$[Fe(L-L)_3]^{3+} (almost colourless) \xrightarrow{Reduction} [Fe(L-L)_3]^{2+} (deep red coloured)$ (L-L = bpy or phen)

(i) SCN⁻ (thiocyanate): Fe³⁺ gives the red coloured complex [Fe(SCN)_x]^{(x-3)-}. This colour is due to ligand to metal charge transfer (LMCT).

Note: • Organic acids like oxalic acid, tartaric acid, etc form the **colourless complexes** with Fe³⁺. These complexes, *e.g.* [Fe(C₂O₄)₃]³⁻, [Fe(C₄H₆O₂)₃]³⁻, etc. are colourless and such organic chelating ligands (having the O-donors) interfere with the complexation by SCN⁻.

- Fluorides can discharge the red colour of [Fe(SCN)_x]^{(x-3)-} due to replacement of SCN⁻ by F⁻ leading to the colourless [FeF₆]³⁻ complex. In fact, Fe(III) being hard prefers F⁻ compared to SCN⁻.
- Hg²⁺ being softer than Fe³⁺ can snatch away the Fe(III)-bound soft SCN⁻/ligand to discharge the red colour. In fact, Hg(II) forms the **more stable** [Hg(SCN)₄]²⁻ complex.
- (ii) Ferron or 7-iodo-8-hydroxyquinoline-5-sulfonic acid:



The tris-chelate is green (LMCT) coloured.

(Note: Fe^{2+} does not react with ferroin under the condition).

(iii) With tiron (i.e. disodium 1,2 dihydroxybenzene-3,5-disulfonate).



(Red complex, LMCT)

Note: 1:1 Complex - blue; 1:2 Complex - violet; 1:3 Complex - red.

(iv) With hydroxamic acid, Fe(III) also gives the characteristic colour (LMCT).



(v) **Cupferron** (*i.e.* ammonium salt of nitrosophenylhydroxylamine)



In aqueous HCl solution, Fe^{3+} gives a reddish-brown (LMCT) precipitate of the complex, $[Fe\{C_6H_5N(NO)O\}_3]$

Ti^{iv}

(i) H₂O₂: In an aqueous sulfuric acid solution, Ti(IV) forms a peroxido complex of orange-yellow colour. The colour appears due to the ligand (*i.e.* O₂²⁻) to metal (*i.e.* Ti^{IV}) charge transfer band (*i.e.* LMCT band).

Because of the high charge/radius ratio of Ti(IV), the species $[Ti(OH_2)_6]^{4+}$ is extensively hydrolysed to produce the polymeric forms having the zigzag -Ti-O the matrix Ti-O chain. In acidic condition, the dilute solution of Ti(IV) may have the predominant species Ti(O)(aq)²⁺ (titanyl cation) or Ti(OH)₂(aq)²⁺.

$$\mathrm{Ti}(\mathrm{IV}) \xrightarrow{\mathrm{H}_{2}\mathrm{O}, \mathrm{H}^{+}} \left[\mathrm{Ti}(\mathrm{OH}) (\mathrm{OH}_{2})_{x} (\eta^{2} \cdot \mathrm{O}_{2}^{2^{-}}) \right]^{+} (\text{orange-yellow})$$

This colour formation reaction may be also utilised for H_2O_2 estimation. The colour is discharged by fluorides due to the formation of more stable $[TiF_6]^{2-}$ complex. Phosphate can also discharge the colour (*cf.* hard-hard interaction, HSAB theory). It may be noted that fluoride and phosphate cannot discharge the colour of the peroxido complex of V(V).

Note: There is a difference in opinion among the workers regarding the composition of the peroxido-complex of Ti(IV). Different species like $\left[\text{Ti}(\text{OH})(\text{OH}_2)_x(\eta^2 - \text{O}_2^{2^-})\right]^+$, $\left[\text{Ti}(\text{OH}_2)_x(\eta^2 - \text{O}_2^{2^-})\right]^{2^+}$, $\left[\text{Ti}(\eta^2 - \text{O}_2^{2^-})(\eta^2 - \text{SO}_4)_2\right]^{2^-}$, etc. have been proposed. The composition depends on pH. Probably at pH < 1, the **predominant species** is $\left[\text{Ti}(\text{OH})(\text{OH}_2)_x(\eta^2 - \text{O}_2^{2^-})\right]^+$. At higher pH, the **polymeric species** like $\left[(\eta^2 - \text{O}_2^{2^-})(\text{aq})\text{Ti} - \text{O} - \text{Ti}(\text{aq})(\eta^2 - \text{O}_2^{2^-})\right]^{2^+}$ may exist. This may give the yellow precipitate of $\text{Ti}(\text{O})(\eta^2 - \text{O}_2) \cdot n\text{H}_2\text{O}$ *i.e.* $\text{TiO}_3 \cdot n\text{H}_2\text{O}$.

(ii) **Chromotropic acid:** In an aqueous sulfuric acid media, Ti(IV) forms a red coloured (LMCT) complex with the ligand.



(i) α -Nitroso- β -naphthol: The ligand forms a green-yellow complex with ZrO²⁺. The ligating behaviour of the ligand has been pointed out in the case of Co(III) complex.

(v) Dioximes:



Dioximes are mainly used for Ni(II), Pd(II). In presence of the masking agent *edta*, selectivity of the dioxime may be increased.

(vi) Cupferron and neocupferron:



The reagent can precipitate Fe(III) (in a strong mineral acid solution) and Cu(II) (in a weakly acidic solution). *It explains the name.* Besides iron and copper, many other metal ions can be precipitated by these chelating ligands.

- (vii) α -Benzoinoxime (Cupron): Ph—CH—OH Ph—CH=NOH
- (viii) Arsenic acids: R-AsO(OH)₂

$$(R = Ph, C_3H_7, etc.): R - As - OH OH OH$$

Used for precipitating the quadrivalent metal ions like Sn^{IV}, Th^{IV}, Ti^{IV} and Zr^{IV} in presence of mineral acids.

11.1.5 Masking or Sequestring Agents in Analytical Chemistry

Masking agent: Many desired reactions are very much unselective. It needs the removal of the interfering substances which can be done without the physical separation, *i.e.* the interfering substances are chemically transformed into the species which cannot participate in the desired reaction. This process of removal of interference is described as **masking** which generally involves the complexation. The ligands used for this purpose are called the *masking or sequestering agents*.

Demasking: In this process, the masked substance can be brought back to its original form.

11.3.4 Complexation in the Rasching Process of Hydrazine Preparation

In this process, hydrazine is prepared by reacting Cl_2 , NaOH and NH₃. The overall reaction is: 2NaOH + Cl_2 + 2NH₃ \rightarrow N₂H₄ + 2NaCl + 2H₂O.

The reaction intermediate NH_2Cl can destroy the product N_2H_4 in the following reaction.

 $N_2H_4 + 2NH_2Cl \xrightarrow{M^{n+}} 2NH_4Cl + N_2$

The above reaction is catalyzed by the transition metal ions M^{n+} (e.g. Cu^{2+}). These are present at trace quantities with the raw materials used in the process. *Thus, the above undesirable side reaction is unavoidable.* To prevent this side reaction, a small amount of gelatin or albumin or glue is added to the reaction mixture. Such an organic matter bears many functional groups to act as the complexing sites to sequester the catalyzing metal ions. The sequestered metal ions cannot catalyze the process.

11.3.5 Complexation in Electroplating Process

For electroplating in the electrolytic bath, instead of free ion, complexed metal ions are generally used. It is done so, because of the following reasons.

(i) **Controlling of deposition potential:** Due to complexation, 2-3 different metal ions can be deposited at a particular decomposition potential. In free state, the deposition potentials of the metal ions are different but through complexation (having different magnitudes of stability constants) their deposition potentials can be made almost the same. For example, the standard reduction potentials (in aqueous solution) of the involved couples in brass deposition are:

$$E_{Cu^{2+}/Cu}^{0} = 0.34 \text{ V} > E_{Zn^{2+}/Zn}^{0} = -0.76 \text{ V}$$

Thus electrolysis of a solution containing both Cu^{2+} and Zn^{2+} will lead to deposition of copper on cathode first. In presence of CN^- , they will produce $[Cu(CN)_4]^{3-}$ and $[Zn(CN)_4]^{2-}$ complexes where the stability constant of $[Cu(CN)_4]^{3-}$ is much higher than that of $[Zn(CN)_4]^{2-}$. Consequently, their reduction potentials becomes comparable, *i.e.*

$$E^{0}_{\left[Cu(CN)_{4}\right]^{3^{-}}/Cu} \approx E^{0}_{\left[Zn(CN)_{4}\right]^{3^{-}}/Zn}$$

This allows the simultaneous deposition of copper and zinc. The details of **simultaneous deposition** of copper and zinc are discussed in Sec. 16.4.4, Vol. 3.

(ii) **Deposition of fine grain:** To have a fine grain of deposit, concentration of the free metal ion to be deposited should be reduced to a small extent. In presence of a complexing agent in the electrolytic bath, concentration of free metal ion is reduced to a significant extent. This allows the deposition of fine grain. In fact, for electrodeposition of copper, silver, gold and cadmium, KCN is used as the complexing agent.

$$M^{2+} + 4CN^{-} \Rightarrow [M(CN)_4]^{2-}, M = Zn, Cd.$$

 $Au^+ + 2CN^- \Rightarrow [Au(CN)_2]^-$

 $Cu^{2+} \xrightarrow{CN^{-}} (CN)_{2} + [Cu(CN)_{4}]^{3-}$, (reduction followed by complexation).

Note: For deposition of copper, the object to be plated is made the cathode and a copper rod is used as the anode. During the electrolysis, in presence of excess CN^- , the following reactions occur.

Anode:
$$Cu + 4CN^{-} \longrightarrow [Cu(CN)_4]^{3-} + e$$

Cathode: $[Cu(CN)_4]^{3-} \longrightarrow Cu + 4CN^{-} - e$