Coordination Chemistry
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Lecture - 35
Reaction Mechanism – I

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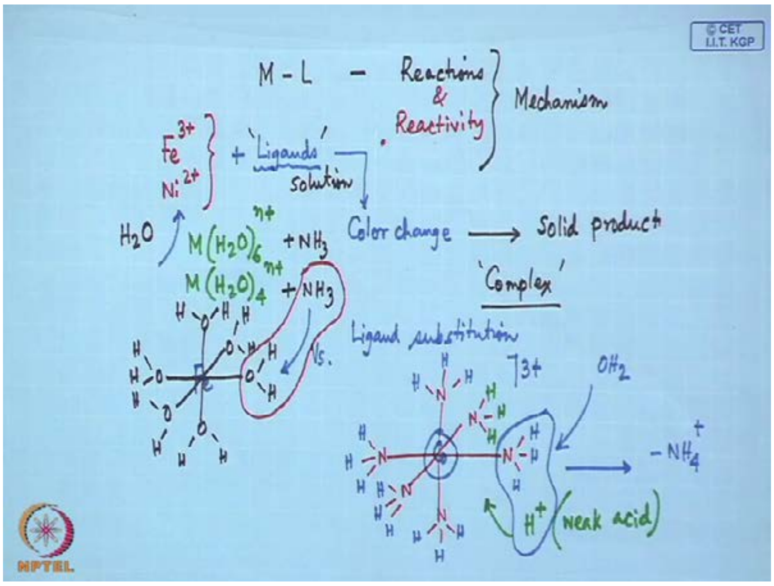

Good evening everybody. Today we will just see how the different metal ions are reacting with the ligands and the type of reactions what we can have. So that nature of reactions, we can also talk all these things in terms of not only the reactions but the reactivity as well. Because if we have certain metal ion, say Fe 3 plus or Ni 2 plus and in a broader sense what we will see that how this can react with the different types of ligands. And when it forms basically, we see initially if they are distinguishable from a color change. So, there will be a color change for this particular reaction, and in all these cases what we can see that the corresponding metal ions which are present as in aqua solution is mostly the corresponding hexa aqua compounds or the corresponding tetra aqua compounds in solution.

So, in a true sense what we will be talking about that the corresponding reactivity of these aqua complexes when water is the reaction medium with that of our ligands. So, we see some color change, that means the metal ion is reacting with the ligand and we get the corresponding interaction with that of metal with that of our ligand. And if there is a solubility difference; that means if the corresponding complex and the nature of the ligand can also tell us that what type of solution we should use for the ligands also. So, sometimes we see that if some big organic molecules are there as the ligands such as bipyridine or orthophenanthroline; they are solvable in non-aqueous medium such as alcohol or acetonitrile or dichloromethane. In that particular case, we if we add the corresponding water solution or aqua solution of the metals salt, there will be color change and some processing for that solution we ultimately get the solid product.

So we can have in our hand the corresponding solid product and we can analyze everything and we know the nature of the corresponding complex. If we find out the corresponding access structure then all other spectroscopic properties, we can used to characterize that particular metal complex. So, what type of ligands we can have that will tell us about the reactions and the reactivity of these metal ions with the ligands, such that ultimately we can propose some mechanism for those reactions. Because since we consider these hexaaqua or the tetraaqua metal ions; they are also in some form they are also metal complexes. So, these metal complexes when they are reacting with any other ligand, say, these are reacting with, say, ammonia molecules, this is also reacting with ammonia molecules. So, when already we have six water molecule surrounding the metal centers, so these are our water molecules.

So, we have six water molecules surrounding this metal ion and what we find that these ammonia molecules will come and basically substitute these water molecules. So, we can compare the corresponding reactivity pattern of this ammonia and water, because why this water molecule will leave the coordination sphere of say iron or nickel, when ammonia is coming to replace the corresponding water molecule as their original ligand. So, what we find in terms of the corresponding reactivity of these aqua complexes. We find it as the corresponding ligand substitution reaction. So, we will have this as ligand substitution reaction and what are the different types of steps we can have and how this mechanistic thing, because it can have two aspects; one is the kinetic aspect and another is the thermodynamic aspect.

What more information we can have for the process of substitution of all these reactions and this particular water molecule is replaced and we are adding ammonia; that means the addition of these ammonia molecules also we can see. So, before starting that particular aspect, that the mechanism of these reaction will finish little bit remaining for these nature of these ligands; that means the nature of the ligands are also very much important to control this reaction, these reactivity pattern and ultimately the mechanism of all these reactions. So, the nature of these ligands, that means we are talking all in terms of the corresponding spectrochemical series. And if we just simply see that how we can compare these two and some more within the spectrochemical series, whether this water will be replaced by the ammonia or ammonia will be replaced by these water molecules because when in some other compound the coordinated groups are all ammonia.

So, six ammonia groups are attaching to the center and if this particular center is our, say, cobalt center. So, it is nothing but hexaamine cobalt 3 cation. So, which is pretty stable we all know and it can be prepared from cobaltous chloride very easily. So, this has all hydrogen's. So, what we can study for this compound is that whether we can go back it; that means whether this ammonia groups can be replaced by these water molecule. So, that is also dependent on the nature of the central metal ion and how strong this particular bond and it is corresponding heat of reaction or enthalpy of formation for this cobalt nitrogen bond where the nitrogen belongs to this ammonia molecule because this was we are talking with, say, iron and nickel. But in this particular case, it is cobalt.

So whether water can replace this ammonia molecule that we can check and for that also we can see or we can check the corresponding reactivity pattern with, say, some proton donor; that means some acid or some weak acid. So, if we have some weak acid in our hand and what will happen there; basically they are very interesting reaction is that way, that this particular proton will come and it will take out these NH3 plus H plus and we will just lose some ammonium ion. And when you lose some ammonium ion and since we are giving some amount of proton into the system and which is acidic in nature. So in that particular case, this water molecule will come and occupy this position.

So, it is basically triggered by the addition of this proton; it is not that you simply do this reaction because we are doing all these reaction the entire reaction and if we go for the corresponding isolated compound, corresponding isolated hexaamine cobalt three compound and if we just simply dissolve it in water, what we should expect? We should expect that if there is direct substitution of this ammonia group by the water molecules, if it can happen with this also, then ammonia groups can also be replaced by these water molecules. But if this is not happening, we need the corresponding addition or the proton to the systems as that your ammonium groups are protonated, and we leave this as ammonium ion and this water molecule will come and occupy some of these positions are all of these positions around this octahedral cobalt ion to give us the corresponding hexaaqua compound.

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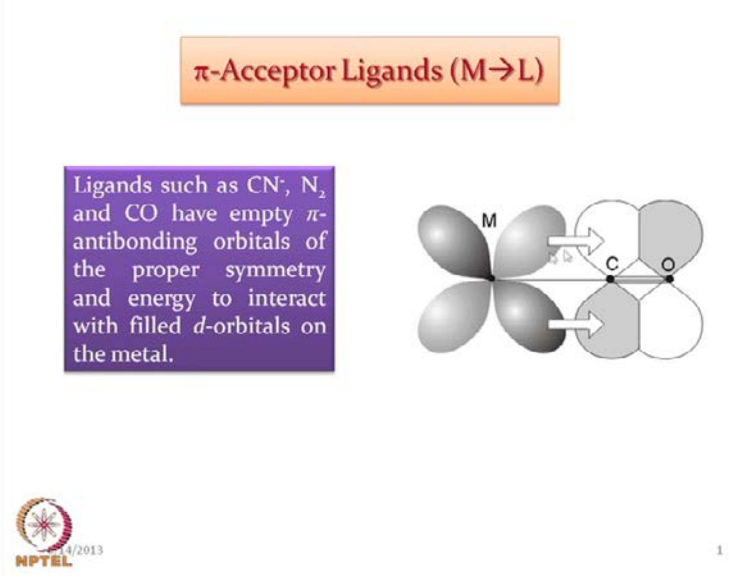

π-Acceptor Ligands (M→L)

Ligands such as CN$^-$, N$_2$ and CO have empty π-antibonding orbitals of the proper symmetry and energy to interact with filled *d*-orbitals on the metal.

So the remaining part what is there for the nature of these ligands what we have seen that the pi acceptor ligands what we are talking about, because this particular thing will tell us about the corresponding nature of this metal ligand bonding strength; how strong they are and how quickly we can remove this ligand from the environment of this particular metal. So, what happens if we have some pi orbital’s and also that orbital is the pi star; that means the anti-bonding orbital which is available for acceptance of electron density from the metal side, we call all these ligands, we group them; these ligands can be grouped as good pi acceptor ligands. So, they are there such as CN minus, dinitrogen and carbon monoxide.

They have anti pi anti-bonding orbital; that means pi star orbitals are available of proper symmetry and energy. Because when we draw the corresponding molecular orbital diagram, we see that energetically if they are mashed, then only we have the good electronic charge transfer from one particular level to the other; otherwise if the symmetry is not mashed, we do not have any good overlap from the site where we have one particular type of metal giving the corresponding molecular orbital of right symmetry and the ligand group orbital's of that group of particular matching symmetry.

So, if the symmetry is mashed and the energy is also favorable energy matching is also favorable, then the corresponding d orbital's can interact which is present on the metal side which interacts with the corresponding empty orbital's on carbon monoxide or CN minus to show the behavior for the corresponding pi acceptance. So, this is the filled one and already we have seen in one of our earlier transparency that this is the carbon monoxide molecule with this particular symmetry level which is not matched; that means this overlap is for anti-bonding orbital formation. So, this is the anti-bonding level on the carbon monoxide molecule, and if the electron density is pushed from here to the carbon monoxide we get the corresponding acceptance.

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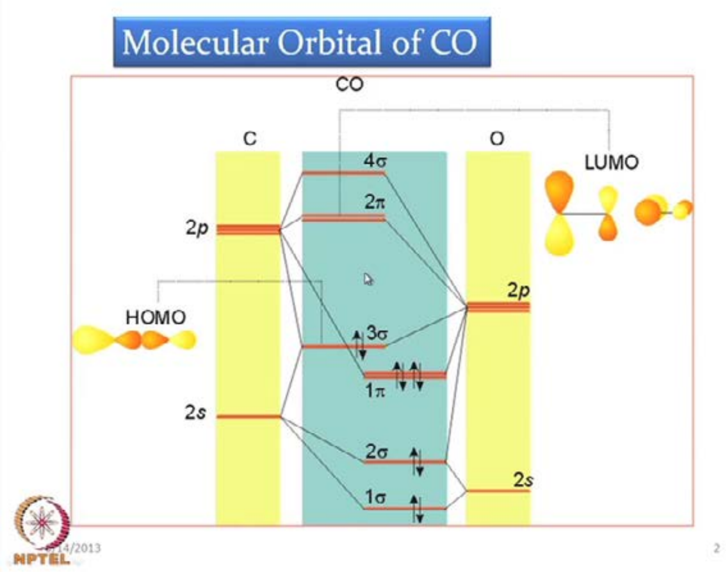

Molecular Orbital of CO

So, if we see that the corresponding molecular orbital picture for the ligand itself. So, if we just simply consider the corresponding molecular orbital picture of the carbon monoxide which is providing us the corresponding number of electron, carbon is providing us four electron and oxygen is providing us 6 electron; so altogether ten electrons we can have. But not that all electrons are donated to the metal center for the formation of the metal carbon bond in the corresponding carbonyl complexes, because there are large number of such metal carbonyl complexes are there such as nickel tetracarbonyl and others. But in this particular case if we see the corresponding molecular orbital picture for carbon side and that of the oxygen side, because oxygen side is having more number of electrons to the 2s level and 2p level are stabilized more and on the left hand side we have the 2s and 2p from the carbon side.

And this 2s when they are having the matching symmetry with the 2s of the oxygen side and 2p basically which can give, you all know that corresponding s p overlap is also allowed because the p x orbital. If the bonding axis is the x axis, then the p x orbital can nicely overlap with the 2s orbital of the carbon and this particular case; that means the p x of carbon can also overlap with the p x of oxygen. So, we have for 1sigma level which is between 2s 2s interaction, then the corresponding 2sigma also this is the corresponding bonding level and this is the anti-bonding level for interaction with the 2s because with respect to this 2s this is higher energy. So, that is basically the anti-bonding level. So, the corresponding anti-bonding level which is having the symmetry level is sigma and it is also filled and which is of lower in energy compared to the 2s level of the carbon atom.

Then we are having that p x and p y orbital's and this p x and p y orbital's have matched symmetry for the corresponding pi interaction and then we can have the p x p x interaction which is also of sigma type. So, when this p x p x interaction from the carbon side to that of the oxygen side giving the 3sigma orbital because this numbering is only for the ordering such as 1 sigma, 2sigma, 3sigma, 4sigma; this energy ordering. The ground one is the lowest one is 1sigma and the highest one is 4sigma. Similarly if in case of pi also it is 1 pi and it is 2 pi. So, this is a simple diagrammatic picture for the carbon monoxide molecular orbital.

So, we have the field 3sigma level. So, this 3sigma level has some overlap from the s level but mainly it is forming from the p x p x interaction from the carbon and the oxygen. So, if we have the corresponding orbitals like these; that means this is the matching orbital from carbon side as well as from the oxygen side and when we have the 3sigma level and this 3sigma molecule orbital which is filled with electrons and this is the bigger lobe which has been shown over here from the carbon side can be donated these two electrons to the metal ion.

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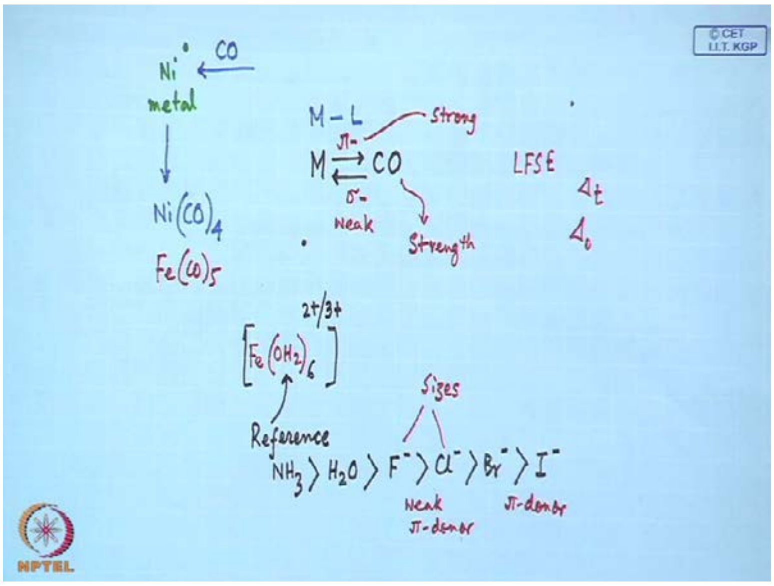

So, this metal ion what we are talking about is nothing but the corresponding metal in zero oxidation state because we know that the nickel is forming in zero oxidation state; that means the nickel is in metallic form and we all know if we have the finally ground or finally powdered nickel in our hand and if we pass carbon monoxide gas on heat and we will be able to produced through the mond process. The Mond first discover that particular thing that we can have the corresponding tetracarbonyl complex of nickel. So, we have from the carbon side we have the lobe and which is basically donated to some of the empty orbital's on the nickel atom. So, nickel is zero oxidation state. So, most of them are filled now because it is in the zero oxidation state, but there are some higher energy orbital's available on nickel which can be utilized for the acceptance from the carbon monoxide side.

So, we have the highest occupied molecular orbital which is the HOMO there in this diagram. So, we have this HOMO in our hand and which is of 3sigma type. So, this homo will be utilized for the donation. Now what about this carbon monoxide molecule which we are classifying it as the good pi acceptor ligand? So, this pi acceptor ligands will be of two types; that means we have the 2 pi orbital's which are of pi star symmetry; that means they are anti-bonding corresponding to this level which is 1 pi and this is 2 pi; that means involving p x and p y this is also involving p x and p y. So, if these two are in p x level; that means it is in the y direction which is in the plane of this terminal and which is perpendicular to this is the corresponding p z.

So p x already utilized for sigma interaction, then p y for 1 pi star and p z for another pi star. So these orbitals will be utilized for acceptance of electron density from the metal. So these are behaving as a LUMO; that means lowest unoccupied molecular orbital. So, unoccupied molecular orbital's will take off the electron density, will receive the electron density from the filled level of, say, nickel 0, because the nickel 0 already have all the filled levels in the d orbital's and if we have some matching symmetry with these LUMOs, then we can have the overlap and electron density can be transformed from the metal side to the ligand side and the ligand can behave as a good acceptor ligand by accepting the electron density in there pi levels; that means they are in there pi star level.

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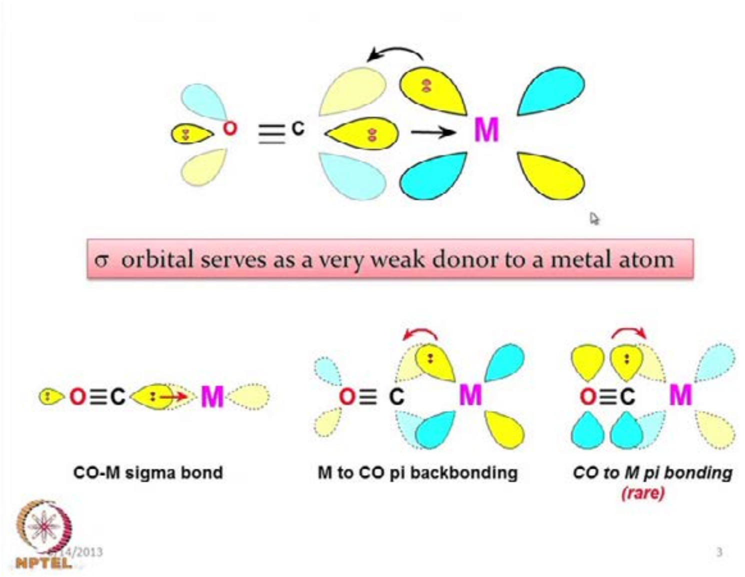

σ orbital serves as a very weak donor to a metal atom

CO-M sigma bond

M to CO pi backbonding

CO to M pi bonding (rare)

So, this the basic diagram for that when we have this; that means when the corresponding 3sigma level is utilized for donation; that mean this orbital is utilized for donation to the metal side and these orbital's are utilized for acceptance. So, this is the sigma orbital from the carbon monoxide side. So, the carbon end is basically utilized for donation. So, this is yellow lobe basically on the carbon side as well as for the oxygen side is utilized for the donation to the metal side. And the metal side if we have some higher energy orbital's which are of this particular axis; that means if we have the corresponding p x, p y or p z or d z square or d x square minus y square which are only pointing towards the Cartesian axis. So these orbital's if they are vacant, then only it can receive some amount of electron density in terms of their sigma orbitals.

So, this sigma donation is very weak in case of carbon monoxide what it is there. So, this weak carbon monoxide sigma donation is basically facilitating the second step; that means the synergistic effect which basically gives us the corresponding thing if that we can have some electron density of this anti-bonding level of this carbon monoxide molecules. So, this anti-bonding level we can have and they are basically vacant. So, electron density can be pushed from the metal side; in this diagram we will be liberating that. So, electron density can be pushed back. So, this can also be considered from carbon to metal and metal to carbon. So, this thing basically we consider whenever we are talking a metal ligand interaction, but the situation has now been changed where the metal ligand interaction is of different type what we are considering that when it is donating to this particular one; that means if we have the sigma donation from the carbon monoxide side.

This is the corresponding sigma donation from the carbon monoxide sides which is little bit weak, but the corresponding pi acceptance from the metal side is strong and this particular nature; that means the pi acceptance will be predominating. So, the nature of this ligand or the strength of the ligand which we will consider it as classification of they are in the spectrochemical series. So, the strength of the ligand will also be controlled by the amount of strong pi acceptance from the metal orbital to the pi star level of this carbon monoxide molecule. So, this we will consider as a synergistic effect and the ultimate result for this interaction between the metal ligand interaction which is always there for the metal complex formation is that, due to this synergistic effect we can have more than one bond order between metal and the carbon of say nickel tetracarbonyl or some other complexes because there are large number of this carbonyl complexes known.

So, we have multiple bonding between this metal and the carbon; so one is sigma another is pi. So, we have a very strong interaction. So, definitely the strong interaction will tell us that carbon monoxide is a very strong ligand though we have a very weak sigma interaction and due to that strength of this carbon monoxide as a ligand, we will be placing this on the right hand side of the spectrochemical serried and will consider this carbon monoxide as a strong ligand. And we will find that the corresponding ligand field splitting and the corresponding ligand field stabilization energy due to, say, delta as corresponding delta t or delta octahedron depending upon the symmetry of the these thing will be bigger due to the strength of this carbon monoxide molecule.

So, the sigma bond is very nice to know that is this particular sigma bond is getting donated to the metal empty orbital. Then we have the pi bond backbonding and another very weak as well as the rare carbon monoxide to pi bonding we can have because these carbon monoxide molecule can have some filled pi orbital's and if the empty orbital's on the metal ion is available. Because this empty orbital's are available for this donation; that means they are basically the corresponding field level, but if the metal orbital's of this particular symmetry; that means depending upon the metal ion whether it is chromium or cobalt or titanium or vanadium, if we have some matching of this orbital of this particular match symmetry with the carbon monoxide pi bond which is filled, then we can push some amount of electron density and there we will consider carbon monoxide as a pi donor ligand.

So it can have two good possibilities; that mean, we can have sigma donation, then pi acceptance from the metal side as well as we have the corresponding pi donation. So if the pi donation is also there, we get something which is above the double bond corrector, but it is not a triple bond corrector, but it is above double bond corrector and that is why we find a very strong interaction between the metal and the carbon that we all discussed in organometallic compounds and in some good catalysts or in some other interactions where carbon monoxide or any carbon monoxide type of molecule is reacting with the metal ion whether it is from the complex or it is from the corresponding metal bearing catalysts.

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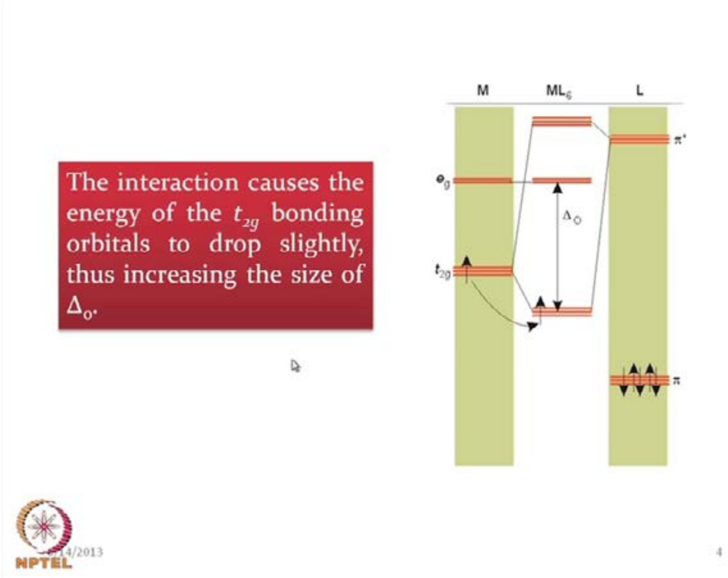

The interaction causes the energy of the t_{2g} bonding orbitals to drop slightly, thus increasing the size of Δ_o.

So, the energy ordering now we can see because we have to compare this energy ordering with that of the corresponding sigma donation. So, we have this pi which is filled. So, these are all the corresponding levels. So, these are all six not five; these are the six electrons in this particular 3 pi level and these are mostly stabilized but this particular interaction; that means the corresponding metal for the t 2g level is interacting with the corresponding pi star level of the carbon monoxide or the other pi accepting ligand. So, if we have the pi level which is available; so this pi level will be interacting with the t 2g symmetry from the metal side and we have the corresponding splitting. So, in essence what we have seen that for sigma donation we have been seeing the situation that we have this particular thing when we have this is the corresponding separation; that means the gap between the t 2g and e g, the t 2g e g gap which we have seen for crystal field theory.

And this gap is basically getting modified, because the theory we are also modifying; we are moving from a crystal field theory to a ligand field theory where we are considering a good overlap between the metal orbital and the ligand orbital and the separation. This particular separation we are considering earlier as the corresponding separation for crystal field splitting and we are talking in terms of the corresponding stabilization in terms of their CFSE; that mean crystal field stabilization energies and the and the amount of stabilization, but when we allow some amount of interaction with the ligand. So, ligands are coming into picture and we are modifying the theory and we are now having the molecular orbitals from the ligands side molecule orbital’s from the metal side. And as a result what we find that earlier we have seen due to the sigma interaction sigma molecular orbital interaction from the ligand side we have this particular gap decreasing, but now this particular gap is increasing when we have the pi acceptorl igand.

That means we are getting a corresponding separation; that means the corresponding splitting if in terms of the corresponding ligand field splitting. So, ligand field splitting will be increased; that means whenever we find a ligand which is of pi accepted type, that will definitely increase the corresponding ligand field splitting and that particular ligand should be characterized as a strong field ligand. So, the interaction causes the energy of the t 2g bonding orbital’s to drop slightly. So, this is the amount of stabilization; that is why we get the corresponding higher energy gap because the e g level we are not modifying due to this interaction and which is therefore increasing the size of this delta octahedral; that means we are pushing the electron towards the strong strength side and the ligands will be of stronger strength.

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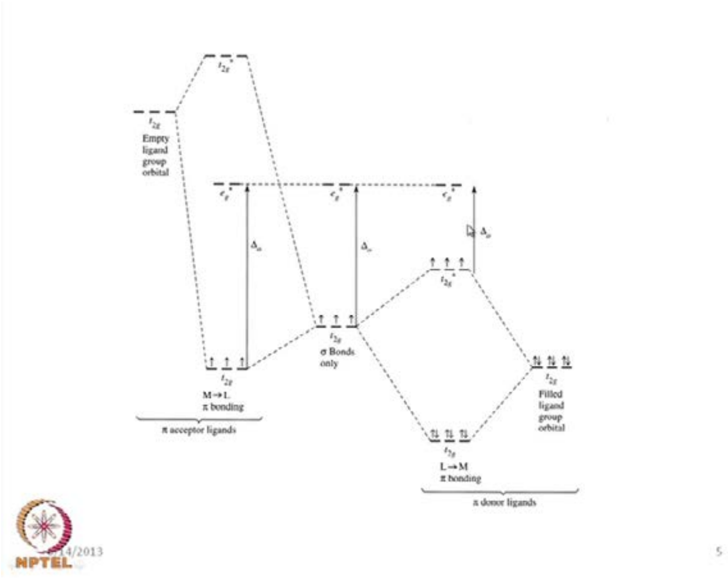

Now if we compare side-by-side these two things; that means earlier we have considered that we have sigma bonding as well as we have pi bonding and if the ligand is of pi type. So, if we have pi bonding, so original separation is this; that means this is the t 2g separation and this has been shown for a situation where it is a d three type of electronic configuration; that means the cobalt three system. And if we have the corresponding sigma bonds only and the sigma bonding interaction, if we just consider it as a point charge interaction and if we do not have any modification in terms of the corresponding crystal field theory, what we get from there that this particular thing basically is not modifying anything.

But when we go for the pi donor; that means the donation from the pi side is there and the ligand to metal pi bonding is available and we have the filled ligand group orbital's which is symmetric match; that means symmetric group orbital or SGOs of six electrons. They will be pushed to the t 2g level which is getting for this molecular orbital formation; that mean the t 2g and the t 2g star. So now this level has basically has been pushed from here to here; that means the t 2g level is now t 2g star level and the energy gap between the t 2g star and e g star has been reduced. And due to pi donation, we will be basically modifying this particular energy gap and whatever we are talking here is the corresponding transition from the t 2g star to the e g star level and this gap is less; that means the ligand if it is only pi donor type, the ligand strength would be less and it can be considered as a weaker ligand.

And the other one just now we have seen for the pi acceptance, the gap will be increasing because the t 2g level is getting stabilized which is not stabilized like this particular case, but it is stabilized little bit due to the interaction from the t 2g empty ligand group orbital because the ligand group orbital's are empty. Because when these are filled we have this are of low energy, but when they are empty this is of high energy. So when this is filled basically over here, we get the corresponding pi donation and when it is empty we considered this ligand as the good pi acceptor ligand such as carbon monoxide. So, we have metal to ligand pi bonding. So, this particular interaction because we have this interaction, we have the stabilization of the t 2g level and now we get the corresponding transition from t 2g bonding to e g anti-bonding level.

So, we should only remember because it is also easy to remember also that whenever we have pi donation from the ligand side, we have the levels involved is both are t 2g star and e g star; then both are of anti-bonding type. But when it is acceptance type one is of bonding type; t 2g level is bonding type and the e g level is anti-bonding type and we will be increasing the corresponding energy gap compared to only sigma bonding interaction. So, basically pi bonding interactions can move the corresponding gap from left to right; in one case it can decrease the corresponding gap and in other case it can increase the corresponding splitting gap.

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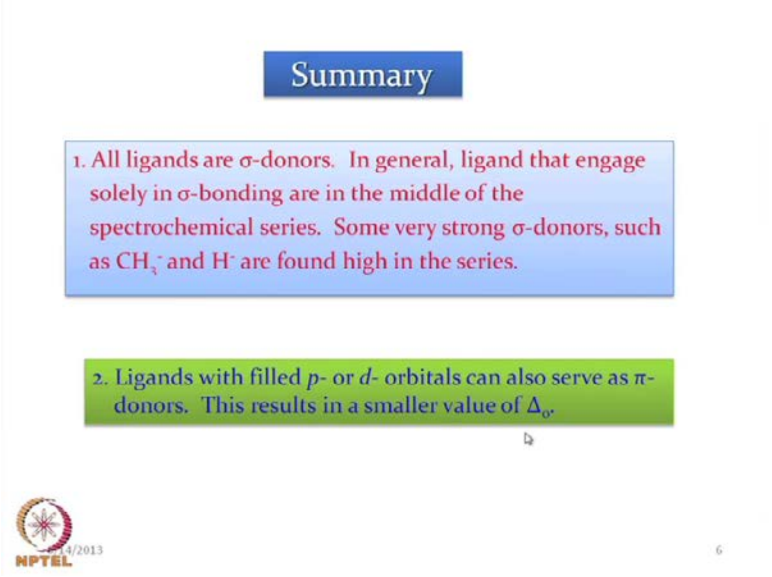

Summary

1. All ligands are σ-donors. In general, ligand that engage solely in σ-bonding are in the middle of the spectrochemical series. Some very strong σ-donors, such as CH_3^- and H^- are found high in the series.

2. Ligands with filled *p*- or *d*- orbitals can also serve as π-donors. This results in a smaller value of Δ_o.

So, that basically gives us the idea that how we can summarize this interaction particularly the pi interactions; that means the ligands are of different type which can show some pi interactions. So, if the ligands are of only sigma donors; that means they do not have any pi electron. They are mostly forming from sigma bonds only; that means the water molecule or ammonia molecule. So, it is basically providing the sigma donation; that means this donation is not very much affecting the corresponding separation between the t 2g level and the e g level. So, the ligands which engage solely in sigma bonding are in the middle of the spectrochemical series; some are very strong sigma donors. So, if we have the entire spectrochemical series; so at the center basically we will have these molecules as ligands where it can show only sigma bonding interactions.

So, if we have only sigma bonding interaction not of special type, but there are some other special type sigma donors which are very strong such as CH 3 minus and H minus; that mean the hydride ion. That hydride ion and methyl ion are found to be high in the series. So they are pretty strong, but they do not have any pi bonding interaction with the metal center. They only show sigma interaction, but their sigma bonding interactions are strong compared to other sigma donor ligands. And then in the second category of this ligand, the ligands with filled p and d orbital's can also serve as pi donors. These are all sigma donors. Then if we have p and d orbital's on the ligand side and which are the filled, they can also serve as pi donors and they basically result in smaller value of sigma octahedron.

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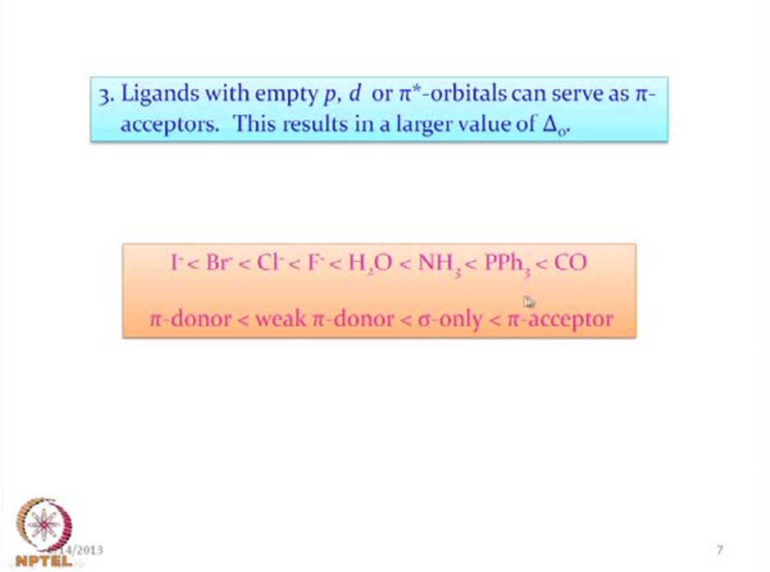

3. Ligands with empty *p*, *d* or π^*-orbitals can serve as π-acceptors. This results in a larger value of Δ_o.

$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < PPh_3 < CO$

π-donor < weak π-donor < σ-only < π-acceptor

Then we have the other category; that means the ligands with empty all; that means if it is in terms of the molecular orbital picture; that means the pi star orbital's or if we have empty p; that means there is no electron in the p level, no electron in the d level but no electron in the molecular orbital which is of pi type. They are serving as good pi acceptors that we have seen just now and we will increase the corresponding value of the delta octahedron. So, we have this corresponding series. So, the part of this spectrochemical series we have taken out for this particular justification that if we have only sigma donors; that means the corresponding sigma donors as this corresponding ammonia and water. So, this can be considered as the typical sigma donor only.

So, they are on this central part of the spectrochemical series because we can also ask that how we can justify in terms of the ligand field theory, the corresponding spectrochemical series. So, spectrochemical series what we have proposed earlier in terms of the crystal field theory, but now we are justifying some part because we are unable to explain position of some of these groups such as triphenylphosphine or carbon monoxide in terms of only crystal field theory; that means only the corresponding charge interaction or ionic interaction. But we should have some covalent interaction for that and to justify the position of these two groups and some others also like cyanide, nitrogen, etc. We have to invoke the pi acceptance of the ligand side. So, this can only be framed or only we can write when we consider the ligand field theory. So, this is basically the corresponding ligand field justification of the spectrochemical series.

So, if we have this water and ammonia. So, these are sigma only and if we have only weak pi donors. So, this will be further weaker than this water and ammonia. So the standard reference, why we are talking all these in case of the standard ligand because whenever we have because these reaction kinetics and reaction mechanisms what will be discussing shortly that if we have the corresponding ferric ion or ferrous ion taking off six water molecules. So, we should have always this particular strength of this ligand. So, the ligand strength is basically the reference for us. So not only water, because this ammonia we all know and ammonia is stronger than water molecule because we know that if we have this water, if we add ammonia, all the six water molecule can be substituted through ligand substitution reaction.

So, if this is the reference and we know in terms of this only sigma bonding interactions. So, if we just only count sigma bond interactions we see that this is greater than this and we have this. So, if we have this and if we just consider that we can have some other groups like the halides. The halides all we know that fluoride, chloride, bromide and iodide and this we all write very nicely. So, they are basically this corresponding weak pi donor. So, they are weak pi donor and they are pi donor, because we do not have anything which is strong pi donor. So here basically, the size basically, why they are; sizes are the main factors. So in this particular case, if we just consider this particular size and as well as the corresponding electronic charge, then this corresponding charge on this particular ion can also tell us that why these are weak pi donor and some pi donor ability.

But the thing is that where we place the triphenylphosphine and carbon monoxide, we have this as the pi acceptor. So compared to all this, basically, the pi acceptor ligands are the strongest ligands. So, they are the very strong ligands and will find in organic chemistry in other related chemicals for the corresponding complexes and as the catalyst, we find that if you have the carbon monoxide they can function as a very good catalyst and triphenylphosphine also can control the corresponding reactivity pattern of the metal center. And we can have large number of metal complexes as the triphenylphosphine because it has a typical steric bulk also and it has the pi acceptance capability also. So, methyl triphenylphosphine interactions are a very important interaction what we can also study when we will be studying the corresponding reactions, reactivity and the mechanisms.

So we just see in that, that how we can utilize these things; that means how we can utilizes this interaction between these metal and ligand for their corresponding reactions in terms of the corresponding reactivity and the mechanism.

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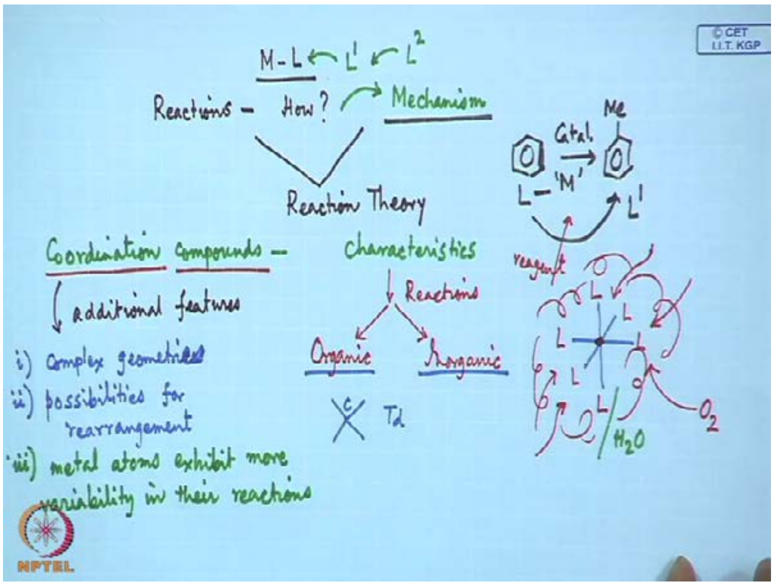

So, if we have M and L and whatever we will be talking here is the reaction; that means certain metal ion is there in our hand and that particular metal ion is reacting with the ligand and how they are reacting that we want to know. So, how this reaction is taking place; that means, if we know that how this reaction is taking place at this particular standard temperature, how fast the reaction is, or how quickly we can substitute this ligand; whether we can substitute these ligands by L 1 or this L 1 can be substituted by L 2. That basically gives us some idea about the corresponding mechanism of these reactions and the substitutions. So basically all these things, but we will consider in this particular class for studying the corresponding reactions in terms of their corresponding reaction theory. So, how theoretically we can explain the corresponding reactivity pattern for these different coordination compounds, because these coordination compounds are very important and very interesting also.

So, whatever coordination compounds we have, they have some important characteristics. Because all these things that means the mechanism particularly, because we always must have some mechanism for any organic reaction or any organic transformation such as how we can get the corresponding benzene; you can have benzene, how we can get the corresponding toluene molecule; that means how we can add the methyl group to the benzene ring through some Friedel-Craft reaction. So basic organic chemistry reaction, we take some time, we take the help of the catalyst and the catalyst is sometime the metal-based. So, how we can know that this catalyst is there and this particular one is not behaving as our ligand; that means, the metal is the corresponding metal center from the catalyst and the ligand is our corresponding molecule which is interacting with the metal center and which is getting modified to, say, L1; that is the L1.

So, these are related to all sorts of reactions particularly the important conversions for any such organic reactions. So, they have some useful characteristics and there is because we are talking about all these reactions and we are focusing attention only on the coordination compounds. So, both organic reactions and typical inorganic apart from this complexes and the coordination compounds, we can have some understanding if we just thoroughly follow the corresponding mechanisms and how the reactions are taking place. But when we talk in terms of the corresponding coordination compounds compared to the very simple transformation of these benzene molecule to toluene and in terms of very simple other inorganic an organic transformations, these coordination compounds we are calling them as the corresponding complexes, and the nature of these and the corresponding feature of these corresponding coordination compounds are little bit complex.

So, they have some additional features therefore and we should always keep in mind those additional features, when we compare the corresponding reactivity pattern as well as the reactions with respect to some organic reaction or some organic molecule or inorganic reaction or with some inorganic molecule. So, these additional features are very important that these molecules have more complex geometries. So, not only the complex architecture; that means the presence of the different metals more than one metals sometime and the different types of ligands and sometime large number of ligand; that means when we talk about the corresponding octahedral compound we have six ligands. So, how these ligands are placed around the metal center because this organic chemistry is mostly dominated by the tetrahedral geometry of the carbons. So, if we have the carbon center is basically only the tetrahedral geometry, but the metal complexes can have octahedral geometry, tetrahedral geometry, square pyramidal geometry, trigonal bipyramidal geometry and much more complex geometries of higher coordination number.

So, these complexes have much more complex geometries. So, complexes have more complex geometries and they have basically more possibilities for rearrangements; so more possibilities for rearrangement. So, since this feature is much more complex; that means since we have, say, in case of octahedral complex, we can have, say, ligand one, ligand two, ligand three, ligand four, ligand five and ligand six. So, the direction in which the corresponding incoming group or the new ligand or some reagent is coming because in presence of catalysts what we are adding over here is the reagent for this sort of transformation. So, at which particular directions, it will have some directional preference for the reactivity and if we have the corresponding symmetry for this geometry is not typically symmetric; octahedral is typically symmetric, but it has no reactional preferences as a result.

But when this same thing is confined in a big biological molecule such as hemoglobin and myoglobin and the metal center is our iron center, then we must have some good sides where the new molecules or the new ligands are coming such as when O 2 is coming into bind the corresponding iron center in hemoglobin and myoglobin. So, it must have some directional preference. So, how this particular geometry if it is square pyramidal or if it is octahedral only; so how O 2 will come and bind these iron centre by substituting, say, some water molecule already bound to the iron side.

So, the possibilities are more and we have the rearrangements are also more and this metal atoms present in these species it can be the corresponding ions also. So, they exhibit more variability. So, variations are there; more variability in their reactions. So, that means their reactions are also much more complex and these reactions what we are getting over here is that this particular reaction is not that for the organic reaction and inorganic reactions are also sometime pretty simple. So, we have to monitor these reactions very critically.

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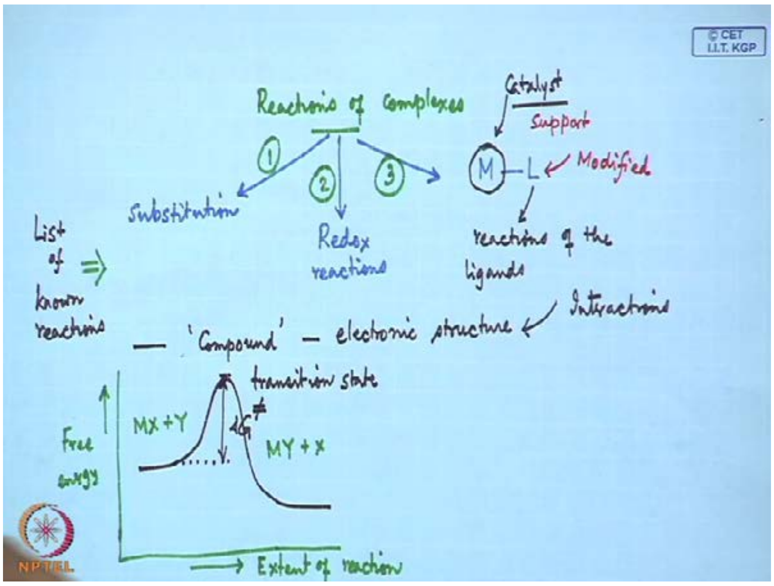

And the reactions what we can have of these complexes are of different types therefore. So, they are of basically three types where we can consider the corresponding substitution; that means the L 1 is substituting L or L 2 is substituting L 1 at the metal side. So, we have the substitution reactions at the metal center. Then we have the oxidation reduction reactions or redox reactions. The ligands are all present, but we can take out one electron from the center and we can donate one electron to the center which is not always possible because we do not have that kind of parallel reaction in case of typical simple organic molecules or inorganic molecules. And sometimes the reactions of the ligands; that means metal is there and ligand is attached to the metal side and what is happening over there the reactions of the ligands, the ligand is basically reacting then without changing their attachment to the metal center; so the reactions of the ligands.

So, if we considered that this particular part is the part of the catalyst, then this reagent or the reactive molecule which is attaching to the catalyst is coming over there and which is attaching to the metal side. So, if the catalyst is basically the support; some solid state catalysts are also known and if this catalysts have good support. So on the catalyst support, the ligand is coming and sitting. So, after sitting on the catalyst we can have some good modification of these ligand; if it is simple benzene ring what example we have given just now that whether we can modify the benzene ring nicely in presence of the catalyst to install it in counterpart or L can be modified to something else which is L 1, L 2, L 3, etcetera. So, when it is sitting over the catalyst, so we can go for the modification. So, ligand can be modified.

So, that basically is our goal; that means how we can change the corresponding reactivity of these ligand side and it can be modified. So, ligand can sow this modification of this particular ligand which is bound to the metal sides. So, for all these three types of reactions, this is one say, this is two, this is three, we can have very detail and elaborate explanations for all these. So, theoretical explanations for all this reactions how the substitution reaction is taking place, how the redox reactions are taking place, and how these reactions are taking place on these molecules. So, we can have such as all these or some more also that least of known reactions we should have in our hand. So, then what we want to understand is the electronic structure of the compounds and their interactions.

So, if we have the complex or the compound and we want to understand basically the electronic structure of that particular compound and this particular compound when we know for this corresponding electronic structure, then only we can have some information related to that of their interactions. So, how this M L interaction is taking place? So, if we find out these interactions with related to that particular metal complex; so very simple interactions what we can talk about is nothing but the corresponding reaction where we have Mx is reacting with y giving rise to the corresponding product which is My plus x. So, this is the very simple reaction if we have the ligand as x or anything else which can be substituted by y by L 1. So, we get the corresponding complex when L 1 will be there and the existing ligand which was L will be kicked out from the medium.

So, if we have this axis as the corresponding free energy change for the reaction; that means for substitution reaction, substitution of x by y and how much we are progressing from the left to right that how faster how quick is the reaction or how far the reaction is going; that means the extent of reaction. So, if we just find the corresponding extent of reaction. So, we get this change only if we have a corresponding potential energy profile or potential energy surface for this reaction is like this. So, what we have that M x plus y is interacting which is here in terms of its free energy. So, we will be gaining some free energy change. The free energy change will be negative and the reaction would be spontaneous.

So, from this free energy axis we should have some gain from the free energy and we are getting this particular product. So, what we get that this particular because we have to cross something some barrier has to be covered. So, this is the corresponding transition state and we will consider more as the corresponding transition state theory and this is the corresponding free energy change and we consider as the corresponding free energy of activation delta g thereby. So, this is the free energy change of activation for the reactions. So we can measure, we can find out these parameters and ultimately we can know the exact form of these reactions and it is mechanisms.

Thank you very much.