Advanced Transition Metal Chemistry – Crystal Field Theory
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Lecture – 14
Crystal Field Theory (CFT) – Jahn-Teller Theorem

Hello everyone. Once again, I welcome you all to MSB lecture series on advanced transition metal chemistry. In my previous lecture after completing valence bond theory, I gave introduction to crystal field theory by going back to historical background and looking into the contribution of several physicists along with chemists to define this very important theory to explain almost all aspects of coordination compounds. So, now let me continue from where I had stopped. I shall introduce soon Jahn-Teller theorem also in this lecture.

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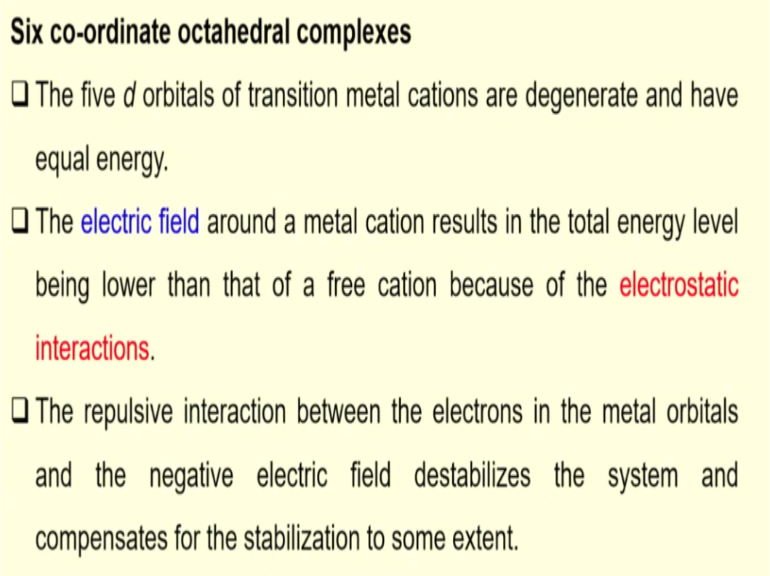

Six co-ordinate octahedral complexes

- ☐ The five *d* orbitals of transition metal cations are degenerate and have equal energy.
- ☐ The electric field around a metal cation results in the total energy level being lower than that of a free cation because of the electrostatic interactions.
- ☐ The repulsive interaction between the electrons in the metal orbitals and the negative electric field destabilizes the system and compensates for the stabilization to some extent.

When we consider six coordinate octahedral complexes, this is how crystal field theory investigation began by considering six coordinated complexes. If you consider any transition metal complex, for that matter, the 5*d* orbitals of these cations are degenerate and have equal energy. The electric field around the metal cation results in the total energy level being lower than that of a free cation because of the electrostatic interactions.

And there will be some repulsive interactions, because ligands are carrying electrons and also metals have electrons, as a result, what happens, the negative electric field destabilizes the system and compensates for the stabilization to some extent.

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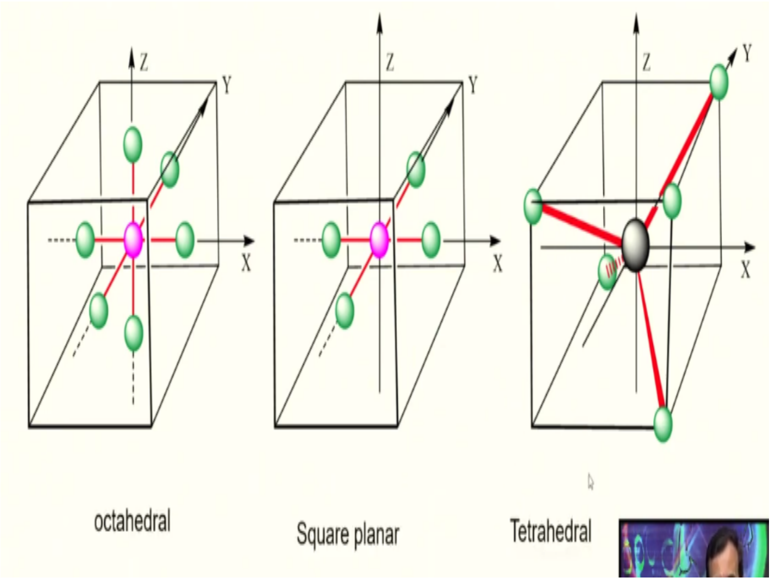

Now, it would be interesting and informative to consider three geometries of octahedral field, square planar as well as tetrahedral field. And for convenient and better understanding, let us try to confine an octahedral molecule, a square planar molecule and a tetrahedral molecule inside a cube with centre occupied by metal ion and surrounding 6 ligands in case of octahedral and 4 ligands in case of both square planar and tetrahedral geometries.

And these green spheres represent ligands and their approach towards the central metal atom to establish metal to ligand bond, and same thing here, and same thing here. If we just look into octahedral molecule, before we begin, we should also consider the Cartesian coordinates and at origin we had kept the metal centre. Now, we can see how the ligand approach direction are coinciding with these Cartesian coordinates.

Why this is important? When we place all 5d orbitals at Cartesian coordinate, we know that d_{z^2} is around the z axis and $d_{x^2-y^2}$ is around x and y axes, and d_{xz}, d_{yz}, and d_{xy} are between the respective axes. This is how the orientation. And now, if we just look into the direction of approach of ligands here, and it is very easy to understand how these ligands will be interacting with five *d* orbitals.

That means in case of octahedral, the 6 ligands will be interacting with two orbitals that are coming in their way: that is d_{z^2} and $d_{x^2-y^2}$, whereas other three remaining orbitals such as d_{xz}, d_{yz}, and d_{xy} are in-between the axis. As a result, what happens? They are having much lesser interactions, and this is where, the splitting of d orbitals into e_g and t_{2g} with the t_{2g} having slightly lower energy and then e_g having higher energy comes into the picture.

Now, let us consider a square planar complex. In this one, 4 ligands are approaching and if we assume this molecule is placed with principal axis being z, so in this case, what happens when the 4 ligands are approaching the metal ion? They are approaching from the x, –x y and –y direction. So in this case, what happens? Since no ligands are coming along z direction that is least affected that means and then rest is very similar to what we saw in case of octahedral complexes.

Now, let us consider tetrahedral complex in which 4 ligands are occupying alternate corners of cube and when these 4 ligands are occupying alternate corners of cube and not this one, you should ignore this one. So, one here, one here, and one here, and one here. So, these 4 ligands are approaching the metal from alternate corners and when they approach and they establish bonds, we will end up with a regular tetrahedron with regular tetrahedral angles here.

So, in this case, again, if you place all the five orbitals around these Cartesian coordinates depending upon their orientations and you will notice clearly that d_{z^2} and $d_{x^2-y^2}$ are not overlapping directly with any of these 4 ligands, in contrast the d_{xz}, d_{yz}, and d_{xy} orbitals would be having larger overlapping with the direction of approach of ligand. As a result, here the energy levels reversal takes place compared to octahedral.

This is what Kramers also depicted much before fully prepared crystal field theory was proposed by Van Vleck. So, in fact this observation was also made by Kramers and others when they were working on crystal field theory before Van Vleck added all these ingredients to explain crystal field splitting in all geometries. So, this is octahedral, this is square planar and this is tetrahedral.

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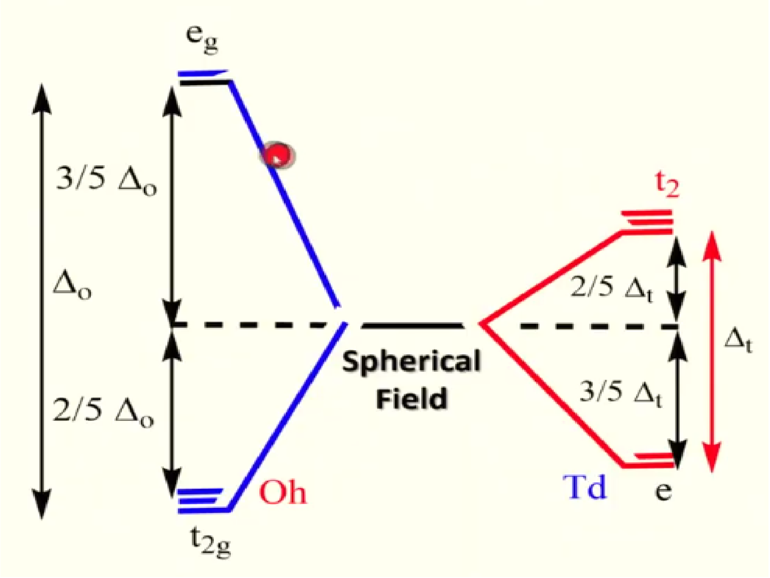

Now, you can see in this one, this is for octahedral and this is for tetrahedral. And if you see the magnitude, also in case of octahedral, and CFS in case of tetrahedral, a remarkable difference is there. And in fact, you can see the difference is quite considerable. That means usually weak field ligands form tetrahedral complexes, whereas strong field ligands prefer octahedral complexes. And whenever we come across a tetrahedral complex, usually the ligand field is smaller and the splitting is smaller and there may be one or two exceptions, but nevertheless this is followed all through uniformly.

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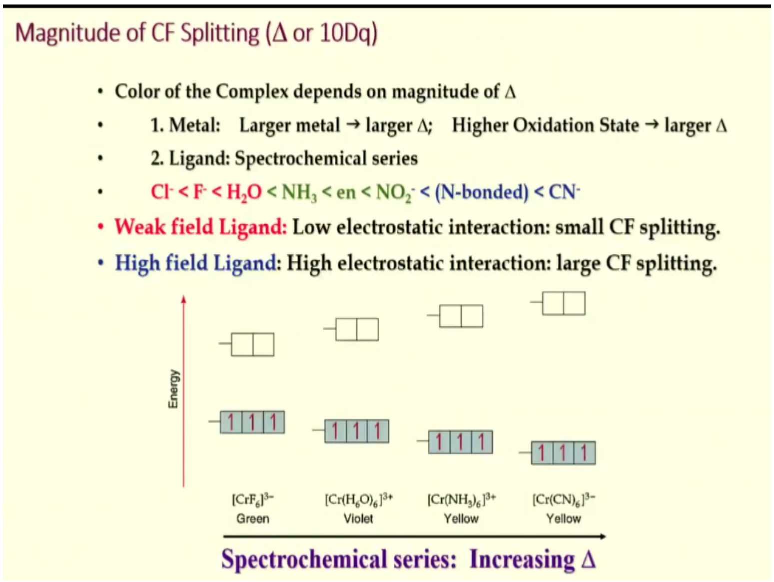

Magnitude of CF Splitting (Δ or 10Dq)

- Color of the Complex depends on magnitude of Δ
- 1. Metal: Larger metal → larger Δ; Higher Oxidation State → larger Δ
- 2. Ligand: Spectrochemical series
- $Cl^- < F^- < H_2O < NH_3 < en < NO_2^- <$ (N-bonded) $< CN^-$
- Weak field Ligand: Low electrostatic interaction: small CF splitting.
- High field Ligand: High electrostatic interaction: large CF splitting.

Spectrochemical series: Increasing Δ

So, now let us look into the magnitude of crystal field splitting, and of course since it can explain the transitions, because crystal field theory says that electrons are no longer degenerate in d-orbitals and did split into two or more levels, as a result what happens one can anticipate electronic transition. Since one can explain electronic transition, we can as well explain colour of the complex using crystal field theory.

And colour of the complex, it depends on magnitude of this crystal field stabilization energy. When we consider a metal, larger metal and we expect larger CFSE and metals with higher oxidation state will be having larger CFSE and for understanding the colour of the complex and magnitude of CFSE, we should look into the positions of ligands in spectrochemical series and this is spectrochemical series for few ligands.

I will be giving a consolidated spectrochemical series much later. And if you see here among them, chloride is the weakest ligand again and then fluoride comes, then water comes and then ammonia, ethylenediamine and nitrate N-bonded one and the cyanide. So, here crystal field stabilization energy is also increasing here and the ligand field strength is also increasing here. What it says is weak field ligands, low electrostatic interaction, as a result crystal field splitting will be very small.

And high field ligands, high electrostatic interaction between the ligands and the metal ion that results in large crystal field splitting. You can see here, how steadily it is increasing as the ligand field strength is increasing. So, that means, it can also give you the magnitude. And also it can give you an idea about the nature of the ligands, whether they are weak ligands, whether they are strong ligands, whether they are of intermediate in nature.

So, this is the origin of spectrochemical series, and here you can see, here the hexafluoro chromium 3– $[CrF_6]^{3-}$ is there, all are octahedral complexes, only ligands have been changed here. When the ligands have been changed from fluoride to water, water to ammonia, ammonia to cyanide and colour also is changing from green to violet to yellow to again yellow and you can see the separation is steadily increasing. That means this clearly shows cyano complexes are much more stable compared to fluoro or halo complexes in general.

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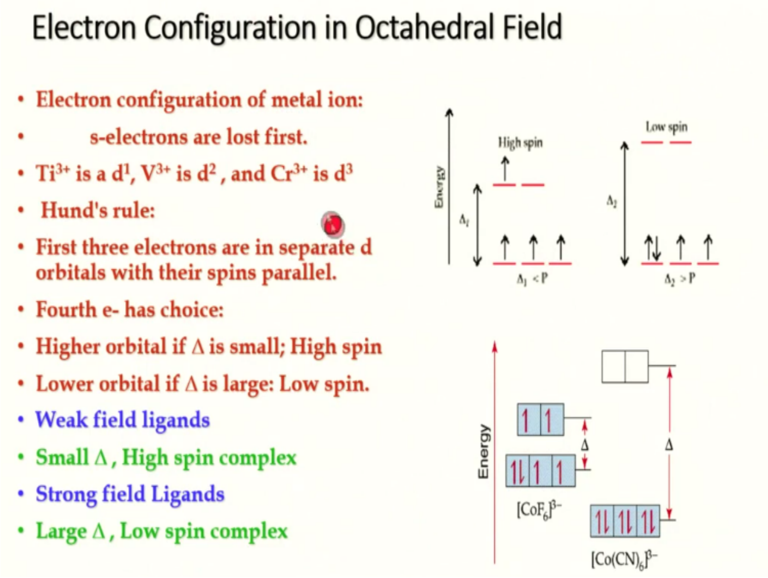

Electron Configuration in Octahedral Field

- Electron configuration of metal ion:
- s-electrons are lost first.
- Ti^{3+} is a d^1, V^{3+} is d^2, and Cr^{3+} is d^3
- Hund's rule:
- First three electrons are in separate d orbitals with their spins parallel.
- Fourth e- has choice:
- Higher orbital if Δ is small; High spin
- Lower orbital if Δ is large: Low spin.
- Weak field ligands
- Small Δ, High spin complex
- Strong field Ligands
- Large Δ, Low spin complex

So, now, let us look into the electronic configuration in octahedral field. When we try to ionize and generate cationic metal ions, what will happen is first s electrons are lost and then that means two electrons present in (n+1)*s*-orbital will be lost and if further oxidation takes place then the electrons will be in a sequence removed from inner d orbitals. For example titanium 3+, we have $3d^2 4s^2$ ground electronic configuration, we are left with one electron, so it is a d^1 system.

Similarly, vanadium 3+ if you consider it is a $3d^3$ $4s^2$ electronic system, if you remove three electrons: it is a $3d^3 4s^2$ electrons system, and if you remove three electrons here, we will be left with the d^2 system here. And then in case of chromium we have $3d^4 4s^2$ system and if you remove three electrons we will be left with d^3 system. And first three electrons are in separate d orbitals with their spin parallel.

That means while filling electrons, Hund’s rule is followed and fourth electron has a choice. For example, if you have three electrons, automatically they will go to individual orbitals, separate orbitals and the fourth electron comes it has a choice of going to fourth orbital or it can also get paired something like this. So, that means here we have to introduce one more term that pairing energy.

Higher orbital if delta (Δ) is small that means high spin complexes and lower orbital if Δ is larger, low spin complexes will be there. That means in case of weak field ligands, this separation is small, as a result what happens electrons will be promoted easily rather than getting paired. That means the CFSE is much smaller than pairing energy. As a result, what happens, it is instead of getting paired, it will go and occupy higher position.

And then in case of strong field ligands, we have larger separation is there, as a result what happens pairing energy will be much smaller than the promotional energy. As a result, what happens they will be get paired instead of going to the higher orbital. So, that results in low spin complexes in contrast, in these cases, where ligand field is small and the separation is small, it is easy to promote electron, we end up with high spin complexes.

And you can see them again magnitude can be very nicely compared here, one with hexaflurocoabaltate here, and your hexacyanocobaltate here. So, you can see one is the weakest ligand, one is the strongest ligand, and that is reflected in the magnitude of the CFSE.

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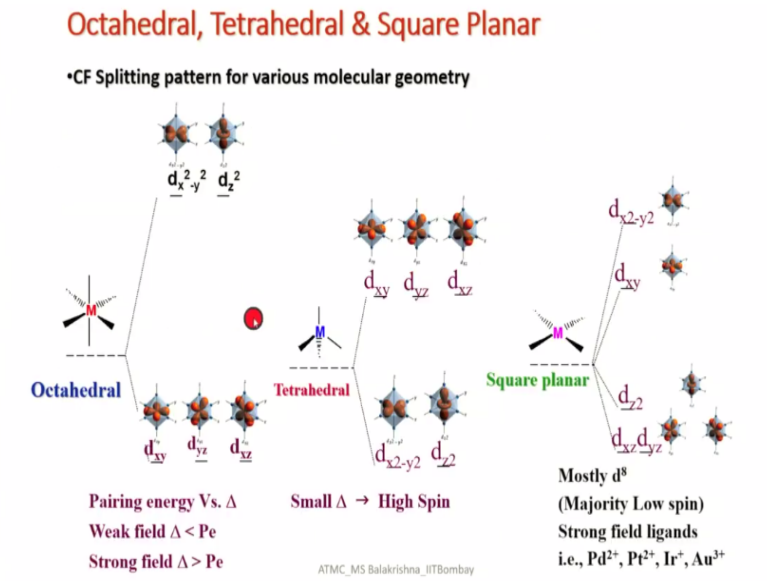

Octahedral, Tetrahedral & Square Planar

- CF Splitting pattern for various molecular geometry

Pairing energy Vs. Δ
Weak field Δ < Pe
Strong field Δ > Pe

Small Δ → High Spin

Mostly d^8
(Majority Low spin)
Strong field ligands
i.e., Pd^{2+}, Pt^{2+}, Ir^{+}, Au^{3+}

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And this compares three important geometries, we come across among coordination complexes. This is a typical octahedral complex and here the corresponding orbitals have shown with relative orientations. And here we have e_g set, we have t_{2g} set. And in case of tetrahedral exactly opposite takes place and *e* are lower in energy and t_2 are higher in energy, but the magnitude is smaller.

And then in case of square planar, what happens, further splitting takes place and mostly d^8, majority of them are low spin complexes with an exception of a few nickel 2+ complexes, for example if you take palladium 2+, platinum 2+, Iridium + and gold 3+ and also rhodium +; most of them they possess the square planar geometry.

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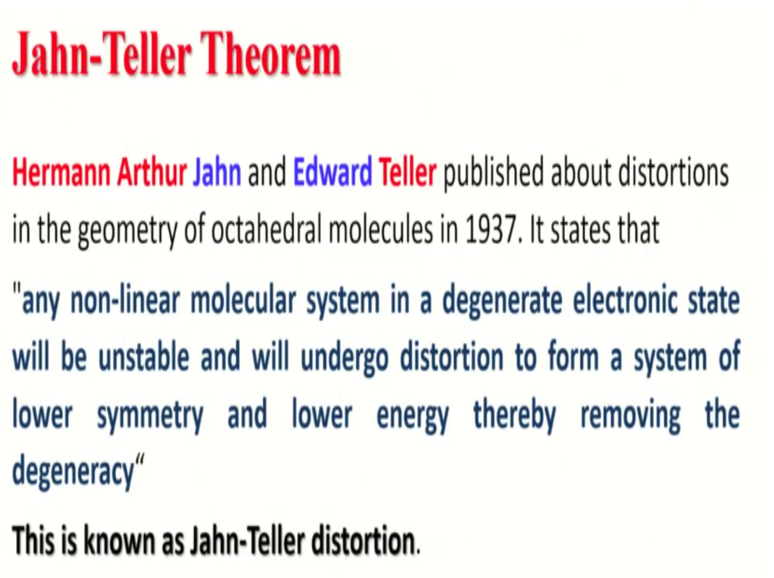

Jahn-Teller Theorem

Hermann Arthur Jahn and Edward Teller published about distortions in the geometry of octahedral molecules in 1937. It states that

"any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy"

This is known as Jahn-Teller distortion.

So, now, let us move on to Jahn-Teller theorem. Hermann Arthur Jahn and Edward Teller full name, mostly books introduce them as Jahn-Teller, but actually the full names are Hermann Arthur Jahn and Edward Teller published about distortions in the geometry of octahedral molecules in 1937. It states that, I quote, any nonlinear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy.

This is called as Jahn-Teller distortion. And especially when we have uneven occupation of electrons in e_g orbitals or e orbital this is what exactly happens. That means odd electrons if they are present in a d^4 system or d^9 system this Jahn-Teller distortion is more pronounced. Ideal examples are d^4 system chromium 2+ and d^9 system with copper 2+.

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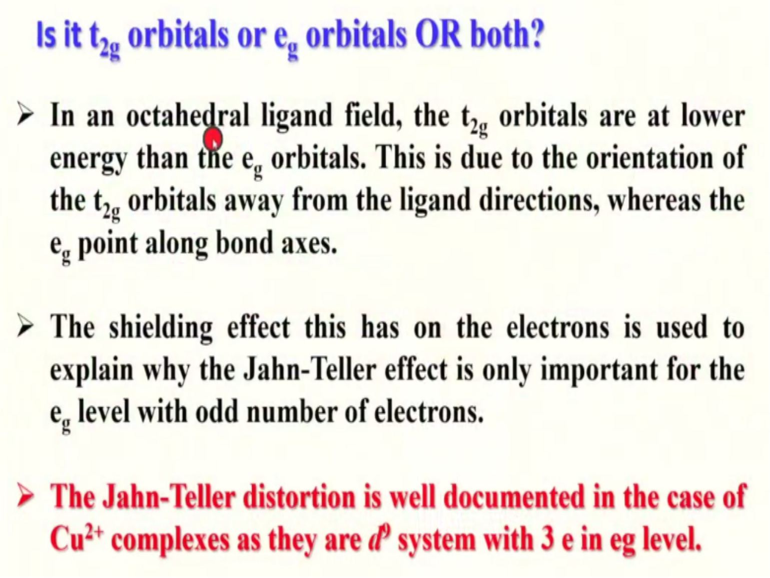

Is it t_{2g} orbitals or e_g orbitals OR both?

- In an octahedral ligand field, the t_{2g} orbitals are at lower energy than the e_g orbitals. This is due to the orientation of the t_{2g} orbitals away from the ligand directions, whereas the e_g point along bond axes.
- The shielding effect this has on the electrons is used to explain why the Jahn-Teller effect is only important for the e_g level with odd number of electrons.
- The Jahn-Teller distortion is well documented in the case of Cu^{2+} complexes as they are d^9 system with 3 e in eg level.

Is it t^{2g} orbitals are e_g orbitals or both? That means here the question is how do the Jahn-Teller distortion is affected? Is it because of filling of t_{2g} orbitals or filling of e_g orbitals or both? Let us try to answer these questions. In an octahedral ligand field, the t_{2g} orbitals are at lower energy than e_g orbitals. This is due to the orientation of t_{2g} orbitals away from the ligand direction that you are all familiar already, whereas the e_g point along bond axes, e g: z, z–, x, –x, and y, y–.

The shielding effect, this has on the electrons is used to explain why the Jahn-Teller effect is only important for the e_g level with odd number of electrons. The Jahn-Teller distortion is well documented in the case of copper 2+ complexes as they are d^9 system with 3 electrons in e_g level.

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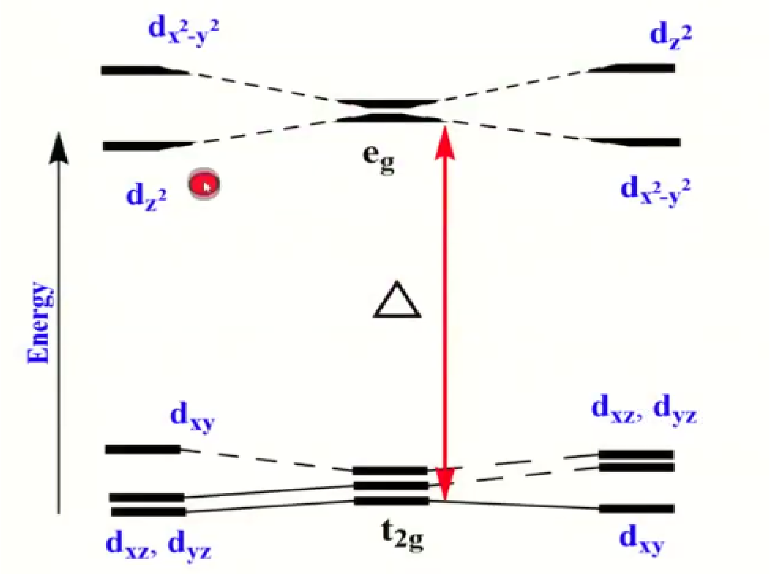

So, that means, when we have 3 electrons in e_g level, we have two options of filling them. That means I can put two electrons in d_{z^2} or I can put two electrons in $d_{x^2-y^2}$, one electron in d_{z^2} and one electron in $d_{x^2-y^2}$. So, what would happen? Let us say I put two electrons in d_{z^2} and one electron in $d_{x^2-y^2}$ so that it has d^9 electronic configuration.

In this case, what is the sequence of this kind of arrangement on stability of the complex. Now, when 6 ligands are approaching the metal ion, what happens, because I have put two electrons here, those approaching from z and –z direction would experience maximum repulsion and try to stay a little away from the metal centre. Whereas here since only one electron is there, 4 ligands approaching around x, –x, y, and –y would undergo or experience less repulsive forces.

As a result, they come a little closer to metal ion compared to what we will see along z direction. In contrast here other way round happens. So here, if you put two electrons in $d_{x^2-y^2}$ and one electron in d_{z^2}, here 4 electrons approaching the metal from x, –x, y, –y direction, experience larger repulsive forces and as a result what would happen, they will stay away from the metal ion relatively compared to two ligands that are approaching along z direction.

They will come a little closer as they have to experience repulsive forces because of only one electron present in dz square. So that means here we have two longer bonds and four shorter bonds. And here we have four longer bonds and two shorter bonds. You can decide yourself which would give you more stability having four weaker bonds and two stronger bonds or four stronger bonds and two weaker bonds.

That means tetragonal elongation is more pronounced when metal ion has an option compared to tetragonal compression, because here, it will be a little less stabilized because you have four longer bonds and two shorter bonds. So, with this information we call this as z, you can see something like this. We can see this one is z-elongation, two long bonds and four short bonds will be there. Whereas in this case z-compression happens.

The compression means basically it comes like this, case of compression. Elongation means it goes like that. When you are pulling up in that direction, the ligands will come closer in the plane. On the other end, if you compress this, z direction along the axis will be coming closer and they will be expanding, so the compression happens in this case.

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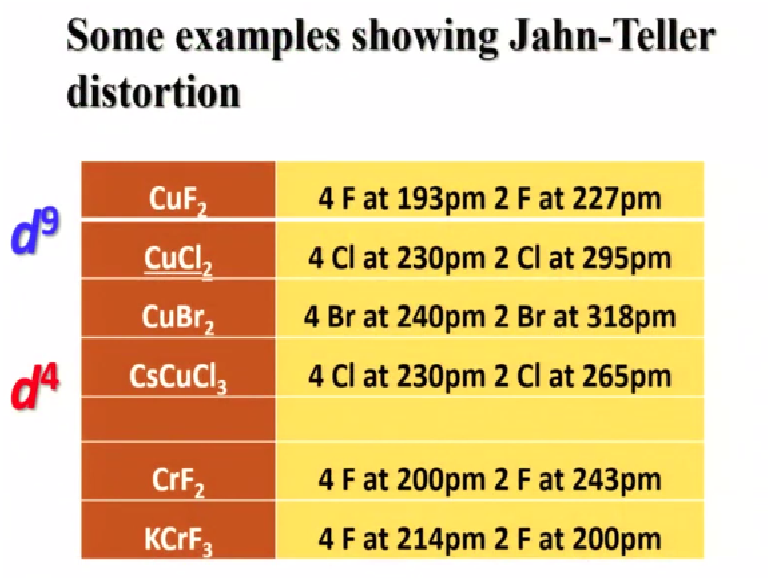

Some examples showing Jahn-Teller distortion

d^9	CuF_2	4 F at 193pm 2 F at 227pm
	$CuCl_2$	4 Cl at 230pm 2 Cl at 295pm
	$CuBr_2$	4 Br at 240pm 2 Br at 318pm
d^4	$CsCuCl_3$	4 Cl at 230pm 2 Cl at 265pm
	CrF_2	4 F at 200pm 2 F at 243pm
	$KCrF_3$	4 F at 214pm 2 F at 200pm

Let us look into some examples where we observe the Jahn-Teller distortions. I have listed some examples here. CuF_2, $CuCl_2$, $CuBr_2$, and here in all of them the metal ion copper is in +2 state and you should not assume just by looking into the composition that they are linear molecules, no, in three dimensional all of them are surrounded by 6 fluorine atoms or 6 halogen atoms in general, in all these cases.

So that means, here if you look into the crystal structure of CuF_2 that means copper is surrounded by 6 fluoride ions; you should remember, 4 fluorine atoms at a distance of 193 picometers, whereas 2 fluorine atoms are at a distance of 227 picometers. So, that means here there are two are longer and four shorter, you can say it is tetragonal elongation. But if you look into $CuCl_2$ again 4 bonds are at 230 picometre and 2 bonds are at 295 picometre.

These two are longer and four are shorter, again tetragonal elongation. In case of bromide, you can see four shorter bonds and two longer bonds along z direction. So, in all these cases, we invariably see tetragonal elongation and same thing is true in this case as well. And that can be extended to d^4 system also. The d^4 system Jahn-Teller distortion is slightly less pronounced because we have only 1 electron here, whereas here we have 3 electrons.

So nevertheless, it also shows Jahn-Teller distortion that is reflected in this bond parameter. If you just look into it 4 bonds at 200 picometre and 2 bonds at 243 picometre. Similarly, if you look into this molecule here 4 bonds are 214 picometre and 2 fluorine are at 200 picometre, so that explains. That means is it possible to see tetragonal compression as well, yes there are examples where we come across tetragonal compression as well.

But if tetragonal compression is there it is very difficult to predict probably it is because of solid state effect. What is solid state effect? By assuming tetragonal compression probably the packing will be very efficient and they can be densely packed and as a result what happens lattice energy increases and stability increases. In those cases, wherever the energy gained through lattice energy by having compression, if it compensates the energy loss due to you know Jahn-Teller elongation in those cases.

What would happen, when one can observe tetragonal compression? There are examples for tetragonal compression as well, but there, you may not be able to explain unless you look into solid state effects or one can verify that one through spectroscopic measurements, electronic spectrum one should record and look into transitions and some time it can guide you.

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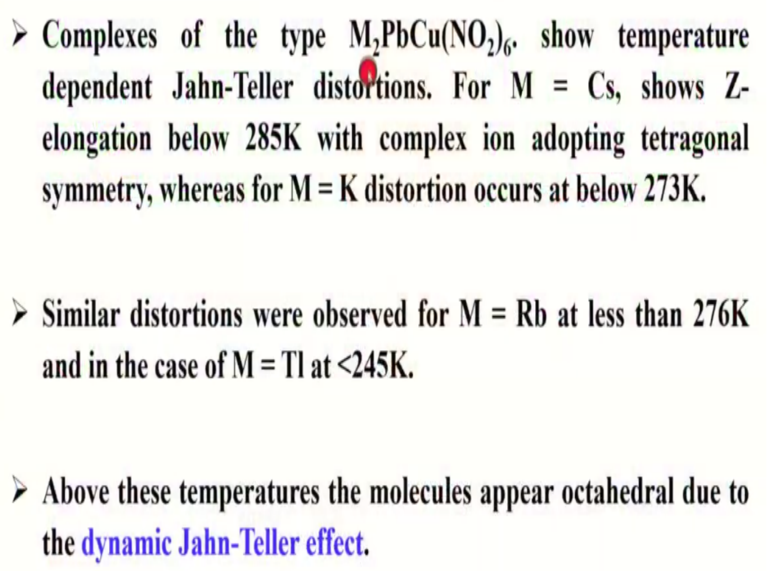

- Complexes of the type $M_2PbCu(NO_2)_6$. show temperature dependent Jahn-Teller distortions. For M = Cs, shows Z-elongation below 285K with complex ion adopting tetragonal symmetry, whereas for M = K distortion occurs at below 273K.
- Similar distortions were observed for M = Rb at less than 276K and in the case of M = Tl at <245K.
- Above these temperatures the molecules appear octahedral due to the dynamic Jahn-Teller effect.

Complex of the type, I have shown here, complexes of the $M_2PbCu(NO_2)_6$ shows temperature dependent Jahn-Teller distortion. For M = caesium, shows z elongation below 285 Kelvin with complex ion adopting tetragonal symmetry, whereas for M = K, distortion occur at below 273 Kelvin. So that means here, temperature assisted Jahn-Teller distortion, one can see.

And similar distortions were also observed with M = rubidium, at less than 276 Kelvin and in the case of M = Thallium, at less than 245 Kelvin. And that means above these temperatures the molecules appear octahedral due to the dynamic Jahn-Teller effect. So that means at a lower temperature what happens, the splitting happens, distortion happens, tetragonal distortion happens but at higher temperature it does not happen.

So, this is called dynamic Jahn-Teller effect. Let me stop here. Continue discussion on Jahn-Teller distortion in my next lecture. Until then have an excellent time reading about crystal field theory.