Advanced Transition Metal Chemistry – Ligand Field Theory
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Lecture – 19
Ligand Field Theory (LFT)

Hello everyone, welcome to MSB lecture series on advanced transition metal chemistry. This is 19th lecture in the series. In my previous lecture, I discussed about the application of molecular orbital theory to main group elements with a couple of interesting molecules where there are controversies when you compare valence bond theory or VSEPR theory. Now, let us continue from where I had stopped. Now, let us try to use molecular orbital theory OR one can also call it as ligand field theory, to explain bonding among coordination compounds.

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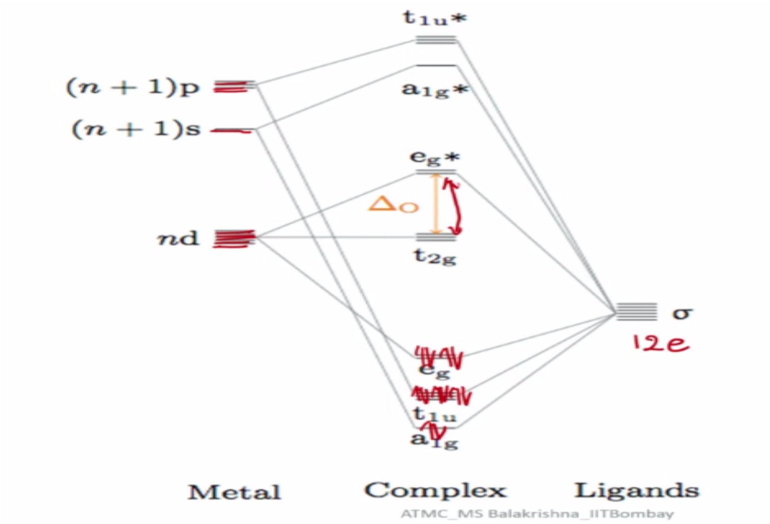

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So, I have just shown a generic MO diagram that depicts bonding in case of metal complexes with the ligands having only sigma bonding properties. A typical MO diagram can be written in this fashion. I am just overwriting on the diagram I have shown to make you familiar with drawing yourself MO diagrams for complexes. For example, in this case what we are considering for any given transition metal n*d* orbitals and the (n +1) *s* and (n + 1) *p* orbitals as valence orbitals.

And the intention is to utilize them for making bonds when the ligands are entering coordination sphere. Here of course, to begin with, we are considering atomic orbitals of metal, here we are considering this 5d orbitals and we are considering (n +1) *s* orbital and then we are also considering (n + 1)p orbitals for which the Mulliken symbol is t_{1u} and here we are considering ligand group orbitals. There 6 ligand group orbitals are there and each one is coming with a pair of electrons.

So, we have a total of 12 electrons that has to be accommodated, let us not worry, how many electrons we have in the d-orbitals of transition metals that is immaterial now. So, now if the 12 electrons are coming from 6 ligands, as six pairs, they will be put here. So, now you can see this is how this molecular orbital that have combined ligand orbitals along with two d orbitals that is in this case it is $d_{x^2-y^2}$ and d_{z^2} to generate this many bonding molecular orbitals in which these 6 pair of electrons are accommodated.

If any electrons are left in t_{2g} that is d_{xy}, d_{yz} and d_{zx} they remain nonbonding and they are placed here. And now this gap what we have here, so this one, this is called Δ_o here and then from here onwards, if you consider, there have antibonding properties, their antibonding molecular orbitals e_g^*, a_{1g}^* and t_{1u}^*. So, this is how one can write a typical MO diagram for a metal complex with octahedral geometry. Of course, the same MO diagram what I showed is also good for ligands having only pure sigma donor properties.

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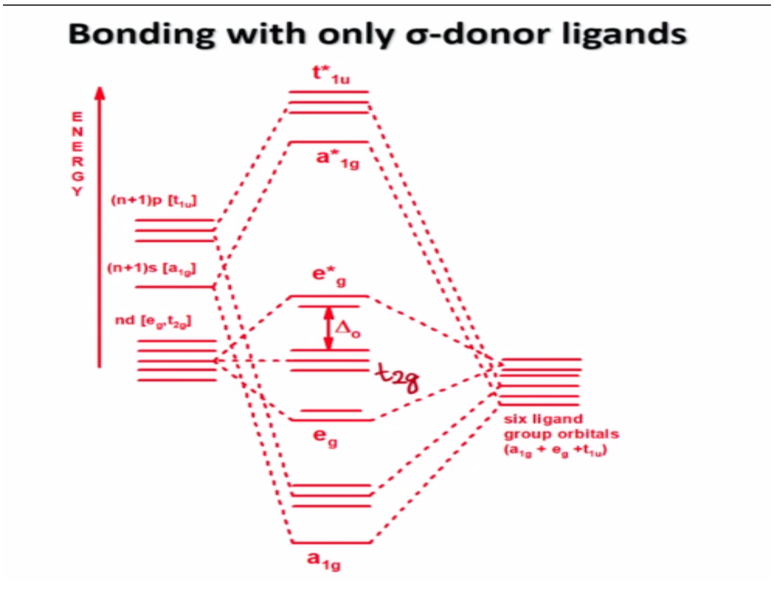

Bonding with only σ-donor ligands

So, again I have shown here, the same what I showed here except for the fact that I have also included the symmetry of the ligand group orbitals so that you can match appropriately with appropriate metal orbitals to generate molecular orbital. This a_{1g} is coming here, along with

a_{1g} is this one, and then when you go for t_{1u}. So, 3 orbitals coming here, and 3 orbitals are coming here, and then t_{2g} e_g is there. Two orbitals are coming here.

And then e_g two orbitals from this d-group will be coming here and then this will remain and this is t_{2g}, so rest would be same. Once you know how to write these diagrams, you should be able to fill the electrons according to the number of electrons you have in a given metal complex. So, this molecular orbital diagram represents ligands having only pure sigma donor properties.

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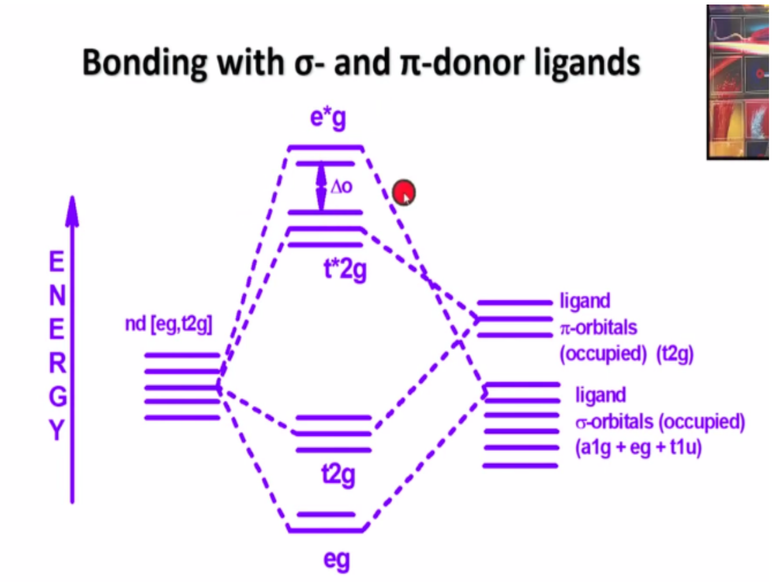

Bonding with σ- and π-donor ligands

Now, let us look into ligands having both sigma donor and pi donor properties. So, in this case I already told you in my previous lecture ligands can have low energy field sigma orbitals and low energy field pi orbitals. When they interact with metal atomic orbitals to generate molecular orbitals, this gap between t_{2g} and e_g or t_2 and e shrinks, this is what exactly happens in case of metal chlorides and fluorides. So, here relatively these compounds are less stable compared to pure sigma donor ligands.

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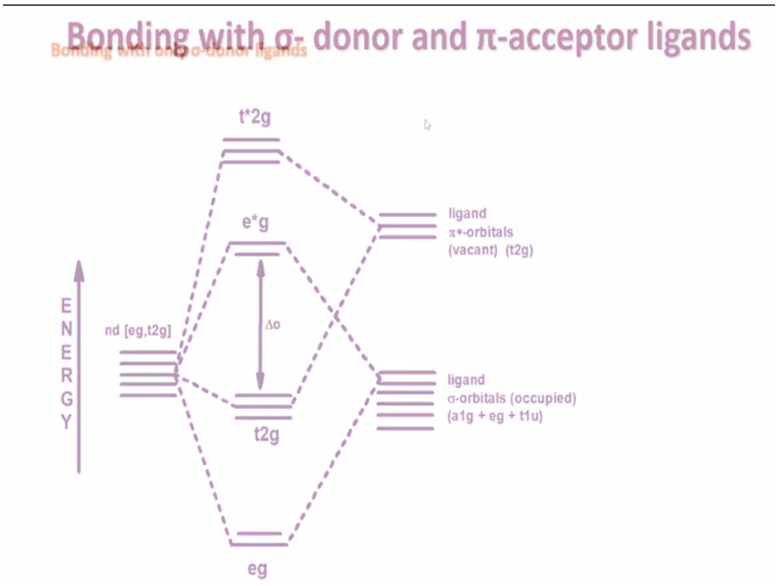

Bonding with σ- donor and π-acceptor ligands

Then the other ligand group we are talking about is bonding with sigma donor and pi acceptor ligands such as carbon monoxide, triphenylphosphine and N-heterocyclic carbene, etc. In this one, here it is again metal valence orbitals nd, (n + 1) s and the (n +1) p and here we have again ligand orbitals, their low energy filled sigma orbitals and high energy empty pi orbitals. So, in this case, you can see the magnitude of this separation has increased remarkably that explains why these complexes are very stable compared to other two class of ligands that I had described.

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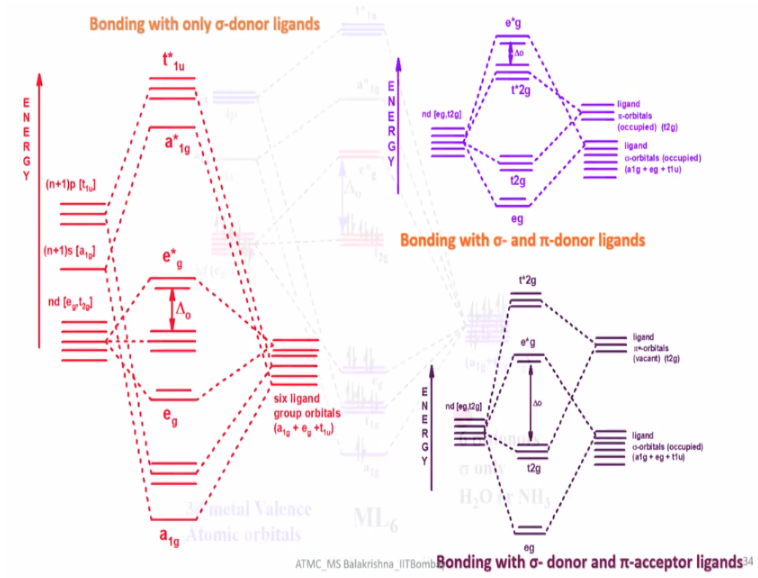

Bonding with only σ-donor ligands

Bonding with σ- and π-donor ligands

ATMC_MS Balakrishna_IITBombay Bonding with σ- donor and π-acceptor ligands 34

For comparison, I have put all the three types MO diagrams here. Clearly distinctly you can see the separation between these two and of course in this case, we also use the term HOMO and LUMO. This is highest occupied molecular orbital and this is lowest unoccupied molecular orbital, between which electronic transition takes place.

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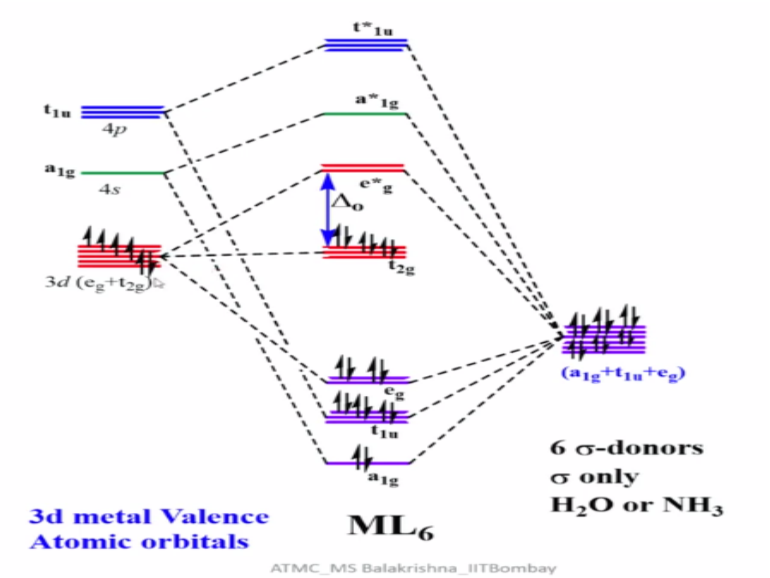

Once again 6 sigma donor ligands such as water or ammonia and they are again coming with 12 electrons. These are the symmetry of the ligand group orbitals that are going to combine with metal orbitals. And here I have just put 6 electrons in the orbital and these 6 electrons remain here as nonbonding and if there is any electronic transition is there, these electrons can be promoted to this higher energy state here.

So, this represents a typical hexamine metal complex our hexaaqua metal complex here. Here you can put whatever the electrons you think the metal possess after required oxidation state is achieved with that metal.

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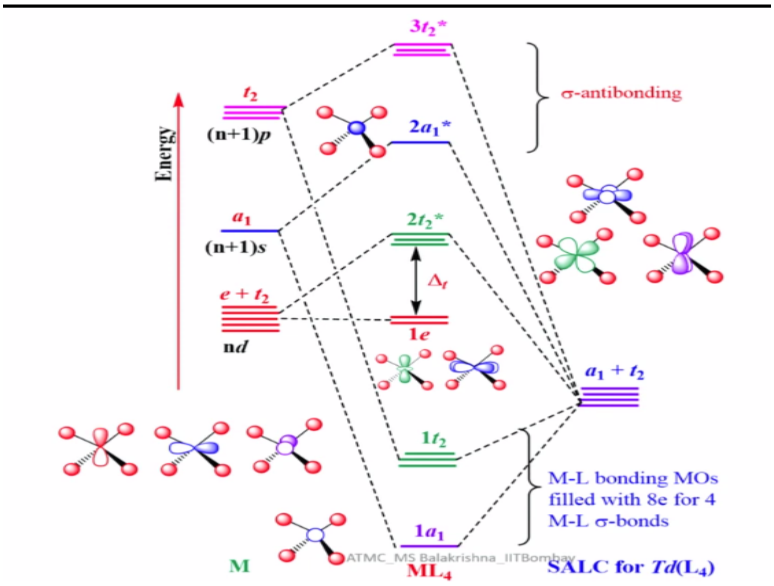

So, this one, you can guess, what geometry it represents. And of course, the moment you see here two orbitals and the symmetry correspond to a_1 and t_2 obviously this is for a tetrahedral complex. In tetrahedral complex, we are talking about four ligands coming with the 8 electrons and here we have five d orbitals again and here the symmetry will be e and t_2 and as usual (n + 1) s orbital having a_1 and this (n + 1)*p* will be having t_2 in case of tetrahedral.

So, here very similar to crystal field theory, the energy of e will be lower compared to energy of t_2 and this remains nonbonding here. In many cases, what happens tetrahedral complexes also have electrons in the antibonding orbitals here. If they have more than 4 electrons, obviously the fifth electron has to be placed in here and these compounds are relatively unstable compared to octahedral complexes, also to an extent, square planar complexes.

Four pairs of electrons coming from the ligands would occupy these 3+1, 4 molecular orbitals here and electrons present in the d orbitals will be filled in this one. If it is more than two electrons; then it would go here, usually here pairing does not start here because this gap is much smaller. So, electrons will be promoted here and they will be usually high spin complexes. And also, I am showing you the orbitals involved in this one, you can see these are the orbitals having this kind of orientation.

Of course, you can also compare them to p_x, p_y and p_z and this is a. And all of them participating tetrahedral geometry can be seen here. This is called symmetry adapted linear combination of atomic orbitals. You can see here this is composite of d_{z^2} and $d_{x^2-y^2}$ you can clearly see how d_{z^2} and $d_{x^2-y^2}$ orbitals are oriented with respect to the direction of approach of ligand.

Once again crystal field theory, whatever we discussed it can be seen here why the energy of these things are lower. And then if you see here, again it is very clear, why the energy of t_2 is higher because they are almost coming on the way of ligand approach here in all these cases. And this is M-L bonding molecular orbitals filled with 8 electrons for 4 M—L sigma bonds and then we call them as antibonding molecular orbitals. And this is how the looks like antibonding orbital.

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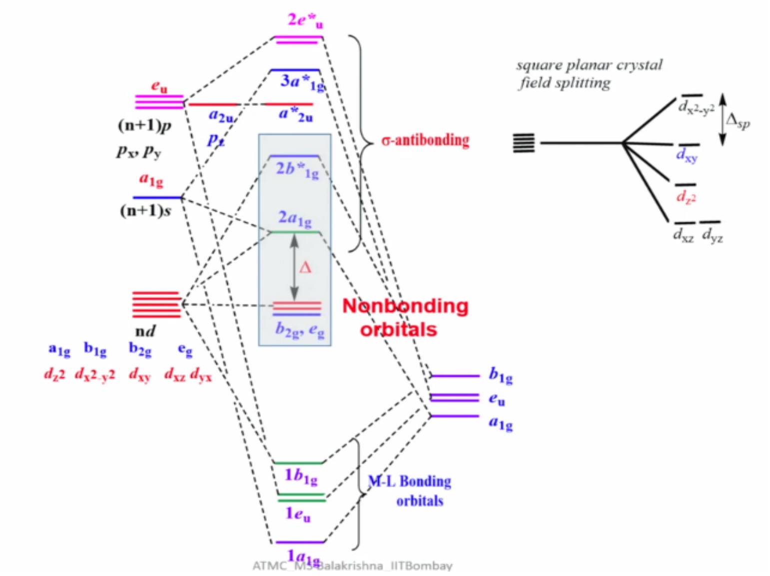

The another one, of course you can see here this is for square planar complex. In case of square planar complex again 4 ligands are coming, but they are having different symmetry or Mulliken symbols depending upon what kind of orbitals that are available for bonding from metal ion or metal atom. So, here nd will be further split into different sets that I should show you and then a_{1g} does not change here.

And since two of the p-orbitals are participating in mixing and others does not, if you recall valence bond theory of *dsp*^{2}, so two p will be mixing as a result what happens? It has two different type of p orbitals here. Then accordingly, they are further split, of course tetragonal elongation, if you remember how it splits one can visualize here also in case of ligand field theory. 11:25

Then, these are the Mulliken symbols given for various d-orbitals: a_{1g}, for $d_z{}^2$, b_{1g} for $d_x{}^2{-}_y{}^2$ and b_{2g} for d_{xy} and d_{xz} and d_{yz} still degenerate, they are called e_g set. And then metal to ligand binding orbitals, again 8 electrons are comfortably placed here as four pairs, they are responsible for making for metal to ligand bonds. And they are antibonding and these are nonbonding orbitals here. This is very important when we are talking about reactivity. And let us now compare bonding in metal carbonyls and metal phosphines.

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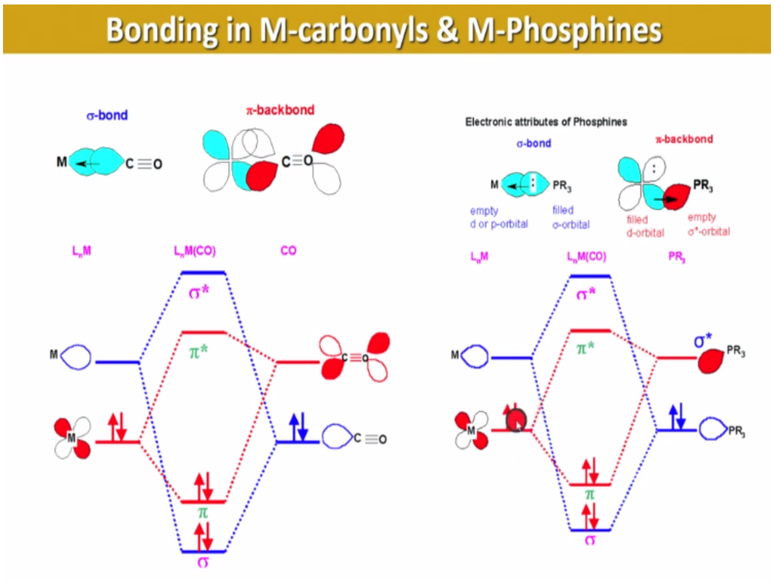

If you see metal carbonyl, in my previous lecture, I showed you about the lone pair present on carbon that is responsible to perform CO as a sigma donor. These electrons from CO would be overlapping with one of the orbitals from M, essentially d_{z^2} or $d_{x^2-y^2}$ to form a sigma bond, then the filled metal orbitals will overlap with π* atomic orbitals of carbon monoxide to take electrons from the metal through back bonding.

And this is how carbonyl ligands stabilize metals in their low valence and overcome interelectron repulsion in the metal by taking comfortably the electrons from metal to π* of carbon monoxide orbitals. So, this is a typical metal carbonyl bonding scheme here and let us assume a pair of electrons is coming from carbon monoxide. These two electrons here, this orbital, and they interact with appropriate metal orbitals to form a sigma bond.

So, we established a metal to carbon sigma bond. Now, the energy of this one quite comparable with pi star of this one that is a t_{2g}. I would say and then they overlap, they interact again to generate a set of bonding and antibonding molecular orbitals. One thing one should remember here is π* is not going to take directly electrons from the metal t_{2g} orbitals. When the metal atom or an ion is ready for giving electrons from its t_{2g}, t_{2g} orbital should be treated as atomic orbitals.

And π* or antibonding orbitals present on carbon monoxide should be treated as atomic orbital. These two combine together to generate again a set of bonding and antibonding orbitals. To the bonding orbitals, what happens? The metal electrons go, so this is how back bonding takes place. If somebody says that σ* or π* in phosphines or carbon monoxide directly takes electrons that is incorrect, they are not going to take, they have to be treated as atomic orbitals.

And t_{2g} orbitals are with pi-symmetry or essentially t_{2g} are: d_{xy}, d_{yx} and d_{xz}, they have to be treated as again atomic orbitals. They combine together to generate a set of bonding and antibonding orbitals and they have pi-symmetry and that is the reason we call it as pi-back bonding. So, same thing I have shown here for phosphorus. Again phosphorus lone pair is there, that goes to a metal to form a sigma bond and then the σ*, when we write PR_3 molecular orbitals PR_3 has a σ*.

That σ* interacts with filled d-orbital to take electrons and this is called back bonding here. Again in this case also σ* orbitals you should treat as atomic orbitals, they interact with filled d-orbitals to generate a set of bonding and antibonding, again they have pi-symmetry and here electrons will be transferred from metal to this bonding molecular orbital and hence we call it as pi bonding.

Very similar here except for the fact that here we are using pi star antibonding orbitals and here we; are using sigma star as antibonding orbitals. And then you can see symmetry pi star and pi, so electrons would be transferred to this place, so that what happens, interelectron repulsion is minimized.

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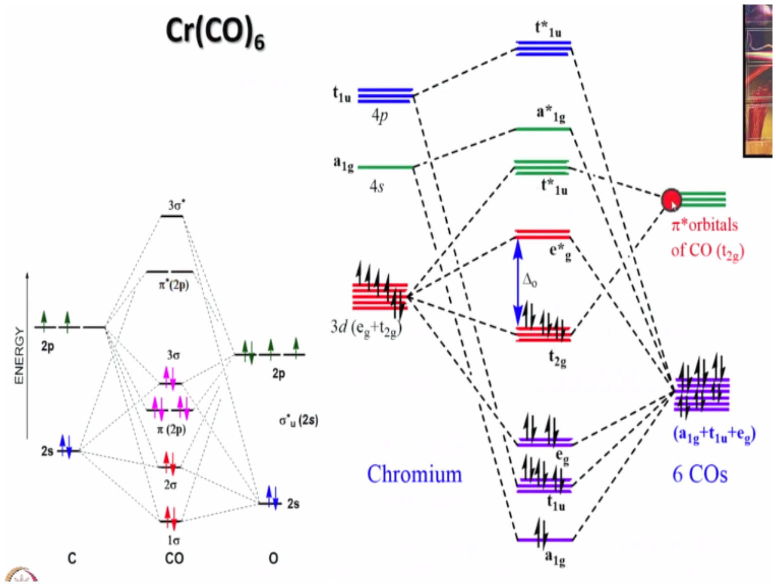

So, now I have shown here for chromium hexacarbonyl. You can see here 6 carbon monoxides are there and the symmetry is referred to a_{1g}, t_{1u} and e_g here. And as usual, they combine here and then I have also given t_{2g} (π^*) orbitals. As I mentioned, these orbitals are now combined with t_{2g} and you can see now this is a bonding and it is antibonding and the electrons are placed here.

And now you can say, the moment it is involved in bonding, the energy of electrons present here, previously it was nonbonding somewhere here, it is lower. So, since it is lower the gap is increased. So, we can say now, the complex is more stabilized because the energy of this one is lower. You can see here. This is the pair I have shown here, this is the one, so that I am considering from 6 carbon monoxide, 6 pairs of these electrons are shown here and then this pi star whatever I have shown here, this is the pi star I am referring to here, this is same as this one.

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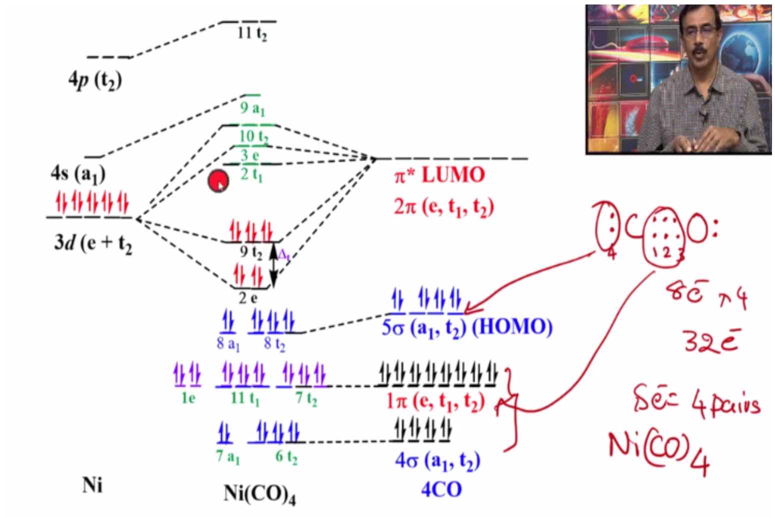

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G.Cooper, K.H.Sze, C.E.Brian, J.Am.Chem.Soc.1989,111,5051-5058

So, I have an interesting case here, nickel tetracarbonyl and normally you do not see MO diagram for nickel tetracarbonyl. Here I have written too many electrons, you may be surprised to see why I have written so many electrons instead of writing just 8 electrons from 4 carbon monoxide, they are making bond with Ni to form $Ni(CO)_4$, but I have written extra electrons. Here you can see 1, 2, 3, 4 pairs are there and 4 and 8 pairs under that.

So, basically, I have shown 16 pairs there. So, that means about 32 electrons I have considered here, 32 electrons where they are coming from? Yes, let me show you here. Let me write Lewis dot structure again. You know how we are establishing a triple bond between carbon and oxygen. So, this pair is 1, 2, 3 and 4 pairs are there, 4 pair means 8 electrons are there and 8 electrons into 4 ligands, 32 electrons are there.

Out of 32 electrons what happen, these 4 pair means, 8 electrons equal to 4 pairs, they are responsible for making bond. So, this is what valence bond theory says, but is it really true? Let us examine that one whether the sigma electrons really participate and interact with appropriate metal orbitals to make Ni—CO bonds. You can see here, these 4 pairs are, I am referring to this one, these are the 4 pairs, I am showing.

And then here 8 pairs, whatever I am showing here, these are the electrons I am showing here together, they remain nonbonding. And to our surprise, if you see these four orbitals should have interacted with this one as well as this one to generate a set of four molecular orbitals to place these 8 electrons very similar to what we saw in tetrahedral complexes in earlier case. But if you see these 4 pairs of electrons remain almost nonbonding here.

Energy is much lower compared to any of the metal orbitals here that indicate there is no sigma bond at all between nickel and carbon monoxide. There is no sigma bond. In order to have sigma bond we should have pulled these orbitals much lower to connect with this one, but that is not happening. So, that indicates the 4s and 4p energy are too high to interact with this sigma electrons from carbon monoxide.

Then in that case, there is no 4 sigma bonds at all in $Ni(CO)_4$. Then how $Ni(CO)_4$ is formed? $Ni(CO)_4$ is formed through only back bonding. You can see here π^* of carbon monoxide that is interacting with here $e+t_2$ with t_2, e, t_1 here and as a result what happens? The electrons here degenerate prior to the formation of $Ni(CO)_4$ is split into two levels as usual e and t_2 and the electrons are placed here, 10 electrons present in nickel.

Nickel(0) means $3d^8 4s^2$, 0 means 10 electrons. These 10 electrons are placed here. That means just by splitting this one what happens? This is stabilized. So valence bond theory says that we are utilizing these orbitals from metal to establish $Ni(CO)_4$ that is not the case at all and of course this, one can see, if you want to read more about that one, you can refer to these papers. Not many textbooks talk about this one and I have not come across in many textbooks describing MO diagram for $Ni(CO)_4$ in this fashion.

But this is very true and also this explains why $Ni(CO)_4$ is highly volatile and more reactive, for the same reason this is stabilized by only back bonding and there is no sigma bonding in

$Ni(CO)_4$ at all. Whereas in case of chromium hexacarbonyl we have sigma bond that I showed you in previous slide. So, there it is a solid and reasonably stable, high melting point white powder, moderately or reasonably stable to atmosphere, whereas this one is highly volatile and it can decompose readily.

So, some of these properties can be explained nicely and bonding also can be explained and that normally we do not see in case of valence bond theory and also crystal field theory of course it does not explain anything about such complexes where metal is in 0 valent state. Let me stop here and continue more interesting stories about transition metal elements in my next lecture.