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 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 centre and M–N–O unit is linear), or as a 10-electron unit (when NO^+ forms a multiple bond with the metal centre and M–N–O unit is bent).

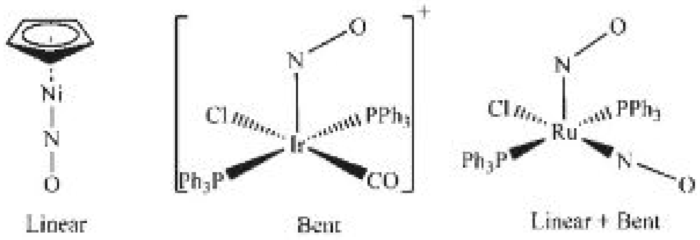


Figure 17. Metal complexes with terminal nitrosyls.

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 example are given below.

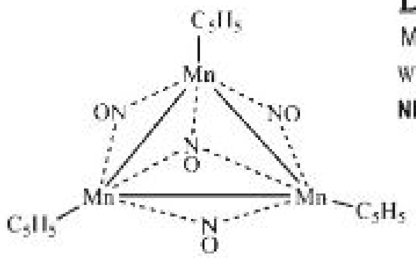


Figure 18. Metal complexes with terminal nitrosyls.

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

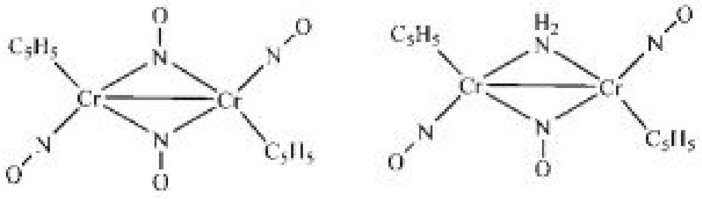


Figure 19. Metal complexes with terminal nitrosyls.

Reactions: i) The nucleophilic attack:

$$[\mathrm{Fe(CN)_5NO}]^{2-} + 2\mathrm{OH}^- \rightleftharpoons [\mathrm{Fe(CN)_5(NO_2)}]^{4-} + \mathrm{H_2O}$$

$$[\mathrm{Fe(CN)_5NO}]^{2-} + 2\mathrm{NH_3} \rightleftharpoons [\mathrm{Fe(CN)_5(NH_3)}]^{3-} + \mathrm{N_2} + \mathrm{H_3O^+}$$

ii) Reduction of metal nitrosyls:

$$[\mathrm{Fe(CN)_5NO}]^{2-} + \mathrm{e} \rightleftharpoons [\mathrm{Fe(CN)_5NO)}]^{3-}$$

$$[\mathrm{Ru(NH_3)_5NO}]^{3+} + \mathrm{e} \rightleftharpoons [\mathrm{Ru(NH_3)_5NO}]^{2+}$$

iii) Reactions of nitrosyls with electrophiles:

$$2[\mathrm{Co(en)_2NO}]^{2+} + 2\mathrm{CH_3CN} + \mathrm{O_2} \rightleftharpoons 2[\mathrm{Co(CH_3CN)_5(en)_2(NO_2)}]^{2+}$$

$$2[\mathrm{Ir(PPh_3)(NO)_2}]^+ + \mathrm{O_2} \rightleftharpoons 2[\mathrm{Ir(PPh_3)(NO_2)(NO)}]$$

iv) Formation of carbon-nitrogen bonds:

$$[\mathrm{Co(CH_3)_2(PMe_3)_2(NO)}] \rightarrow [\mathrm{Co(CH_3)(PMe_3)_2(CH_3NO)}]$$

$$\begin{aligned} 2[\mathrm{(C_5H_5)Mo(CO)_2(NO)}] &+ 3\mathrm{PPh_3} \\ &\rightarrow [\mathrm{(C_5H_5)Mo(PPh_3)(CO)(NO)}] + \mathrm{CO} \\ &+ [\mathrm{(C_5H_5)Mo(CO)(PPh_3)(NCO)}] + \mathrm{PH_3PO} \end{aligned}$$

➢ *2. Metal Dinitrogen Complexes*

Metal dinitrogen complexes are the coordination compounds that contain the dinitrogen ligand (N_2) attached to a metal centre. The first complex of dinitrogen, $[Ru(NH_3)_5(N_2)]^{2+}$ was reported by Allen and Senoff in 1965, which is consisted of a 16e-$[Ru(NH_3)_5]^{2+}$ centre 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:

$$[\mathrm{CoH_2(PPh_3)_3}] + \mathrm{N_2} \rightarrow [\mathrm{Co(PPh_3)_3(N_2)}] + \mathrm{H_2}$$

$$[\mathrm{RuH_4(PPh_3)_3}] + \mathrm{N_2} \rightarrow [\mathrm{RuH_2(PPh_3)_3(N_2)}] + \mathrm{H_2}$$

$$[\mathrm{CoH_3(PPh_3)_3}] + \mathrm{N_2} \rightarrow [\mathrm{CoH(PPh_3)_3(N_2)}] + \mathrm{H_2}$$

$$[\mathrm{FeH_4(PEtPh_2)_3}] + \mathrm{N_2} \rightarrow [\mathrm{FeH_2(PEtPh_2)_3(N_2)}] + \mathrm{H_2}$$

ii) From compounds containing chains of nitrogen atoms:

$$[\mathrm{Ru(NH_3)_5L}]^{n+} + \mathrm{N_3^-} \rightarrow [\mathrm{Ru(NH_3)_5}(N_2)]^{2+} + \mathrm{L}$$

$$trans\text{-}[\mathrm{Ir(Cl)(CO)(PR_3)_2}] + \mathrm{RCON_3} + \mathrm{EtOH} \rightarrow trans\text{-}[\mathrm{Ir(Cl)(N_2)(PR_3)_2}] + \mathrm{RCONHCO_2Et}$$

$$trans\text{-}[\mathrm{Rh(Cl)(CO)(PR_3)_2}] + \mathrm{RCON_3} + \mathrm{EtOH} \rightarrow trans\text{-}[\mathrm{Rh(Cl)(N_2)(PR_3)_2}] + \mathrm{RCONHCO_2Et}$$

$$[\mathrm{OsH_4(PR_3)_3}] + \mathrm{CH_3C_6H_4SO_2N_3} \rightarrow [\mathrm{OsH_2(N_2)(PR_3)_3}]$$

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

$$[\mathrm{Fe(CN)_5NO}]^{2-} + \mathrm{N_2H_4} \rightarrow [\mathrm{Fe(CN)_5(N_2)}]^{2-}$$

$$\mathrm{RuCl_3} + \mathrm{Zn} + \mathrm{NH_3} \rightarrow [\mathrm{Ru(NH_3)_6}]\mathrm{Cl_2} + [\mathrm{Ru(NH_3)(N_2)}]\mathrm{Cl_2}$$

$$[\mathrm{Os(NH_3)_5(CO)}]^{2+} + \mathrm{HNO_2} \rightarrow cis\text{-}[\mathrm{Os(NH_3)_4(N_2)(CO)}]^{2+} + 2\mathrm{H_2O}$$

$$[\mathrm{Ru(NH_3)_6}]^{3+} + \mathrm{NO} + \mathrm{OH^-} \rightarrow [\mathrm{Ru(NH_3)_5(N_2)}]^{2+} + 2\mathrm{H_2O}$$

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

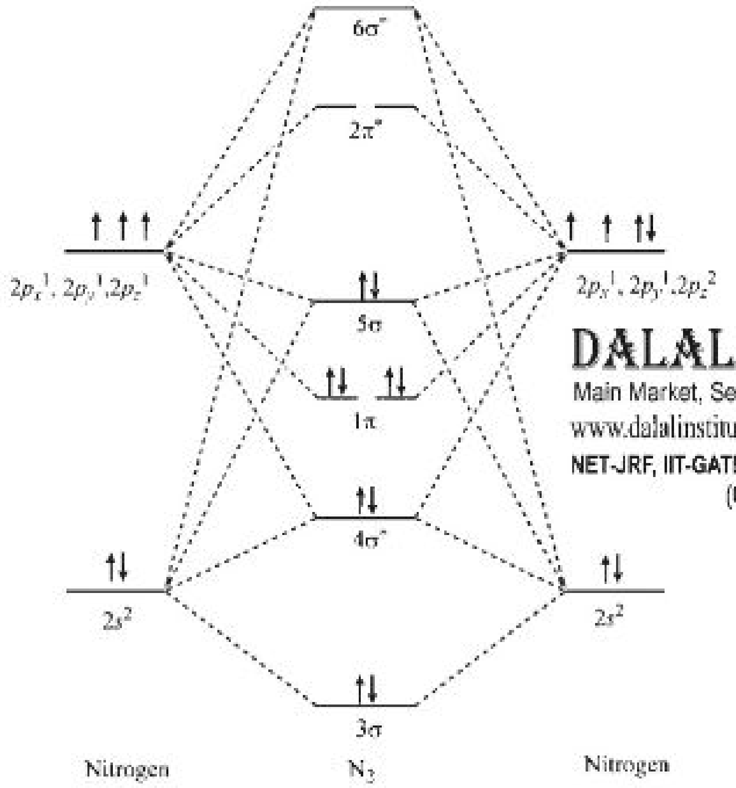
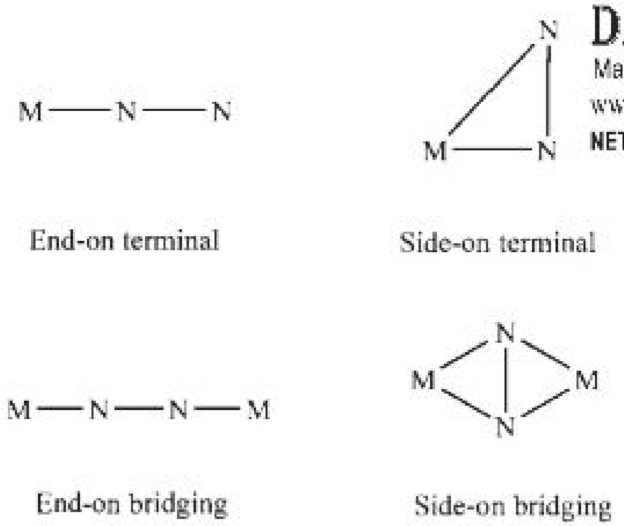


Figure 20. The molecular orbital diagram of dinitrogen molecule.

Though the N_2 molecule is isoelectronic with CO and NO^-, it does not form 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 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.



End-on terminal Side-on terminal

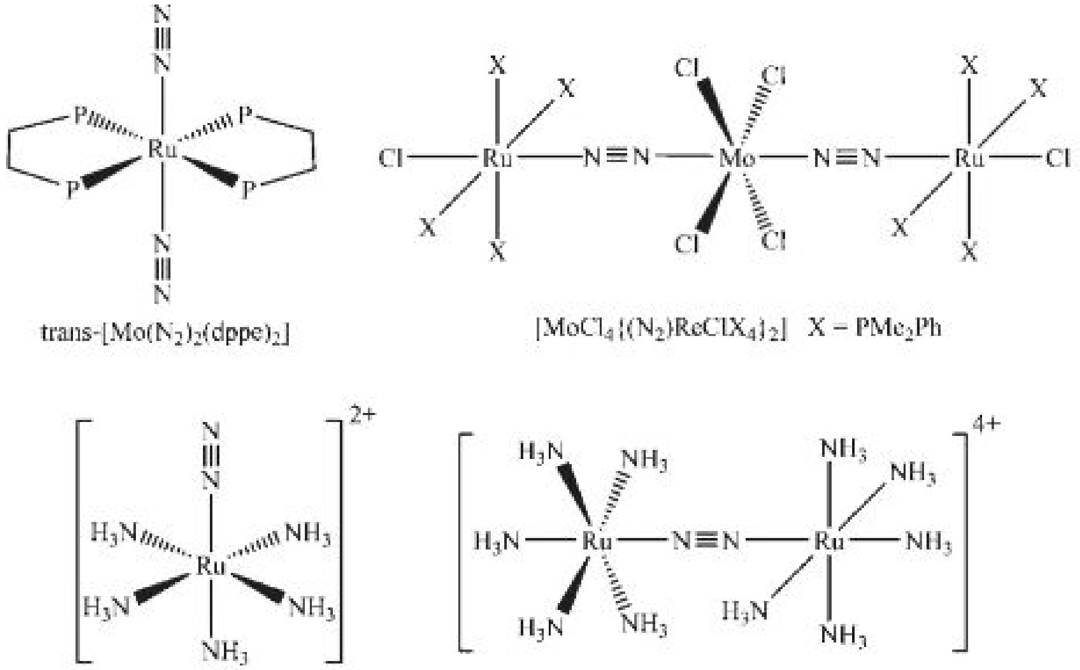
End-on bridging Side-on bridging

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

The most common binding mode of dinitrogen ligand with transition metal centre 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 extant of backbonding from filled *d*-orbital the metal centre 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 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 contain 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.



trans-$[Mo(N_2)_2(dppe)_2]$

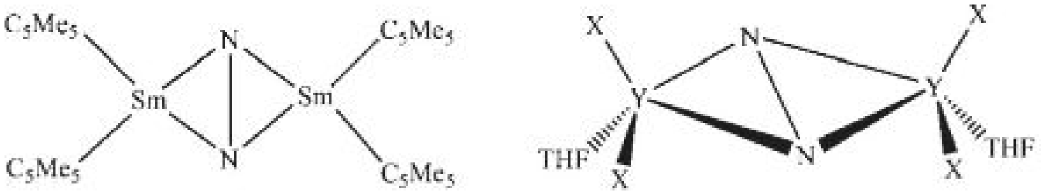
$[MoCl_4\{(N_2)ReClX_4\}_2]$ X = PMe_2Ph

$[Ru(NH_3)_5(N_2)]^{2+}$

$[\{Ru(NH_3)_5\}_2(\mu\text{-}N_2)]^{4+}$

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. One of the most common examples are given below.



$[Sm(C_5Me_5)_2]_2(N_2)$

$[Y(THF)X_4]_2(N_2)$ X = $N(SiMe_3)_2$

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

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

$$trans\text{-}[\mathrm{Mo(N_2)_2(dppe)_2}] + 2\mathrm{C_2H_4} \rightarrow trans\text{-}[\mathrm{Mo(C_2H_4)_2(dppe)_2}] + 2\mathrm{N_2}$$

$$trans\text{-}[\mathrm{Mo(N_2)_2(dppe)_2}] + 2\mathrm{RNC} \rightarrow trans\text{-}[\mathrm{Mo(RNC)_2(dppe)_2}] + 2\mathrm{N_2}$$

$$trans\text{-}[\mathrm{Mo(N_2)_2(dppe)_2}] + 2\mathrm{CO} \rightarrow trans\text{-}[\mathrm{Mo(CO)_2(dppe)_2}] + 2\mathrm{N_2}$$

ii) Reactions of Ligating N_2 with Lewis Acids:

$$[\mathrm{ReCl(N_2)(PMe_2Ph)_4}] + [\mathrm{Mo(Cl_4)(THF)_2}] \xrightarrow{\mathrm{CH_2Cl_2,\,MeOH}} [\mathrm{(PMe_2Ph)_4ClReN_2MoCl_4(OMe)}]$$

$$[\mathrm{ReCl(N_2)(PMe_2Ph)_4}] + [\mathrm{MoCl_4(PPh_3)_2}] \rightarrow [\mathrm{MoCl_4\{(N_2)ReCl(PMe_2Ph)_4\}_2}]$$

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

$$trans\text{-}[\mathrm{Mo(N_2)_2(dppe)_2}] + 2\mathrm{HCl} \rightarrow [\mathrm{MoCl(NNH_2)(dppe)_2}]\mathrm{Cl} + \mathrm{N_2}$$

$$trans\text{-}[\mathrm{W(N_2)_2(dppe)_2}] + 2\mathrm{HBF_4} \xrightarrow{\mathrm{THF}} [\mathrm{WF(NNH_2)(dppe)_2}][\mathrm{BF_4}] + \mathrm{BF_3.THF} + \mathrm{N_2}$$

iv) Formation of carbon-nitrogen bonds:

$$[\mathrm{W(N_2)_2(dppe)_2}] + \mathrm{RCOCl} + \mathrm{HCl} \rightarrow [\mathrm{WCl(N_2HCOR)(dppe)_2}]\mathrm{Cl}$$

$$[\mathrm{Mo(N_2)(RCN)(dppe)_2}] + \mathrm{PhCOCl} \rightarrow [\mathrm{MoCl(NNCOPh)(dppe)_2}]$$

$$[\mathrm{Mo(N_2)_2(dppe)_2}] + \mathrm{RCOCl} + \mathrm{HCl} \rightarrow [\mathrm{MoCl(N_2HCOR)(dppe)_2}]\mathrm{Cl}$$

➢ *3. Metal Dioxygen Complexes*

Metal dioxygen complexes are the coordination compounds which contain O_2 ligand attached to a metal centre. 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 the 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 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

$$[\mathrm{IrCl(CO)(PPh_3)_2}\ ] + \mathrm{O_2} \rightleftharpoons [\mathrm{IrCl(CO)(PPh_3)_2O_2)}]$$

$$[\mathrm{Co(DMG)_2}] + \mathrm{O_2} + \mathrm{Pyridine} \rightarrow [\mathrm{Co(DMG)_2(O_2)(Pyridine)}]$$

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

$$2[\mathrm{Rh(PPh_3)_3}Cl] + 2\mathrm{O_2} \rightarrow [\mathrm{Rh(PPh_3)_2(O_2)Cl}]_2$$

$$2[\mathrm{Co(histidine)_2}] + \mathrm{O_2} \rightarrow [\mathrm{Co_2(histidine)_4(O_2)}]$$

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

$$[\mathrm{Ru(PPh_3)_2(CO)_2(SO_2)}] + \mathrm{O_2} \rightarrow [\mathrm{Ru(PPh_3)_2(CO)_2(SO_4)}]$$

iv) Displacement of free oxidized ligand:

$$[\mathrm{Pt(PPh_3)_4}] + 2\mathrm{O_2} \rightarrow [\mathrm{Pt(PPh_3)_2(O_2)}] + 2\mathrm{Ph_3PO}$$

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 O_2 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 O_2 is given below.

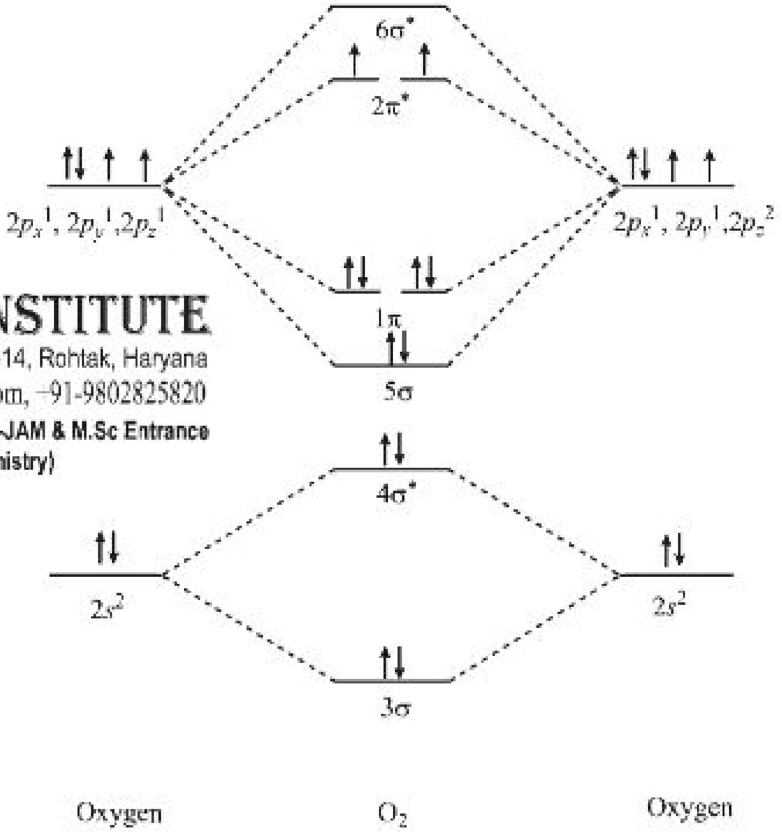


Figure 24. The molecular orbital diagram of dioxygen molecule.