

PGI - Sem-II

Subject → Chemistry

Paper → C-C - VI

Unit → IV

Dr. Kumud Kumari,  
Associate Professor,

Dept. of Chemistry,  
H.D. Jain college, Arz.

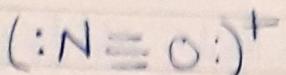
## Transition Metal Nitrosyls : —

Transition metal nitrosyls are complexes that contain nitric oxide ( $\text{NO}$ ) 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 ( $\text{NO}$ ) as ligand e.g.  $\text{Fe}(\text{NO})_4$ ,  $\text{Co}(\text{NO})_3$  and  $\text{Ru}(\text{CO})_9$ . Most of metal nitrosyls occur as mixed ligand complexes in conjugation with other  $\pi$ -bonding low oxidation state stabilizing ligands (e.g. carbonyl/ halides/ thio) cyano) nitrosyl are known e.g.  $[\text{M}(\text{NO})_2\text{Cl}_2]$ ,  $\text{Na}[\text{Fe}(\text{NO})_2\text{S}]$ ,  $[\text{Co}(\text{NO})_2(\text{CO})_2]$ ,  $[\text{Fe}(\text{NO})_2\text{I}]_2$ ,  $\text{Na}_4[\text{Fe}(\text{CN})_6]$ ,  $\text{Na}_4[\text{Fe}(\text{CN})_5\text{NO}]$  etc.

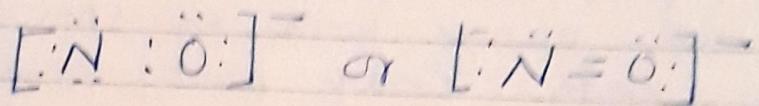
In these compounds nitrogen of the nitrosyl group is directly bonded to the atoms or ions. Nitric oxide is an odd electron molecule having an unpaired electron. It readily units with other elements by direct addition.

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  $\text{NO}^+$  is formed due to the loss of an electron. The structure is



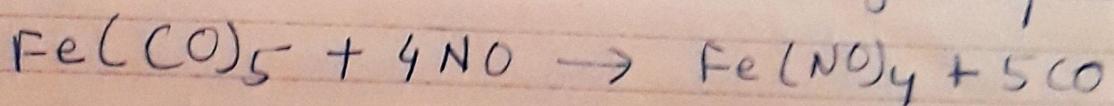
(ii) A negative ion  $\text{NO}^-$  is formed due to the gain of an electron from electropositive metal. The structure of  $\text{NO}^-$  is



(iii) Nitric oxide also act as electron coordinating group by donating an electron pair. A coordinating nitric oxide may be  $\text{NO}$ ,  $\text{NO}^+$  or  $\text{NO}^-$ .

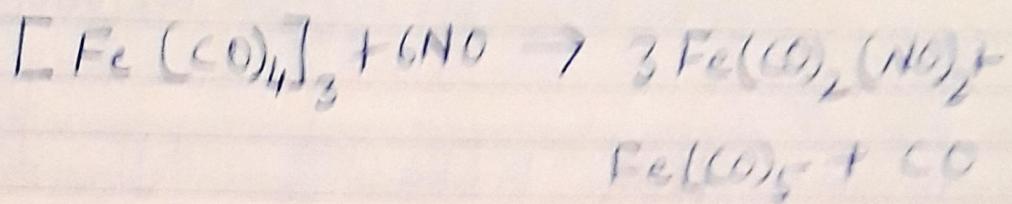
Preparation of transition metal nitrosyl

D The  $\text{Fe}(\text{NO})_4$ ,  $\text{Ru}(\text{NO})_4$  and  $\text{Co}(\text{CO})_4$  can be prepared by the action of nitric oxide on their carbonyl compounds.

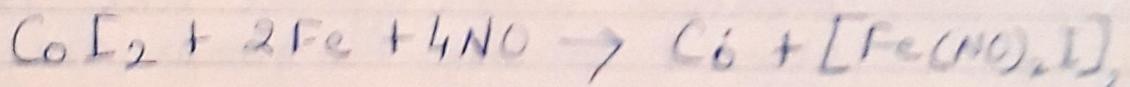
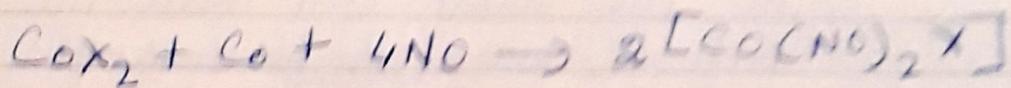


(3)

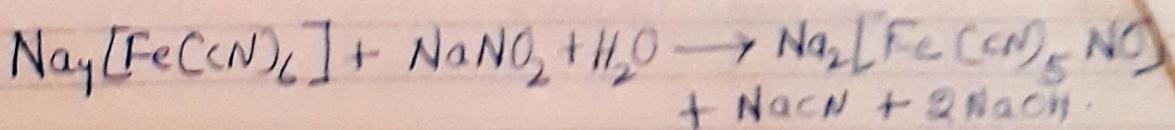
- (2) The nitrosyl carbonyl complexes of cobalt and iron can be prepared by the action of nitric oxide on their polynuclear carbonyls.



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



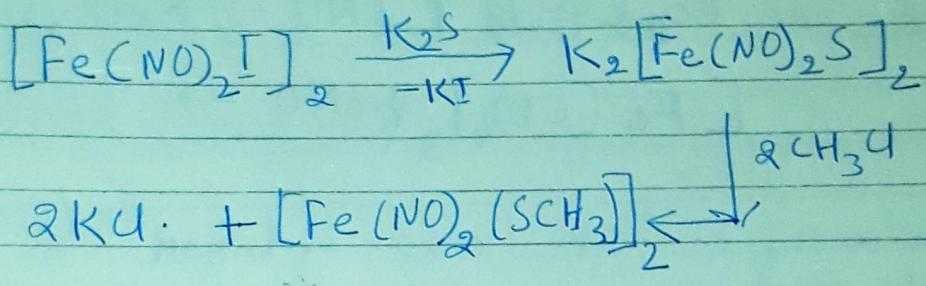
- (4) When hexacyanoferrate II complex compound was treated with <sup>sodium</sup> nitrite ~~oxide~~ it gives Sodiumnitroprusside. It is one of the important mixed ligand compound of nitrosyl.



(4)

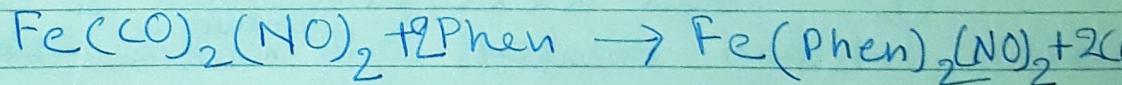
## Properties →

- (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.

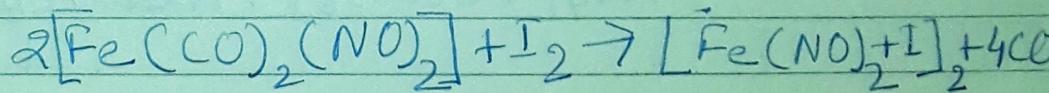


## Properties ← Important Reactions:-

- (i) Substitution Reaction :— In metal carbonyl nitrosyls,  $\text{NO}^+$  ions are more firmly attached with the metal ion than the CO groups. Therefore, when <sup>π</sup>-bonding metal carbonyls nitrosyls are treated with ligands like  $\text{PR}_3$ ,  $\text{CNR}$ , Phen etc, it is only CO groups are replaced by these ligands.

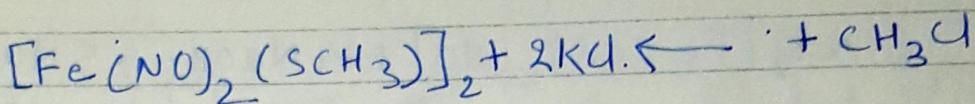
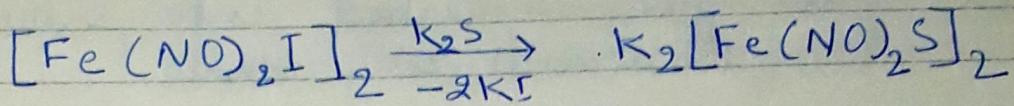


- (ii) Action of halogen :— Metal carbonyl nitrosyl when treated with halogens gives metal nitrosyl halides.



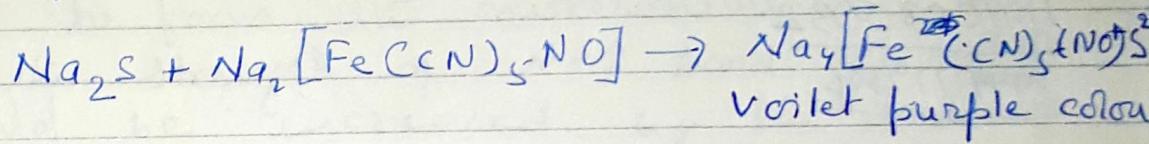
(5)

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



(iv) Sodium pentocyanonitrosoyl ferrate II or sodium nitroprusside is an important compound of transition metal nitrosoyl.

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



(b) Alkaliesulphites give a rose red colour because of the formation of  $Na_4[Fe(CN)_5NO]$ . This reaction can be used to distinguish sulphite from thiosulphates which do not gives this reactions.

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

