Basics in Inorganic Chemistry
Prof. Debabrata Maiti
Department of Chemistry
Indian Institute of Technology, Bombay

Lecture - 10
Crystal Field Theory: Octahedral vs. Tetrahedral complex

We have seen the octahedral complexes; we have seen the tetrahedral complexes. These are the two most important classes of compounds that are present over the let us say whatever chemistry known so far. There are other complexes as you have seen it could be you know penta coordinated.

The metal complex can be penta coordinated, two different types of geometry is possible for penta coordination. Out of that trigonal bipyramidal is one of the preferred geometry. So, there are lot of things that we can definitely go on and discuss about it, but it is literally impossible to discuss each and every structure in detail.

Each and every metal complex kind of different geometry in detail and how they are know ligand field will affect the d orbital splitting. So, geometry changes d orbital splitting pattern changes, I think just by learning octahedral and tetrahedral you have got that sense.

Now, it has all to do with the way the ligand is approaching, sometime ligand is approaching directly towards the atomic orbital of the of each of those metal or d orbital of the metals and thereby you can see the extent to which it gets stabilized or destabilize is deferring, right.

So, if you take technically speaking, if you take a trigonal bi-pyramidal perhaps you would be able to at least understand why the splitting in such that, ok. In the syllabus we for you guys we do not have any other geometry to discuss octahedral and tetrahedral, if possible you can look at a little bit at trigonal bi-pyramidal; TBP, ok.

Now, square pyramidal or square planner in something which will come soon. Square planner is basically nothing, but octahedral geometry you are having you take out 2 z axis; you have octahedral scenario you take out 2 z axis that is becomes square planner. So, we will discuss that.

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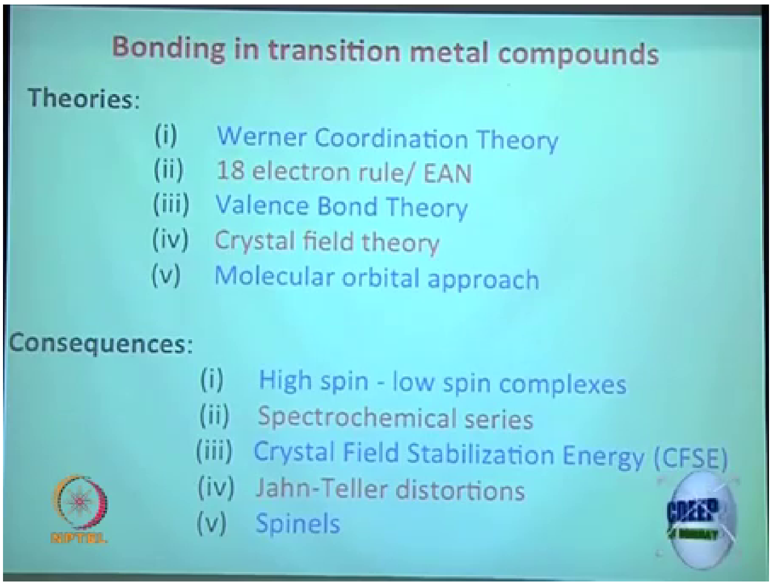

Bonding in transition metal compounds

Theories:

(i) Werner Coordination Theory
(ii) 18 electron rule/ EAN
(iii) Valence Bond Theory
(iv) Crystal field theory
(v) Molecular orbital approach

Consequences:

(i) High spin - low spin complexes
(ii) Spectrochemical series
(iii) Crystal Field Stabilization Energy (CFSE)
(iv) Jahn-Teller distortions
(v) Spinels

So, in the last class once again we were discussing Werner coordination theory, 18 electron rule, valence bond theory and how good it is and then how bad it is and how good the crystal field theory is. Really we will stop there how good the crystal field theory is and not too much we will get into the MO approach Molecular Orbital approach, ok.

There are I mean no end to learning, I think for this course purpose we will stop in there not too much afterwards, ok. So, the major objective for this syllabus or for this chapter and the next chapter is definitely giving you an idea about these high spin - low spin complexes, the spectrochemical series. I hope you have come across this term in the last class crystal field stabilization energy, Jahn-Teller distortion and spindle these are the last two topics we will discuss today. I will briefly give you an overview what we have discussed in the last class.

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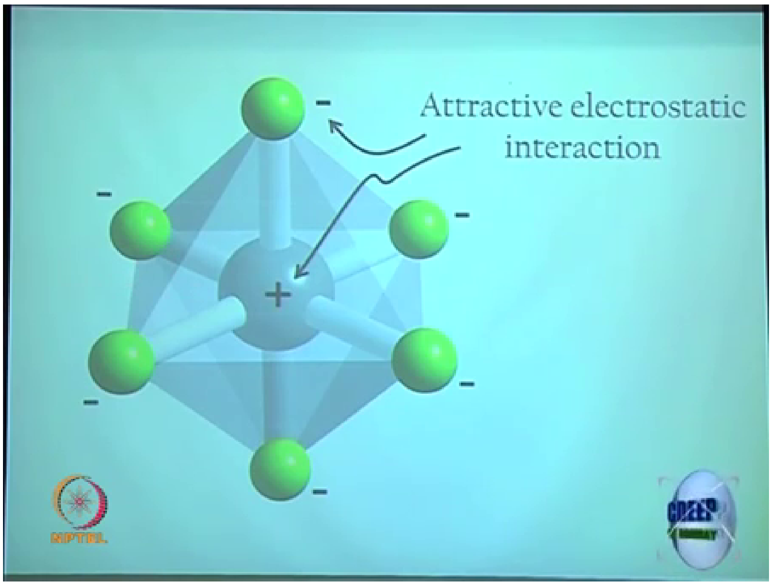

So, this is an octahedral complex, metal center is they are at the middle of it. So, that is at the center of the geometry it is a metal center. Metal and ligand are almost having electrostatic interaction. It is a positive charge and negative charge are the ligand which are interacting with the metal center.

Remember in the valence bond theory we were mainly assuming it is a covalent structure, ok. As you see this is axial position that is also axial position, this is the direction where d z 2 orbital is d z square or d z 2. Now, these are the direction, these 4; 1, 2, 3, 4. These 4 are the ones where we have d x 2 d y 2 orbital directly, it is not indirect this is where is actually dx 2 y 2.

So, therefore, from this you can understand why d z 2 and d x 2 y 2 orbital is most destabilized for octahedral geometry. Because, they are the one which facing the music basically they are now one of which is getting repelled most, because ligand electrons and the d orbital electrons are repelling each other, very simple.

Now, all other orbitals d xy, d yz, d xz they are not facing these ligands directly, they are in between somewhere here, here, here, here so, in between. So, they are by they are not going to get rippled too much; they are going to get rippled, but not too much, ok. Relative to dx 2 y 2 and d z 2 they are going to stabilize, ok.

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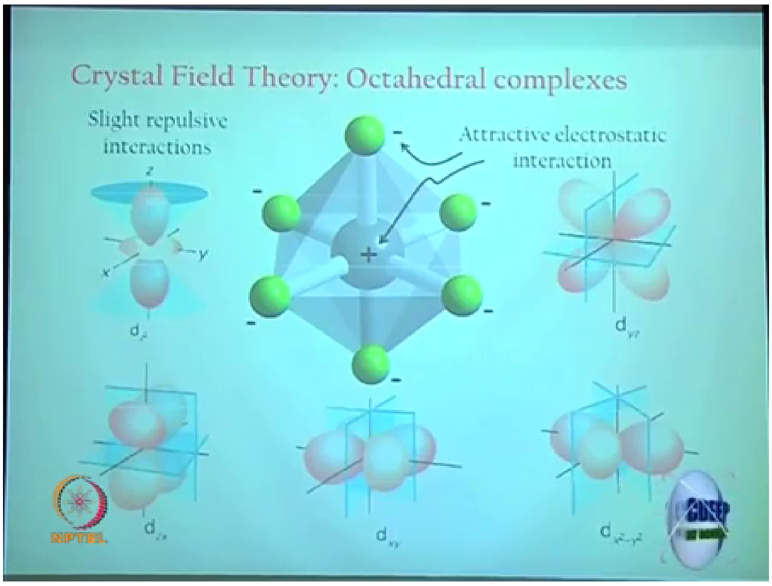

Crystal Field Theory: Octahedral complexes

Slight repulsive interactions

Attractive electrostatic interaction

So, just a quick look at the orbitals what we have discussed in the last class d z 2 orbital d x 2 y 2 orbital, ok. Now, these are the other orbitals with respect to these three other orbitals you can see where the ligands are. Therefore, you can understand the stabilization or the destabilization of this, ok.

Student: (Refer Time: 06:15).

That is a good question. Usually, that is where we will come to Jahn-Tellar distortion ok, that I guess that that you will be able to clearly understand when we are discussing the Jahn-Teller distortion. That is the actually the origin of the Jahn-Teller distortion and z elongation and z in, ok; we will come back.

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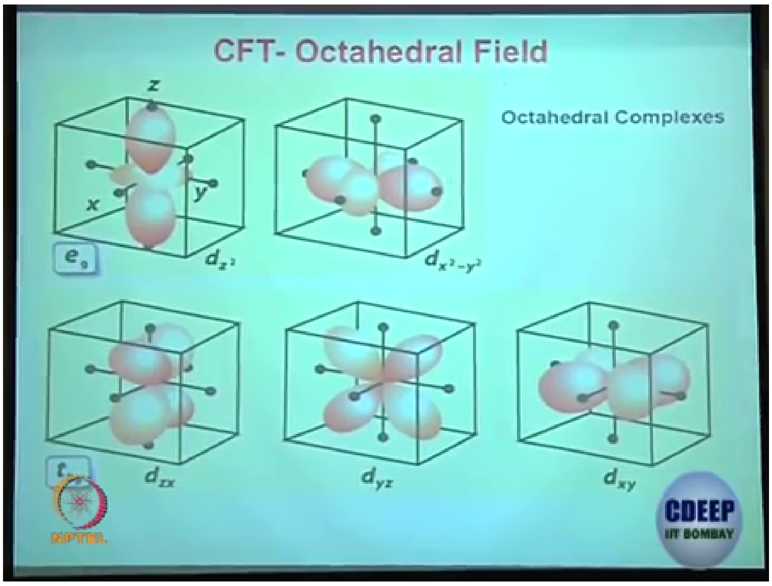

CFT- Octahedral Field

Octahedral Complexes

Now, this is the same thing in a different bottle, I think whatever splits you. You just look at it, it gives you a very clear idea. These are the ligands the black balls are the ligands and the metal orbitals or d orbitals are shown in here clearly ok, no confusion, right.

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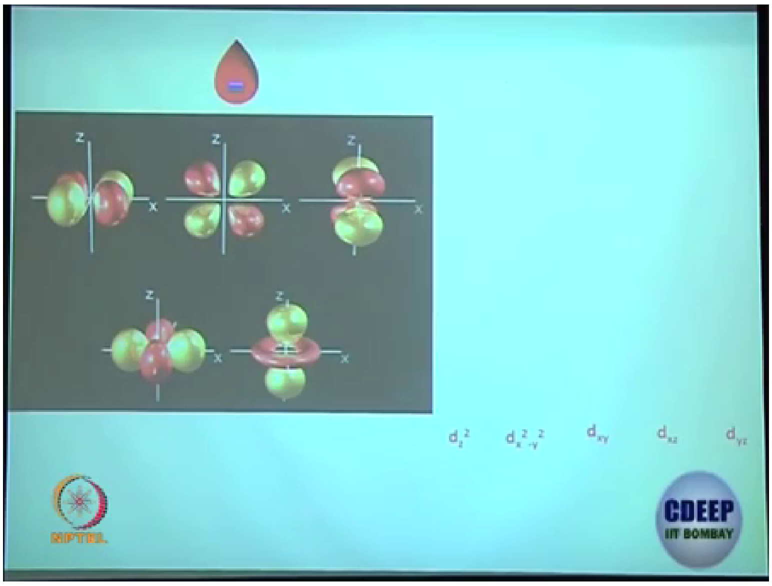

Now, as you are showing in the last class. So, these are d orbitals and this is let us say ligand electrons; ligand electrons are coming for this orbitals to overlap, right.

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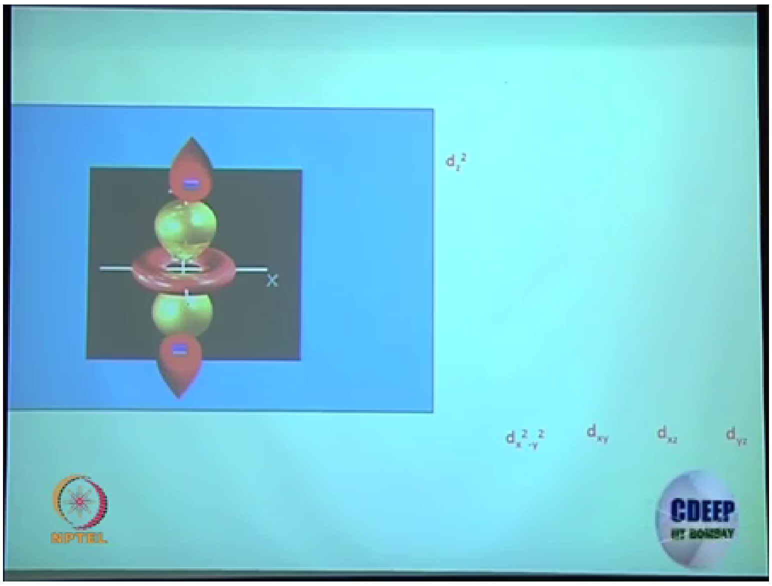

d_{z^2}

$d_{x^2-y^2}$ d_{xy} d_{xz} d_{yz}

Now, first instance we will discuss the d z 2 interaction with the ligand. Ligand electrons comes they will be rippling each other therefore, d z 2 will be destabilized; d z 2 is facing the ligand once again directly.

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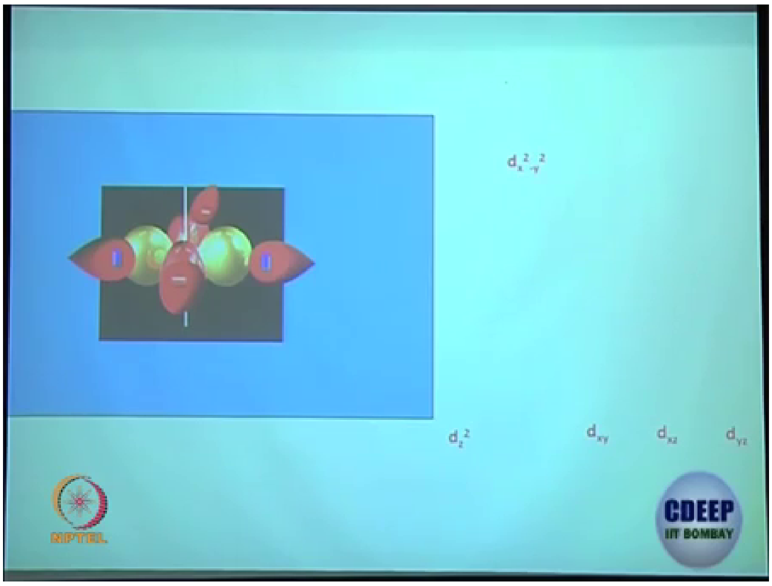

This is the d x 2 y 2 1 ok, now here you see that the 4 ligands are coming along all these axis to answer to the previous question. One of the way you can see is these are 4 lobes; 4 lobes divided by 4 ligand and 2 lobes divided by 2 ligands kind of that is how perhaps it is you know you do not have to worry usually. But, finer details when it is unsymmetrically filled right d z 2 and d x 2, although they are of same energy, but if they are unsymmetrically filled. Let us say 1 is there in the e g orbital or 3 is there in the e g orbital then the problem comes, ok.

Now so, you have seen the you have seen how they are coming and they are by they are also getting these orbitals are getting destabilized, ok.

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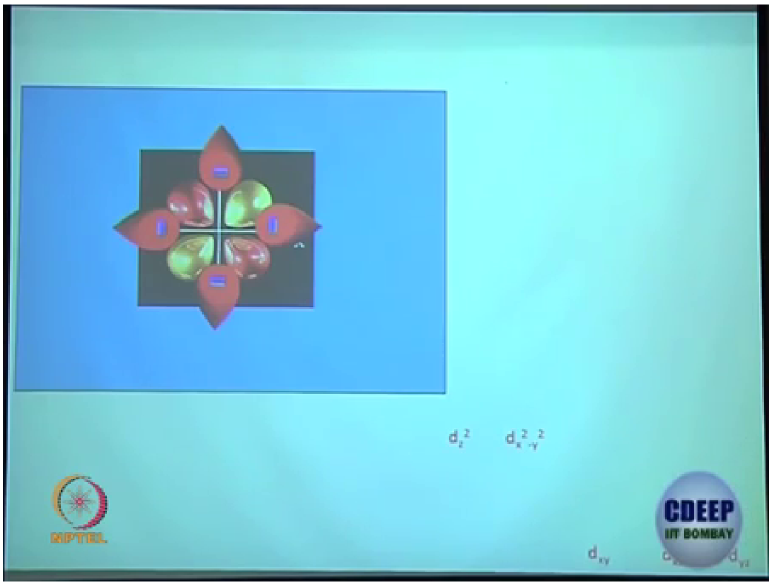

All other d orbital like these three are like d xy, d xz and d yz they are really not facing the orbitals directly as you can see they are sitting right in between and they are why you can see so, for example, over here we have shown d xz same is true for d xy and d yz.

Thereby these orbitals are relatively mind you relatively stabilized with respect to d z 2 and d x 2 y 2. If you compare the free metal ion with respect to free metal ion everything is destabilized, because free metal ion has no ligand there by no repulsion. The moment ligand comes repulsion starts; so, the systems energy goes up, ok.

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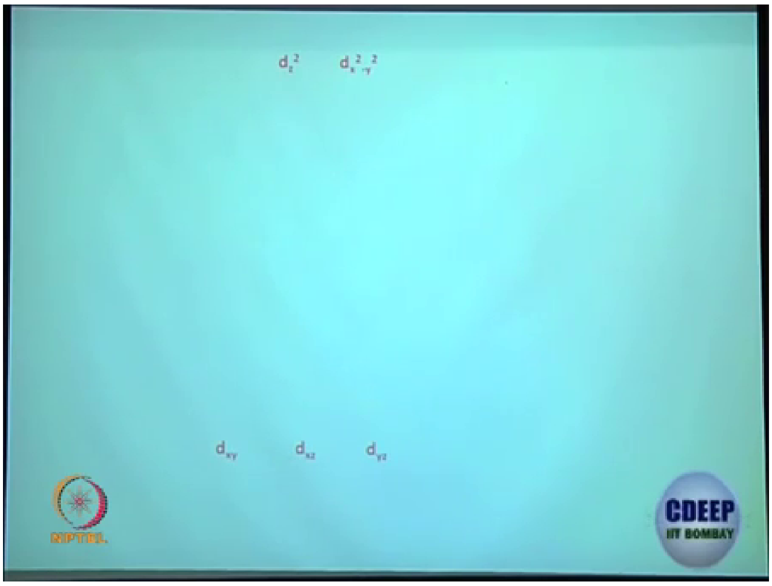

Now, overall therefore, you have two up three down ok, but net stabilization with respect to that barycenter the center in the middle. The net stabilization or destabilization for a completely filled d orbital let us say d 10 or d 5 in a high spin situation which we have discussed should be the 0 stabilization. If it is completely filled total stabilization and total destabilization has to be the same, ok.

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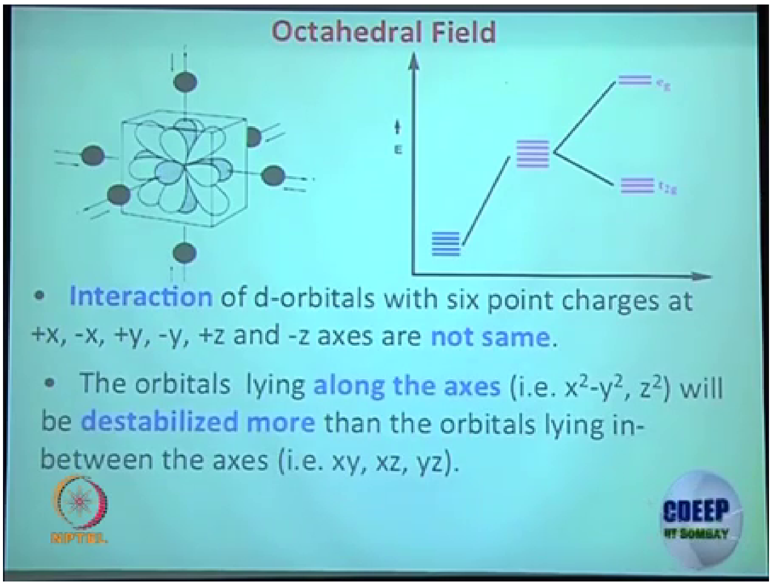

Octahedral Field

- **Interaction** of d-orbitals with six point charges at +x, -x, +y, -y, +z and -z axes are **not same**.
- The orbitals lying **along the axes** (i.e. x^2-y^2, z^2) will be **destabilized more** than the orbitals lying in-between the axes (i.e. xy, xz, yz).

Now, this is where again once again this is kind of a clear picture this is the octahedral field, we were showing 6 ligands coming at these box. So, if you are assuming that this is a box, 6 ligands are facing the way it is shown 1, 2, 3, 4, 5, 6. Now, this is the free metal ion this is the metal complex, 3 of the t 2 g got stabilized, 2 of the eg got destabilized, ok. Now, this is e g not e, e will be for tetrahedral; t 2 g not t 2, ok. Now, of course, I think I have discussed these information already.

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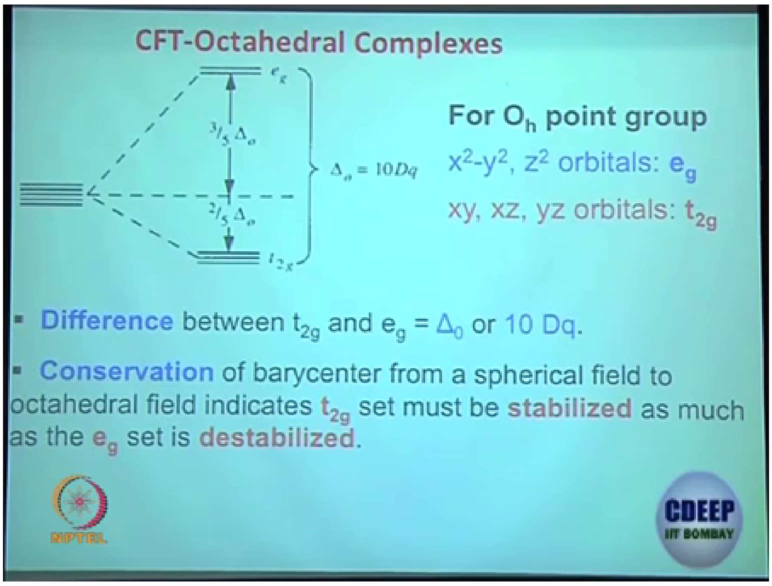

CFT-Octahedral Complexes

For O_h point group

x^2-y^2, z^2 orbitals: e_g

xy, xz, yz orbitals: t_{2g}

- **Difference** between t_{2g} and e_g = Δ_0 or 10 Dq.
- **Conservation** of barycenter from a spherical field to octahedral field indicates t_{2g} set must be **stabilized** as much as the e_g set is **destabilized**.

Now, since this is 3 of them, this is 2 of them this distance between this barycentre and the steb stabilization for t 2 g.

Student: Sir, ligand maybe different. So, this not effect to the (Refer Time: 11:05).

Ligand may be different. Here, we are thinking say we have to ideal deal with the idealistic world at the beginning ml 6 ligands are same ml 6. We are not thinking like 3 of the chloride, 3 of the fluoride that is a mixed situation, ok. For just to this of course, those situation comes often comes, but this is if we do not understand I mean very simple situation how can we go complex, ok.

So, of course, let us say if you have 3 chloride and 3 cyanide what will be the situation right, that is a special you know topic on this how finer details, you will can get in the d orbital splitting. Initially, it may split and then they may further split. If you have all of them let us say weak field like 3 fluoride and let us say 3 chloride they may be having, they have been same, but the moment you have one weak field one strong field ligand things will be a little bit complicated, ok.

So, overall how much ligand I think overall you have to see whether it is a strong field ligand or weak field ligand, whether it is a first point whether it is a octahedral geometry or tetrahedral geometry and they are by go for it. For the exam purpose for this course, I do not think we will be tricking into anything which is mixed little bit more complicated than that.

For exam purpose or for this course purpose you have to just know octahedral field splitting and tetrahedral, and we will be discussing briefly about the square planner because that is kind of comes automatically. Furthermore, if you want to learn maximum go to trigonal bi pyramidal we will give those split it. But, you know as again it is a more complex than we would like to think, we are just dealing idealistically; that is a good question.

So, over here we see that the stabilization should be 0.4, 2 by 5 delta 0; 0.4 delta 0 this destabilization would be 0.6 delta 0. We have discussed it or 4 Dq, 6 Dq if it is delta 0 or 10 Dq, we have discussed, right.

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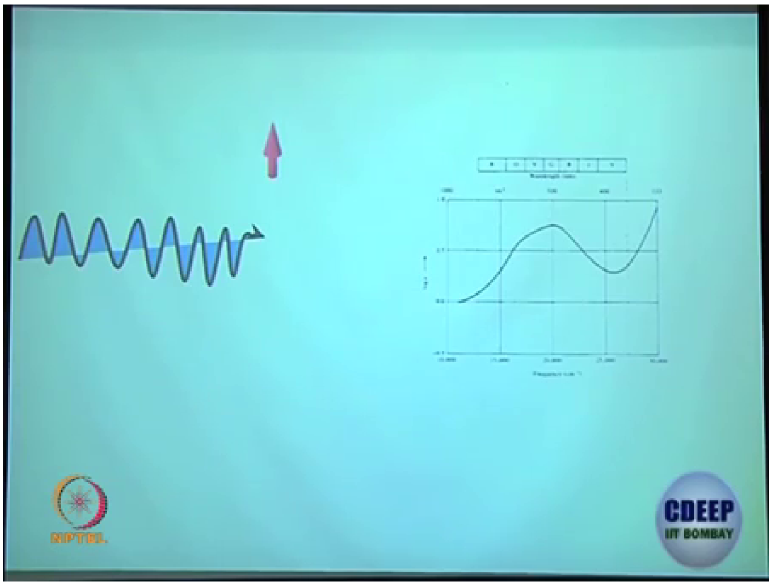

Now, the first advantage of this a crystal field theory is you can explain the magnetic properties, you can expect to explain the you know spectro spectroscopic behavior; let us say you will be studying why certain peaks are coming. So, this is where I we were telling that if you have a unpaired electron, if you are moving from t 2 g to e g the spectra you get will be something like this absorption maximum.

Of course, we are not getting into finer details of the spectra, but this is the major origin where from electrons are moving and where it is going. So, from t 2 g this is a d 1 electronic configuration, 1 electron is there. So, t 2 g 1 ; that means, over here t 2 g 1; 1 electron was over here you all these three orbitals are degenerate same energy only way it can go is up to here. Now, if you think, if e g is splitted further these 2 orbitals are dx 2 y 2 and d z 2.

If it in splitted further so, the electron can go to 2 different levels right. Therefore, you can expect 2 different peaks, whether intensity will be high or low that is of course, then you have to think about the symmetry and lot of other things which will not be discussing. But, you can sense where the spectra is coming from and where the electron is you know moving from; I mean, which orbital to where it is going. So, this is fine.

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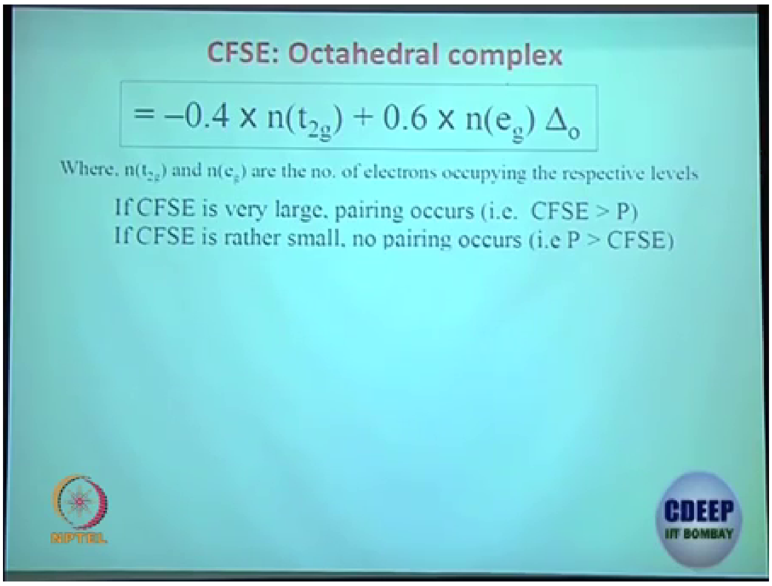

CFSE: Octahedral complex

$$= -0.4 \times n(t_{2g}) + 0.6 \times n(e_g)\, \Delta_o$$

Where, $n(t_{2g})$ and $n(e_g)$ are the no. of electrons occupying the respective levels

If CFSE is very large, pairing occurs (i.e. CFSE > P)
If CFSE is rather small, no pairing occurs (i.e P > CFSE)

So, you get the spectra, now we have also seen crystal field stabilization energy. So, you calculate you are given I think you have to really master this you should be able to do it in your dream, ok. D 3 electronic configuration, what is the crystal field stabilization energy if octahedral? D 5, what is if it is octahedral how many scenarios are there, 2 scenarios; how high spin and low spin, right. So, what will be the crystal field stabilization energy?

Any question in specially in exam if you see before even thinking too much I would say just imagine the scenario. Only three scenarios you have octahedral 2 scenario, high-spin low spin and tetrahedral only high spin scenario, 99 percent case. We will discuss one case today which is otherwise, but that is it octahedral 2 scenario and tetrahedral 1 scenario done.

So, once you have that I think the answer should come out almost like why something is preferred, why something is not preferred. At least I would say out of 25 mark question, 5 marks to 7 marks will be based on that indirectly; I mean of course, it will not be given perhaps on a platter definitely will be able to figure out better.

So, please do familiar you should not be fearing about calculating an electronic configuration should be always correct, there should not be any mistaken, ok.

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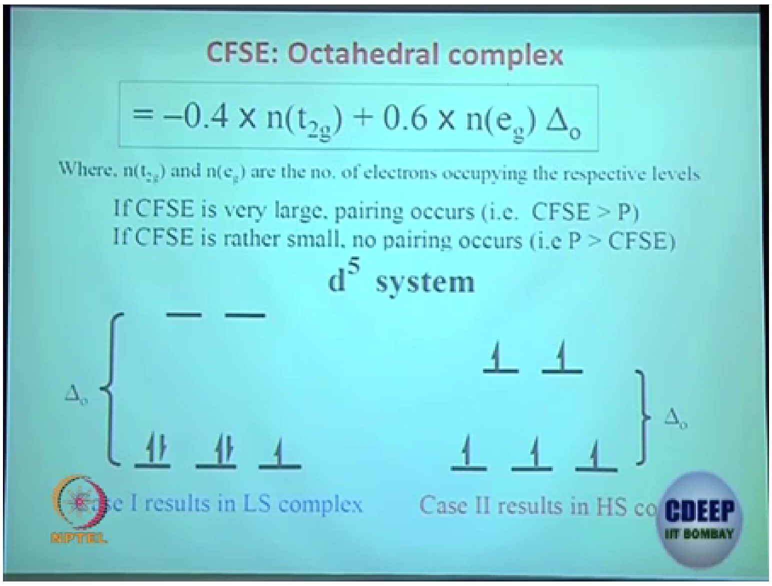

CFSE: Octahedral complex

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If CFSE is very large, pairing occurs (i.e. CFSE > P)
If CFSE is rather small, no pairing occurs (i.e P > CFSE)

d^5 system

se I results in LS complex

Case II results in HS co

Now, should be 5 system for example, one case we were giving. So, this is the d 5 high spin; that means, 3 stabilization 2 destabilization CFSE should be 0, right that is what I was trying to say. So, net stabilization and destabilization should be 0, if it in symmetrically field, ok. So, this is 0 you do not have to even calculate, if it is d 10 it is again 0, d 10 means all of them are full. So, stabilization is equals to destabilization.

So, that is where let us say you are given d 7 and this is the configuration 5, 6, 7. So, 5 take out 5 because 5 3 plus 2 had stabilized destabilized and cancelled each other out. Now, you just deal with 2; 2 will be d 7 2 will be over here and here right. So, that will be minus 8 Dq or 0.8 delta 0 or delta octahedral.

You should be able to do it really quick without calculating and going through the simple math. Now, of course, d 7 you can have also high spin and low spin configuration for example, this one what would be the CFSE, minus.

Student: (Refer Time: 18:06).

So, of course, minus that is out of question it stabilization each of them are 0.4. So, 5 of them 20 minus 20 or minus 2 sorry minus 2 delta 0 ok, that is it; delta 0 means delta octahedral delta o I mean different people pronounce it different way, ok. So, this is it I mean if you do it really simply I am sure 5 to 7 mark question will be there; I mean, invariably whatever it is the question is based on that, it is going to be based on that.

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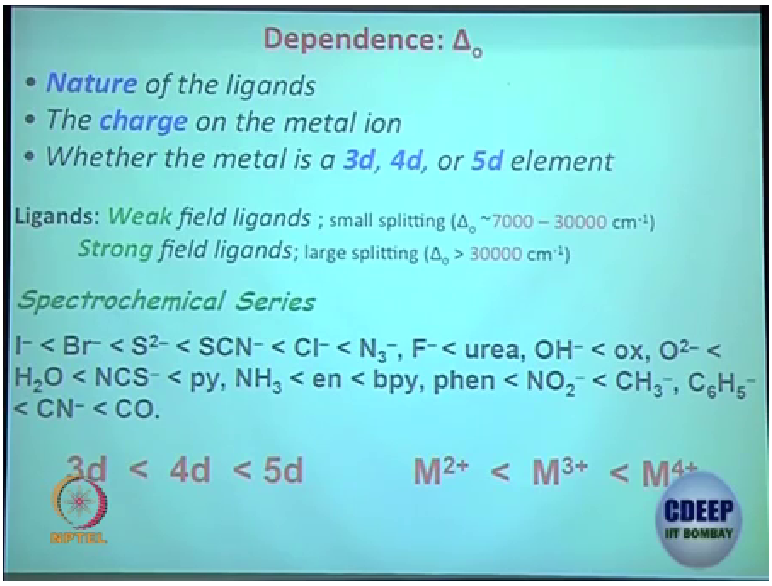

Dependence: Δ_o

- *Nature of the ligands*
- *The charge on the metal ion*
- *Whether the metal is a 3d, 4d, or 5d element*

Ligands: *Weak field ligands* ; small splitting (Δ_o ~7000 – 30000 cm^{-1})
Strong field ligands; large splitting (Δ_o > 30000 cm^{-1})

Spectrochemical Series

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^-$, $F^- <$ urea, $OH^- <$ ox, $O^{2-} < H_2O < NCS^- <$ py, $NH_3 <$ en $<$ bpy, phen $< NO_2^- < CH_3^-$, $C_6H_5^- < CN^- < CO$.

3d < 4d < 5d

$M^{2+} < M^{3+} < M^{4+}$

Now, of course, we have discussed it once again two scenarios high spin, because the spin is maximum high spin, low spin means spin is minimum you see one unpaired spin. Now, if you look at the, I will come back to the magnetic behavior; magnetic behavior is nothing, but due to the unpaired electron, right.

So, the moment you have unpaired electrons magnetic behavior comes, because the parallel spin will cancel each other you want to spin on that direction and I want to spin on this direction. So, it will be cancel out, cancelling. So, this is the one will have low magnetic value magnetic moment value, this is the one will have high magnetic value, this is the origin for molecular magnet; a lot of molecules are magnet ok.

And, these are the ones you see the application almost everywhere literally everywhere, you take any electronic gadgets you take almost anything which is electronic in nature, which had some fancy application. It is the material, it is the material which are having magnetic properties and that is why they are used how expensive, it is based on that you know you will get your material. Of course, in lot of other cases you see the use of these things I will show 1 or 2 case today, ok.

So, dependence of delta 0 like how much splitting is going on that depends on the nature of the ligands as I was trying to tell you whether it is a weak field ligand or strong field ligand. Strong field means the splitting will be very high, weak field means the splitting between t 2 g and e g will be small.

And therefore, for weak field ones we will always see high spin means spin will not be pairing up, ok. And the charge on the metal of course, if it is a high higher charge you will have higher separation, if it is 5 d you will have higher separation compared to 3 d, right.

So, this is the spectro electro chemical series with respect to different ligands, these are the stronger one stronger ligands. These will these are the one which almost always will give you the low spin; sorry, high which one low spin complex because the splitting will be high, strong field ligand splitting will be high. So, the spin pairing will happen it cannot go from t 2 g to e g, ok.

These are the one which have likely to give you low spin complexes is it getting clear. If it is you are getting; I mean, some time it is little bit confusing, it is either yes or no type of answer question. I mean the understanding is either yes or no high spin or low spin, right. So, just get it clear.

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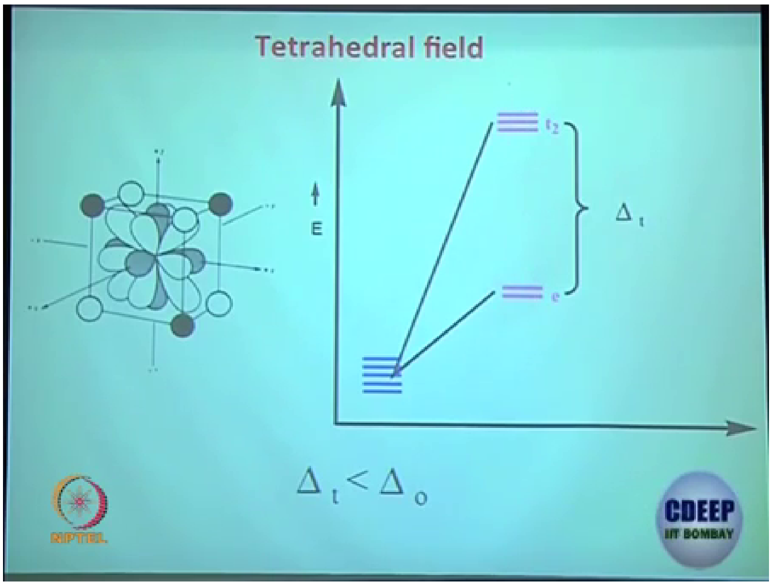

Tetrahedral field

$\Delta_t < \Delta_o$

Now, this is the trend we have shown for tetrahedral case we were dealing with a completely different scenario which can be clearer from this picture. If you remember the previous picture for octahedral case which was nothing, but direct confrontation. Here it is like more of a political approach you know diplomatic approach you do not go direct you just talk with.

So, they are talking, they are not directly confronting, they are by the scenarios are completely different since it is not interacting directly overlapping directly with let us say those e g orbitals. Previously, we have seen for octahedral cases d x 2 y 2 and d z 2.

D z 2 is over here actually and see the ligand where it is; ligand is here, d z 2 is here actually those orbitals are the once those e g, orbital for octahedral case are the ones which are farthest from the ligand which are farthest and thereby they are the one which will get stabilized. The other 3 orbitals d xy, d yz, d xz those are the ones which are nearer not directly overlapping, but closure and they are by they are destabilized, ok.

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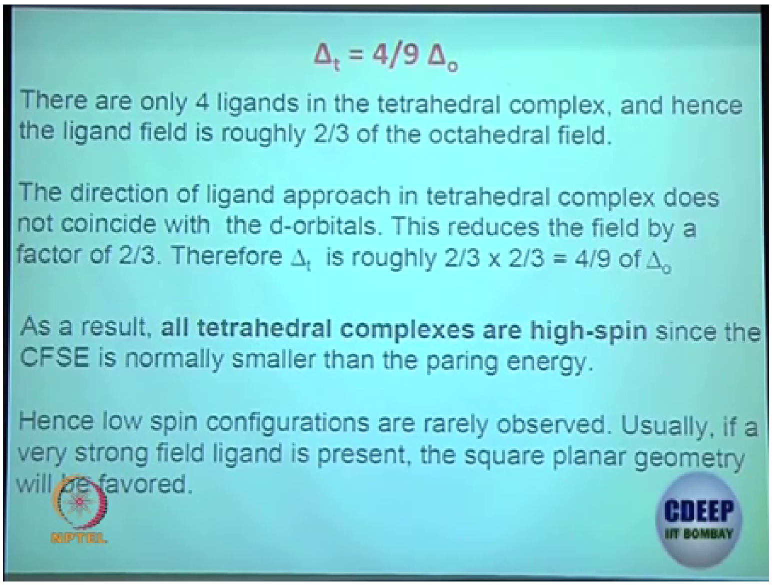

$\Delta_t = 4/9\ \Delta_o$

There are only 4 ligands in the tetrahedral complex, and hence the ligand field is roughly 2/3 of the octahedral field.

The direction of ligand approach in tetrahedral complex does not coincide with the d-orbitals. This reduces the field by a factor of 2/3. Therefore Δ_t is roughly 2/3 x 2/3 = 4/9 of Δ_o

As a result, **all tetrahedral complexes are high-spin** since the CFSE is normally smaller than the paring energy.

Hence low spin configurations are rarely observed. Usually, if a very strong field ligand is present, the square planar geometry will be favored.

Now, this difference is called delta t, and this delta t is going to be four-ninth of the delta o or delta 0. Two-third coming from the number of ligands 6 to 4 octahedral to tetrahedral, another two-third coming from indirect approach not from direct approach. If it was directly approaching that is the case of octahedral case, but here indirect approach basically you can calculate based on the angle which angle it is coming, ok.

So, roughly these are like rough calculation it is becoming two-third times two-third, four-nine of delta 0. So, delta t is always less therefore, you never see almost never ever see low spin case for tetrahedral. Since, the splitting is very less always you end up getting high spin case. So, never ever calculate tetrahedral for high spin sorry, low spin.

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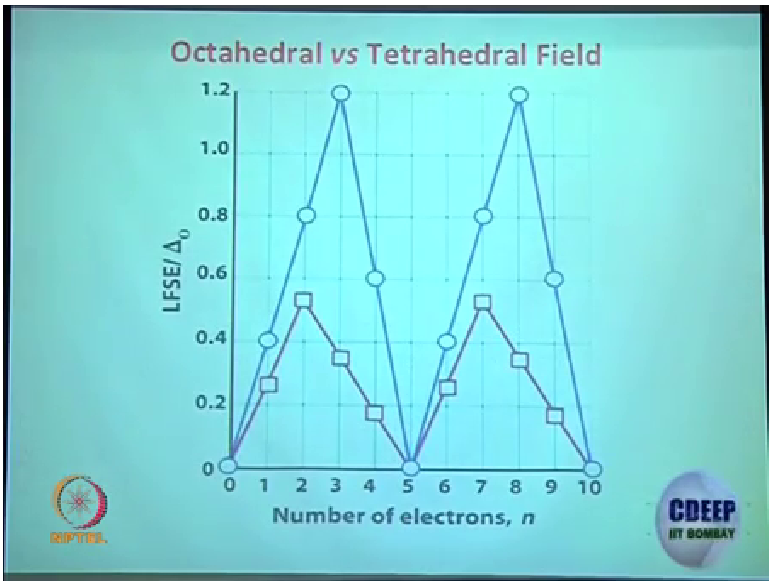

Now this is the electronic configuration and they are respecting stability if you are comparing delta octahedral and delta tetrahedral directly. So, what happens how much stability is there if it is d 1 for octahedral case, d 1 for tetrahedral case and we are comparing apple versus apple ; that means, high spin versus high spin..

High spin of octahedral and high spin of tetrahedral, tetrahedral cannot have low spin. In tetrahedral case, we have to normalize the value with the four-nine of delta 0, these two you do it you will get this should be you should be able to get it.