

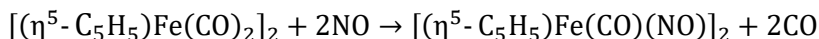
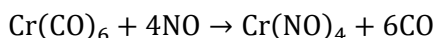
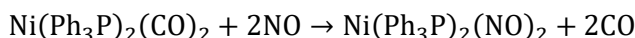
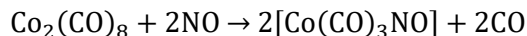
❖ Preparation, Bonding, Structure and Important Reactions of Transition Metal Nitrosyl, Dinitrogen and Dioxygen Complexes

Besides carbon monoxide, there are many other important ligands which form π -complexes with transition metal center; some of them are NO, N₂ and O₂ molecules. The methods of preparations, nature of bonding, structure and their important reactions are discussed in detail below.

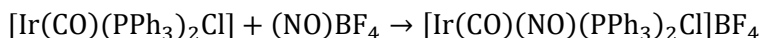
➤ 1. Metal Nitrosyl Complexes

Metal nitrosyls are the complexes that contain nitric oxide (NO) bonded to a metal center (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 labeled as isoleptic nitrosyls. They are very rare, one of the special members of this class is Cr(NO)₄. On one hand, polycarbonyl complexes are very much common, even trinitrosyl complexes are rare on the other.

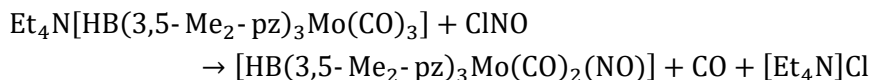
Preparation: i) Metal nitrosyl complexes can be prepared via many routes, but direct formation from nitric oxide gas is much more common. For example:



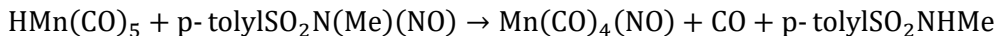
ii) From nitrosonium salts:



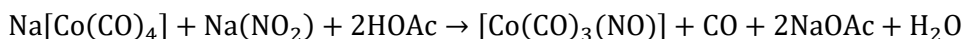
iii) From nitrosyl halides:



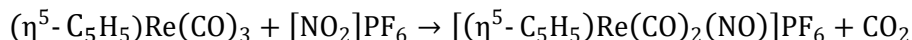
iv) From N-nitrosamides:



v) From nitrite salts:



vi) From nitronium (NO₂⁺) salts:



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 2, respectively; and therefore, in order to rationalize the nature of the bonding between metal center and the nitrosyl ligand, we must understand molecular orbital diagram for the nitrosyl ligand first.

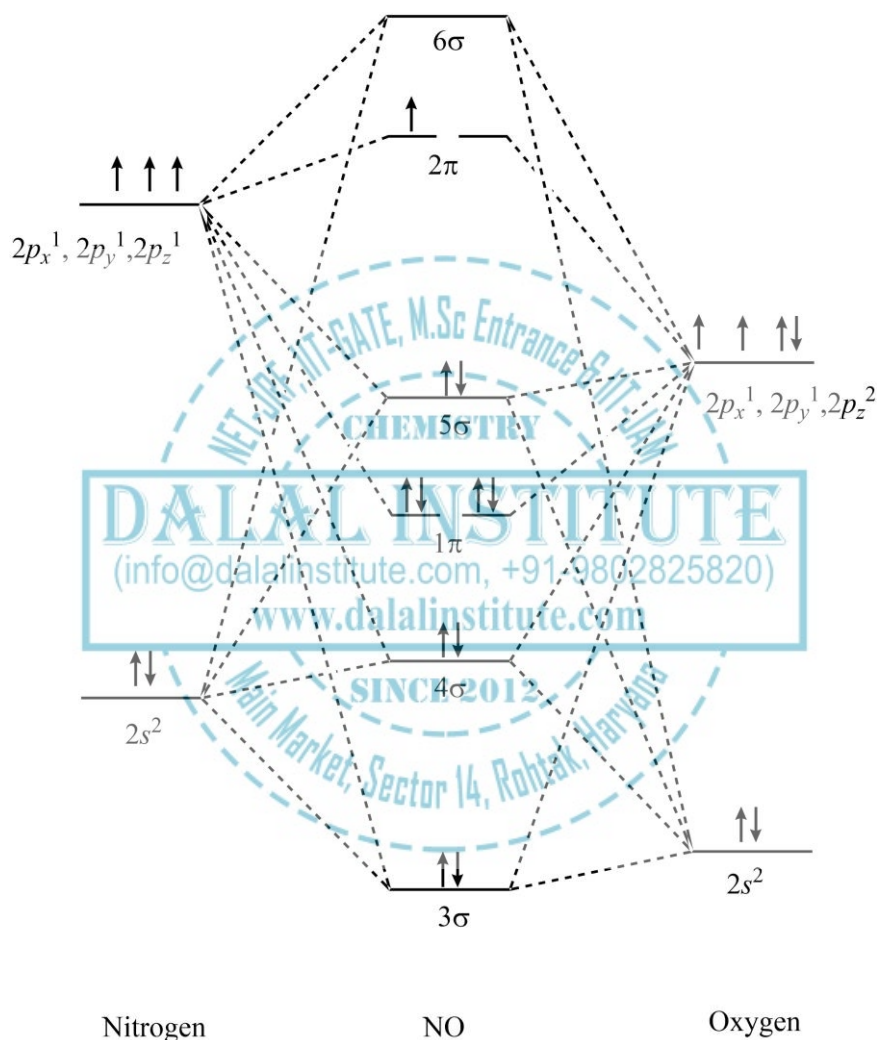


Figure 15. The molecular orbital diagram of nitric oxide (NO).

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 donors, depending upon the type of orbital used in bonding. If the electron present in π^* -orbital resides on NO, i.e., not transferred to the metal center, 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 $[\text{Fe}(\text{NO})_2(\text{CO})_2]$ and $[\text{Co}(\text{NO})(\text{CO})_3]$, 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 $[\text{Cr}(\text{NO})(\text{CN})_5]^{3-}$ and $[\text{Mn}(\text{NO})(\text{CN})_5]^{2-}$, 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 the nitrosyl group is actually transferred to the metal center making NO as NO^+ ligand. Thus, we can say that the coordination of neutral nitrosyl is highly unlikely.

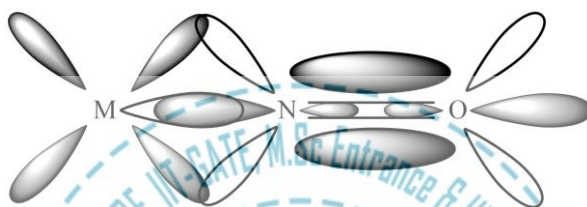


Figure 16. The nature of σ and π overlap in metal nitrosyl complexes.

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 is also very obvious from the comparison of infrared absorption wavenumbers of free NO (1880 cm^{-1}) with the nitrosonium salts ($2200 - 2300 \text{ cm}^{-1}$); 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 $[\text{Mn}(\text{CO})(\text{NO})_3]$ and $[\text{Fe}(\text{NO})_2(\text{CO})_2]$ complexes are 36 for each, which is possible only if the NO ligand act as NO^+ i.e. three electron donor.



In the initial step, the π^* electron of the NO transfers to the metal center, 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, the total number of electrons 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 in a considerable decrease in the nitrogen-oxygen bond order. The infrared absorption peak of NO^+ in metal nitrosonium complexes lies in the range of $1900 - 1600 \text{ cm}^{-1}$ 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 the metal center to its antibonding molecular orbital forming a NO⁻ ion. The metal center in this process would get oxidized from Mⁿ⁺ 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, the total number of electrons 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 are 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 center to antibonding molecular orbital on nitrosyl ligand. For example, during the formation of [Co(CN)₅(NO)]³⁻ and [Co(NH₃)₅(NO)]²⁺ complexes (passing NO through amine and cyanide salts of Co²⁺), 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 [Co(CN)₅Br]³⁻ and [Co(NH₃)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 analyzed 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.



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 π -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⁻.

Structure: The structure of metal nitrosyls can mainly be classified into three categories; first as the metal-complex systems that contain NO as a terminal ligand only, the second one as having only bridging nitrosyl group, and the third one with nitrosyl groups with the terminal as well as bridging profile.

i) *Metal complexes with terminal nitrosyl:* The NO group as a monodentate ligand in metal complexes acts either as a 12-electron unit (when NO^- forms a single bond with the metal center and M–N–O unit is linear), or as a 10-electron unit (when NO^+ forms a multiple bonds with the metal center and M–N–O unit is bent).

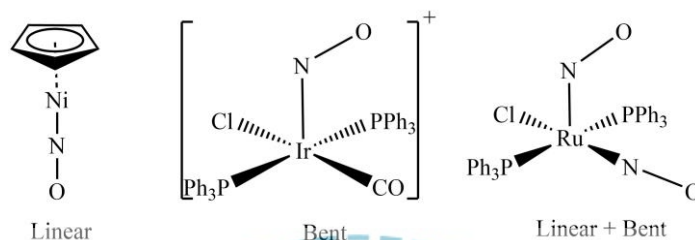


Figure 17. Metal complexes with terminal nitrosyls.

ii) *Metal complexes with bridging nitrosyl:* In some of the metal nitrosyl complexes, all NO groups are present in bridging mode. One of the common examples is given below.

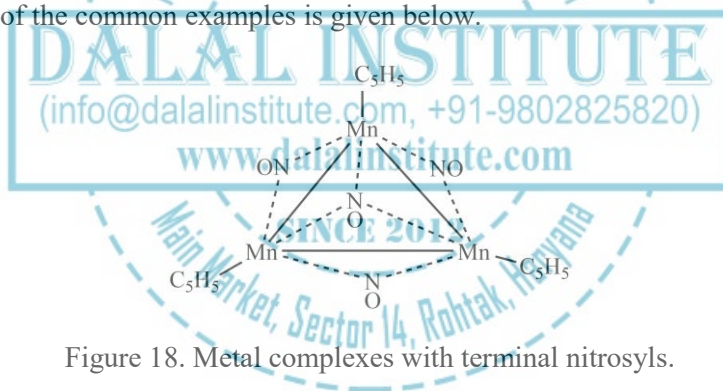


Figure 18. Metal complexes with terminal nitrosyls.

iii) *Metal complexes with the terminal as well as bridging nitrosyl:* In some of the metal nitrosyl complexes, NO groups are present in the terminal as well as in bridging mode. Some of the common examples are:

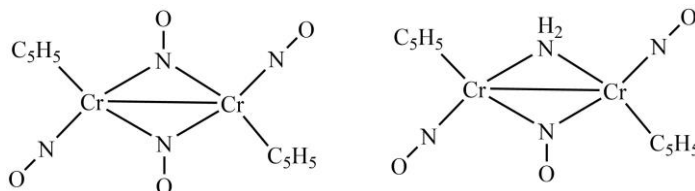
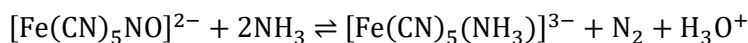
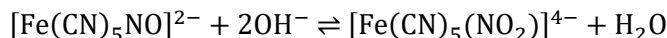
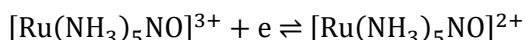
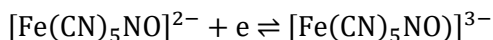


Figure 19. Metal complexes with terminal nitrosyls.

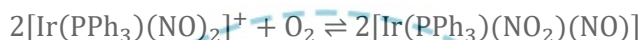
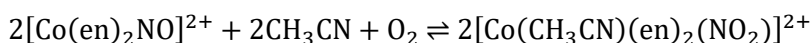
Reactions: i) The nucleophilic attack:



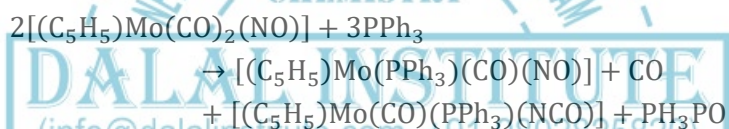
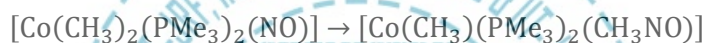
ii) Reduction of metal nitrosyls:



iii) Reactions of nitrosyls with electrophiles:



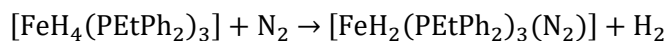
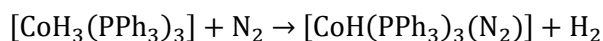
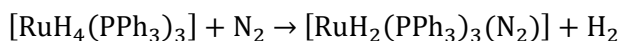
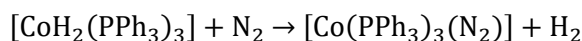
iv) Formation of carbon-nitrogen bonds:



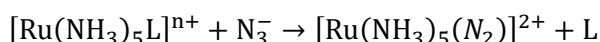
➤ 2. Metal Dinitrogen Complexes

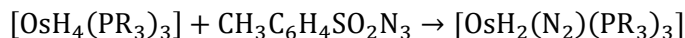
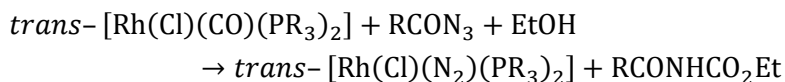
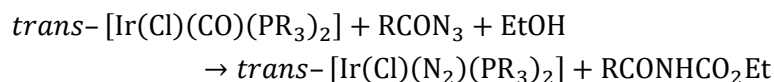
Metal dinitrogen complexes are the coordination compounds that contain the dinitrogen ligand (N_2) attached to a metal center. The first complex of dinitrogen, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+}$ was reported by Allen and Senoff in 1965, which is consisted of a 16e- $[\text{Ru}(\text{NH}_3)_5]^{2+}$ center attached to one end of N_2 . The interest in such complexes arises because N_2 comprises the majority of the atmosphere and there are many useful compounds containing nitrogen atoms.

Preparation: i) Metal dinitrogen complexes can be prepared via many routes, but direct formation from dinitrogen is very common. For example:

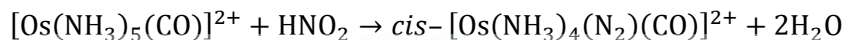
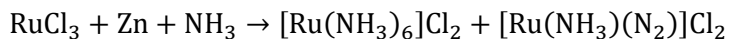
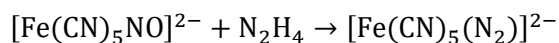


ii) From compounds containing chains of nitrogen atoms:





iii) Preparations in which two nitrogen atoms are combined to give a dinitrogen group:



Bonding: In order to rationalize the nature of the bonding between the metal center and the N_2 , we must understand the bonding within the dinitrogen ligand first. The molecular orbital diagram for N_2 is given below.

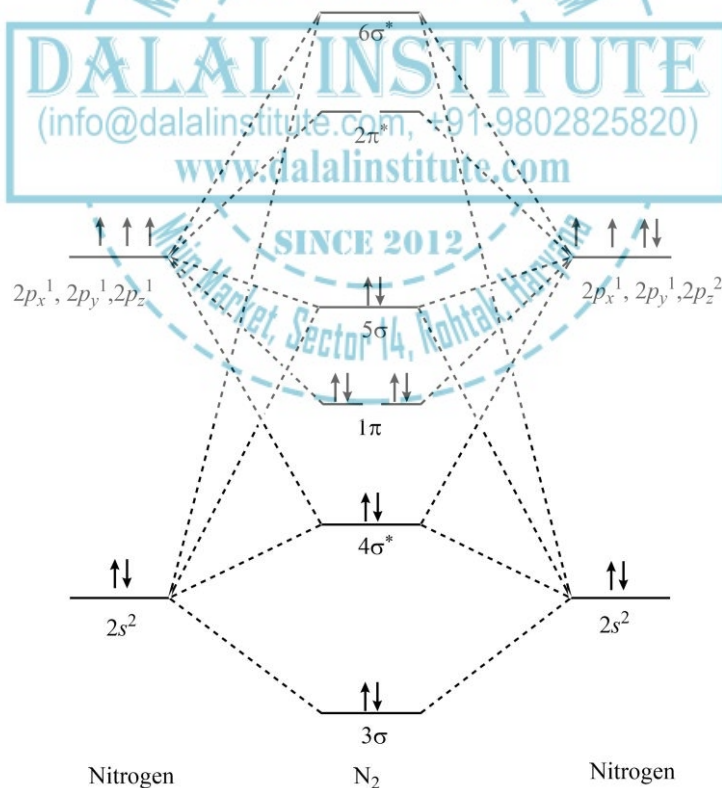


Figure 20. The molecular orbital diagram of dinitrogen molecule.

Though the N_2 molecule is isoelectronic with CO and NO^+ , it does not form a large number of metal complexes like the two. This is obviously due to the fact that it is a poor ligand and cannot act as a strong π -acceptor due to the lack of polarity. In other words, N_2 ligand is neither a good σ -donor nor good π -acceptor as there is no polarity in N–O bond. The different bridging modes of dinitrogen ligand are given below.

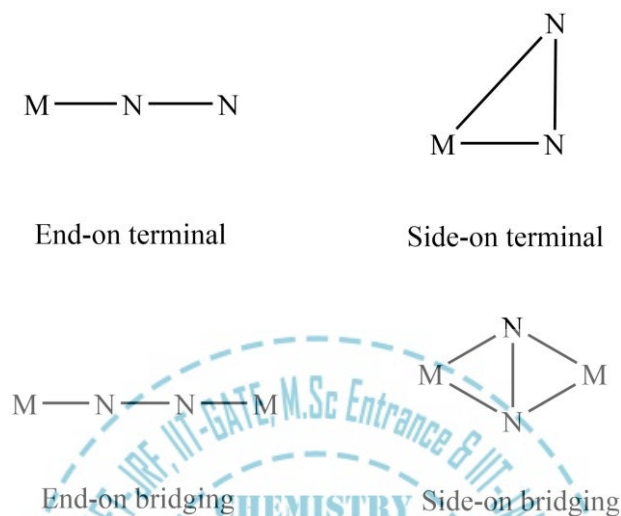


Figure 21. Bonding modes of N_2 ligand in metal-dinitrogen complexes.

The most common binding mode of dinitrogen ligand with transition metal center is end-on i.e. just like in the case of isocyanides, carbon monoxide and nitric oxide. These observations are also supported by the theoretical treatment of some dinitrogen complexes which indicated that end-on bonding is more beneficial than side on as far as the stability of the complex is concerned. The end-on bonding involves the donation of the lone pair of N_2 to the empty metal orbital and, the back-donation from filled metal d -orbital to the empty π^* orbitals of N_2 ligand. In contrast, the side-on bonding comprises of electron donation from the π and σ bonding molecular orbital of the dinitrogen to the empty orbitals of the metal and the back-donation of electron density from filled orbitals of the metal to the π^* molecular orbital of the N_2 ligand. Though the side-on bonding mode is quite common in metal-acetylenes and metal-olefin complexes, there are very few reports of side-on bonded dinitrogen complexes. Consider the example of $[Ru(NH_3)_5(N_2)]^{2+}$ complex, Ru–N bond length in Ru–N–N unit is shorter than Ru–N bond length in Ru– NH_3 unit. This shows that there is some extent of backbonding from filled d -orbital the metal center to the empty π^* molecular orbital of dinitrogen. This is also very obvious from the vibrational Raman stretching frequency of free N_2 (2331 cm^{-1}) and infrared active stretching frequency of metal coordinated ligand (2105 cm^{-1}) in $[Ru(NH_3)_5(N_2)]Cl_2$ complex. However, it is also worthy to note that metal-carbon bond in carbonyl complexes is stronger than the metal-nitrogen bond in dinitrogen complexes, which shows that CO is definitely a stronger σ -donor a better π -acceptor as highest occupied molecular orbital (HOMO) is predominantly concentrated on carbon due to high polarity.

Structure: The structures of metal-dinitrogen complexes can mainly be classified into two categories; metal-complex that contains N_2 as an end-on ligand and with N_2 group as a side-on ligand.

i) *Metal complexes with end-on dinitrogen:* As a ligand, N_2 usually binds to metals as an end-on ligand, as illustrated by Allen and Senoff's complex. Such complexes are usually analogous to related CO derivatives.

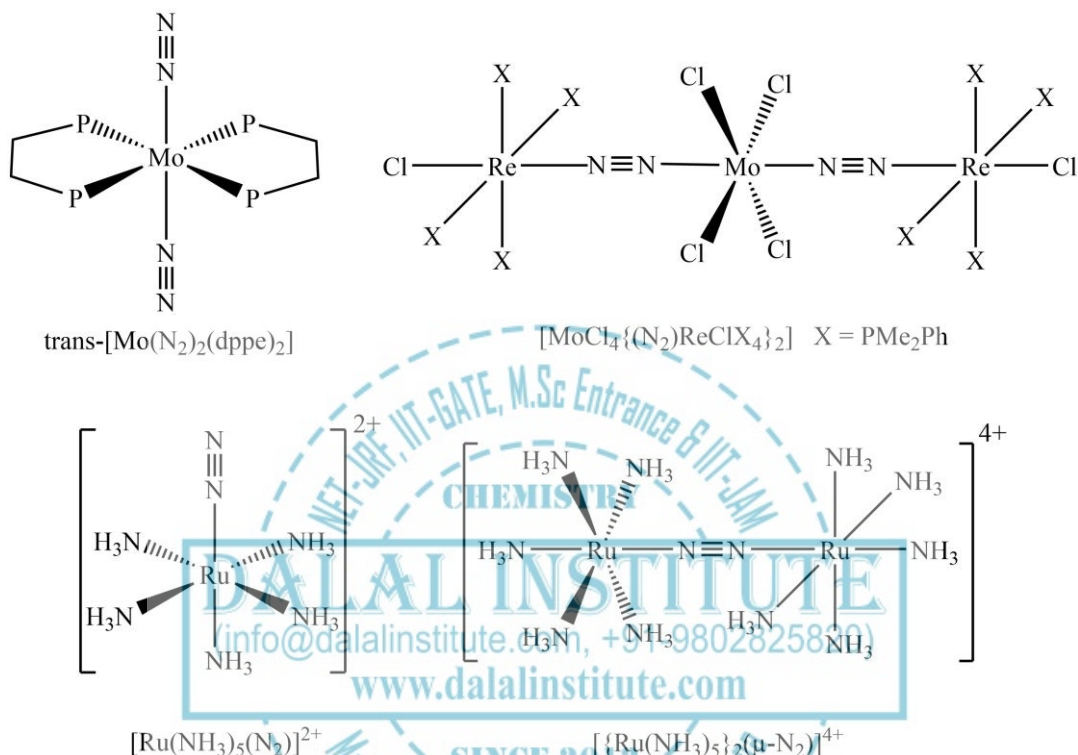


Figure 22. Metal-dinitrogen complexes with end-on N_2 ligand.

ii) *Metal complexes with side-on dinitrogen:* In some of the metal-dinitrogen complexes, the N–N vector is perpendicular to the M–M vector. Some of the most common examples are given below.

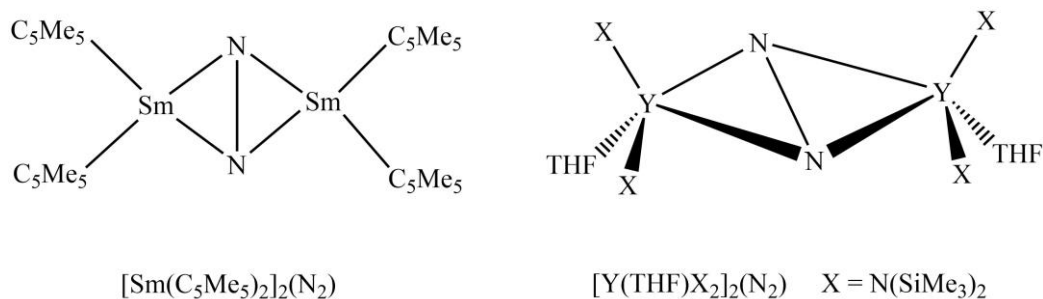
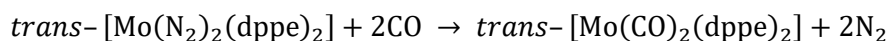
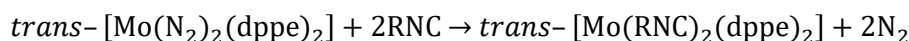
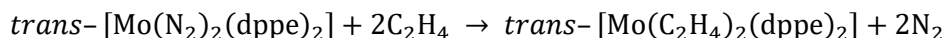
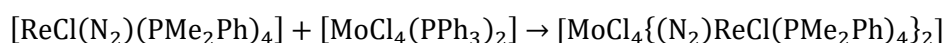
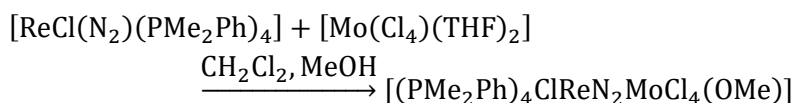


Figure 23. Metal-dinitrogen complexes with side-on N_2 ligand.

Reactions: i) The displacement of dinitrogen ligand by some other groups:



ii) Reactions of Ligating N_2 with Lewis Acids:



iii) Formation of metal-hydrazido complexes from ligating N_2 :



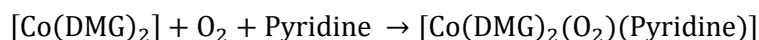
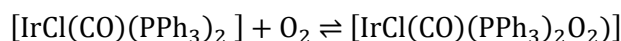
iv) Formation of carbon-nitrogen bonds:



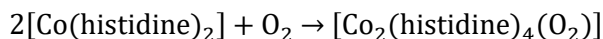
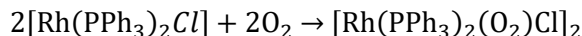
➤ 3. Metal Dioxygen Complexes

Metal dioxygen complexes are the coordination compounds which contain O_2 ligand attached to a metal center. The principal driving force behind the analysis of these compounds are oxygen-carrying proteins such as myoglobin, hemoglobin, hemocyanin, and hemerythrin. Many transition metals form complexes with O_2 , and many of these complexes form reversibly. The binding of O_2 is the first step in many important phenomena, such as cellular corrosion, respiration and in industrial chemistry. The first synthetic oxygen complex was demonstrated in 1938 with Co^{2+} complex reversibly bound O_2 . Most of the organometallic metal-dioxygen complexes are synthesized by the reaction of gaseous molecular oxygen with complexes (having d^7 , d^8 , or d^{10} electronic configuration) solution.

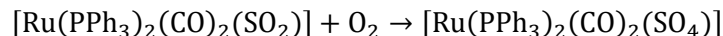
Preparation: i) Formation of a mononuclear dioxygen adduct with or without displacement of ligands



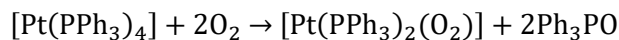
ii) Formation of a dimer or a binuclear dioxygen adduct:



iii) Oxidation of ligands with the oxidized ligand remaining coordinated:



iv) Displacement of free oxidized ligand:



Bonding: The nature of bonding in metal-dioxygen complexes is usually evaluated by single-crystal X-ray crystallography, focusing both on the overall geometry as well as the O–O distances, which reveals the bond order of the O₂ ligand. However, in order to rationalize the initial idea of the metal-ligand bonding, we must understand the bonding within the dioxygen ligand first. The molecular orbital diagram for O₂ is given below.

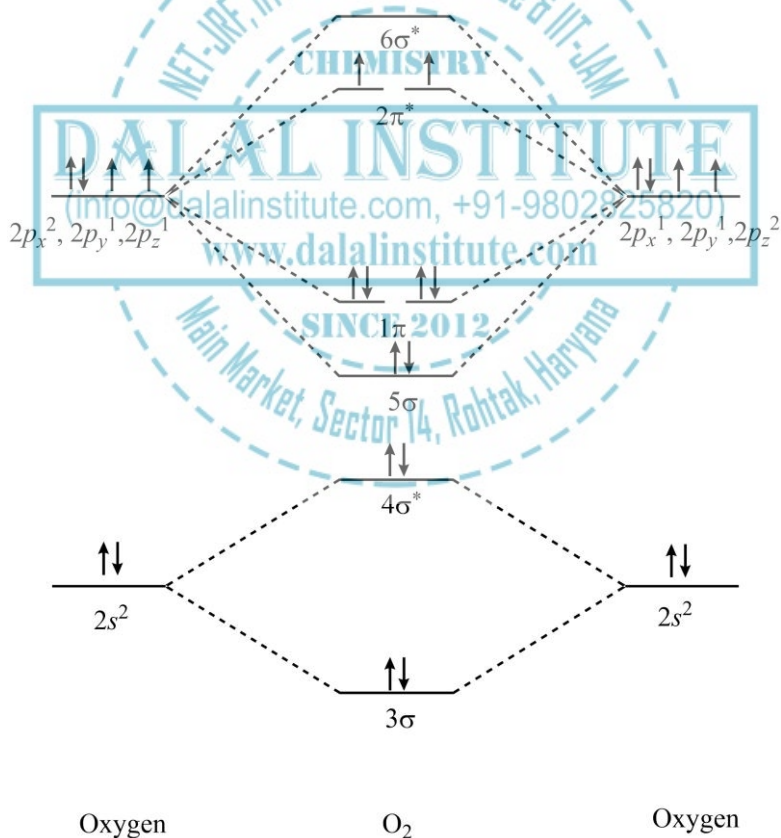


Figure 24. The molecular orbital diagram of the dioxygen molecule.

The experimental results show that the bent structure of the dioxygen unit in oxyhemoglobin is actually diamagnetic in nature; which suggests that π^*2p_x and π^*2p_y orbitals are not completely degenerate in the complex as they are in free dioxygen. A linear M–O–O structure would result in a degenerate set of π^*2p_x and π^*2p_y orbitals with a triplet state. In addition to the σ -bonding, there are two types of interactions between the d -orbitals of the metal and the π^* orbitals of the dioxygen. One is through an overlap of the $3d_{xz}$ of the metal with the π^* orbitals perpendicular to the Fe–O–O plane; while the other is through the overlap of the $3d$ orbital of the metal with the π_y^* orbital in the Fe–O–O plane. The different bridging modes of dinitrogen ligand are given below.

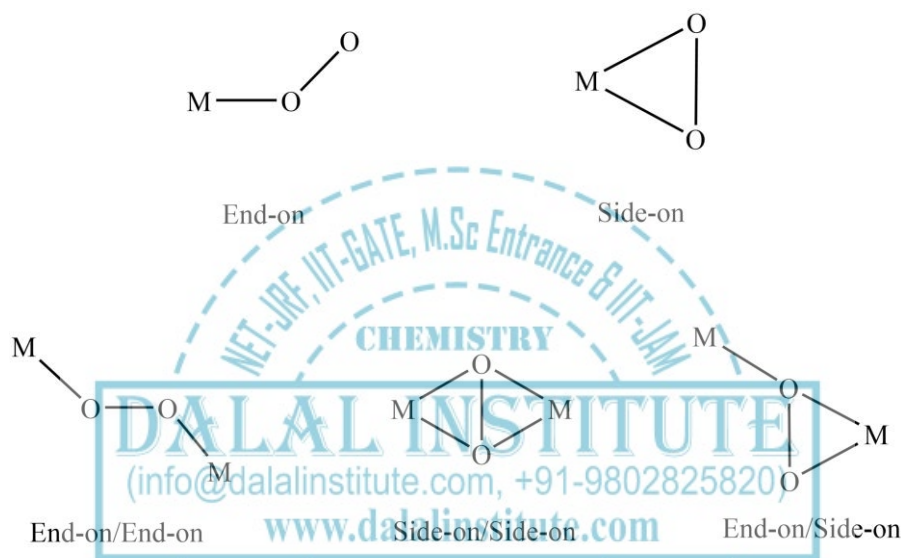


Figure 25. Bonding modes of O_2 ligand in metal-dioxygen complexes.

The O_2 ligand binds to a single metal center either end-on (η^1 -) or in a side-on (η^2 -) manner. Dioxygen adducts derived from Co^{2+} and Fe^{2+} complexes of porphyrin (and related anionic macrocyclic ligands) exhibit this bonding mode. The hemoglobin and myoglobin are two famous examples, and many other synthetic analogs have been reported which behave in a similar manner. Binding of O_2 is usually described as proceeding by electron transfer from the metal(II) center to give superoxide (O_2^-) complexes of metal(III) centers. The η^2 -bonding is the most common motif seen in the coordination chemistry of dioxygen. Since O_2 has a triplet ground state and Vaska's complex is a singlet, the reaction is slower than when singlet oxygen is used. Complexes containing η^2 - O_2 ligands are fairly common, but most are generated using hydrogen peroxide, not O_2 . The O_2 can bind to one metal of a bimetallic unit via the same modes discussed above for mononuclear complexes. A well-known example in nature is hemerythrin, which features a diiron carboxylate that binds O_2 at one Fe center. The dinuclear complexes can also cooperate in the binding, although the initial attack of O_2 probably occurs at a single metal. These binding modes include μ^2 - η^2 , η^2 -, μ^2 - η^1 , η^1 -, and μ^2 - η^1 , η^2 -. Depending on the degree of electron-transfer from the dimetal unit, these O_2 ligands can again be described as peroxo or superoxo. In nature, such dinuclear dioxygen complexes often feature copper.

Structure: The structures of metal-dioxygen complexes can mainly be classified into two categories; the first one as the metal-complex that contains dioxygen (O_2) ligand attached to one metal center and the second one with O_2 group connected to two or more metal centers. A brief discussion on both of the categories is given below with suitable examples.

i) *Mononuclear metal-dioxygen complexes:* As a ligand, O_2 can bind to a single metal-center either as an end-on ligand or as a side-on ligand. The structures of some representative metal-dioxygen complexes of such type are given below.

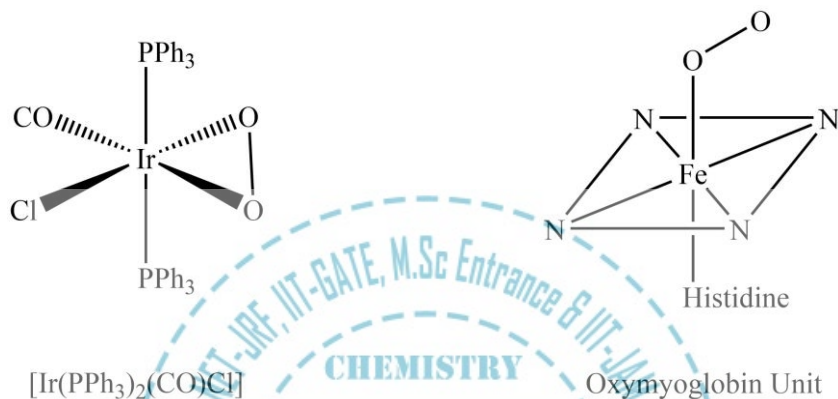


Figure 26. Mononuclear metal- O_2 complexes.

ii) *Binuclear metal-dioxygen complexes:* In binuclear metal-dioxygen complexes, the O_2 molecule can bind either to one or both metals center as an end-on/end-on, end-on/side-on and side-on/side-on ligand. The structures of some representative metal-dioxygen complexes of such type are given below.

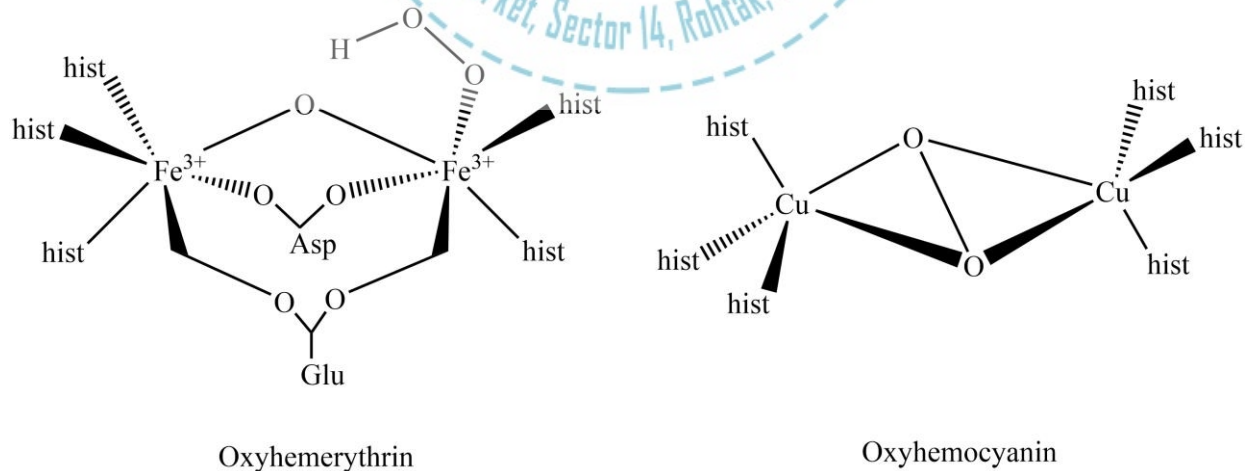
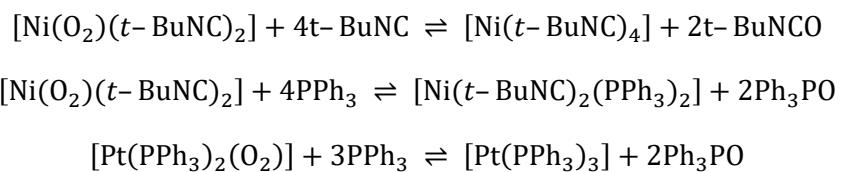
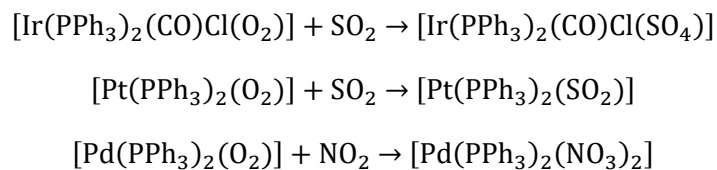


Figure 27. Metal-dioxygen complexes with side-on O_2 ligand.

Reactions: i) The displacement of molecular oxygen by some other ligand:



ii) The formation of complexes of oxidized substrates:



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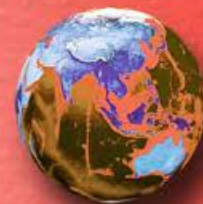
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