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CHEMISTRY
11: Inorganic Chemistry-III
10: Molecular orbitals of NO and structure and bonding of metal nitrosyls

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1. Learning Outcomes

After studying this module, you shall be able to learn about:

- the basics of molecular orbital theory.
- the molecular orbital diagram of nitrosyl.
- Structure and bonding in metal nitrosyl.
- Metal complexes possessing a non-linear (bent) coordination of NO.
- polynuclear metal-nitrosyls.

2. Introduction

Molecular orbital theory:

Valence bond and hybrid orbital theories provided the way to rationalize the geometries of simple molecules. The idea behind the bonding theories started from writing simple Lewis electron-dot structures to visualizing the atomic orbitals in order to provide valid explanations for the obvious question “why do atoms combine?”. However, these theories could explain the bond formation in simpler molecules like methane and to some extent the geometries of these molecules, the link between the molecular properties and the aspects of bonding was still missing. These were unsuccessful to explain, for example, the phenomenon of light absorption followed by molecular excitations and light emission. For example, MO theory can explain “why O₂ is paramagnetic?”

Molecular orbital (MO) theory describes the electrons in molecules by using specific wave functions called molecular orbitals. Molecular orbitals are formed by the linear combination of two atomic orbitals. Two atomic orbitals (AOs) combine to form two molecular orbitals namely bonding molecular orbitals and anti-bonding molecular orbitals. MOs have many of the similar characteristics as atomic orbitals. MOs, like AOs, can hold a maximum of two electrons and have definite energy. Unlike AOs, MOs are associated with the entire molecule and not with a single atom. Two *s*-orbitals and two *p*-orbitals combine in different ways to give rise to one bonding MO (σ_{1s}) and one anti-bonding (σ^*_{1s}) MO as shown below (fig-1 and fig-2).

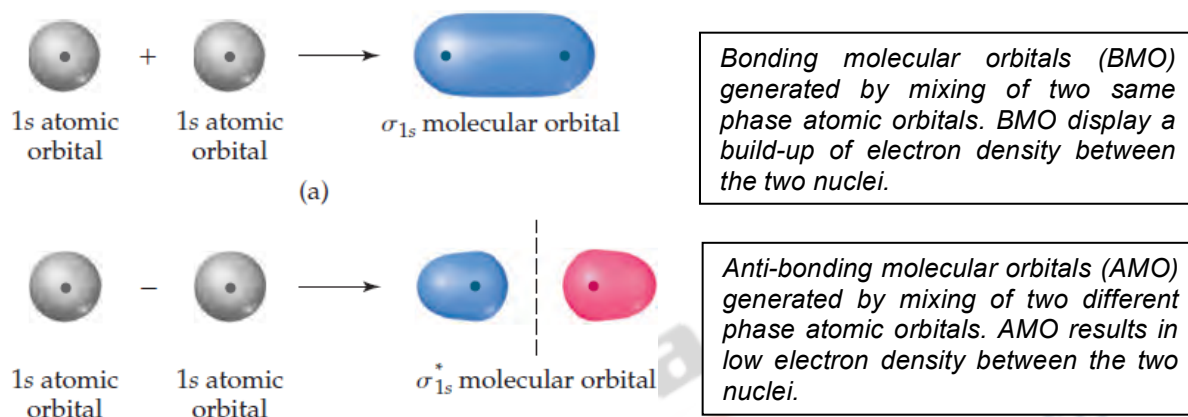


Fig. 1: Mixing of two atomic s -orbitals to generate two molecular orbitals.

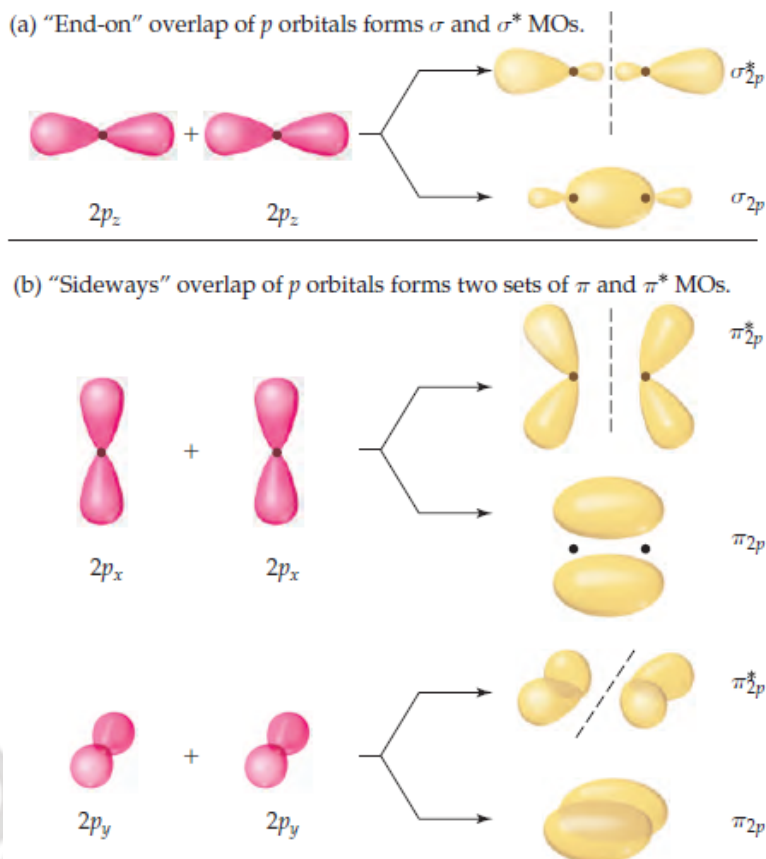


Fig. 2: Mixing of two atomic p -orbitals to generate two molecular orbitals. (a) "End-on" overlap results in a σ -bond. (b) "Sideways" overlap results in a π -bonds. Mo diagrams of H_2 and He_2 molecules is shown in fig-3

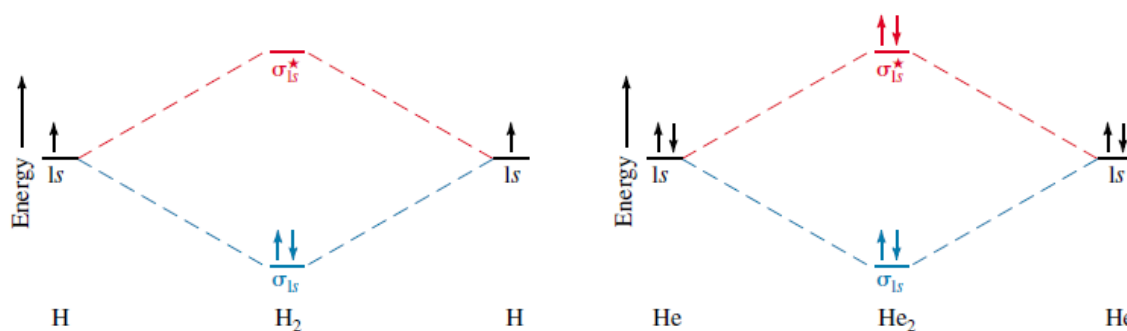
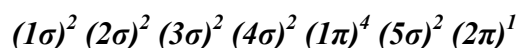


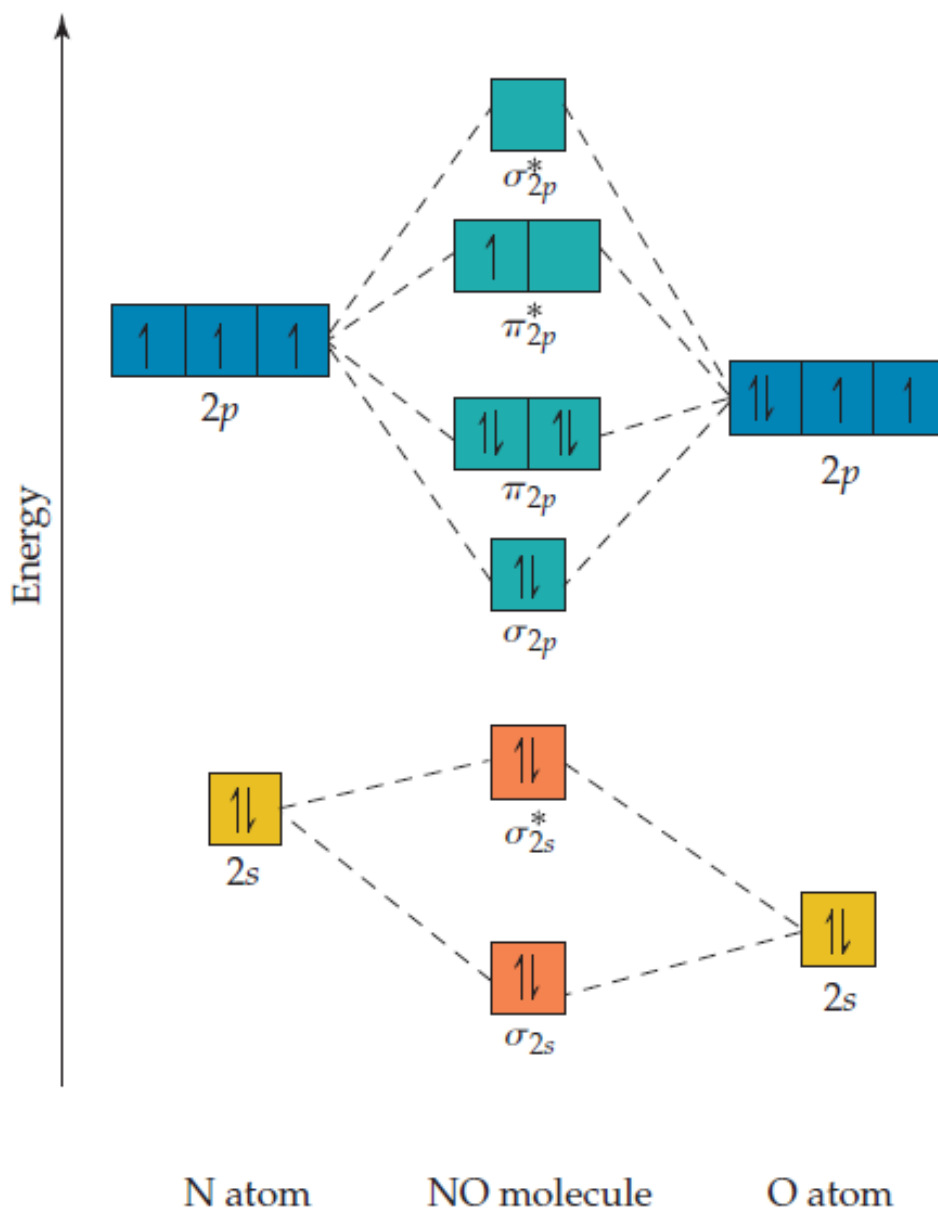
Fig. 3: Molecular orbital diagram of H_2 and He_2 .

3. Molecular Orbitals of NO

Nitric oxide (NO) has total 15 electrons and 11 electrons in valence shell. The molecular orbital electronic configuration can be written as:



The energy level diagram displaying the filled MOs of a molecule in the increasing order of their energies is called a molecular orbital energy level diagram. The number of molecular orbitals (MOs) formed is equal to the number of atomic orbitals that are combined. Following these principles, the MOs of NO can be filled to make an energy level diagram as shown in the figure below.

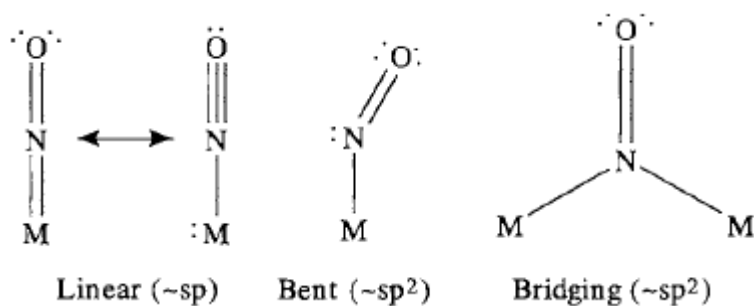


When two atomic orbitals are combined, one of the resulting MOs is at a lower energy than the original atomic orbitals; this is a bonding orbital. The other MO is at a higher energy than the original atomic orbitals; this is an anti-bonding orbital. The electrons in the MOs are filled according to the Aufbau principle, the Pauli's exclusion principle and the Hund's rule of maximum multiplicity. A maximum of two electrons of opposite spin

can occupy a molecular orbital (Pauli's exclusion principle). The orbitals of same energy must be singly filled before pairing. The unpaired electrons must have parallel spins (Hund's Rule). The atomic energies of the more electronegative atom will be lower in energy than those of the less electronegative element and are placed on the two opposite ends of the diagram. Therefore, the $2\sigma_s$ MO is closer in energy to the 2s atomic orbital of oxygen. As a result, the bonding MOs of NO molecule has more oxygen-like atomic orbital character, and the anti-bonding orbitals have more nitrogen-like atomic orbital character. The greater the energy differences between the bonding and anti-bonding MOs, the more polar the bond joining the two atoms and hence greater is its ionic character. The energy difference is also a measure of degree of orbital overlap between atomic orbitals; the more the orbitals overlap, greater is the covalent character of the bond. Since NO has 15 valence electrons, it has a bond order of 2.5, short nitrogen-oxygen bond length of 1.15 Å, a low dipole moment of 0.15 D and a high bond energy of 891 kJ/mol. The σ_{2p} molecular orbital of NO is also localized on nitrogen and act as donor orbital, although this is a poorer donor as compared to the σ_{2p} molecular orbital of CO because the higher electronegativity of nitrogen. The π^* orbital of NO act as degenerate pair of acceptor orbital similar to those of CO but the higher electronegativity of N makes them better acceptor than C.

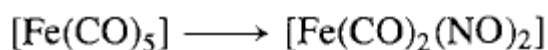
4. Structure and bonding in metal nitrosyls:

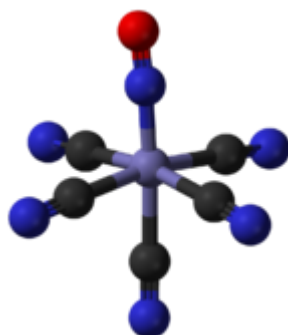
Nitric oxide as ligand displays a variety of coordination modes in their metal complexes as shown in the figure below:



5. Metal complexes possessing a linear coordination of NO

NO has one more electron than CO, hence it often acts as a three electron donor. Hence in metal carbonyl complexes, the replacement of CO by NO is compensated by a matching decrease in the atomic number of the metal centre. Therefore, 3 CO can be easily replaced by 2 NO. For example, the nitroprusside anion, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, an octahedral complex containing a "linear NO" ligand is shown as:





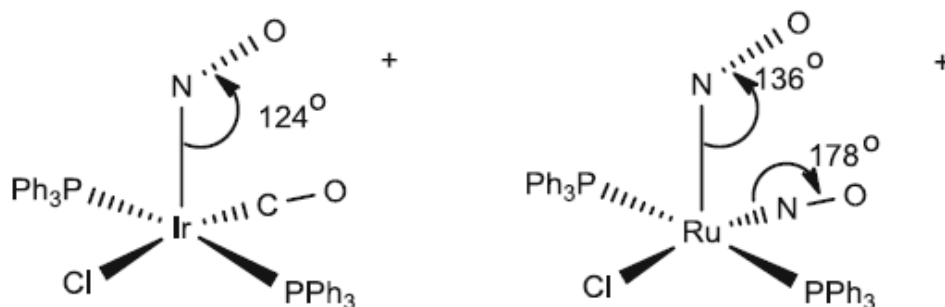
In these and analogous complexes, the M-N-O group is linear. The bonding in these compounds can be discussed in terms of a preliminary transfer of 1 electron from NO to the metal center. The resulting NO^+ then coordinates with the reduced metal centre as a 2 electron σ -donor and π - acceptor. A variety of nitrosyl complexes possessing the linear nitrosyl group are shown in the table below.

| Compound | Angle M-N-O | ν (N O)/ cm^{-1} |
|---|-----------------------------|-------------------------------|
| <i>Linear</i> | | |
| $[\text{Co}(\text{en})_3][\text{Cr}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$ | 176° | 1630 |
| $[\text{Cr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{NO})_2]$ | $171^\circ, 166^\circ$ | 1823, 1715 |
| $\text{K}_3[\text{Mn}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$ | 174° | 1700 |
| $[\text{Mn}(\text{CO})_2(\text{NO})(\text{PPh}_3)_2]$ | 178° | 1661 |
| $[\text{Fe}(\text{NO})(\text{mnt})_2]^-$ | 180° | 1867 |
| $[\text{Fe}(\text{NO})(\text{mnt})_2]^{2-}$ | 165° | 1645 |
| $[\text{Fe}(\text{NO})(\text{S}_2\text{CNMe}_2)_2]$ | 170° | 1690 |
| $\text{Na}_2[\text{Fe}(\text{CN})_5(\text{NO})] \cdot 2\text{H}_2\text{O}$ | 178° | 1935 |
| $[\text{Co}(\text{diars})(\text{NO})]^{2+}$ | 179° | 1852 |
| $[\text{Co}(\text{Cl})_2(\text{NO})(\text{PMePh}_2)_2]$ | 165° | 1735, 1630 |
| $\text{Na}_2[\text{Ru}(\text{NO})(\text{NO}_2)_2(\text{OH})] \cdot 2\text{H}_2\text{O}$ | 180° | 1893 |
| $[\text{RuH}(\text{NO})(\text{PPh}_3)_3]$ | 176° | 1645 |
| $[\text{Ru}(\text{diphos})_2(\text{NO})]^+$ | 174° | 1673 |
| $[\text{Os}(\text{CO})_2(\text{NO})(\text{PPh}_3)_2]^+$ | 177° | 1750 |
| $[\text{IrH}(\text{NO})(\text{PPh}_3)_3]^+$ | 175° | 1715 |
| <i>Bent</i> | | |
| $[\text{CoCl}(\text{en})_2(\text{NO})]\text{ClO}_4$ | 124° | 1611 |
| $[\text{Co}(\text{NH}_3)_5\text{NO}]^{2+}$ | 119° | 1610 |
| $[\text{Co}(\text{NO})(\text{S}_2\text{CNMe}_2)_2]^{(aq)}$ | $\sim 135^\circ$ | 1626 |
| $[\text{Rh}(\text{Cl})_2(\text{NO})(\text{PPh}_3)_2]$ | 125° | 1620 |
| $[\text{Ir}(\text{Cl})_2(\text{NO})(\text{PPh}_3)_2]$ | 123° | 1560 |
| $[\text{Ir}(\text{CO})\text{Cl}(\text{NO})(\text{PPh}_3)_2]\text{BF}_4$ | 124° | 1680 |
| $[\text{Ir}(\text{CO})\text{I}(\text{NO})(\text{PPh}_3)_2]\text{BF}_4 \cdot \text{C}_6\text{H}_6$ | 124° | 1720 |
| $[\text{Ir}(\text{CH}_3)\text{I}(\text{NO})(\text{PPh}_3)_2]$ | 120° | 1525 |
| <i>Both</i> | | |
| $[\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2]^+$ | $178^\circ, 138^\circ$ | 1845, 1687 |
| $[\text{Os}(\text{NO})_2(\text{OH})(\text{PPh}_3)_2]^+$ | $\sim 180^\circ, 127^\circ$ | 1842, 1632 |
| $[\text{Ir}(\eta^3\text{-C}_3\text{H}_5)(\text{NO})(\text{PPh}_3)_2]^+$ (see text) | $\sim 180^\circ, 129^\circ$ | 1763, 1631 |

6. Metal complexes possessing a non-linear coordination of NO

There are metal complexes in which the M-N-O group features slightly bent coordination geometry where the M-N-O bond angles are in the range of 165° - 180° . For example, the cationic complex $[\text{Ir}(\text{CO})\text{Cl}(\text{NO})(\text{PPh}_3)_2]^+$ was found to have a bond angle of 124° and there are a large number of other nitrosyl complexes. On the other hand, in a related complex $[\text{RuCl}(\text{NO})_2(\text{PPh}_3)_2]^+$, in which the CO ligand has been replaced by a second NO

molecule, have both linear and bent M-N-O as shown in the figure below. In this complex, the basal nitrosyl is linear Ru-N-O (178°) whereas the apical nitrosyl was found to be bent (136°). The metal-nitrogen bond lengths in the complex are in accordance with the presented structure. The Ru-N bond length in the linear system is shorter (1.73 \AA) as compared to the bent system (1.85 \AA). This indicates that there is substantial π -bonding in the linear system whereas the bent system is a σ -only metal-nitrogen bond.

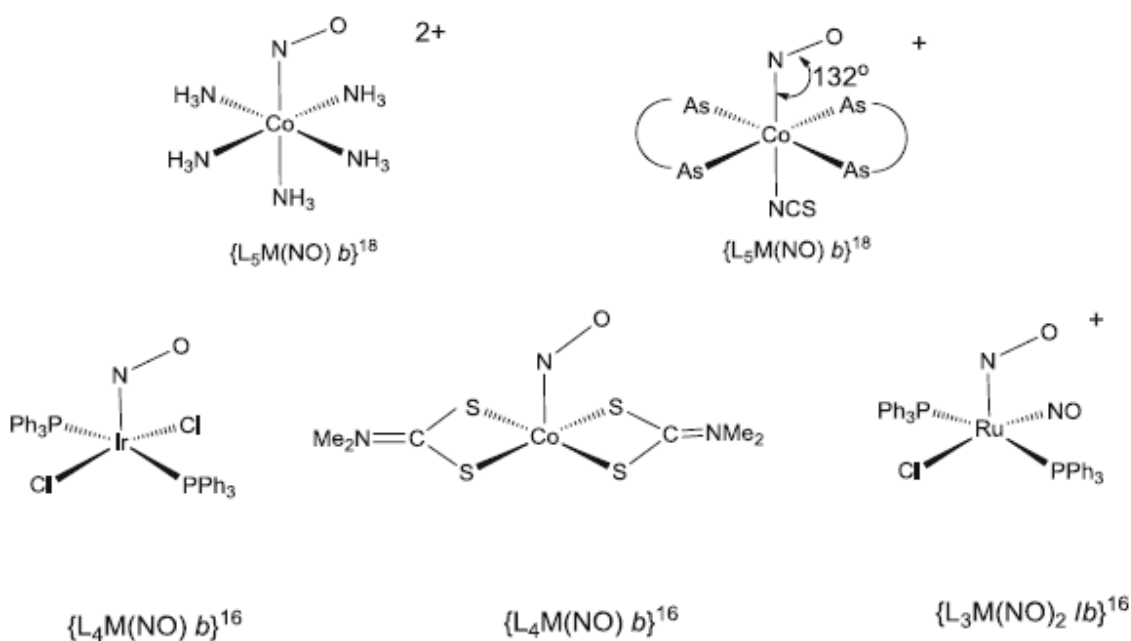


In $[\text{Co}(\text{NO})(\text{en})_2\text{Cl}]^+$ (where “en” is ethylenediamine), the NO takes a bent coordination mode. In this complex, the Co-N bond distance (1.820 \AA) in Co-NO bond was found to be considerably different from Co-N bonds with the ethylenediamine ligand (1.964 \AA). This indicates that the NO ligand retains significant multiple bond character because of back donation from a filled metal d-orbital to the remaining empty π^* orbital of the NO ligand. The first well-characterized example of a metal complex containing the bent nitrosyl was found in a derivative of Vaska’s complex.

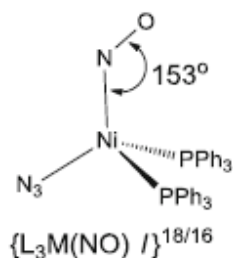


The product has a square pyramidal structure with a bent nitrosyl ligand having an Ir-N-O angle of 124° . The question of whether the nitrosyl ligand would adopt a linear or bent coordination mode can be answered by looking at the MO picture of the final complex. If

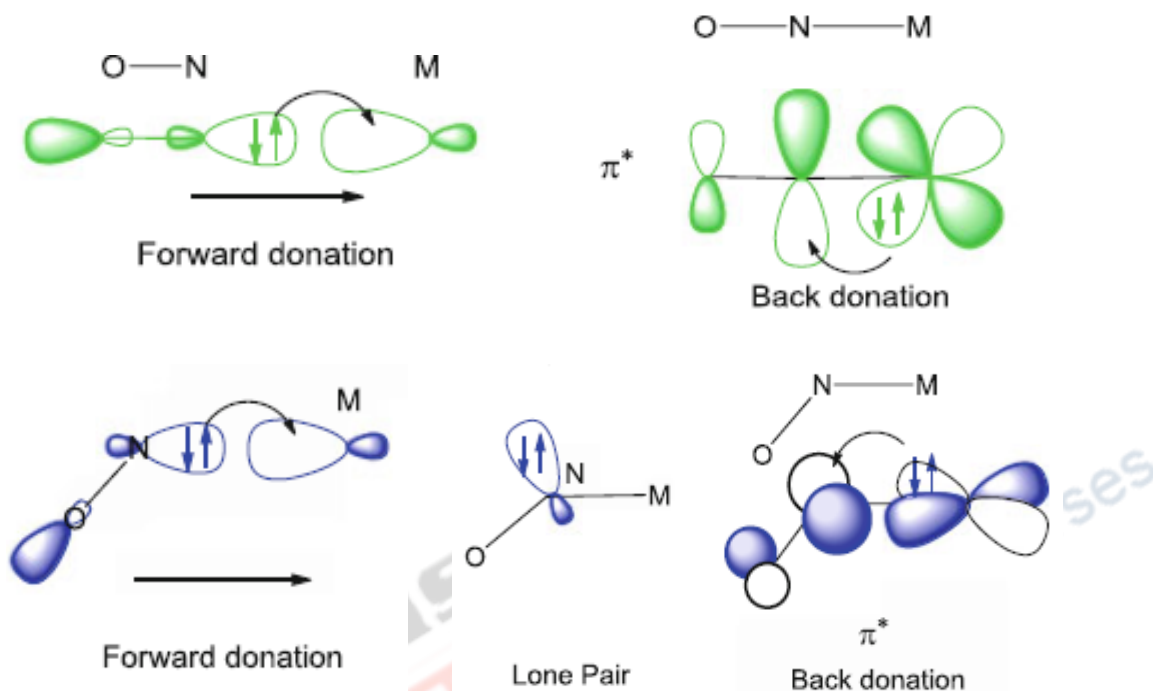
there are available non-bonding MOs on the electron poorer metal, the electron pair on the nitrogen of NO can reside there and the nitrogen functions as a sp donor system with an associated π -back donation from the metal to the NO. Thus, NO adopts linear coordination mode in this situation. On the other hand, when the low-lying orbitals of metal are already filled (electron-rich system), the pair of electron must occupy a basically non-bonding orbital on the nitrogen of bonded NO, resulting in sp^2 hybridization and a bent coordination geometry of the NO.



Complexes with bent b nitrosyls - NO is a 1 electron donor

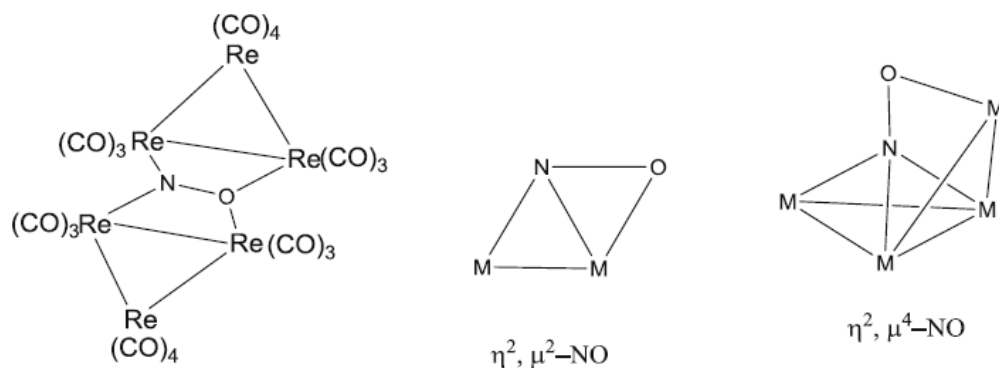


Complex with an intermediate l nitrosyl - NO is a 3 or 1 electron donor

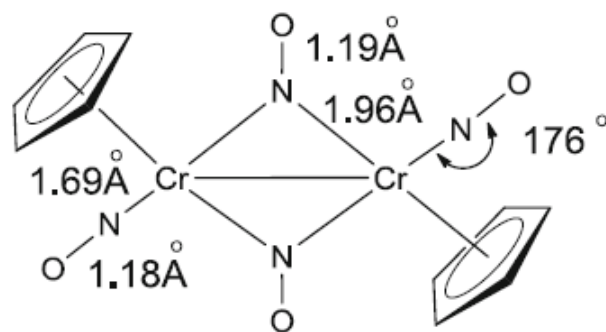


7. Polynuclear metal nitrosyl complexes

A number of metal-metal bonded complexes with transition metals possessing linear, doubly bridging and triply bridging nitrosyl ligands. An example containing unusual bridging modes of nitrosyl is $[\{\text{Re}_3(\text{CO})_{10}\}_2(\mu\text{-NO})]$ where the bridging NO bonded through both N and O to two pairs of rhenium atoms from the two triangular Re_3 fragments. There are also examples of cluster complexes where the nitrosyl ligand bands simultaneously with nitrogen and oxygen through π -electrons of nitrosyl.



One such example containing nitrosyl ligand in both linear and bridging coordination modes.



polynuclear metal-nitrosyls.

8. Summary

- Molecular orbital (MO) theory describes the electrons in molecules by using specific wave functions called molecular orbitals. In molecular orbitals, electrons are filled by using aufbau principle, Hund's rule of maximum multiplicity and Pauli's exclusion principle.
- NO has 15 valence electrons, it has a bond order of 2.5, short nitrogen-oxygen bond length of 1.15 Å, a low dipole moment of 0.15 D and a high bond energy of 891 kJ/mol.
- NO possess one unpaired electron in the anti-bonding π -orbital.
- NO display linear, bent and bridging coordination modes in their metal complexes.
- The nitroprusside anion, $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ possess linear NO as ligand.
- The first well-characterized example of a metal complex containing the bent nitrosyl was found in a derivative of Vaska's complex.
- With electron poores metal ions, NO acts as a three electron donor and possess linear coordination mode.