

Class - P.G. Sem II

Subject - Chemistry

Paper - CC-VI

Unit - II

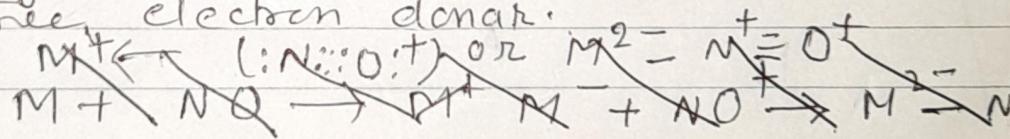
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## Structure Of Transition Metal Nitrosyls:-

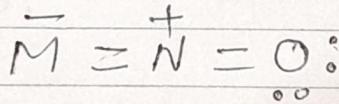
In metal nitrosyls nitric oxide is bonded to the metal centre. There various kind of nitrosyl complexes which vary in respect of coligand, structure and nature of bonding. Nitric oxide ( $\text{NO}$ ) has an additional electron in antibonding  $\pi$  molecular orbital, which may be readily lost to form the nitrosonium ion  $\text{NO}^+$ .

So the strength of N-O bond in  $\text{NO}$  should be increased by the loss of the antibonding electron. It is also confirmed by the increase in the N-O stretching frequency from  $1878\text{ cm}^{-1}$  in free nitric oxide to  $2200 - 2300\text{ cm}^{-1}$  in nitrosonium salts. Thus the majority of metal nitrosyls are formed by donation from the nitrosonium ion ( $\text{NO}^+$ ) to the metal atom with the  $M-\text{N}$  bonding. So  $\text{NO}$  must be considered a three electron donor.



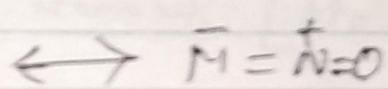
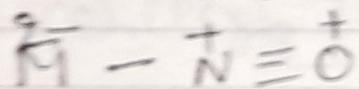
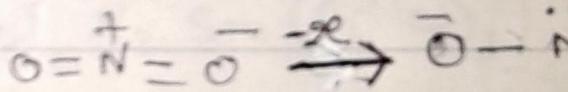
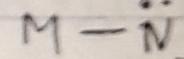
(2)

In  $\text{NO}$  both atoms are potential donor but the nitrogen atom coordinates preferentially, avoiding a large formal positive charge on the more electronegative oxygen atom. Although most nitrosyl ligands are linear, with  $\text{sp}$  hybridisation of nitrogen but some case of bent nitrosyls are also known. A bent nitrosyl ligand is an analogue of an organic nitroso group or the  $\text{NO}$  group in  $\text{Cl}-\text{N}=\text{O}$ . In bent nitrosyl the nitrogen is  $\text{sp}^2$  hybridised and bear a lone pair that cause the nitrosyl group to be bent. In the neutral atom counting method electron counting, a linear nitrosyl ligand is regarded as a three electron donor and a bent nitrosyl ligand is regarded as a one electron donor. In linear case the count includes the nonbonding electron pair on nitrogen as well as the unpaired antibonding electron in  $\text{NO}$ .



(3)

In the oxidation state method, the ligand is viewed as a coordinated nitroso form  $\text{NO}^+$  when linear and a coordinated  $\text{NO}^-$  when bent; it is two electron donor in both forms. In bent nitroso the pair of electrons will be forced to reside in an orbital on the nitrogen atom and in linear nitroso there is a low-lying metal based molecular orbital available to it. If there are available nonbonding MO's on the metal, the electrons pair can reside there and allow the nitrogen to function as an  $\text{sp}$  & donor with  $\pi$  back bonding or  $\pi$  acceptor. On the other hand if all the low lying orbitals on the metals are already filled, the pair of electrons must occupy an essentially nonbonding orbital on the nitrogen, requiring trigonal hybridisation and a bent system.

Linear  $\text{sp}$  hybridisationbent  $\text{sp}^2$  hybrid

(4)

In the linear nitrosyls there is a short metal ligand bond indicating substantial  $\pi$  bonding. The bent system show a relatively long  $\sigma$ -metal-nitrogen bond. Therefore the N-O bond also longer in case of bent nitrosyls than linear one.