

METAL NITROSYLS

Nitrosyls are the compounds in which the nitrogen of the nitrosyl group is directly bonded to the atoms or ions.

or

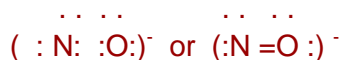
The compounds containing nitric oxide group are called nitrosyl compounds.

- Nitric oxide molecule as such is an odd electron molecule having an unpaired electron.
- On account of its structure, it readily unites with other elements by direct addition to form nitrosyl compounds.
- Nitric oxide might form nitrosyl compounds by the following three ways:

(i) A positive ion, NO^+ , is formed due to the loss of an electron which then combines with atom or molecule. It may have the following structure :



(ii) A negative ion NO^- is formed due to the gain of an electron from some electropositive metal and it has probably the structure :



(iii) Nitric oxide may act as a co-ordinating group through the donation of an electron pair. Such behaviour might involve neutral molecule or NO^+ or NO^- group.

CLASSIFICATION

In terms of the above considerations, the nitrosyl compounds are classified as given below:

I. Simple Compounds Containing the NO^+ group :

Examples are:

- (i) NOHSO_4 and $(\text{NO})_2\text{S}_2\text{O}_7$,
- (ii) Nitrosyl Halides (NOX , where $\text{X} = \text{F, Cl, Br}$).
- (iii) NOCIO_4 , NOBF_4

(iv) $(\text{NO})_2\text{SeO}_4$, NOHSeO_4 .

(v) NOSCN .

(vi) $\text{NO}[\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]$

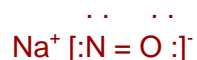
(vii) NOSbCl_6 , NOAsF_6 , $(\text{NO})_2\text{PtCl}_6$ and NONO_3 .

II Compounds containing NO^- Groups:

- The only example of this type is sodium nitrosyl.
- Sodium nitrosyl is prepared by the action of dry nitric oxide on sodium in liquid ammonia.



- Sodium nitrosyl is a white substance which is unstable.
- This compound is diamagnetic which clearly confirms the presence of NO -group.
- It is a white and unstable solid. Magnetic properties suggest the presence of the NO group.
- It is decomposed by water with the evolution of nitrous oxide and the formation of sodium hydroxide, sodium hyponitrite and traces of sodium nitrate.
- Its probable structure is :



- The bond angle is around 125° in this molecule.

III. Coordination Compounds or Metal Nitrosyls

- These are the compounds in which the nitrogen of the nitrosyl group is directly bonded to them atoms or ions. These compounds are also known as metal nitrosyls.
- Metal nitrosyls occur mostly as mixed ligand complexes in conjugation with other pi-bonding low oxidation state stabilising ligands.
- The properties and compositions of these compounds vary widely, therefore, it is best to consider them under the broad heading of coordination compounds.

- In metal nitrosyls or co-ordination compounds, the nitric oxide acts as a co-ordinating group through the donation of an electron pair to the metal atom or ion. Such behaviour might involve the neutral molecule or the NO^+ or NO^- group.

(1) Co-ordination compounds containing neutral nitric oxide molecule :

The co-ordination by neutral nitrosyl group is unlikely due to the lack of experimental evidences. Some of these are considered below :

(i) Iron pentacarbonyl carbonyl on reaction with nitric oxide forms volatile nitrosyl carbonyl $\text{Fe}(\text{NO})_2(\text{CO})_2$. The similarities of this compound with metallic carbonyl $[\text{Fe}(\text{CO})_5]$ suggest coordination by neutral nitric oxide molecules. As the neutral nitric oxide molecule contains one unpaired electron, it clearly suggests that $\text{Fe}(\text{NO})_2(\text{CO})_2$ must be paramagnetic but actually it is diamagnetic. Thus, this example clearly indicates that coordination by neutral nitric oxide molecule is unlikely.

(ii) If the neutral nitric oxide molecules were involved, they could be replaced by neutral molecules without any change in the compound type. When nitrosyl carbonyls are treated with pyridine, it replaced carbonyl group without affecting the nitrosyl groups. It confirms that coordination by neutral nitros group is unlikely

(2) Coordination compounds containing NO^- group :

In general, this type of coordination compounds is also unlikely because only positive evidence for this is $[\text{Co}(\text{NH}_3)_5\text{NO}]^+$ where cobalt (II) apparently transfers an electron to the NO group. There are two isomers of $[\text{Co}(\text{NH}_3)_5(\text{NO})]^{2+}$ red and black. The red isomer is dimeric, and the black isomer is monomeric. Actually this structure is reasonable in some ways but puzzling in others. This is a diamagnetic pink compound containing NO^- group

(3) Coordination compounds containing NO^+ group :

The evidence for the coordination compounds containing NO^+ group is more convincing. This nitric oxide cation NO^+ is similar to the neutral carbon monoxide molecule and the cyanide ion.



Corresponding similarities have been reported among compounds containing these materials. Examples are :



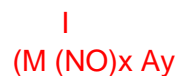
$K_3[Fe(CN)_5CO]$ and

$K_4[Fe(CN)_6]$

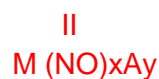
The co-ordinated nitrosyl compounds may be classified as:

(A) Nitrosyl carbonyls and related compounds

(B) Nitrosyl compounds of type



(C) Nitrosyl compounds of the type



(D) Nitrosyl compounds of the type



(E) Nitrosyl derivatives containing groups of the type



STRUCTURE OF NITROSYLS COORDINATION COMPOUNDS

If we compare the electronic structure of nitric oxide with carbon monoxide, it is observed that NO has an additional electrons in antibonding pi M.O. which may be readily lost to form the nitrosonium ion NO^+ . With the result, the strength of N-O bond in NO should be increased by the

loss of the antibonding electron. Actually, it has been confirmed by the increase in the N-O stretching frequency from 1878 cm^{-1} in free nitric oxide to $2200\text{--}2300\text{ cm}^{-1}$ in nitrosonium salts.

The additional electron present in π^*z molecular orbital of neutral nitric oxide can be supplied to metal atom thus increasing its effective number by one unit and neutral nitric oxide is itself converted into NO^+ ion. Then, this NO^+ ion is co-ordinated through nitrogen with the metal atom by donating its lone pair to the metal.

(i) Cobalt atom may increase its effective atomic number from 27 to 28 by accepting an additional electron from a neutral molecule of nitric oxide.



Cobalt anion may then combine with one NO^+ group and three carbon monoxide molecules to form stable compounds $\text{Co}(\text{NO})(\text{CO})_3$.



In this compound, the effective atomic number of cobalt is $27+1+2+6=36$ which is that of stable krypton gas.

(ii) Similarly, the formation of $\text{Fe}(\text{NO})_2(\text{CO})_2$ can be explained.

In 1934 Sidgwick and Bailey reported that the NO group is attached to the metallic atom by a link of two shared electrons; both being contributed by the nitrogen atom of nitric oxide group. Besides this, nitrogen atom loses its third electron to the metal, thereby, increasing its effective number by three.

The virtual accumulation of charge on the central atom favours strong π -bond formation with the attached groups.

Thus, the majority of metal nitrosyls are best regarded as being formed by donation from the nitrosonium ion to the metal atom with the M-O back-bonding in a manner entirely analogous to that in the M-C bond in carbonyl. In simple words. NO must be considered as a three-electron donor:



The infra-red and structural data clearly support the nitric oxide as three electron donor. Also, the structural studies of nitrosyls confirm that M-N-O groups are linear.

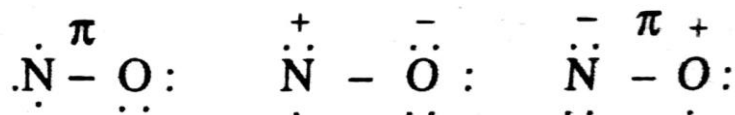
Since oxygen is more electronegative than nitrogen, it is nitrogen atom of NO^+ ion which coordinates to M^- ion to form the nitrosyl complexes.

In other words it means that the coordination of NO^+ ion to M^+ ion occurs through the lone pair of electrons residing in the hybrid orbital on N atom .

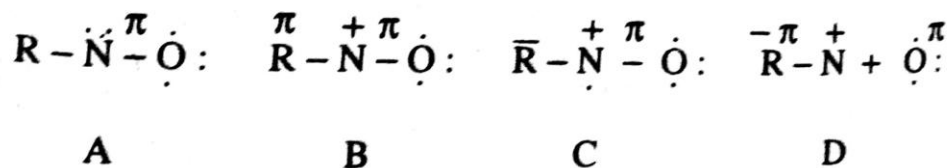
Although the concept of bonding involving three electrons accounts for the structure of many nitrosyl complexes, it suffers from the general criticism that an unlikely negative charge gets accumulated on the metal atoms.

An alternative is the four electron arrangement in which the metal acts as both as a donor and an acceptor.

The molecule of nitric oxide may be regarded as a resonance structure of the following form:



On the basis of the resonance structures of nitric oxide, the metallic nitrosyls may be formulated as follows:



In the above structures, R is one atom of the metal.

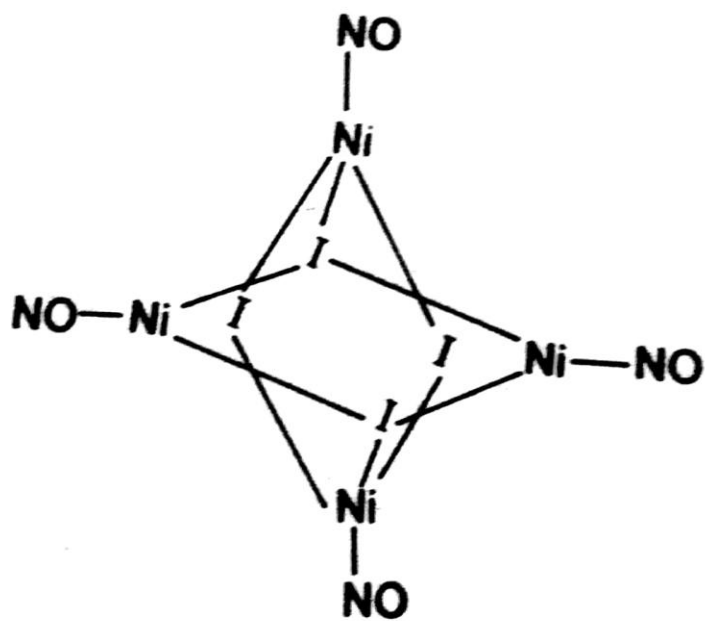
- (i) In configuration B, one electron from nitrogen atom gets transferred to some orbital of the metal other than two orbitals which are engaged in bonding the nitrogen atom to the metal.

(ii) In configuration C, the nitrogen donates a lone pair of electrons to the metal atom and thus a co-ionic bond is established. This configuration is paramagnetic due to an unpaired electron on nitrogen atom.

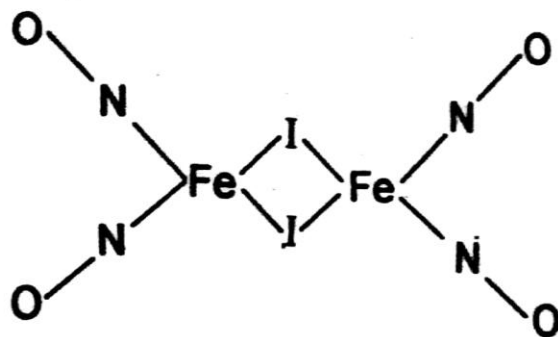
(iii) In configuration D, the unpaired electron of the nitrogen forms a pi-d bond with the metal

Structures of some important coordination compounds are as follows:

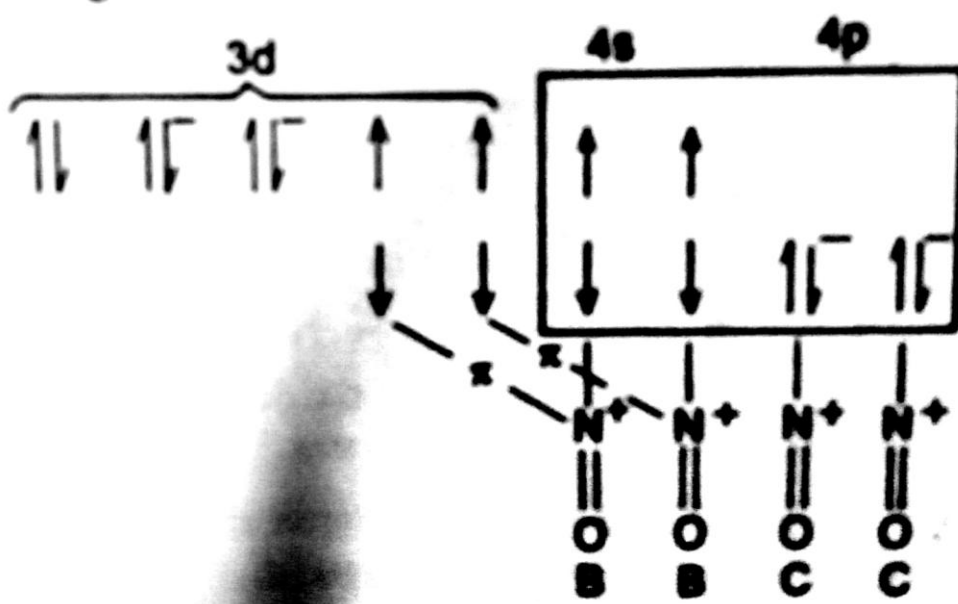
Configuration of [Ni(NO)]₄



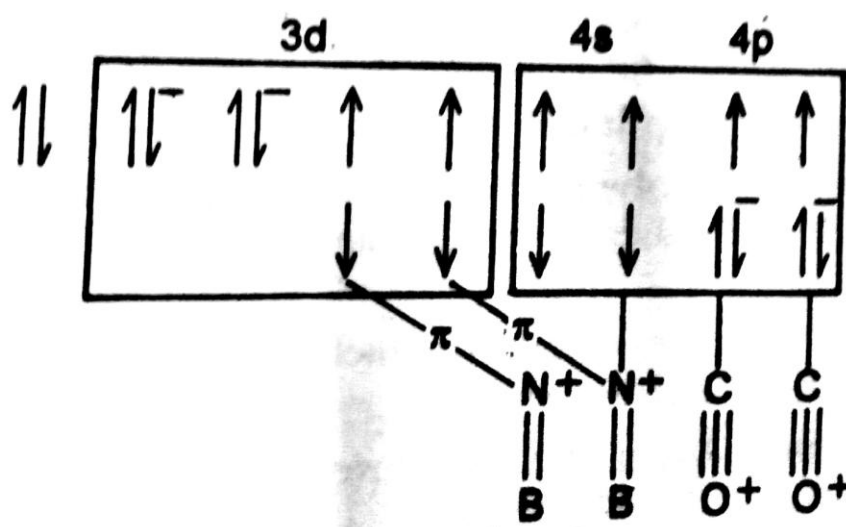
Configuration of $\text{Fe}(\text{NO})_2\text{I}$



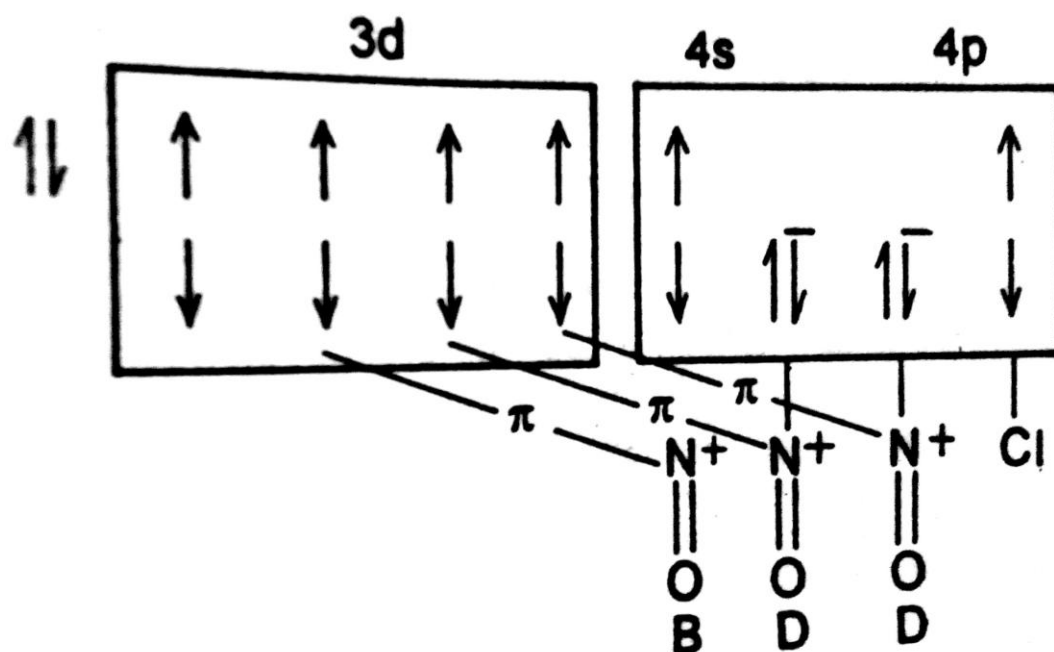
$\text{Fe}(\text{NO})_4$: Orbital diagram is given below



$\text{Fe}(\text{NO})_2(\text{CO})_2$: Its orbital diagram is



$\text{Fe}(\text{NO})_3\text{Cl}$: Its orbital diagram is



Effective atomic number (EAN) rule as applied to metallic nitrosyls :

Metallic nitrosyls also obey the EAN rule as demonstrated below for certain nitrosyls. In these cases NO is assumed to be a unipositive ion, NO^+ and hence acts as a two-electron donor. Metal atoms are, therefore, in negative oxidation state.



$$\text{Co}^- = 27e^- + 1e^- = 28e^-$$

$$3\text{CO} = 3 \times 2e^- = 6e^-$$

$$\text{NO}^+ = 1 \times 2e^- = 2e^-$$

$$[\text{Co}^-(\text{CO})_3(\text{NO}^+)] = 36e^- \text{ (Kr)}$$

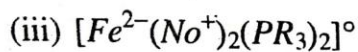


$$\text{Fe}^{2-} = 26e^- + 2e^- = 28e^-$$

$$2\text{CO} = 2 \times 2e^- = 4e^-$$

$$2\text{NO}^+ = 2 \times 2e^- = 4e^-$$

$$[\text{Fe}^{2-}(\text{CO})_2(\text{NO}^+)_2] = 36e^- \text{ (Kr)}$$



$$\text{Fe}^{2-} = 26e^- + 2e^- = 28e^-$$

$$2\text{NO}^+ = 2 \times 2e^- = 4e^-$$

$$2\text{PR}_3 = 2 \times 2e^- = 4e^-$$

$$[\text{Fe}^{2-}(\text{NO}^+)_2(\text{PR}_3)_2] = 36e^- \text{ (Kr)}$$



$$\text{Mn}^{3-} = 25e^- + 3e^- = 28e^-$$

$$\text{CO} = 1 \times 2e^- = 2e^-$$

$$3\text{NO}^+ = 3 \times 2e^- = 6e^-$$

$$[\text{Mn}^{3-}(\text{CO})(\text{NO}^+)_3] = 36e^- \text{ (Kr)}$$