➢ *6. Formation of Metal Carbonyl Nitrosyls or Metal Nitrosyls*

The metal carbonyl complexes react with nitrosyl ligand to form either metal carbonyl nitrosyls or metal nitrosyl complexes. For example:

$$Fe(CO)_5 + 2NO \rightarrow [Fe(CO)_2(NO)_2] + 3CO$$

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

$$Fe_3(CO)_{12} + 6NO \rightarrow 3[Co(CO)_2(NO)_2] + 6CO$$

$$Ni(CO)_4 + 4NO \rightarrow [Ni(NO)(NO)_2] + 4CO + N_2O$$

The displacement of carbonyl by the nitrosyl cation may be achieved using $[NO][BF_4]$ i.e nitrosyl tetrafluoroborate. On applying to the hexacarbonyls of tungsten and molybdenum, the NO binds to the metal. Some indirect methods involve the use of NO group from some other species, usually accompanied by oxidation and reduction processes. For instance, the brown ring test in which the nitric oxide ligand is actually supplied by the nitrate ion.

➢ *7. Disproportionation Reactions*

Many metal carbonyls show disproportionation reactions when exposed to some other coordinating ligands. For instance, $Fe(CO)_5$ reacts with amines to produce hexaaminoiron(II) tetracarbonylferrate(−II); or $Co_2(CO)_8$ reacts with amine to form Hexaamminecobalt(II) bis-tetracarbonylcobaltate(−I) as:

$$2Fe(CO)_5 + 6NH_3 \rightarrow [Fe(NH_3)_6]^{2+}[Fe(CO)_4]^{2-} + 6CO$$

$$Co_2(CO)_8 + 6NH_3 \rightarrow [Co(NH_3)_6][Co(CO)_4]_2$$

The driving force for the above two reactions can be understood in terms of the ease of formation of the carbonylate ions and the favourable coordination number for iron(II) involved. The disproportionation in both the cases generates a positive metal centre and a metal centre with a negative oxidation state. The carbonyl ligand, being a soft base, prefers to bind to the softer acids i.e.metal centre with negative charge; on the other hand, the ligands with nitrogen as donor site are hard Lewis bases, and therefore, prefer to bind to the harder acid i.e. metal centre with more positive charge on it.

A variety of carbonylate complexes can be synthesized via these disproportionation reactions which makes this type quite important as far as the practical applications are concerned. For example, the $[Ni_2(CO)_6]^{2-}$ anion and $[Co(CNR)_5][Co(CO)_4]$ can be synthesized by the following reactions.:

$$3Ni(CO)_4 + 3phen \rightarrow [Ni(phen)_3][Ni_2(CO)_6] + 6CO$$

$$Co_2(CO)_8 + 6NH_3 \rightarrow [Co(CNR)_5][Co(CO)_4] + 4CO$$

It is also worthy to note that the range of coordinating agents that will cause disproportionation is rather wide.

❖ Preparation, Bonding, Structure and Important Reactions of Transition Metal Nitrosyl, Dinitrogen and Dioxygen Complexes

Besides carbon monoxide, there are many other important ligands which form π-complexes with transition metal centre; some of them are NO, N_2 and O_2 molecules. The methods of preparations, nature of bonding, structure and their important reactions are discussed in detail below.

➢ *1. Metal Nitrosyl Complexes*

Metal nitrosyls are the complexes that contain nitric oxide (NO) bonded to a metal centre (usually transition element). There are various kinds of nitrosyl complexes known so far, which vary in respect of coligand, structure and nature of bonding. Metal complexes having nitrosyl ligands only are labelled as isoleptic nitrosyls. They are very rare, one of the special member this class $Cr(NO)_4$. On one hand, polycarbonyl complexes are very much common, even trinitrosyl complexes are rare on the other.

Preparation: i) Metal nitrosyl complexes can be prepared via many routes, but direct formation from nitric oxide gas is much more common. For example:

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

$$Ni(Ph_3P)_2(CO)_2 + 2NO \rightarrow Ni(Ph_3P)_2(NO)_2 + 2CO$$

$$Cr(CO)_6 + 4NO \rightarrow Cr(NO)_4 + 6CO$$

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2 + 2NO \rightarrow [(\eta^5\text{-}C_5H_5)Fe(CO)_2(NO)]_2 + 4CO$$

ii) From nitrosonium salts:

$$[Ir(CO)(PPh_3)_2Cl] + (NO)BF_4 \rightarrow [Ir(CO)(NO)(PPh_3)_2Cl]BF_4$$

iii) From nitrosyl halides:

$$Et_4N[HB(3,5\text{-}Me_2\text{-}pz)_3Mo(CO)_3] + ClNO$$
$$\rightarrow [HB(3,5\text{-}Me_2\text{-}pz)_3Mo(CO)_2(NO)] + CO + [Et_4N]Cl$$

iv) From N-nitrosamides:

$$HMn(CO)_5 + p\text{-}tolylSO_2N(Me)(NO) \rightarrow Mn(CO)_4(NO) + CO + p\text{-}tolylSO_2NHMe$$

v) From nitrite salts:

$$Na[Co(CO)_4] + Na(NO_2) + 2HOAc \rightarrow [Co(CO)_3(NO)] + CO + 2NaOAc + H_2O$$

vi) From nitronium (NO_2^+) salts:

$$(\eta^5\text{-}C_5H_5)Re(CO)_3 + [NO_2]PF_6 \rightarrow [(\eta^5\text{-}C_5H_5)Re(CO)_2(NO)]PF_6 + CO_2$$

Bonding: Most of the metal nitrosyl complexes can be viewed as derivatives of the nitrosyl cation (NO^+) or anion (NO^-). The nitrosyl cation (with a bond order of 3) is isoelectronic with carbon monoxide, thus the bonding between a nitrosyl ligand and a metal follows the same principles as the bonding in carbonyl complexes. However, the bond order of neutral nitrosyl and anion are 2.5 and zero, respectively; and therefore, in order to rationalize the nature of the bonding between metal centre and the nitrosyl ligand, we must understand molecular orbital diagram for the nitrosyl ligand first.

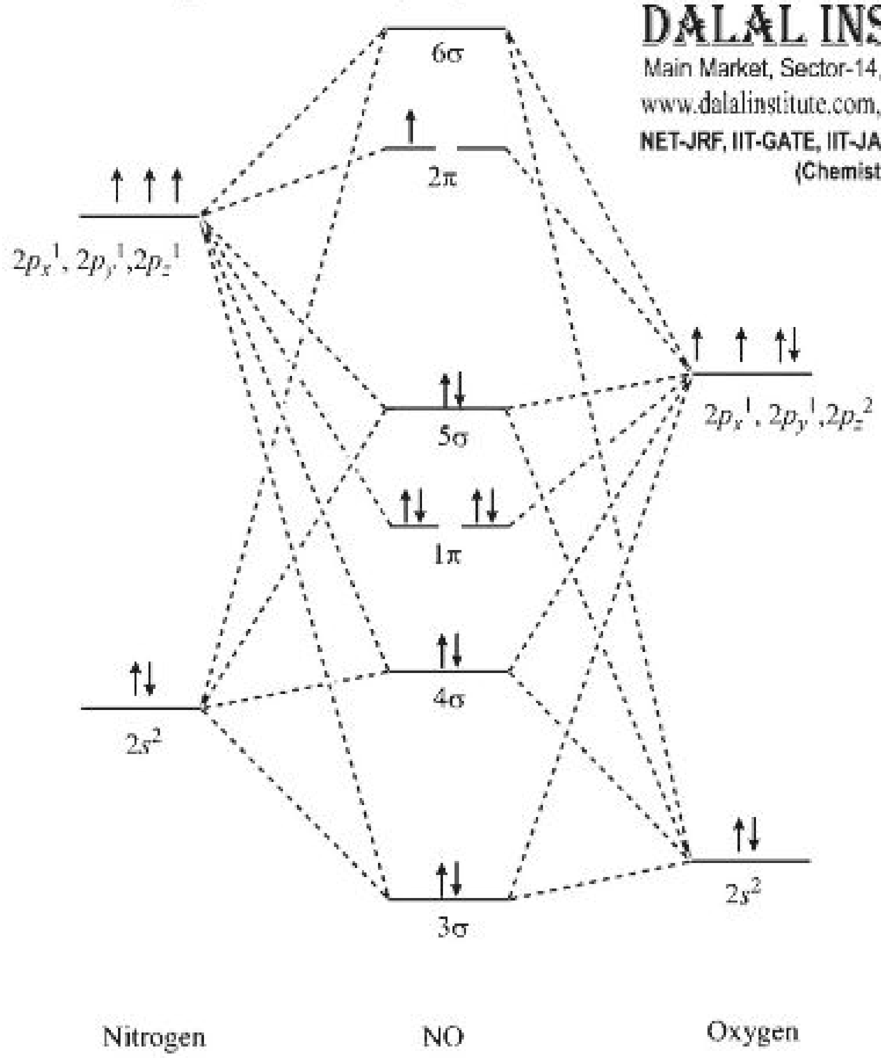

Figure 15. The molecular orbital diagram of nitric oxide (NO).

After looking at the molecular orbital diagram for NO, one can immediately recognize the difference from the carbonyl ligand that there is one extra electron in the π^*-orbital. This suggests that NO ligand can be one, two or three electron donor, depending upon the type of orbital used in bonding. If the electron present in π^*-orbital resides on NO i.e. not transferred to metal centre, nitrosyl ligand would behave as a two electron donor, and the nature of metal complex should be paramagnetic. There are some nitrosyl complexes of iron and cobalt such as $[Fe(NO)_2(CO)_2]$ and $[Co(NO)(CO)_3]$, which were thought to be derived from neutral NO ligand but these compounds are diamagnetic in nature; and therefore do not contain unpaired electrons. This suggests that the nitrosyl ligand is not neutral in these complexes. This assumption is also supported by the fact that the displacement of a previously attached ligand by any other neutral ligand in metal carbonyl nitrosyl complexes is always accompanied by the release of CO group. Moreover, there are also many complexes like $[Cr(NO)(CN)_5]^{3-}$ and $[Mn(NO)(CN)_5]^{2-}$, which are actually paramagnetic and were also thought to be having neutral nitrosyl ligand. However, in the later years, it was found that the unpaired electron of nitrosyl group is actually transferred to the metal centre making NO as NO^+ ligand. Thus, we can say that the coordination neutral nitrosyl is highly unlikely.

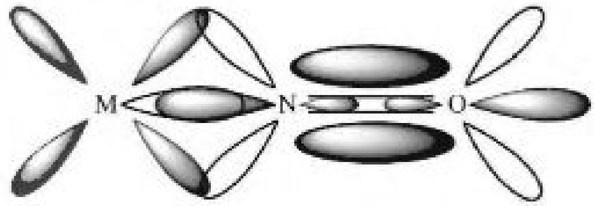

Figure 16. The nature of σ and π overlap in metal nitrosyl complexes.

i) Complexes containing NO^+: Nitric oxide molecule can easily release the odd electron from its antibonding molecular orbital to form a stable nitrosonium ion (NO^+). This also very obvious from the comparison of infrared absorption wavenumbers of free NO (1880 cm^{-1}) with the nitrosonium salts (2200 – 2300 cm^{-1}); and can be explained in terms of increased bond order from 2.5 to 3, and consequently the force constant value. Actually, most of the metal nitrosyls exist with nitrosyl ligand as three electron donor. For instance, the effective atomic numbers (EAN) for $[Mn(CO)(NO)_3]$ and $[Fe(NO)_2(CO)_2]$ complexes are 36 for each, which is possible only if the NO ligand act as NO^+ i.e. three electron donor.

$$M + NO \longrightarrow M^- + :N\equiv\overset{+}{O}: \longrightarrow \overset{2-}{M}\leftarrow\overset{+}{N}\equiv\overset{+}{O} \xleftrightarrow[\text{bonding}]{\pi\text{-back}} \overset{-}{M}\leftrightarrows N\equiv\overset{+}{O}$$

In the initial step, the π^* electron of the NO transfers to metal centre, reducing M to M^- and itself forming NO^+ ion. Then NO^+ donates a lone pair of electron via N just like the carbon in metal carbonyls. However, total number of electron donated by NO in this case would be three while carbonyl can donate only two. The back donation of electron charge from filled *d*-orbital of metal to π^*-orbital of NO would result a considerable decrease in the nitrogen-oxygen bond order. The infrared absorption peak of NO^+ in metal nitrosonium complexes lies in the range of 1900−1600 cm^{-1} which is far less than what has been observed in nitrosonium ionic salts. Moreover, the magnitude of decrease in carbonyl stretching frequency is less than the magnitude of decrease in nitrosonium stretching frequency as we go from their corresponding free unit to metal-coordinated unit. This, therefore, confirms the better π-acceptor strength of NO^+ ligand; which is further increased by an accumulation of negative charge on nitrosonium complexes.

ii) Complexes containing NO^-: Nitric oxide molecule can also accept an electron from metal centre to its antibonding molecular orbital forming a NO^- ion. The metal centre in this process would get oxidized from M^{n+} to $M^{(n+1)+}$ ion. Then the NO^- ion donates a lone pair of electron via N just like the carbon in metal carbonyls. However, total number of electron donated by NO in this case would be one while the carbonyl can donate only two. The infrared absorption wavenumbers of NO^- in metal nitrosyl complexes is found in the range of 1100–1200 cm^{-1} (much lower than NO), which can be explained in terms of complete transfer of one electron from *d*-π orbital of metal centre to antibonding molecular orbital on nitrosyl ligand. For example, during the formation of $[Co(CN)_5(NO)]^{3-}$ and $[Co(NH_3)_5(NO)]^{2+}$ complexes (passing NO through amine and cyanide salts of Co^{2+}), the Co(II) gets converted into low spin Co(III) with t_{2g}^6 configuration. Both of these complexes, in respect of charge and magnetic moment, resemble to $[Co(CN)_5Br]^{3-}$ and $[Co(NH_3)_5Cl]^{2-}$, respectively.

In nitrosyl complexes, the M−N−O unit is generally linear, or no more than 15° from linear. However, in some complexes, especially where back-bonding is not that much important, the M−N−O angle can largely deviate from 180°. The linear and bent NO ligands can be differentiated using infrared spectroscopy. The linear M−N−O groups absorb in the range 1650–1900 cm^{-1} (close to metal coordinated NO^+); whereas the bent nitrosyls absorb in the range 1525–1690 cm^{-1} (close to metal coordinated NO^-). The difference of vibrational frequencies reflects the difference in N−O bond orders for linear (triple bond) and bent NO (double bond). The bent NO ligand is sometimes described as the anion, NO^-. Prototypes for such compounds are the organic nitroso compounds, such as nitrosobenzene. A complex with a bent NO ligand is trans-$[Co(en)_2(NO)Cl]^+$. The adoption of linear vs bent bonding can be analysed with the Enemark-Feltham notation. In their framework, the factor that determines the bent vs linear NO ligands is the sum of electrons of π-symmetry.

Linear Bent

Complexes with "π-electrons" in excess of 6 tend to have bent NO ligands. Thus, $[Co(en)_2(NO)Cl]^+$, with seven electrons of π-symmetry (six in t_{2g} orbitals and one on NO), adopts a bent NO ligand, whereas $[Fe(CN)_5(NO)]^{3-}$, with six electrons of pi-symmetry, adopts a linear nitrosyl. In a further illustration, the M−N−O *d*-electron count of the $[Cr(CN)_5NO]^{3-}$ anion is shown. In this example, the cyanide ligands are "innocent", i.e., they have a charge of −1 each, −5 total. To balance the fragment's overall charge, the charge on Cr−N−O is thus +2 (−3 = −5 + 2). Using the neutral electron counting scheme, Cr has 6 *d*-electrons and NO has one odd electron for a total of 7. Two electrons are subtracted to take into account that fragment's overall charge of +2, to give 5. Written in the Enemark-Feltham notation, the *d*-electron count in Cr−N−O unit is five. The results are the same if the nitrosyl ligand were considered NO^+ or NO^-.