Coordination Chemistry
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Lecture - 17
Bonding in Complexes – II

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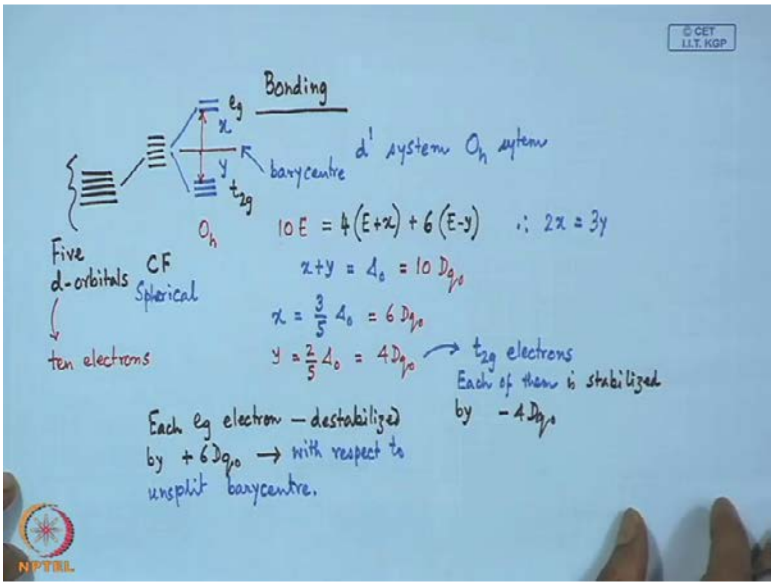

Bonding

d^1 system O_h system

$$10E = 4(E+x) + 6(E-y) \quad \therefore 2x = 3y$$

$$x + y = \Delta_o = 10\,Dq_o$$

$$x = \frac{3}{5}\Delta_o = 6\,Dq_o$$

$$y = \frac{2}{5}\Delta_o = 4\,Dq_o \rightarrow t_{2g} \text{ electrons}$$

Each of them is stabilized by $-4\,Dq_o$

Each e_g electron – destabilized by $+6\,Dq_o$ → with respect to unsplit barycentre.

Good evening everybody. So, we are still with the bonding for the different metal complexes, and in this part, we have been seeing that how the different d-orbitals which are of same energy undergoing splitting within a crystal field. So, if we put the corresponding crystal field, how the ordering of the different d-orbitals will change, and in which particular symmetry the orientation would be of one type, and in another symmetry the orientation can be of different type.

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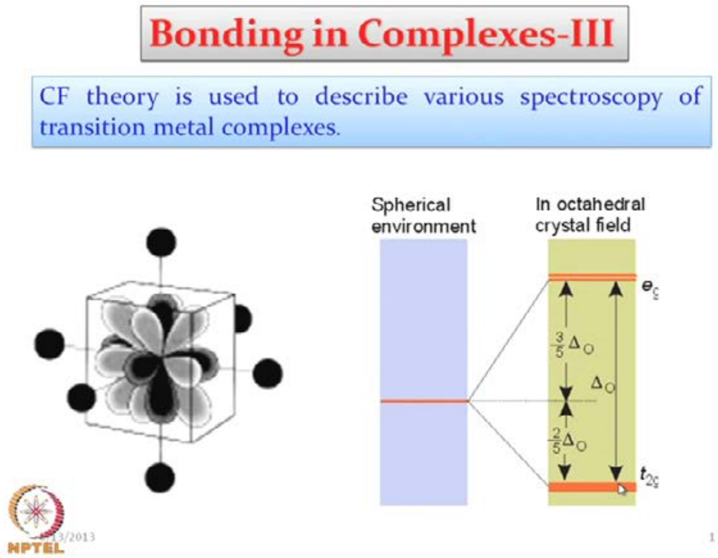

Bonding in Complexes-III

CF theory is used to describe various spectroscopy of transition metal complexes.

So, we will see that this bonding in complexes of part three that crystal field theory what we have seen, it can be used to describe particularly the different types of spectroscopic assignments of the different transition metal complexes; so if we see the corresponding spectroscopic signature of all these metal complexes, how we can classify them in terms of this particular theory?

So, here we are basically assuming that a particular metal ligand interaction is purely electrostatic in nature, and that is why we think that everything is within a environment, where a crystal is operating. So, in a particular octahedral crystal field, so we have all the different types of orbitals, the metal ion orbitals, which is sitting inside a cube, and if we just considered the different types of these interactions and which are all electrostatic in nature; and if we consider the metal ion has all the s orbitals then the p orbitals and the different d orbitals. And since the d-orbitals are the outermost orbitals, so we will mainly focus our attention on the interaction of the d-orbitals with these dipoles of the 6 ligands. And these dipoles or the negative ends of the ligands are facing towards this particular metal center from the 6 faces of the cube, and which is basically giving rise to the corresponding octahedral geometry.

So, center of each and every face is occupying the ligand, and this particular ligand is then interacting directly with the metal orbitals; and this particular interaction can give rise to a particular type of splitting, and that splitting we will call as the crystal field splitting. So, this particular theory basically tells us that how crystal field theory telling us that the corresponding splitting of the different d-orbitals will take place in a particular symmetry.

So, if we have the spherical environment, so in the spherical environment, so energy of all the 5 d levels will be raised. So, the crystal field which is spherical in nature; so so this particular spherical crystal field is operating on this particular 6 d levels, and these 6 d levels then will undergo splitting into two sets; one is the corresponding t 2 g set, and another is the corresponding t 2 g set. So, in this particular class we will just consider the different spherical arrangement; so if the arrangement is from a octahedral field will get the corresponding splitting, and the amount of splitting with respect to the unsplitted bary centre which is the center where we have the corresponding energy level in which particular case we do not have the splitting.

So, before splitting we have some energy level for the d level and after splitting we have some of these orbitals we will have some lower energy and some of them are going up. And the entire amount of this particular splitting that the separation between these two levels one we call it as a t 2 g level, and another we are calling as the e g level. So, the separation between this t 2 g and e g level is known as the corresponding crystal field splitting. So, this is the corresponding crystal field splitting parameter or splitting energy for the octahedral crystal field, and we will find out that how we determine this particular amount of stabilization for the t 2 g set, which is two fifth delta 0 and the amount of de-stabilization for the e g set will be three-fifth delta 0.

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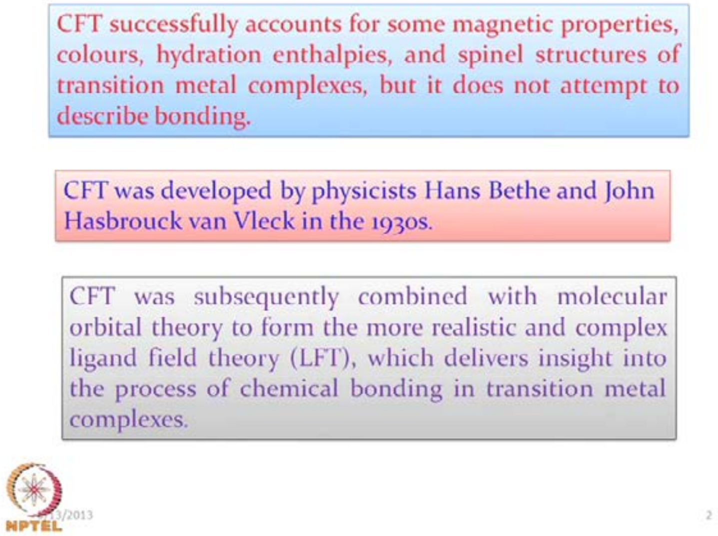

CFT successfully accounts for some magnetic properties, colours, hydration enthalpies, and spinel structures of transition metal complexes, but it does not attempt to describe bonding.

CFT was developed by physicists Hans Bethe and John Hasbrouck van Vleck in the 1930s.

CFT was subsequently combined with molecular orbital theory to form the more realistic and complex ligand field theory (LFT), which delivers insight into the process of chemical bonding in transition metal complexes.

So, this particular theory successfully accounts, which the previous one; that means, the valence bond theory could not explain for some magnetic properties. The some of the magnetic properties we can explain nicely, which we could not explain through valence bond theory or VBT. Then the color of the compounds, then hydration enthalpies, because most of the salts what have seen when we dissolve this salts particularly, the chloride salts or the sulfate salts or the nitrate salt in water, they form the corresponding hydrated complexes or the aqua-complexes. So, how these hydration enthalpies are getting changed through this particular type of hydration that can also be determine from the corresponding crystal field stabilization energies.

Then the spinel structures; that means, the corresponding mixed oxides the mixed oxidation states of the oxides and some these oxides are present with some spheres in tetrahedral field, and some of them are in octahedral field. And if these two fields are predominating then we can find out which particular metal ion whether the bivalent or the tetravalent such as Fe 3 O 4, which is a mixed valent spinel structure. So, that particular structure whether the ferrous ion will be in the tetrahedral field or the ferric ion in the tetrahedral field that can be determined, if we find out the corresponding occupancy of those metal ions in the different environments.

So, the spinel structure can also be explained in terms of the corresponding metal complexes, but and most of the cases it does not attempt to describe the typical nature of these bonding. So, for the exact bonding nature, we have to use the corresponding other type of theory, where the crystal field theory can be mixed up with the that corresponding molecular orbital theory and that molecular orbital theory will account for the corresponding ligand field theory.

It is Hans Bethe and John Hasbrouck Van Vleck these two people and they are basically the physicists they considered this corresponding interaction in terms of the corresponding crystal type of interactions; and they developed and proposed this particular crystal field theory in an around 1930's.

So, this two people basically considered as the father of the crystal field theory, and this particular theory subsequently combined with molecular orbital theory to form the more realistic and complex ligand field theory. So, ligand field theory would be a little bit complex to an where will find that most of these part is belongs to the molecular orbital theory, but it can be explained for some of its part as the corresponding crystal field theory; that means, the crystal field theory can be derived from the ligand field theory for some basic explanations like magnetic properties the color and the spinel structure or the hydration enthalpies. And which therefore, delivers insight into the process of chemical bonding in transition metal complexes.

So, we now onwards some of our future classes will be considering this particular theory to know the exact nature of the bonding in transition metal complexes, whereas we have the corresponding donation from ligand to metal or the metal to ligand back bonding. So, before that will just focus our attention on the corresponding crystal field stabilization.

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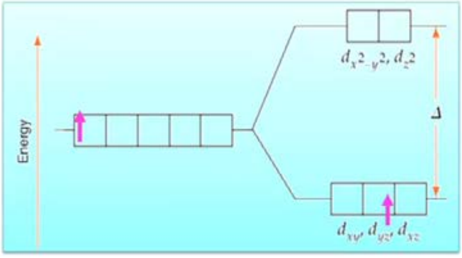

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So, for a d 1 system, so in d 1 system in octahedral field, if we have the in octahedral system what we find that the overall we have all the 5 d-orbitals. So, on the left hand side we have 5 d-orbitals, and the energies of these 5 d-orbitals are basically when we consider that all together we have ten electrons, so 5 d-orbitals means we have therefore, 10 electrons and these 10 electrons can have the corresponding occupancy before the splitting and after the splitting also. So, we have the corresponding crystal field in a typical octahedral geometry where you find that if this particular energy we can have that means, one is x and another is y. So, we can have 4 electrons here the occupancy be 4 electrons; so if this is x and this is y, then we can have these all together ten electrons will be distributed between these two levels; one is t 2 g level another is the corresponding e g level. So, these two levels we have.

So, the upper one would be therefore, E plus x, because this is the energy for this particular level, the unsplitted level is e, and the lower would be E minus y. So, this particular case, what we find that the t 2 g level and the e g level has the total of 4 electron and e g level has 6 electrons; so altogether these electrons we can have which give rise to Becky Valency of 2 x with 3 y, and the entire this x plus y value is nothing but the corresponding crystal field splitting in octahedral geometry. Therefore, by combining these two we get x is equal to three-fifth delta octahedral, and y is equal to two-fifth delta octahedral. So, if x plus y is equal to delta octahedral is equal to 10 D q o also we explain in some cases it as 10 D q o, then this would be equal to 6 D q o octahedral and this equal to 4 D q octahedral.

So, we have therefore, the t 2 g electron, these t 2 g electrons are therefore, in this particular level. So, t 2 g electrons, they are in this particular level are stabilized. So, each of them is stabilized by minus whole D q o that means, in a stabilization which is lower in energy. And therefore, the reverse; that means, each e g electron which are in the upper level would be de-stabilized by plus 6 D q o, and all these are with respect to the bary centre which is our this one. So, all these are therefore, with respect to the unsplit beay centre; that means, the total energy of the system is conserved before and after splitting.

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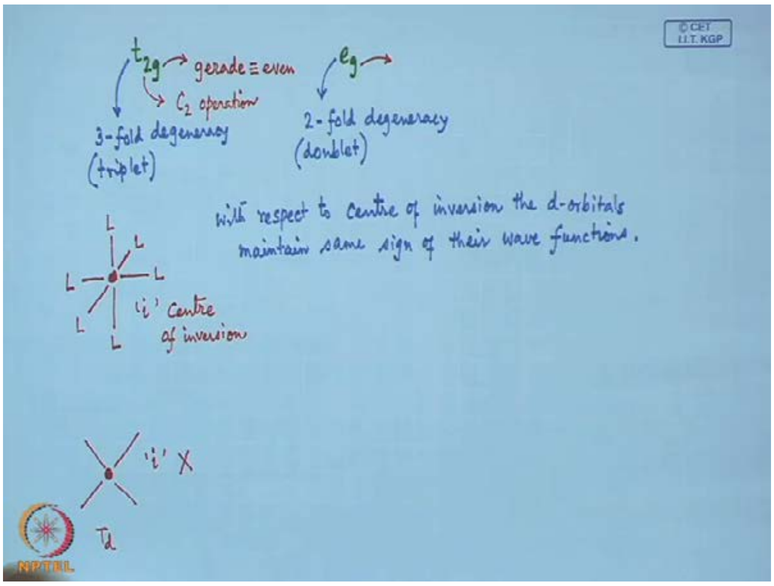

with respect to centre of inversion the d-orbitals maintain same sign of their wave functions.

And we have these two levels, which we are considering one as the t 2 g level and another as the e g level, and in these cases e stands for the corresponding 2-fold degeneracy, and t stands for the triplet one, this is therefore, 2-fold means doublet one. So, that degeneracy is doublet. And here the t stands for a 3-fold degeneracy or triplet, and this g basically the other level is their g, g is related to the symmetry which is gerade which means even; that means, the metal ion which is sitting inside the octahedral environment which is at the centre of inversion i, which is centre of inversion. That means, if we transform, that means if we go for the corresponding symmetry operation with respect to this i operation, we will get the same sign of the wave function and the same molecule; that means, the environment if we have all L at all these positions, they are even in nature that is why the level is g. But when will be moving for the corresponding tetrahedral symmetry in T d symmetry, i is not there.

So, we cannot level those orbitals which will be splitting within a tetrahedral crystal field as a corresponding level as g. So, g will be dropped there. Similarly this is also even with respect to the corresponding inversion symmetry operation, and this particular value two is also related to and C 2 operation, for this corresponding symmetry. So, these are the corresponding symmetry levels with respect to the corresponding inversion. So, what we do with respect to centre of inversion the d-orbitals. The d-orbitals basically maintain same sign of there wave functions that is why under this crystal field, the two sets of these orbitals, the t 2 sets and the e g set will be leveled with a level which is known as the corresponding g level that means the even level.

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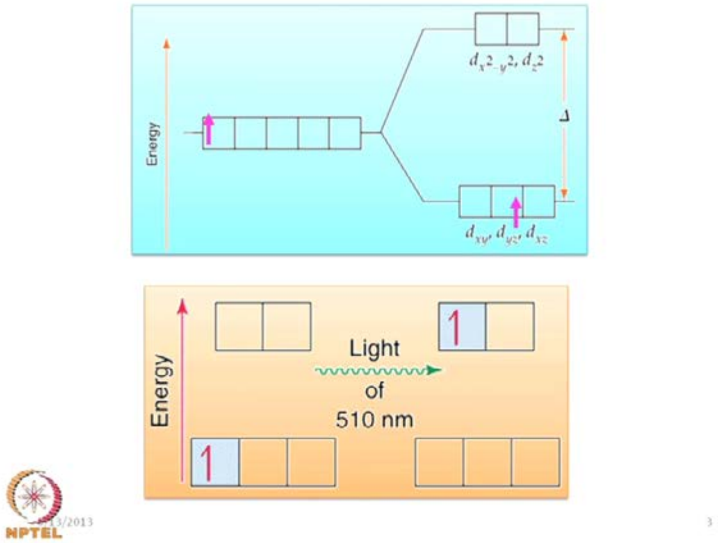

So, that basically gives us some information that already we have seen that we can have the sets of t 2 g as d x y d y z and d x z; and e g set is d x square minus y square d z square and we have the corresponding delta, and delta o this is basically for this. So, only three orbitals will be available, which are degenerate for the corresponding occupancy of the electron, when we have the corresponding crystal field splitting; and for the electronic configuration d 1, the d 1 system it can be 3 d 1 can be three d 4 d 1 or 5 d 1 we have the corresponding electronic configuration which can be leveled as t 2 g 1.

Since the other level is available for this corresponding occupancy for the single electron. So, we can promote this single electron, which are in the t 2 g level to the e g level, and there will be corresponding transition, and we have the corresponding absorption and we get the corresponding color for the compound having this particular electronic configuration.

So, when light of wave length of 500 train nanometer is passed from this particular configuration is passed through this electron configuration, the electron in the t 2 g level can be promoted to the e g level, and we have the corresponding absorption is 510 nanometer and the corresponding color. So, 510 nanometer is a corresponding color range for the visible region, and which will be absorbed and with the corresponding color of the solution would be its complementary color, and we observe all these as the solution color would be the corresponding complementary color of the solution due to this transition.

So, continuously this can relax back to the ground state again we can push the electron from the lower level to the higher level, and this basically consider which is not allowed though as the typical d to d transition, we all consider it is a d t transition. So, that is why the crystal field theory can explain to some extend the corresponding d d transition for the origin of the color for the different complexes.

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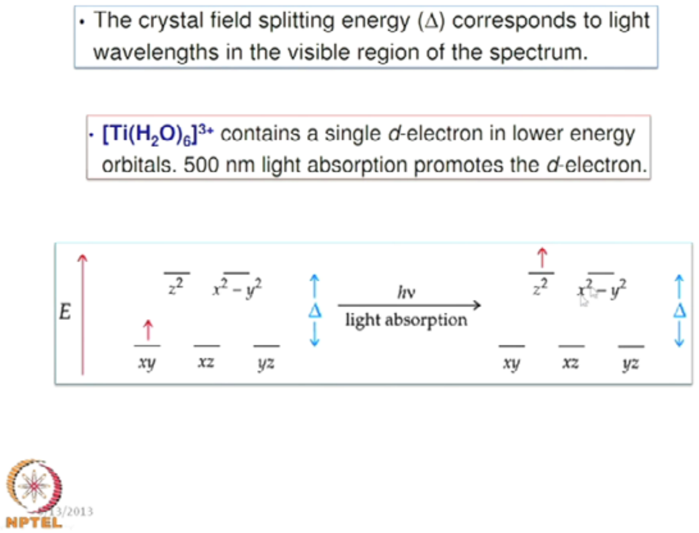

- The crystal field splitting energy (Δ) corresponds to light wavelengths in the visible region of the spectrum.

- $[Ti(H_2O)_6]^{3+}$ contains a single *d*-electron in lower energy orbitals. 500 nm light absorption promotes the *d*-electron.

Then will see that this delta whether it can be leveled as with a subscript o means for octahedral and t for the corresponding tetrahedral symmetry. Therefore, the crystal field splitting energy corresponds to the light wave lengths in the visible region of the spectrum. That is why the h nu value or the e value for the corresponding wave length what we are focusing on the solution is all in the visible region that is why most of this compounds would be colored, and there will be a change in color if we change the corresponding ligands. That we have seen that around nickel, if we have all the 6 water molecules we have a typical color, and through ligand substitution, if we replace all the 6 water molecules by ammonia, we will get h color change. Then all the 6 ammonia molecules by 3 ethylene-di-amine we again see some color change. So, the 3 d one configuration belongs to that hexa aqua titanium 3 plus cat-ion.

So, this is the corresponding aqua complex of titanium in trivalent state, which has one and only one d electron in lower energy orbital; that means, the t 2 g level. And 500 to 510 nanometer of light absorption can take place for the promotion of the electron from the t 2 g level to the e g level and that is why the titanium solutions can show the corresponding absorption in this particular region. So, any compound whether we prepare it from titanium chloride or titanium nitrate or any other source of titanium, if we dissolve it in water or a water solution is made, and if we suspect that the corresponding hexa aqua-titanium compound is generated in the solution, we run the corresponding electronic spectrum and we see the typical absorption. So, the nature of the absorption band and it is corresponding lambda max value in the range of 500 to 500 nanometer will immediately tell us that the species present as a complex species as a complex compound in solution is the corresponding hexa aquatitanium 3 ion.

So, we just then responsible for this particular transition and light absorption can take place, and we can promote this electron either to d z square or d x square minus y square.

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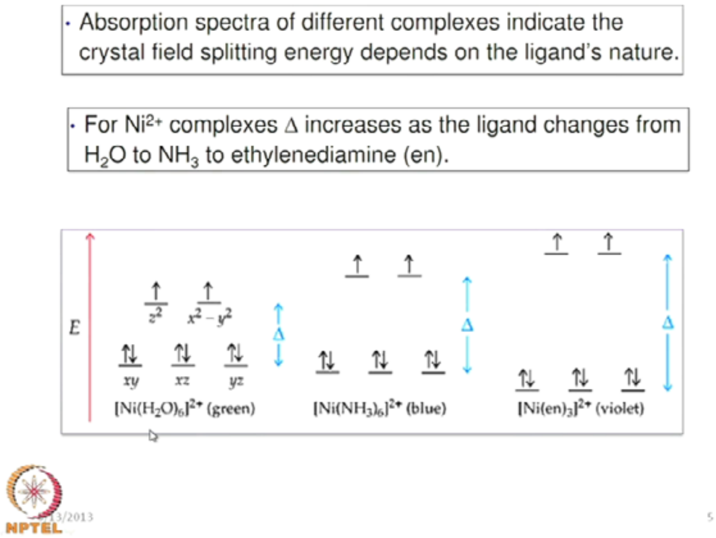

- Absorption spectra of different complexes indicate the crystal field splitting energy depends on the ligand's nature.

- For Ni^{2+} complexes Δ increases as the ligand changes from H_2O to NH_3 to ethylenediamine (en).

So, this absorption spectra of different complexes therefore indicate that the crystal field splitting energy depends on the nature of the ligand.

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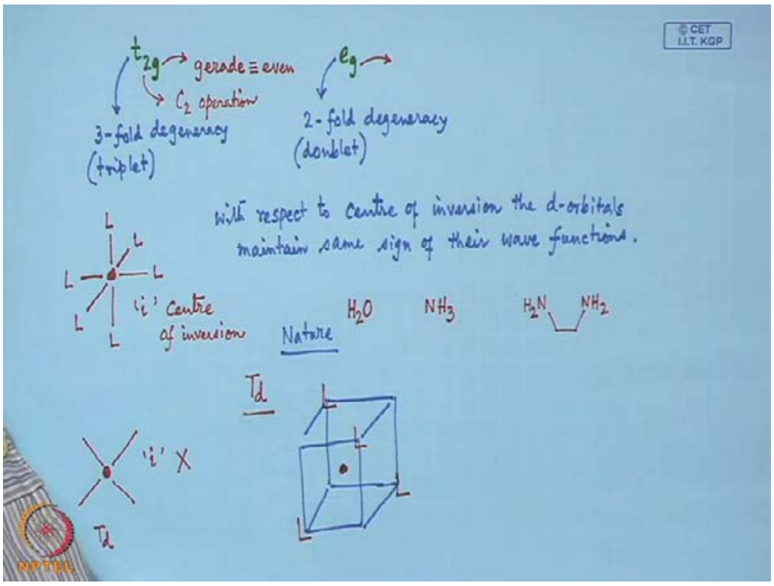

with respect to centre of inversion the d-orbitals maintain same sign of their wave functions.

So, if have the corresponding metal ion surrounded by water molecule or surrounded by ammonia or ethylene-di-amine. So, the corresponding absorption energy, the corresponding absorption will depend on this nature of these ligands. So, the nature of the ligand is therefore very much important to see the corresponding absorption. So, for Ni 2 plus complex delta increases as the ligand is changed from water to ammonia to ethylene-di-amine; that means, we will be increasing the delta value that will see how we can order the different delta values for all these particular spectral change.

So, in case of if we have the corresponding red line as the corresponding energy scale, we have the hexa aqua nickel 2 plus and we get the corresponding separation between the t 2 g set and e g set and we have a nickel 2 plus means is a 3 d 8 system; that means, 8 electrons to be placed in all 5 d levels. So, this is the corresponding spin state; that means, all the levels in the t 2 g level are filled, and we have two unpaired electron in the e g level. So, the separation between these two will be changing as we go from the green solution of hexa aqua nickel 2 plus to blue solution where the separation is bigger compared to the water molecule. That means, we can also correlate to be a solution to be seen as blue, the corresponding lambda max for the absorption for the crystal field transition would be of higher energy; that means, lower wave length.

Similarly if we move from blue hexa amine nickel 2 ion to violate tris ethylene-di-amine nickel 2 ion will get the delta is far more higher, the separation is bigger compared to the amine complex also, and we will have more energy requirement for transition of the electron from the lower level to the upper level. So, we can push this electron say to this particular level, and the amount of energy required for that particular transition will be given by the delta value, and this is known from measurement of the simple electronic spectrum. So, if we measure the electronic spectrum will be able to tell that why this particular solution is valid, but not green which is for the corresponding hexa aqua compound.

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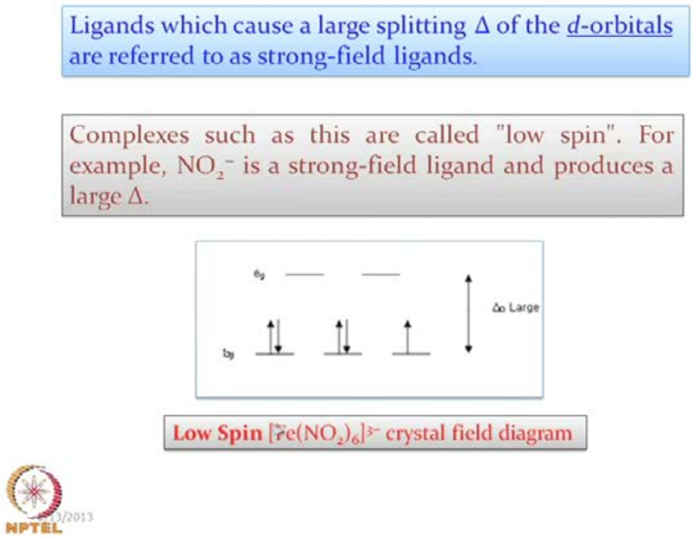

Ligands which cause a large splitting Δ of the *d*-orbitals are referred to as strong-field ligands.

Complexes such as this are called "low spin". For example, NO_2^- is a strong-field ligand and produces a large Δ.

Low Spin $[Fe(NO_2)_6]^{3-}$ crystal field diagram

So, ligands which cause a large splitting of delta value of the d-orbitals are referred as corresponding strong field ligands. So, some of these ligands will be considering as the strong field; that means, it is providing us a corresponding crystal field, which is strong enough. And as we move such as in case of nickel, we just see the corresponding separation is changing, the separation is increasing as we move from water to ammonia to ethylene-di-amine. That means, ethylene-di-amine has a strong ligand field compared to the water molecule, once we know the corresponding separation between these levels.

So, there are some complexes such as that of the corresponding nitrite ion, they called as they called a low spin for example, NO 2 minus is a strong field ligand and produces a large delta value. So, like ethylene-di-amine around nickel 2 plus, this NO 2 minus say around iron 3 plus can provide a corresponding strong field environment and the delta value is higher.

So, up till now, we can define that the corresponding field is strong enough, if we see that the delta is bigger; and if the delta is small, we consider corresponding weak field strength for the corresponding ligands. So, if delta octahedral delta o is large we see for a electronic configuration of 3 d or 4 d or 5 d 5; that means, 5 electrons there, and if this is large that means, this delta o is large these 2 electrons instead of going to this e g level they will be paired up; that means, this delta value is higher than the corresponding pairing energy for pairing in the t 2 g level; that means, we have less number of unpaired electron. If we do not have the corresponding pairing in these two levels we have this electron in this level, and this electron also in this level. So, altogether 1, 2, 3, 4 and 5 unpaired electrons we were having, but since this delta is large, we will push those 2 electrons from this e g level to the t 2 g level downward, and this will reduce the corresponding number of available unpaired electron from 5 to 1; that means, we get a corresponding compound which are known as the low spin compounds.

So, we have therefore that means, we have if we have the large splitting of delta, the crystal field is large enough we will push those electrons from the upper field to the lower one, and we get basically low spin compound; that means, low spin compounds are those compounds where the available number of unpaired electrons are small. This is the situation for a low spin compound of iron 3, which is Fe NO 2 whole 6 3 minus, and this can be considered as it is corresponding crystal field diagram, where we see the corresponding number of electrons in this level is t 2 g 5 only. So, simply we have the t 2 g 5 electronic configuration for these iron, and we get the corresponding low spin compound.

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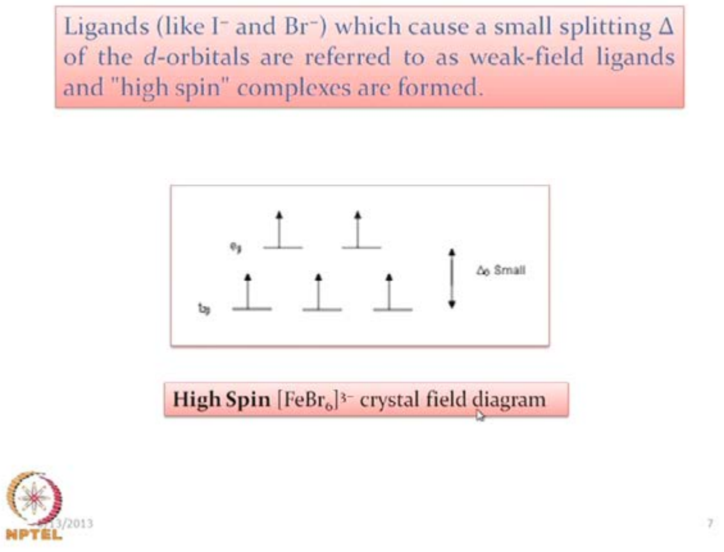

Ligands (like I^- and Br^-) which cause a small splitting Δ of the *d*-orbitals are referred to as weak-field ligands and "high spin" complexes are formed.

High Spin $[FeBr_6]^{3-}$ crystal field diagram

Similarly the other two ligands like iodide and bromide; if we compare them with nitrite they cannot cause very large splitting as we have seen in case of nitrite ion. So, bromide and iodide that means, the corresponding bromo and iodo compounds of iron, we have a splitting which is less than that we have observed just know for the nitrite complex. So, small splitting of delta of the d-orbitals will be considered as the weak field ligands, and as a result high spin complex is result. That means, whatever compound we will be getting with iodo and bromo ligand, they are all of high spin that means, the maximum number of unpaired electrons can be there.

So, all the five levels the t 2 g level as well as the e g level, all will be singly occupied. So, there are 5 electrons, 3 in the t 2 g level, and 2 in the e g level, and all will be singly occupied that if we write them as the off-spin that means we have 5 unpaired electron and the magnetic movement, the determined magnetic movement would be high also which will corresponds to 5 unpaired electron, which was not possible in case of the corresponding low spin compound. So, this is Fe Br 4 2 minus. So, the hexa bromo ferric three ion, and it is crystal field diagram showing that the compound is a high spin compound.

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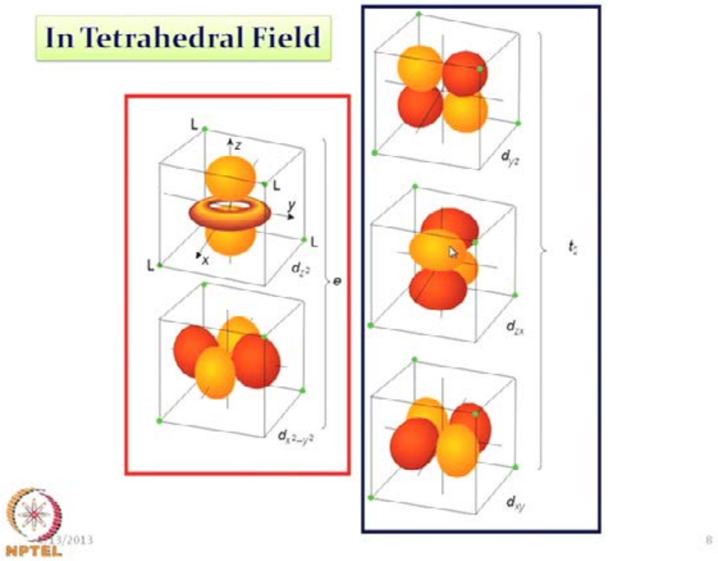
In Tetrahedral Field

So now, if we move to the tetrahedral field, and in this particular tetrahedral field will find that the situation is changing now, because in case of the corresponding octahedral field we are just looking at the 4 plus 2 6 faces, and the centre of the faces are occupied by the ligands. Now to generate a corresponding tetrahedral field, which is t d crystal field, the t d crystal field will have alternate corners would be occupied by the ligands, and centre of this cube will be occupied by the metal ion.

So, we get the corresponding crystal field, and you see these L are the 4 ligands; and within the cubic field, because this is also a cubic field; and within this particular cubic field if we place all these 5 d orbitals, we will see like that of our octahedral geometry that they will now face differently. In earlier case we have seen that the ligand is here for octahedral geometry ligand in all 6 faces of the corresponding cubic geometry. And they are directly facing the d x square minus y square and d z square orbital that is why they are mostly destabilized and we get the corresponding e g set in octahedral geometry.

But in this particular case these are hap diagonal distance we have, you have this diagonal of the one cube face and it is pointing towards the centre of this particular face. So, is hap diagonal distance is facing one particular ligand to the low of d z square orbital or the d x square minus y square, because this is the corresponding x direction, and this is the corresponding y direction; again if we look at this particular face it is pointing towards the hap diagonal distance from the ligand.

So, they will be more stabilized compared to the other three orbitals, and these two belongs to the e set now. And g will be dropped from their nomenclature, because we do not have the corresponding centre of inversion with respect to the metal ion centre. So, with respect to the inversion operation it is not even is a odd symmetry, and that odd symmetry will be designated as any low level as g as its subscript. Similarly these particular orbitals which are facing in these edges of this cube, so this is the hap edge distance. So, they are facing the d y z d x z and d x y. So, hap of this edge basically and hap of this edge is nearer compared to hap diagonal distance. So, hap edge distance is shorter compared to hap diagonal distance that is why all three; that means, d y z d x z and d x y orbitals will face these orbital strongly and that is why we have the higher energy t 2 set not t 2 g this will be leveled as t 2 for their interactions.

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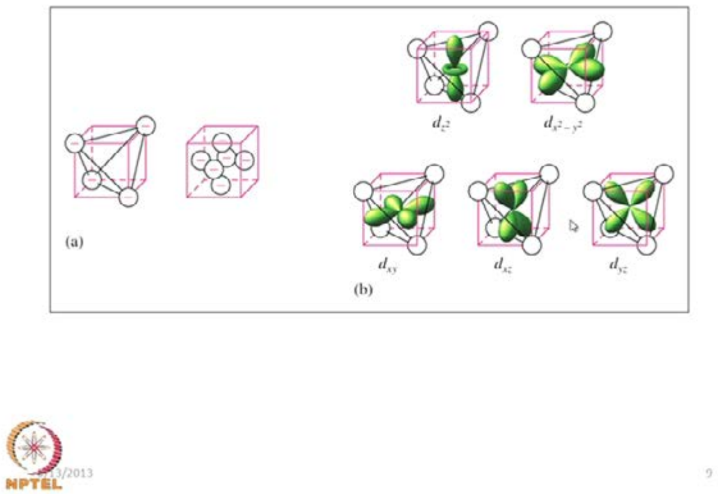

So, this is basically the exact drawing of the corresponding tetrahedral. So, this is the tetrahedral, and we have either the negative ligands, negatively charged ligands or the negative end of the dipolar units compared to the octahedral geometry, because if this is the octahedral geometry means all 6 faces are occupied, but here alternate corners will be occupied for the corresponding tetrahedral geometry. And once we place all the d-orbitals within the field, we will find that this are basically corresponding level; that means, this will be the corresponding e set. So, these will stabilized, because we have the hap diagonal distance compared to the hap edge distance. So this is the Hap edge distance and hap edge is obviously, is also very much pointing towards this particular point, where we do not have any ligand here.

So, if we consider these two ligands in this particular direction, which is the corresponding diagonal distance; that means this is the corresponding diagonal distance, and the ligand low is facing half way from this particular edge. So, they are the corresponding thing; that means, they are little bit nearer than that is corresponding ligand system, and they will be therefore, destabilized.

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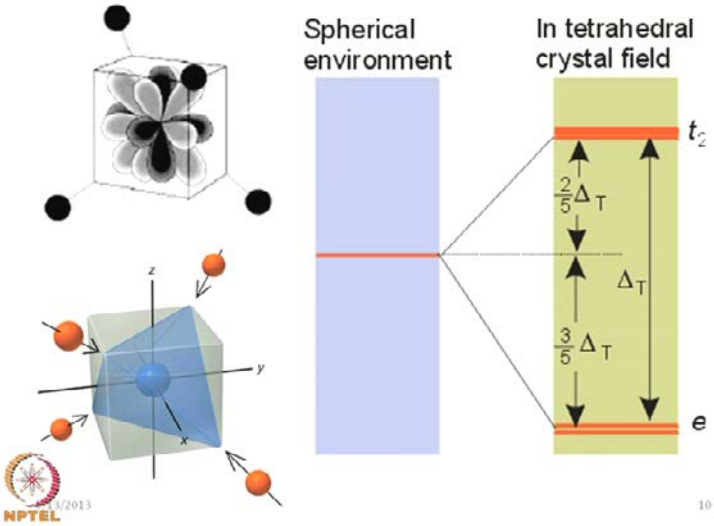

So, this is like that of our octahedral symmetry, this is the corresponding symmetry geometry for the tetrahedral thing, and we have the corresponding ligands along these four corners of this cube, and we have the corresponding splitting. So, this splitting is completely different from that of the octahedral splitting, and we have now the e set and the t 2 set, and the corresponding splitting is known as corresponding delta t either the capital T or the small t. So, these delta t will be there and if we just simply consider that corresponding to the octahedral environment that this will be stabilized by 3 fifth of delta t and this will be destabilize by two-fifth of delta t which is exactly the reverse one as we have seen for the corresponding octahedral geometry.

So, here we just also see that this particular destabilization with respect to the bary centre is due to the corresponding electrons in these levels, and the other cases the corresponding electrons in the t 2 level. And cis few one number of ligands are facing the metal ion compared to the octahedral geometry, we have only four ligands. So, the interaction with the metal center is less, and the less interaction is also responsible for the corresponding amount of splitting; and this particular crystal field splitting would be there for less compared to any octahedral splitting. So, it is four ninth times to that of any octahedral crystal field splitting, if we consider the same situation for the same metal ion and the same set of ligands.

If we want to compare the splitting what we see for the octahedral symmetry and the tetrahedral symmetry, the tetrahedral symmetry we have the less amount of splitting, and that is why in tetrahedral symmetry we do not get any low spin complexes. Since the splitting is less most of the cases or all the time we get only high spin compounds.

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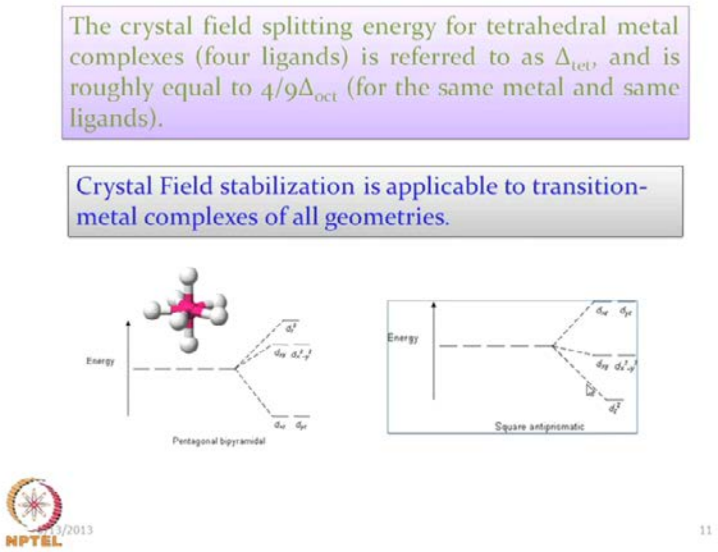

The crystal field splitting energy for tetrahedral metal complexes (four ligands) is referred to as Δ_{tet}, and is roughly equal to $4/9\Delta_{oct}$ (for the same metal and same ligands).

Crystal Field stabilization is applicable to transition-metal complexes of all geometries.

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Therefore, this is the four-ninth of the corresponding splitting, and the corresponding splitting energy for the tetrahedral metal complexes, where we have 4 ligands is referred to as delta capital t delta small t or delta tet all is there we can write anything of them. And is roughly equal to 4 ninth of the delta oct or delta o; that means, the octahedral one for the same set of metal ion and the same ligand system. So, we get almost basically half of the corresponding splitting, what we observe for the corresponding octahedral splitting. And therefore, we have the corresponding crystal field stabilization, and we can calculate out the corresponding crystal field stabilization energy, which can also be applicable to other transition metal complexes.

So, the different types of transition metal complexes we can have in different geometries, the way we have seen the corresponding geometries for the octahedral geometry; this is for the octahedral geometry; this is for the tetrahedral geometry. Now if we can go for the other type of geometries will find that there are also the corresponding splitting. So, if we have a corresponding pentagonal bi-pyramidal geometry.

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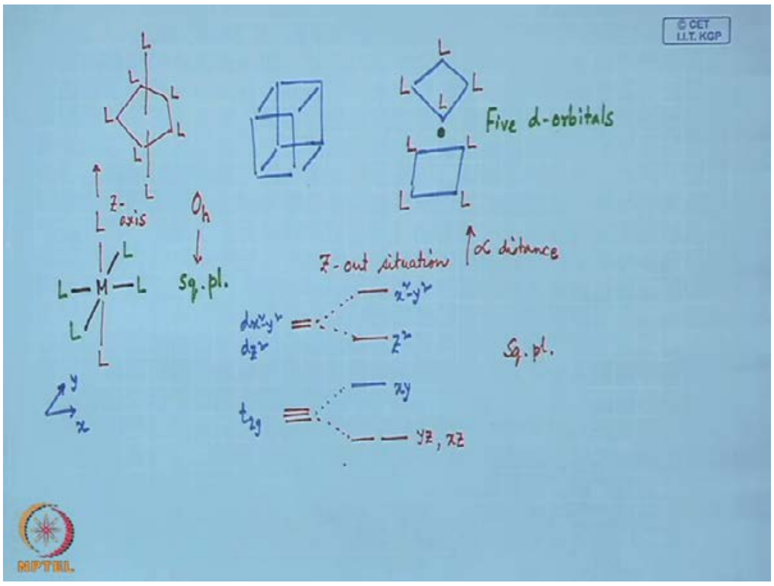

This pentagonal bi-pyramidal geometry, what will find that we have in plane a pentagon and one ligand above this pentagonal plane and one ligand below this. So, we have 5 plus 2 - 7 ligands around the metal centre. And we have therefore, the corresponding interaction with these orbitals; that means, the 5 d orbitals, since these two; that means, the corresponding these two which are in z direction; and we can consider that along this z direction, we have this corresponding ligands, and they are facing directly the d z square orbital.

So, this ligand and this ligand will be facing this particular d orbital along this particular z axis, and their interaction is very high that is why d z square orbital is mostly destabilized with respect to the corresponding crystal field splitting. And then the other two orbitals, which are in the x y plane; that means, d x square minus y square and d x y, they are basically in this particular plane that means, the pentagonal plane, so if the pentagonal plane is in the x y plane. So, these two these two orbitals basically will be next destabilized by facing 5 ligands within this plane. So, we have 4 plus 4 - 8 lopes for x y and d x square minus y square orbitals and they are equally sharing the corresponding points along the pentagon in this particular plane.

So, they are the second destabilize ligands with respect to the d z square. So, the remaining two which are having the z components, the x z and y z; so they will be in between; so they are along the z direction in x plane and the y plane; that means, they are having the z components. So, the orbitals having the z components in a set of d x z and d y z they are the most stabilized one. So, since they are not directly facing any of the ligand which are in this particular plane, since these two orbital's are away from the plane; that means, they are away from the z axis, and also they are away from the x y plane, they will be mostly stabilized for their corresponding separation from this particular splitting.

So, the pentagonal bi-pyramidal geometry will give rise to a corresponding separation like these; that means, the d x z and d y z will be more stabilized one. So, this is basically a doublet set. Then another doublet set we have the d x y and d x square minus y square, so these two are e set this is e set this is e set and we have the final set which has d z square which is singlet set which can be leveled as small a. So, we can have another geometry for the square Anti-prismatic geometry which is a corresponding geometry is a complex once anti-prismatic geometry square.

So, if we have the square prism which is nothing but the cube geometry, and if we have this is the corresponding square anti-prismatic geometry, and if we put all the orbitals that means, we have the metal ion here, and which has the corresponding 5 d orbitals. So, all those 5 d-orbitals will have different types of interactions from the ligands along these directions, and we get some point of interactions, where the ligands which were mostly stabilized in pentagonal bi-pyramidal geometry will be destabilized in this particular case that mean d x z and y z are mostly destabilized, then we have the d x y and d x square minus y square and finally, the most stable arrangement is d z square, because this will not face any of the ligand in square anti-prismatic geometry.

So, interestingly like that of the situation what we have seen in case of the octahedral and tetrahedral geometry that one particular type of splitting is a reverse to the other. Similarly this pentagonal bi-pyramidal geometry having a coordination number of seven and square anti-prismatic geometry with a coordination number of eight, they have the similar type of reverse relationship that means, here the d z square is the mostly destabilized here, the d z square is stabilized, and these two are the stabilized orbitals here it will be most destabilized orbital. So, is a reverse relationship we can have with this type of splitting for square anti-prismatic geometry.

So, if we now then move on to a geometry like square planer, which is mostly a interesting geometry for us, because whatever ligand we were just seeing that in case of a particular octahedral geometry, what we see that these are the two L along the z axis. So, along the z axis, if we can have these L, and if we just simply remove all these L from these z axis will be remaining with only these 4 ligands in a square planer. So, we will end up with a square planer geometry.

So, those orbital's which are interacting with the ligands along z axis will no longer be there that means, if we remove these L, these 2 L, these two ligands to an infinite distance along the z axis will end up with a square planer geometry from an octahedral geometry. So, any octahedral geometry can give rise to a corresponding square planer geometry, if we move these 2 L from a particular intermediate M L distance to an infinite distance.

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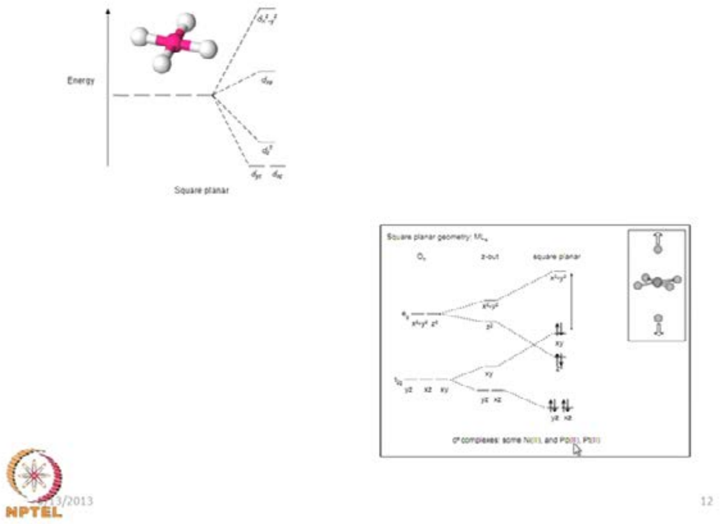

Square planar geometry: ML_4

d^8 complexes: some Ni(II) and Pd(II), Pt(II)

And that basically gives us corresponding splitting like this, and this particular splitting we can have from the corresponding octahedral splitting also. So, that t 2 g set and the e g set we can have, and there we have seen that d x square minus y square and d z square where the e g set and t 2 g is d x y d y z and d x z levels. So now, if we just remove these two groups from above this particular square plane and below this particular square plane along the z axis. That means, the z components the orbital having z components will be mostly stabilized; that means, d z square and d y z and d x z will be stabilized they will form basically the ground level with some separation.

But the orbitals which are in the x y plane if we consider that x y plane is the corresponding molecular plane; that means, where we have the 4 M L bonds; that means, within the x y plane, we have one metal ion and four ligands. So, one metal ion and four ligands will give rise to the corresponding square plane and in this particular square plane we have the most destabilized orbital's should be the d x square minus y square, because these ligands facing the metal ion along the x along the y axis. So, they are directly facing the x square minus y square orbitals so that particular orbital is the most destabilized one. And the intermediate one is the corresponding d x y orbital which is in between x and y axis. And this be the next one. So, we have the corresponding separations. So, we have one separation here we can have another separation between these two orbitals and the third type of separation is between d x y and d x square minus y square.

So, most of these cases particularly the nickel 2 plus in square planer geometry we find that this compounds are diamagnetic in nature, because in that particular case, these 4 orbitals should be available like from the valence bond picture as the d s p 2 hybridization. So, these four orbitals will be available for occupying the eight electrons available for nickel 2 plus. So, here two, here two, here another two and lastly the last 2 electrons would be the d x y. So, we do not have any electron in the d x square minus y square level, when the molecule will become a diamagnetic one.

So, we have the corresponding situations like this, where we have from the octahedral geometry. So, if we just move from the octahedral geometry, we remove these two that means, we remove these L, so this particular along the z axis if we remove them. So, the situation will be the corresponding situation is would be known as z out situation. So, when z out situation is there, we have the t 2 g and the e g level. So, when we are removing this when z is taking away from the environment and here we have d z square. So, this thing which will be stabilized will be z square and x square minus y square will be above.

Similarly for the t 2 g set which belongs to that y z x z and x y. So, we will have separation like these; that means, since it is in the x y plane, this particular plane is x and

y. So, the component which are having both x and y; that means, the d x y will be most destabilized with respect to the t 2 g and the other two will be here which are y z and x z. So, this is basically not the final situation which is only the z out situation, where we have M L distances are longer compared to the other M L distances which are present in the x y plane.

So, when we take this z; that means, z’s are moved to some infinite distance, we will end up with a square planer environment, and in that particular situation this is the, this particular ligand has been removed this particular ligand has been removed. And in that particular case, the z square is further stabilized, and x y is further destabilized, similarly x y is further destabilized and these two are also further destabilized.

So, our splitting is changing and we are ending with a corresponding compound for the square planer environment, and we are having basically the separation between this d x square y minus y square and d x y as the corresponding most important crystal field splitting parameter for the square planer environment

That is why any d 8 complex in this particular case will all be paired in these four levels and we will get the diamagnetic compound. Though we have one separation, two separation and three separation, but it will be mostly controlled by this particular separation between d x square minus y square, and d x y level, and that will push this electron from this level to that level, and all 4 orbitals will be paired up, and we get a diamagnetic situation for nickel 2, palladium 2 and platinum 2.

Thank you very much.