

**Advanced Transition Metal Chemistry – Metal-Metal Multiple Bonding**  
**Prof M. S. Balakrishna**  
**Department of Chemistry**  
**Indian Institute of Technology – Bombay**

**Lecture – 23**  
**Metal-Metal Multiple Bonds (Quadruple and Quintuple Bonding)**

Welcome to MSB lecture series on advanced transition metal chemistry. In my previous lecture, I had initiated discussion on metal-metal multiple bonding and also I gave you some background to metal-metal multiple bonding by the work carried out by Cotton's group especially while working with rhenium salts. Let us continue from where I had stopped. Before we try to establish a bonding concept such as molecule orbital theory to understand the nature of these bonds, let us try to classify the metal-metal bonds we come across among coordination compounds and organometallic compounds.

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### Metal-Metal Bonding

There are three general class of M-M bonding



**Covalent:** Electron precise bonds. M-M bond counts as one electron from each metal center. Most common type of M-M bonding

**Dative:** One metal uses a lone pair from its filled d orbital to coordinate to an empty orbital on a second, more unsaturated metal. For simple electron count purpose, they can be considered as covalent bonds

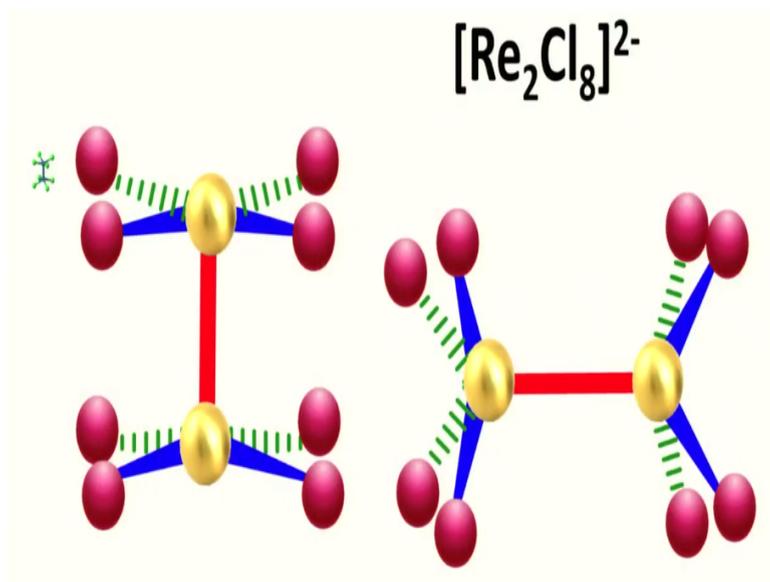
**Symmetry:** Weak metal-metal interactions caused by molecular orbital symmetry interactions of filled and empty M-M bonding and/or antibonding orbitals. Seen in  $d^8$  metals. Less common

In general, there are three class of metal-metal bonding we come across in coordination chemistry as well as in organometallic chemistry. First one is covalent bond. So, here they are electron precise bonds, M-M bonds count as one electron from each metal centre. So, most common type of metal-metal bonding we use while electron counting and also to know whether a given complex satisfies 18 electron rule or not, especially when you have more than one metal centre in a complex, so that means this is a covalent bond.

And then we have another type of bonding called dative bonding. So, one metal uses a lone pair from the filled d orbital to coordinate to an empty orbital on a second, more unsaturated metal. For simple electron count purpose, can be considered as covalent bond, but here what happens one metal is electron rich, other metal is the electron poor and it has vacant orbital so that the electrons can be given very similar to what we come across in case of acid-base interaction, Lewis acid and Lewis base interaction, that is called dative bond.

For example, if I take a metal centre having 18 electrons and other metal having 14 electrons, so it can give, that can also become 16 electron complex, if not 18 electron. Now, we have the last one, very rare one that is called symmetry metal-metal bonding. What does it mean? So, weak metal-metal interactions caused by molecular orbital symmetry interactions of filled and empty metal-metal bonding and or antibonding orbitals seen in case of  $d^8$  metals, but they are less common in nature.

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Now, let us come back to  $[\text{Re}_2\text{Cl}_8]^{2-}$ . Here you can just imagine this molecule in this fashion or in this fashion and here this xy plane is there and principal axis is, z-axis in which two rhenium atoms are establishing a metal-metal bond. And now we have 4 chlorides here and 4 chlorides are here. And here for our practical purpose let us consider this as z axis here and then this is xy plane.

And then accordingly, we have to consider that d-orbitals for the overlapping to establish various bonds to accommodate these electrons present on metal to arrive at different bonds between two metal centres. So, here we have a quadruple bond that is 4 bonds between two

rhenium atoms, and we have to show convincingly using MO diagram. **(Video Starts: 03:41)**

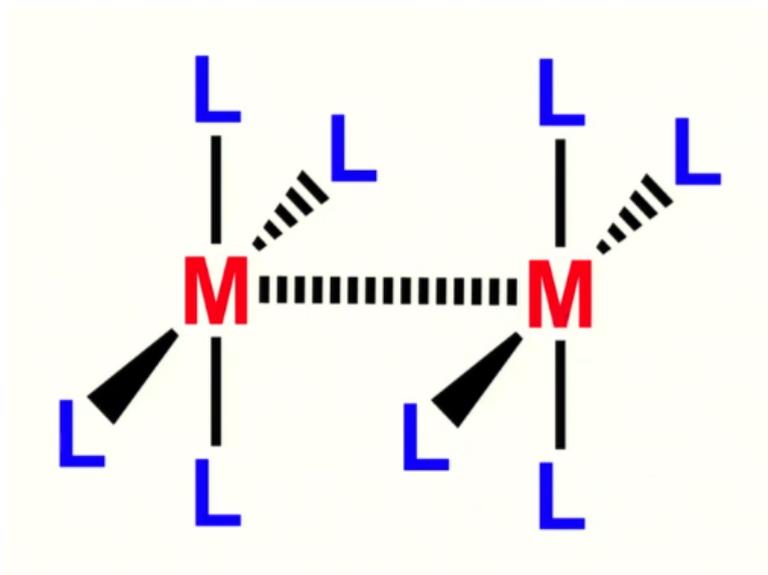
Let us say, if you consider, this is the z axis.

If it is z-axis, what happens, we have  $d_{x^2-y^2}$  is there and then little angle we have  $d_{xy}$  at  $45^\circ$  in the same plane and then we have  $d_{xz}$  and then  $d_{yz}$  is there and  $d_z^2$  be in this fashion. So, that means, now if two rhenium atoms are in z axis, let us say they can overlap something like this, this is  $d_z^2$ . So, this overlapping you can call it as  $\sigma$ -bond. And now, if we talk about  $\pi$ -bond, let us assume this is  $d_{xz}$  and this is another  $d_{xz}$ .

And if they overlap, this is pi-overlapping, this is one  $d_{xz}$  and then this one is  $d_{yz}$ . So, this will degenerate, so that accounts for two  $\pi$ -bonds, and then this one is  $d_z^2$  accounts for one  $\sigma$ -bond. Now, we have  $d_{xy}$  is like this. If the  $d_{xy}$  orbital is like this, now they do not have any option other than overlapping like this. This kind of overlapping we do not come across in main group chemistry or in organic chemistry, when we talk about pi-bonds, because this is not pi bond, pi-bonds will be something like this.

This is  $d_{xz}$  and this is  $d_{yz}$  and then this is  $d_z^2$ . And now if you look into the orientation the  $d_{xy}$  is like this, so they overlap sideways. So, this is the  $d_{xy}$ , so this is responsible, this is called delta bond ( $\delta$ -bond), the higher energy. Energy of this one is very high and the lowest one is  $d_z^2$ . **Okay (Video Ends: 05:21)** And the next one will be these two  $d_{xz}$  and  $d_{yz}$  and then we have the  $d_{xy}$ .

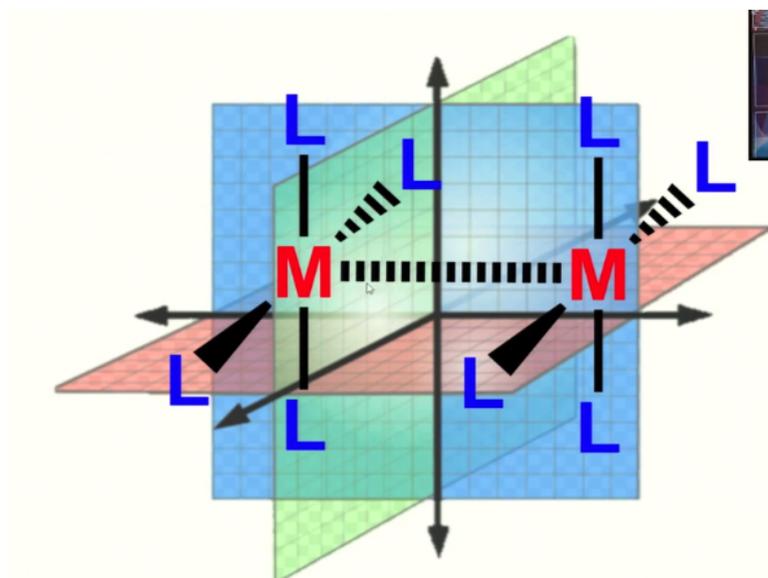
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Now, assume like this. It is there, this is the z-axis and one  $d_z^2$  is there, another  $d_z^2$  is there. And now, if you ask me why we are using only 4 orbitals such as  $d_z^2$ ,  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$ ; why not  $d_{x^2-y^2}$ ? If you just look into this  $ML_4$  square planar complex formation, and if you recall again valence bond theory, in valence bond theory we are using  $dsp^2$  hybrid orbitals. If it is  $dsp^2$  hybrid orbitals, the d-orbital used is  $d_{x^2-y^2}$ .

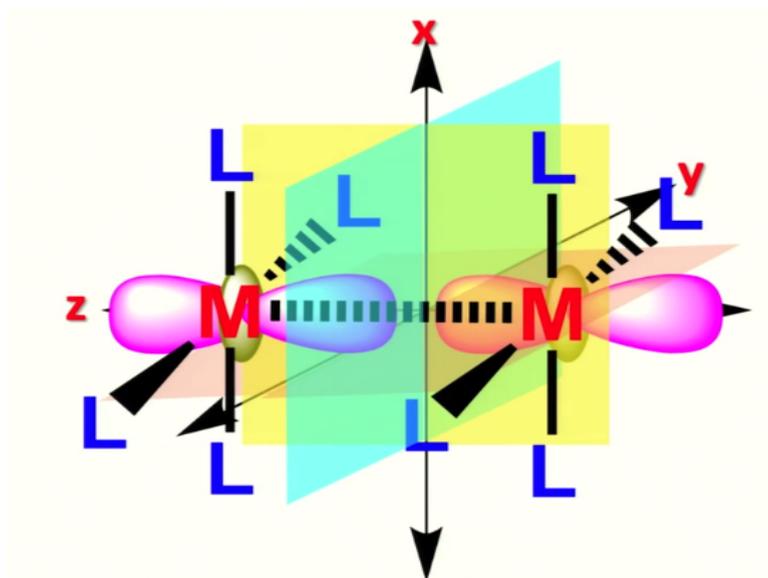
That means,  $d_{x^2-y^2}$  is already participated in making metal to ligand bond, as a result that is not available for metal-metal bonding that is the reason we are not considering. So, other orbitals that are left unutilized while making metal to ligand bond are:  $d_{x^2-y^2}$  is used,  $d_{xy}$  is not used,  $d_{xz}$  is not used,  $d_{yz}$  is not used and also  $d_z^2$ . That is the reason we are using these four unutilized bonds to establish bonds between two metal centres.

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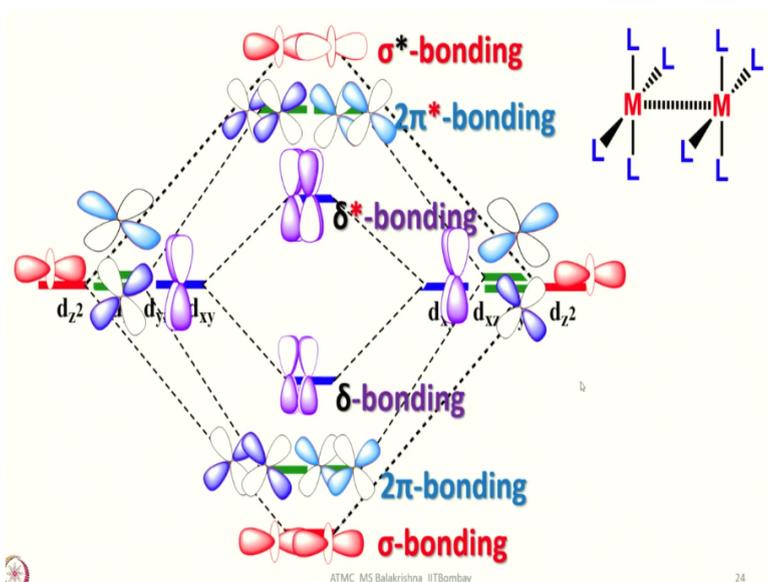
Now, so you bring this Cartesian coordinate, so that can give you precisely the orientation of different orbitals.

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Once again you take this one here, another plane, so another plane. So, now we put. Now, this is what we are considering, two are in this plane, you can see now how sigma-bond is established between two  $d_z^2$  which are on z axis.

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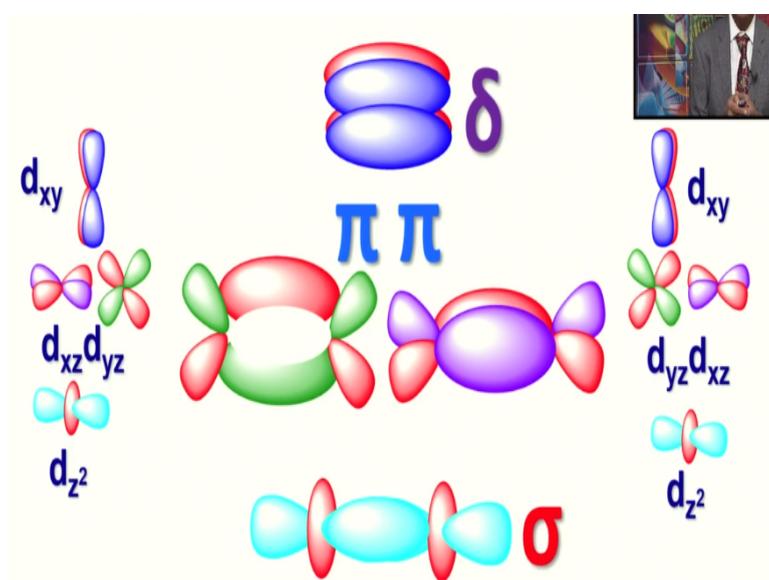


So, now with this one let us continue forming other bonds. So, one bonding molecular orbital is formed, one antibonding is formed here, now this is sigma bonding ( $\sigma$ ) and this is sigma star ( $\sigma^*$ ) bonding. If two electrons are there, one electron here, one electron here, they come here and one sigma bond will be established. Next, we have  $d_{xz}$  and  $d_{yz}$ , they degenerate here. So, they overlap like this to generate bonding and antibonding molecular orbitals having pi symmetry.

So two are there, so capacity is 4 electrons. Now, consider  $d_{xy}$ , and this  $d_{xy}$  will be forming delta ( $\delta$ ) and this will also be delta but this is sigma bonding and this is delta antibonding ( $\delta^*$ ). This is delta bonding whereas this one is delta antibonding. So, this is how you can explain quadrupole bonding here. If you have 4 electrons: 1, 2, 3, 4; so here 2 electrons are there, here 4 electrons are there, here 2 electrons are there, 8 electrons are there, here we do not have any electrons.

So, bond order would be:  $8 - 0 / 2$ , that is 4 bonds. So, that explains the delta bonding or quadruple bond between two rhenium atoms.

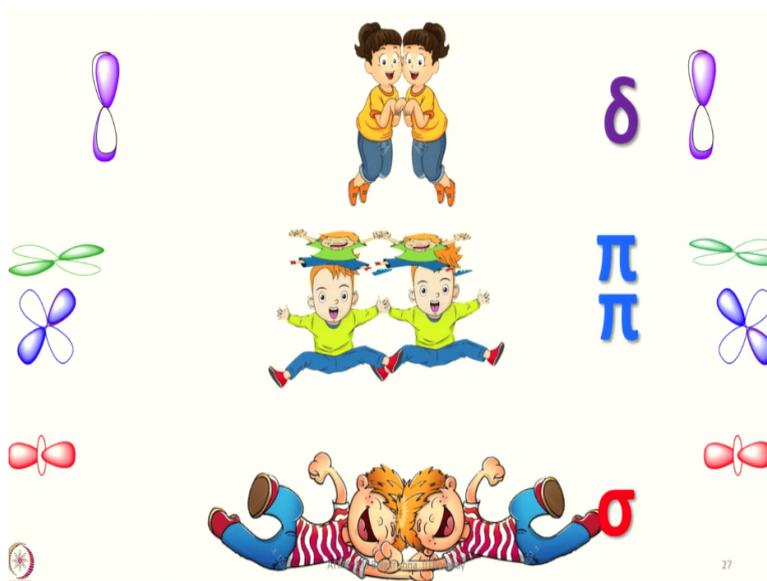
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So, now to make it clear again I am showing you. **(Video Starts: 08:39)** So this is sigma bond. This is one of the pi bonds and this is the second pi bond and then this is the delta bond with the  $d_{xy}$  through sideways overlapping. And now that leads to this sigma molecular orbital and this one, and this one, two pi bonds in this fashion, are orthogonal to each other and then we have the delta bond. **(Video Ends: 09:15)**

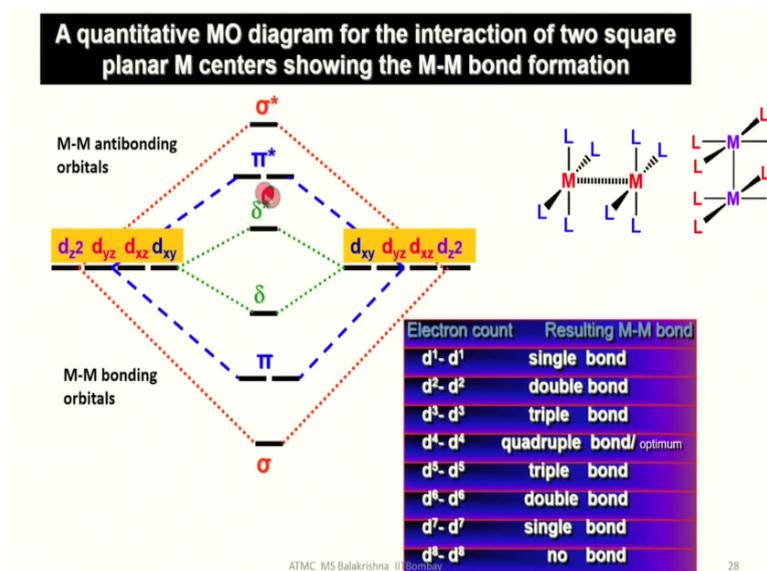
So, that means we have a sigma bond, two pi bonds and one delta bond. They are responsible for making bonding molecular orbitals and remaining will go in the same sequence delta, pi and sigma; they will be antibonding orbitals. So, this is how in a very simple way one can explain the multiple bonding between two metals in coordination chemistry.

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To even further simplification I have use these cartoons. You can see this is sigma bond, head on collision and this is one of the pi bonds. Now, this is orthogonal another pi bond and now we have delta bond. I hope it is very clear now, how to write bonding molecular orbitals and antibonding orbitals to show the magnitude of bonding among coordination compounds if there are metal-metal bonds.

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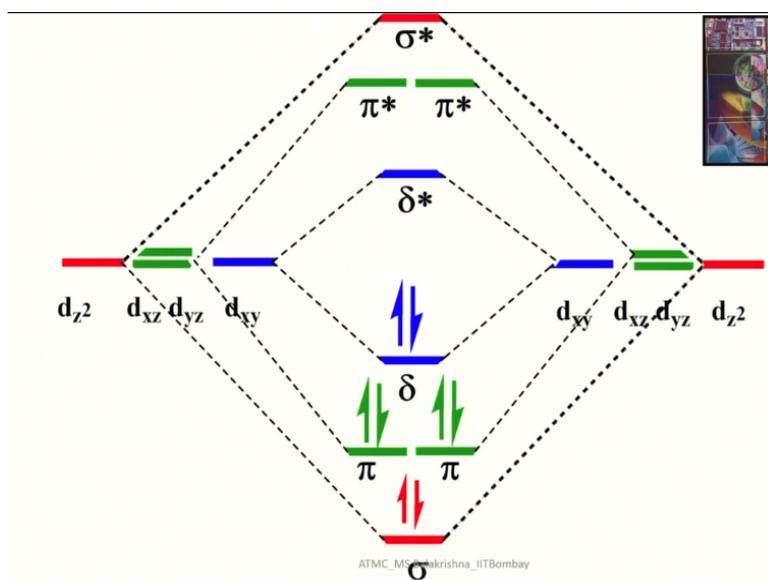
So, now I have shown here, what would happen if we have more than 4 electrons, so that means d<sup>1</sup> - d<sup>1</sup> may put 2 electrons here that results in a single bond; and d<sup>2</sup> what happens we will be having 2 electrons here and 2 electrons. So, bond order will be 2, so it will be a double bond. If you have triple bond we will be having 2 + 2 + 2 here 6 electrons, 3 from each, so we have a triple bond.

And if we have 4 electrons from that is  $d^4$  system we will be having a maximum bond order of 4 that is called quadruple bonding. And then the fifth one will be, if we have one more electron, so that goes here a pair, so that means 2, 4, 2, 2, 10. Now, the bond order will decrease, so it will become a triple bond. Similarly, if you go to the  $d^6$  electrons, then it will become double bond and  $d^7$  up to here completely filled, you have a single bond.

If  $d^8$  system both bonding and antibonding are completely filled, so bond order is 0, no net bonding results in case of  $d^8$  system in this fashion. So, this can give you an idea about the nature of the bond through simple electron counting here, simple electron counting and placing them here. What you should remember how you should remember one sigma, two pi, delta, delta star, pi star, sigma star that is it.

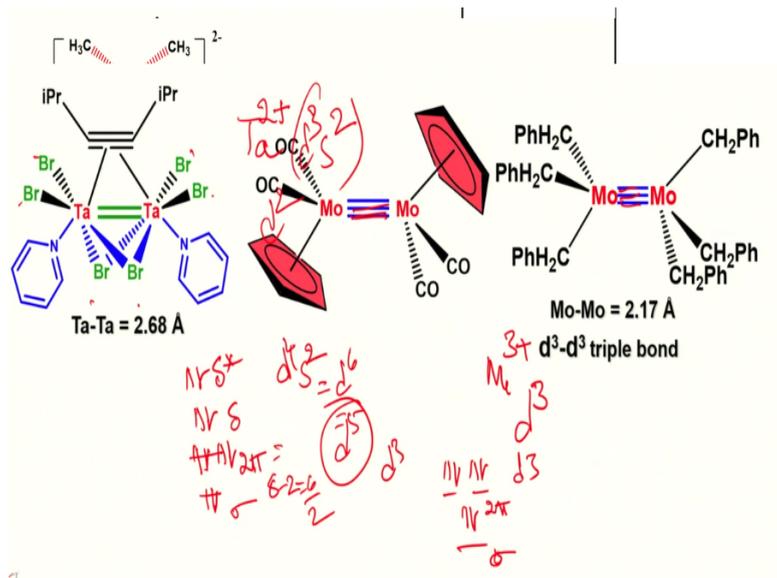
And  $d_z^2$  is responsible for sigma bond and  $d_{xz}$  and  $d_{yz}$  are responsible for two pi bonds and  $d_{xy}$  is responsible for delta bond and in a similar fashion, so we can see the corresponding antibonding molecular orbitals.

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Now, let us look into some examples here. So, for electrons as I mentioned you can start putting here 2, 2 first they are singly occupied and then you have they doubly occupied, 6 six and then yes. So, this explains, now 8 electrons are there in the bonding. So bond order is 4.

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For now, let us look into this molecule here. First you have to identify tantalum, nothing doing, identify tantalum metal here. Tantalum means when it comes you should know; vanadium, niobium, tantalum that means it has  $d^3s^2$ , means 5 electrons are there and you have to identify anionic ligands. So, we have 1, 2, 3, 4, 5, 6; 6 are there. It has a symmetric structure.

So, that means, each one would contribute 3 electrons so that the tantalum is in +2 state  $d^3s^2$ ,  $d^3s^2$  loses 3 electrons and then we have a  $d^2$  system here. If  $d^2$  system is there, you can go back to the previous diagram and see whether we have a double bond between two tantalum atoms. We have a double bond between two tantalum atoms and then here the Ta—Ta bond is 2.68 angstrom units. Now, let us go to another example here.

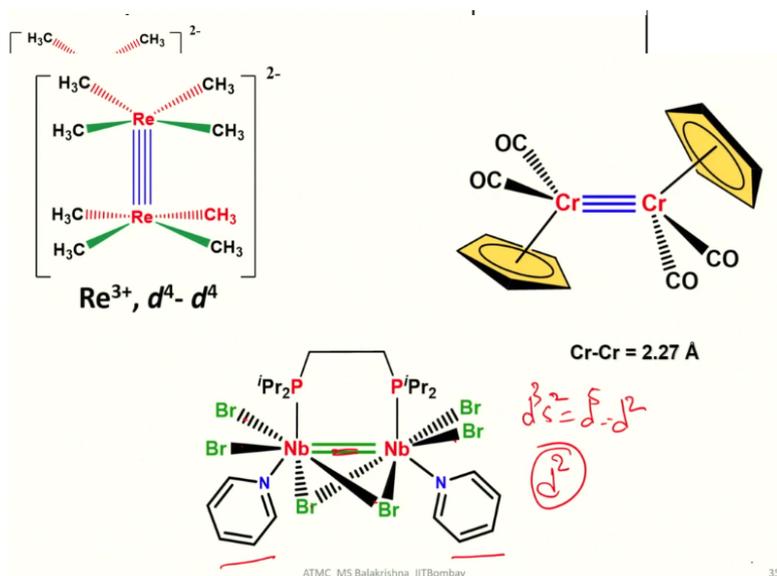
So, now look into this one. Each molybdenum has two carbonyl groups and one Cp group is there. And of course, here molybdenum is, let us consider  $d^4s^2$ , 6 electrons are there. Now one is negative. So, molybdenum should be in +1 state, as a result what happens? This  $d^6$  becomes  $d^5$ , if  $d^5$  is there, you should recall the previous diagram I showed you. So,  $d^5$  will result in how many electrons, so if you put here 2 electrons, 4 electrons here and then 2 electrons here and 2 electrons here.

So, this is sigma, 2 pi and then delta, delta star. So,  $10 - 2 = 8$ ,  $8 - 2 = 6$  by 2, so yes there should be a triple bond. So, triple bond is there. So, now you go to this one here. So, here we have trianionic ligands are there. So, molybdenum,  $d^4s^2$ , but molybdenum is in +3 state,

means what we have is out of 6 three,  $d^3$  system. So,  $d^3$  system how to write? So, here 6 electrons are from one  $d^3$  here and another  $d^3$  here.

So what we have is 1 sigma, 2 pi, so it should be 3, triple bond. So, triple bond is there. So this is how you should be able to identify the magnitude of metal-metal bond simply by electron counting and then adding those electrons to already established MO diagram that I have given to you in the order sigma, 2 pi, delta, delta star, 2 pi star and then sigma star again. So, here molybdenum-molybdenum distance is 2.17 angstrom units and it has a triple bond.

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This is almost identical with  $[\text{Re}_2\text{Cl}_8]^{2-}$ , so  $d^4$  system. This is again  $d^4$  system and what is interesting is despite  $\text{CH}_3$  groups are very bulky, still it prefers eclipse confirmation so that it can establish delta bond. What happens, the other one turns this way, what happens  $d_{xy}$  would not be having in the same fashion? It will be something like this, they have to be something like this both the  $d_{xy}$  orbitals.

If at all something like this, there is an overlapping. So, in order to have this one facing each other exactly like this for sideways overlapping, they have to be eclipsed. That is the reason despite it overcomes kinetically stable staggered conformation and prefer eclipsed, of course in order to minimize what happens it lifts these 4 orbitals little up and this one down so that it can have a quadruple bond.

So, now this is very similar to what I showed for molybdenum again, you should anticipate a triple bond between these two chromium atoms. Here, chromium-chromium distance is 2.27

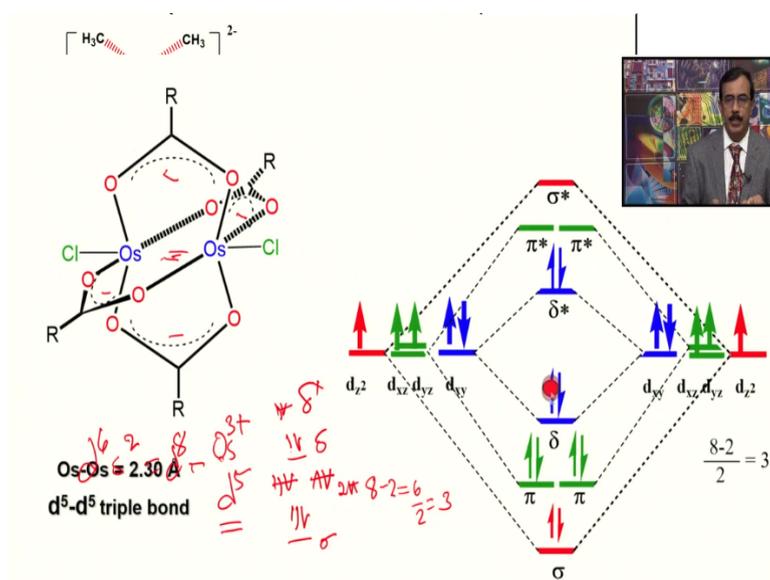
angstrom units. Now, let us look into this example here. In this example, again we have this pyridine is there on each, one neutral ligand and we have a bisphosphine bridging two metal centres, two niobium, and we have again a  $d^5$  system: 1, 2, 3, 4, 5, 6 are there.

That means you have to get rid of 3 electrons for each one. So, it is  $d^3s^2$ , Let us assume  $d^5$ , to remove three electrons it becomes  $d^2$ . In  $d^2$  system you will be having a double bond between these two. So, that means, in this one, it has a double bond between niobium atoms. It is very simple. It is much simpler than doing 18 electron rule, but do not mix up 18 electron rule with this way of electron counting, they are two different entities.

You should remember, you should not even make an attempt to make it satisfy or obey electron rule because early metals or metal ions having less than 6 electrons in their d orbital which are available for bonding, you cannot, even with octahedral geometry, satisfy 18 electron rule. So, 18 electron rule is a different concept and then looking into the nature of metal-metal bond in this kind of molecule is a different concept.

Please do not try to mix up even if somebody asks you a question, they are referring to different concepts. One need not have to worry about that one, but there is no harm in verifying whether for a given molecule, the magnitude of the bond metal-metal bond can be explained using both the methods. We may have some examples, but you cannot generalize for all complexes or coordination compounds, both the methods.

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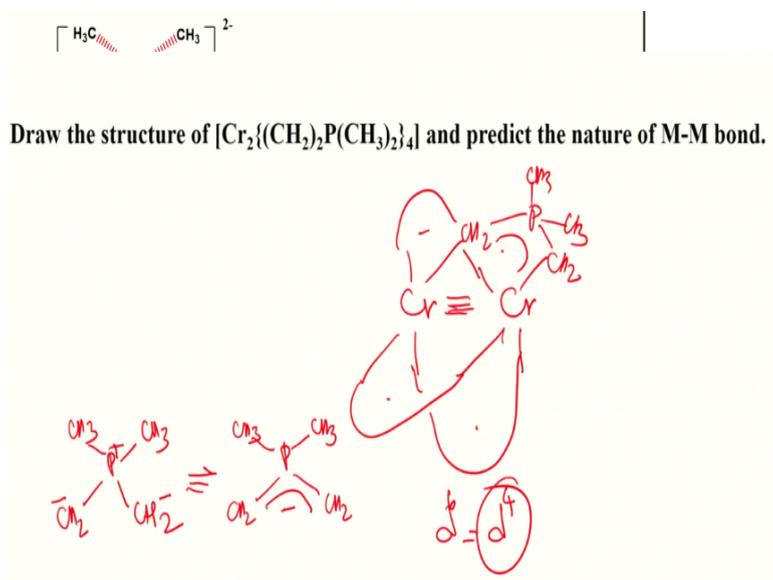


Now, let us look into another interesting molecule here. We have osmium compound, we have 4 acetates and also we have a osmium-chloride bond on each one. So, that means here you should know that acetate is a monoanionic: 1, 2, 3, 4 monoanionic ligands are there and two negative ligands are there, so that means basically 6 anionic ligands are there, each one should go to osmium, so they pull out 3 electrons from each osmium metal.

Osmium is a  $d_6s^2$ . So out of 8 electrons, we have to take out 3, 3 means it will be osmium +3, this is a  $d^5$  system, will be having a triple bond. How,  $d^5$  system will be triple bond, again two pairs here, sigma, pi, 2 pi and delta we have 2 electrons and then delta star we have 2 electrons. So 10 electrons are accommodated. And now what we have is a triple bond. So,  $8 - 2 = 6 / 2 = 3$ .

So, you should have triple bond, so easy, so you can see now triple bond. So, this is how no matter which metal ion is given, you can also say how many bonds are there, whether the bonding is possible or not, all those things you can analyse simply using this as very general MO diagram.

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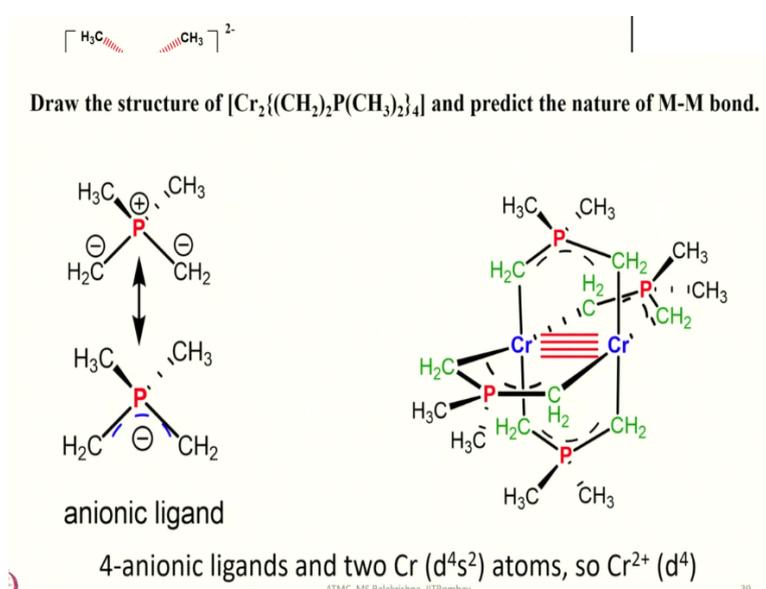


So, now I have another interesting molecule here. Just molecular formula I have given here and how to write the structure. Yes, you can take the compound here. So, this is how the ligand is described. If you see here, the valence is not satisfied, this should be negative charge, this should be negative charge and this is phosphonium positive charge. So, that means two negative charge and one positive charge is there.

And then, one can write something like this. So, now this looks almost isoelectronic with acetate. That means, we have four of them. How these four will be forming bonds? Something like this 1, 2, 3 and 4. So, that means just one I will write, so then another one should be something like this; I can write, another one I can write something like this, another one something like this; now four are there.

And let us assume we have 6 electrons; 1, 2, 3, 4 anionic are there, two each. So, it will be a  $d^4$  system. If it is a  $d^4$  system, very similar to rhenium case, you can anticipate a quadruple bond between them.

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You can see, yeah anionic ligand and then resonance structure when you write, yeah this is how the structure you can write. And you can see, yes, this molecule has a quadruple bond. So, 4 anionic ligands and 2 chromium atoms are there. And chromium is in +2 state. Once in +2 state it is a  $d^4$  system. Obviously, it shows quadruple bonding. Let me stop here.

Another interesting question that comes to your mind is whether we can have more than four bonds between two metal centres. Yes, we can also have five bonds that is called quintuple bond. So, what are the conditions for a metal complex to have a quintuple bond, let us discuss with a couple of examples in my next class. Until then enjoy metal-metal multiple bonding concept reading and understanding.