Coordination Chemistry
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Lecture - 16
Bonding in Complexes – II

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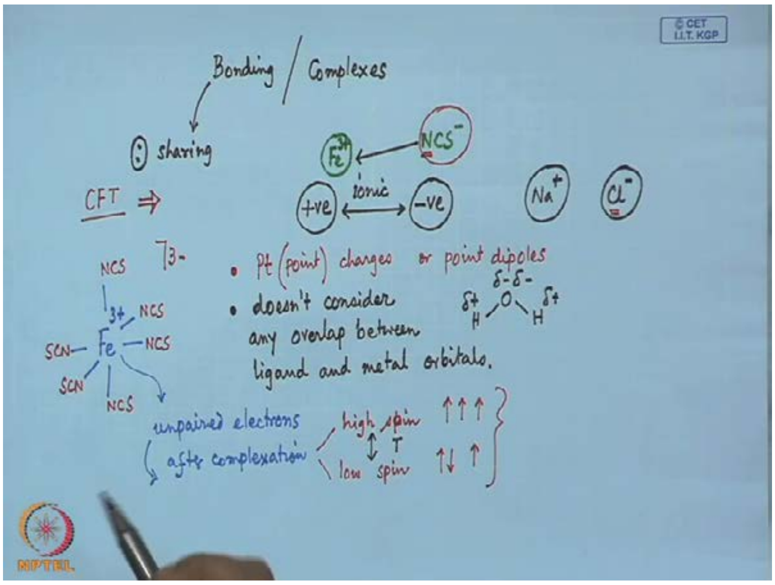

Good evening everybody. So, we will continuing with the types of bonding what is present in complexes. So, so at this particular point, when people were talking about this bonding, so quantum mechanics was not developed at that time, and the only idea was there that electron pair can be utilised for sharing.

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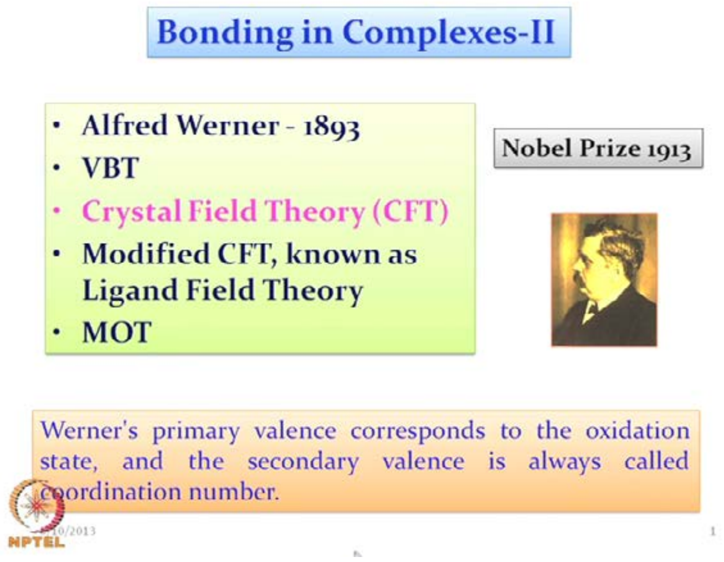

Bonding in Complexes-II

- Alfred Werner - 1893
- VBT
- Crystal Field Theory (CFT)
- Modified CFT, known as Ligand Field Theory
- MOT

Nobel Prize 1913

Werner's primary valence corresponds to the oxidation state, and the secondary valence is always called coordination number.

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So, the historical perspective for this bonding nature, if we consider in this second part of bonding in complexes, we will see that during 1893 when Alfred Werner proposed this sort of complexes, and at that time the bonding idea between 2 atoms was not so clear. And he proposed that a particular type of metal ion can bind to so many ligand system, such as water molecule, ammonia molecule, or ethylene diamine molecule; and give some important characteristics for those species, which we can derive when the metal is bond to the ligand system.

And, at that particular point, when the Werner bond theory was gained account, and we see that a coherent bond can be formed from sharing of the electron pair between the 2 atoms. And following this time frame, that means, around 1893 or so after that this theory, the valence bond theory gained ground; and we are able to explain some of the geometrical features, the compositions and little bit of the structural aspects of these metal complexes.

But, it could not explain so many other things like the colour, the magnetic property, and the reactivity of some of these complexes we could not explain using the valence bond theory. So, slowly, the crystal field theory which was originally proposed for the crystals was gained ground; and people are utilising the crystal field theory for explaining the bonding nature, the types of bonds, in all these metal complexes.

So, in this particular class and the following one also, we will focus our attention on this particular theory that how crystal field theory can explain so many important properties and aspects of the metal complexes; then we will just follow that crystal field theory with the modification, the ligand field theory; and finally to the different molecular orbital's to the entire molecule, that means, the molecular orbital theory.

So, Alfred Werner who just proposed the concept of this complex formation, and 2 types of bonding he proposes at that particular time. And immediately after say, 20 years, he got the Nobel Prize for this idea of getting this complex species in solution as well as in the solid state. And he proposed 2 things that one is the primary valence and the second is the secondary valence. And whenever, we are talking about the valence bond theory, we should know about, we should have good idea about the valence structure of the species. So, the primary valence which basically corresponds to the oxidation state, so it is nothing with relation to the corresponding coordinate bond; it is simply like that of the presence of 3 chloride ions around aluminium centre in aluminium chloride, or 2 chloride, chlorine, chloride ions around barium in barium chloride.

But the most important thing, or most interesting thing is this secondary valence. So, this secondary valence can be correlated to the coordination number. So, this secondary valence, when it is fulfilled by the metal centre, we found that certain metal centres can have a coordination number of 2; and in some other cases, the coordination number can go to 3, or can go to 6. So, depending upon the number of coordination, we can have the corresponding geometry also.

And, the valence structure of the metal centre can give some proposition, what we have seen on our previous class, that the hybridisation scheme which was originally proposed by Linus Pauling. That the hybridisation scheme can be applied to these complexes, to explain to some extent the geometry and the corresponding property, at least the corresponding magnetism of these complexes, which were very much important, because most of this compounds first studied by Alfred Warner is on chromium, is on cobalt; that means, the first transition elements which were, nearly all of them are paramagnetic.

But, if we find that during the complex formation, the paramagnetism is lost; that means, the compound becomes from a paramagnetic site to a diamagnetic one. That means, the coordination is doing something very great to this particular complex formation; that particular information and that knowledge is very much helpful, when we consider some of these biological molecules like myoglobin and haemoglobin. The magnetic properties of these biological centres are very much useful to identify the corresponding oxygenation reaction, because oxygen molecule itself is also paramagnetic. So, when the centre, which we can consider as the metal complex, is also binding to another centre, which is also paramagnetic. So, what should be the overall property of the metal bound species, whether that would be diamagnetic or paramagnetic, that gives us some idea from the studies on this particular type of complexes.

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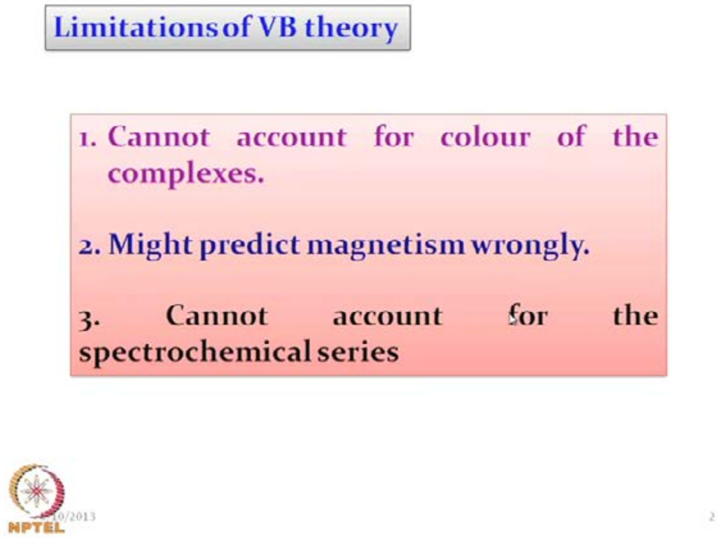

Limitations of VB theory

1. Cannot account for colour of the complexes.
2. Might predict magnetism wrongly.
3. Cannot account for the spectrochemical series

So, we have seen that, the valence bond theory were unable to explain so many important things. It cannot clearly account the colour of the complexes, whether the solution colour of the complexes would be green, would be blue or would be violet. So, for this particular bonding, that means, d 2 s p 3 or s p 3 d 2 type of hybridisation for octahedral complexes are around the nickel 2 plus ion, cannot nicely explain the colour, or to be specific the colour change, how the colour change is taking place.

As we change the ligand centre around the metal ion, it might predict the magnetism wrongly; that means, it cannot say nicely that what should be the precise magnetic moment of that particular complex species. And which is very much important for a large molecule, like a large bio molecule, like myoglobin or haemoglobin, to know the magnetism nicely; then only we can have some idea about the interaction of the metal centre with some other paramagnetic species like dioxygen.

It also cannot account for the spectrochemical series; that we will see afterwards that, in a spectrochemical series we can arrange the ligands according to their strength, and that strength will change the corresponding colour of these complexes. If we can have some 5 or 10 ligands in our hand, and all of them are interacting with a particular metal centre say, nickel 2 plus or copper 2 plus, then we find that depending upon the binding or the complexation of all these ligands, we find that there are changes in the corresponding colour. So, how we arrange those ligands in a particular series, and that series will be called as the corresponding spectrochemical series. So, valence bond theory cannot explain nicely, the corresponding colour of these complexes; and it cannot arrange this corresponding ligands.

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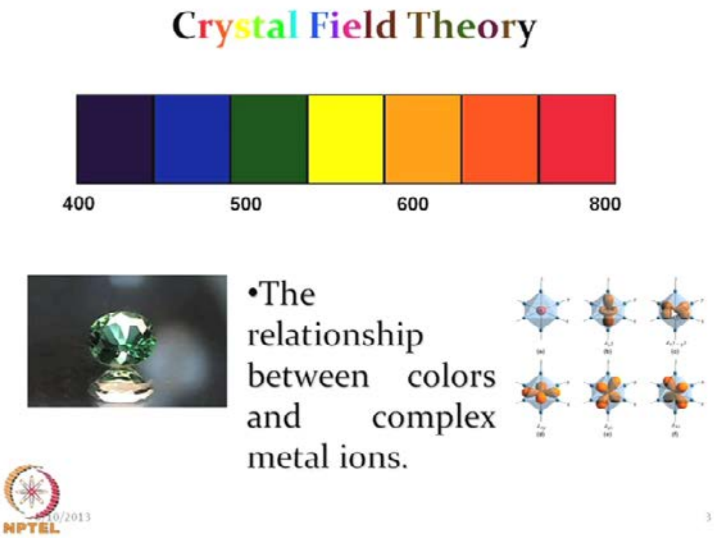

Crystal Field Theory

•The relationship between colors and complex metal ions.

So, we will just proceed towards the crystal field theory. So, crystal field theory gained ground from the assumption that, a particular metal complex is forming say, iron 3 plus is forming the metal complex with thycynate anion. So, iron 3 plus, which is a hard metal centre. So, according to hard and soft acid base theory, it is the nitrogen end of this thycynate anion will bind to the ferric ion; and the interaction is that this is a positively charged species, and this is also a negatively charged species.

So, the interaction between the positive centre and the negative centre can be considered nicely, by assuming that the one particular centre is basically from the crystal lattice; and this interaction is purely ionic in nature. So, this particular assumption is very much true when we consider the interaction between N a plus and C l minus. So, (( )) proposed this idea that if we just simply consider that this particular metal centre, that means, the ferric ion, equivalent to that of the sodium plus in sodium chloride lattice and C l minus is our ligand like that of our thycynate anion.

So, the ligands what we can have in this particular theory; so we have the CFT, the crystal field theory which can ground slowly after the identification and the establishment of the metal complexes. So, we have this ligand; this is also the corresponding ligand which is binding to the iron centre; and this is in the sodium chloride centre. So, the ligands binding to the metal centre through the atom, that means, either through nitrogen or though C l minus. So, they can be considered as point charges, maybe it is as p t point charges or point dipoles. So, we are considering as them as point charges or point dipoles, so such that, the charges centred, basically at the centre of gravity of the species. So, point charges and point dipoles; if we have water molecule also we will have a delta minus, delta minus dipole charges. So, this particular charge the negative charge which is centred on oxygen can be considered as a corresponding point dipole.

And, it does not consider any overlap between ligand and metal orbitals, which we proposed basically in case of valence bond theory. But this particular case we are not consider this thing, because we are considering on the crystal, crystal, read the crystal lattice, the cation anion interactions which are purely ionic in nature. So, these overlaps basically gives rise to some information’s, what we can get from this particular theory that the basically the visible spectrum the colour, say from 400 to 800 nanometre, starting from violet to red.

So, if we can find that the 3 d elements, the transition series elements in the first series or the second series or the third series; when they are in solution interacting with different point charges or dipoles to give the corresponding complex species, even if that particular metal salt is dissolved in water it is interacting with the aqua molecules, or through deprotonation; it is interacting with the hydroxide ion or oxide ion. So, is basically gives the colour. So, it can also little bit explain the origin of the colour in the solid state also, say some spaces (( )) material or the mineral which is colourful, where due to the presence of the transition metal ion. So, transition metal ion in the solid state also in some crystalline environment can also be considered as the interaction such as the corresponding crystal field theory, which can little bit explain the relationship between colour and the complex metal ion.

So, what is the complex metal ion, whether it is in the solution or in the solid state, we can get some idea, if we consider that the corresponding metal ions in the d levels are responsible for the transitions to give a particular metal complex, green or light green to blue to violet. And we will be considering slowly the all the different orbitals, corresponding orbital’s we can have, sorry, this is the corresponding octahedral, octahedral geometry where we can have this; that octahedral geometry where we can have the central metal ion, and the 3 Cartesian axis x, y and z. And this is basically giving rise to the corresponding octahedral crystal field, but the basic assumption behind that the, all the 5 d orbitals. These are the 5 d orbital, which are placed inside an octahedral crystal field. So, how the d orbitals will behave in this particular crystal field?

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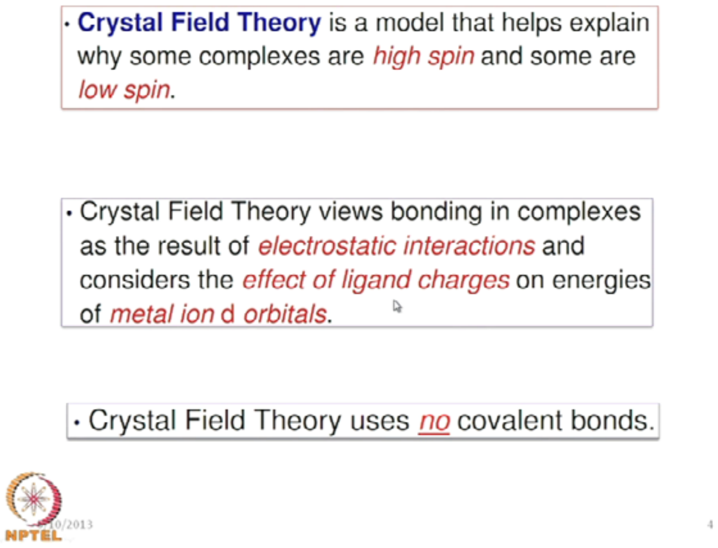

- **Crystal Field Theory** is a model that helps explain why some complexes are *high spin* and some are *low spin*.

- Crystal Field Theory views bonding in complexes as the result of *electrostatic interactions* and considers the *effect of ligand charges* on energies of *metal ion* d *orbitals*.

- Crystal Field Theory uses *no* covalent bonds.

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So, this particular theory is therefore, a model. So, we will by using this particular theory as a model to explain some of the known facts, or some of these experimental facts. So, this is basically a theoretical justification for all this metal complexes about their bonding pattern. So, it can explain the, whether some complexes are high spin and some are low spin. So, high spin and low spin complexes, what we will get that if we have this particular iron centre what is there, and is binding to say 6 thycynate anions. So, NCS, NCS, and overall charge is 3 minus. So, this basically gives us, because we all know the free ion magnetic moment; that means, how many unpaired electrons it has.

So, after complexation, we can have 2 situations: one, we have a paramagnetic situation, or another one is the diamagnetic or closed to diamagnetic one. So, in one case we will see that the magnetic moment is high; that means, it has high spin values. That means, the number of unpaired electrons would be more. In another case, the situation will give us a low spin configuration, where some of these are paired up. So, the number of unpaired electrons available would be less, compared to this high spin molecule. So, we get another low spin type of molecule. So, 2 types of molecules we can have, due to complexation. So, these are the results for complexation reaction. So, we can have the high spin and low spin complexes for that particular purpose.

And it also views the binding in complexes as a result of electrostatic reactions. So, we are talking about the ionic interactions. So, the interaction between the metal centre and the ligand is purely electrostatic in nature. And it considers the effect of ligand charges on the energies of the metal ion d orbitals. How the ligand charge, which we are considering as point charges, how they are interacting with the metal d orbitals; and it is changing the corresponding energetics of the metal d orbitals.

Otherwise, in absence of that particular crystal field of the metal complex, all the 5 d orbitals are degenerate. So, the degeneracy will be lifted when we put the ligands in a particular coordination environment; and the number of ligands around the metal centre is also specific and important. So, when we consider that only electrostatic interactions are operating, we should not consider any kind of covalent interaction. Thus crystal field theory uses no covalent bonds.

That is why valence bond theory has been discarded, because where we have considered that the hybridised orbitals are overlapping with the ligand orbitals. So far, the development of crystal field theory above the valence bond theory gained ground only by considering that the interactions between the metal and the ligand; and the interactions what we all know now, that the interaction between the iron centre in haemoglobin with that of the dioxygen molecule. When we use the dioxygen molecule for our respiration can also be considered as electrostatic in nature. But that is not purely true fact, because afterwards when we modify the crystal field theory by ligand field theory, or purely the molecular orbital theory, we will see that slowly that the pure electrostatic interactions is not the only fact, but we can have some amount of covalent interactions at the same time.

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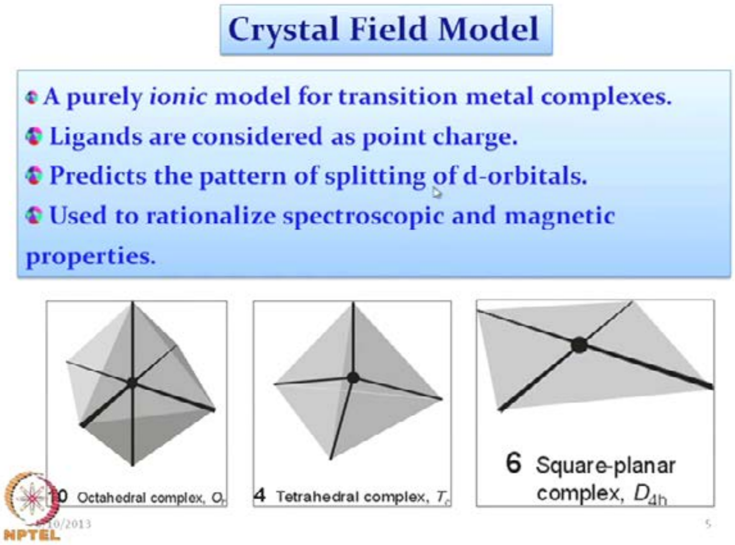

Crystal Field Model

- A purely *ionic* model for transition metal complexes.
- Ligands are considered as point charge.
- Predicts the pattern of splitting of d-orbitals.
- Used to rationalize spectroscopic and magnetic properties.

So, what model we can use for this particular type of crystal field theory, is that a purely ionic model. Therefore, we are discarding any kind of covalent interaction, whether some percentage of covalent interaction can be available from there. But we are not considering that particular interaction. The ligands are considered as point charge, that already we have told you.

It predicts the pattern of splitting of d orbital, which is the important fact. So, the number 3, the point number 3 is the most useful one; how we consider the splitting of the d orbital, generally the 2 types of d orbitals we will have, in a particular coordination geometry. And one d orbital is available for giving the electron for the transition to the other d level and will get the d d transition, and which cannot be rationalised for the corresponding colour of the complexes. So, this particular occupancy, the differential occupancy of the d orbitals which are non degenerate now in presence of the crystal field, can be rationalised for the spectroscopic signatures what type of absorption spectra we get?

And, the magnetic properties, whether the compound is paramagnetic, whether it is diamagnetic, or it can have some intermediate magnetic moment, or it can have some dependence with that of the temperature; that means, the temperature dependence of the magnetism can also be very nicely explained, if we just consider that there is some equilibrium between these two states; that means, the high spin state and the low spin state has some temperature dependent equilibrium; then we will find that due to the variation in the temperature we can have one particular geometry than the other.

So, what we have seen that, we know the corresponding field, that means, the octahedral crystal field. And this octahedral crystal field can have 6 ligands around the 3 axis, 3 Cartesian axis x, y and z. And if we just simply consider that particular metal ion is there, and the corresponding orbital's under interaction with the point charges of the ligand. So, what will happen, if we also consider not only the d orbitals, but the s and p orbitals.

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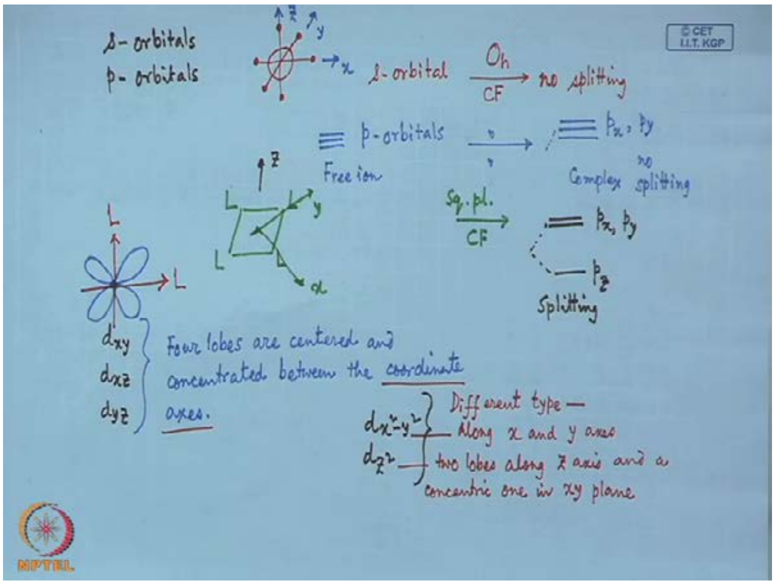

s- orbitals
p- orbitals

s- orbital $\xrightarrow[CF]{O_h}$ no splitting

p-orbitals $\longrightarrow$ p_x, p_y no splitting

Free ion Complex

$\xrightarrow[CF]{Sq. pl.}$ p_x, p_y p_z Splitting

d_{xy}, d_{xz}, d_{yz} } Four lobes are centered and concentrated between the coordinate axes.

$d_{x^2-y^2}$ } Different type — Along x and y axes

d_{z^2} — two lobes along z axis and a concentric one in xy plane

So, we can have s orbital's, we can have p orbital's. So, s orbital, we all know, is spherically symmetric in shape, which has electron density around all the 3 axis. So, when we have the s orbital in octahedral crystal field, we put this in crystal field. Since, the ligands are there in all 3 Cartesian axis, these are the point charges which will interact with the metal centre at the centre of the geometry. So, when the s orbital is facing all the 6 ligand symmetrically, from all the 3 Cartesian axis, we do not get any kind of splitting. So, it will not give any splitting for their energies. So, if we have more than 2 s orbital's, we do not expect any kind of splitting due to the crystal field available from the ligands in a particular coordination geometry, which is octahedral.

Then, what happens for the p orbitals? So, when we have p orbitals, they are 3 in number, p x, p y and p z. And if we put the same octahedral crystal field, we will find that if this is the z direction, this is the x direction, and this is the y direction, then the p x and p y will face the ligands, as well as the ligand will also face the z direction. So, all 3 were there before interaction; that means, the free ion p orbitals and the complex p orbital's; only the energy can be increased little bit, but there is also no splitting. So, if we have certain amount of preferential coordination through some axis, then only we can have some kind of splitting from one particular direction.

So, now, if we can put the p orbitals in x y plane that means the square planar one. So, if we just that in the square planar one, then we will find that this particular thing will change differently. That means, now the crystal field is square planar. And the square plane is such that, we have the 4 ligands in a particular square plane along the x and y axis. So, since these 2 ligands are in x and y direction, so p x and p y will face only the point charges the ligands. So, they will face them; and p z will not face any such interaction, because along this we do not have any ligand. So, the p z orbital will be stabilised, and p x and p y will go up energetically, so there will be splitting in square plane environment. So, p orbital's can also give rise to splitting in a geometry which is different from the octahedral geometry, and can have some preference for the interaction with the ligand centres.

So, now, will just see, how the 5 d orbital's of different sets can be placed within a octahedral field, which, if we have the octahedral field we have the 6 ligands, along the x y and z direction. How all these 5 d orbital's can interact with the tetrahedral complex having a t d geometry; where only 4 directions will be occupied by the ligands; and then with the square planar one which has a symmetry level of D 4 h. So, just now we have seen that in square planar environment, since the p z orbitals is perpendicular to the x y plane, the coordination plane, the p z orbital will not interact with the ligand centres, the ligand point charges. So, that is why the p z orbital is only stabilised; p x and p y will have some higher energy, and there will be splitting within the all p levels.

Similarly, how the 5 d orbitals will split in a particular square planar complex, also will see; and we will see the other geometries as well, because we have discussed so many coordination numbers; we can have the 5 coordinated square pyramidal geometry; we can have the 5 coordinate trigonal bipyramidal geometry. So, how the 5 d orbital ordering we can get? And how we can predict the pattern of splitting of d orbitals? So, this is the most important point for the crystal field model, is how we can predict the different patterns of splitting of d orbital's in different coordination geometries.

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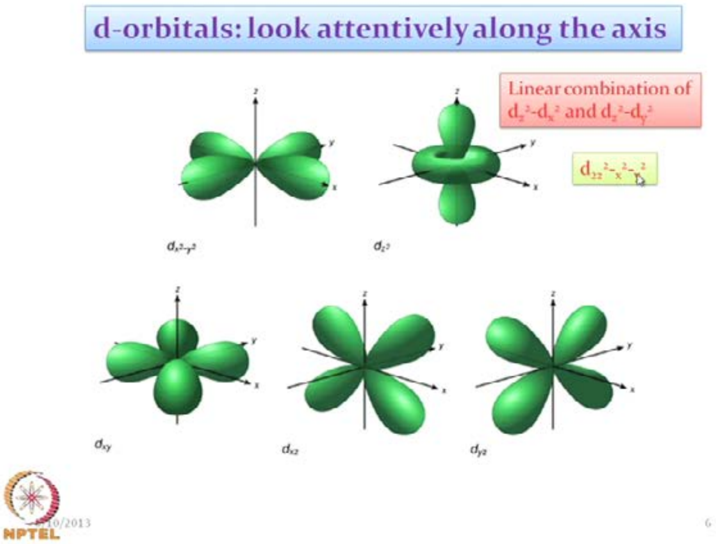

d-orbitals: look attentively along the axis

Linear combination of d_{z^2}-d_{x^2} and d_{z^2}-d_{y^2}

$d_{2z^2-x^2-y^2}$

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So, if we look now, the different d orbital's along the axis. So, this is one particular set the d x y, d x z and d y z; and this is d x square minus y square and d z square. So, this is one particular set, because d x y, d x z and d y z, these 3 orbitals have, all of them have 4 lobes. So, the shape of the orbitals are of same type. So, the 4 lobes which are available, are centred, and concentrated between the coordinate axis.

So, what we are talking? We are talking that the ligands which will approach along the coordinate axis, but this set of orbitals will be concentrated between the coordinate axes. That means, we have the coordinate axis like this, and our orbitals will be inbetween; and our ligands will be from this side and from this side. So, they will not face directly towards the ligands. So, they will away from the ligands. So, there are interactions, but the interactions, the magnitude of the interactions, the point charge interactions between the metal centre and the ligand centre, ligand as the point negative charge or the point dipole would be less, compared to the other orbitals if they are facing directly to the ligand centres.

So, these basically will give us some idea that, when we have the d x y, d x z and d y z, so we see that the lobes are concentrated between the x and y axis. The 4 lobes are in between the 2 axis, x and y. Similarly, y z is also between y and z; and x z and y z is also between y and z, so between these 2 Cartesian axis. So, this particular orbital is a planar nature occupying the particular plane, where it is designate as x y. If it is designate as d x y, it will be lying only in the d x y plane; and along the z direction we have no electron density. In a similar fashion, we will see that the p orbital's, the way they have been splited in a square planar environment, similarly the interaction for the square planar geometry for the x y plane would be different compared to the other orbitals that we see. So, these are one particular set of orbitals.

The other set is d x square minus y square, where the lobes are directly along the Cartesian axis. In case of d x square minus y square, it is along the x axis and along the y axis. Because this d x y is in between x and y, and d x square minus y square will be along x and y axis; and d z square is nothing but we have the lobe along the z axis and a circular lobe along the x y plane. Basically, it can be considered as d z square x square minus y square minus x square minus y square; that means, we have the concentric lobe along the x axis and along the y axis.

So, these 5 orbital's when we place nicely within the octahedral field, this is the octahedral field. So, we will place that, all 5 orbitals will be placed along the octahedral field; and this is now got is a combination of d z square minus d x square, and d z square minus d y square. So, d z square is nothing but d z square minus d x square minus d y square. So, this can be written as d 2 z square minus x square minus y square, so which we abbreviate simply as d z square.

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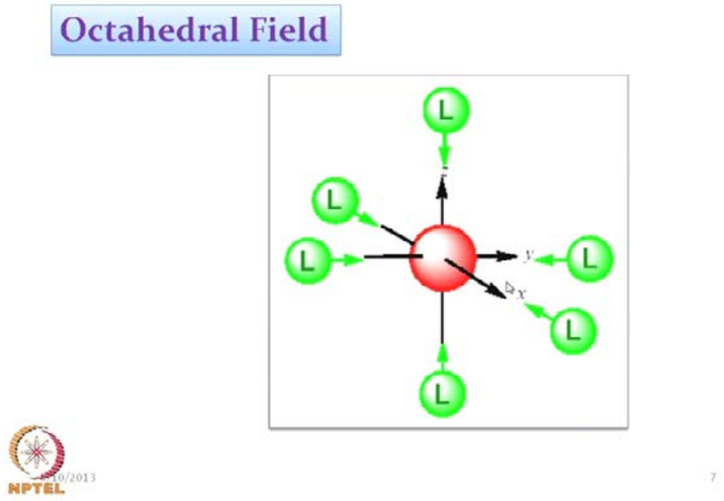

Octahedral Field

So, we can have the octahedral field. First we will start from the octahedral field, not with that of our linear field like a coordination number of 2 or a coordination number 3 or 4, but we will considerably go for the simplest example, where we can have the octahedral field, and we have the 6 ligands along the 6 directions, along the Cartesian axis x, y and z.

So, just now what we have seen that, d x y, d x z and d y z have 4 lobes concentrated between the coordinate axis. Similarly, what we have seen that, d x square minus y square and d z square; these 2 orbitals are of different type, not like that of d x y, d x z and d y z. So, this d x square minus y square has lobes along x y axis, along x and y axis; and d z square has 2 lobes along z axis; and a concentric one in x y plane. So, thus we can have some very good idea about how the lobes are placed for the 5 d orbitals.

So, if all of them are placed in a octahedral field. So, now, we can visualise that where we have the x, where we have the y, and where we have the z; and how the 5 types of orbitals, we can now have the 5 different types of orbitals; how they will interact with the ligand system; and whether the energy of the 5 d orbitals will be raised or not, that we will see if we just simply monitor the corresponding interaction in this particular field.

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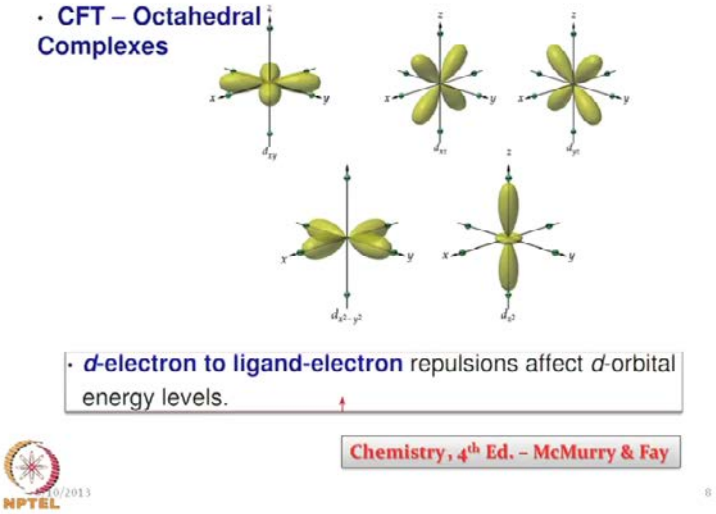

- **CFT – Octahedral Complexes**

- ***d*-electron to ligand-electron** repulsions affect *d*-orbital energy levels.

Chemistry, 4th Ed. – McMurry & Fay

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So, we bring the ligands around a crystal field which is octahedral in nature. So, if we have the d x y orbital, and the 5 this small green points are the ligands. So, the 5 ligands or 6 ligands along x, y and z are there. So, these 4 ligands in the x y plane are close to these orbitals, and they are interacting with the ligand point charges or dipoles in a particular manner.

Similarly, the other 2 also, the d x z and y z, so they are not directly facing the corresponding ligand point charges. See here, this is the d y z; the lobes are between y and z axis, but the ligands are along the y and along the z, so this is quite away from this lobe. Similarly, this ligand is also quite away from this lobe. So, since they are not quite headed away head to head interaction, the head to head electrostatic interactions we are not getting for this type of interaction for the metal and the ligand.

But this particular one; that means, the d x square minus y square, we now see that the 4 lobes along the x and y axis are facing directly for the 4 ligands. So, they will interact differently compared to this 3 set. Similarly, d z square also, along the z axis we have the 2 ligands; this is one and this is another one. And they are directly facing the lobe, because this concentric lobe in the x y plane is a very small one, and which is not interacting much with the ligands present in the x and y direction. So, we put all the 5 ligands in a particular octahedral crystal field. So, we find the repulsions, the d electron to the ligand electron repulsions affect the d orbital energy level. So, these d electrons which are present there, they will now interact differently with the different ligands. So, this we can have from the book of McMurry and Fay, say forth edition.

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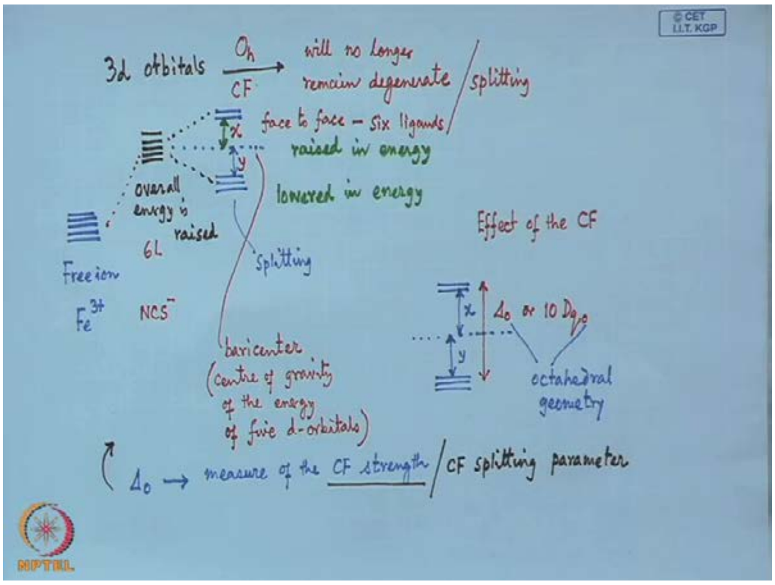

So, if we have the 3 d orbitals which are 5 in number; and the way we have placed the crystal field the, over the s orbitals and over the p orbitals. We will see that the same octahedral crystal field, if we put on the 3 d orbital's, so there will be different types of interactions; and the d orbital's will no longer remain degenerate, will no longer remain degenerate. So, we will have the corresponding splitting. So, there will be difference in energy for these 5 orbitals. So, one set will face different interaction compared to the other set.

So, if we have, thus the 3 ion orbital's, the 3 ion orbital's are 5 in number; say if it is F e 3 plus, we have the 5 d orbitals available for F e 3 plus. Then we put the ligand, if they are octahedral we put 6 L, such as we have seen that we can have 6 thycynate anions and we have a characteristic blood red colouration for that. So, we have, when the 6 ligands are bringing together, so overall energy of the 5 orbitals will be raised. So, overall energy is raised, and the situation we expect before, immediately before the splitting. So, we do not have splitting at this particular point, but the overall energy will be raised over there, and after that we have the splitting. And 2 sets of orbitals, the d x y, d x z; and y z set of orbitals, they are away from the ligands. So, they will be lower in energy. And the 2 other, the d x square minus y square and d z square; they are face to face with the 6 ligands. So, these 2 orbitals are face to face with the ligands, face to face with the 6 ligands. So, they will be raised in energy that is why we are here. And the other they do not go for any interaction directly like this, they will be lower in energy, lower in energy.

So, we have 2 sets of orbitals. One will be lower in energy and another will be higher in energy. So, we have the splitting. So, here we have the splitting. So, crystal field theory thus gives us the splitting. And this particular centre, which we get here, after the raise in energy when 6 ligands are brought together around the metal centre, such as 6 thycynate anions around the ferric ion. So, it has a centre of energy and that energy is known as the corresponding barycentre, which is nothing but the centre of gravity of the energy, of the energy of 5 d orbitals. So, with respect to that we have the splitting. So, we have one magnitude of splitting, this we can consider as x and another is y. So, if now we have the total splitting; that means, we have 2 levels in one set of orbitals, in another case we have another set of orbitals; and this is the barycentre; and this we are considering as the amount of splitting is y; and this is the amount of splitting is x. So, this is now well known to us.

So, now, we can just simply consider this, what is the effect of the crystal field. So, the effect what we are now looking; effect of the crystal field. Effect of the crystal field is therefore, the splitting in 2 groups. So, two groups of orbitals will be there. And we just consider this as the crystal field splitting is delta o, delta o for octahedral or we can consider as 10 D q o. And this o, the level for o are for octahedral geometry. So, this o and this o are octahedral geometry. So, this particular delta 0 or delta o can be defined as the corresponding crystal field splitting; and is a measure of the crystal field strength.

It is therefore, a typical measure how we can measure. So, if the delta o is bigger, we have bigger crystal field strength; if it is smaller, we have a smaller crystal field strength. Or, we can consider it as a crystal field splitting parameter; and we just simply measure, by measuring this delta o that we can measure the corresponding strength. So, if we just measure the corresponding delta o, we will be able to measure the corresponding crystal field strength. So, that is our choice now; that how we can measure the corresponding crystal field strength.

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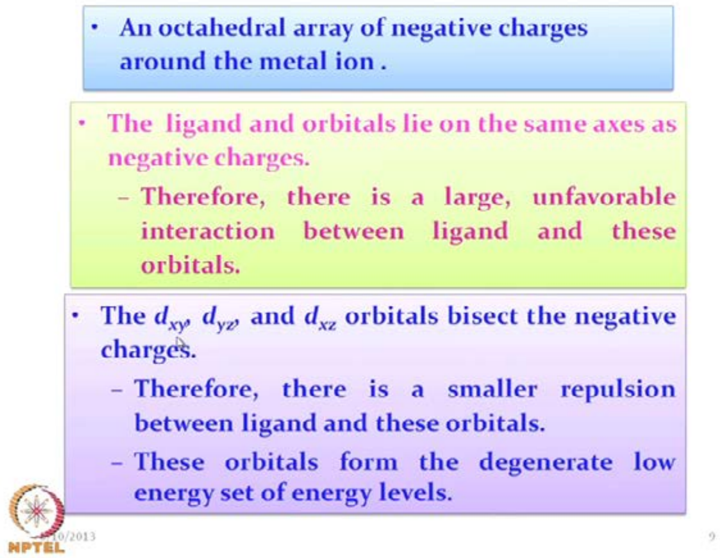

- **An octahedral array of negative charges around the metal ion .**

- **The ligand and orbitals lie on the same axes as negative charges.**
  - **Therefore, there is a large, unfavorable interaction between ligand and these orbitals.**

- **The d_{xy}, d_{yz}, and d_{xz} orbitals bisect the negative charges.**
  - **Therefore, there is a smaller repulsion between ligand and these orbitals.**
  - **These orbitals form the degenerate low energy set of energy levels.**

By looking at the different splitting of these orbitals where we find that an octahedral array of negative charges around the metal ion we have. The ligand and the orbitals lie on the same axes as negative charges. Therefore, there is a large, unfavourable interaction between the ligand and these orbitals. So, we should have an unfavourable interaction between the ligand and these orbitals. So, the corresponding electrons on the different orbitals will stay away.

The d x y, d y z and d x z orbitals bisect the negative charges, that we have seen nicely. Therefore, there is a smaller repulsion between the ligand and these orbitals. And these orbital therefore, form the degenerate low energy set of energy levels. So, they are lower in energy, but they are all again degenerate. And degenerate low energy set of orbitals in an octahedral crystal field is therefore, comprising of d x y, d y z and d x z orbitals.

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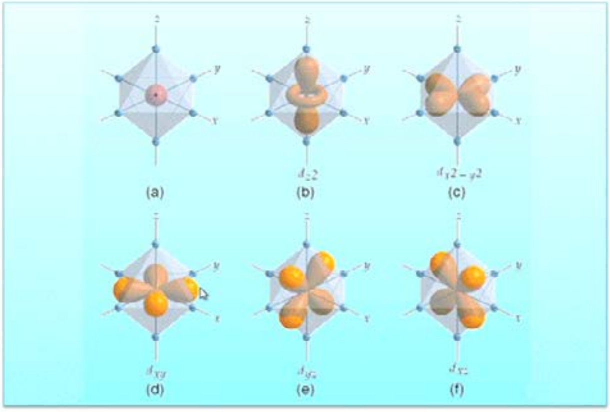

So, now, is a clear view from all the orbitals within the crystal field; that means, the crystal field is octahedral field. So, how the octahedral field, then where the ligands are? And how they are going to interact with different orbitals, can be seen.

So, the same thing we can have also, if can just simply draw the other coordination geometry. So, best thing to do is, that we have the coordination geometry, whether it is a trigonal bipyramidal geometry or square pyramidal geometry, we will try to put that geometry on an above this ligand related centres where we have the metal orbitals are available. So, metal orbitals are there and we put the ligands, and then the ligands around the corners of a regular geometry. And then we can visualise about the amount of interaction between the ligand point charges with the different d orbitals. If the interaction is more, then the energy of those orbitals will go up; and if the interaction is less, the energy of those d orbitals will go down, and they will remain as the lower energy level.

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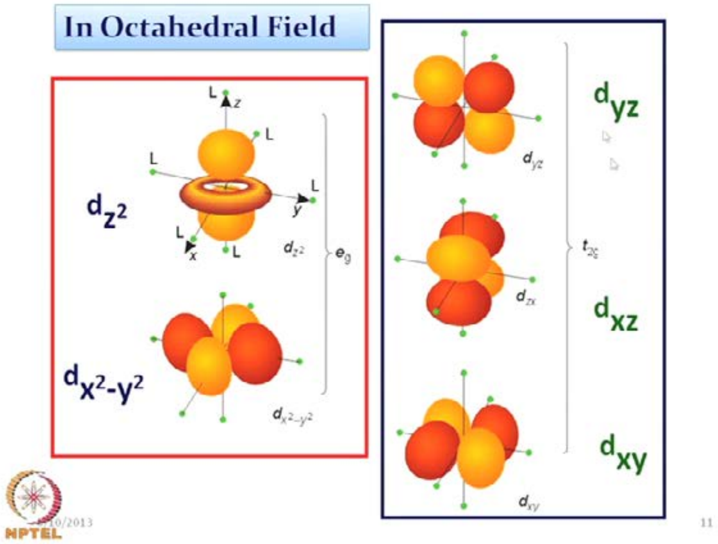

In Octahedral Field

So, what we get therefore, in the octahedral field? We have all these legends in all these different points. So, this is giving us one particular set; and this is giving us another set. So, from some spectroscopic terminology we level these as the doublet set, because it has 2 orbitals only. So, it will be levelled as the e g set.

And, the other 3 those who are lower in energy can be considered as the t 2 g set. So, t 2 g set will have the orbitals d y z, d x z and d x y. They are degenerate, and we have a triplet set. That is why t stands for triplet and e stands for doublet; and within these they are now degenerate. So, the electron can move from this to the other level, to the other level very nicely, without being pushed for the corresponding barrier, which is now our crystal field barrier, for the transition from the lower energy to the higher energy state.

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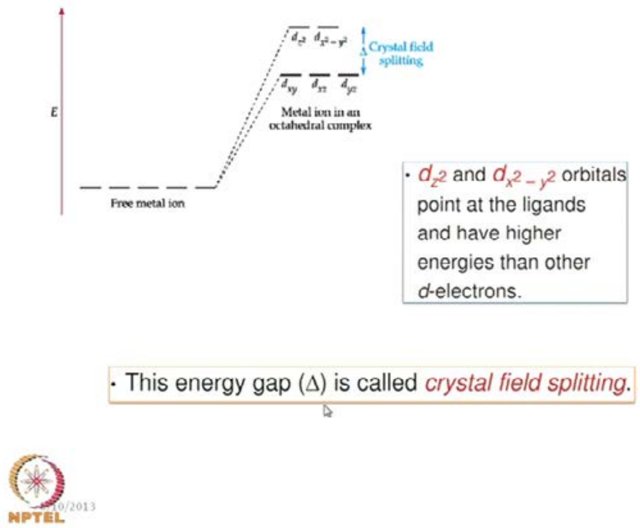

- d_{z^2} and $d_{x^2-y^2}$ orbitals point at the ligands and have higher energies than other *d*-electrons.

- This energy gap (Δ) is called *crystal field splitting.*

So, we just see now that what we seen the magnitude. So, free iron, metal ion then somewhere, in between we have the corresponding one, where the overall energy is raised. And that overall energy raising is giving rise to the 2 sets of orbitals. The metal ion in an octahedral field gives rise to the delta o or delta 0, as the corresponding crystal field splitting. So, we want to measure the amount of splitting, what we can have between these 2 levels. And the d z square and d x square minus y square point at the ligands and have higher energies than the other d electrons. And energy gap, which we will consider as delta is called the corresponding crystal field splitting.

So, depending upon the geometry, if it is octahedral will be levelled it as delta o; and if it is in tetrahedral geometry we level it as delta t; and already we have seen that we have levelled this as the t 2 g set and the e g set. Thus, the corresponding available crystal field can split them into 2 sets: one is t 2 g and the other is e g. So, then next we will continue the other part; that means, how we go for the corresponding values in a regular way.

Thank you very much.