</b>	279 GPa					
<b>Shear modulus</b>	115 GPa					
<b>Bulk modulus</b>	160 GPa					
<b>Poisson ratio</b>	0.21					
<b>Mohs hardness</b>	8.5					
<b>Vickers hardness</b>	1060 MPa					
<b>Brinell hardness</b>	1120 MPa					
<b>CAS registry number</b>	7440-47-3					
<b>Most stable isotopes</b>						
Main article: Isotopes of chromium						

iso	NA	half-life	DM	DE (MeV)	DP
<sup>50</sup> Cr	4.345%	> 1.8×10 <sup>17</sup> y	εε	-	<sup>50</sup> Ti
<sup>51</sup> Cr	syn	27.7025 d	ε	-	<sup>51</sup> V
			γ	0.320	-
<sup>52</sup> Cr	83.789%	<sup>52</sup> Cr is stable with 28 neutrons			
<sup>53</sup> Cr	9.501%	<sup>53</sup> Cr is stable with 29 neutrons			
<sup>54</sup> Cr	2.365%	<sup>54</sup> Cr is stable with 30 neutrons			

### **Occurrence**

Chromium is the 21st most abundant element in Earth's crust with an average concentration of 100 ppm.[74] Chromium compounds are found in the environment, due to erosion of chromium-containing rocks and can be distributed by volcanic eruptions. The concentrations range in soil is between 1 and 3000 mg/kg, in sea water 5 to 800 µg/liter, and in rivers and lakes 26 µg/liter to 5.2 mg/liter.[75] The relation between Cr(III) and Cr(VI) strongly depends on pH and oxidative properties of the location, but in most cases, the Cr(III) is the dominating species,[75] although in some areas the ground water can contain up to 39 µg of total chromium of which 30 µg is present as Cr(VI).[76]

Chromium is mined as chromite (FeCr<sub>2</sub>O<sub>4</sub>) ore.[77] About two-fifths of the chromite ores and concentrates in the world are produced in

South Africa, while Kazakhstan, India, Russia, and Turkey are also substantial producers. Untapped chromite deposits are plentiful, but geographically concentrated in Kazakhstan and southern Africa.[78]

Though native chromium deposits are rare, some native chromium metal has been discovered.[79][80] The Udachnaya Pipe in Russia produces samples of the native metal. This mine is a kimberlite pipe rich in diamonds, and the reducing environment helped produce both elemental chromium and diamond.[81]

### ***Isotopes***

Naturally occurring chromium is composed of three stable isotopes;  $^{52}\text{Cr}$ ,  $^{53}\text{Cr}$  and  $^{54}\text{Cr}$  with  $^{52}\text{Cr}$  being the most abundant (83.789% natural abundance). Nineteen radioisotopes have been characterized with the most stable being  $^{50}\text{Cr}$  with a half-life of (more than)  $1.8 \times 10^{17}$  years, and  $^{51}\text{Cr}$  with a half-life of 27.7 days. All of the remaining radioactive isotopes have half-lives that are less than 24 hours and the majority of these have half-lives that are less than 1 minute. This element also has 2 meta states.[82]

$^{53}\text{Cr}$  is the radiogenic decay product of  $^{53}\text{Mn}$ . Chromium isotopic contents are typically combined with manganese isotopic contents and have found application in isotope geology. Mn-Cr isotope ratios reinforce the evidence from  $^{26}\text{Al}$  and  $^{107}\text{Pd}$  for the early history of the solar system. Variations in  $^{53}\text{Cr}/^{52}\text{Cr}$  and Mn/Cr ratios from several meteorites indicate an initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratio that suggests Mn-Cr isotopic composition must result from in-situ decay of  $^{53}\text{Mn}$  in differentiated planetary bodies. Hence  $^{53}\text{Cr}$  provides additional evidence for nucleosynthetic processes immediately before coalescence of the solar system.[83]

The isotopes of chromium range in atomic mass from 43 u ( $^{43}\text{Cr}$ ) to 67 u ( $^{67}\text{Cr}$ ). The primary decay mode before the most abundant stable isotope,  $^{52}\text{Cr}$ , is electron capture and the primary mode after is beta decay.[82]  $^{53}\text{Cr}$  has been posited as a proxy for atmospheric oxygen concentration.[84]

## Chromium(III)

The oxidation state +3 is the most stable, and a large number of chromium(III) compounds are known. Chromium(III) can be obtained by dissolving elemental chromium in acids like hydrochloric acid or sulfuric acid. The  $\text{Cr}^{3+}$  ion has a similar radius (63 pm) to the  $\text{Al}^{3+}$  ion (radius 50 pm), so they can replace each other in some compounds, such as in chrome alum and alum. When a trace amount of  $\text{Cr}^{3+}$  replaces  $\text{Al}^{3+}$  in corundum (aluminium oxide,  $\text{Al}_2\text{O}_3$ ), the red-colored ruby is formed.

Chromium ions tend to form complexes; chromium ions in water are usually octahedrally coordinated with water molecules to form hydrates. The commercially available chromium(III) chloride hydrate is the dark green complex  $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl}$ , but two other forms are known: pale green  $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2$ , and the violet  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ . If water-free green chromium(III) chloride is dissolved in water then the green solution turns violet after some time, due to the substitution of water for chloride in the inner coordination sphere. This kind of reaction is also observed in chrome alum solutions and other water-soluble chromium(III) salts. The reverse reaction may be induced by heating the solution.

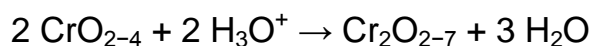
Chromium(III) hydroxide ( $\text{Cr}(\text{OH})_3$ ) is amphoteric, dissolving in acidic solutions to form  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , and in basic solutions to form  $[\text{Cr}(\text{OH})_6]^{3-}$ . It is dehydrated by heating to form the green chromium(III)

oxide ( $\text{Cr}_2\text{O}_3$ ), which is the stable oxide with a crystal structure identical to that of corundum.[85]

## Chromium(VI)

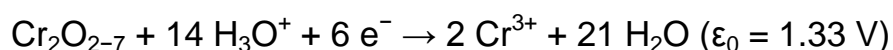
Chromium(VI) compounds are powerful oxidants, and, except the hexafluoride, contain oxygen as a ligand, such as the chromate anion ( $\text{CrO}_{2-4}$ ) and chromyl chloride ( $\text{CrO}_2\text{Cl}_2$ ).[85]

Chromium(VI) is most commonly encountered in the chromate ( $\text{CrO}_{2-4}$ ) and dichromate ( $\text{Cr}_2\text{O}_{2-7}$ ) anions. Chromate is produced industrially by the oxidative roasting of chromite ore with calcium or sodium carbonate. The chromate and dichromate anions are in equilibrium:

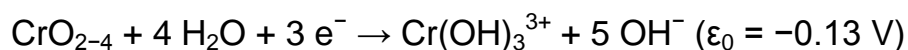


The dominant species is therefore, by the law of mass action, determined by the pH of the solution. The change in equilibrium is visible by a change from yellow (chromate) to orange (dichromate), such as when an acid is added to a neutral solution of potassium chromate. At yet lower pH values, further condensation to more complex oxyanions of chromium is possible.

Both the chromate and dichromate anions are strong oxidizing reagents at low pH:[85]



However, they are only moderately oxidizing at high pH:[85]



Chromium(VI) compounds in solution can be detected by adding an acidic hydrogen peroxide solution. The unstable dark blue

chromium(VI) peroxide ( $\text{CrO}_5$ ) is formed, which can be stabilized as an ether adduct  $\text{CrO}_5 \cdot \text{OR}_2$ . [85]

Chromic acid has the hypothetical structure  $\text{H}_2\text{CrO}_4$ . Neither chromic nor dichromic acid can be isolated, but their anions are found in a variety of compounds, the chromates and dichromates. The dark red chromium(VI) oxide  $\text{CrO}_3$ , the acid anhydride of chromic acid, is sold industrially as "chromic acid". [85] It can be produced by mixing sulfuric acid with dichromate, and is an extremely strong oxidizing agent.

## **Applications**

- Metallurgy
- Dye and pigment
- Tanning
- Refractory material

## ***Other use***

Several chromium compounds are used as catalyst. For example the Phillips catalysts for the production polyethylene are mixtures of chromium and silicon dioxide or mixtures of chromium and titanium and aluminium oxide. [86] Chromium(IV) oxide ( $\text{CrO}_2$ ) is a magnetic compound. Its ideal shape anisotropy, which imparted high coercivity and remanent magnetization, made it a compound superior to the  $\gamma\text{-Fe}_2\text{O}_3$ . Chromium(IV) oxide is used to manufacture magnetic tape used in high performance audio tape and standard audio cassette. [87] Chromates can prevent corrosion of steel under wet conditions, and therefore chromates are added to the drilling muds. [88] The long known influence of chromium uptake on diabetes conditions suggested the positive influence of dietary supplement containing chromium(III) also on healthy persons. For this reason, dietary supplement or slimming aid usually contain chromium(III) chloride, chromium(III) picolinate,

chromium(III) polynicotinate or amino acid chelate, such as chromium(III) D-phenylalanine. The benefit of those supplements is still under investigation and is questioned by some studies.[89][90]

- Chromium hexacarbonyl  $\text{Cr}(\text{CO})_6$  is used as a gasoline additive.[91]
- Chromium(III) oxide is a metal polish known as green rouge.
- Chromic acid is a powerful oxidizing agent and is a useful compound for cleaning laboratory glassware of any trace of organic compounds. It is prepared *in situ* by dissolving potassium dichromate in concentrated sulfuric acid, which is then used to wash the apparatus. Sodium dichromate is sometimes used because of its higher solubility (5 g/100 ml vs. 20 g/100 ml respectively). Potassium dichromate is a chemical reagent, used in cleaning laboratory glassware and as a titrating agent. It is also used as a mordant (i.e., a fixing agent) for dyes in fabric.

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