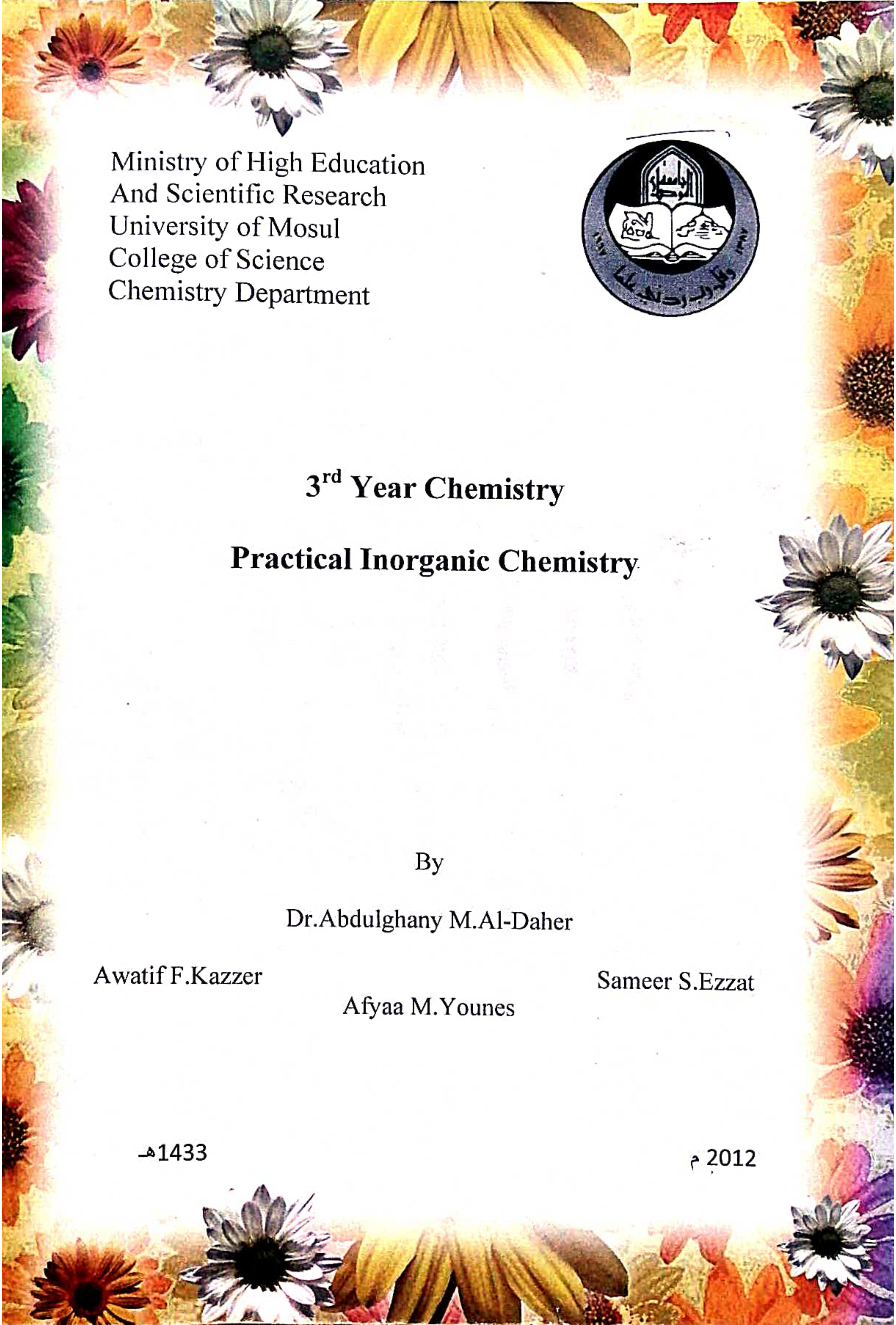

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3^{rd} Year Chemistry

Practical Inorganic Chemistry

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Part (I)

Introduction

Transition metals, due to their characteristic electronic configurations, form a large number of complex compounds. These complexes are very important in both solid state and solution chemistries of transition metals.

Complex compounds are composed of central metal ion (usually positively charged ions) bonded to a number of ions (usually negatively charged ions) or neutral molecules called ligands. There are a large number of ligands that able to form complex compound with central metal ions.

The ligand is defined as : an atom, ion, or molecule having lone pair of electrons able to donate it to positively charged central metal ion forming coordinate-covalent bond producing complex compound. The formed complex compound may be neutral as $[Fe(acac)_3]$, anionic e.g $[Fe(CN)_6]^{-3}$ or cationic e.g $[Fe(H_2O)_6]^{+3}$.

Ligand can be classified according to the number of coordinate bonds that formed with the central metal ion. Monodentate ligands are those attached to the central metal ion by one bond, sharing only a single pair of electrons with the metal ion (e.g. NH_3, H_2O, Cl^-).

Bidentate ligands are those having two atoms each have a lone pairs interact with the same metal , the resulting complex is called chelate compound, e.g. $[Ni(en)_3]^{+2}$ the ligand en (ethylenediamine) is a chelate ligand. Molecules that have the capacity to attach to the central ion at more than two positions, for example, dien and EDTA may be attached to three and six positions, respectively, such group is called a multidentate ligand, it also called tridentate and hexadentate ligand respectively.

Two other general types of ligands are the common bridging ligands, which defined as those containing two pairs of electrons shared with two metal atoms simulataneously (e.g. NH_2^-, Cl^-, OH^-), and the ambidentate ligands, which can use one of two different atoms to share a pair of electrons with a metal (e.g. SCN^-, NO_2^-).

Nomenclature of complex compound recommended by IUPAC

Rules for nomenclature:

1. Name the cation, then the anion.
2. Nonionic compounds are given a one-word name .
3. Name ligands:

a. Ligands are named first and central atom last.

b. Ligands are named in alphabetical order.

c. Neutral ligands are named the same as the molecule (except aqua and ammine).

d. Anionic ligands are named by adding –o to the stem of the name (chloride becomes chloro).

e. The ligand name is preceded by Latin or Greek prefix to indicate how many are present di, tri, tetra, penta, hexa, pentakis .... If one of these is part of the ligand name, use, bis, tris, tetrakis,. For bridging ligands, the prefix indicating the number of ligands is placed after the μ.e for example if there are two bridging chloride ligands, they are indicated as μ-dichloro.....

g. Two ways to handle ambidentate ligands. One is to use a slightly different form of the name, depending on the atom that is donating the electrone pair to the metal. The second is to put the symbol of the donating atom before the name. So –SCN might be called thiocyanate or S-thiocyanato, wheras –NCS would be isothiocyanato or N-thiocyanato.

4. In a neutral or cationic complex, the name of central metal is followed by its oxidation number in Roman numerals in parentheses (I), (II), (III), (IV).....
5. In anionic complex, the suffix-ate is added to the name of the central metal, followed by its oxidation number in Roman numerals in parentheses. Some metals, such as copper, iron, gold and silver, use the Latin stem for the metal and become cuprate, ferrate, aurate and argentite, respectively of the ligand.

Examples:

1. $Na_3[Co(CO_3)_3].3H_2O$.
   Sodium tricarbonatocobaltate (III) trihydrate.
2. $[Co(NH_5)CO_3]. NO_3$.
   Pentaamminecarbonatocobalt (III) nitrate.
3. $[Ni(en)_2Cl_2]$.
   Dichlorobis(ethylenediamine)nickel (II)
4. $[Fe(acac)_3]$.
   Tris (acetylacetenato) iron (III).
5. $[Co(NH_3)_5NO_2] Cl_2$.
   Pentaammine-N-nitrocobalt (III) chloride.

Experiment No. 1:

Geometrical isomerism

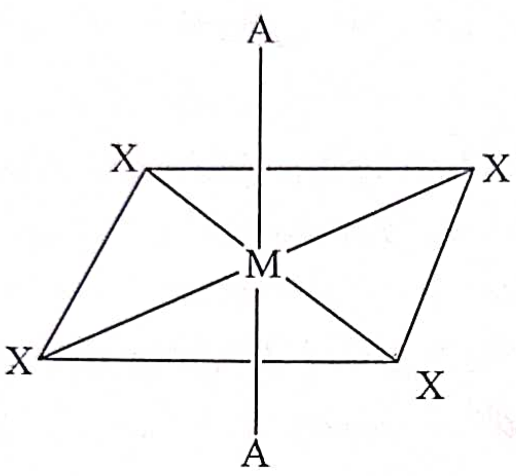
Theory:

An isomer is one of several species that have the same atomic composition (molecular formula), but have different constitutional formula (atom connectivities) or different sterio chemical formula. Isomers exhibit different physical and/or chemical properties.

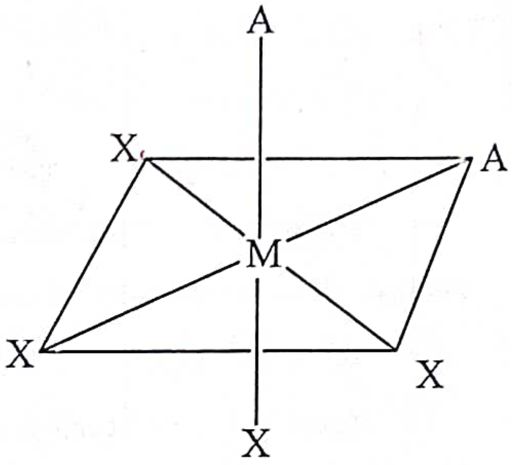
Metal complex forms many types of isomers, one of these are the geometrical isomers. Geometrical isomers have the same structural framework, but differ in the spatial arrangement of the atoms. Geometrical isomers differ somewhat in physical properties and can be isolated under ordinary conditions. Geometrical isomers are generally named by the use of the terms cis- to designate adjacent (90° apart) positions and trans- for opposite (180° apart) positions.

Metal complexes of coordination numbers 2 & 3 and regular tetrahedral 4-coordinate complexes exist in only one geometrical form, so they not form geometrical isomers. Cis-, trans- isomers are common in square planner and octahedral complexes.

For octahedral complexes there are, naturally, more possible geometrical isomers. An octahedral complex of formula MX_6 or MX_5A can exist is only one form, but MX_4A_2 complexes can exist as cis- and trans- isomers in which ligands A are at adjacent or opposite positions, respectively.

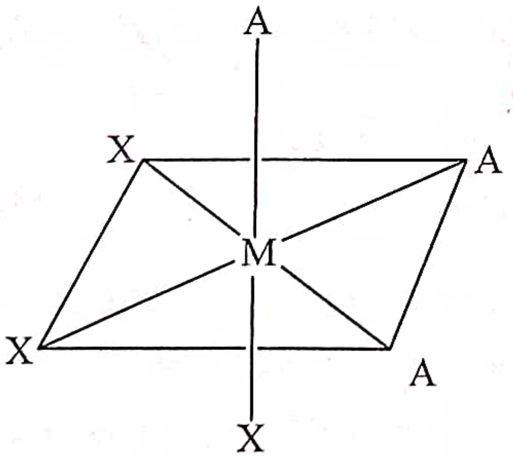


trans-isomer

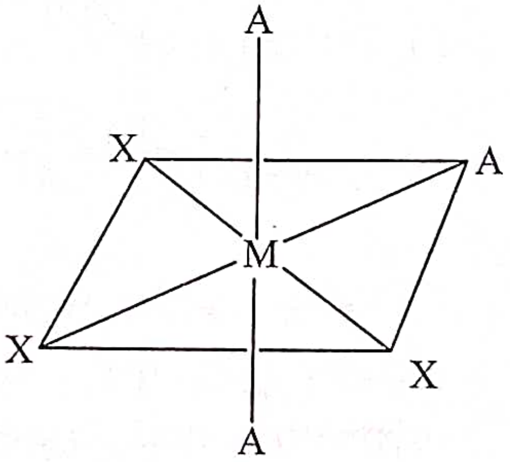


cis-isomer

Another type of octahedral complexes that form geometrical isomers are those have the formula MX_3A_3 in which the three groups may all be adjacent, i.e. at the cormers of one face of the octahedron, or they may occupy three positions such that two are trans to each other, which are commonly called the facial (fac) and meridional (mer) isomers, as shown below:



face-isomer

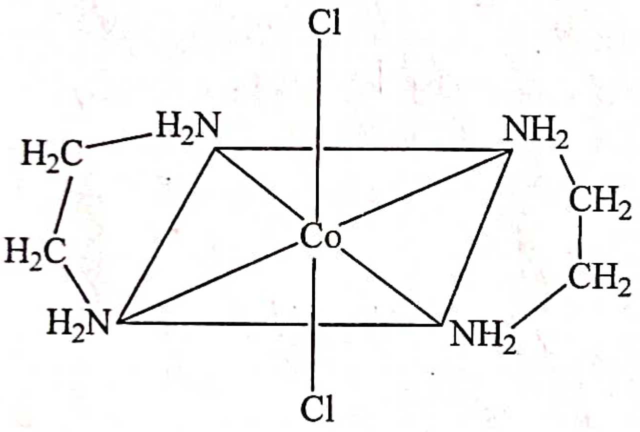


mer-isomer

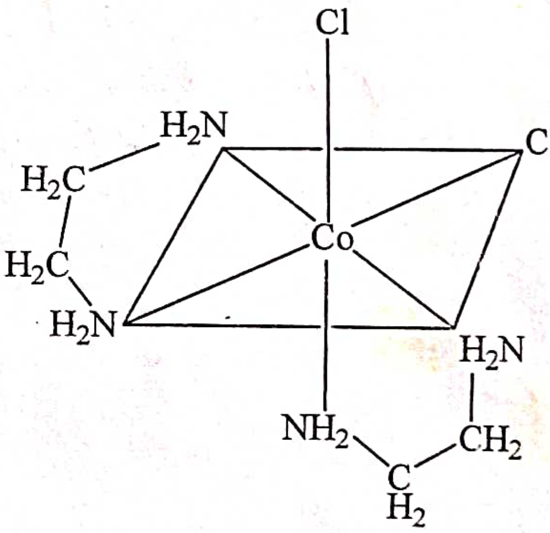
Simple example of MX_4A_2 and MX_3A_3 complexes are those of cobalt (III) formed with ammonia and chloride ion as ligands, namely the cations cis- and trans-$[CoCl_2(NH_3)_3]^+$, and the neutral molecules fac- and mer- $[CoCl_3(NH_3)_3]$.

The use of chelate ligands for example ethylenediamine (en) in octahedral complexes and the presence of two ligands give complexes of the type $[M(AA)_2X_2]$ (where AA refers to a symmetric chelate). This type of complexes form cis- and trans- isomers.

A simple example is the octahedral complex $[Co(en)_2Cl_2]^+$ that has two ethylenediamine (en) chelate and two monodentate chloride ions coordinated to the Co(III) Central metal ion.



trans-$[Co(en)_2Cl_2]^+$



Cis-$[Co(en)_2Cl_2]^+$

The isomerization reactions (conversion of one isomer to other) is of important in coordination chemistry to isolate different isomers of the complexes. The kinetic of isomerization usually ivestigted spectrophotometricccally.

In this experiment, you prepare the trans and cis isomers of dichlorobis(ethylenediamine)cobalt(III) chloride. Cobalt (III) forms large number of octahedral complexes. The ligand substitution reactions of these complexes are slower than other transition metal complexes due to relatively higher stability which made these complexes are of special importance in isomerization reaction investigation.

Cobalt (III) complexes usually prepared using Co(II) salts as starting material. This is because the usual oxidation state of cobalt in its simple salts is (II). The oxidation state (III) becomes the stable form only when cobalt is coordinated to certain types of ligands. Furthermore, it is convenient to start with salts of Co(II) complexes undergo substitution reactions very rapidly, whereas reactions of Co(III) complexes are very slow.

The preparation of Co(III) complexes therefore proceeds by fast reaction between Co(II) and the ligand (en) to form cobalt (II) complex which is then oxidized to corresponding Co(III) complex, as in the preparation of trans-$[Co(en)_2Cl_2]Cl$, using hydrogen peroxide as oxidizing agent.

Reaction equations:

$$2CoCl_2 + 4(en) + 4HCl + H_2O_2 \longrightarrow \cancel{2}\ \text{trans-}[Co(en)_2\,Cl_2]Cl + 2HCl + 2H_2O$$

$$\text{trans-}[Co(en)_2\,Cl_2]Cl \xrightarrow{H_2O} \text{cis-}[Co(en)_2\,Cl_2]Cl$$

Procedure:

A. Preparation of trans-dichlorobis(ethylenediamine) cobalt(III) chloride.

1. Dissolve (2 gm) of hydrated cobalt (II) chloride in (5 ml) of water.
2. Add (7.5 ml) of 10% ethylenediamine with continuous stirring.
3. Cool the solution in an ice bath for (15 min.).
4. Add (5 ml) of 6% hydrogen peroxide dropwise to the solution with continuous stirring, during (8 min.), keeping the temperature of the solution below 10 °C during the addition.

5. Leave the solution to settle for (7 min.) at room temperature.
6. Heat the solution to 40 °C for (5 min.).
7. Add slowly, during (25 min.) 4 ml of concentrated hydrochloric acid.
8. Evaporate the solution at temperature 100 °C to about (10 ml) [or until the precipitation of green solid].
9. Leave the solution to stand for 24 hrs.
10. Filter the bright green precipitate in a dry filtration apparatus (note that the precipitate is very soluble in water).
11. Wash the solid with (10 ml) ethanol then with (10 ml) diethylether.
12. Dry the solid complex in an oven at 110 °C for (30 mins.) during which the crystalline precipitate converted into dark green powder.
13. Weigh the solid product and calculate the %yield.

B. Preparation of cis-dichlorobis(ethylencdiamine)cobalt (III) chloride.

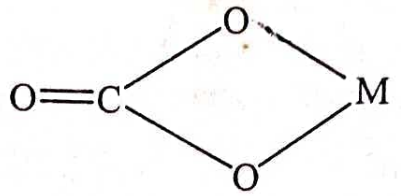
1. Weigh (0.5 gm) of the dry trans-isomer that prepared in section (A) and dissolve it in (10 ml) water using small beaker.
2. Neutralize the solution using diluted ammonia solution.
3. Evaporate the solution on a water bath to dryness (violet colour solid).
4. If some of the trans-isomer is not converted to the cis-isomer repeat the steps (1-3) above (dissolving in water, followed by neutralization and evaporation to dryness) until the violet colour solid formed.
5. Weigh the solid and calculate the %yield.

Experiment No. 2:

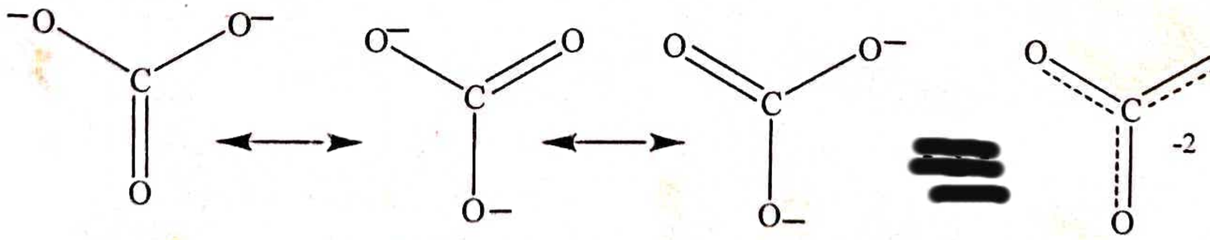
Preparation of cobalt (III) complex with bidentate ligand $Na_3[Co(CO_3)_3].3H_2O$

Theory:

The dinegative carbonate ion $[CO_3]^{2-}$ may act as bidentate ligand coordinating to the central metal ions through two oxygen atom in metal complexes.



The carbonate ion is planner and possesses D_3h symmetry with all C-O bonds of length 129 pm. A delocalized bonding picture involving (p-p)π-interactions is appropriate. The valance bond theory describes the ion in terms of three resonance structures, shown below. In which the carbon atom orbitals are SP^2 ($S+P_X+P_Y$) hybridized interact with the P orbitals of three oxygen atoms forming three single bonds. The remaining P_Z orbital of carbon atom form the additional π-bond with oxygen atoms. The C-O bond distance in $[CO_3]^{2-}$ is longer than in CO_2 (O=C=O) and consistent with formal bond order of 1.33, and the equivalent distribution of negative charge on the three oxygen atoms.



Resonance structure

The structural formula $[Co(CO_3)_3]^{-3}$ is rrefered to the anionic complex compound produced from the oxidation of cobalt (III) salts by hydrogen peroxide in the presence of sodium bicarbonate. The complex formed under these conditions was found to have the formula $Na_3[Co(CO_3)_3].3H_2O$. This complex compound is of special importance since it used in the preparation of large number of cobalt (II) complexes by its reaction with ligands in their acidic form producing carbone dioxide and water as by products.

The complex sodium tricarbonatocobaltate(III) trihydrate is olive green colour solid, insoluble in water, stable under dry condition and decompose without melting at 93 C°.

Reaction equations:

اكسدة

$$2Co(NO_3)_2.6H_2O+H_2O_2+10\ NaHCO_3 \longrightarrow 2Na3[Co(CO_3)_3].3H_2O+4NaNO_3+4CO_2+12H_2O$$

Procedure:

1. Prepare solution of cobalt (II) nitrate hydrate (1.5 gm) in (2.5 ml) water, then add to the solution (0.5 ml) of 30% hydrogen peroxide.
2. Dissolve (2.1 gm) of sodium carbonate in (7.5 ml) water (heat if necessary until complete dissolution). Cool to 0°C in an ice bath. Add the solution prepared in step (1) above dropwise to the cold carbonate solution with continous stirring.
3. Stir the mixture by magnetic stirrer for 30 min. at 0 °C.
4. Filter the precipitated olive green colour solid and wash it with ethanol then with ether.
5. Dry the solid, note that any water should be discarded since it causes the decomposition of the complex to black solid.
6. Calculate the % yield of the complex.

$Co(NO_3)_2\ 6H_2O$

Experiment No. 3:

Aluminium complexes

$K_3[Al(C_2O_4)_3]. 3H_2O$

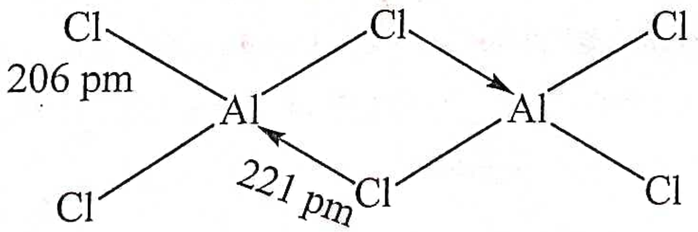
Theory:

Metal complexes are not formed by transition metals only but most of the non-transition elements form complexes also, these later are usually have white colour or colourless.

عديد/ كثير Aluminium does not occur free in nature, but its compounds are numerous and widely distributed. It is the most وافر abundant metal in the earth's crust, it comes third, after oxygen and silicon.

Aluminium is the second elements of group 13 in the periodic table. Its outer electronic configuration is $3s^2 3p^1$. Oxidation state +3 is مميزة characteristic of aluminium. It is readily oxidizes in air, it dissolves in dilute mineral acids but passivated by concentrated HNO_3. Aluminium reacts with aqueous NaOH or KOH, liberating H_2. Reactions of aluminium with halogens at room temperature or with nitrogen on heating give Al(III) halids or nitride. Aluminium is often used to reduce metal oxides, e.g. in the thermite process which is highly exothermic.

Aluminium tends to يحرز/ يبلغ attaine the nobel gas electronic configuration forming trihalide dimers for example Al_2Cl_6.



Solid $AlCl_3$ يتخذ adopts a layer structure with octahedrally sited Al. The vapours consist of dimeric molecules and these also present in solutions in inorganic solvents. Only at high temperatures does dissociation to monomeric $AlCl_3$ trigonal planer يوجد/ يحدث occure, but in the dimer, a tetrahedral بيئة/ محيط environments results from Cl → M coordinate bond formation involving a halogen lone pair of electrons.

When water is dripped on the solid $AlCl_3$, vagrous hydrolysis occurs, but in dilute aqueous solution, $[Al(H_2O)_6]^{+3}$ and Cl- ions are present the aqua-complex $[Al(H_2O)_6]^{+3}$ is six-coordinated with octahedral structure containing six water molecules surrounding the aluminium (III) ions which has high hydration energy due to its high charge and small volume.

In coordinating solvents such as Et_2O or Et_3N $AlCl_3$ forms adducts such as:

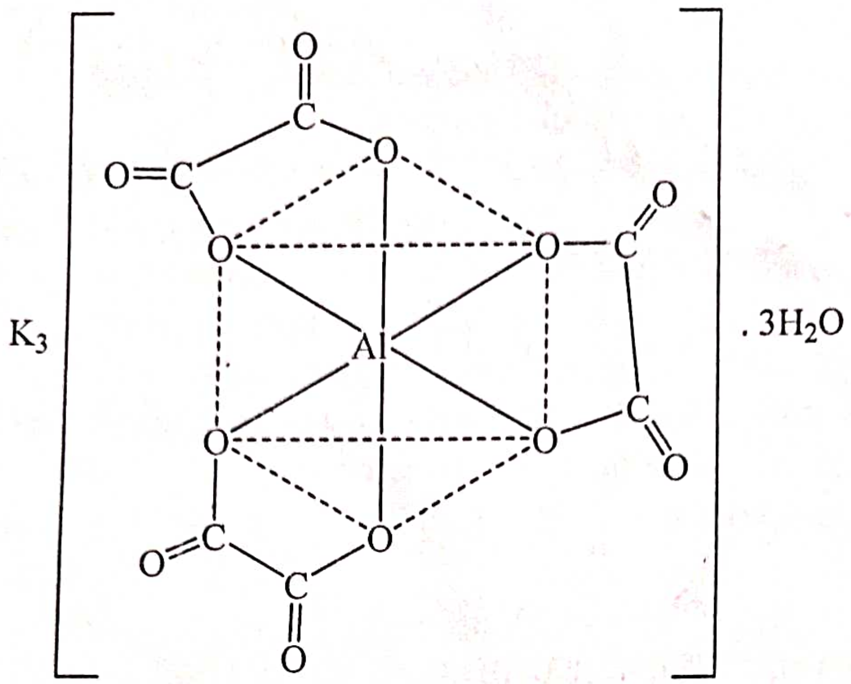
$(Et_2O: \longrightarrow AlCl_3)$ and $(Et_3N: \longrightarrow AlCl_3)$

Solution spectroscopic studies show that in acidic media, Al(III) is present as octahedral $[Al(H_2O)_6]^{+3}$, but raising the pH leads to the formation of polymeric species such as hydrated $[Al_2(OH)_2]^{+4}$ and $[Al_7(OH)_{16}]^{+5}$. Further increases in pH causes $Al(OH)_3$ to precipitate, and in alkaline solution.

The aluminate anion $[Al(OH)_4]^-$ (tetrahedral) and $[Al(OH)_6]^{-3}$ (octahedral) and polymeric species such as $[(HO)_3Al(\mu\text{-}O)\,Al(OH)_3]^{2-}$ are present.

Increasing numbers of coordination complexes of aluminium are becoming known, octahedral coordination is common e.g. $[Al(acac)_3]$, $[Al(ox)_3]^{-3}$. The structure of $[Al(ox)_3]^{-3}$ is shown below. The bidentate 8-hydroxy quinoline form neutral octahedral complex after deprotonation which has a number of applications. For example Al^{+3} may be extracted into organic solvents as the octahedral complex $[Al(8\text{-}quin)_3]$ providing a weighable form for the metal in gravimetric analysis.

Most of aluminium complexes are colourless due to empty d-orbitals. The structure of the potassium trioxalatoaluminate(III) trihydrate can be represented in the following figure $K_3[Al(C_2O_4)_3].3H_2O$



Procedure:

1. Weigh (0.25 gm) aluminium foil and cut it to small pieces then put it in a (200 ml) beaker.
2. Add (2.5 ml) of warm water covering the aluminium pieces, then add (7.5 ml) of potassium hydroxide KOH (prepared by dissolving 1.5 gm solid KOH in 7.5 ml distilled water), gradually until the reaction started.
3. Heat the solution to boiling temperature to complete dissolution of aluminium.
4. Filter the solution (to get rid of the black solid), through glass wool (use filter paper if not available).
5. Add (2.5 ml) distilled water to the filterate then heat to boiling temperature.
6. Dissolve (3.5 gm) of hydrated oxalic acid and add it gradually in portions to the warm solution (the precipitated hydrated alumina re-dissolved by continous heating).
7. Leave the solution to cool then neutralize with KOH solution prepared by dissolution of (3 gm) of solid potassium hydroxide in (7.5 ml) distilled water (note that the color of litmus paper that is for pH=6-7.

8. Filter the neutralized solution using filter paper (neglect the solid).
9. Add (15 ml) of ethanol to the filtrate (if any precipitate formed before the ethanol addition re-filter the solution and get rid of the solid) then stir the solution well.
10. Cool the solution in an ice bath with continous stirring until minute colourless crystals of the oxalato complex formed (it may need vigorous stirring to initiate the crystallization of the complex).
11. Filter the precipitated crystalline solid and wash it with mixture of equal volumes of water and ethanol (2 ml water + 2 ml ethanol), then with (5 ml) ethanol and finally dry in air at room temperature.

Determination of % oxalate in the complex

1. Prepare (50 ml) (0.1 N) solution sodium oxalate using 50 ml volumetric flask and homogenize the solution by shaking the flask well.
2. Prepare 100 ml (0.1 N) potassium permanganate $KMnO_4$ in 100 ml volumetric flask and homogenize the solution as above.
3. Transfer 10 ml of (0.1 N) sodium oxalate solution to 250 ml concal flask using suitable pipet then add 10 ml of 2N H_2SO_4 (previously prepared).
4. Fill a suitable burret with 0.1N $KMnO_4$ solution to the mark.
5. Warm the solution in the conical flask to about 60 C and titrate against $KMnO_4$ solution (note that $KMnO_4$ is self indicator) record the volum of permanganate solution required to change the colour of solution from colourless to pale pink).
6. Repeat the titration three times and calculate the mean value.
7. Calculate the exact normality of potassium permanganate by applying the formula.

   N_1V_1 (permanganate solution) = N_2V_2 (oxalate solution)

8. Weigh accurately (0.2 gm) of the prepared complex and transfer it to 500 ml conical flask then add 50 ml (2N) H_2SO_4 then heat the content flask to the boiling temperature.

9. Titrate the solution of the complex against potassium permanganate solution and record the volume of $KMnO_4$ solution required to change the colour of the solution from colourless to pale pink.

10. Repeat the titration three times and find the mean volume.

11. Calculate the normality of the prepared oxalate complex by applying the same above formula.

12. Calculate the % of oxalate group $(C_2O_4)^{2-}$ in the complex using the normality equation.

N × V × M(eq.wt) = W (gm)

N = the exact normality of $KMnO_4$ from the first titration.

V= the volum of the $KMnO_4$ solution from the second titration.

M(eq.wt) = the equivalent weight of oxalate = 88/2.

W (gm) = the practical weight of oxalate group in the complex

% oxalate in the complex can be calculated as follows:

$$\% = \frac{W\ (gm)}{0.2} \times 100$$

Compare the % of oxalate found practically with that calculated from the proposed formula of the complex $K_3[Al(C_2O_4)_3].3H_2O$.

Experiment No. 4:

Preparation of cobalt (III) complex with hexadentate ligand

$Ba[Co(EDTA)]_2.4H_2O$

Theory:

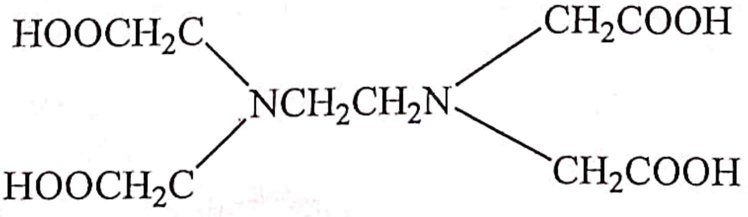
The cobalt metal is ferromagnetic and present in many crystalline forms. Its common oxidation states are Co(II) and Co(III) and its highest oxidation state is (III) but the oxidation state (II) is more stable in aqueous solution and its oxidation to Co(III) is difficult.

$$[Co(H_2O)_6]^{+3} + e^- \xrightarrow{\qquad\qquad} [Co(H_2O)_6]^{+2} \qquad E^o = +1.84\ V$$

Oxidation state (III) is stable in low spin complexes and there are large number of these complexes specially with nitrogen donor ligands.

$$[Co(NH_3)_6]^{+3} + e^- \xrightarrow{\qquad\qquad} [Co(NH_3)_6]^{+2} \qquad E^o = +0.1\ V$$

The low value of E° means that oxidation of cobalt (II) coordinated to ammonia to cobalt (III) is easy. The molecules or ions that have two donor atoms able to coordinate to a central metal ion is called bidentate ligands for example, ethylenediamine (en) and oxalate ion $(C_2O_4)^{-2}$. Other polydentate ligands may have three, four or more donor atoms able to coordinate to the central metal ions an example of these the hexadentate ligand, ethylenediaminetetraaceticacid (EDTA) (its structure shown below).



EDTA

The six donor atoms (2N + 4O) that exist in EDTA when coordinated to the central metal ion will strongly bond the ligand to the central metal ion and very stable complex will be formed. Thus such ligands have many important applications. It may be used as drug for lead (Pb) poisoning treatment and as water hardness removel in some cleaning product (e.g. shampoo). It may also used as food additive to act as masking agent for some metal ion that catalyze oxidation processes that cause food expire.

The ligands that attached to two positions or more of a central ions at the same time forming one or more ring structures are called chelating ligands. The chelating ligand EDTA form soluble very stable complexes. The stability of these complexes is due to the presence of many groups in this ligand molecule that able to form chelate rings surrounding the metal ion and inhancing the stability of the complex. The figure below show the structure of one of EDTA complexes in which the six donor atoms of the ligand coordinated to the central metal ion (Co^{+3}) forming many ring structures.

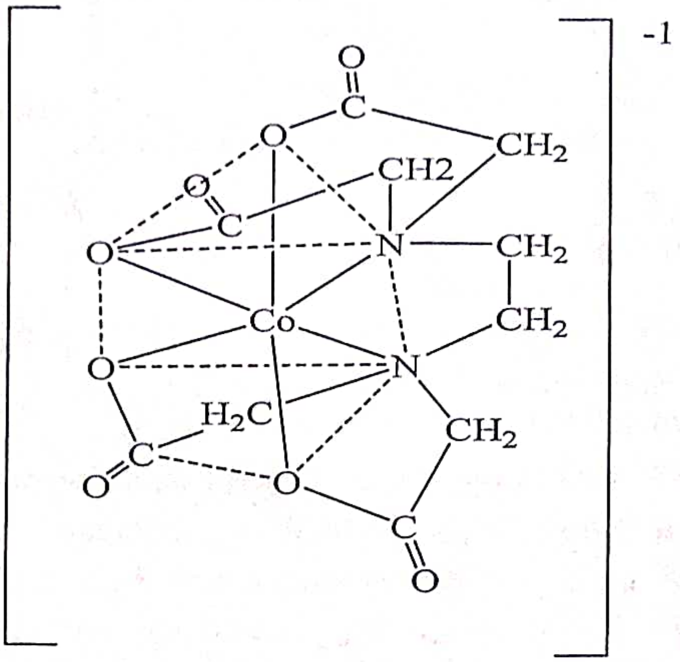
Equations:

$$\underset{\text{EDTA}}{CoCO_3 + C_{10}H_{16}N_2O_8} \longrightarrow [Co(C_{10}H_{\underline{\underline{14}}}N_2O_8)] + CO_2 + H_2O$$

كل مرحلة يفقد 2H

$$2Co(C_{10}H_{14}N_2O_8) + 2H_2O_2 + BaCO_3 + 2H_2O \longrightarrow Ba[Co(C_{10}H_{\underline{\underline{12}}}N_2O_8)]_2.4H_2O + CO_2$$

(Note : use cobalt(II) chloride hexahydrate $CoCl_2.6H_2O$ instead of cobalt carbonate $CoCO_3$ because the later is not available in the labarotary)



$[Co(EDTA)]^{-1}$
complex

Procedure:

ذرة مركزية

1. Weigh (2.37 gm) cobalt(II)chloride hexahydrate $CoCl_2.6H_2O$ (2.92 gm) EDTA ليكند and dissolve them sucessivly in (10 ml) distilled water in (100 ml volume) beaker.
2. Heat the solution with continuouis stirring up to 75 °C (use thermometer) then leave it at this temperature with stirring for (10 7 min min.).
3. Cool the solution to room temperature.
4. Add (2.5 ml) of 30% hydrogen peroxide dropwise with continuous stirring for at least (8 10 min.). عامل مؤكسد يؤكسد Co من Co^{+2} إلى Co^{+3}
5. Add slowly batchwise (0.99 gm) barium carbonate $BaCO_3$ powder with continuous stirring at room temperature. عامل مرسب
6. Continue stirring the solution for at least (15 min.) until complete evolution of carbon dioxide gas (no more gas bubles evolved).
7. Leave the solution at room temperature for at least (30 20 min.) then filter using Buchner filtaration techniques, finally wash the precipitate with (3 ml) distilled water then with (5 ml) ethanol.
8. Dry the precipitate in an oven at 60°C for at least one hour.
9. Weigh the precipitate the calculate the % yield.

Experiment No. 5:

Acetylacetone complexes

Theory:

Manganese is relatively abundant, constituting about 0.085 % of the earth's crust. Among the heavy metals, only Fe is more abundant. It is on the top of group 7 (VIIB) of the periodic table.

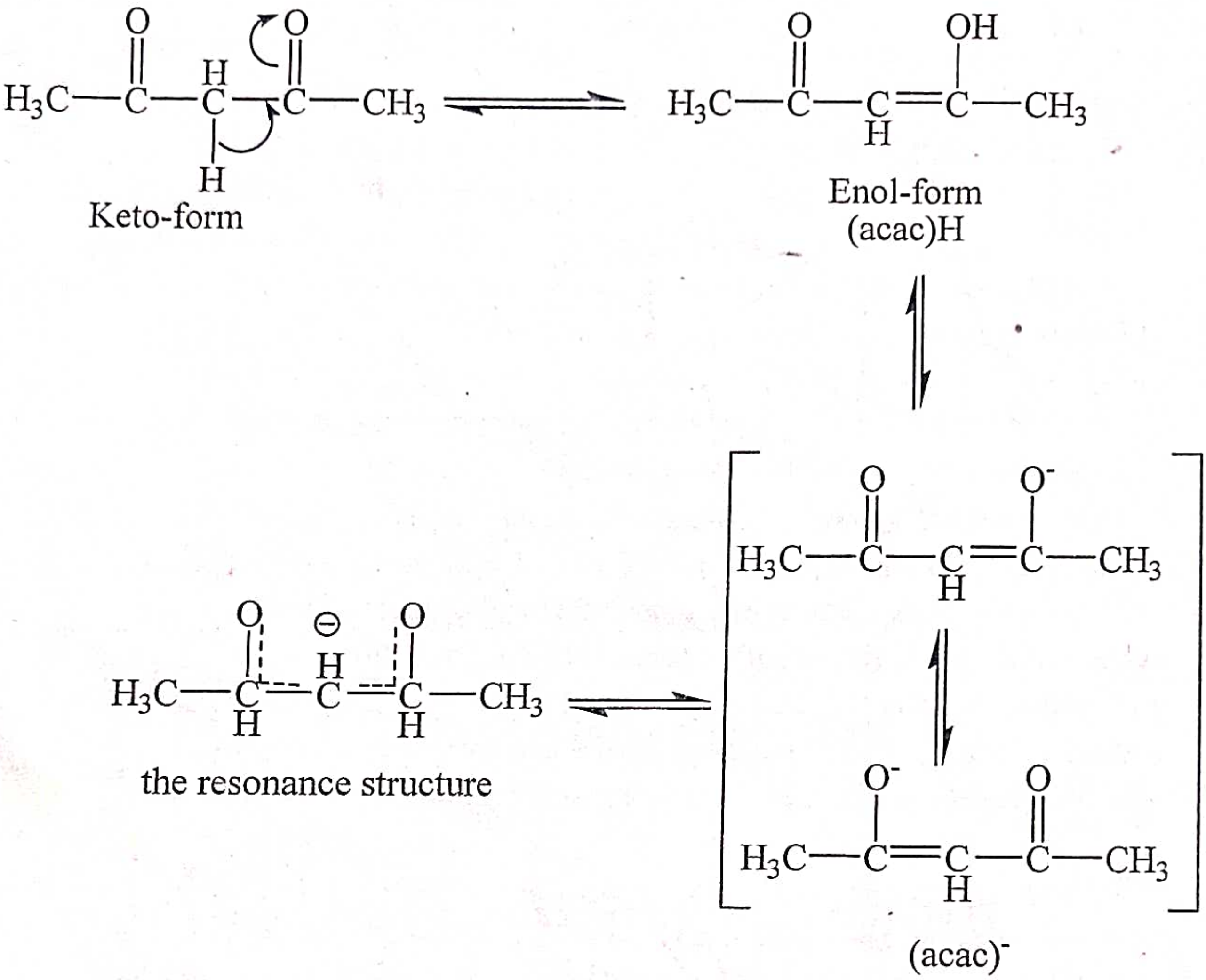
Manganese exhibit the widest range of oxidation states of any of the first series transition metals. Its oxidation states are in the rang +1 to +7, and the most common oxidation states are +2, +4, and +7.

The divalent states (+2) is the common and most stable oxidation state. It is very stable in acidic medium and in most divalent manganese salts which are sparingly soluble in water. In neutral or acid aqueous solution there is the very pale pink hexaaqua ion $[Mn(H_2O)_6]^{2+}$, which is resistant to oxidation. In basic the hydroxide $Mn(OH)_2$ is formed, this is very easily oxidized by air.

The trivalent state (+3) is an important specie in manganese chemistry. In solution stable manganese (III) can be obtained in the presence of anions like sulfate, oxalate or pyrophosphate.

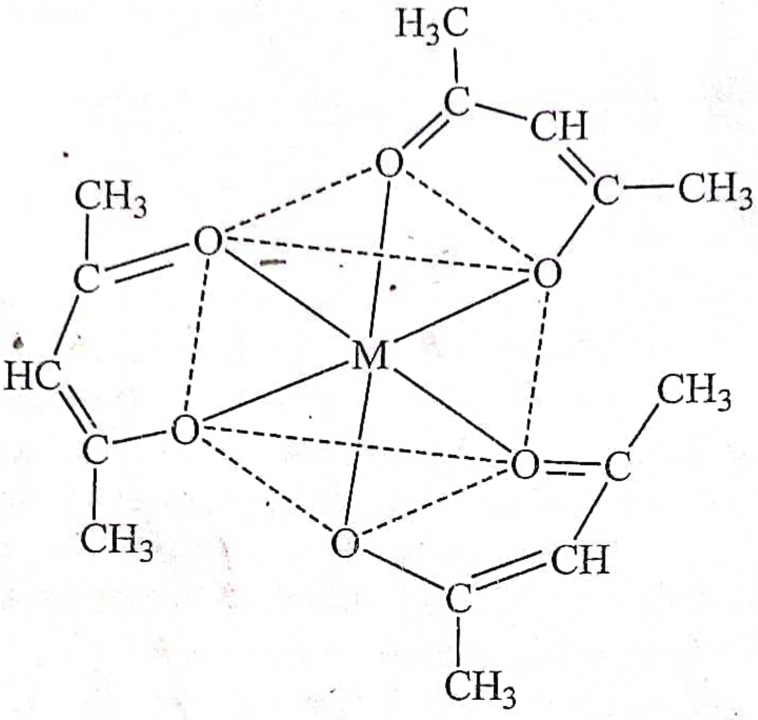
Iron is the most important of all metals, is also one of the most abundante in the earth's crust, being second only to aluminium. The most important ores are haematite, Fe_2O_3, magnetite, Fe_3O_4, and siderite, $FeCO_3$. It is the first element in group 8 (VIII). Most of the chemistry of Fe involves Fe(II)(+2) Fe(III)(+3) with Fe(IV)(+4) and Fe(VI)(+6) is rare. The (+6) is the highest oxidation state of iron, since it has no stable oxidation state in which it lose all its (eight) outer orbitals electrons as in the case of manganese. The most important oxidation states are +2 and +3. The trivalent state has the electronic configuration $3d^5$ in which the d-orbitals are half-filled as in the case of manganese (II), that made these oxidation state more stable. Iron (III) form complexes with most known anions except the species that reduce it to Fe(II).

Acetylaceton undergo keto-enol tatomerism like other β-diketons, which can form anions as a result of this enolization, the equilibrium of keto-enol forms depend on the experimental condition.



Acetylacetonate (acac)$^-$ which is the commonest ligand of β-diketone form very stable chelate complexes with most metal ions. Among the commonest types of acetylaceton complexes are those neutral complexes with stoichiometries $M(acac)_3$, and $M(acac)_2$. The former all have structures based on an octahedral disposition of six oxygen atoms. (see structure below)

Substances of composition $M(acac)_2$ are very often oligomeric, thereby allowing coordinative saturation of the metal. Thus acetylacetonate chelate complexes $Zn(acac)_2$, $Ni(acac)_2$ are trinuclear, while $Co(acac)_2$ is tetranuclear, all have bridging acetylacetonate groups.



M(acac)$_3$ M = Mn(III) or Fe(III)

1. Preparation of tris(acetylacetonato)manganese (III) [Mn(acac)$_3$]

Equations:

$$\underset{}{MnCl_2} + \underset{(acac)H}{2HC_5H_7O_2} + 2NaC_2H_3O_2 \rightleftharpoons \underset{Mn(acac)_2}{[Mn(C_5H_7O_2)_2]} + 2NaCl + 2H_2C_2H_3O_2$$

$$\underset{Mn(acac)_2}{4[Mn(C_5H_7O_2)_2]} + KMnO_4 + \underset{(acac)H}{7HC_5H_7O_2} + HC_2H_3O_2 \rightleftharpoons \underset{Mn(acac)_3}{5[Mn(C_5H_7O_2)_2]} + KC_2H_3O_2 + H_2O$$

المعقد الناتج متعادل

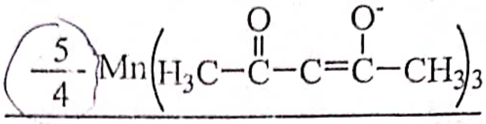
Procedure:

1. Weigh (0.65 g) manganese (II) chloride tetrahydrate $MnCl_2.4H_2O$ and (1.7 g) sodium acetate hydrate then dissolve them in (25 ml) distilled water at a 250 ml conical flask.
2. Add to the solution (2.5 ml) acetylacetone.
3. Prepare a solution of (0.13 g) potassium permanganate ($KMnO_4$) (8.5 ml) of distilled water and add it gradually (to the above solution in step(2)) with continuous stirring ver at least (15 min.)
4. Prepare another solution by dissolving (1.7 g) of sodium acetate hydrate in (8.5 ml) of distilled water and add it to the solution (from step 3) gradually with stirring over at least (20 min.).
5. Heat the mixture at 40°C for (10 min.) then cool the product to room temperature followed by cooling in an ice bath.
6. Filter the solution under vacuum (using Buchner filteration technique) and wash the precipitate with (2.5 ml) distilled water.
7. Re-crystalize the precipitate by dissolution in (20 ml) hot benzene then filter the solution while hot. Evaporate the benzene solution to 7 ml volum then cool.
8. Add (20 ml) petrollium ether to the cold solution to precipitate the complex compound then filter under reduced pressure (Buchner).
9. Dry the precipitate in an oven at 60°C for at least one hour, then weigh the precipitate and calculate the %yield of the product.

Complex properties:

The complex is bright dark black to brown crystals under reflected light, and dark green in a trasperant light. It is not melt at sharp temperature but decompose above 150 °C. it dissolve in some organic solvents like benzene, chloroform, and ethylacetate while it is sparingly soluble in water.

Calculations:

$MnCl_2.4H_2O$	 $\frac{5}{4}\,Mn\left(H_3C-\overset{O}{\overset{\|}{C}}-C=\overset{O^-}{\overset{|}{C}}-CH_3\right)_3$
198	440
0.65	X

X = Theoritical weight of product

لماذا نضرب × $\frac{5}{4}$ حتى نحصل
على مول واحد من المعقد

$$\% \text{ yield} = \frac{\text{the product weight}}{X} \times 100$$

B. Preparation of tris(acetylacetonato) Iron (III)

[Fe(acac)₃]

Reaction equation:

$$FeCl_3.6H_2O + 3(acac)H + 3CH_3COONa.3H_2O \rightarrow Fe(acac)_3 + CH_3COOH + 9H_2O + 3NaCl$$

Procedure:

1. Weigh (0.85 g) ferric chloride hydrate $FeCl_3.4H_2O$ and dissolve it in (5 ml) distilled water in a conical flask with glass rubber stopper.
2. Add (1 ml) acetylaceton (using graduated cylinder) and use (2-5 ml) ethanol to transfer any acetylacetone remained in the cylinder.
3. Shack the conical flask content (by hand) for (20 min.) to complete the reaction.
4. Weigh (2-7 g) sodium acetate trihydrate ($CH_3COONa.3H_2O$) and add it gradually (1.0 g a batch). Shake well after each addition.

5. Cool the mixture in an ice-bath for at least (20 min.) until bright red crystalline solid formed. Filter the red solution to separate the precipitate.
6. Re-crystalize the precipitate as follows:

a- Dissolve the red precipitate in boiling (20-25 ml) ethanol and filter while hot (hot filteration) quickly under reduced pressure (Buchner).

b- Cool the filtrate to room temperature then in an ice-bath, add few drops of distilled water from time to time until precipitation started (water initiate crystallization). Continue cooling in ice-bath until complete precipitation.

c- Filter the solution under reduced pressure (Buchner) and wash with (5 ml) ice-cold distilled water (cool water before washing).

7. Dry the bright red precipitate in an oven at 60°C for at least one hour.
8. Weigh the precipitate and calculate the % yield of the product.

Experiment No. 6:

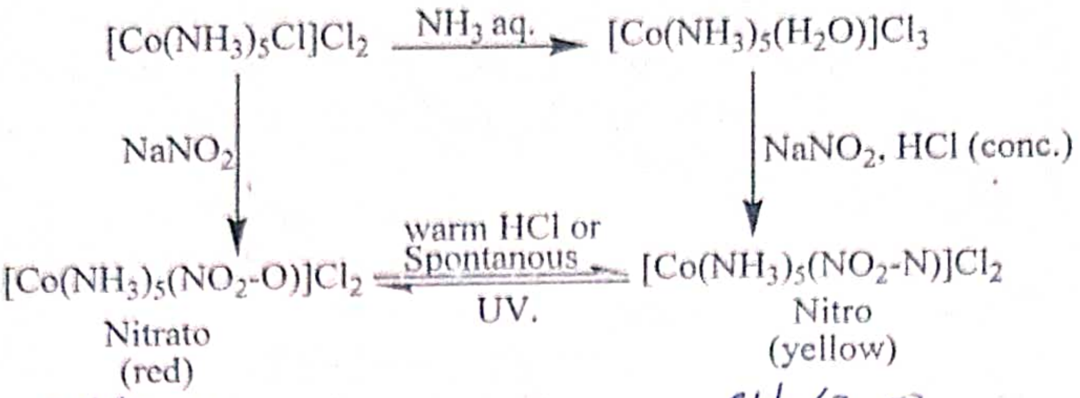
Linkage isomerism

Theory:

Linkage isomerism is one of many important type of isomerism in metal complexes.

There are a number of molecular ligands that contain two different atoms carrying lone pairs, both capable of coordination to a metal ion. These are called ambidentate ligands, distinguished by their capability for binding a metal ion through either of the different donor groups. (see figure below). A simple example is the thiocyanate anion (SCN^-), which offers either a N atom (NSC-N isomer) or a S atom (NCS-S isomer) to metal ions, which one a metal ion selects depends on metal ligand preferences. For example the "hard" Co(III) ion prefers to form Co-NCS complexes with the "hard" N-doner whereas the "soft" pd(II) ion prefers the "soft" S-donor and forms pd-SCN complexes.

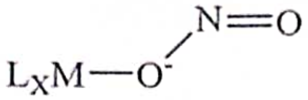
Another classical example is nitrite ion, which offers N or O atoms as donors. This example has been deeply studied, and the way it behaves is fairly understood. The O-bound isomer converts (isomerizes) to the thermodynamically stable N-bound isomer (see equation below), sometimes even in solid state, by intramolecular process (without the ligand departing the coordination sphere) in inert complexes. Another feaure of ambidentate ligands is that they can display a tendency to "bridge" between two metal ions, with each of the two different donor atoms attached to one of two metal ions.



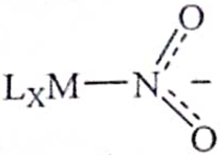
pH (7-6)

pH ≤ (3-5)

NO_2^-



O-nitro (or nitrito)



N-nitro

SCN^-

$L_XM—S^-—C \equiv N$

S-thiocyanato

$L_XM—N^-=C=S$

N-thiocyanato

Procedure:

A. Preparation of the complex, Chloro pentaamminecobalt(III) chloride $[Co(NH_3)_5Cl]Cl_2$.

مركب وسطي للحصول على Nitro و Nitrato

(Note: carry out the first steps in a fumehood and without heating)

1. In a 250 ml conical flask dissolve (2.5 g) ammonium chloride (NH_4Cl) in (15 ml) of concentrated ammonia solution. تحضير المعقد بالليكند
2. Stir by magnetic stirrer (put a small magnet in the solution) and add with continuous stirring (5.0 g) cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$) powder batchwise slowly (do not add more powder until the first portion completely dissolved. Note that solid hexaammincobalt(II) chloride precipitated and heat is liberated. (exothermic reaction). تحضير المعقد بذرة الفلز المركزية

عامل مؤكسد يحول $Co^{+2} \rightarrow Co^{+3}$

3. Add slowly (10 ml) of 30 % hydrogen peroxide (H_2O_2) (from a buret) with continuous stirring (do not heat, the reaction is exothermic). Note that after the reaction subset, red solution of aquapentammine salt is formed. عامل مرسب
4. Add (10 ml) concentrated hydrochloric acid (HCl) over a period of at least (10 min.) (note that the solution will warm because the reaction is exothermic also).
5. Note the formation of pink precipitate and the colour of solution is pale greenish blue (if the pink precipitate is not formed add excess concentrated HCl until precipitation started).
6. Heat the mixture on a water bath for at least (20 min.) (the water bath temperature should not exceed 80°C), then cool the solution to room temperature.
7. Filter the product under reduced pressure (use Buchner technique). Wash the precipitate with (2.5 ml) cold distilled water then by (2.5 ml) of (6M) (six molar) HCl solution.
8. Dry the precipitate in an electrical oven at 60°C for at least one hour.
9. Weigh the precipitate and calculate % yield.

B. Preparation of the complex, Nitropentaamminecobalt (III) chloride $[Co(NH_3)_5NO_2]Cl_2$.

1. Weigh (1.25 g) of the prepared complex (in section A above), chloropentaamminecobalt (III) chloride and dissolve it in (15 ml) distilled water in a 250 ml conical flask.
2. Add to the solution (1.0 ml) concentrated ammonia solution and heat the solution at 50°C with continous stirring (using magnetic stirrer) for at least (5 min.)
3. Filter while hot to get rid of any undisolved chloro pentaamminecobalt (III) chloride complex then cool the filtrate to room temperature, (neglect the precipitate).
4. Acidify the solution with diluted HCl, add it dropwise until pH in the range (3-5) using pH-meter or pH-paper.
5. Add (1.5 g) solid sodium nitrite ($NaNO_2$) batchwise. Note the formation of red solid in few minutes of complete addition.

Leave the solution to stand for at least (5 min.) at room temperature to complete precipitation.

6. Heat the dissolve the red precipitate. Remove any undissolved precipitate by filtration under reduced pressure (Buchner technique).
7. Add slowly (16 ml) of concentrated HCl through a buret over a period of (30 min.) (in fumehood).
8. Cool the mixture in an ice-bath. Yellowish-brown precipitate will form. Filter under reduced pressure.
9. Dry the precipitate in an oven at 60°C for at least one hour.
10. Weigh and calculate the %yield of the product.

$[Co(NH_3)_5ONO]Cl_2$

C. *Preparation of the complex, Nitritopentaamminecobalt (III) chloride*

1. Weigh (0.6 g) of the complex chloropentaamminecobalt (III) chloride $[Co(NH_3)_5Cl]Cl_2$ (prepared in section A) and dissolve it in a mixture of (10 ml) distilled water and (2.3 ml) concentrated ammonia solution in a 250 ml conical flask.
2. Filter the solution to get rid of any undissolved chloropentaamminecobalt (III) chloride complex.
3. Neutralize the filtrate by dropwise addition of diluted HCl until pH at (6-7) using pH-meter or pH-paper.
4. Weigh (0.6 g) sodium nitrite and dissolve it in the solution by shaking mechanically.
5. Add (0.6 ml) of 6M hydrochloric acid (HCl) to the solution.
6. Leave the solution to stand at room temperature for at least (15 min.) for a red precipitate to form.
7. Filter the solution under reduced pressure (Buchner) and wash the precipitate with (5 ml) cold distilled water.
8. Dry the precipitate in an oven at 60°C for at least one hour.
9. Weigh the precipitate and calculate %yield of the product.

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