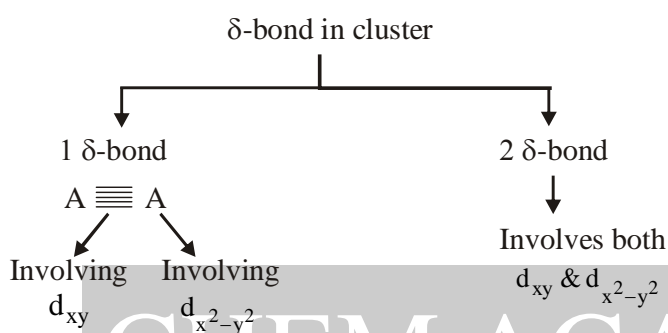


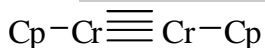
Organometallics

Metal clusters having δ -bonding:

- * δ -bond is formed by 4 lobes interaction
- * $d_{x^2-y^2}$ and d_{xy} can form δ bond, If z is considered as intermolecular axes.



Binuclear Compounds Containing Quintuple Bond



One of the electrons of each chromium atom is used for bonding with substituted aryl group. The remaining ten electrons of the two chromium atoms are distributed in molecular orbitals with the electronic configuration $\sigma^2\pi^4\delta^4$.

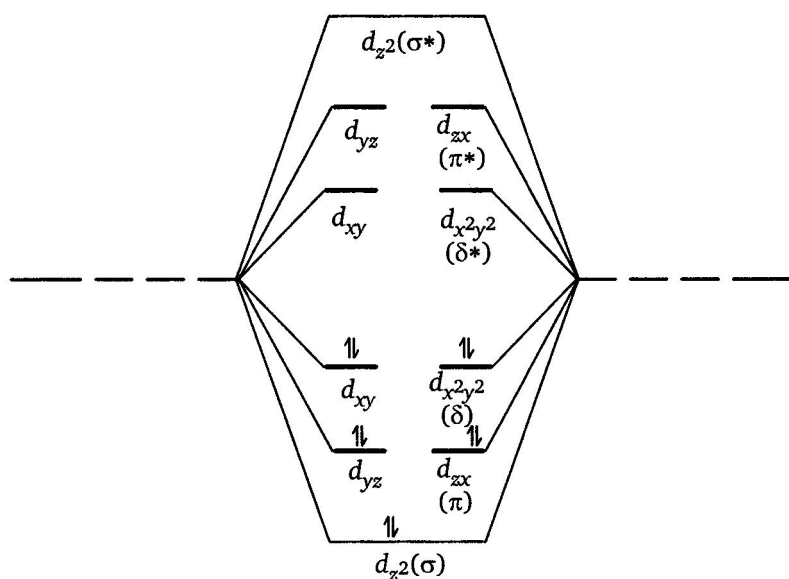
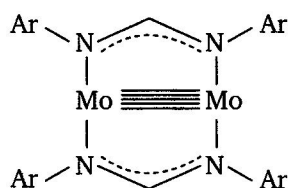


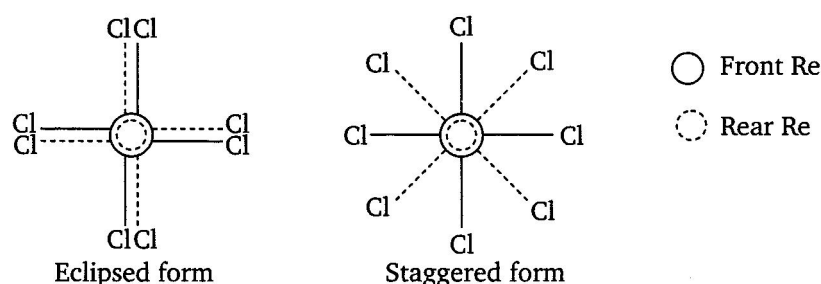
Figure: Molecular orbital diagram for metal-metal quintuple bond

The δ - orbitals are highest occupied molecular orbitals (HOMO) and δ^* are the lowest unoccupied molecular orbitals (LUMO). Bond order according to this MO diagram is $(10 - 0) / 2 = 5$. A dimolybdenum compound with quintuple bond and two diimido bridging ligands has been synthesised.



Binuclear cluster involving d_{xy} for delta bond

In $[\text{Re}_2\text{Cl}_8]^{2-}$ ions, the Re-Re distance (224 pm) is extremely short compared with an average Re-Re bond distance. Structural analysis has shown that the Cl atoms are eclipsed rather than staggered.



Both of these features can be recognized due to quadruple M-M bonds. Each rhenium atom is bonded to four chlorine atoms that are almost in a square planar array. The $d_{x^2-y^2}$ orbitals of the two metals are used for bonding to Cl ligands. The Re-Cl bonds are formed by using dsp^2 hybrid orbitals on both metals utilizing $d_{x^2-y^2}$ orbitals. This leaves four orbitals d_{z^2} , d_{yz} , d_{zx} and d_{xy} and the four electrons on each Re^{3+} ion (d^4). The metal d_{z^2} and p_z orbitals may hybridize to form two dp hybrid orbitals: one orbital directed towards the other rhenium atom and a second orbital directed in the opposite direction. The former hybrid orbital overlaps with the similar on the second Re atom to form a Re-Re σ -bond.

The d_{xz} and d_{yz} orbitals of each metal atom overlap to form two π -bonds in xz and yz planes respectively. Finally sideways overlap of d_{xy} orbitals of the two metals form a δ bond. The formation of the δ bond causes the eclipsed conformation because overlap of the d_{xy} orbitals is possible only in geometry. If the chlorine atoms are staggered the two d_{xy} orbitals will likewise be staggered which results in zero overlap.

A qualitative molecular orbital diagram for the formation of M-M bonds is shown in Figure. The Re-Cl bonds are regarded as coordinate bonds between Re^{3+} ions and the Cl^- ligands. The eight d -electrons from two Re^{3+} ions (four electrons from each Re^{3+} ion) occupy a σ -bonding, two π bonding and one δ bonding molecular orbital to form the quadruple bond. Therefore, the electronic configuration in $[\text{Re}_2\text{Cl}_8]^{2-}$ ion will be $\sigma^2\pi^4\delta^2$.

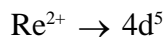
$[\text{Re}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4]^{2-}$:

Let the oxidation state of Re = x

$$2x - 4 + 0 = 0$$

$$2x = +4$$

$$x = +2$$



Therefore number of d-electrons on two Re^{2+} ions = 10, Electronic configuration in this compound is $\sigma^2 \pi^4 \delta^2 \delta^{*2}$

$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(8 - 2) = 3.0$$

All electrons are paired, therefore, it is diamagnetic.



Let the oxidation states of two Re atoms are x and y.

$$x + y - 4 = +1$$

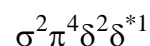
$$x + y = +5$$

$$x = +2, y = +3$$



Therefore, number of d-electrons on Re^{2+} and Re^{3+} ions
 $= 5 + 4 = 9$

Electronic configuration in this cluster ion is



$$\text{Bond order} = \frac{1}{2}(8 - 1) = 3.5$$

There is one unpaired electron, therefore, it is paramagnetic.

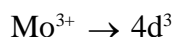


Let the oxidation states of Mo atoms are x and y.

$$x + y - 8 = -2$$

$$x + y = +6$$

$$x = +3, y = +3$$



Number of electrons in two M^{3+} ions = 6

Electronic configuration in this cluster ion is: $\sigma^2 \pi^4$

$$\text{Bond order} = \frac{6 - 0}{2} = 3.0$$

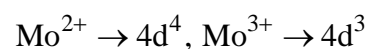
Since all electrons are paired, therefore, this cluster ion is diamagnetic.



$$x + y - 8 = -3$$

$$x + y = +5$$

$$x = +2, y = +3$$



Number of valence electrons on Mo^{2+} and Mo^{3+} ions is = 7

Electronic configuration in this cluster ion is : $\sigma^2 \pi^4 \delta^1$

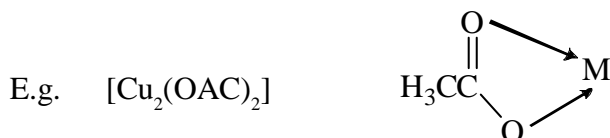
$$\text{Bond order} = \frac{7-0}{2} = 3.5$$

Since there is one unpaired electron, therefore, this ion is paramagnetic.

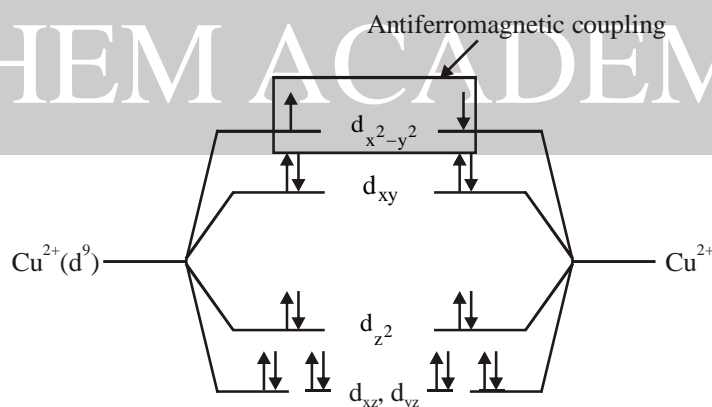
The energy difference between δ and δ^* orbitals lie in the visible region of the electromagnetic radiations. Therefore, most of the complexes with quadruple bond are of intense colour. For example, $[\text{Re}_2\text{Cl}_8]^{3-}$ and $[\text{Mo}_2\text{Cl}_8]^{4-}$ are royal blue and dark yellow respectively. The colour of compounds containing M–M quadruple bonds is due to $\delta - \delta^*$ transition.

Involvement of $d_{x^2-y^2}$ orbital in δ bonding

Sometimes $d_{x^2-y^2}$ orbitals are used when dimerisation of 3-d series elements take place.



In square planar complexes of $\text{Cu}^{2+}(d^9)$ when octahedral complexes have high Z out. Therefore $d_{x^2-y^2}$ orbitals increase to very high energy. Which results in antiferromagnetic coupling by the formation of δ bond.



Note:

The electron density on both complexes should be high for better coupling
As extent of coupling increase, lesser will be the magnetic moment.