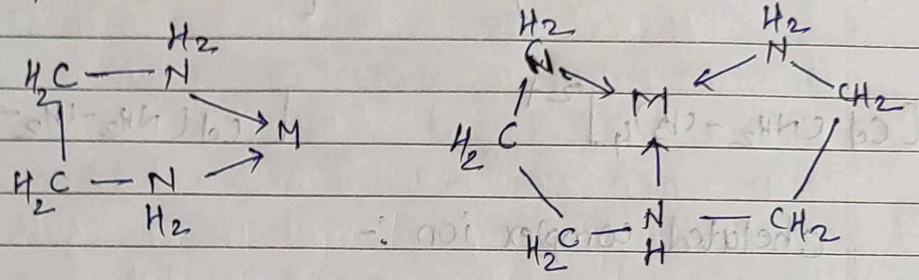
B. CHELATES

Introduction :-

Chelates are coordination compounds. It is defined as, "A chelate is formed upon the reaction of metal ion and a substance containing two or more groups with electron donar properties such that one or more rings are formed as result of reaction."

Example :-



(i) Morgan and Drew proposed term chelate for that cyclic structure formed by union of metallic atom with organic and inorganic molecules. The ring of such compounds are called chelate rings and phenomenon as chelation.

(ii) The term chelate is derived from Greek word, 'chele' or 'chelos' means crab's claw. Because ligand captures metal ion with the help of donar atoms.

(iii) Such complexes are also called as chelated complexes or cyclic complexes and term chelation also called cyclization.

(iv) Chelate comp also defined as, complexes in which donar atom are attached to each other as well as to metal so that metal become part of heterocyclic ring.

Eg: ethylenediamine Form a chelate with Cadmium ion as shown below :

Normally chelated complexes are more stable than non-chelated complexes. The more rings, the more stable is complex. chelated rings contain five or six member rings including metal ion, which reduces strain and are more stable.

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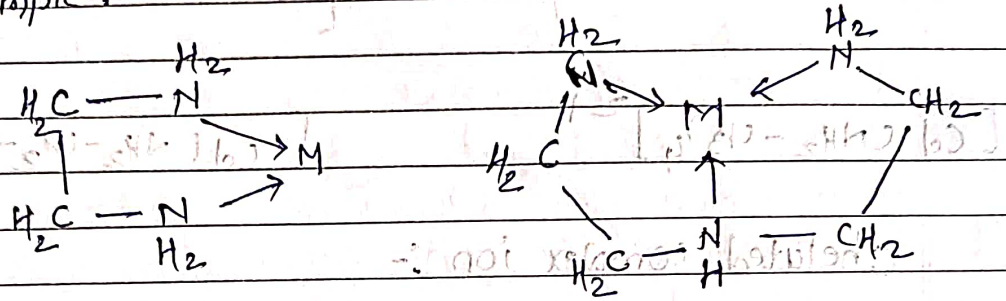

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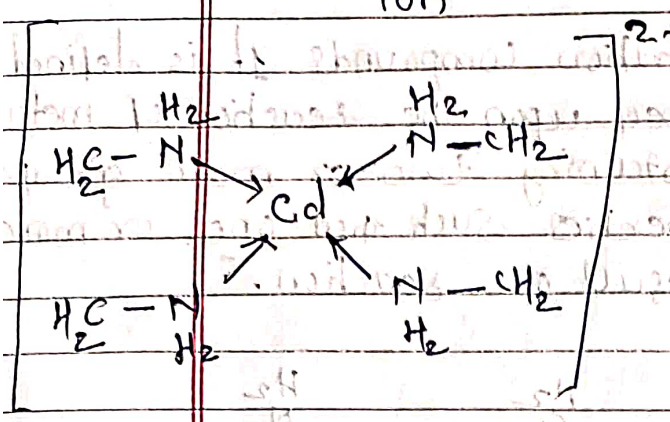
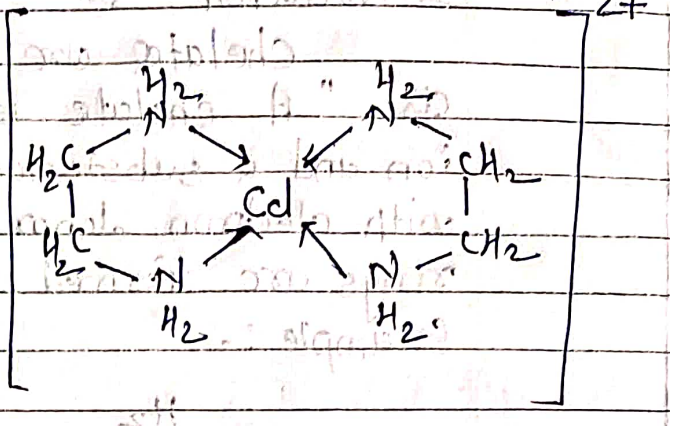
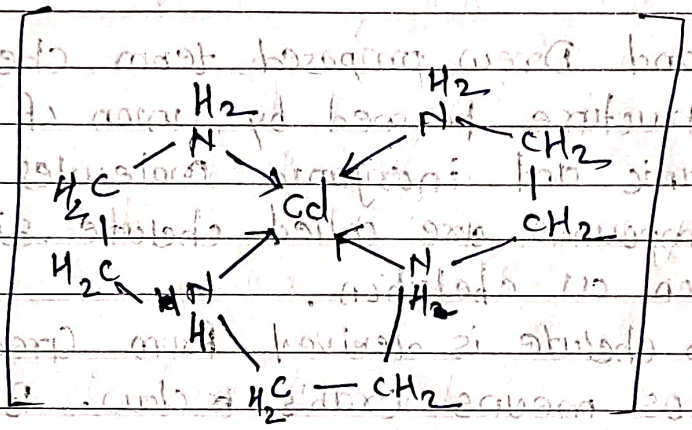
Non-chelated complex ion :- chelated complex ion





$[Cd(NH_2-CH_3)_4]^{2+}$ $[Cd(NH_2-CH_2-CH_2-NH_2)_2]^{2+}$

Chelated complex ion :-



$[Cd(tetrien)]^{2+}$

Chelated complex ion :-

Martell and Clavin given an summary and applications of chelating agents. They roughly divide chelating agents into two classes.

① Sequestering agents :-
These are chelating agents that form water-soluble chelates. These are very useful for effective removal of objectionable metal ion in aqueous soln. They have applications in laundering into boiler scale removal and to speed up the elimination

of harmful radioactive metals from body fluids.

(2) Chelating agents :-
These are the reagents that precipitate out the metal chelates.
Chelation has been fully appreciated as prominent chemical principle. progress in chemistry of metal chelate has received an more importance because of its many biological application. Metal chelates ~~get~~ aquire extraordinary features when metal ion links with organic molecule. They play essential role in life processes.

eg:- Chlorophyll, it is green ~~colour~~ pigment of plants is a magnesium chelate while hemin, red colouring matter of earth is an iron chelate.

Basic concept :-
Metal chelates may be examined from following three point of view,
(1) The central metal atom
(2) The chelating molecule
(3) The nature of bonds linking the CMI with chelating molecule and influence of each and all of these on behavior of metal chelates.

(1) The Central metal atom :-
The properties of metal complex are affected by nature and oxidation state of CMI.
Example : chelates formed by Cu(II) and Ni(II) with dimethyl glyoxime have totally different properties. Cu(II) chelate is soluble in water while Ni(II) chelate is highly insoluble in water.

Cu(II) chelate is tetragonal pyramidal molecule while nickel chelate is square planar molecule. These difference is due to difference in size and electronic config-uration of two metal atom.

oxidation state and coordination number also affect the structure and property of chelates.

(ii) The chelating molecule :-

If molecule is to function as a chelating agent, it must fulfil following two conditions.

(a) It must possess at least two appropriate functional group which ~~are~~ can bound ~~et~~ to metal.

(b) The functional group present in molecule must permit the formation of ring with metal atom as a closing member.

Steric effect of ligand also affect chelation.

Eg: 8-hydroxyquinoline form tris complex with Al(III) but 2-methyl-8-hydroxyquinoline prevent formation of such complex.

(iii) The metal-ligand bond :-

The stability of chelate also depend upon metal-ligand (M-L) bond. The nature of M-L bond depends upon the size and electronegativity of metal ion (M) and nature of atom of ligand (L) which form bond with metal atom.

Classification of chelates :-

The chelates are classified on the basis of number and kind of attachment of ligands to CMI. The polydentate ligand may bind to CMI through two types of functional groups namely acidic and coordinating group. They form coordinate linkage and ~~coord~~ covalent bond. chelate ring may be formed by formation of only covalent bonds or

only coordination bonds or by combination by both.

(i) Covalent bonds are are formed by replacement of one or more H atoms from acidic group of ligand by metal atom.
Eg: $-COOH$ (carboxylic), SO_3H (sulphonic), $-OH$ (enolic hydroxyl), $=NOH$ (oxime).

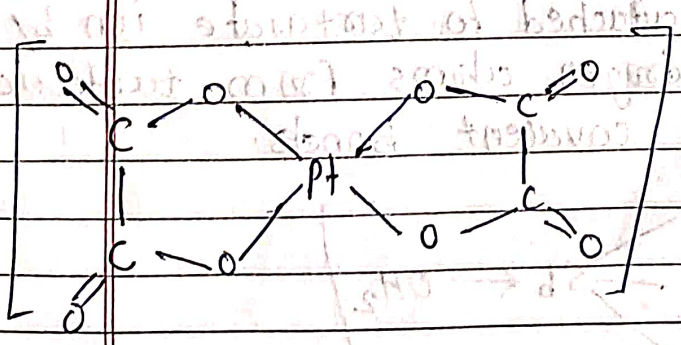
(ii) Coordinate bonds are formed by donation of electron pair from ligand to metal ion.
Eg: $-NH_2$ (1° amines), $>NH$ (2° amines), $>N-$ (3° amines), $=NOH$ (oxime), $-OH$ (alcoholic hydroxyl), $C=O$ (carbonyl) and $-S-$ (thio ethere).

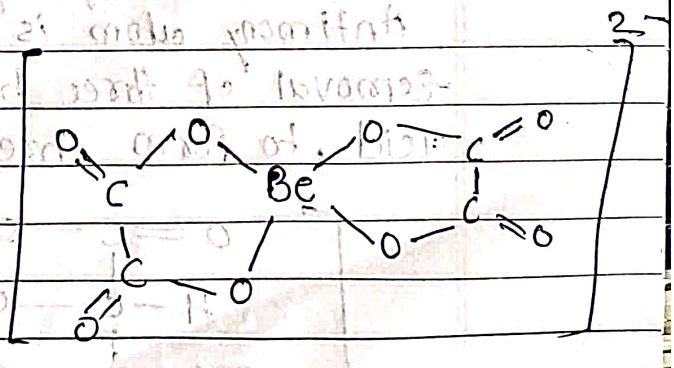
Chelating agent which supplies two donors to metal so as to form a single chelate ring is said to be bidentate. similarly, tri, tetra, penta and hexa ligands bind metal in three, four, five and six positions respectively.

The chelates may be classified into following groups

1. Bidentate chelating groups

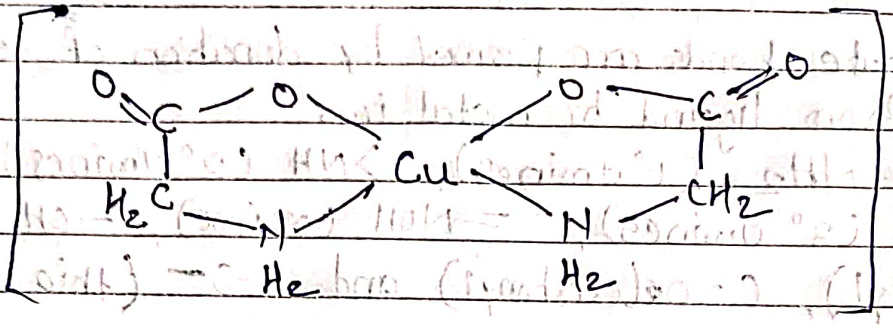
(a) Two acidic groups :-
In this complexes cation is combined through Covalent bonds only. Ring of these type are formed by replacement of two Hydrogen atoms of ligand by metallic cations.





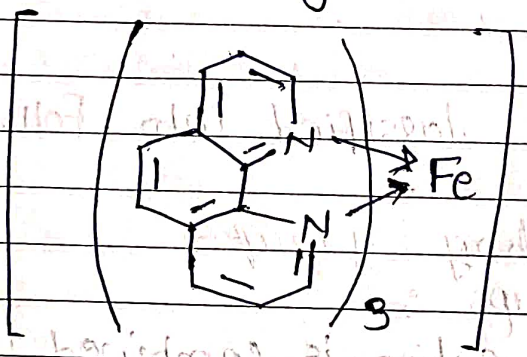
(b) One acidic group and one Coordinating group :-

Cu^{2+} ion reacts with glycine (CH_2NH_2COOH) to produce copper glycinate. Glycine molecule is attached to copper atom by one covalent bond & one coordinate bond.



(c) Two coordination groups :-

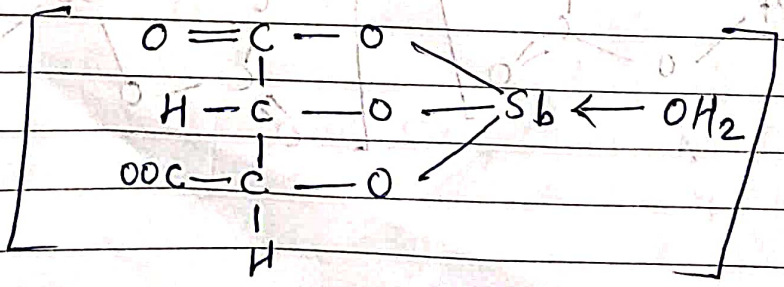
Fe^{2+} ion combines with three molecule of O-Phenonthroline which contain two nitrogen atoms in heterocyclic ring.



(2) Tridentate Chelating ~~agent~~ groups :-

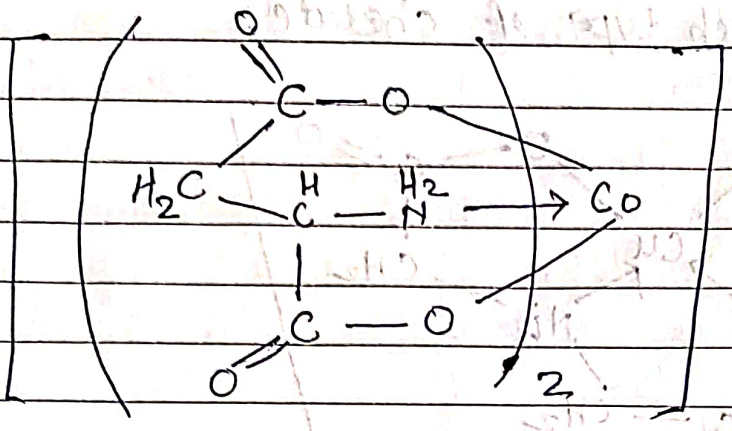
(a) Three acidic groups :-

Antimony atom is attached to tartarate ion by removal of three hydrogen atoms from tartaric acid, to form three covalent bonds.



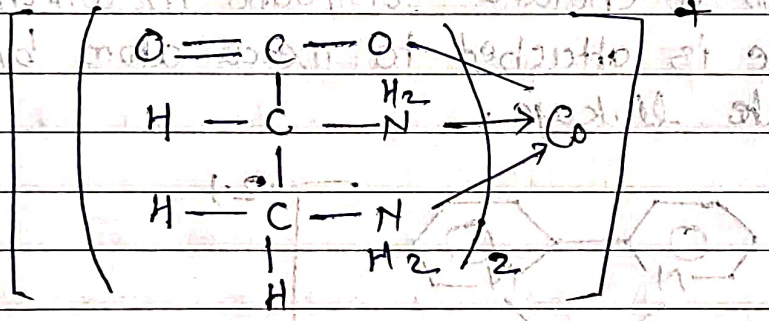
(b) Two acidic group and ~~two~~ one coordinating group :-

Aspartic acid combines with Co^{3+} to form water soluble tridentate ~~ligand~~ compound.



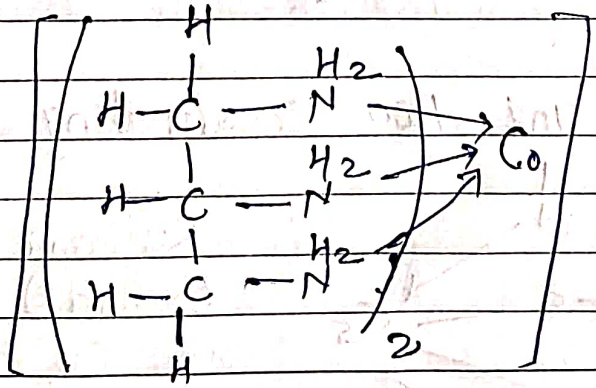
(c) One acidic group and two coordinating group :-

Alpha, Beta diamine propionic acid combines with Co^{3+} to form a chelate.



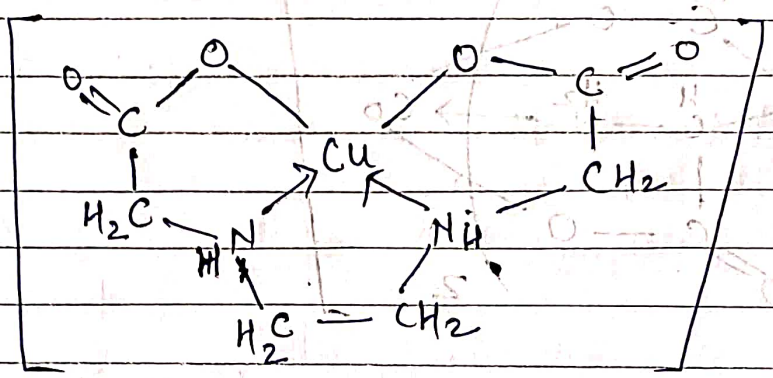
(d) Three coordinating group :

Triaminopropane combines with Co^{3+} to form Chelates.



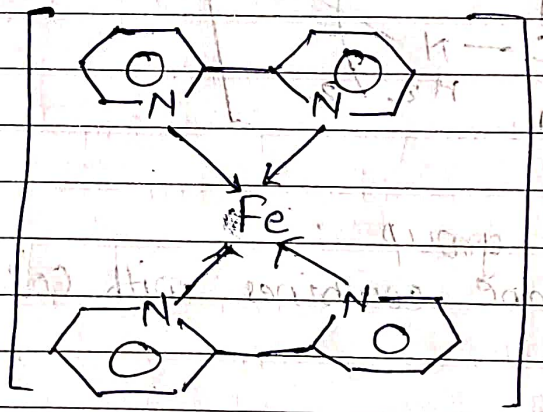
(3) Quadridentate chelating groups :-

(a) Two acidic and two coordinating groups : Ethylene diamine acetic acid [$(HOOCCH_2)\cdot NH\cdot CH_2-CH_2-NH\cdot (CH_2COOH)$] combine with Cu^{2+} to form such type of chelate.

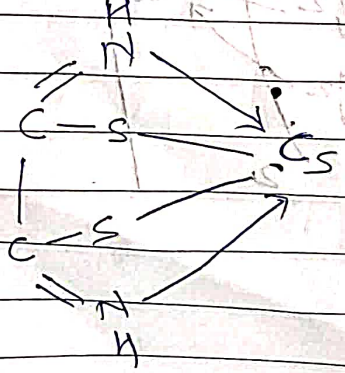


(b) Four coordinate groups :-

2,2'-bipyridyl reacts with Fe^{2+}, Co^{2+}, Ni^{2+} & Zn^{2+} to form a chelate compound in which the organic molecule is attached to metal atom by four coordinate linkage.



(c) Two covalent and two coordinating group :-

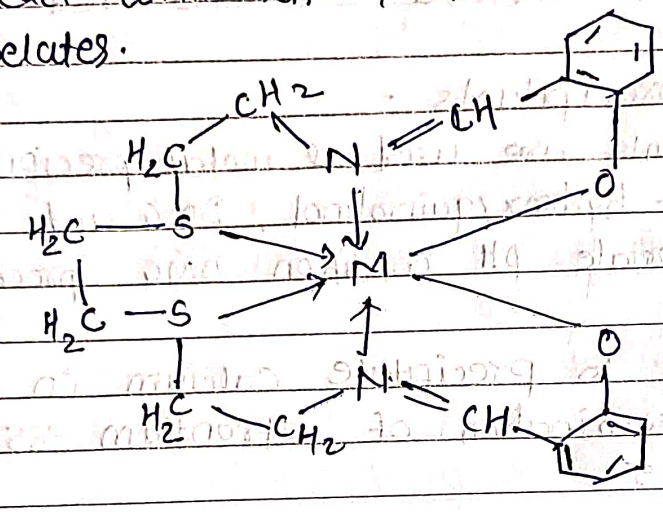


Rubeanic acid (dithio oxamide) combines with Cu^{2+} to form such type of complexes.

4. Hexadentate chelate group :-

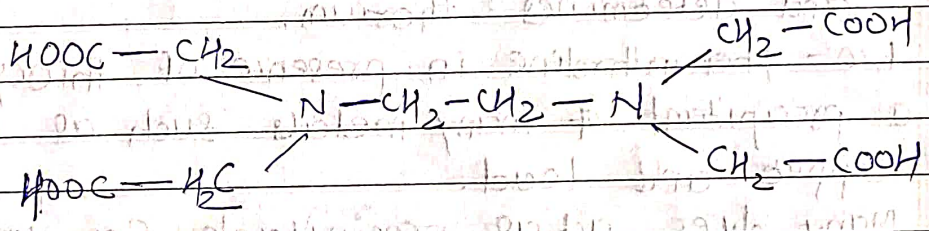
(a) Two acidic and four coordinating group :-

1,8 - bis - salicylidineamino - 3,6 - dithiooctane react with Zn^{2+}, Ni^{2+} or Co^{2+} ion to form chelates.

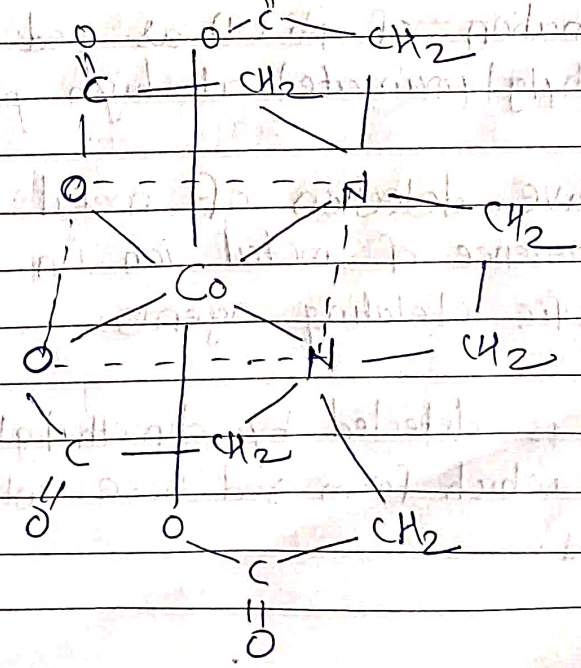


(b) Four acidic and two coordinating group :-

EDTA reacts with number of metal ion to form chelates. The structure of EDTA and its complex is is



Ethylene Diamine tetra acetic acid (EDTA) complex :-



Application of chelates in Analytical chemistry

Chelating agents are of increasing importance in analytical chemistry. Some principle applications of chelates are described here.

(a) As metal precipitants :
Chelating agents are used as metal precipitents.
Example : 8- hydroxyquinolinol, DMG and oxalates.

(i) Under appropriate pH condition DMG precipitate only nickel.

(ii) oxalate used to precipitate calcium in a radio chemical determination of strontium -85 and Calcium - 45.

(iii) The tungusten is gravimetrically estimated by 8- quinolinol.

(iv) Many carboxylic acid chelates used to precipitate variety of cations.
Eg : dihydroxy maleic acid used as precipitant and determines thorium.

(v) 1,10- phenanthroline in presence of thiocyanate, is a precipitant of many metals such as nickel, cobalt copper and lead.

(vi) Many dyes act as precipitants for variety of metal cations.
Eg : Estimation of Ni (II) as red coloured bis (dimethylglyoximate) at high pH.

(b) Qualitative detection of metal ions :
The presence of metal ion in sol^n can be detected by specific chelating agents.
Eg :-

(i) Ni (II) is detected by dimethyl-glyoxime in alkaline medium, which form red rose coloured chelate compound.

(ii) Co (II) of same gp can be detected by use of thiocyanate chelating agent. The complex form is blue in colour.

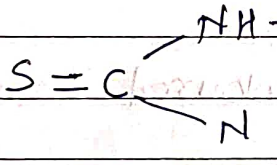
(iii) Copper ion are detected by formation of its blue coloured complex with ammonia. ferric ions are found to form blood red hexakis (isothiocyanate) iron (III).

© Application in qualitative analysis :
Spot test for basic radicals :-

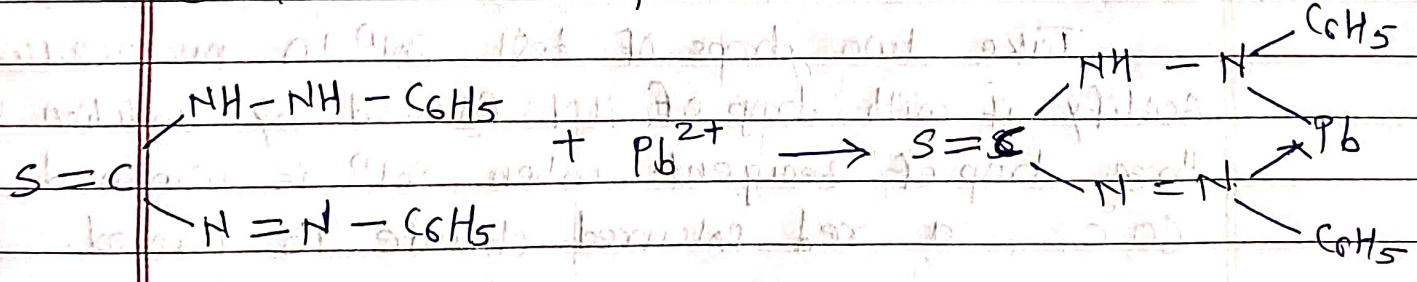
Chelating agents forms coloured chelates with specific metal ions (basic radicals). hence they are useful in qualitative determination of basic radicals.

(i) Spot test for Group I (Pb^{2+}, Hg^{2+} & Ag^{+}) :

Eg :- Test for Pb^{2+} : chelating agent used is



Take two drops of test soln in semimicro test tube. Add few crystals of KCN followed by two drops of reagent. If the green colour of reagent changes to red, it contain Pb^{2+}.

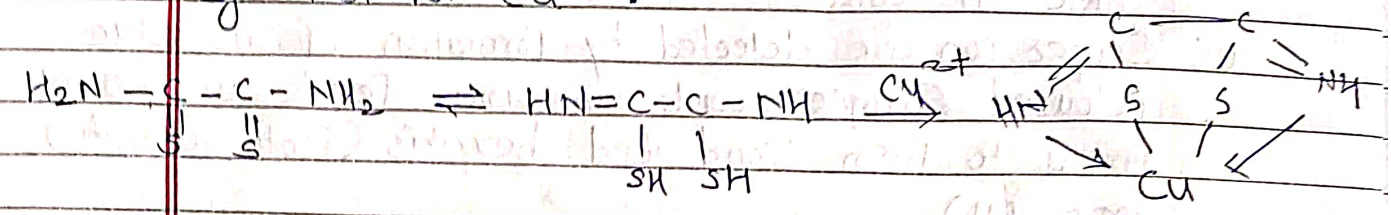


(Green) (Red)

Dithizone — Lead complex of dithizone.

(ii) Spot test of group II A (Hg^{2+}, Bi^{3+}, Cu^{2+} & Cd^{2+})

Eg: Test for Cu^{2+}:

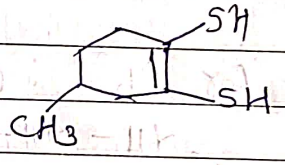


Take a drop of test solution in semimicrotest tube. Neutralise it with a drop of NaOH solution followed by two drops of acetic acid and drop of rubeanic acid which is a reagent. A green black ppt of Cu^{2+} ion is obtained.

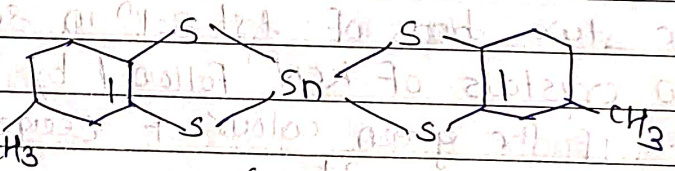
(iii) Spot test for group II B (As^{3+}, Sb^{3+} & Sn^{2+}) :-

Eg: Test for Sn^{2+} :

Chelating agent is



This chelate form red coloured complex with Sn^{2+} ion as follows.



(Red colour)

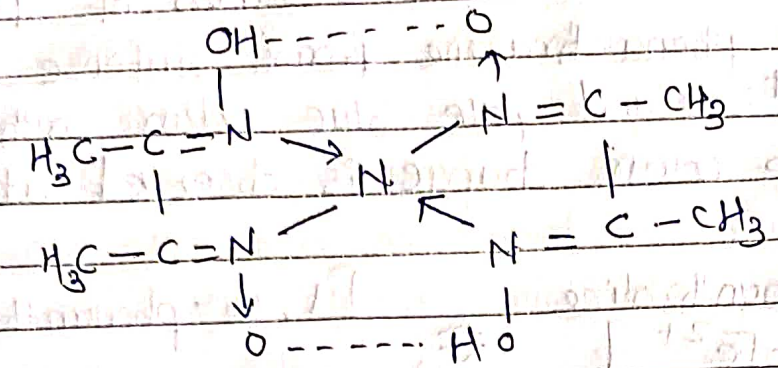
Take two drops of test soln in microcrucible. Acidify it with drop of HCl followed by addition of three drop of reagent. when soln is warmed to 60°C, a red coloured chelate is formed.

(d) Application in Gravimetric analysis :-

In gravimetric analysis metal like K^+, Ni^{2+}, Al^{3+}, Cu^{2+}, Zn^{2+} etc are determined by using different complexing agents.

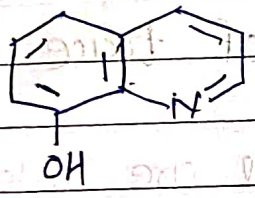
Example :

① Gravimetric estimation of Ni^{2+} ion by using dimethyl glyoxime as a complexing or chelating agent.

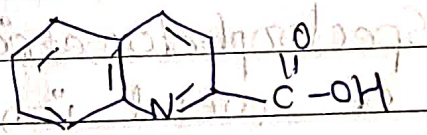


Ni - DMG complex (Red)

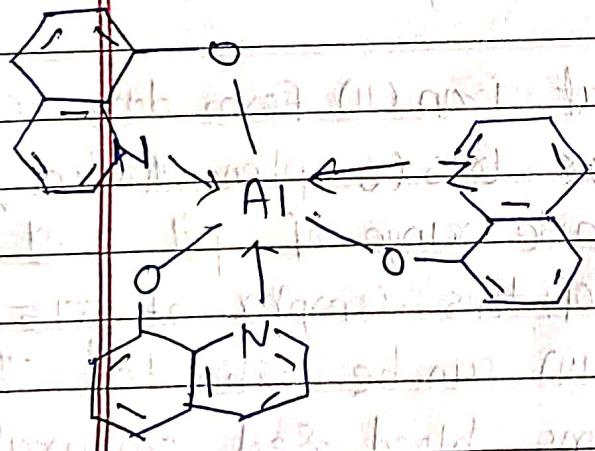
② 8 - Hydroxy quinoline is used as the complexing agent for determination of Al^{3+}, Mg^{2+}, Zn^{2+} etc. Quinaldic acid is used for Cu^{2+}.

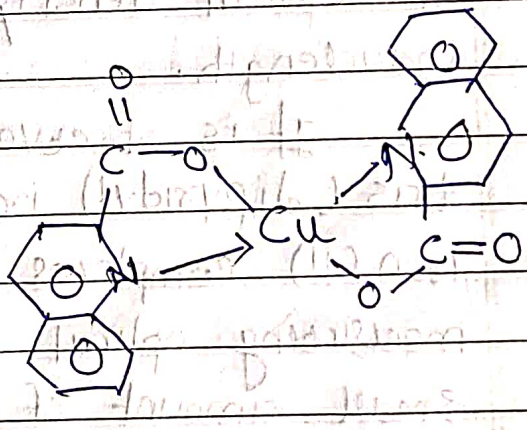


8-hydroxy quinoline (~~oxine~~) (oxine)



Quinaldic acid





(e) Application in volumetric analysis :-

(a) 1,10 - phenanthroline complex of iron may be used as redox indicator in redox titration of Fe^{2+} to Fe^{3+}. This 1,10 - phenanthroline forms intense red colour with Fe^{2+} ion and pale blue colour with Fe^{3+}. This sharp colour change is observed at end point.

[1,10 - phenanthroline $-Fe^{2+}$] $\rightleftharpoons$ [1,10 - phenanthroline $-Fe^{3+}$]

Red colour complex — pale blue complex.

(b) The nitro derivative of 1,10 - phenanthroline becomes an excellent redox indicator for oxidation reaction with Ce(IV).

(f) Spectrophotometric estimation of trace quantities of metal ions :-

Many transition metal complexes are intensely coloured and show high absorption. By using this property some metal ion can be determined from measurement of optical density data of complex at optimum wavelength.

It is observed that iron (II) form dark red tris (dipyridyl) iron (II) or tris (o - phenanthroline) iron (II) complexes over wide range of pH 2-9. By measuring optical density of this complex at 515 mμ small amount of iron (III) can be estimated. The soln of iron (III) ion forms blood red colouration when mixed with excess of thiocyanate soln in acidic medium. The complex formed is $[Fe(SCN)_6]^{3-}$ for this also, optical density measurement can be applied.

Besides these applications, Chelates have application in several fields like industrial, in biological system and as drugs.

Stability of Chelates :-

The stability of chelates can be explained on the basis of following factors.

A) Basic strength of ligand :

The stability of complex depends upon the tendency of ligands to donate electron pairs to CM I. This tendency increases with increase in basic strength of ligands. Higher is basic strength of ligand, greater is tendency of ligand to form stable metal complexes.

Eg : ① NH_3 is more basic than H_2O. So NH_3 form more stable complexes than H_2O with same metal ion.

② F^- should form more stable complexes than Cl^-, Br^- & I^-.

B) The nature of donar atom in ~~chelating~~ chelating ligand :

The donor atoms of low polarizability and high electronegativity like N, O, F etc can form more stable chelates than that of high polarizability & low E.N. like P, Cl, Br, I etc.

C) Number of metal chelate rings :

Larger the number of chelate rings, greater is the stability of complex, thus,

ⓐ chelated complex are more stable than similar complexes with unidentate ligand.

ⓑ Amongst the chelates, more the ring more is stability.

Eg :-

$[Ni(NH_3)_4]^{2+} < [Ni(en)_2]^{2+} < [Ni(trien)]^{2+}$

No chelate ring — Two chelate ring — Three chelate ring

→ increasing stability order.

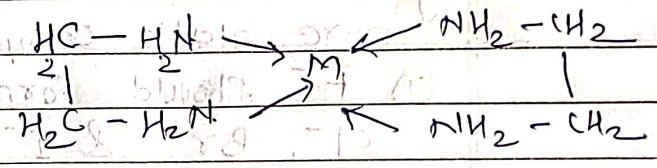
$[Ni(NH_3)_4]^{2+}$ is least stable as it has no chelate ring and $[Ni(trien)]^{2+}$ is most stable as it has three chelate rings.

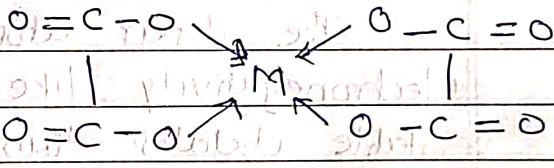
(3) Number of atoms in each ring :

Stability of complex also depend upon number of atom in each ring. The 5 or 6 membered ring have greater stability than 4 or more than 6 membered chelate ring. This is because 5 or 6 membered rings cause less strain to the molecule.

Staturated ligands gives more stable product with 5-membered chelate rings whereas unsaturated ligands gives more stable product with 6-membered chelate rings.

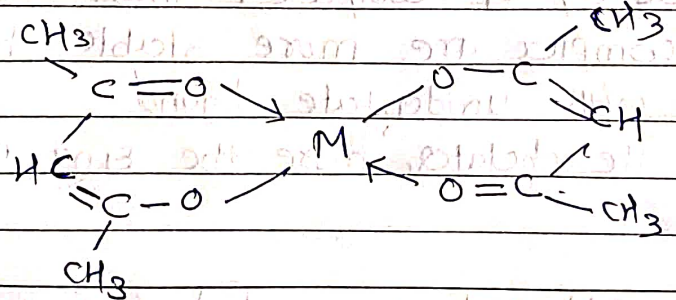
Eg: Complexes with 5-membered rings :





Chelates with saturated five member chelate ring

Complex with 6-membered rings



Acetylacetonato chelate

chelate with unsaturated six membered chelate ring.

(E) Steric effect :-

When bulky group is present on chelate, it cause mutual repulsion among them. This result in ~~weakening~~ weakening of M-L bond & therefore stability of chelates decreases.

Thus steric effect decreases the stability of chelates.

Eg : Ni^{2+} complex with en is more stable than tetra derivative of en with Ni i.e, $(CH_3)_2N-CH_2-CH_2-N(CH_3)_2$.

(F) Entropy change (ΔS) or entropy effect :-

As the number of independent species increases, entropy is increases. This is because entropy is the measure of disorder.

A reaction resulting in increase in entropy is always favoured and gives stable product.

$$[Ni(H_2O)_6]^{2+} + 3en \longrightarrow [Ni(en)_3]^{2+} + 6H_2O$$

1 3 1 6

4 7

In above reaⁿ no. of independent species is increases and hence entropy increases.

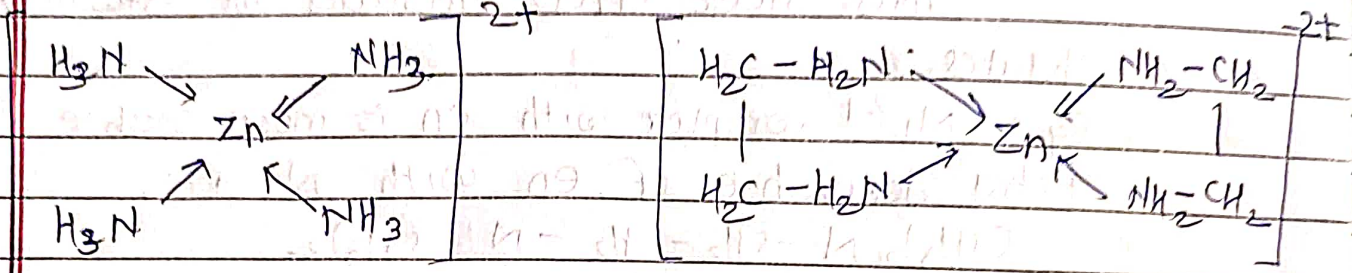
Thus, more is the increase in entropy during chelation process more is the stability of that chelate.

(G) Chelate effect :-

Complexes with chelating agent like 'en' is more stable than those with unidentate ligands like NH_3. This is because ~~heterocyclic~~ chelating agents form heterocyclic rings which are comparatively more difficult to break.

" The enhanced in stability of complex containing one or more chelate rings as compared to similar complex with unidentate ligands is termed as chelate effect."

Eg : $[Zn(en)_2]^{2+}$ is more stable than $[Zn(NH_3)_4]^{2+}$



less stable complex

$K = 2.88 \times 10^9$

more stable complex

$K = 117 \times 10^9$

In above eg when NH_3 ligand is replace by 'en' the stability constant K increase. This increase in value of K is due to chelate effect.

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