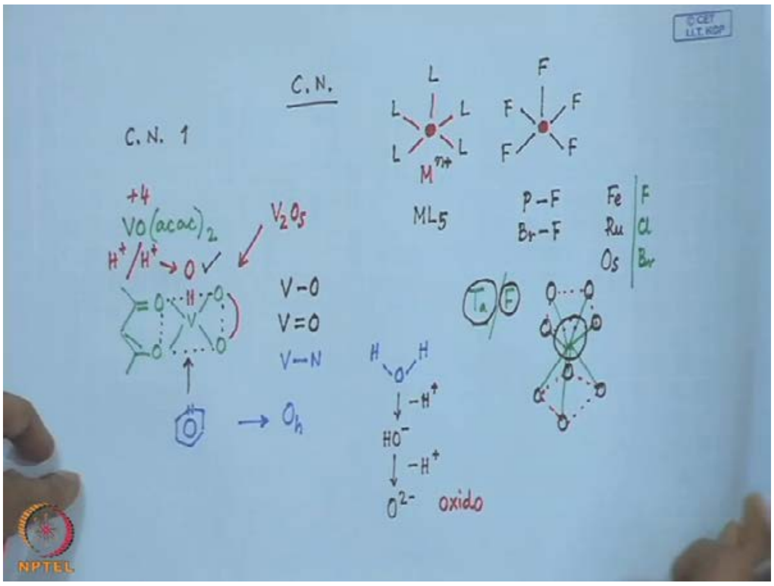
# Coordination Chemistry
## Prof. Debashis Ray
## Department of Chemistry
## Indian Institute of Technology, Kharagpur

## Lecture - 9
## Coordination Number - III

(Refer Slide Time: 00:26)



Good evening everybody. So, today we will just still continue with the different other co-ordination numbers of metal complexes. So, we have started our journey from a very low co-ordination number. We have also seen some examples for the co-ordination number of one. So, this is not very usual, but really unusual situation where we can consider a situation where can have a co-ordination number one. So, we just simply, if we go on increasing the number of ligands around the metal ion center or some other non-metal center.

So, it can be our metal center, where we see that this metal center having some charge on it, it can be bivalent or trivalent; then we can put several ligands around it. So, we get a corresponding situation, if we are just considering, today we are starting from there basically; a co-ordination number of 5. So, M L 5 would be the immediate situation where we can accommodate 5 ligands around the central metal ion.

In the same way, if we just consider that a non-metal center is there, it can be phosphorus, it can be bromine or it can be some other non-metal center, and in that case also if we just see that if the ligands are now the fluorine atom. So, in that case also very much similar to that of the metal complex, where we can see that a particular center is again surrounding in a corresponding typical geometry, where we can have the phosphorus-fluorine bond or the Br-F bond or in some other cases some other bigger type of geometry, we can have.

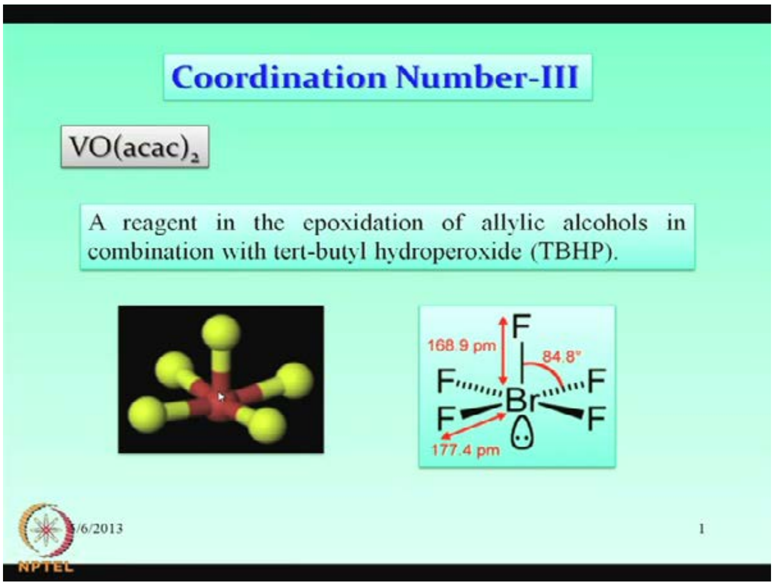
So, side by side, we are just comparing some examples only, that how we can accommodate a situation where we have the metal ligand assembly and in some other case, a typical fluoride, chloride, bromide or any other metal fluoride or metal fluoride is there. Because we can go up to a situation where we can have the other transition metal ions say iron from the first series or ruthenium from the twenty series, or osmium from the 5 d. We see in all these cases, there are the chances of having the corresponding fluoride salt or corresponding chloride salt or corresponding bromide salt.

So, way the metal salts the corresponding alloys are there in the same fashion. These metal ions or some other metal ions say tantalum, etcetera, can form the corresponding metal salt or as the corresponding fluoride, when they are binding to the fluoride center; in that particular case, what we are just thinking that as we go for higher co-ordination number beyond four, we are just increasing the size of the corresponding central element and the size of the ligand is also less.

So, we can have a bigger size and we can have the smaller atoms surrounding the species. So, at one case, we see that we can have the corresponding number of the smaller spheres which are our ligand in a typical situation, where we can have this is one square plane above this bigger sphere, and this is another square planer below the corresponding bigger sphere.

So, we have to consider the all these, that means we have to consider in that particular situation, as a corresponding co-ordination number, as if they are all binding to the central element. So, we can have a corresponding co-ordination number of 1 2 3 4 5 6 7 8. So, in this way, we can just go up from one level to the other and finding how they are involving in the corresponding co-ordination numbers of these different elements.

(Refer Slide Time: 05:57)



## Coordination Number-III

**$VO(acac)_2$**

A reagent in the epoxidation of allylic alcohols in combination with tert-butyl hydroperoxide (TBHP).

/6/2013

So, in this third part of this class, we just considering the different types of co-ordination numbers and one example we are started discussing, that is the vanadyl acetylacetonate, which is VO acac whole 2; and all we know that the acetylacetone molecule is providing two oxygen atom to the metal center through de-protonation. So, it is a mono negative ligand. So, one half is binding like this, in a same way the other orbital is also binding to the metal center, and we have a vanadium oxygen bond as the vanadium species.

So, this particular situation is very different compared to the other, because we can have that all these vanadium oxygen bonds, what we are having, they are made of vanadium oxygen single bond and one is vanadium oxygen double bond. So, defiantly this bond length will be shorter compared to that of our vanadium oxygen single bond; and all these four oxygen atoms which are coming from the to acetylacetonate ligands will remain in a square planer geometry. So, this is our corresponding square planer geometry, and when all four positions in a particular square planer are occupied, we do not have any other option to think of that the vanadium double bond oxygen will be either above the plane, either above this particular square plane, or below this particular square plane.

So, what we get? We are basically getting a square pyramidal geometry is a square plane and the pyramid is the corresponding vanadium oxygen double bond. And we have some room for this reactions, that means we have some positions; that means, if some groups like pyridine is allowed to react with this particular vanadyl acetylacetonate molecule, it can go and start finding some position to have a corresponding vanadium nitrogen bond which would be defiantly longer, corresponding to this vanadium oxygen and the vanadium double bond oxygen. But in that particular situation, we have the option that the situation will go from a typical square pyramidal geometry to an distorted octahedral geometry.

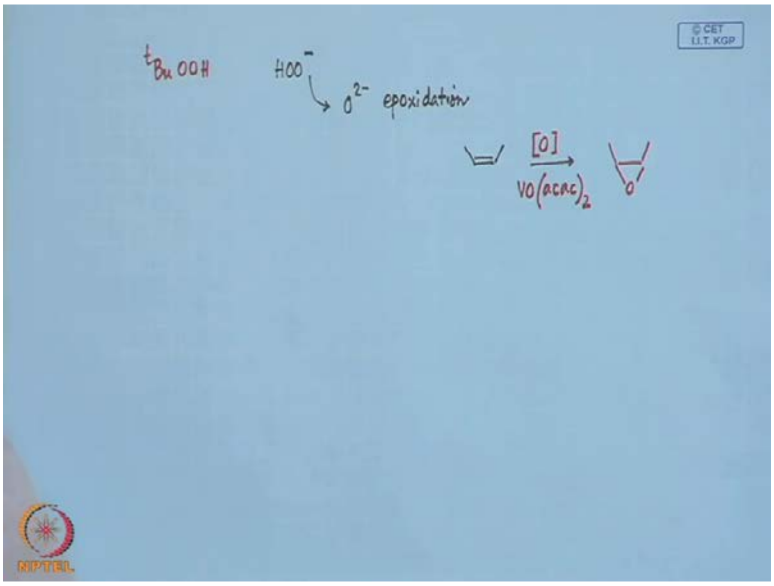
So, not only from the structural point of view, but also some other reactivity pattern, we can see how this particular new groups are coming and entering to the vanadium center or vanadium co-ordinance sphere and how this particular double bond will react further, because whenever we can think of a oxygen double bond, an oxygen double bond to any metal center at the same time, we can consider that through one step of de-protonation, it can go to HO minus; again another step of de-protonation will leave to O 2 minus, which is the oxo anion and this particular one is our typical oxo anion.

So, when it is in the isolated form that means, when it is simply present as O 2 minus, we can consider as, it as a corresponding oxido ligand. And defiantly, it is corresponding property towards the protons which has been last from hydroxido group or the hydroxido group which was generated from the water molecule, the affinity for their getting back the corresponding proton to all these anionic species would be different, when it is bound to a particular metal center such as vanadium in plus 4 oxidation state; this particular vanadium center is in plus 4 oxidation state.

So, what we will see that whenever we have the corresponding one, this is the most able species which can be synthesis, what we have seen in our previous class that how we can synthesis it from V 2 O 5, vanadium pentoxide, it can be generated from vanadium pentoxide. So, once it is formed, it is the most able form of the corresponding vanadium oxo compound or the vanadyl acetylacetonate compound, but there will be chance that it can convert this vanadium double bond o, can be converted like the conversion of oxido group to the hydroxido group or to the water molecule.

So, we can have the corresponding situation where we can put one proton or another proton to this oxido oxygen on the vanadium center. So, that will give us some information that how we can think of some reactivity pattern on this vanadium acetylaceton molecule; because it is very well known that is a very good reagent in the epoxidation of allylic alcohol, this special type of alcohol where the allylic group is present in combination with tertiary-butyl hydroperoxide.

(Refer Slide Time: 12:37)



So, tertiary-butyl hydro peroxide which is used. This is a typical organic peroxide and that organic peroxide can also give rise to the corresponding hydro peroxide anion and it can deliver to the system the corresponding oxido anion, for the reaction which is known as the corresponding epoxidation reaction.

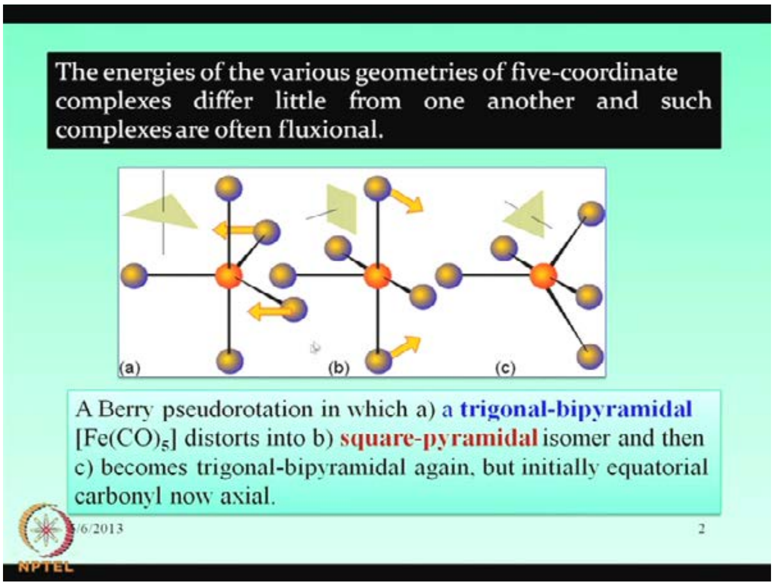
So, if we have a corresponding allylic group for the… Can consider as it is their double bond, so the corresponding epoxidation can take place on it and we get the corresponding epoxide; and this is very much catalyzed by VO acac whole 2. So, we have a typical co-ordination number for this which is very much useful for its corresponding reaction. So, not only the metal ion, its co-ordination number, its co-ordination geometry, but also the corresponding reagent as well as the nature of these ligands are useful for a particular co-ordination compound to function as a good catalyst. Because this is the most important aspect of this particular part of chemistry of these elements, that they can also nicely perform the job of a good catalyst, but the corresponding individual metals or say it is V 2 O 5, but any other vanadyl compound which may not be useful for this simple epoxidation reaction of allylic alcohols.

So, we can take only the help of one particular type of the ligand system, that means the acac ligand system which is bond to the vanadyl system and deliver the corresponding catalytic activity. Similarly just now, what we are discussing that if we have instead of this vanadium center, if we can have the corresponding bromine as the center part and we have the corresponding interhalogen type of compound that Br F 5. So, this will also have a similar geometry corresponding to Br F 5. Here vanadium center is occupying the bromine position, these oxygen is occupying the axial oxygen which is double bonded to the vanadium center, and for other oxygen atoms of the acac ligand is occupying the four other positions in the equatorial position of the square plane giving rise to VO 4 plane in this particular case.

So, what we see in case of the Br F 5 molecule also, which has a similar geometry to that of our this complex vanadium is also square pyramidal in geometry, and when this fluorine, which is, they are present as the corresponding axial ligand. We have a bond angle of close to 90 degree, but its little bit deviated which is 84.8 degree. So, that this means that this fluorine is little bit tilted towards this particular fluorine making the angle less then 90 degree, and the bond angles are also, these bond angles are different, they are 1.77 angstrom, but this particular one is 1.68 angstrom which is axial in nature

So, not only these complex but also we get some inorganic compound which has a close similarity of their structure which is square pyramidal in geometry. So, this particular ball and stick model will also depict the geometry of either the vanadylacetylacetonate molecule or the Br F 5 molecule showing nicely, the corresponding square plane where we have this particular square plane is there, and the epical side, epical side is occupied by this either the fluorine atom in case of Br F 5 or oxygen of this vanadyl acetylacetonate molecule. So, we have now in our hand, the corresponding square pyramidal geometry, for a typical coordination number of 5.

(Refer Slide Time: 17:30)



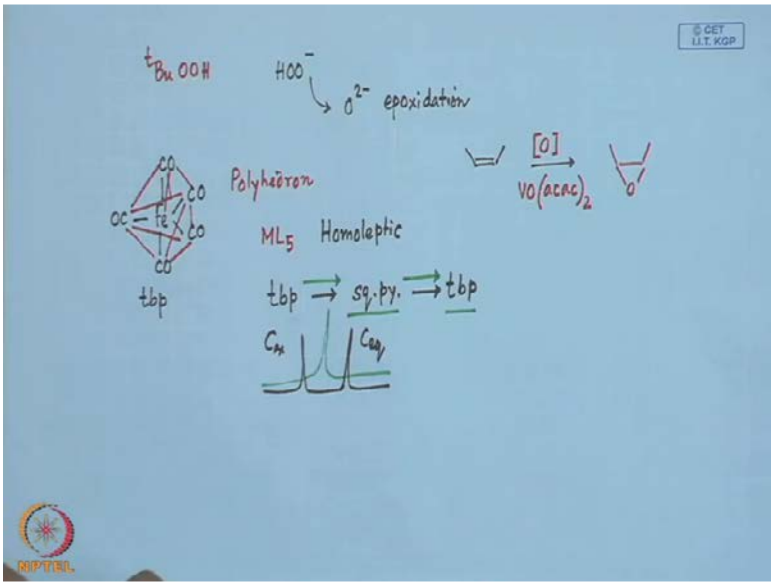
**The energies of the various geometries of five-coordinate complexes differ little from one another and such complexes are often fluxional.**

A Berry pseudorotation in which a) a **trigonal-bipyramidal** $[Fe(CO)_5]$ distorts into b) **square-pyramidal** isomer and then c) becomes trigonal-bipyramidal again, but initially equatorial carbonyl now axial.

/6/2013

So, if we can have any other alternative geometry, which is 5 coordinates. So, all these 5 coordinate complexes can have some differences in energies. So, we can state in these fashion, the energies of various geometries, if there are two possibilities of these two geometries, already we have discussed that out of these two geometries, one is just now we have concluded our discussion about the corresponding square pyramidal geometry, and the second one is that trigonal bipedal metal geometry. So, if they differ little from one geometry to the other, we see that these complexes can function as a corresponding fluxional molecule. So, a fluxional molecule is such that with slight energy change from one form to the other, they basically go from one structure to the other. So, any spectroscopic technique or any other physical technique, if we used to monitor the corresponding structure, it is very difficult to monitor the corresponding geometry in one form only, because they are continuously interchanging from one form to the other. So, one such example is, a very simple example is iron panta carbonyl compound.

(Refer Slide Time: 19:08)



So, this iron penta carbonyl compound will be very much similar to that of what we are seeing for vanadyl acetylacetonate molecule or Br F 5 molecule. So, this penta carbonyl compound has one form which is trigonal bipyramidal in geometry. So, this t b p geometry is present and when we have this corresponding polyhedral. So the, the corresponding polyhedral is trigonal bipyramidaline structure. So, in one particular form, this will be stabilized with this geometry; and if we have these two geometries which are interconvertible means, we can go from one particular geometry to the other with a slight energy change.

So, if we just move from a trigonal bipyramidal geometry to a square pyramidal or vice versa, we see that one isomer will have a different geometry to that of the other and we consider a typical pseudo rotation, and berry propose this particular pseudo rotation in this particular molecule, that is why it is known as berry pseudo rotation, in which a particular geometry in t b p is moving towards square pyramidal isomer and then again becomes trigonal bipyramidal, but the initially equatorial carbonyl is now axial.

So, if this particular molecule can be monitor for the geometry by simple say, C 13 n m r; the carbon 13 n m r will be a very good tool to identify these two geometries. And we find that the corresponding position for the axial and equatorial, that means, which are above the trigonal plane and which are in plane, they resonate at different frequencies for their corresponding C 13 signal in n m r, then once they move from one geometry to the other is very difficult to identify these two groups of carbon monoxide ligands differently, because one, when it is present in the equatorial geometry, it becomes axial and axial molecules of carbon monoxide will become equatorial ligand. So, if they are interconvertible from one form to the other.

So, this is the typical geometry which we can show is that this is the trigonal plane and one above this trigonal plane and another below the trigonal plane, so considering these three spheres. So, these are the corresponding carbon monoxide groups. So, these three spheres basically, they are forming this particular trigonal plane. So, this trigonal plane, one above this sphere and another below is this sphere, and we get a corresponding trigonal bipyramidal geometry. So, how this particular pseudo rotation can take place is very easy to understand from there, that all this three, that means, this three.

So, this also we can consider, they are in one particular plane will remain intact. Only these two carbon monoxide molecules, the arrow, the leveled as two arrows, they will move in these two directions, on the left hand side of figure a, and when they are moving in this particular direction and they are forming, this is the carbon atom and this is also the carbon atom for the carbon monoxide molecule and this red sphere is the iron.

So, initially when they are present in this trigonal bipyramidal geometry, this carbon-iron carbon bond is 120 degree. And due to the movement, we are just increasing the corresponding bond angle between carbon-iron carbon from 120 degree to 180 degree, it has become 180 degree in this particular situation.

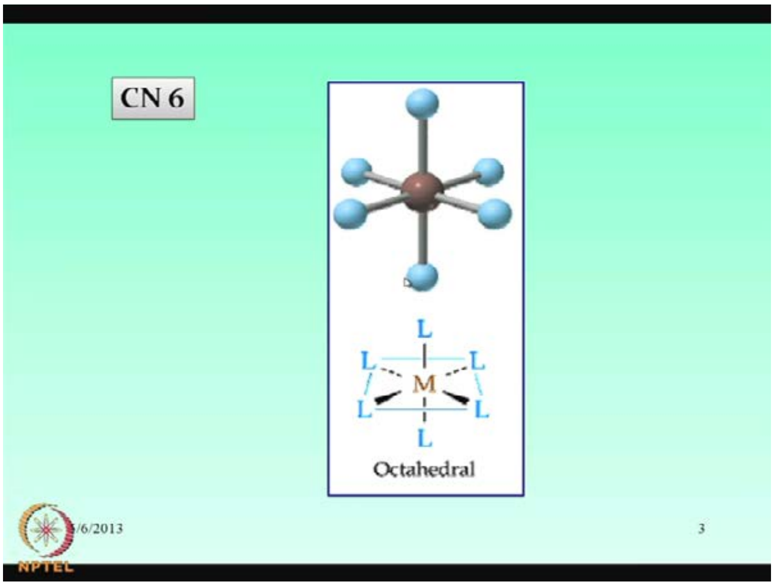
And at this point, the geometry is changing; that means, all these four carbon monoxide molecules have come to a particular square plane; this is the square plane; first one, second one, third one and fourth one. They are present in this square plane; and this particular carbon monoxide has become the corresponding pyramidal one. So, from this direction, we get a square pyramidal geometry. So, t b p geometry has changed to a square pyramidal geometry. So, it is a fluxional molecule in one particular form is changing to the other form and from this particular form, we can get a different type of square pyramidal to trigonal bipyramidal geometry, if we go for because initially in figure a, these two carbon monoxide molecules are moving from here to left, and from here to left again.

Now, these two carbon monoxide molecules which have already moved, they will remain stationary; only the other two in the shown arrow position. So, these two carbon monoxide molecule will move in this direction such that we have these carbon-iron carbon bond originally at 180 degree will now decrease and will make the corresponding including this one to the corresponding trigonal plane. So, after movement, we have now the new trigonal plane like this, and carbon-iron carbon bond which was 180 degree in figure b; will be 120 degree in figure c and as a result, we get a new trigonal plane which is completely different from figure a. Here the trigonal plane is forming through this three spheres. Now, we have three other spheres which are already present over here as the axial carbon monoxide is now equatorial, and equatorial carbon monoxide will be now axial. So, these two types of interchanges is very difficult to identify, which carbon monoxide molecule will be axial and which one is equatorial, in any spectroscopic measurements such as c 13 n m r spectroscopic.

So, we get a change trigonal bipyramidal geometry, but the geometrical pattern will be close to that of a new trigonal bipyramidal one. So, which is true for a molecule which we consider as a homoleptic molecule that means, M is present which has bond to 5 ligand system and all the ligand systems are same, that means, the nature of the ligand are all same, and we call them as, they are homoleptic ligands binding same type of ligand to the metal center. So, when they are changing from trigonal bipyramidal to square pyramidal geometry to again t b p geometry, where not getting back the original geometry in this particular case; and the corresponding axial groups or axial molecules which are present from this groups are changing to equatorial position and equatorial groups are changing towards the axial position. So therefore, in the spectroscopic signature or in the spectrum, we get the corresponding signal positions which will be averaged out, that means, if we have one position for the corresponding axial one and another position for the equatorial one.

So, carbon monoxide, the carbon signal which is coming for axial and which is coming for equatorial; and if we can go for corresponding temperature dependence, that means, if we just simply increase the temperature, that means, we have a very first interconversion between this two geometries t b p to square p and this square p to t b p, and which are becoming very first and we will just lend up with some average signal which will merge these two signals into one. So, that is the basic idea that how we can just differentiate these two types of groups, if we just low down, we can go down to a lower temperature, that means, we can freeze this two individual structures, that means, if we can freeze that this t b p structure and this square pyramidal structure, then these two having two types of say c os groups attached to the iron center for t b p geometry, and two types for the square pyramidal geometry and if their positions for identifications are all different, theoretically we should have four signals, two from this square pyramidal geometry and two from this trigonal bipyramidal geometry, and much more complex pattern, we can have for this type of pseudo rotation for two different types of geometries.

(Refer Slide Time: 30:11)


CN 6

Octahedral

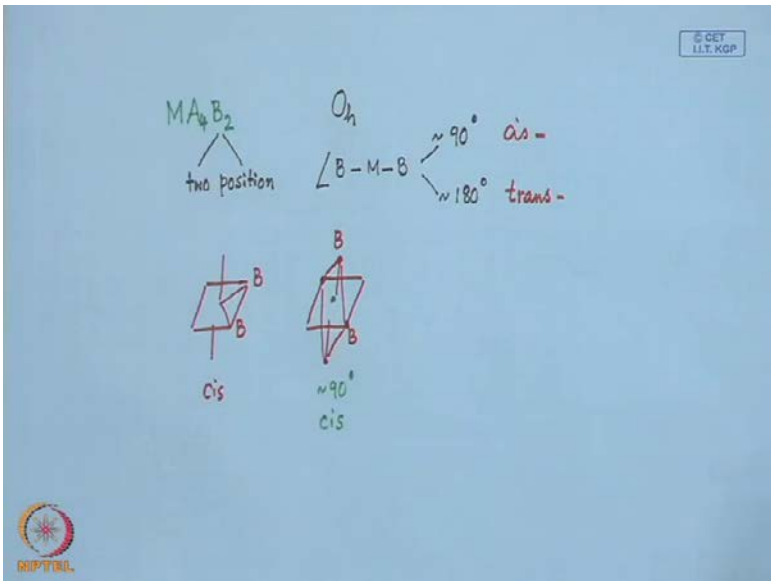
/6/2013

3

So, if we next move to the corresponding higher one, that means, the coordination number of 6; and in that situation, we have the most important geometry, we can have their is the corresponding octahedral geometry. So, 6 groups of ligands which are bound to the metal center, four will be in this particular plane, one will be above this plane, and another will be below this plane and the typical polyhedral structure as 8 faces, 4 above and 4 below the square plane. So, that is known as therefore, the octahedron, and the corresponding geometry is the octahedral geometry, and the metal complex is defiantly the corresponding octahedral metal complex, so will be just talking about the corresponding co-ordination number of 6.

So, most important example which are plenty in number and we have large number of all this examples where the co-ordination number of 6 is only found in these octahedral structures; one such example is trans tetramine dichloride tetramine cobalt 3 compound, and this example we have earlier also seen, which is a metal A 4 B 2 type of compound.

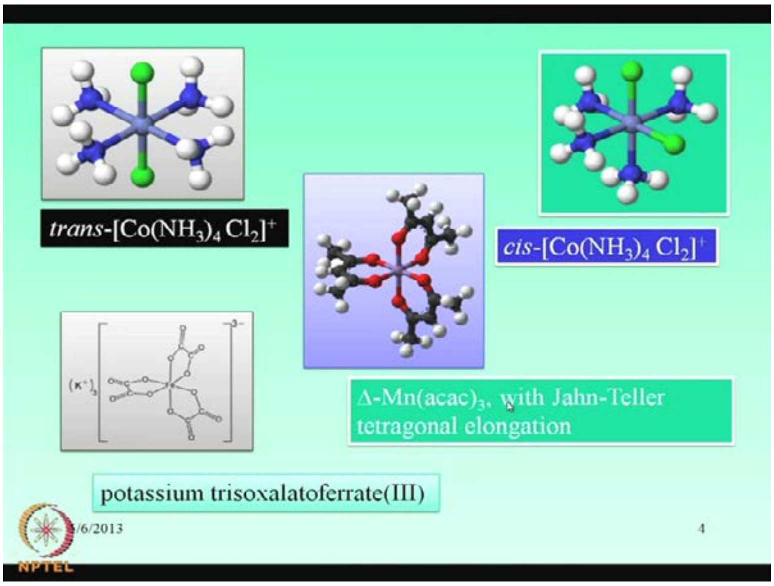
(Refer Slide Time: 31:42)



So, when we fix this particular geometry and we get a corresponding octahedral geometry; and we can have these two positions. So, B 2 can have two positions, and these two positions, that means B M B angle, it can have two types of angles, one would be close to 90 degree and another will be close to 180 degree. So, when this B M B angle which is also true for square planer geometry, we get when these are opposite to each other, we get a corresponding isomer as trans-isomer, we will all discuss this when we will study the isomerism, and this is the corresponding geometry which is a cis geometry. So, when we talk about the corresponding positions of B and B in a octahedral geometry. So, immediately considering this particular square plane, we can consider that we have 90 degree situation in this particular case. So, it would be cis geometry. Similarly, we should also some have some idea, how we get the corresponding geometry if the position of these are like this. So, this is considering this, this, this position and this position is also another square plane.

So, in this particular case also, we have the B and B angle, B and B angle which is close to 90 degree. So, this would also be a cis geometry. So, we can similarly change the positions, not only in the, this particular square plane, but in other square plane, because in this side also, we have another square plane. So, we can have other positions at the same time.

(Refer Slide Time: 34:40)



*trans*-$[Co(NH_3)_4Cl_2]^+$

*cis*-$[Co(NH_3)_4Cl_2]^+$

Δ-$Mn(acac)_3$, with Jahn-Teller tetragonal elongation

potassium trisoxalatoferrate(III)

/6/2013

4

So, when four ammonium molecules are attached to the cobalt center and 2 Cl as the ligand, we get the trans when the chlorine cobalt chlorine bond angle is 180 degree, when chlorine cobalt chlorine angle is 90 degree, close to 90 degree, we get the corresponding isomer as the cis isomer, we level it as cis CoNH 3 whole 4 Cl 2 plus. So, this is the corresponding structure; these green spheres are the corresponding chlorine atom and 4 NH 3 molecules are in plane. So, this in plane is little bit crowded, is surrounded by 4 NH 3 groups which are blue in color. So, you have four cobalt nitrogen bonds in this particular square plane; and the green cobalt chlorine bond and this green sphere bond to the cobalt center one is above the square plane and another is below the square plane.

Similarly, this is the situation where we see that if we consider this particular square plane, already we have this particular chlorine atom in it. So, these two positions are therefore important, if we interchange these two positions, bring the chlorine to the nitrogen position and the nitrogen to the chlorine position. So, these two positions, if these two positions are interchanged, we get the corresponding cis compound. So, cis compound will be in our hand and we get another geometry in the octahedral co-ordination.

Similarly, if we have 3 bidentate ligands. So, these are COO COO is the oxalate anion. So, oxalate is a very good bidentate ligand system, binding to the metal center with 2 oxygen atoms; and when these two oxygen atoms are bound to the iron center, we get one bidentate circulation over here, second from here and third from here. So, it is basically iron trisilicate and since the oxalate anion has two negative charge, we get over all 3 into 2, 6 minus negative charge and iron is in plus 3 oxidation state. So, after balancing the negative charge of 6 units by 3 positive units from the metal center will remain with 3 negative charges which should be counterbalanced by the corresponding potassium ion giving to the center; therefore, we get a corresponding potassium salt of the corresponding tris oxalato compound.

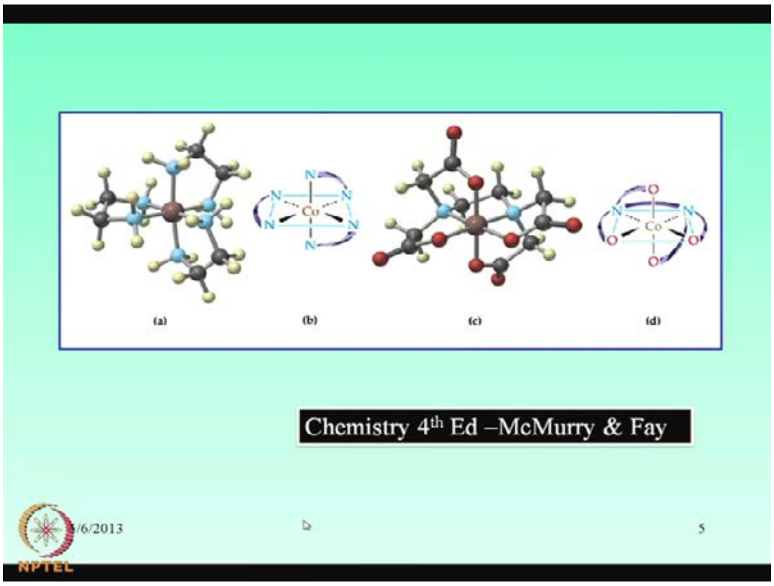
So, is known as potassium tris oxalato ferrite three; and since this molecule do not have any other second type of donor atom, we do not get the corresponding trans geometry or the cis geometry out of this molecule; and only again a homoleptic situation is occurring there, and Fe O 6 co-ordination sphere is generated through tris binding of the three oxalato groups to the ferric iron.

So, this is the situation. In one more case where we have the corresponding acetylaceton group. Just now, we have seen in case of vanadium also, and this delta nomenclature will shortly discuss it, about what is the meaning of this delta nomenclature; before any trischelation, this is the trischelate similar to that of our oxalatechelating is acac chelating and manganese is in plus 3 oxidation state and acac ligand is mono negative ligand. So, this mono negative acac ligand will give rise to three chelation and these red spheres are the oxygen atoms from the acac ligand; this is from the first ligand, this is from the second ligand and this is from the third ligand.

And the interesting property for the manganese in the trivalent state which is a 3 d 4 system is that unequal occupancy of the two levels that means, the t 2 g and e g level that we will discuss, when we will discuss about the electronic structures of these molecules and the crystal field theory. We will find that there will be some Jahn Teller elongation; but right now, what we can consider it is that we have a tetragonal plane this particular type of plane where we have a square plane. So, we have a tetragonal plane and above this tetragonal plane, we have one oxygen and below this tetragonal plane, we have another oxygen; and if these particular axis, if we consider these axis as a z axis, when this is the x axis, one oxygen manganese oxygen axis is the x axis, second oxygen manganese oxygen is the y axis. So, the third is the z axis

So, we will find this particular elongation that this bond that means, along z axis that manganese oxygen bonds are longer compared to the manganese oxygen bonds which are available in the x axis and the y axis. So, the electronic situation is such that we have an elongated octahedral geometry.

(Refer Slide Time: 40:40)



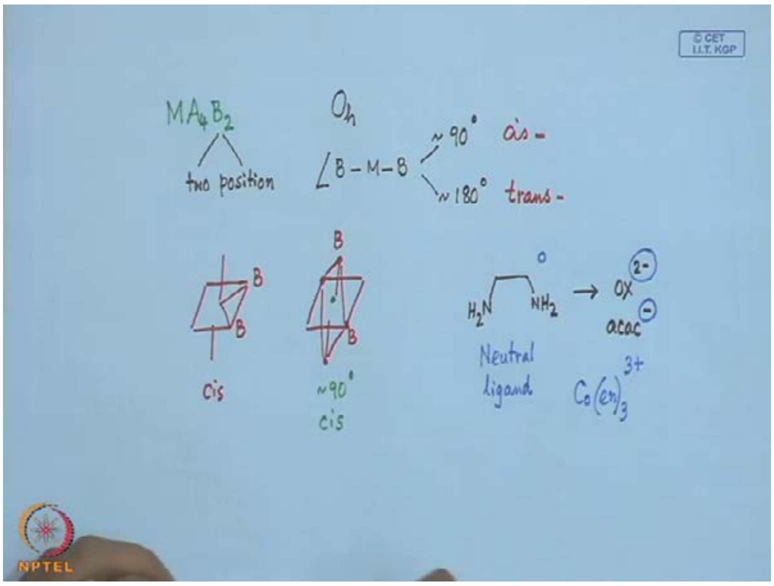
Chemistry 4th Ed –McMurry & Fay

/6/2013

5

Similarly, if we just simply go for ethylene diamine, this particular ligand is our ethylene diamine, and when a two nitrogen atoms of the ethylene diamine molecule. What we know that…

(Refer Slide Time: 40:59)



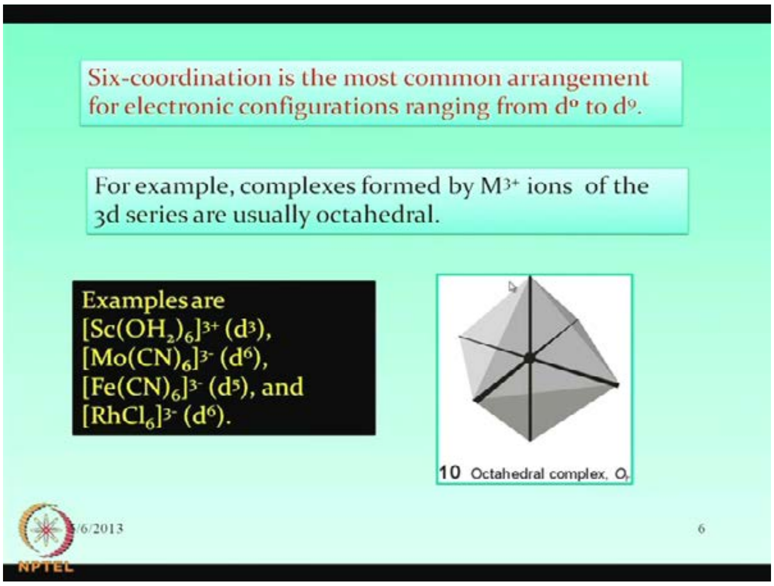
So, this particular ligand is also similar, what to that what we have seen just now to oxalate anion or acac, acetylacetone anion. So, from these three examples, we get, we basically three different types of ligands, where we have in case of oxalate ligand, we have after deportonation, two negative charge; in case of acetylacetone, we have one negative charge; and in case of ethylene diamine, we do not have any other charge which is a neutral molecule

So, this neutral ligand, when it is bound to the metal ion center such that cobalt, we get cobalt of three types that means, tris ethylene diamine cobalt and if the cobalt center is in trivalent state, we get three positive charge on it. So, this is the thing where we have this is the ethylene diamine backbone, NH 2 CH 2 CH 2 and NH 2; this is the first chelate ring, this is the second chelate ring and this is the third chelate ring. So, when first chelate ring is showing. So, this is the ball and stick diagram, usually when you do the axis structure, we get this type of ellipsoid, that means, the atoms are, we are getting as the corresponding sphere, showing the corresponding electron density related to that particular atom, but in the diagrammatic form, we see that this is the corresponding nitrogen, so this nitrogen is starting from here. So, this is the first chelate. So, this is the first chelate; this is the second one from this nitrogen to this nitrogen; and this is the third one from this nitrogen to this nitrogen.

So, when we see that three dimensional view, we see this particular chelate. So, this is the front nitrogen and this is the back nitrogen. So, that is why, this particular curly ring is bold in this particular side, and is thinner on the other side. Similarly, this nitrogen is in this particular plane of the paper, but this nitrogen is back of the plane of the paper. So, the bold is this side, but it is thin in other side. Similarly, we see another situation for cobalt where the ligand is not ethylene diamine, but is E d t a.

So, for this ball and stick diagram, what we see, this is the only backbone related to this one, which is the ethylene diamine backbone; and this ethylene diamine backbone is present over there, and from these ethylene diamine backbone, we have 4 carboxylic acid groups, two from the right hand side and two from the left hand side, so this nitrogen is functionalite through one oxygen and though another oxygen. So, this is one half, similarly this nitrogen is functionlite to this oxygen and through this oxygen. So, this is another one which is ethylene diaminetetracidic acid; that means, the Ed t a. So, when we ride the cobalt Ed t a complex, the diagrammatically, the diagram of this particular ligand would be like this. So, this, all these in formations and all this structures, we can have from the Mcmurry and Fays book.

(Refer Slide Time: 44:57)



Six-coordination is the most common arrangement for electronic configurations ranging from $d^0$ to $d^9$.

For example, complexes formed by $M^{3+}$ ions of the 3d series are usually octahedral.

Examples are
$[Sc(OH_2)_6]^{3+}$ ($d^3$),
$[Mo(CN)_6]^{3-}$ ($d^6$),
$[Fe(CN)_6]^{3-}$ ($d^5$), and
$[RhCl_6]^{3-}$ ($d^6$).

10 Octahedral complex, $O_h$

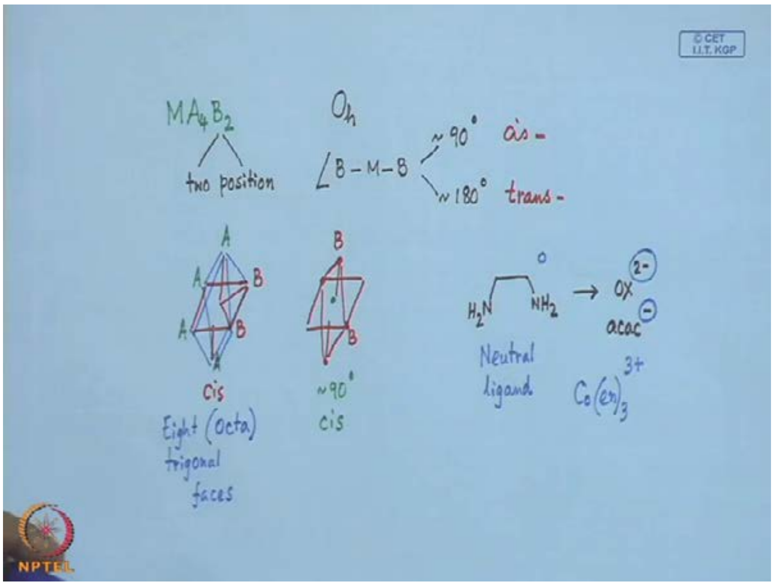
/6/2013

6

So, what you see that most of these geometry, the 6 coordination is most common arrangement for electronic configuration ranging from d 0 to d 9, if the center is divide of any d electron that means, molybdenum in plus 6 oxidation state, which is d 0 system, but in the 4 d level. So, is the 4 d 0 system, but it also prefers a co-ordination number of 6 in octahedral geometry, similarly a d 9 system which is cobalt 2. So, if we have cobalt 2 sorry copper 2. So, this particular copper 2, we can get for the corresponding 3 d 9 situation and that also gives rise to a typical octahedral geometry.

So, further examples, we can have the complexes by metal ion in trivalent series which are in the 3 d series, they are all usually octahedral. So, if we have iron in the trivalent state, cobalt in the trivalent state, all will prefer to have a co-ordination number of 6 in octahedral geometry. Some more examples are there apart from iron or cobalt, and this are belonging to the situation where we have is the polymer in the range of d 0 to d 9, but they are d 3, d 6, d 5 and again d 6. So, for a d 3 molecule, we have the scandium hexaco molecule, 6 water molecules are surrounding the scandium center in octahedral geometry. Similarly, these two are cyano metallates, where we have the molybdenum which is a 3 d 6 system. Similarly, this molybdenum, this is iron which is also heaxcyano, it is a d 5 situation, and rhodium also which is a d 6 situation, and where we have the 3 charge on the complex and we get all as the corresponding octahedral geometry.

(Refer Slide Time: 47:41)



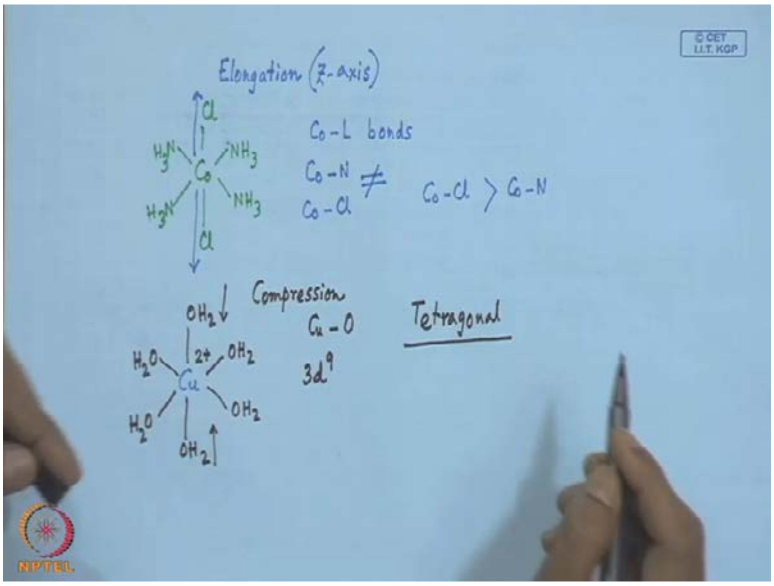
So, if we just consider the typical octahedral geometry from the corresponding polyhedron that means, how the polyhedron will look like the way we have drawn the corresponding geometry is that, in this particular case what we have seen that, if we have

A 4 B 2 molecule which are in cis geometry, and the polyhedron, we can draw, is this particular polyhedron. So, there are basically, this A A B, these are all trigonal faces sorry trigonal, sorry trigonal faces are four in number. So, this is one trigonal face, this is second one, this is third one and this the fourth one. So, four trigonal faces above this A 2 B 2 square plane and 4 below. So, we have 8 trigonal faces. So, this 8 trigonal faces give rise to the name which is octa. So, that is why we have octahedral that means, 8 faces we can have. So, this is the typical structure of this octahedral complex. So, this is one particular trigonal plane, this is the second trigonal plane, this is the third one and the fourth one is not visible, which is above this square plane.

So, this is the metal center and 6 donor atoms are showing. So, this is a corresponding polyhedral arrangement, what we can see from this particular situation and this one particular trigonal plane is visible nicely from here. So, diagonally opposite side, on the back of this figure, back of this polyhedron, we have another trigonal face, but which are completely in reverse direction that means, this trigonal face joining this point, this point and this point, which is the another trigonal face, which is on the back side of this figure.

So, if we have a corresponding distortion. So, how we can get a corresponding distortion in the octahedral geometry? Because whenever we have these different types of donor atoms like that of our cobalt compound, what we have seen that cobalt with four ammonium groups which are, and two chlorine groups.

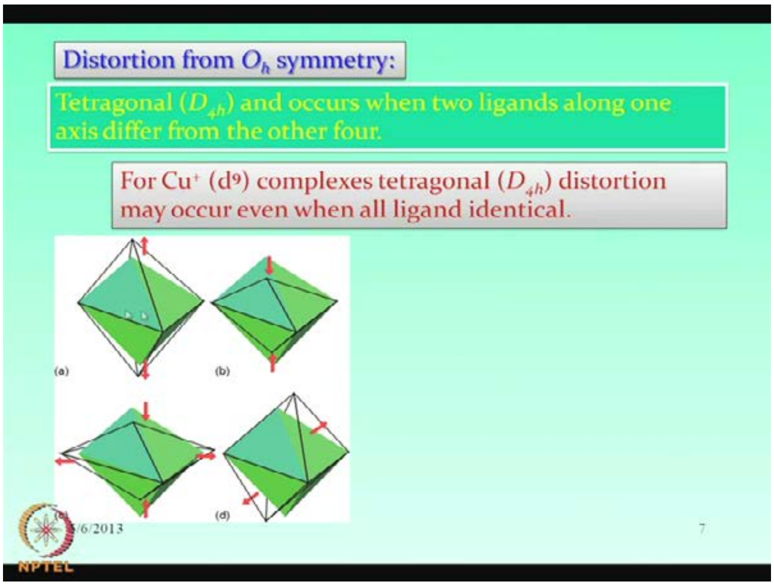
(Refer Slide Time: 50:20)



So, in this particular situation, they are not homoleptic, they are heteroleptic complex, because we have two types of ligand groups present. So, it is a M A 4 B 2 type situation and obviously, we will have 6 cobalt ligand bonds are present; two are cobalt sorry four are cobalt nitrogen and two are cobalt chlorine bond. So, if they are, these two bonds defiantly will be not equal to each other, what we see that if the cobalt chlorine bond is longer than the cobalt nitrogen bonds.

What we see that this particular one that means, we have this cobalt chlorine bonds are longer compared to the four cobalt nitrogen bonds which are in plane; as a result, what we see that we cannot consider this as a regular octahedron, because by definition, the regular octahedron is a such polyhedral arrangement, where all the metal ligand distances are same. So, it has some elongation. So, we consider this as elongation along this direction. So, if the elongation is along the z axis, we consider that the elongation has taken place along these z axis and therefore, it is an elongated structure of a corresponding typical octahedral.

(Refer Slide Time: 52:52)



Distortion from $O_h$ symmetry:

Tetragonal ($D_{4h}$) and occurs when two ligands along one axis differ from the other four.

For $Cu^+$ ($d^9$) complexes tetragonal ($D_{4h}$) distortion may occur even when all ligand identical.

/6/2013

7

So, we have two types of tetragonal distortions; one is the tetragonal distortion like that what we have just seen, and the symmetry level which can change from O h symmetry, because the symmetry was O h, it can be changed to D 4 h symmetry. When two ligands along one axis differ from the other four that was we are discussing that the two cobalt chlorine bond length are different, which are longer compared to the cobalt nitrogen bonds, which are four in number in one particular plane. In case of copper also, in plus 1 oxidation state, which is a d 9 situation the tetragonal distortions which may occur; when all ligands are identical also; that means, the john teller distortion is operating over there.

So, this is the situation, the first situation what we have seen just now; that means, we have the elongation either through different types of ligand co-ordination like this cobalt bound to two different types of ligand rule; one is NH 3 and another is Cl or we can have the copper, which is a 3 d 9 situation, which is not 1 plus its 2 plus. So, copper in 2 plus which is 3 d 9, and when all the ligands are same that means, if all of them are water molecules, we expect that the, all the cobalt oxygen bonds, sorry copper oxygen bonds, copper oxygen bonds are same; but in actual practice, it is not happening, we get unequal occupancy of the electrons in two levels, which are in one t 2 g level and another is the e g level that we will discuss in our some of our future classes, and we see that since the electronic configuration is 3 d 9, we will have two types of copper oxygen bonds, and we will have a corresponding situation where we get a either compression or elongation. So, this is the elongation, this is the compression.

So, this for the corresponding tetragonal system where we find that this tetragonal system is changing along the z axis. So, the z axis is either elongated or it can also be compressed. So, when we get that this two bonds are shorter compared to the other 4 bonds, we get a situation where we have that instead of tetragonal elongation, we get a situation where we can consider it as a tetragonal compression. So, this is one sought of situation where the, we are talking about as the distortion which is tetragonal in nature. So, next we will discuss about the corresponding trigonal distortions.

Thank you very much.