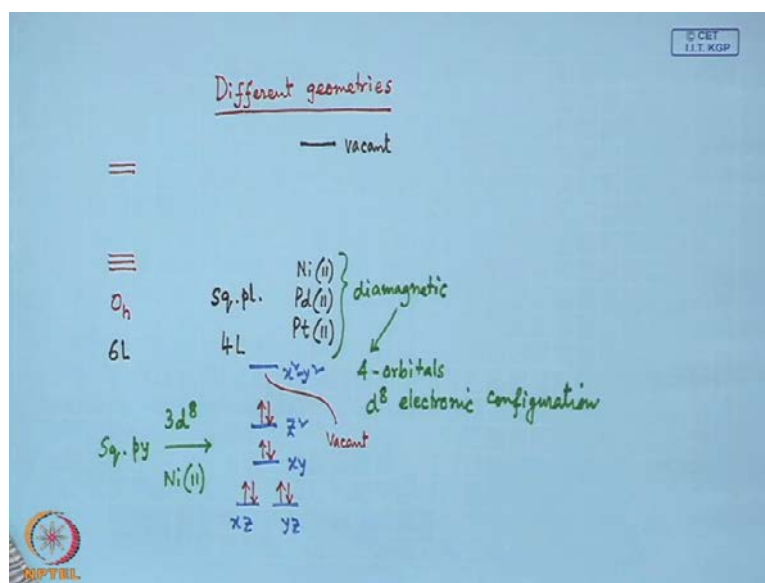


Coordination Chemistry
Prof. Debashis Ray
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Lecture - 18
Bonding in Complexes - IV

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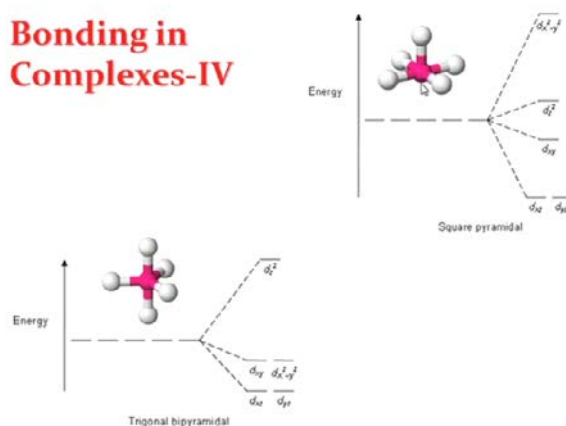


Good evening, all of you. The next part of this class on bonding, we will see that the different geometries how can affect the corresponding d orbital ordering in a particular crystal field. So, if we have an octahedral crystal field and if we can move to a square planar one, we all know that, this is obtained by putting 6 ligands around the metal centre and this by putting 4 ligands around the metal centre. And since the splitting is different, we can have the different ordering of these orbitals. And these orbitals can take of these different types of electrons. And the properties of the corresponding complex what we can have, which is a square planar one, and that we have seen in case of nickel 2, palladium 2 and platinum 2. These all we know from our school days about the corresponding valence bond feature that these compounds are all diamagnetic; that means only 4 orbitals would be available for the occupancy of 8 electrons from the d 8 level. So, we have the d 8 electronic configuration. And these electrons can be accommodated within 4 orbitals. So, these 8 electrons will remain paired within the 4 orbitals and one of the orbital will be the corresponding second orbital. So, all these

properties and reactivities and all will be changing as we move from one particular environment to the other. And this particular vacant orbital is most important and most interesting and it can play some important role in the corresponding compounds of nickel, palladium and platinum.

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Bonding in Complexes-IV



Next, we will move for the next part that means, the bonding in complexes part 4; we will see here that, if we just move. That means, if we add one more ligand to the square planar geometry; or, in a reverse direction, if we consider that, you take out the bottom ligand from the xy plane in an octahedral geometry; in an octahedral geometry, you take out one ligand from the bottom of the xy plane or you put one extra electron to the square planar geometry; how the corresponding ordering of the different d orbitals can take place? So, that basically gives us some idea that, how we derive it starting from the corresponding octahedral geometry or a corresponding square planar geometry. So, if we take out that particular ligand from an octahedral geometry, what we see that, originally, in octahedral geometry, this d xz, d yz and d xy – these three belong to that t_{2g} set and dx square minus y square and dz square – these two were in the e_g set.

Now, what is happening, we are just stabilizing the particular axis, that means, the z-axis. So, instead of double z out situation, this is a single z out situation from the octahedral compound. So, one of the ligand, we are pushing from ml distance to an infinite distance. So, we are just pushing it towards the infinity. So, this particular orbital will be

stabilized. So, the orbitals having z component will definitely be stabilized. So, from the e g set, the dz square will be stabilized. So, dz square will be of low energy compared to the dx square minus y square.

Similarly, from the t_{2g} set, the orbitals having the z component like d x z and d y z would be stabilized compare to d x y. So, this is a very simple crystal field diagram to be drawn for a square pyramidal geometry, where you see that we have a doublet, one singlet, one singlet and one singlet. So, three levels will be singlet and one will be doublet. So, if we can have the corresponding electron occupancy for the system such as for nickel 2 plus, we will find that, 1, 2, 3, 4 orbitals will paired and then this particular geometry also we expect the nickel 2, palladium 2 and platinum 2 in basically a corresponding square pyramidal geometry in the biannual, will all be diamagnetic. So, not only square planar geometry, but also, the square pyramidal geometry for these metal irons can give us to diamagnetic compounds.

And, we should all be able to write the corresponding electronic configuration in this particular geometry. If we are going to write it, how we can write? We can write it in square planar to square pyramidal. If it is say for nickel 2 plus, which is 3 d 8; and this 3 d 8 situation can be tackled very nicely. If we just consider it as the corresponding levels as x z and y z; then we have the x y; then z square, and finally x square minus y square. So, it would be d x z 2, d y z 2, d x y 2 and d z square 2. So, compared to this square planar (()) we have the vacancy here. Similarly, here also, we have this one also – a vacant level in the xy plane for the square pyramidal geometry. So, we will be able to write this configuration – particular configuration in a particular geometry, which is square pyramidal in nature.

Next, we will just go from this geometry to the other well-known geometry for a coordination number of 5, what we have discussed in detail for the different types of coordination number. And the coordination geometry is therefore, the trigonal bipyramidal one. The 3 ligands in the trigonal pen; and out of these, 2 other ligands: one will be above the trigonal plane and the other will be below the trigonal plane. So, in this particular case, we have now, these two of the ligands surfacing now z square. So, compared to this one, here we have this is directly facing. So, dz square would be the most destabilized level. So, the dz square will be most destabilized one, which is facing directly the two ligands in this particular direction. Then we have 2 orbitals d xy and d x

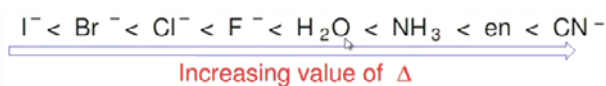
square minus y square in this particular trigonal plane. So, within this trigonal plane, we have these two orbitals in xy plane. So, if xy plane belongs to this particular trigonal plane, we have these two and these two are the most destabilized one in that particular case. So, we have d_{xy} and $d_{x^2-y^2}$. They will form as a doublet. So, there will be no splitting between d_{xy} and $d_{x^2-y^2}$. So, they will form the doublet here.

And, two others having z component will be the ground state as another doublet. So, nicely, we have two doublets. This is also e state; this is also e state; and, one singlet a. So, this particular geometry compared to this one is a different one. And if we get this particular interconversion due to the very few rotations; that is, if we have any compound, which is interconverting between square pyramidal and trigonal bipyramidal geometries, we will find that, the corresponding magnetic property will not change for nickel 2, palladium 2 and platinum 2 compound, because all these 4 levels will be occupying by 8 electrons and all of them will be paired. So, pairing in these levels will give rise to a situation, which is diamagnetic and we have the vacant orbital which is different.

So, while looking at the vacant orbital, we can differentiate between the square pyramidal and trigonal bipyramidal geometries. In one case, it is the $d_{x^2-y^2}$ level, which is for square pyramidal geometry; and in other case, if the d_{z^2} level is vacant, our geometry is trigonal bipyramidal. So, that way, we can differentiate these. And we should be able to write in the same fashion the way we have written the corresponding electronic configuration. In this square pyramidal geometry, we should also be able to write the same nickel electronic configuration in trigonal bipyramidal geometries. So, we should be careful while writing this particular electronic configuration that, which particular level is vacant. Here $d_{x^2-y^2}$ is vacant; here d_{z^2} is vacant. So, we should not put any electron in d_{z^2} level or $d_{x^2-y^2}$ level while writing the corresponding metal complex having a coordination number of 5 in these two geometries.

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• In general, the crystal field splitting energy increases as the ligand varies in the following order.



• This is known as the *spectrochemical series*.

• Ligands which lead to small values of Δ are called *weak-field ligands*. Those which lead to large values of Δ are called *strong-field ligands*.



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Next, we will see, how basically, the different types of splitting we can have. So, we have the delta value; that means the splitting parameter, the crystal field splitting energy also we can calculate; and other is the corresponding pairing energy term. So, in general, the crystal field splitting energy increases as the ligand varies in the falling order; that means we can try to locate the electrons in a particular order; the way we have seen in case of Ni 2 plus, the ordering for water, ammonia and ethylene diamine. So, in that particular case, the weakest one is the water and the strongest one is the ethylene diamine.

So, water would be less than ammonia and less than ethylene diamine. So, this particular part we can put and we can extend that for large number of other groups. So, here we will see that, this is water; this is ammonia; and this is ethylene diamine. So, this part is fine; the way we have seen simply the color of the compounds with respect to nickel 2 that, how bivalent nickel 2 plus is interacting with water molecule or ammonia molecule or ethylene diamine; and how the colors are getting changed. We can simply or straight away we can write this particular ordering.

Similarly, for the halides, we know the weakest one is hydride. So, it basically follows the reverse order in the group, what is there in the halogen group in the periodic table. So, reverse order for that since these are very weak and is a bigger one. Iodide ion is the soft one and the bigger one; and therefore, is the weakest one. So, iodide, which is less

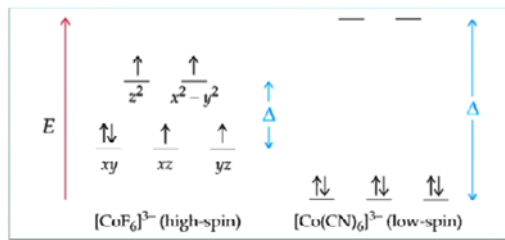
than bromide is less than chloride and less than fluoride. So, after fluoride, we will put the water. So, then again, (()) immediately get the 3... And we put here; we will expand it further also for other type of ligands. But here right now, we have this CN minus is well-known; that for cyanide, (()) is a strong field one and that gives the square planar complex for nickel 2 plus, which is a tetracyanonickelate ion. And immediately, it goes for the square planar geometry. And in the square planar geometry, the corresponding crystal field splitting for CN minus would definitely be higher than that of ethylene diamine. So, as we write in increasing the value of delta, this is more or less the straight cut order for 4 plus 4 – 8 ligands. So, 8 ligands if we can have; and if all of them are interacting with say nickel 2 plus, we can get the typical ordering for increasing value of delta for all these 8 ligands around nickel 2 plus.

So, this particular part is not the full one. We will come back to this particular series again. So, this particular part, that means, ordering of some ligands in a particular sequence from weak field to strong field with increasing delta; that means, I minus – the iodide ion has the smaller delta value compared to CN minus, which has the highest possible delta value in this particular series, is known as spectrochemical series. Since it is effecting the spectra – the optical spectra, the electronic spectra, the ligands which are effecting and which are giving a corresponding order in this particular sequence – we consider it as the corresponding spectrochemical series.

On the left hand side – what we have on the left-hand side, I minus, Br minus, Cl minus and F minus, which can be considered as very weak ligand, so ligands which lead to small values of delta. So, the ligands which are on the left-hand side; that means, this delta value is increasing from left to right. So, the ligands, which are on the left-hand side will be weaker in nature, will provide small delta values and are called weak field ligands. So, iodide ion and bromide ion are therefore, weak-field ligands. So, whenever they form complex (()) they provide very small delta value and the corresponding electronic transition can also be correlated with that of the very small delta value for the complex. But in the case of the ligands, which are on the right-hand side of the series such as en or CN minus will find that this lead to large delta values. And therefore, they are known as strong-field ligands. So, we can now have two different types of ligands: one is weak-field ligand and another is the strong-field ligand. And some of them will be in between. They are intermediate type of ligands.

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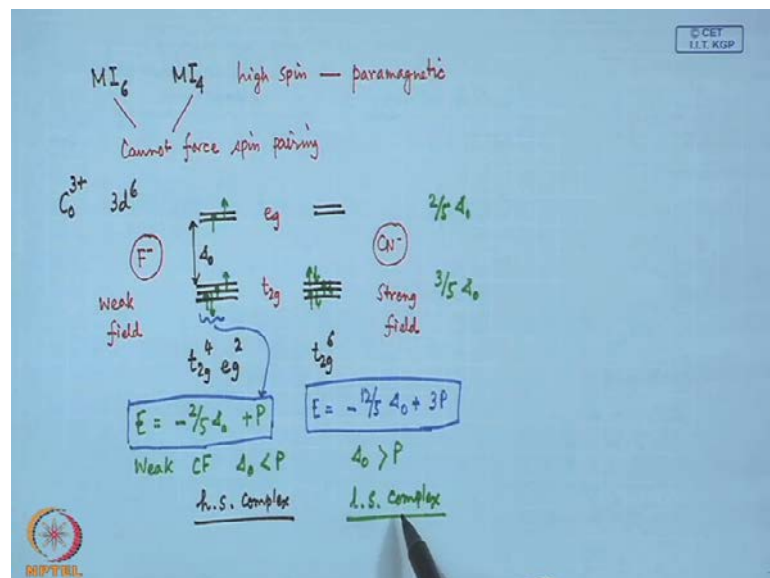
- **Crystal Field Splitting** can also account for magnetic properties in terms of high- and low-spin complexes.
- *Weak-field ligands* lead to *high-spin paramagnetic* systems.
- *Strong-field ligands* lead to *low-spin diamagnetic* systems.



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We can have the delta. And this delta gives us the corresponding crystal field splitting. And it can account for magnetic properties in terms of high- and low-spin complexes. So, this high-spin and low-spin complexes we can have depending upon the nature of the ligand and depending upon the amount of splitting. So, weak-field ligands lead to high-spin paramagnetic systems that, we have the corresponding ligands such as the iodide or bromide. So, we can have...

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If we have the corresponding metal and if we have the iodide 6 or MI_4 , the expectation is that, in these cases, we can have high spin compounds. Since high spin, therefore, we have large number of three spins present in the complex. And that is why, the compounds would be paramagnetic. Since free spins are available, where the I minus ligands – iodide ligands cannot force the spin pairing. So, this I and this I cannot force spin pairing, for the other type, the strong-field ligands... These are weak-field ligands. So, we can have strong-field ligands as well lead to low-spin diamagnetic systems. So, if the field is such that we can pair off all the available electron spin we will get of yellow spin compound; and when s is equal to 0; when all the free spins can be paired up, we get the corresponding diamagnetic system. So, if we cannot force all the spin to the different orbitals, it cannot be diamagnetic, but it can be paramagnetic with a low-spin value.

These are the two situations, where we can have the corresponding cobalt, hexafluoro and the cobalt hexacyano species. In one case, we have, since the cobalt is in plus 3 oxidation state, we have the cobalt having 6 electrons. So, is the $3d^6$ stem. One case, we have the high spin situation; that means, this is the only known example of cobalt 3, where the corresponding stabilization is much more. If we get the corresponding paired up situation in hexacyano cobalted ion, which is $3-$ cobalted 3 ion, which is low spin; where, all the 6 electrons will be in the t_{2g} set. So, since this is having some Δ value is less, because fluoride we all know, is in the left-hand side of the spectrochemical series after iodide, bromide, chloride. Therefore, it can have low Δ value and giving rise to a high spin situation compared to a situation, where we get the corresponding cyanide ligand from the extreme right-hand side of the spectrochemical series; where the Δ value is very high, we get only the corresponding low-spin compound.

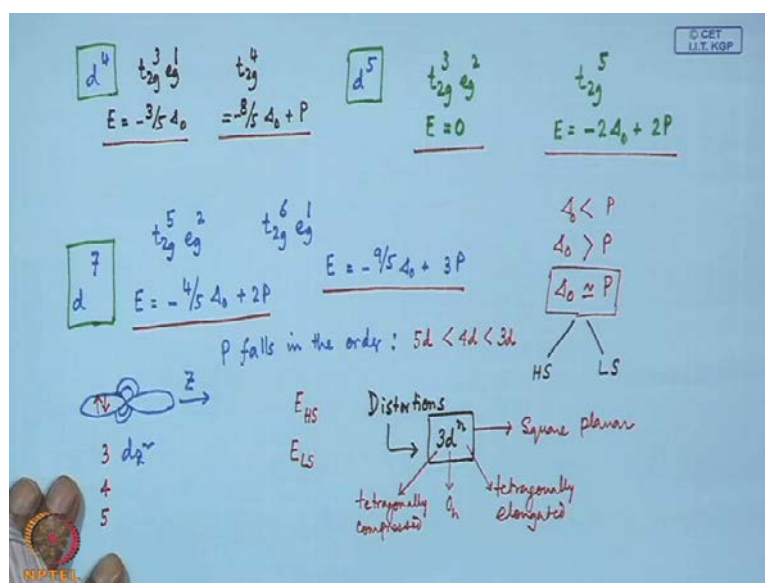
In this situation, what we find? That is, cobalt 3, which is the trivalent cobalt, which is the $3d^6$ situation; and we can have the levels like t_{2g} and e_g . So, in one case, we have the ligand as the weak-field ligand, which is F^- . And another case we have CN^- , which is strong field. So, the electron occupancy would be like this – 1, 2, 3, 4, 5 and 6, which is for the corresponding weak field. And for the strong field, we have all will be paired; all in the t_{2g} level. So, these two are the t_{2g} ; these two are e_g level. So, in this particular situation, this one, we can write it as $t_{2g}^4 e_g^2$; and this is t_{2g}^6 . So, in terms of the corresponding crystal field stabilization energy, if we can find out the E value for this configuration as well as this configuration ($t_{2g}^4 e_g^2$), we can compare these

values also. We will find this corresponding stabilizations, what we can have earlier; what we have seen earlier that, this particular level – this t_{2g} and the e_g level. The t_{2g} level was stabilized by corresponding value for this was the three-fifth Δ_o ; and the e_g set was two-fifth Δ_o . So, this 4 will be multiplied by this value and 2 will be multiplied by this value. And this is stabilization, which is negative in sign. So, if we add up these two, that means, the paired electron occupancy will have the corresponding stabilization for minus three-fifth Δ_o and paired occupancy in the e_g level is the two-fifth Δ_o . We get this value as minus two-fifth Δ_o plus P ; P is the corresponding pairing energy. So, we put this is for this p . So, this is the corresponding pairing and this pairing is this corresponding pairing energy.

Similarly, for the right-hand side, we have minus twelve-fifth Δ_o plus 3 units of corresponding pairing energy term. So, this is the situation – a weak crystal field. So, this will be the balance between this pairing energy and the corresponding splitting. And if we find that – a weak crystal field, that means, this is the weak field. So, in case of weak crystal field... On the left-hand side, we have a weak crystal field. And in that situation, Δ_o octahedron is less than P ; that means, this separation is very important – this particular, which is less than the corresponding pairing energy. That is why all these electrons will go from lower to the upper level. So, this Δ_o is very less compared to the pairing energy. So, will have less pairing and we get the corresponding high spin complexes having 4 unpaired electrons. So, that is why we have the high spin complexes. So, here we just develop the corresponding high spin complex.

Similarly, on the right-hand side, we have this, is the maximum stabilization. And here this is greater than P though we have the three pairing energy term. But since Δ_o is greater than P , we get the situation, where we have the low spin complex. So, straight away, we just go from one example, which is for the cobalt that, how we calculate these values for the other systems, because these are very important; how we calculate out the E values for these. From there we can compare the corresponding energy for the high-spin fragment and the low-spin fragment.

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We get for the situations for d 4, d 5; d 6 already we have seen; and d 7. So, for d 4, we have the corresponding configurations, which are $t_{2g}^3 e_g^1$; E would be equal to minus three-fifth delta 0 and we do not have any pairing. So, P term is not there. This is for high spin. And for low spin, we have t_{2g}^4 and E is equal to minus eight-fifth delta 0 plus P. Similarly, in case of the corresponding d 5 configuration – for d 5, and we will calculate for d 7 also. For d 5, we have two situations: one is $t_{2g}^3 e_g^2$ and there is t_{2g}^5 . So, for the high-spin situation, the E is equal to 0; no crystal field stabilization. And for the low spin, E is equal to minus 2 delta 0 plus 2 P. And for the d 7 situation, we have $t_{2g}^5 e_g^2$ and $t_{2g}^6 e_g^1$. And in the former case, E is equal to minus four-fifth delta 0 plus 2 P. And in the latter case, it is equal to minus nine-fifth delta 0 plus 3 P.

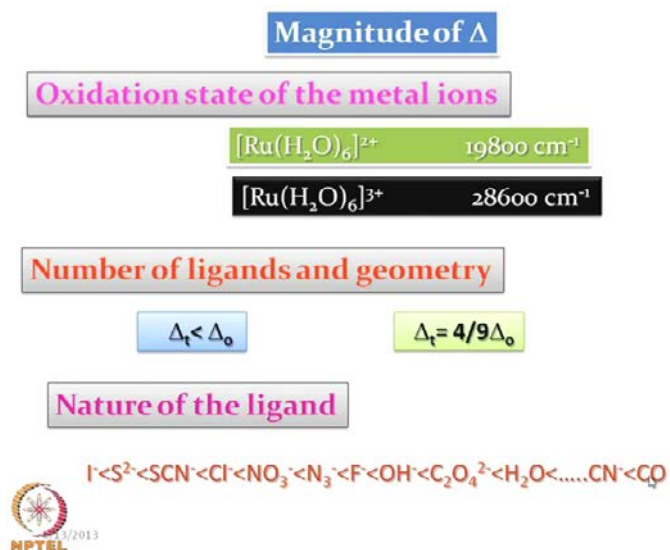
So, these are the different energy values for the system. And for a particular type of complex, we should compare the corresponding situation for high-spin and low-spin situation. And then we just compare the corresponding terms for these delta 0 and P values, because we know that these two situations we can have the delta 0 is either less than P or delta 0 is greater than P.

And, in some cases also, we discussed that, when this is close to P value, which is typically an equilibrium situation, which will discuss shortly about the corresponding spin-state equilibrium. But what about the nature of this P for the different compounds that, this P value basically falls in the order. P is nothing but when we have large number

of electrons like these three such pairing and two such pairing; and one orbital is shared by 2 electrons. So, if we can have one particular orbital; if it is in the z direction; that means, d_{z^2} ; and we can have... When this level is filled, we can have a paired electron in this particular level. So, compared to $3d_{z^2}$, $4d_{z^2}$ and $5d_{z^2}$; when the principal quantum number is changing from 3 to 4, 4 to 5, the size of these d levels are increasing; that means, the maximum amount of repulsion can be observed when two electrons are present in the d_{z^2} level only; where, this size is bigger compared to $3d_{z^2}$ to $4d_{z^2}$. The size is bigger. So, the repulsion, which is been experienced by 2 ligands should be less in case of 4 and in case of 5 also. So, that is why the P, the pairing energy for the pairing of these electrons in these levels basically can fall in the order, where 5 d level has the lowest pairing energy compared to 4 d and then 3 d.

If we just simply compare for these values, we just compare all these in a different way such that if we have the corresponding energy for the high-spin and corresponding energy for the low-spin situation, we just simply compare. So, when we have two different types of energies, there will be situation, where we have a value like this, which is the critical crystal field. So, the critical crystal field can give rise to two types of situations, where we have either the low-spin or the high-spin complex depending upon the situation. So, we see that, from this configuration of $3d^6$ in two situations, we can have the high spin and low spin. And we can calculate out the corresponding energy; that means, E_{HS} and E_{LS} for these two situations.

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Then, we see that, how the pairing energy is changing. Now, you see the magnitude of delta. It can be delta o for octahedral geometry or delta t for the tetrahedral geometry. So, it depends on the variation in the oxidation state of the metal ions. So, if the oxidation state is getting changed, we can have the different values for this, such as we have the ruthenium in class 2 oxidation state; where, we have 6 water molecules present; and 6 water molecules are surrounding this particular ruthenium in octahedral geometry. And in inverse centimeter scale, it would be 19800.

And, this can also have some idea about the corresponding pairing energy term, which is also known for the ruthenium system. And we can compare what type of spin state we can have; whether we get this compound as a high-spin or a low-spin one. But the effect of the oxidation state is drastically absorbed if we just move from plus 2 to plus 3; that means, the trivalent ruthenium in the same environment; that means, 6 water molecules surrounding in octahedral geometry giving us to a corresponding delta value for 28,600 centimeter inverse. So, definitely, with oxidation state, it is changing. The more and more crystal field is observed as we move from lower-oxidation state to higher-oxidation state.

Then the number of ligands and geometry, which is very important and which is also very much crucial, that how the number of ligands can change a particular geometry as well as the delta value. So, as we have already seen that, since more number of ligands

are present for octahedral geometry, the Δ_o is always greater than Δ_t , which is for the tetrahedral geometry with less number of ligands; that means, 4 ligands compared to 6 ligands. And we have seen also that, Δ_t will be equal to – almost Δ_t equal to four-ninth of Δ_o . And as a result, we do not expect any low-spin compounds in tetrahedral geometry. So, all the tetrahedral complexes in all the cases are high spin in nature; whether it is tetrachloroferrous ion or tetrachloro or hexachloronickel ion, all will be in the high-spin geometry. Then the nature of the ligand – that the nature of the ligand can also change the corresponding environment, which we already seen that, we have little bit elaborated value now – the corresponding spectrochemical series. This spectrochemical series, what we have seen earlier is that, iodo, bromo, chloro, fluoro; then we have the water; then ammonia and ethylene diamine.

Now, we have added some more ligands to that particular series such that we can have an extended series involving most of the common ligand systems. So, if we put sulfide and thiocyanate, sulfide will be less than thiocyanate. And this is basically incorporated between I minus and Cl minus. So, they have intermediate strength of crystal field between I minus and Cl minus, between Cl minus and F minus. So, we have these two: that means, NO₃ minus – the nitrate ion and the azide ion.

Then, we have the hydroxide ion, and then oxalate ion and the water. And lastly, the two well-known strong field ligand systems, what we have already discussed in case of the corresponding nickel compound or the cobalt compound: hexacyanocobaltite and hexatetracyanonickelate, that cyanide is stronger than water or ethylene diamine. Further, we can consider though carbon monoxide is neutral one, but it is typical nature of the bonding that we will discuss in case of molecular orbital picture that, CO will exert more than that of the corresponding Δ value compared to CN minus though CN minus has charged. But the neutral CO will have better effect in terms of the corresponding splitting. So, CO will be considered as the strongest possible ligand in the spectrochemical series compared to CN minus.

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Crystal Field Stabilization Energy (CFSE)

- In Octahedral field, **configuration is: $t_{2g}^x e_g^y$**
- Net energy of the configuration relative to the average energy of the orbitals is
$$= (-0.4x + 0.6y)\Delta_O$$
$$\Delta_O = 10 Dq$$

BEYOND d^3

- In weak field: $\Delta_O < P$, $\rightarrow t_{2g}^3 e_g^1$
- In strong field $\Delta_O > P$, $\rightarrow t_{2g}^4$
- P - pairing energy



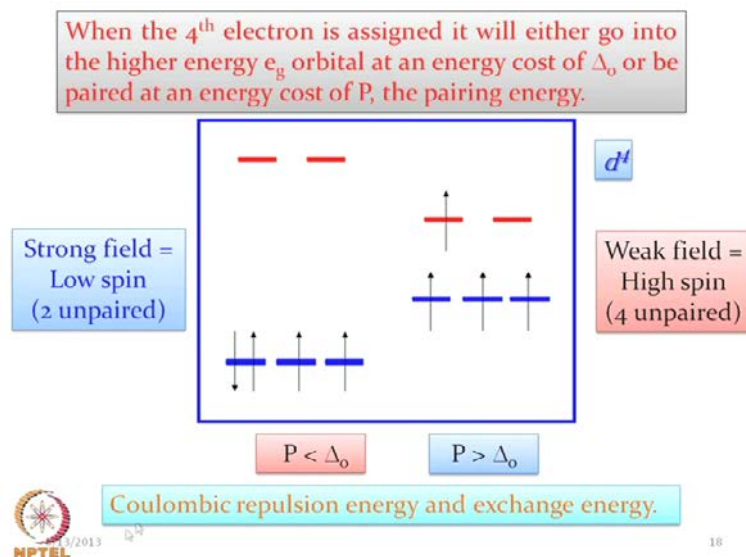
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Now, we just what we have just seen, the corresponding crystal field stabilization energy; we have calculated in detail for d^4 , d^5 , d^6 and d^7 . And what we have seen in terms of the corresponding delta octahedral or $10 Dq$ values in terms of the corresponding x and y values. And those values are basically giving rise to corresponding the amount of energy from the barycentres. So, in octahedral field, we can write in general, the corresponding configuration as $t_{2g}^x e_g^y$. This we have seen how we can write a corresponding configuration for d^7 or d^5 . When we have the d^7 configuration, we have the $t_{2g}^5 e_g^2$. So, we are writing it in the form of $t_{2g}^x e_g^y$, because in the energy term, we have considered one as x and another as y . So, occupancy for x and y can be simply very quickly multiplied for the total energy calculation. So, the net energy of the configuration relative to barycentre energy, which is the barycentre energy of the orbitals is $-0.4x + 0.6y$ into Δ_O ; that means, the octahedral geometries, where Δ_O is $10 Dq$.

And, we have seen that, beyond d^3 , what we can have. When we have the d^4 , d^5 , d^6 and d^7 situation, we have seen just now that, in weak field case, Δ_O is less than P and in strong field case Δ_O is greater than P . We have the t_{2g}^4 configuration compared to $t_{2g}^3 e_g^1$ configuration; where, P term also we have considered as the corresponding pairing energy, which will control the corresponding spin state.

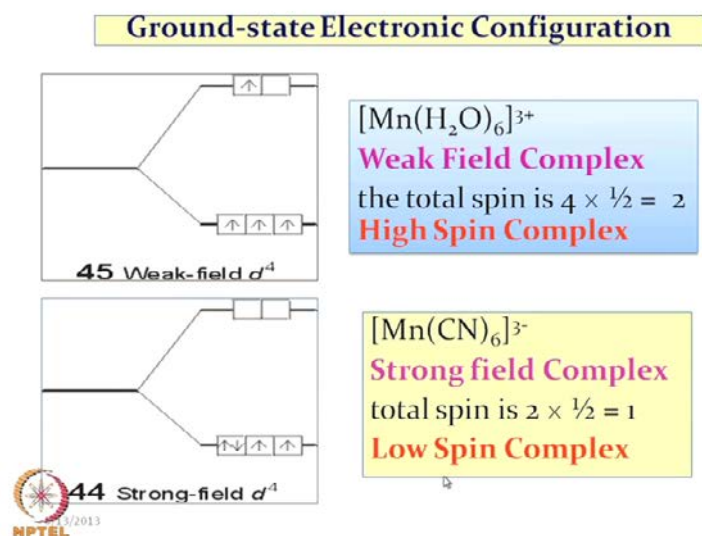
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When we go for the fourth electron, what can happen, it can go either to the t_{2g} level or the e_g level at an extra energy cost of Δ_o or be paired at the energy cost of P . So, balance is between the Δ_o and P . So, for d^4 situation, whether this electron will go up or will be paired over here; that will be dictated by the relative magnitude of Δ_o and P . So, these are the levels. These reds are e_g level and blue are t_{2g} level. So, this is a situation, where P is less than Δ_o . So, we have the corresponding low-spin situation. So, is a strong field situation. We have only two unpaired electrons. And when P is greater than Δ_o , we get the corresponding weak field or high-spin situation with 4 unpaired electrons.

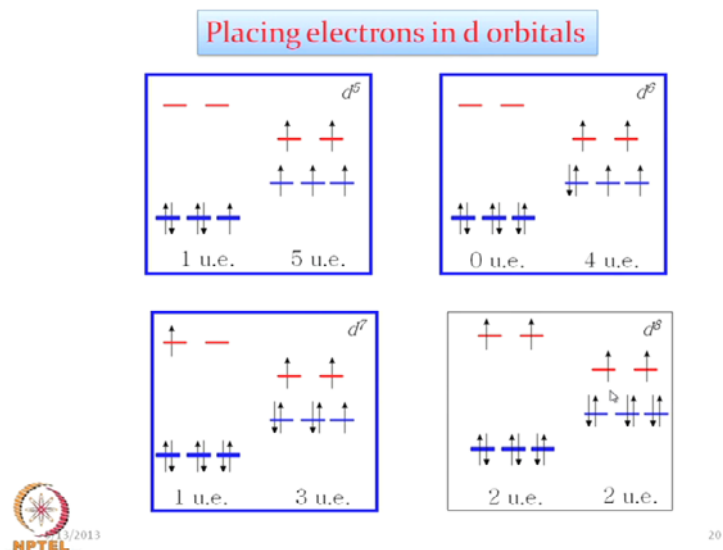
So, we can write it in these two forms: whether we can write in P relative to Δ_o or Δ_o relative to P . But we should be careful which way we are writing and how we are dealing with the strong field and the weak field situation by looking at the number of electrons in these two levels. And also, we are considering since the energy levels, what we are talking about; all are electrostatic in energy. So, this particular Δ_o term is related to the Coulombic repulsion energy for the interaction; and the P term is the corresponding exchange energy for the pairing.

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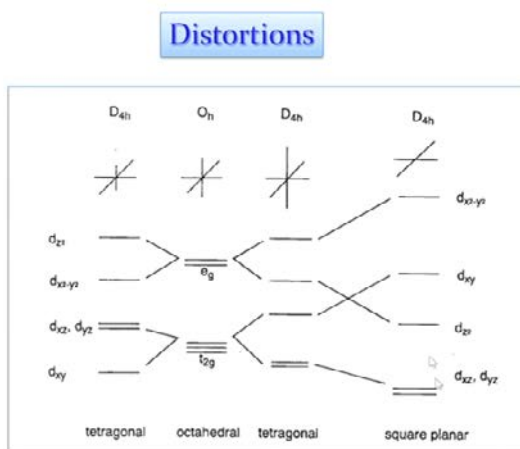
Then, how we find the ground-state electronic configuration, we have seen just now. So, this is the simplest form of writing diagrammatically. So, how we draw the corresponding diagram for the d^4 situation; and example is well-known for manganese system, where we have the hexaco manganese (()) though manganese is in trivalent state; but we get a weak field situation in water environment. So, water environment manganese in the trivalent state. Still we have a high spin complex; that means, we have 4 unpaired electrons. So, in this particular situation, the trivalent manganese cannot force the corresponding pairing in the lower level; that means, the Δ_0 is less in case of this hexaco manganese compound. And is well-known like that of power cobalt cyanide compound that, when you move from aqua to cyanide compound, it would be strong field complex; and the total spin in that particular case would be with 2 unpaired electrons; the two is one; and we are having the low spin complex only.

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Then, how we place these electrons; that what we have seen just now, is pictorially we can elaborate it with the number of unpaired electrons. In case of this low spin one, we have 1 unpaired electron; in case of high spin, we have 5 unpaired electrons for d^5 situation. In d^6 situation, we have the corresponding number of unpaired electrons 0 and 4. In case of cobalt, we have discussed in detail. In case of 7 also, we have the situation here and we have calculated the corresponding energy values also. And in the d^8 situation, we have the situation. In both these cases, which is true for nickel in octahedral geometry that, both the two situations, we have two unpaired electrons; that means, the crystal field will not be able to force the spin pairing for nickel 2 plus whether it is weak field or strong field; we will have two unpaired electrons whether the splitting is less or splitting is more.

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Now, we will just move on to the different types of distortions what we can have from a regular geometry. So, this we will see that, for octahedral geometry, in this octahedral situation, what we find that, all the $m l$ bonds are same. So, when all the $m l$ bonds are same, we can have the regular geometry, which is related to the typical octahedral geometry and which is t_{2g} and e_g in these 2 levels and is octahedral in size and say. And when we try to elongate this along the z-axis, that means, the z out situation; the z out situation, the interaction in the z level is less, which will give rise to the stabilization of the d_{z^2} orbital. So, this is d_{z^2} and this is $d_{x^2-y^2}$. And the situation for the t_{2g} set is also different. So, the t_{2g} set will undergo splitting for tetragonal elongation. So, we have the corresponding crystal field pattern for tetragonal elongation geometry is that, the d_{xz} and d_{yz} will form the doublet; the d_{xy} is here, which will be destabilized compared to this d_{z^2} and we have the other two levels.

And, if we further take out this z-axis to infinite distance, which we have discussed right now that, is a situation, where the symmetry is not changing from d_{4h} to d_{4h} ; but we do not have two electrons. The coordination number around the metal ion is changing from 6 to 4. And we have taught that destabilization of $d_{x^2-y^2}$ orbital and for the stabilization of d_{z^2} orbital, because we do not have any z interaction along the z-axis. And that gives rise to further stabilization of d_{z^2} orbital. And at the expense of that stabilization, we have destabilization of the d_{xy} orbital and stabilization of d_{xz} and d_{yz} . So, we get the ordering for square planar geometry. So, as we move

from octahedral to square planar, more and more we are taking away, pooling away the z-axis ligands. So, we have direct correlation for this t_2g set to this doublet set, this t_2g set to this d_{xy} level.

Similarly, for e_g for this d_{z^2} square and e_g for this $d_{x^2-y^2}$ square level, and now, if we go in the opposite direction, that means, which is known as tetragonal compression. So, this is tetragonal elongation on the right-hand side. And on the left-hand side, it is tetragonal compression. So, in case of compression, the ordering for the elongation is completely reversed. So, doublet will now be destabilized compared to d_{xy} . And these two, that means, $d_{x^2-y^2}$ and d_{z^2} would be again splitted, but in the reverse order as we have seen for the corresponding elongation. So, this d_{z^2} would be up and $d_{x^2-y^2}$ will be down.

So, in a tetragonally compressed form, the d_{z^2} would be the most destabilized one; and which we will find that, which is the compressed one means we have a short metal ligand distance, we have the ligands, and the situation is completely different compared to the square planar situation. And in the square planar situation, we do not have any ligand in the z direction. But here we have the interaction is more in the z direction and we have a short metal ligand distance in the z direction. That is why the d_{z^2} is mostly destabilized in tetragonal compression; whereas, d_{z^2} is stabilized in square planar geometry.

Similarly, this $d_{x^2-y^2}$ is comparatively stabilized compared to d_{z^2} square, which was mostly destabilized in case of the square planar geometry. So, these are the relative ordering. So, if we have a typical electronic configuration for say $3d^n$; this $3d^n$ configuration. And we should be able to write the corresponding electronic configuration quickly if we have an octahedral geometry or a tetragonally compressed or tetragonally elongated or square planar. So, if we have some idea about all these, we should be able write down the electronic configuration for any $3d^n$ system for these typical distortions. So, if we have distortions on any $3d^n$ electronic configuration in all these 4 geometries, we should be able to write down their electronic configuration nicely from these orderings of these different d levels.

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Jahn -Teller effect

It describes the geometrical distortion of molecules and ions that is associated with certain electron configurations.

When orbitals of a highly symmetrical nonlinear polyatomic molecule are degenerate, the degeneracy is resolved by distorting the molecular framework to attain lower symmetry and thus lower energy.



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Then, we can have little extent to a next also that, how these distortions can be very much effective for the corresponding Jahn-Teller effect. So, this is a very simple and effective effect. This can be known from the corresponding interactions if we can have a geometrical distortion of molecules and ions that is associated with certain electronic configurations. So, the electronic configuration will now dictate the corresponding distortion, Just now what we have seen that, the geometry, which we can have a particular type of geometry, can distort the corresponding molecule and the ordering for the different levels. For the electrons, the different d levels are changing. But now, we find that, the differential occupancy of these levels can also distort the structure. So, this is the reverse effect. Now, we have a different electronic configuration. And due to that different electronic configuration, we see the distortions. So far, we have discussed about the distortions first. Then on the bases of those distortions, we are looking for the corresponding electronic configurations.

Now, we see that, this JT effect or Jahn-Teller effect is only operative for certain electronic configurations. And those electronic configurations are sensitive for this particular effect; would be sensitive for this particular effect. So, when orbitals of a highly symmetrical non-linear polyatomic molecule are degenerate, the degeneracy is resolved or lifted; we do not have the degeneracy. Degeneracy means we do not have all the levels together; that means, we have seen that, we have a triplet level, the t_{2g} level or a doublet level, which is a corresponding e_g level. So, this triplet level and the

doublet level have some degeneracy of 2 and 3. So, that particular degeneracy will be resolved or lifted if we have a particular type of electronic configuration, which will be able to distort the molecular framework to attend lower symmetry, thus lower energy. So, we will have the distortion due to this electronic configuration. And the symmetry of the system will be changed, such as the corresponding elongated situation from the octahedral geometry.

And, as a result, we will have the corresponding energy term, which will be also lowered due to that particular splitting. So, if we have a splitting, we would be able to generate some of these levels, which will be lower in energy compared to the other; that means, at the expense of some level, we get a lower energy situation and a higher energy situation. And since the electronic configuration will dictate that, it will go for one particular level compared to the other. So, we will see that, if this can be a regular geometry; but if it is for a copper ion, the copper 2 plus, which have some unequal occupancy in the e g level. So, this particular molecule would be able to go for some kind of distortion, where we get this through some electronic configurations, which will be applicable for tetragonally elongated one. So, that will give rise to the corresponding Jahn-Teller effect. And that we will discuss in detail in our next class.

Thank you very much.