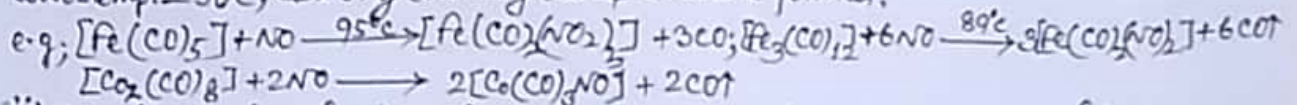


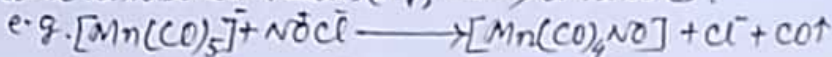
Compounds containing NO (nitrosyl gr.) as ligand, i.e., M-NO linkage are usually called metal nitrosyl complexes. They are metal- π complexes, and generally formed by transition metals. In most nitrosyl complexes, NO^+ (nitrosonium ion) present, which forms an $\text{M} \leftarrow \text{N} \equiv \text{O}^+$ bond by transferring 3 electrons to transition metal (M). A few complexes containing only nitrosyl (NO) as ligands, e.g., $[\text{Co}(\text{NO})_3]$, $[\text{Fe}(\text{NO})_4]$ etc. But many mixed carbonyl/halide/thio/cyano-nitrosyl complexes are known e.g., $[\text{Mn}(\text{CO})_5]$, $[\text{M}(\text{NO})_2\text{Cl}_2]$, $\text{Na}[\text{Fe}(\text{NO})_2\text{S}]$, $[\text{Co}(\text{NO})(\text{NH}_3)_2]^+$, $[\text{Fe}(\text{NO})(\text{CN})_5]$, $[\text{Ru}(\text{NO})\text{Cl}_5]^{2-}$ etc.

Preparation: Metal nitrosyl complexes are prepared by a number of methods:

1. From metal carbonyl: When metal carbonyl is treated with NO (nitric oxide) gas at lower temp. $\approx 90^\circ\text{C}$, carbonyl nitrosyl complexes are formed.

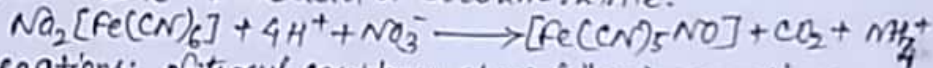


(ii) Recently, carbonyl-nitrosyl complexes prepared from metal carbonyl by treatment with nitrosonium salts (e.g., NOCl) or nitrites.



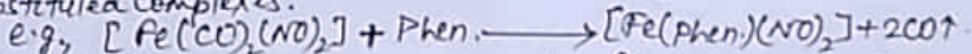
2. From metal halides: when metal halides is treated with nitric oxide (NO) in the presence of a suitable metal (as halogen acceptor), e.g., Zn, Co, Fe etc, metal nitrosyl halides are formed. $2\text{NiI}_2 + 12\text{Zn} + 8\text{NO} \longrightarrow 2[\text{Ni}(\text{NO})\text{I}] + 12\text{ZnI}_2$.

3. Specific method: Sodium nitroprusside is prepared by treating sodium hexacyano ferrate (II) with conc. nitric acid or sodium nitrite.

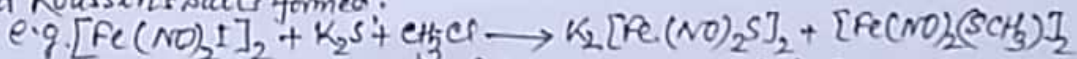


Important Reactions: Nitrosyl complexes show following reactions:

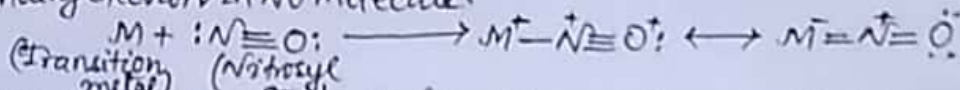
1. Substitution reactions: Metal carbonyl-nitrosyl complexes, NO^+ (ligands) are more firmly bonded than carbonyl (CO) ligands. When such complexes treated with ligands like phenanthroline, PR_3 , CNR etc., only CO ligands are substituted giving substituted complexes.



2. Formation of Roussin's salts: metal nitrosyl halide reacts with potassium sulphide (K_2S) and chloromethane (CH_3Cl), a dark red colour compound, $\text{K}_2[\text{Fe}(\text{NO})_2\text{S}]_2$ & $[\text{Fe}(\text{NO})_2(\text{SCH}_3)]_2$ called Roussin's salts formed.



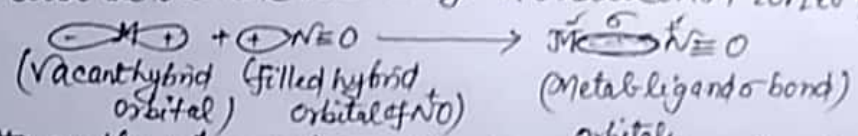
Structure & Bonding: Most nitrosyl ligands appear to be linear ($\text{N} \equiv \text{O}$), consistent with the sp hybridisation of N-atom. A few cases of bridging bent NO ligand (NO) are known. A bent nitrosyl is an analogue of an organic nitroso group in $\text{Cl-N}=\text{O}$, where the N-atom can be sp^2 hybridised with a lone pair. Due to presence of lone pair, nitrosyl group is bent. A linear nitrosyl ligand ($\text{M}-\text{N} \equiv \text{O}$) is regarded as a three-electron donor and a bent nitrosyl as a one electron donor. Linear nitrosyl includes the non-bonding electron pair on N-atom and the unpaired antibonding electron in NO molecule.



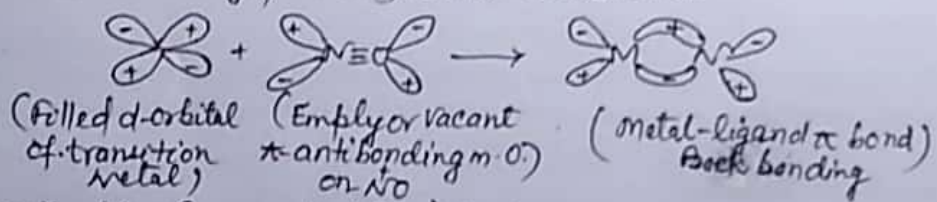
In oxidation state method, the ligand is viewed as a coordinated nitrosyl ion (NO^+) when linear and a coordinated NO when bent, two electrons donor in both cases.

(2)

On the basis of MOT, the hybrid orbital on nitrogen containing a lone pair, z^2 e, $(sp)^2 N_2$ overlaps with the suitable vacant hybrid orbital on M^+ ion to form $ON^+ \rightarrow M \sigma$ bond.



Now, the empty π_z^* or π_y^* (antibonding π orbitals) molecular orbitals can overlap with the filled d-orbitals to form $M^+ \rightarrow NO \pi$ -bond, z^2 e, back bonding transfers, some electronic charge/cloud from M^+ to NO ions.



The ν_{NO} vibrations frequencies (ν_{NO}) for linear $M-N \equiv O$ groups verify the idea of extensive metal to nitrogen π -bonding leading to appreciable population of π^* orbitals. The infrared frequencies in the range $1800-1900 \text{ cm}^{-1}$ characteristic of linear MNO groups in metal nitrosyl complexes having zero/small charge.

In linear metal nitrosyls, there is short $M-N$ bond (173.8 pm) indicating appreciable π -bonding as seen in metal carbonyls. In the bent metal nitrosyls, a relatively long, essentially σ -only $M-N$ bond (185.9 pm) is present. It should be expected that the $N-O$ bond of a bent nitrosyl would be longer than of a linear nitrosyl.

Cobalt nitrosyl $[Co(NO)_3]$ shows two $N-O$ stretching frequencies (ν_{NO}), it must be pyramidal rather than planar but the detailed structure not known. However, $[Co(NH_3)_5(NO)]^{2+}$ contains nitrosyl as NO^- (bent) shown by a very low $N-O$ stretching frequency of 1170 cm^{-1} and a long $N-O$ bond.