

11.1: Complexes with Multiple Metal-Metal Bonds

Molecular orbital considerations in Dinuclear Metal Complexes with Multiple M-M Bonds

Let us begin a new chapter and think about dinuclear transition metal complexes with multiple metal-metal bonds. What is the maximum bond order that we could expect? The transition metals have five d-orbitals available, and in order to determine the maximum possible bond order we need to see how they overlap to form molecular orbitals (Fig. 11.1.1).

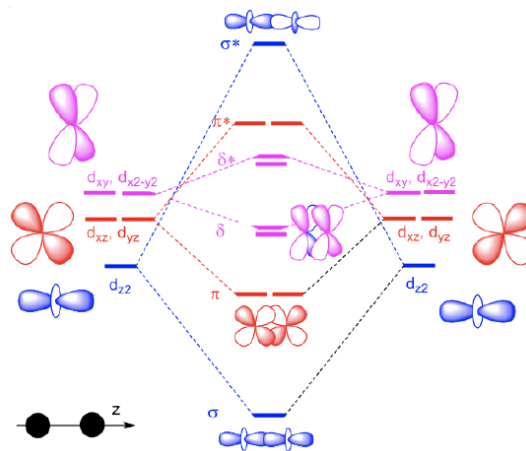


Figure 11.1.1 Molecular orbital overlap of metal d-orbitals forming M-M bonds

If we define the M-M bond axis as the z-axis, then two d_{z^2} -orbitals can overlap in σ -fashion to form a bonding and an anti-bonding σ -molecular orbital. A d_{xz} , and a d_{yz} can overlap with another d_{xz} and another d_{yz} in π -fashion to form two degenerated bonding π and two degenerated anti-bonding π^* -orbitals. π -overlap is smaller than σ -overlap, therefore the split in energy between the bonding and the anti-bonding π -orbitals is smaller than the split between the bonding and the anti-bonding σ -orbitals. The d_{xy} orbital can overlap with another d_{xy} orbital in δ -fashion, and so can the $d_{x^2-y^2}$ with another $d_{x^2-y^2}$. This gives two bonding δ -orbitals and two anti-bonding δ -orbitals. The δ -overlap is even smaller than the π -overlap, therefore the energy split between the bonding and the anti-bonding δ -orbitals is even smaller than those for the π and π^* -orbitals. So what would be the maximum bond order that could be achieved? The maximum bond order would be achieved when all bonding MOs were full, and all anti-bonding MOs were empty. We have overall five bonding MOs that we could fill with ten electrons from two metal atoms with d^5 -electron configuration. The maximum bond order BO would therefore be $BO=5$. However, in practice only bond orders up to 4 are well known. This is because the $d_{x^2-y^2}$ orbital is usually too involved in the bonding with the ligands thereby becoming unavailable for metal-metal interactions. The $d_{x^2-y^2}$ orbital makes the strongest interactions with the ligands because most ligands approach on or near the x and the y-axes.

Electron Configurations and Multiple M-M Bonds

We can easily predict now which electron configuration leads to which metal-metal bond order. The bond order increases from 1 to 4 with the electron configuration changing from d^1 to d^4 . At d^4 all bonding MOs are full with eight electrons.

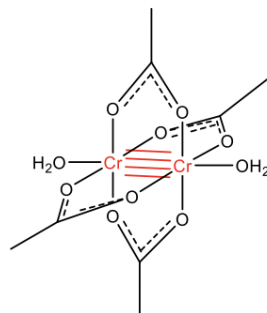


Figure 11.1.2 Tetraacetatodiaquadichromium complex

An example of a complex with a bond order of 4 is the tetraacetatodiaquadichromium complex shown (Fig. 11.1.2). Cr is in the oxidation state +2, which makes the chromium a d^4 species. We can quickly show this by counting the valence electrons. A neutral Cr atom has 6 VE, and an electron configuration $3d^5 4s^1$. There are four acetate ligands having a 1- charge each which gives four negative charges overall. The complex is overall neutral which means that each Cr must have formally a 2+ charge, and the electron configuration is $3d^4$.

d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8
1	2	3	4	3	2	1	0

Figure 11.1.3 Relationship between metal-metal bond order and electron configuration

With even more electrons in the metal d-orbitals the bond order begins to decrease again as anti-bonding MOs need to be filled (Fig. 11.1.3). The combination of two metals with d^5 electron configuration leads to a triple bond, two d^6 -metals give a double bond, and two d^7 metals give a single bond. A metal-metal bond should not exist for two d^8 -metals because then the bond order is zero.

Evidence for M-M Multiple Bonds

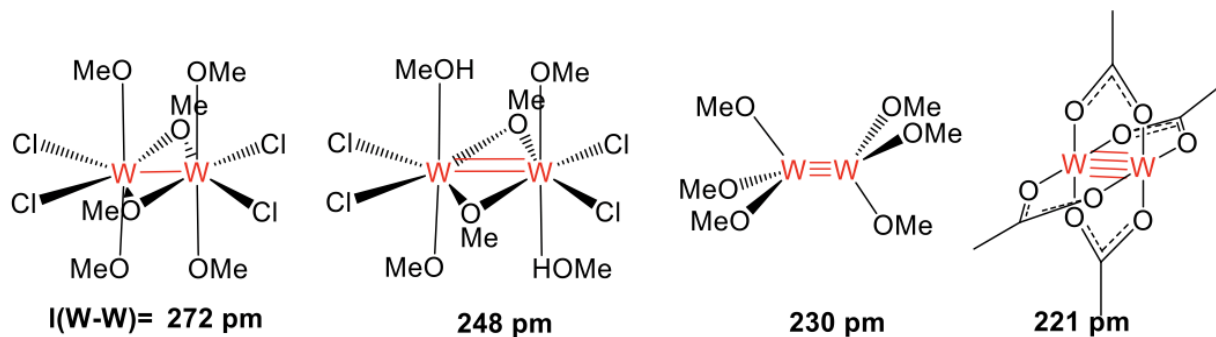


Figure 11.1.4 M-M bond length in four tungsten complexes

What experimental evidence can support the existence of a particular bond order (Fig. 11.1.4)? One argument is the bond length which can be obtained through the crystal structure determination of the complex. The shorter the bond, the higher the bond order. For instance, in the four tungsten complexes shown the bond lengths decrease from 272 pm, to 248 pm, to 230 pm to 221 pm corresponding to a single, double, triple, and quadruple bond, respectively.

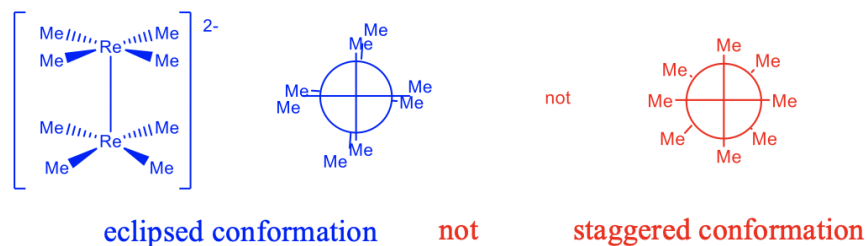


Figure 11.1.5 ReMe_4 conformations

Another hint can be the conformation of a molecule (Fig. 11.1.5). For instance, the two square-planar units of the $\text{Re}_2\text{Me}_8^{2-}$ complex anion show eclipsed conformation. Steric repulsion arguments would favor the staggered conformation, so there must be a reason why the two ReMe_4 units are eclipsed. The rhenium is in the oxidation state +3, thus it is a d^4 species, and we would argue that there may be a Re-Re quadruple bond. This quadruple bond can only form when the d_{xy} orbitals are in eclipsed conformation, and this is only possible when the two ReMe_4 fragments are in eclipsed conformation. The very short bond length of 218 pm further supports the existence of the quadruple bond.

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