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## Transition Metal Nitrosyls :—

Transition metal nitrosyls are complexes that contain nitric oxide (NO) bonded to a transition metal. Many kinds of nitrosyl complexes are known which vary both in structure and coligands. Only few complexes are known which have only (NO) as ligand e.g $Fe(NO)_4$, $Co(CNO)_3$ and $Ru(CO)_9$. Most of metal nitrosyls occure as mixed ligand complexes in conjugation with other $\pi$-bonding low oxidation state stabilising ligands (e.g carbonyl/ halides/ thio/ cyano) ~~nitrosyl are known~~ e.g $[M(NO)_2Cl_2]$, $Na[Fe(NO)_2S]$, $[Co(NO)_2(CO)_2]$ $[Fe(NO)_2I]_2$, ~~$Na_4[Fe(CN)_6]$~~ $Na_4[Fe(CN)_5NO]$ etc.

In these compounds nitrogen of the nitrosyl group is directly bonded to the atoms or ions. Nitric oxide is an odd electron molecule having an unpaired electron. It readily units with other elements by direct addition

to form nitrosyl compounds. Nitric oxide form nitrosyl compounds by the following three ways: Nitric oxide form nitrosyl compound by the following three ways:

(i) A positive ion $NO^+$ is formed due to the loss of an electron. The structure is

$$(:N \equiv O:)^+$$

(ii) A Negative ion $NO^-$ is formed due to the gain of an electron from electro positive metal. The structure of $NO^-$ is

$$[:\ddot{N}:\ddot{O}:]^- \text{ or } [:\ddot{N}=\ddot{O}:]^-$$

(iii) Nitric oxide also act as ~~electron~~ coordinating group by donating an electron pair

~~may~~ A coordinating nitric oxide may be $NO$, $NO^+$ or $NO^-$.

Preparation of transition metal nitrosyl

① The $Fe(NO)_4$, $Ru(NO)_4$ and $Co(CO)_3$ can be prepared by the action of nitric oxide on their carbonyl compounds.

$$Fe(CO)_5 + 4NO \rightarrow Fe(NO)_4 + 5CO$$

(2) The nitrosyl carbonyl complexes of cobalt and iron can be prepared by the action of nitric oxide on their polynuclear carbonyls.

$$Co_2(CO)_8 + 3NO \rightarrow 2Co(CO)_3NO + 2CO$$

$$[Fe(CO)_4]_3 + 6NO \rightarrow 3Fe(CO)_2(NO)_2 + Fe(CO)_5 + CO$$

3. Nitrosyl halides of cobalt and nickel can be prepared by the action of nitric oxide on cobalt halide or nickel halides.

$$CoX_2 + Co + 4NO \rightarrow 2[Co(NO)_2X]$$

$$CoI_2 + 2Fe + 4NO \rightarrow Co + [Fe(NO)_2I]_2$$

(4) When hexacyanoferrate II complex compound was treated with sodium nitrite ~~oxide~~ it gives sodiumnitroprusside. It is one of the important mixed ligand compound of nitrosyl.

$$Na_4[Fe(CN)_6] + NaNO_2 + H_2O \rightarrow Na_2[Fe(CN)_5NO] + NaCN + 2NaOH$$

~~Properties~~ →

(5) Iron nitrosyl halide react with alkali sulphide ~~to form~~ and alkyl halides to form dark red iron nitrosyl thio complex which is known as Roussin's salts.

$$[Fe(NO)_2I]_2 \xrightarrow[-KI]{K_2S} K_2[Fe(NO)_2S]_2$$

$$\downarrow 2CH_3Cl$$

$$2KCl + [Fe(NO)_2(SCH_3)]_2$$

Properties — Important Reactions :—

(i) Substitutio Reaction :— In metal carbonyl nitrosyls, $NO^+$ ions are more firmly attached with the metal ion than the CO groups. Therefore, when metal carbonyls nitrosyls are treated with π-bonding ligands like $PR_3$, CNR, Phen etc, it is only CO groups are replaced by these ligands.

$$Fe(CO)_2(NO)_2 + 2Phen \rightarrow Fe(Phen)_2(NO)_2 + 2C$$

(ii) Action of halogen :— Metal carbonyls nitrosy when treated with halogens gives metal nitrosyl halides.

$$2[Fe(CO)_2(NO)_2] + I_2 \rightarrow [Fe(NO)_2I]_2 + 4CO$$

(iii) Iron nitrosyl halide react with $K_2S$ and $CH_3Cl$ to form dark compound, known as Roussin's salts.

$$[Fe(NO)_2I]_2 \xrightarrow[-2KI]{K_2S} K_2[Fe(NO)_2S]_2$$

$$[Fe(NO)_2(SCH_3)]_2 + 2KCl \leftarrow + CH_3Cl$$

(iv) Sodium pentacyanonitrosyl ferrate II or sodium nitroprusside is a important compound of transition metal nitrosyl.

(a) when this compound added to the compound having sulphide ion a purple violet colour is produced which confirm the presence of shulphide ion

$$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5(NO)S]$$

violet purple colour

(b) Alkali sulphites give a rose red colour because of the formation of $Na_4[Fe(CN)_5(NO)S]$. This reaction can be used to distinguish sulphite from thiosulphates which donot gives this reactions.

(c) When this compound is treated with silver nitrate a flesh coloured compound is obtained.

$$2AgNO_3 + Na_2[Fe(CN)_5NO] \rightarrow Ag_2[Fe(CN)_5NO] + 2NaNO_3$$