

B.Sc. Part-II Hons. Paper-III B (Inorganic Chemistry)

Group C: Uses of Organic reagents in Inorganic analysis

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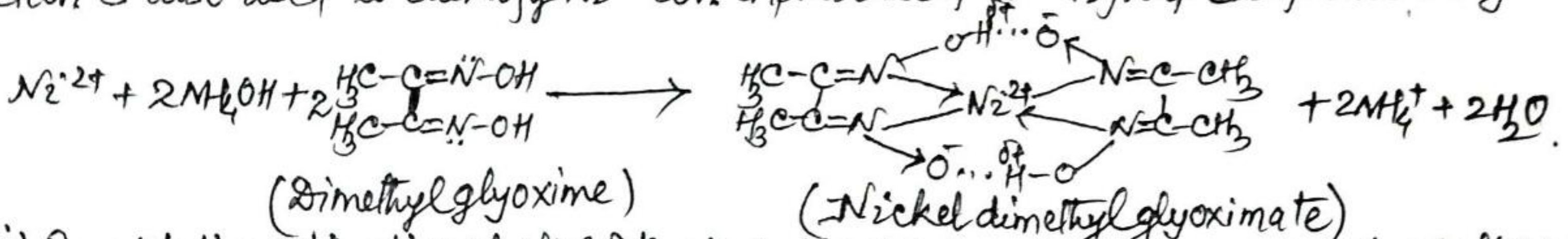
Unit-2  
I. Dimethyl glyoxime

It is an oxime of dimethyl glyoxal and has formula:  $\begin{array}{c} \text{HC-C=N-OH} \\ | \\ \text{H}_3\text{C-C=N-OH} \end{array}$

It is a colourless solid and insoluble in water.

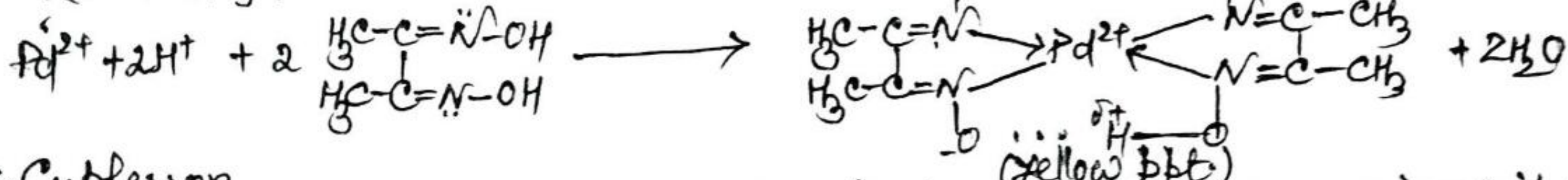
Applications: It is used in alcohol (1%) solution for identification of  $\text{Ni}^{2+}$  ion as well as quantitative estimation of Ni & Pd.

(i) Detection of  $\text{Ni}^{2+}$ :  $\text{Ni}^{2+}$  ion is detected by adding dimethyl glyoxime to ammoniacal solution of  $\text{Ni}^{2+}$  salt. A pinkish red precipitate of complex compound is formed. This reaction is also used to identify  $\text{Ni}^{2+}$  ion in presence of  $\text{Co}^{2+}$  in group-III B of salt analysis.




(ii) Quantitative estimation of Ni & Pd: Nickel (Ni) is precipitated as a complex salt on treatment with alcoholic dimethyl glyoxime solution in presence of ammonium hydroxide  $\text{pH} \approx 9$ . The precipitate is digested, filtered, washed till the free ions, dried at  $100-120^\circ\text{C}$  and weighed as such. From this percentage composition of  $\text{Ni}$  salt solution can be determined. Palladium (Pd) metal is estimated similarly by precipitating from acid solution ( $\text{HCl}/\text{H}_2\text{SO}_4$ )

Reaction of  $\text{Ni}^{2+}$  is same as above.

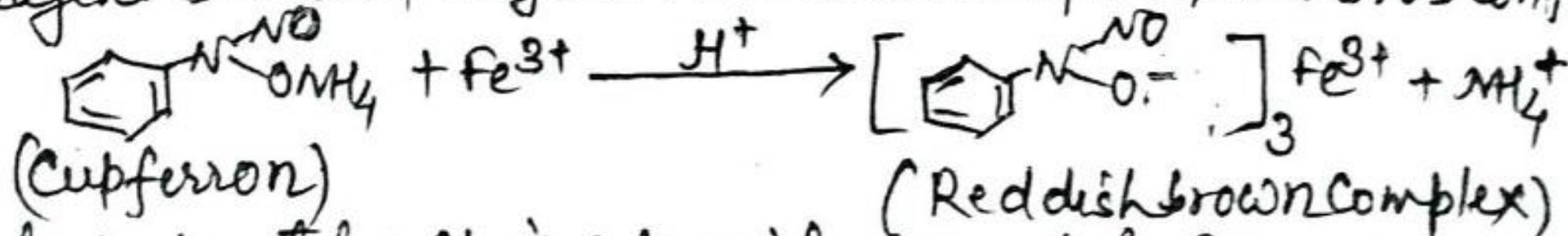


2. Cupferron

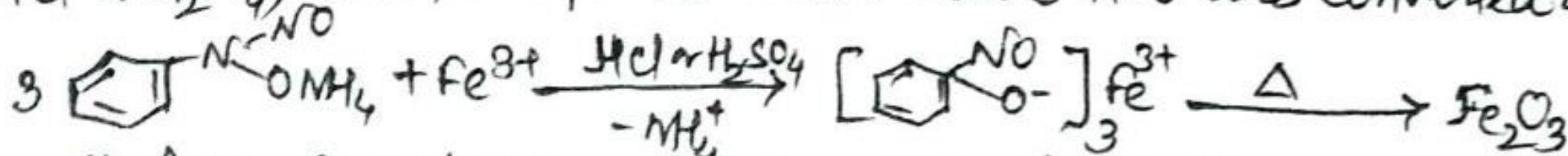
It is ammonium salt of nitrosophenylhydroxylamine, i.e., ammonium nitroso-phenylhydroxylamine. Its formula is 

Applications: It's 2% aqueous solution is used as reagent and always used freshly prepared reagent solution. It is mainly used in detection of  $\text{Fe}^{3+}$  and quantitative analysis of Fe, Ti & Zr. It is also used in spot test of  $\text{Fe}^{3+}$ .

(i) Detection of  $\text{Fe}^{3+}$ : To a drop of the salt ( $\text{Fe}^{3+}$ ) solution strongly acidified with HCl, a drop of the cupferron reagent is added to give reddish brown precipitate. This confirms the presence of  $\text{Fe}^{3+}$  (spot test).

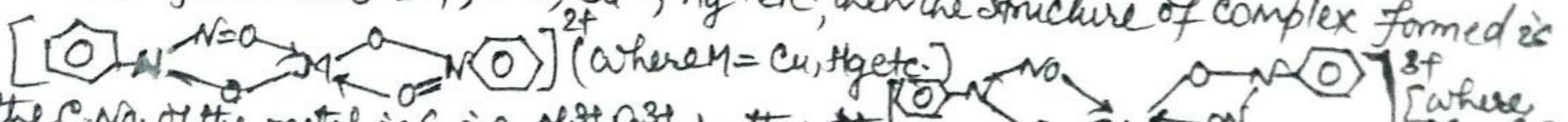


(ii) Quantitative analysis of metals: It is a specific reagent for Fe, and Fe can be estimated in presence of Cu, Ni, Cr, Mn etc. It gives sparingly soluble salt with Fe in which  $\text{NH}_4^+$  is replaced by one equivalent of the metal. The precipitation is done in strongly acidic medium ( $\text{HCl}$  or  $\text{H}_2\text{SO}_4$ ). The precipitate is not stable & so it is converted into oxide & weighed as such.

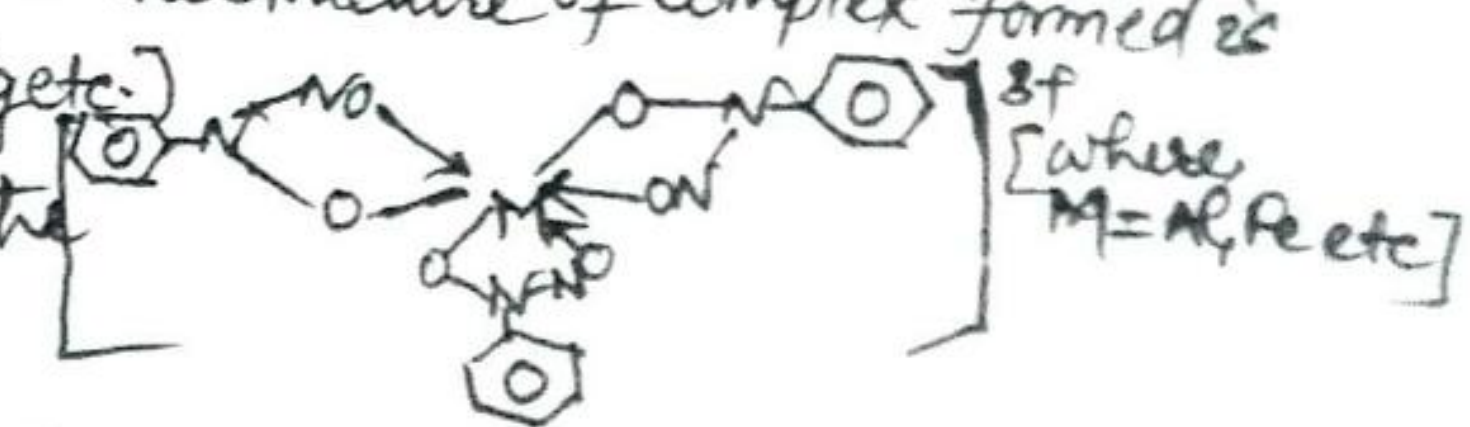


It form complex compounds with metals both in coordination no. 4 & 6.

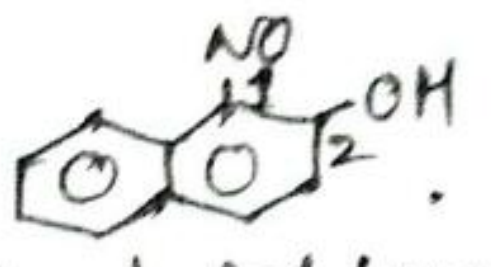
If the c.No. of the metal is 4, i.e.,  $\text{Cu}^{2+}$ ,  $\text{Hg}^{2+}$  etc, then the structure of complex formed is



If the c.No. of the metal is 6, i.e.,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$  etc, then the structure of complex compound formed is



### 3. $\alpha$ -Nitroso- $\beta$ -naphthol (1N2N)



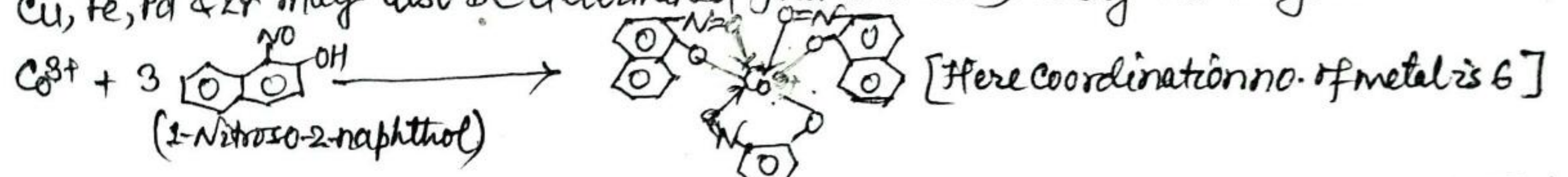
It is 1-nitroso, 2-hydroxy derivative of naphthalene. Its formula is Oc1ccc(cc1)[N+](=O)[O-].

It is orange-brown coloured crystalline solid, insoluble in water but soluble in alcohol, benzene etc.

Applications: It is used in detection of  $Co^{2+}$  &  $Ni^{2+}$  and quantitative estimation of Fe, Co, Ni, Cu, Mo, V, Pd, Zr etc. The principal use of this reagent is in the separation of Co from large amount of Ni after any ferron iron present has been removed.

(i) Detection of metal ions ( $Co^{2+}$ ,  $Ni^{2+}$ ): It is used in spot test of  $Co^{2+}$  &  $Ni^{2+}$ . To a drop of salt solution a drop of the reagent in 50% acetic acid aqueous solution was added when brownish red precipitate, soluble in HCl is obtained. This confirms presence of  $Co^{2+}$ , while formation of brown precipitate, soluble in HCl indicates the presence of  $Ni^{2+}$ .


(ii) Quantitative analysis of metals: It is mainly used in the estimation of Co. When cobalt salt is treated with reagent solution, a bulky brick red precipitate of Cobalt Complex compound is obtained. Cobalt can be estimated by gravimetric, volumetric and colorimetric methods. Cu, Fe, Pd & Zr may also be determined gravimetrically using this reagent.

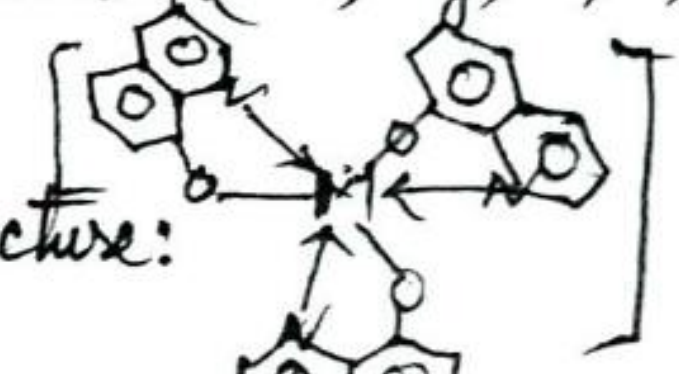


Cobalt can be indirectly determined volumetrically. Cobalt salt is first precipitated by  $\alpha$ -nitroso- $\beta$ -naphthol. The precipitate is then dissolved in acetone and titrated against standard solution of  $Mo^{3+}$  salt. Mo reduces the nitroso group to amino gr/compound. An excess of molybdenum solution is used, and residual molybdenum solution <sup>( $Mg^{3+}$ )</sup> determined by titrating with ferric amm. sulphate solution using methylene blue as indicator.

### 4. 8-Hydroxyquinoline or Oxine

Oxine is 8-hydroxyquinoline, i.e., hydroxy derivative of quinoline, a heterocyclic base. Its formula is Oc1ccc2ncncc2c1. It is buff coloured heterocyclic compound, insoluble in water but

soluble in alcohol, acetone and acetic acid. It forms a sparingly soluble coordination compds. with different metal ions in different C. Nos. If C.No. of the metal is 4 (i.e., Mg, Zn, Cu, Cd, Pb, Sr), then the complex compds have structure: 

If the C.No. of metal is 6 (i.e., Al, Fe, Bi, Ge), the complex compds have structure: 

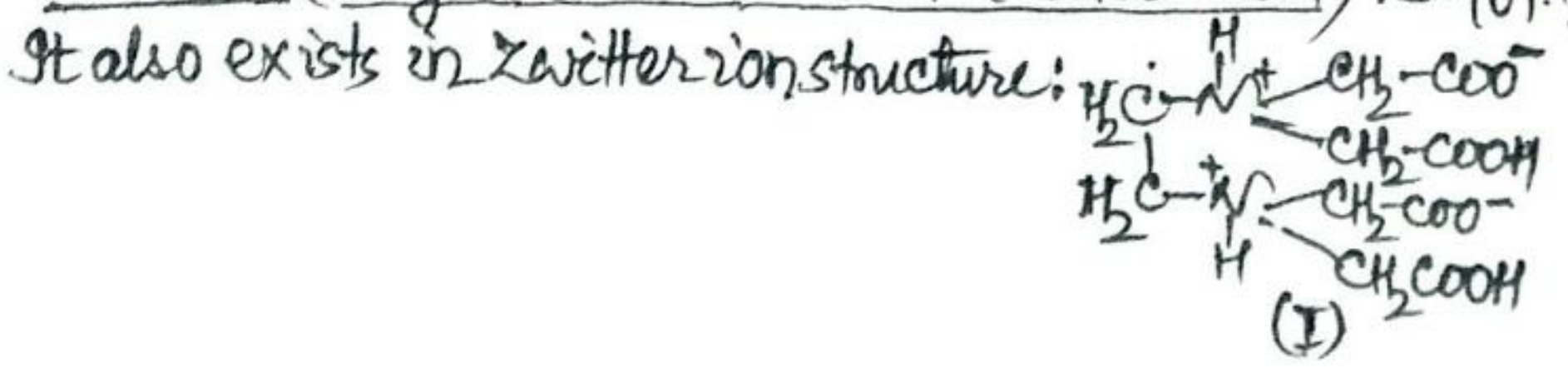
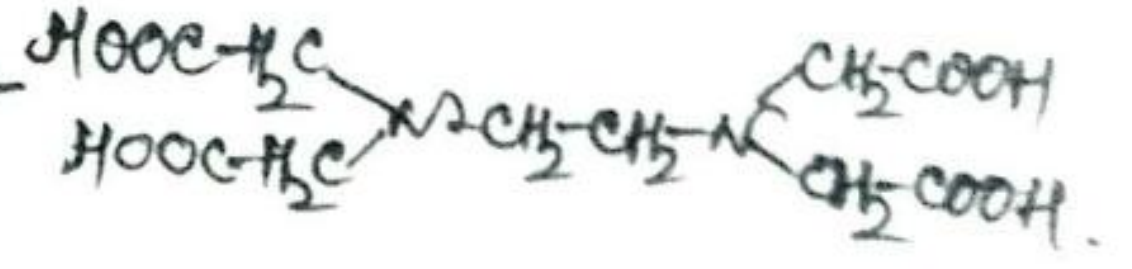
Metals like Ti, Zr form complexes with Oxine in C.No. 8.

Applications: This reagent is used in quantitative estimation (gravimetric & volumetric) of metal ions  $Mg^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Cd^{2+}$ ,  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Bi^{3+}$  etc.

(i) Gravimetric analysis: The reagent solution is added to a cold solution of the metal salt. A yellow colour of the liquid indicates that the reagent is present in excess. After the addition of the reagent the liquid is heated below  $70^{\circ}C$  to facilitate the coagulation of the ppt. The precipitated complex is filtered, washed, ignited to oxide and then weighed. Amount of metal can be known by calculation.

(ii) Volumetric analysis: Precipitate, obtained by the treatment of the reagent with salt solution, is dissolved in HCl solution. The solution is titrated with standard potassium bromate-bromide ( $KBr-KBrO_3$ ) solution.

### 5. EDTA (Ethylene diamine tetraacetic acid): Mol. formula -



(3)

It is a complex forming reagent of remarkable possibilities in analytical chemistry. It is hexadentate ligand (anion) and forms stable complexes with metal ions having no. 6 or 8. The complexes formed are of chelate (5 membered ring) type. For simplicity EDTA is given the formula  $H_4Y$ , the disodium salt  $Na_2H_2Y$  and yields the complex forming ion ( $H_2Y^{2-}$ ) in aqueous solution. 1:1 complexes are usually formed by EDTA with all metal ions.

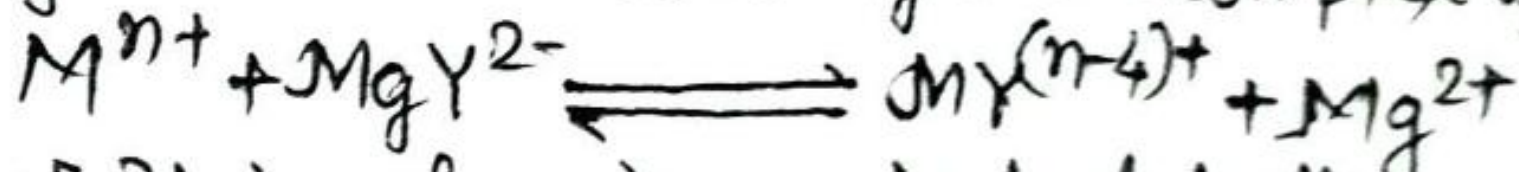
Applications: It is used as follows: (1) EDTA is an important masking agent. For example,  $Pb^{2+}$  is not an oxidising agent in its presence  $Fe^{3+}$  can be precipitated quantitatively as hydroxide by  $NH_4OH$  in presence of  $Al^{3+}$  or  $Fe^{3+}$ .

(2) EDTA is colourless but it intensifies the colour of some coloured ions like  $Cu^{2+}$  &  $Fe^{3+}$ . Hence, it is used in the determination of certain ion by colourimetry.

(ii) EDTA is a versatile reagent for titration of metal ions. This is done by number of methods:

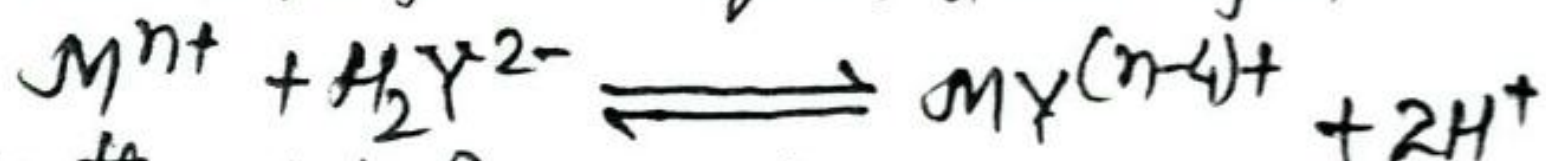
(a) Direct titration: The solution containing the metal ion to be determined is buffered (adding buffer solution) to the desired pH and titrated directly with the solution EDTA solution. In order to avoid the precipitation of the hydroxide of the metal, complexing agents, such as tartarate or citrate is added. At the end point the magnitude of the concentration of metal ion being determined, decreases sharply. It is accomplished by the change in colour of a metal indicator which responds to change in  $pM (-\log M^{n+})$ .

(b) Displacement or substitution titration: Such titration may be employed for metal ion that do not react with metal indicator, or for metal ions which form EDTA complexes that are more stable than those of other metals such as  $Mg$  &  $Ca$ . In such cases metal cation ( $M^{n+}$ ) to be determined may be titrated with  $Mg$  or  $Zn$  complex of EDTA, when the following reaction occurs:



The amount of  $Mg^{2+}$  or  $Zn^{2+}$  ion free is equivalent to the cation present and can be titrated with a standard solution of EDTA and a suitable metal indicator.

(c) Alkalimetric titration: When a solution of disodium ethylenediaminetetraacetic acetate ( $Na_2H_2Y$ ), is added to a solution containing metallic ions, complexes are formed with liberation of two equivalents of  $H^+$ .



The  $H^+$  ion thus set free can be titrated with a standard solution of an alkali using an acid-base indicator.

(d) Miscellaneous method: A number of anions have been determined indirectly with EDTA by reaction based upon precipitating as the silver halides, the latter dissolved in a solution of  $[Ni(CN)_4]^{2-}$  to form an equivalent amount of free  $Ni^{2+}$  ions, which is then titrated rapidly with standard EDTA solution using m. ox indicator.



The end