

Advanced Transition Metal Chemistry_Summary and Conclusions
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Module - 12
Lecture - 60
Summary and Conclusions

Hello everyone. I once again welcome you all to the last lecture of MSB lecture series on Transition Metal Chemistry. In this lecture, I shall consolidate whatever I discussed in last 59 lectures in the form of summary and conclusions. To begin with, what I did was I gave a historical background to the periodic table. Why I gave? It is very important to know how many of these people contributed to bring all the known elements in the form of a table to understand their chemistry and also to do comparison and also giving some order.

As I had mentioned, periodic table is nothing but place for every element and every element in its place. So, meticulously it was done, and it was published by Dmitri Mendeleev in 1869. But however, at least 50 years before this concept came into the mind of Dmitri Mendeleev, several other alchemists or physicists, chemists in general, scientists worked very hard to arrange those elements in an organised manner. In that context, I call all these people as periodic table scientists.

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Periodic Table Scientists

 <p>Antoine Lavoisier 1743-1794</p>	 <p>Jons Jakob Berzelius</p>	 <p>William Ramsay 1852-1916</p>	<p>Albert Ghiorso (July 15, 1915 – December 26, 2010) was an American nuclear <i>scientist</i> and co-discoverer of a record 12 <i>chemical elements</i> on the periodic table. His research career spanned six decades, from the early 1940s to the late 1990s.</p>			
 <p>Dmitri Mendeleev</p>	 <p>Henry Moseley</p>	 <p>John Newlands</p>	 <p>Julius Lothar Meyer</p>	 <p>Yuri Oganess...</p>	 <p>Glenn T. Seaborg</p>	 <p>Albert Ghiorso</p>

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You can see here, among them who stands taller if you ask me, it is Antoine Lavoisier. He changed the perception of understanding of science and chemistry at the time when people

were not going in a different direction to propagate the advancement of science. At that time, he brought the concept of quantitative analysis instead of qualitative analysis, and he can be called as father of modern chemistry.

And of course, he named oxygen and hydrogen. And also, he named several other elements, he also discovered silicon. And unfortunately, at the age of 51, he was guillotined. Next, Mendeleev published his periodic table in 1869, but before that, triad system came into picture by John Newlands. And then, he also talked about octave. And then, Jons Jakob Berzelius named several elements and gave symbols for them.

And when periodic table was published by Dmitri Mendeleev, he gave an important statement that physical and chemical properties of elements are periodic functions of their atomic weight; but later, Henry Moseley through extensive photoelectron spectroscopy, he determined atomic number and several properties of elements and eventually he modified the understanding of periodic table giving importance to atomic number, and thus it was modified as the periodic functions of atomic number, that means physical and chemical properties of elements are periodic functions of their atomic number.

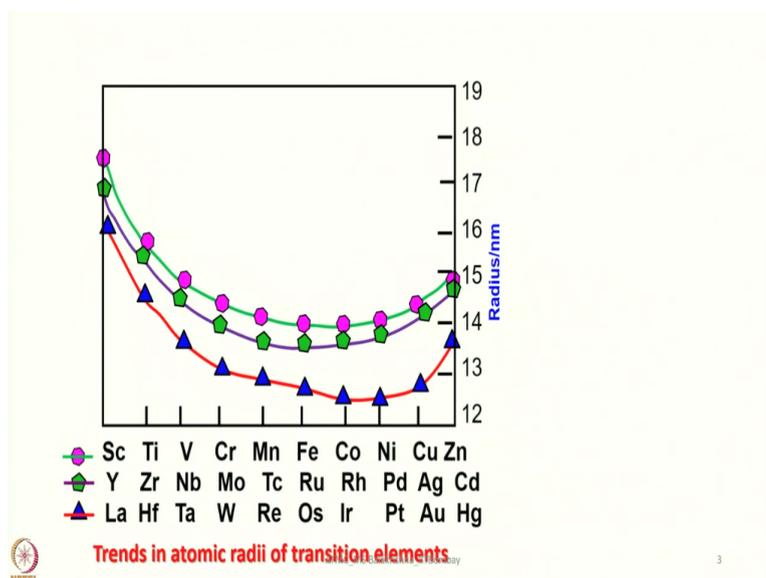
Now we know that how valuable the atomic number is, that is electronic configuration and number of electrons. And once we know the electronic configuration and with basic understanding of periodic trends and periodic properties, we should be able to deduce all properties and understanding their reactivity, stability, etcetera. And during the same time, when Dmitri Mendeleev presented his periodic table, Julius Lothar Meyer from Germany was almost ready even 1 year before, but somehow he did not publish.

It does not mean that he did not contribute, his contributions are very significant. And due to some reason, he did not publish his periodic table that was very similar to what Dmitri Mendeleev presented. And however, we can see even in NCERT books, Lothar Meyer's plot about trends among transition elements. And of course, Glenn Seaborg and Yuri Oganessian were given distinction by naming elements with atomic number 207 and 218 after their name.

And in fact, when element with atomic number 207 was named as seaborgium, Glenn T. Seaborg was extremely happy and he said that this honour of naming an element after his

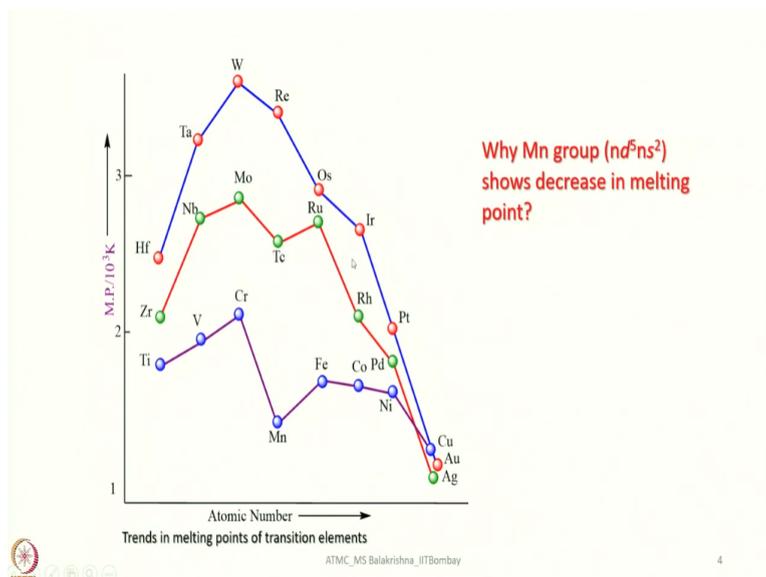
name is more than getting a Nobel Prize. In fact, these are the only 2 people whose names were considered for 2 elements when they were alive.

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And of course, one should understand the trends in atomic radii or melting point, boiling point, ionisation energy and try to analyse to understand the properties, how it varies within the group and also along the period when you start filling from d^0 to d^{10} electronic configuration.

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For example, you can see why manganese group shows decrease in melting point. All these things are clearly spelled out in my lecture. Please give importance and attention to these things so that you can understand the behaviour in a better way. It is very appropriate to remember Alfred Werner for his coordination theory.

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Coordination Theory

Alfred Werner
Zurich University Zurich, Switzerland
Coordination Theory 1893
"Electron" discovery by J. J. Thomson 1896
Nobel Prize in 1913 (at the age of 47)

$\text{Co}(\text{NH}_3)_6\text{Cl}_3$ is the first coordination compound discovered by Tassaert in 1798



Alfred Werner 1866-1919

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Again, when he started working on coordination compounds of cobalt, octahedral cobalt compounds and square planar complexes of platinum, there were no support of any analytical or spectroscopic tools. And not only that one, even atomic model, atomic structure was not known and even electrons were not known. In fact, he proposed his coordination theory in 1893, but electrons were discovered much later by J. J. Thomson in 1896.

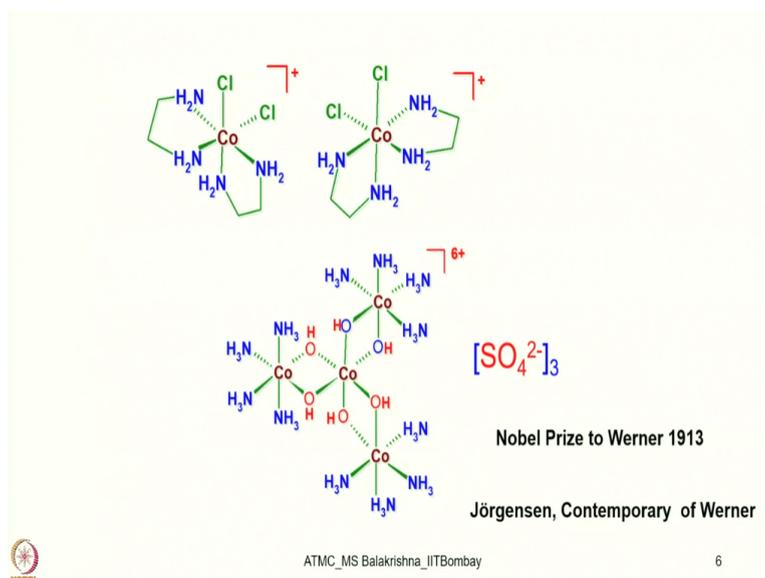
However, he did not leave any stone unturned. With his synthetic ability and analytical thinking, he could make all possible isomers and also, he brought isomerisation concept, and also, he said why coordination number 6 would prefer octahedral geometry; when you have coordination number 4, why certain molecules prefer square planar geometry, why certain molecules prefer tetrahedral geometry; all those things very nicely he analysed and he eventually proposed his coordination theory.

During his time, his contemporary, who had more inclination towards organic chemistry, Jorgensen was always opposing and ridiculing discoveries of Alfred Werner, because he was proposing a theory called chain theory and always telling that no coordination compound can have coordination number more than 3. And also, I showed you how the bonding was shown in octahedral compounds of having different number of ammonia and chloride in his chain theory.

And chain theory was a total flop, but however, he was also ridiculing coordination theory proposed by Alfred Warner. But in fact, it even went to a personal abusing level, but however,

he tolerated all those things and he quietly worked hard and eventually he made everything very clear. And then, eventually he got the Nobel Prize in 1913.

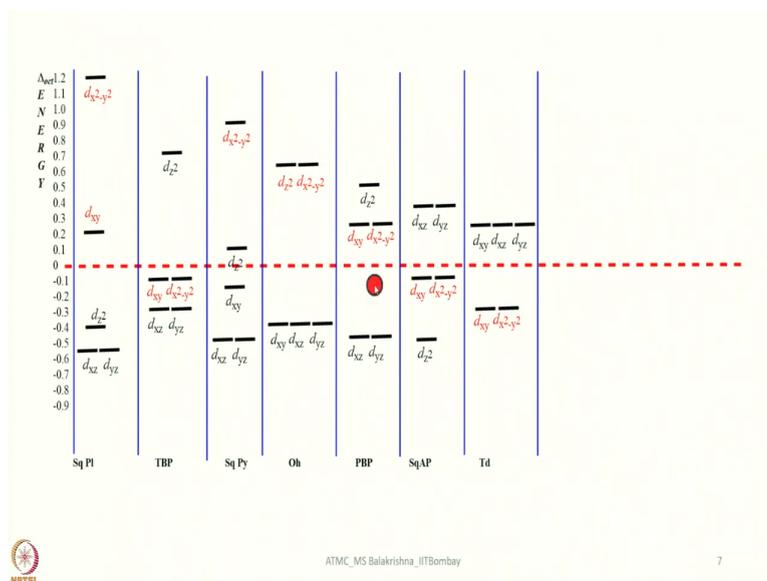
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And one more thing we should remember is about making an optically active coordination compound having no carbon atoms. In fact, Jorgensen was again telling, one cannot make any optically active compound without having a chiral carbon centre. So, with this, what he did was he made this compound. You can see, there are no carbon atoms, only O and N are coordinating.

He made this chiral compound; he isolated both the enantiomers; and then, for his painstaking work and of recognising this synthesis, he was given Nobel Prize in 1913. So, now we know, most of the concepts still we were using, whether it is reaction mechanism or whether it is isomerism or whether it is understanding bonding concepts.

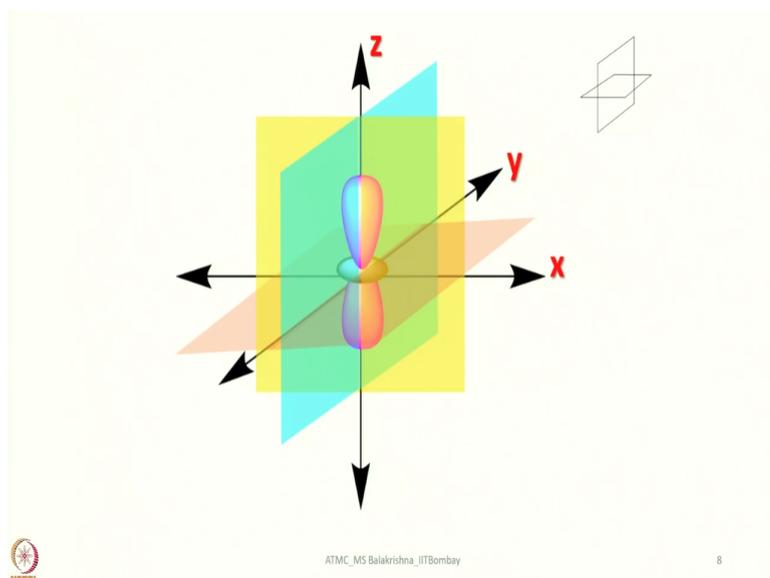
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And of course, crystal field theory is a very nice theory to explain bonding among coordination compounds, to an extent organometallic compounds but there is also a flaw was there, and nevertheless it is a fantastic bonding concept and it can explain many things; only thing is, it does not consider covalent character in the bonding, metal to ligand bonding. However, the best from the valence bond theory that is mixing of orbitals that is the hybridisation, and then the crystal field theory about a splitting of d orbitals were nicely imbibed into the molecular orbital theory to come up with ligand field theory.

Now, ligand field theory having all these very good ingredients from these bonding concepts can literally explain everything including reactivity, stability and all those things. So, this is how coordination chemistry progressed from Werner's coordination theory. And also in between, I also told you earlier, attempts to explain bonding using electroneutrality principle and Kepert's model for using VSEPR theory to explain bonding, all those things.

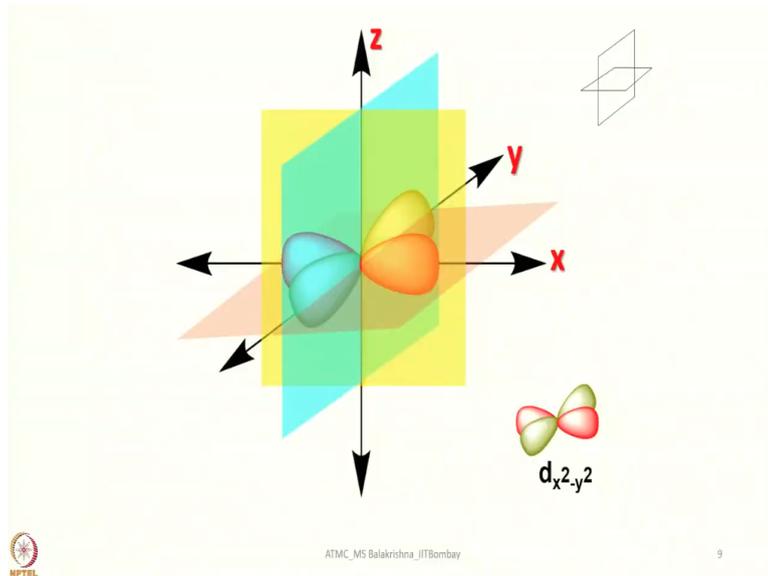
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And of course, crystal field theory is very important. In order to understand and to write crystal field splitting diagrams, now one should remember 2 things; one is relative orientation of d orbitals with respect to Cartesian coordinates, and also the direction of approach of ligand towards metal in different geometries. Once we know these things, understanding and writing crystal field splitting diagram for any geometry would be rather easy.

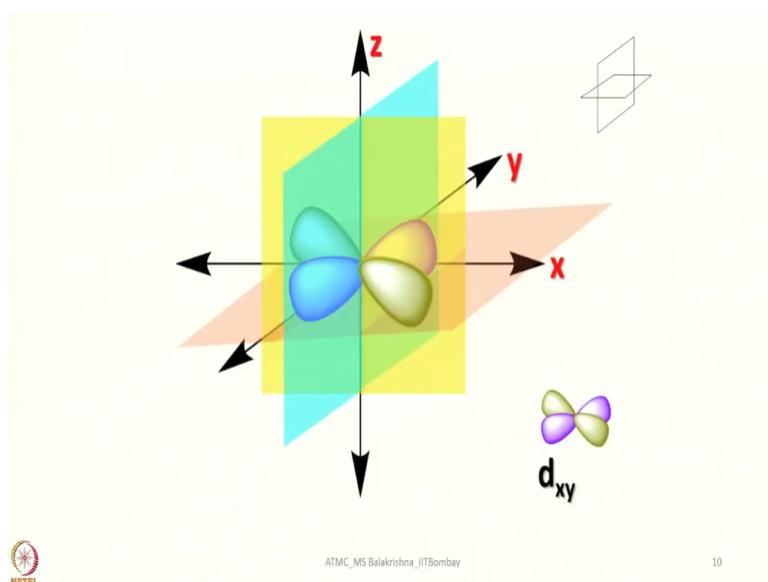
So, again to emphasise I am showing you the orientation of orbitals and also the planes we come across xy plane, and then xz plane and zy plane. So, now, if we arrange all the orbitals and if we place ligands coming from different directions to establish a certain geometry, we can know now, because of these interactions, what would happen to the energy and how the degeneracy is destroyed and how they are arranged. Once we know, understanding rest of chemistry would be rather easy.

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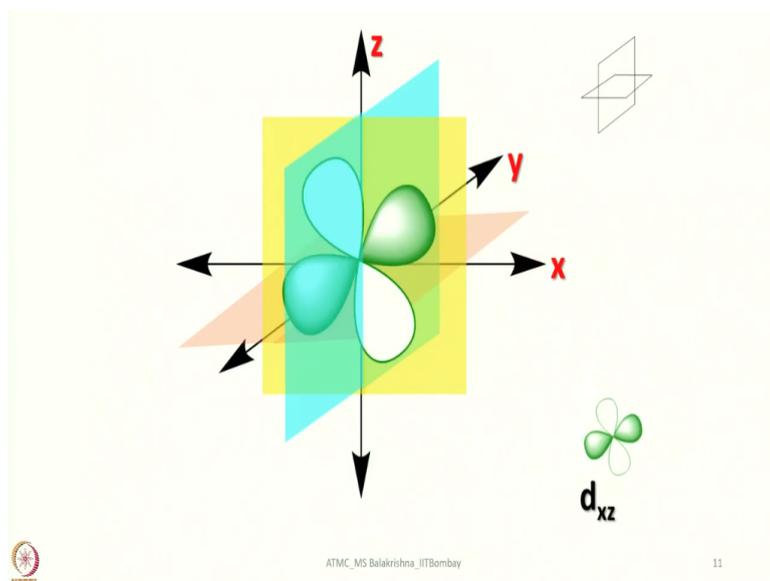
This is for $d_{x^2-y^2}$.

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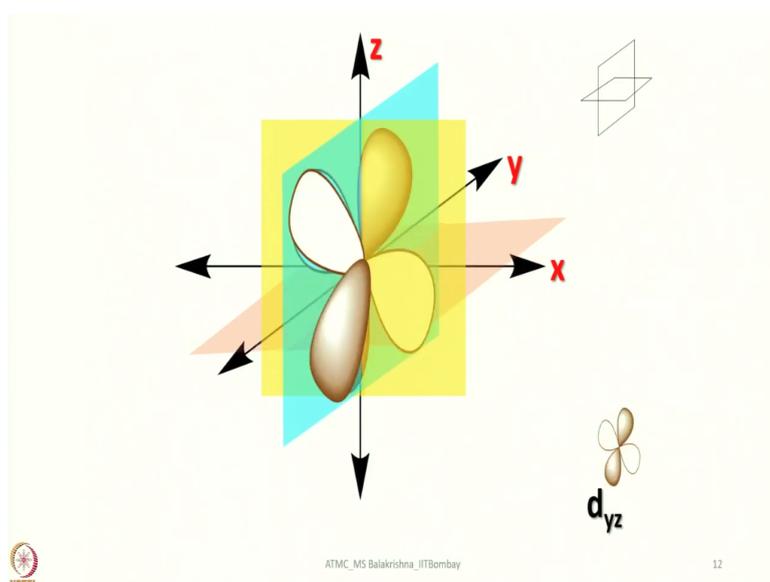
And this is for d_{xy} .

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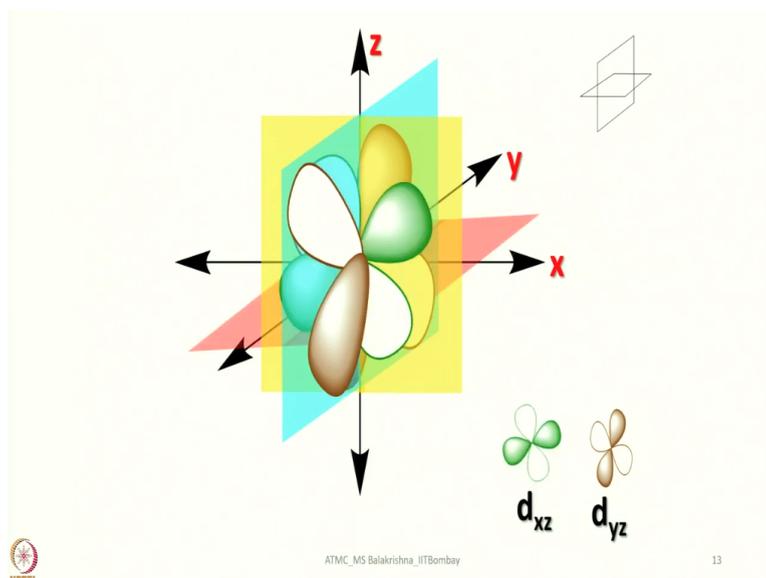
And then this is for d_{xz} .

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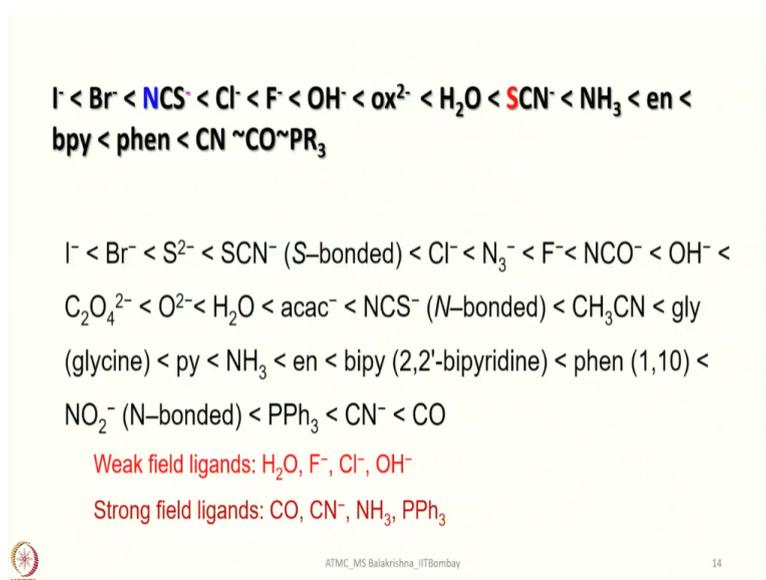


And this is for d_{yz} . Once we know these things, and also, we know the geometry of our ligand field, we can write crystal field splitting very easily for any given geometry.

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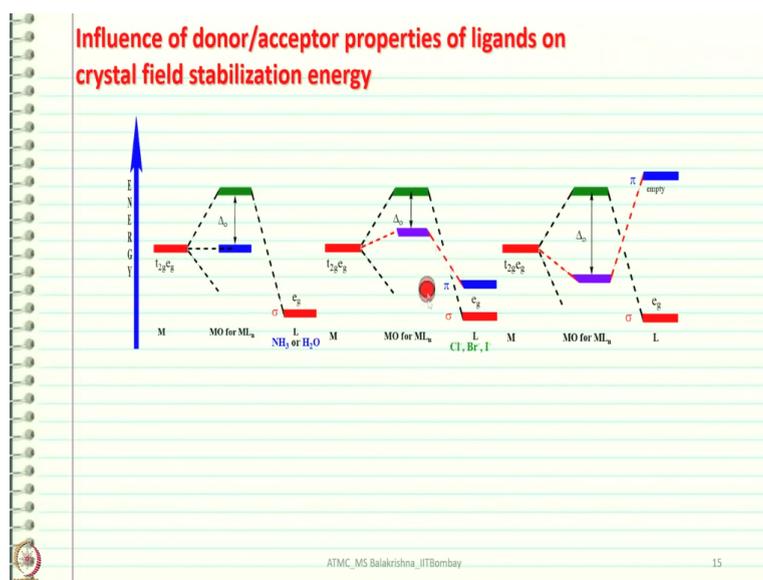
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So, now, this is very important, spectrochemical series. And spectrochemical series, the position of ligands in spectrochemical series can be checked by looking into UV-visible spectra of complexes having these ligands. But on the other hand, why a given ligand has taken or occupied a position somewhere here or here in the spectrochemical series cannot be explained by CFSE.

CFSE can also only tell you where it is positioned, but why it is positioned you cannot tell. For that one, one has to understand the nature of the ligands and what kind of electrons they have and where in the donor orbitals are located or whether it has donor and acceptor properties or it has only donor property or it has both donor and acceptor properties.

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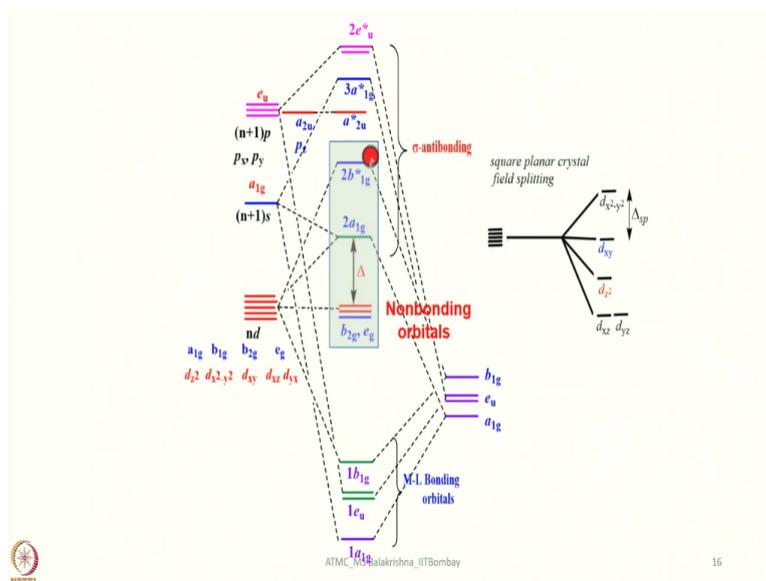


So, in that context, these pictures are very significant. So, here you can see, I have written 3 diagrams. Again I am emphasising, we talked about pure sigma donor ligands; in that case, CFSE would remain like this. And when we consider a sigma donor and pi donor ligands; for example, low-lying filled sigma donor and low-lying filled pi donor orbitals. In that case, what would happen, because of overlapping and generation of molecular orbitals, the CFSE drops significantly.

That is the reason these ligands are called as weak field ligands. So, the CFSE does not tell why they are weak field ligands because of these two here, low-lying filled sigma orbitals and filled pi orbitals having low energy compared to metal t_{2g} would signify why they are weaker ligands. And similarly, if we look into sigma donor and pi acceptor, low energy filled sigma orbitals are there, high energy empty pi orbitals are there.

In this case what happens, because of their overlapping, the CFSE in this fashion increases. So, that means, we should remember this one, the classification of ligands should be based on these 3, that is 2 sigma donors, and sigma donors and pi donors, and sigma donors and pi acceptors. Once we know those things, understanding chemistry and utilising them in some application would be very easy.

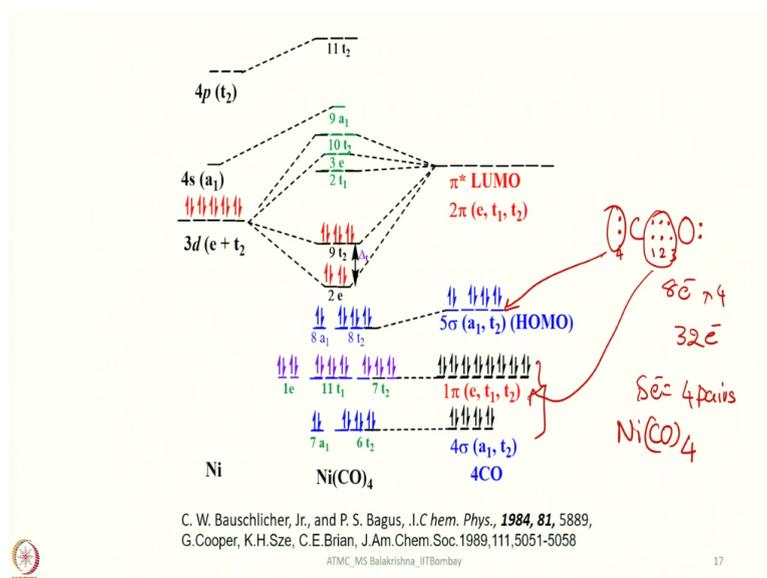
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Now, let us look into MO diagram for square planar complex. If you just look into CFSE crystal field splitting here, this is the gap that determines CFSE among square planar complexes. And again here, if you just look into it, this is a gap that we call it as frontier orbitals I would say, and this is HOMO and LUMO gap here. And if you consider here 8 electrons, 8 electrons are filled here; so, up to here, 8 electrons are filled; and then, this will be HOMO and this will become LUMO.

So, that means, by extending this one, considering this crystal field splitting diagram and then considering what kind of hybridisation one can anticipate for square planar complexes, getting information from VBT. And then we consider these 2 and put into molecular orbital theory; this ligand field theory comes and it can expand very nicely all those things. And also I have given Mulliken symbols for various d orbitals. Just go through it and just look into it and try to understand.

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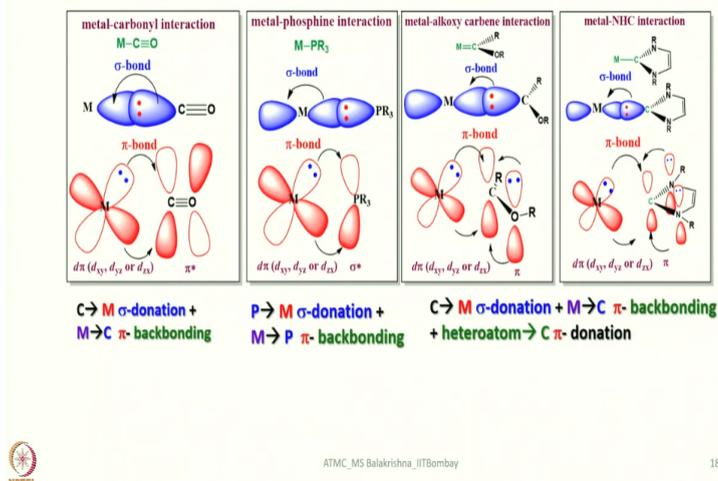
So, now, one more MO diagram I have given here for nickel tetracarbonyl. You can see here, nickel tetracarbonyl, this lone pairs are placed here, higher in energy among all. And this one essentially should go to the metal, sp^3 orbitals to establish metal to ligand bonds, nickel to carbonyl bonds; but however, if we just look into this diagram, they are not participating, there is no overlapping of this one with s and p because they are too high in energy.

So, that means you should know the fact that $Ni(CO)_4$ does not have sigma bonding at all. That means, how this molecule is formed? It is because of back-bonding only; you can see here. So, these t_{2g} electrons are getting placed in the molecular orbitals generated by pi star and t_{2g} of metal. So, that means, only the back-bonding from nickel to carbon monoxide antibonding orbital is responsible for the existence of $Ni(CO)_4$.

So, that is the reason they are very unstable and also, they are volatile, whereas, in case of a metal carbonyl such as chromium hexacarbonyl, tungsten or even pentacarbonyl, we have seen the participation of both sigma as well as pi-orbitals. In fact, all metal hexacarbonyls are stable and solids having moderate stability.

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Bonding interactions between metal and various σ/π ligands



So, now, these 4 diagrams will tell you non-classical ligands having sigma donor and pi acceptor capabilities, carbon monoxide and phosphines and also Fischer carbene and N-heterocyclic carbene. All of them are non-classical ligands having sigma donor and pi acceptor capabilities. And of course, there is relative difference in their donor and acceptor properties.

Carbon monoxide may be very good sigma donor and also good pi acceptor, no doubt; but phosphines can also compete well with carbon monoxide in terms of their sigma donor ability and pi acceptor ability, but in contrast to carbon monoxide, we can vary these things, we can vary these properties to an extent that it can even perform as a better pi acceptor compared to carbon monoxide, when we have electron withdrawing groups or electronegative substituents on phosphorus.

That means, we should know that electronically we can tune the phosphines to make them better than carbon monoxide. For example, if you put more electron releasing groups on phosphorus, it can be a good sigma donor and a poor pi acceptor. On the other hand, if you put electron withdrawing groups on phosphorus, it can become poor sigma donor, but very good pi acceptor.

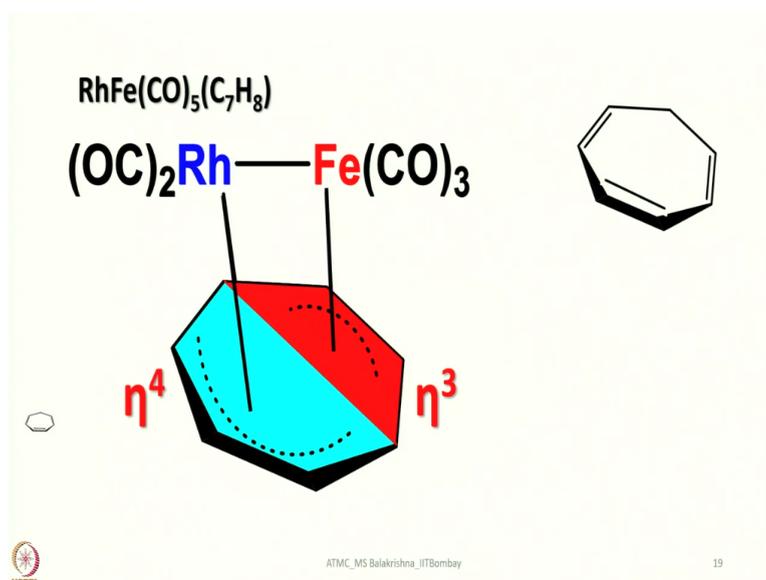
So, this kind of flexibility in its synthesis, you cannot come across in carbon monoxide. That is the reason the tuning is very easy. And hence, phosphines are very popular when we use metal complexes containing phosphines as catalysts in homogeneous catalysis for several organic transformations. And similarly, Fischer carbynes also there; here also back-bonding is

there; back-bonding one can anticipate in the same way as carbon monoxide, but here already we have lone pairs within the ligand.

As a result, what happens, this intra-back-bonding is more facile compared to inter back-bonding that is from metal to ligand. As a result, what happens, they become poor pi-acceptors. So, this also you can call it as an intra backbonding, also you can call it as negative hyper conjugation. Same thing is true in case of N-heterocyclic carbenes also, you should remember.

N also has a lone pair. This lone pair can also go to the pi star of carbene. As a result, what happens, they are also poor pi acceptors but they are good sigma donors. So, this is how you can compare these non-classical ligands in terms of their donor and acceptor properties.

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And then, 18-electron rule is very important. It is not a must to have a stable complex because many square planar complexes with 16 electrons are stable; for example, rhodium 1, iridium 1 and also all d^8 system, nickel 2, palladium 2, platinum 2, gold 1, all those things; but counting 18 electron gives some idea about their possible utility in some reactions and other things.

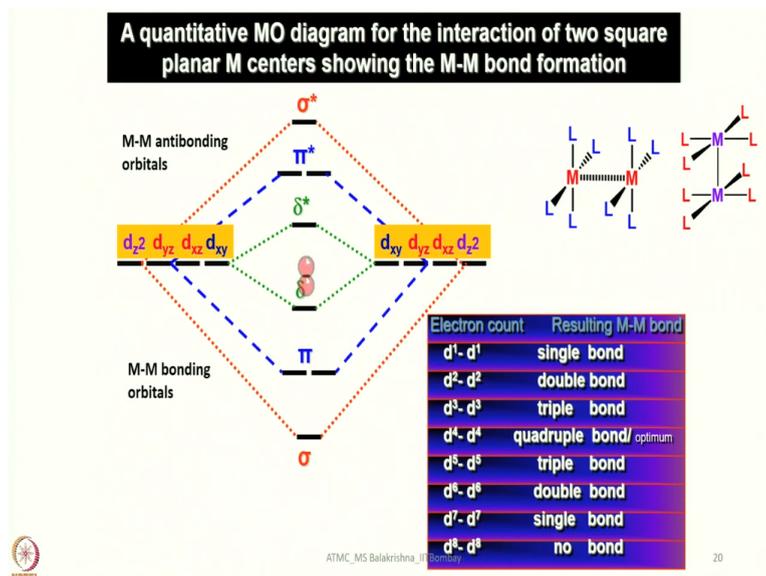
For example, if there are 18 electron complexes, you cannot use them for oxidative addition reaction or catalysts; prior to that we have to get rid of a couple of ligands or you have to remove some electrons so that it is ready for oxidative addition reaction. And also, it is very interesting to count electrons. I have taken this interesting molecule again.

We have here rhodium and iron and we have 5 carbonyl groups are there and a C_7H_8 is there, cycloheptatriene is there, and that I have shown here. So, now, let us see how it satisfies 18-electron rule. First you should think of a formal rhodium to iron bond, and also why I have put more carbon monoxide on iron is because it has less electrons compared to rhodium; it is a d^7s^2 system, whereas iron is d^6s^2 system.

So, now, 2 are there and 1 rhodium-iron bond is there. And now, you should place in such a way that both of them would be having 18 electrons; at least 17 electrons so that this comes through, one comes through rhodium-iron metal-metal bonding. So, this how you can show η^4 and η^3 . So, this is again very interesting. So, like that, many examples I have discussed.

Go through it and also you can find lots of examples in textbooks, try to solve them, or best thing is, every time you come across a metal complex, try to count electrons to see whether it satisfies 18-electron rule or not.

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So, now, it is about a metal to metal multiple bonding. This is very important with square planar complexes and having eclipsed geometry. Of course, I have discussed in length how they identified rhenium complexes in the group of F. A. Cotton when he was in MIT. And now we know, how to explain the bonding up to 5 bonds, not 4 bonds like quadruple bond; up to 5 bonds are possible between 2 metal centres.

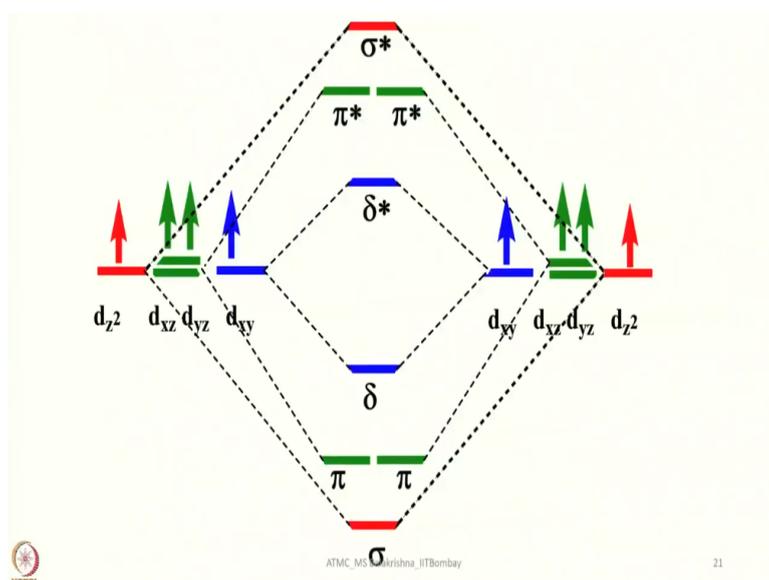
And then how the bond formation takes place can be readily explained using even molecular orbital picture like this. And here you should remember the fact that d_z^2 ; and for this one what happens, 2 metal complexes having square planar geometry should be eclipsed to each other. And in this case, if you just ask me why not $d_x^2-y^2$, because that is already used for the formation of metal to ligand bond, if you recall dsp^2 hybridisation from Valence bond theory.

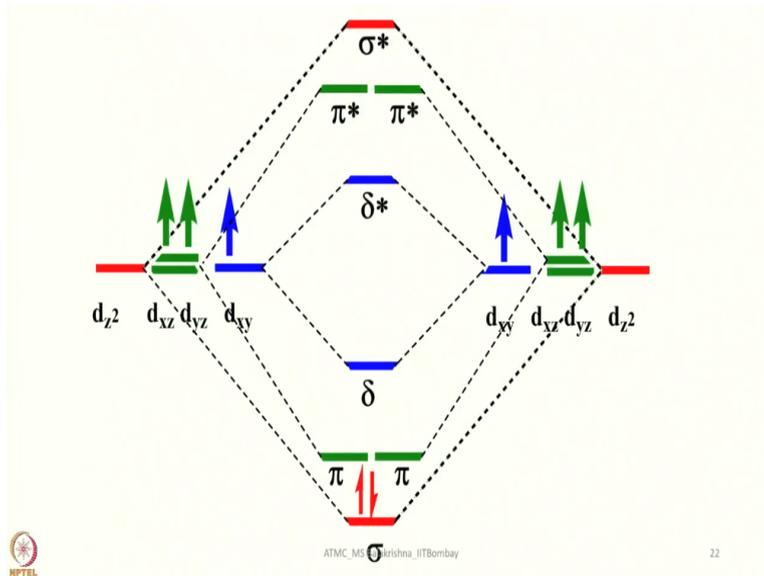
So, that means 4 orbitals are left here, d_z^2 , d_{yz} , d_{xz} and d_{xy} . Now, one can comfortably use from 2 metals to establish metal-metal bond like this. So, this one is a sigma bond, **(Video Starts: 20:26)** head on collision, $d_z^2 - d_z^2$; and d_{xz} is like something like this; and then, d_{yz} is something like this; they are degenerate, they can accommodate 2 electrons each; and then, we have d_{xy} is there.

So, this is a weak interaction, something like this. So, one is this d_z^2 ; one is a d_{xz} ; another, d_{yz} ; and then this is d_{xy} ; d_{xy} will be like this. So, now, that is called δ -bonding between them, weakest overlapping among orbitals. **(Video Ends: 20:55)** What would happen to the number of electrons one have?

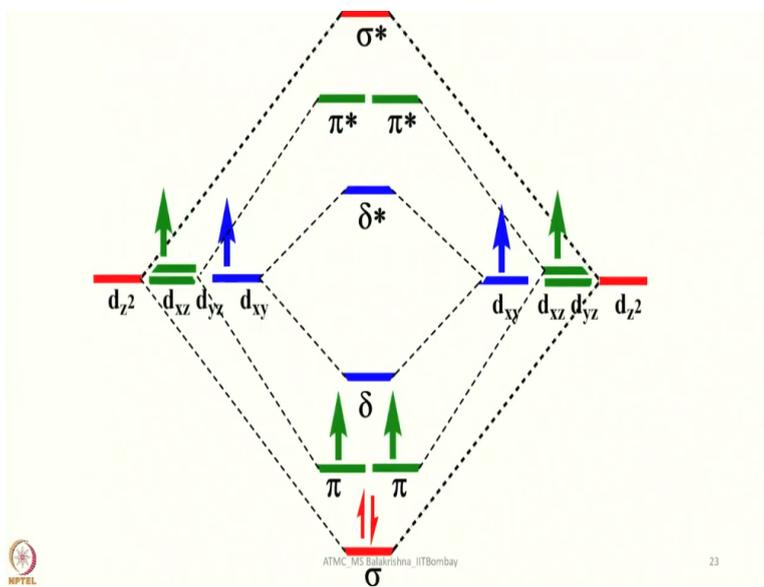
d^1 , one electron is there, so, then you can have 1 electron from each, results in sigma; 2, double bond; 3, triple bond; and 4, quadruple bond; if you have 5, again we start filling antibonding orbitals, so, triple bond; d^6 , double bond; d^7 , single bond; and d^8 , everything is filled, so, bond order is 0, you cannot see a formal metal-metal bond in d^8 system.

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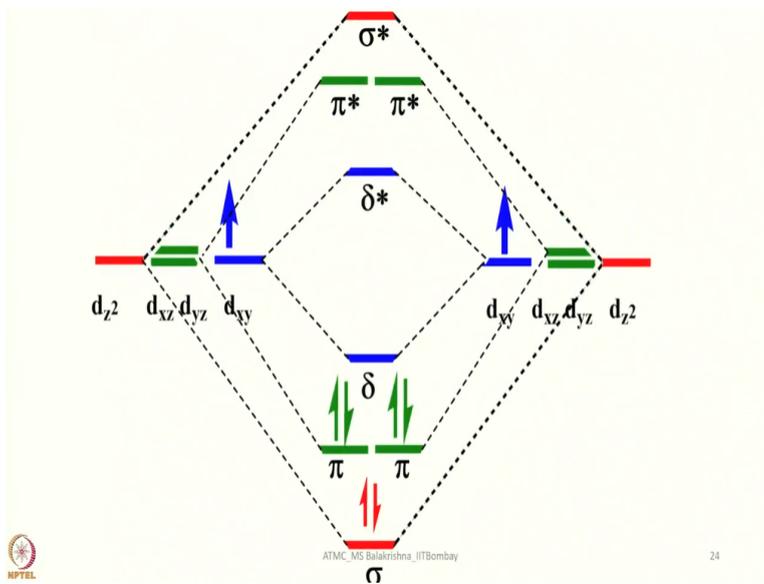




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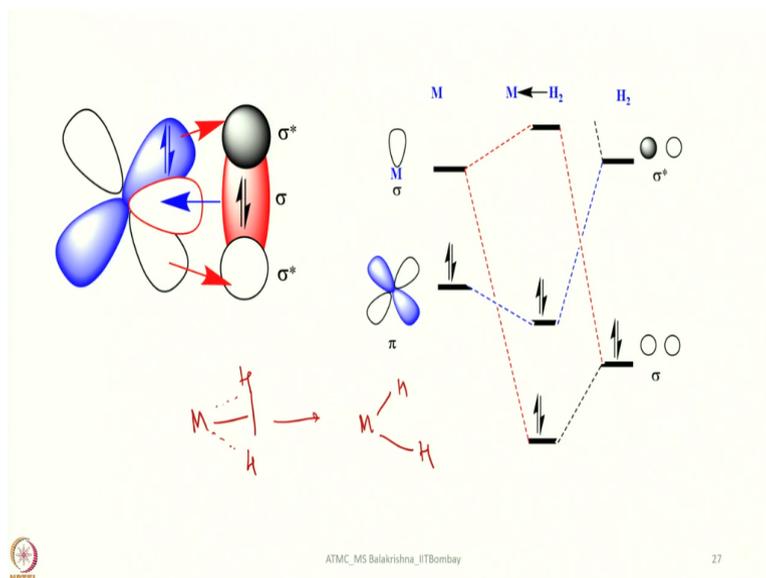


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Now, $d_{x^2-y^2}$ at an angle of 45 degree are degenerate, similar to dxz and dyz ; so, you can have here 10 electrons.

So, bond order is 5. So, this is how you can explain very nicely using MO diagram, quintuple bonding as well. I have given quite a few examples. Again go through it, and in case if there is a problem, always you can write to me.

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And this is important about hydrogen bonding to metal. In fact, it is very significant, H_2 , H-H bond is quite strong and it is endothermic; it is not easy to break. As I mentioned, if you take any unsaturated hydrocarbon and put high pressure hydrogen into it and in a closed vessel and if you try to heat it for several hours, even hydrogenation happens with very low conversion, about 5% or 6%.

But on the other hand, you add a metal complex; so, that can happen even at room temperatures. Why that happens? Because how very nicely it drifts the electrons present between H through sigma bonding and also it pushes its own electrons through back-bonding to sigma star. So, that means you are taking away bonded electrons and you are pushing electrons to the antibonding.

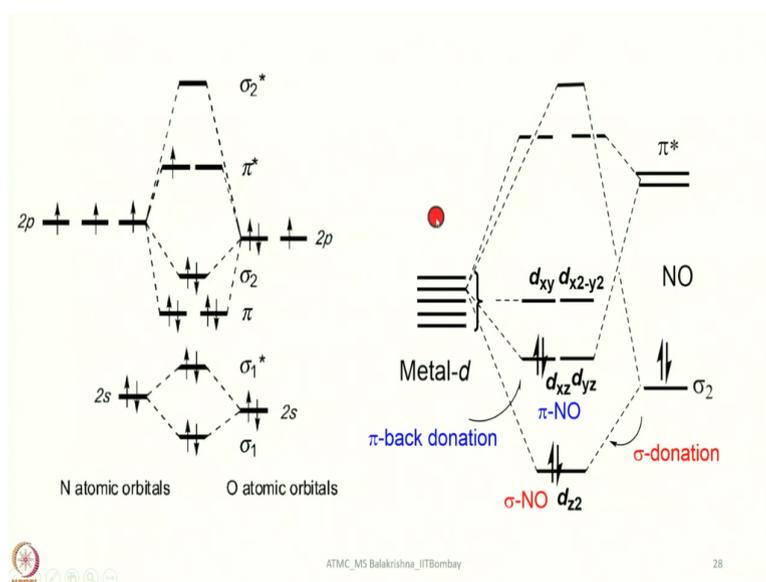
As a result, what happens, H-H bond becomes weaker. And then, earlier it is a **(Video Starts: 23:36)** η^1 bonding, it becomes, what happens, a very nicely it acts oxidatively to form 2 MH bonds. **(Video Ends: 23:42)** So, this is very significant. Because of this property, metal complexes have been extensively used in organic transformation in homogeneous catalysis.

So, whether it is a HS bond, whether it is a CH bond, whether it is a CC bond or any other heteroatom to hydrogen bond, they can do very conveniently.

As a result, we come across the application of these complexes in many organic transformations. Of course, still we have not succeeded or achieved to use in the industrial scale the CC bond breaking. For that one has to make very ideal compound, where metal is highly electron deficient and the ligands are of poor sigma donor and low coordination is there; in that case what happens, it should be ready to grab literally anything that comes on its way to expand its coordination number.

In this case, probably I would say, if you put octane, it can go very nicely and it can break into 2 butyl groups. If that happens with base metals such as iron, cobalt, nickel or something, one can make fortune out of it. So, there is enormous scope to activate CC bond using metal complexes, but with cleverly designed ligands.

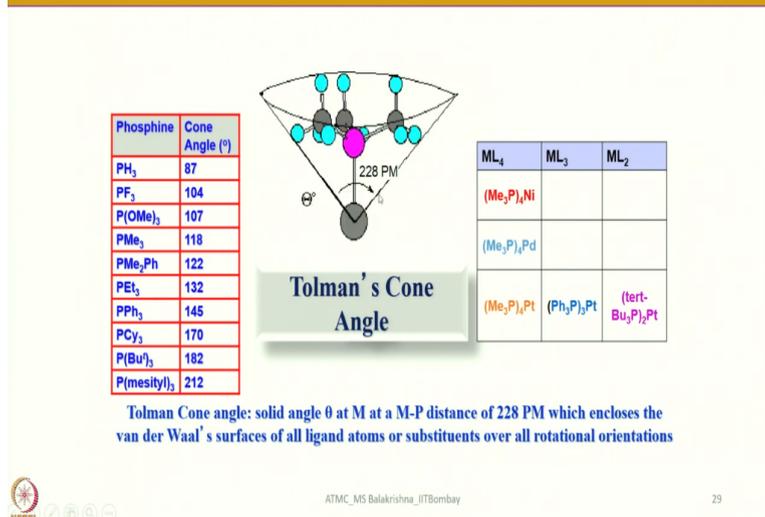
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And of course, here I showed you why NO^+ is stable, because if you once get rid of this 1 electron from pi star, it will be having bond order of 3; that is the reason it would be more stable. And also here I am showing you, once this electron is gone and now NO^+ is there, this can also behave very similar to other non-classical ligands and act as pi acceptor ligand. You can see here I have shown sigma donation as well as pi acceptor. So, NO can also be used as a pi acceptor ligand. And in some metal complexes, we can see these things.

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Steric attributes in Phosphines

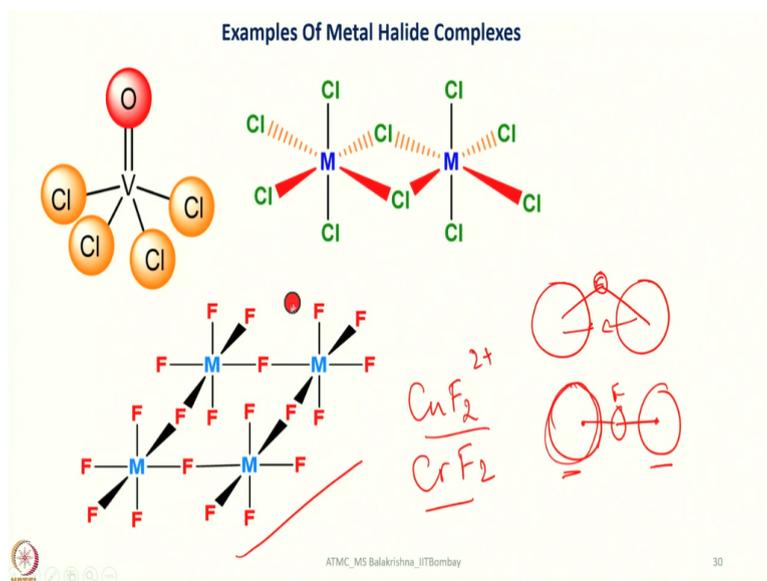


And when we talk about phosphines, I mentioned about electronic properties and steric properties are very important. The steric influence, the magnitude of steric influence can be measured using Tolman's cone angle. What happens here, you take the ligand, make a bond to the metal with a distance of, average distance of 2.28 angstrom units or 228 picometre. Now, imagine a conical surface at the metal that encloses the van der Waals surfaces of ligand substituents over all possible rotational orientations.

How this controls the steric attributes, you can see by looking into the cone angles shown by different ligands having different substituents. As bulkiness of the phosphorous substituents increases, cone angle increases. In that case what happens, you can have because of steric congestion, you can stabilise metal with fewer ligands. In that case what happens, we are automatically we are generating a low coordinated system having less electrons.

In that case what happens, these compounds are electron deficient and also coordinatively unsaturated. As a result, they can readily undergo oxidative addition. For example, if you take a compound here, phosphines, 4 phosphines are there in tetrahedral 18-electron system is there; the moment you put into solution, because of the steric condition, 2 ligands go out, so, dissociation would be very easy.

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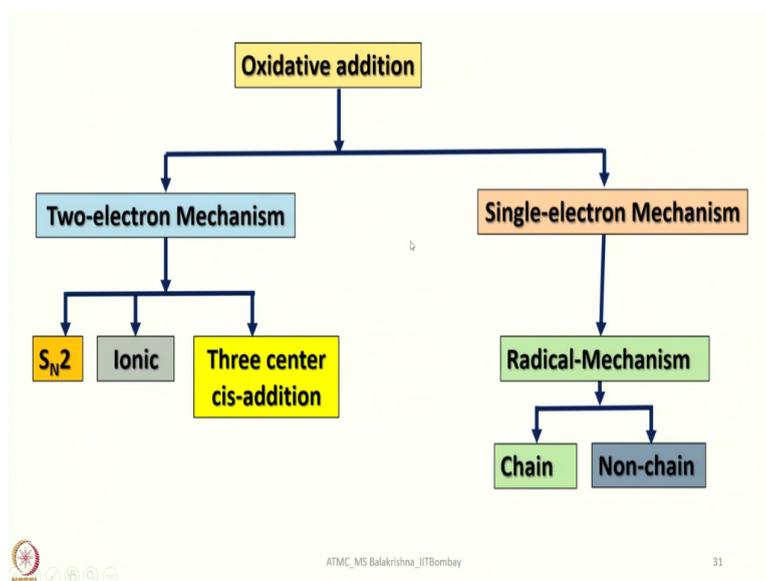


And now, let us look into the metal to halide bonds. Metal to halide bonds also I discussed in length about how certain metal complexes have tetrameric structure and some of them have dimeric structure. Taking aluminium itself, aluminium fluoride if you look into it, it has a tetrameric structure like this, whereas aluminium chloride has a dimeric structure like that AlCl_3 become Al_2Cl_6 .

Al_2Cl_6 , it is not aluminium oxide, it is a metal complex here, it is a transition metal complex; but nevertheless, the reason is the smaller size. When the smaller size is there, because of more electrons are there, fluoride assumes a bent structure when it is bridging to 2 metal centres; in the bent structure what happens, 2 cations come very close to it, they repel. As a result, what happens, they will try to have a linear geometry.

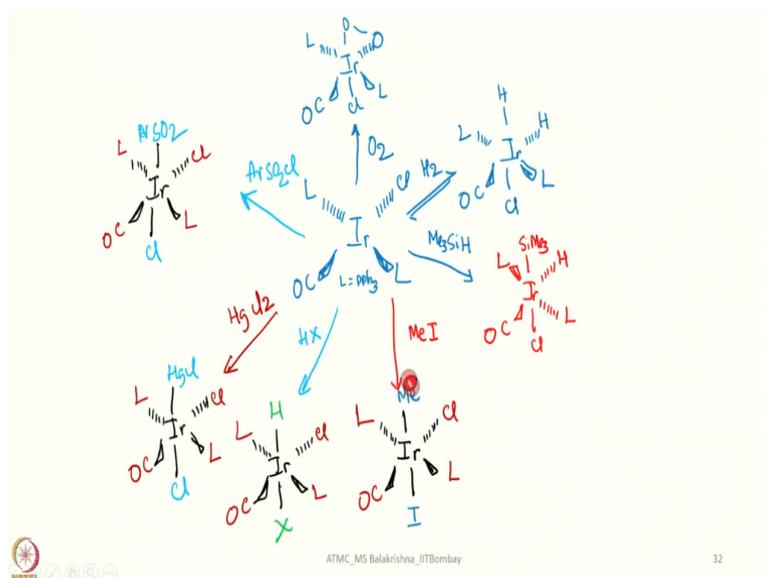
In that case, if you want to see association that has to be minimum of tetrameric or in some cases trimeric also we come across. The preferred one is tetrameric. And hence, if you look into CuF_2^{2+} or CrF_2^{2+} , although it looks like they have linear geometry, it is not linear geometry. The composition of copper to fluorine is 1:2 but they have octahedral geometry something like this.

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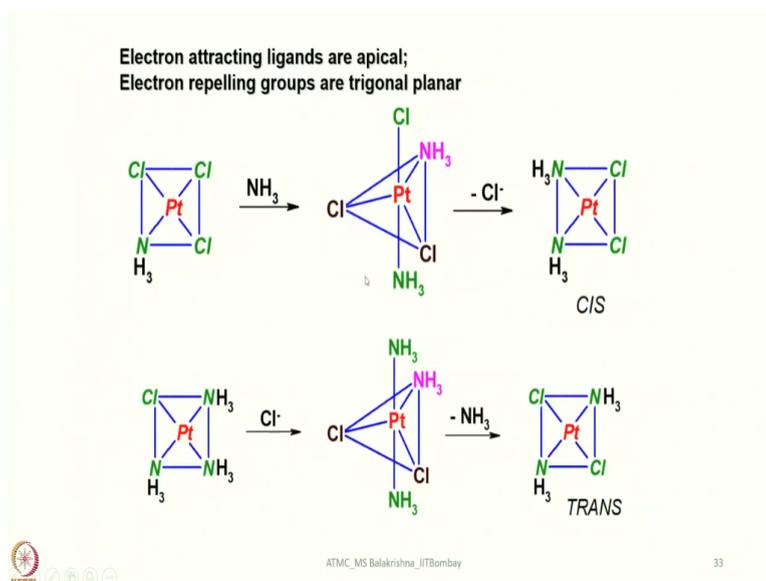
And then, oxidative addition is very important and I also discussed in length about different possible mechanisms. We have 3 bond concerted addition and nucleophilic substitution reactions are there and also radical mechanism also there.

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And also, I discussed all those things. And you can see, polar solvents are going to the trans-positions, whereas nonpolar bonds are going to the cis positions. So, we can see, clearly distinguish between concerted addition and also nucleophilic oxidative addition.

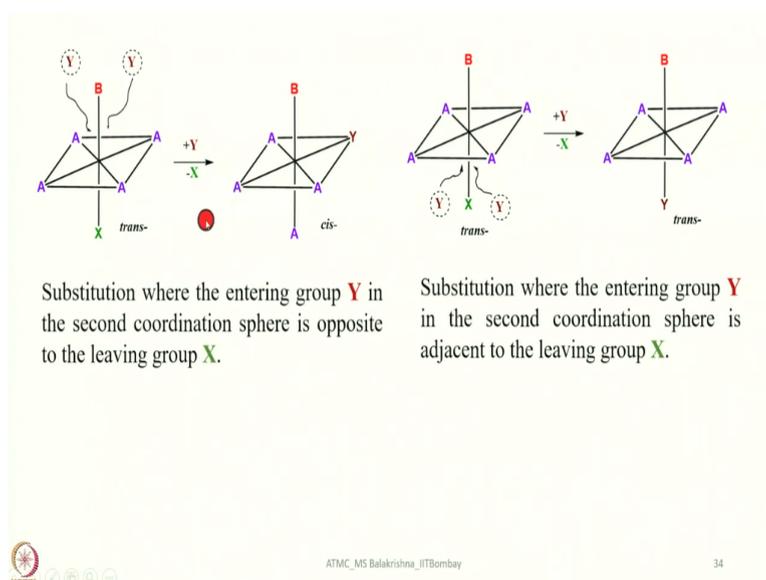
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And also, I discussed about steric chemical consequences also. And then, trans effect is very important when it comes to substitution reactions in square planar complexes. What one should remember is, in a given complex, electron attracting ligands are apical and electron repelling groups are trigonal planar. So, when the incoming ligand is there, a pair having trans influencing group and a group trans to it and the incoming plane will be trigonal planar and other 2 will be axial; and in this case, we have to identify which is electron attracting group and which is repelling group.

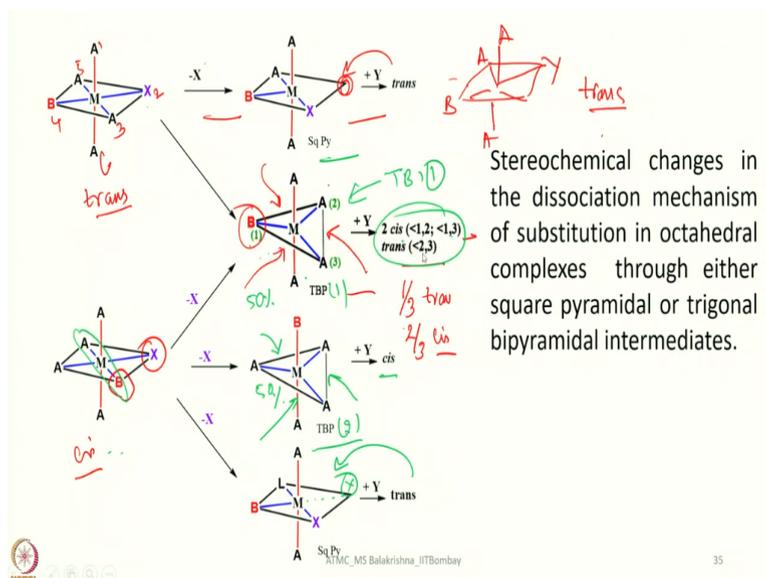
And accordingly, if you generate the intermediate, the moment you generate intermediate, you will come to know the confirmation, what kind of confirmation we are going to get at the end after substitution is completed.

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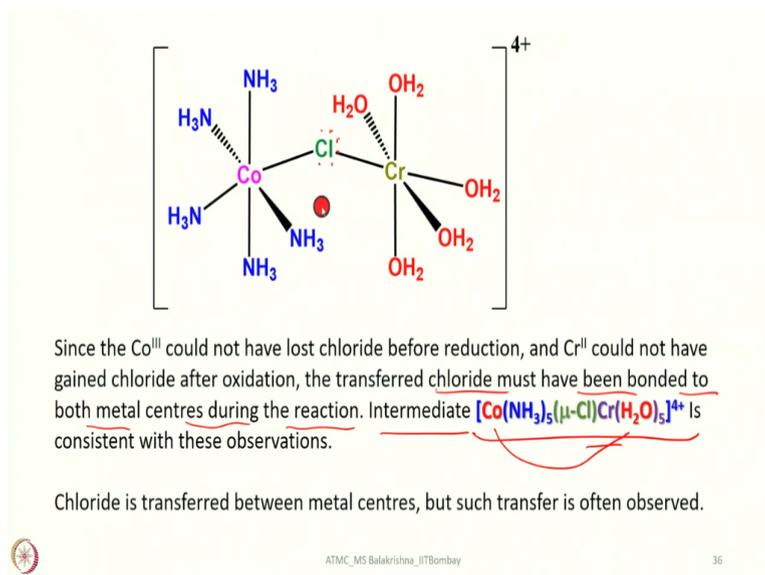
And of course, in case of octahedral complexes, I did mention about substitution, how it happens. Incoming ligands can come on the same side of the group or they can come on the opposite side. And accordingly, what happens, you can see how that influences the formation of cis isomer or trans isomer.

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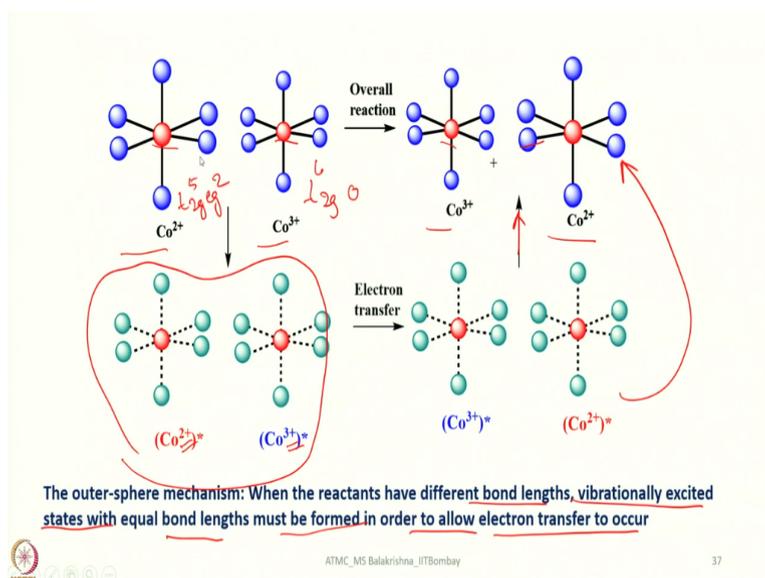
And also I discussed about stereochemical changes or stereochemical consequences in a substitution reaction and octahedral complexes.

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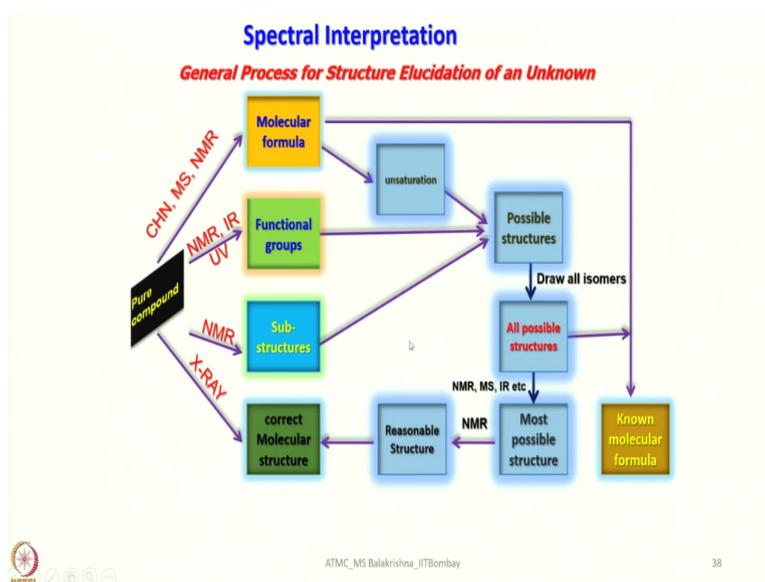
And when it comes to redox reactions, we have 2 types: inner sphere coordination and outer sphere coordination. And in case of inner sphere coordination theory, we need a bridging ligand and this is how the intermediate would be there. And you can see here, once electron-transfer is over, this also moves towards the other one or that is getting oxidised.

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And then of course, in an outer sphere mechanism, we have to keep Franck-Condon Principle in mind. And now you can see here, $t_{2g}e_g$ is there in this one, it is a high spin complex, where it is a low spin complex. Before electron is transferred, both of them should have an optimum bond length and bond angle, and now we can call it as intermediate stage where electrons can run smoothly so that this does not disobey Franck-Condon Principle. Once the electron-transfer takes place, they will revert back to different ones. So, this becomes high spin and this becomes low spin.

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And then spectral interpretation. I made an effort to make you familiar with UV-visible spectroscopy and also NMR spectroscopy, to an extent IR spectroscopy so that you can analyse those compounds, or if you come across some spectra, you should be able to

interpret. And the various methods and how we can arrive at the structure, all those things I have shown in this chart.

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Total Angular Momentum Quantum Number J
 The total **orbital angular momentum** of an atom ($L=2l$), and the total **spin angular momentum** of an atom ($S=2s+1$) combine to form total angular momentum, a number that is quantized by the number J . L and S do not necessarily have to be pointing in the same direction. Therefore J can range from $L+S$ to $|L-S|$.

Illustration of L-S coupling. Total angular momentum J is purple, orbital L is blue, and spin S is green.

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And of course, angular momentum quantum number and spin angular momentum, how they interact, I have shown here very nicely. LS coupling: LS coupling is also very important when we talk about UV-visible spectroscopy and also when we look into magnetic properties.

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d^0, d^{10} are usually colorless

d^1, d^4, d^6, d^9 } colored (They absorb in visible region)

d^2, d^3, d^7, d^8 }

d^5

HgI ₂	Brick Red	d^{10}
KMnO ₄	Intense Purple	d^0
BiI ₃	Orange Red	$d^{10}s^2$
KFe ^{III} Fe ^{II} (CN) ₆	Blue (prussian blue)	

ML + UV light → M⁺L⁻ (MLCT)

ML + UV light → M⁻L⁺ (LMCT)

Also, LLCT, MMCT

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And then of course, I classified all d-electronic configuration into 4 groups here. There is a significance why I have done like this here, you can see only charge transfer transitions. If the compounds are colour, it is because of charge transfer. In this one, ligand to metal; in this one, metal to ligand; and in these cases, we have 1 electron, 1 less than half-filled, 1 more than half-filled and 1 less than completely filled here.

In the same way, we have 2 electrons and 2 less than half-filled, 2 more than half-filled and 2 less than completely filled. So, these complexes show invariably 1 d-d transition; here they show invariably 3 d-d transitions, of course, d^5 is spin-forbidden and Laporte forbidden and compounds are weakly coloured or pale coloured compounds. And of course, all those things I discussed in depth.

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ΔE and Magnet Strength

Energy difference is proportional to the magnetic field strength.

$$\Delta E = h\nu = \frac{\gamma h}{2\pi} B_0$$

*Gyromagnetic ratio, γ , is a constant for each nucleus
(26,753 $s^{-1}gauss^{-1}$ for H).
A 60 MHz photon is required to flip a proton in a 14,092 gauss field.
Low energy, radio frequency.

*It is the ratio of its magnetic moment to its angular momentum

And this equation is very important when we talk about NMR. And using this equation, we can literally explain anything about NMR transition and other things.

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$\Delta S = 0$ UV visible spectroscopy
 $\Delta S = \pm 1$ NMR spectroscopy

Tyler Moore, 2011

And what one should remember is, if you look into spin selection rule, ΔS equals 0; so, that means basically an electron with upward spin should go like upward spin only, whereas

in case of NMR, it is plus or minus 1. The flipping of nuclear spin I mentioned. So, electron with upward spin should go to excited state, it will be having lower spin, alpha becomes beta or something like that. So, this is very important.

(Video Starts: 32:44) And you can see here in this diagram, precision results in the flipping. This is through radio frequency applied in a direction perpendicular to the magnetic field; you can see clearly here. So, you should remember these things. **(Video Ends: 32:56)**

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Magnetism

$$\mu_{s,o} = 2\sqrt{S(S+1)} \text{ BM}, S = \sum s, \frac{1}{2} \text{ for } 1 \text{ e}, 1 \text{ for } 2\text{e}, \frac{3}{2} \text{ for } 3\text{e} \dots$$

$$= \sqrt{n(n+2)} \text{ BM} \quad n = \text{no. of unpaired electrons}$$

$$\mu = \sqrt{L(L+1) + S(S+1)} \text{ BM}$$

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And then magnetism; I did not have time to discuss about magnetism. Of course, you can find these things in standard books, pretty easy. And we use 2 equations and of course, here we are using s is this summation of number of unpaired electrons here. For example, s, if 1 electron is there, s equals half; 2 electrons are s = 1; and then 3 electrons, 3 by 2, it goes like that.

Here, n is number of unpaired electrons; both are essentially same. And if we can also use this one where of course, you know already how to find out L as well as S.

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Magnetism

$$\mu = g\sqrt{S(S+1)}$$

μ = effective magnetic moment

$g = 2.0023$

$S = \frac{1}{2}$ for one electron, 1 for two e, 3/2 for three e.

g is sometime written as 2, spin only treatment is a decent approximation, but is not accurate even to two significant digits.

If the splitting of orbital energy levels is larger relative to kT (k = Boltzmann constant), then

$$\mu = g\sqrt{J(J+1)} \quad g = 1 + \frac{S(S+1) - L(L+1) + J(J+1)}{2J(J+1)}$$

$J = L+S$, usually used for the lanthanide and actinides



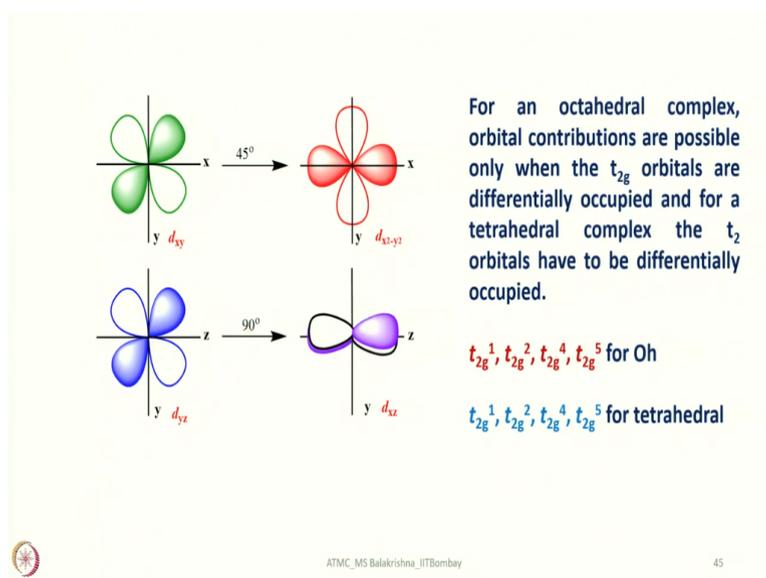
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Or in case of lanthanides and actinides, we have to find out g ; g is 2.0023. And if in some cases only whenever we come across spin only treatment, we can always consider g as 2. The splitting of orbital levels is larger relative to kT (k = Boltzmann constant). Then, one can use this equation here g into square root of $J(J + 1)$. g can be calculated provided we find out from electronic configuration what is S and what is L .

Of course J , one can also use value $L \pm S$ depending upon whether the orbital is less than half-filled or more than half-filled. If it is more than half-filled, we use $L + S$; if it is less than half-filled, we use the $L - S$.

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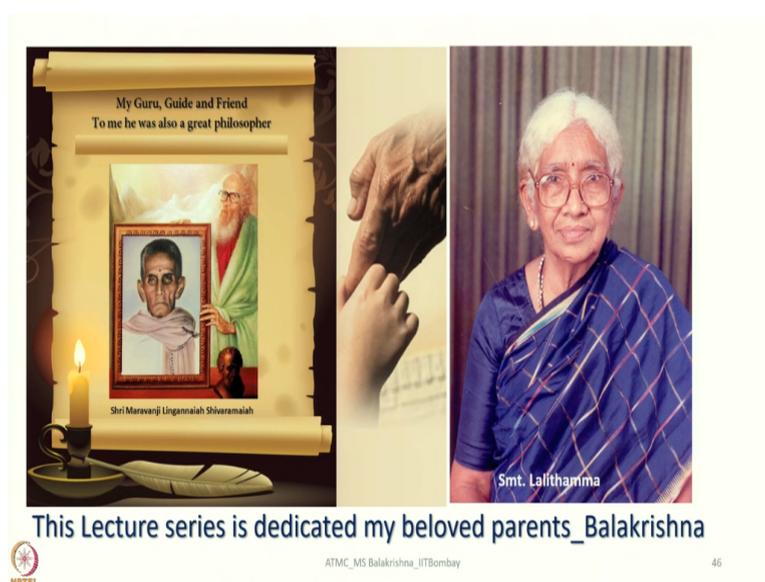
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Where we should consider orbital contribution? We have to see there should be differentially; especially t_{2g} orbitals in case of octahedral complexes and t_2 orbitals in case of tetrahedral

complexes should be differentially occupied. In that case what happens, you can see spin orbital contribution. The moment you look into the electronic configuration you should be able to make out whether spin orbital contribution is coming or not.

For example, in case of octahedral, t_{2g}^1 , t_{2g}^2 , t_{2g}^4 and t_{2g}^5 have unsymmetrical filling. In that case, you come across orbital contribution. And same thing is true in case of tetrahedral except of course here g should be removed because it does not have centre of symmetry. It should be t_2^1 , t_2^2 , t_2^4 and t_2^5 for tetrahedral complexes. And you can see here, with 45 degree rotation, d_{xy} can become $d_{x^2-y^2}$. And similarly, with 90 degree rotation, d_{yz} can become d_{xz} .

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So, at last, I dedicate this lecture series to my beloved parents, my father and my mother. 1 year before I submitted my thesis; my father passed away and 2 years back my mother passed away. And these people taught high ethics in me, and because of them what I am today. So, I dedicate this lecture series to my parents. And also you should remember, parents always work hard to make you better citizen and educated, and they sacrifice everything.

So, in that context, always try to remember parents. And of course, in some cases what happens, I have seen students; parents force their children to opt for a particular topic in which the student, a son or daughter is not interested. In that case what happens, you should try to convince them why you are interested in this one and why you are not interested in what they are imposing.

Certainly you can convince them and you can take a right path and achieve greater success. And I am sure I had conveyed some chemistry through this 60 lectures. And I have put lot of effort; you should remember, lot of effort I have put in generating some of the slides to convincingly teach some chemistry. And when you understand the chemistry behind these 60 lectures and pass exams with good grades, and if you at the end if you think that yes, I got something out of this course, I will be very happy.

And in case if you have any problem, you can always write to me. And later when you achieve higher success and in case if you think that this course has contributed to your improvement, your knowledge, and when you achieve greater success and achieve something and make a mark, and if you just send me a mail, I will be the happiest person, and that brings millions worth happiness to me.

So, with this, I wish you all very best and God bless you all. Enjoy chemistry, thank you so much. Learning never stops. Even now I am learning; I can say without any hesitation, I am a good student of learning, underline good student of learning, because I do not claim anytime that I am a teacher because I have to learn a lot even now. And that means, no matter what you do, learning should never stop. So, learning should continue so that we can have more and more knowledge. And when we have enough knowledge, it is our sincere duty to dissipate it to others. Thank you once again.