Coordination Chemistry
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Lecture - 15
Bonding in Complexes - I

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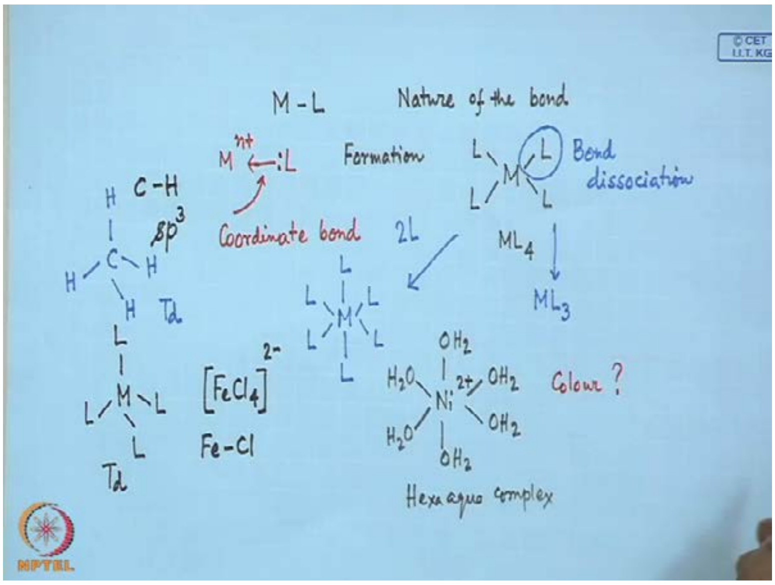

Good evening everybody. So, today we will see how the different metal complexes are forming and what type of interactions we are talking about so far, where we can consider a particular metal ligand bond; that means, the nature of the bond which always plays some important role. Because once we have the metal ion, it can form with the ligand, whether the ligand is a neutral one or anionic one, it can form the corresponding bond. And this particular nature, what we all know now, that it is basically a coordinate bond, where both the lone pair of electrons, if they are available on the L, they can be donated to the metal. So, both the electron pair, which is forming that particular bond are coming from the ligand itself.

So, not only the formation of the bond, it can be more than one, because we know that a particular metal complex can be formed depending on its coordination number and preference of that particular metal ion. So, if it is forming 4 such bonds, we get a corresponding M L 4 species. So, the nature of this bond, the type of the bond and the strength of the bond is basically also reflected when we talk about the corresponding removal of this bond or the breaking of this particular bond. That means, the bond dissociation. So, this bond dissociation would also be very much important, because in that particular case if one L dissociates, will end up with a species like M L 3.

Or sometime, we get the formation of new compound by the addition of two more ligands. Such that this particular M can immediately be converted from a square panel geometry to an octahedral geometry. So, knowledge of the type of the bond is always very much important, the way we know for the different covalent compounds like the formation of the methane molecule from carbon and 4 hydrogen atoms in a particular tetrahedral geometry. So, this tetrahedral geometry will all the time tells us that, we have the carbon centre, and that particular carbon centre is attaching forming 4 C H bonds.

Similarly, a metal can have same type of geometry, we all know that this can be obtained like species F e C l 4 2 minus. So, here also we have 4 such F e C l bonds compared to 4 C H bonds. So, the organic chemistry mainly relying on how good we are handling the corresponding methane molecule, and how we can break the corresponding C H bonds. So, C H bond breaking process as well as the new C H or C C bond making process always we talk about in these in typical organic chemistry synthesis reactions and mechanisms.

Similarly, in coordination chemistry, if we consider the formation of this M L 4 species, and its conversion, and its reactivity, all the time we should focus our attention on the nature of these bonds. So, likewise, if we see that F e C l 4 2 minus compound is also tetrahedral in geometry, and we have 4 such F e C l bonds. So, how we get the corresponding species? Because we know that this particular molecule is forming through some hybridisation. The hybridisation concept was introduced in the time when we people are talking about how the electron pairs are shared between two atoms during the formation of the covalent bond, and the same hybridisation concept was extended towards the formation of this metal complexes also.

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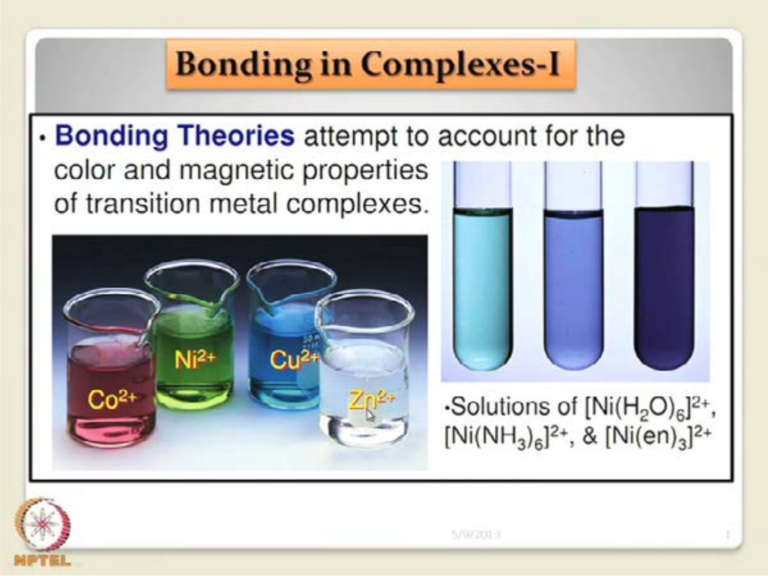

Bonding in Complexes-I

- **Bonding Theories** attempt to account for the color and magnetic properties of transition metal complexes.

- Solutions of $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, & $[Ni(en)_3]^{2+}$

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So in this particular class, where we will talking about bonding in complexes. So, we will be very much interested to know, how the hybridisation concept can be introduced in dealing with the corresponding bonding nature of the metal ligand bonds. Because these bonding theories are very important, starting from the simple chemistry what we all talk about; because we have to explain the colour and magnetic properties of different transition metal complexes. How this colour is originating, the pink red colour for the cobalt 2 plus when we dissolve any cobalt 2 solved in water; or nickel 2 plus, when we dissolve this nickel salt, nickel chloride or nickel sulphate in water; and the blue colour of copper 2 plus in water medium; and the zinc in aqua solution.

So, in all these cases, we all know that whenever we dissolve any nickel salt in water, the preference for that particular nickel centre is, that it will immediately bind 4 water molecules taking from the medium, and they are the ligands in the metal complex that hexa aqua complex. So, we have the hexa aqua complex; and this particular species which is forming in solution, we have to explain the colour. How the colour is originating from the particular species? What is forming immediately in the solution?

Similarly, for other metal ions, where the zinc is also colourless that has to also be explained, why the zinc is also colourless? And if we go further taking this nickel solution, and these are not well matched colours, as the colours are little bit different, because this nickel hexa could be green in colour. And the bluish colouration of the hexa amine compound and the corresponding darkening of the tris ethylene diamine nickel compound can also be explained from a typical bonding, that theory we all expect.

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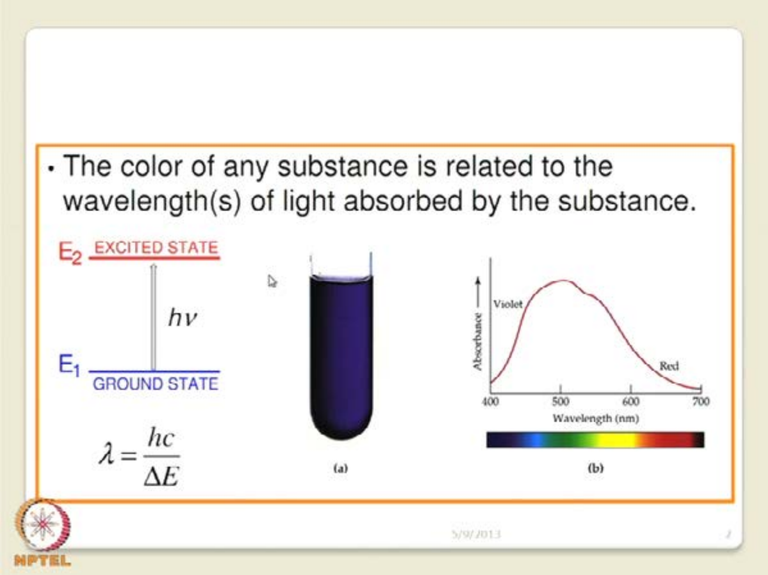

- The color of any substance is related to the wavelength(s) of light absorbed by the substance.

$$\lambda = \frac{hc}{\Delta E}$$

So, this particular colour, what we all know now that, this can be related to the wavelength of the light which is absorbed by the corresponding compound or the corresponding solution. So, why this is coloured blue? Because it has a strong absorbtion band in close to 510 nanometre, this is in the Nanometre scale. And this particular case, it is the corresponding absorption. So, this particular part of the electromagnetic radiation; that means, the greenish part is being absorbed. So, this part when is absorbed, the corresponding colour what we will be getting as the corresponding solution colour is the corresponding emitted colour.

Because in the ground state, we have some electronic transition to the excited state, when the corresponding h nu as the radiation is absorbed. And we can calculate out the corresponding energy gap which u 1 minus u 2 is the corresponding energy gap as delta E, and that energy gap corresponds to a rich new value and the h c can be calculated, and the lambda value can be found out for the corresponding absorption. So, we should have some idea about the gap between the ground state and the excited state for a corresponding colour, what we will be getting for a corresponding compound in solution.

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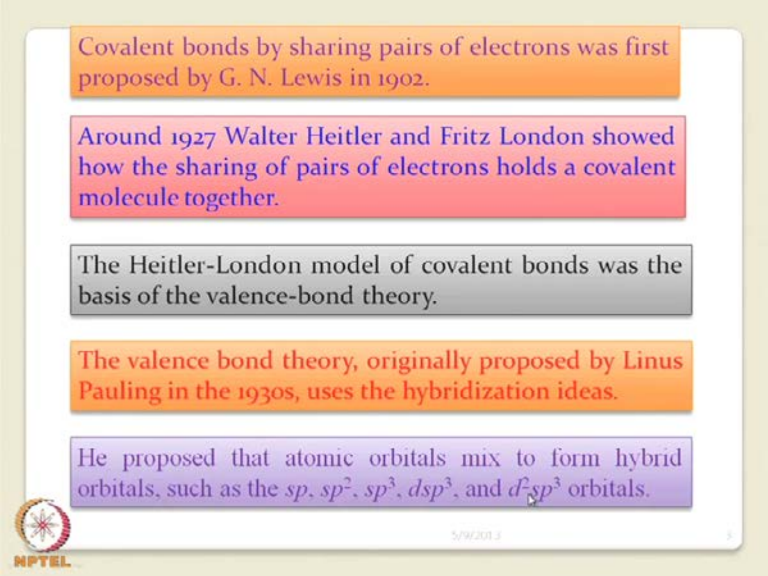

Covalent bonds by sharing pairs of electrons was first proposed by G. N. Lewis in 1902.

Around 1927 Walter Heitler and Fritz London showed how the sharing of pairs of electrons holds a covalent molecule together.

The Heitler-London model of covalent bonds was the basis of the valence-bond theory.

The valence bond theory, originally proposed by Linus Pauling in the 1930s, uses the hybridization ideas.

He proposed that atomic orbitals mix to form hybrid orbitals, such as the *sp*, *sp*^{2}, *sp*^{3}, *dsp*^{3}, and *d*^{2}*sp*^{3} orbitals.

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So, if we can have a corresponding bonding theory for the metal and ligand interaction, such as the interaction between the metal centre and the water molecule itself.

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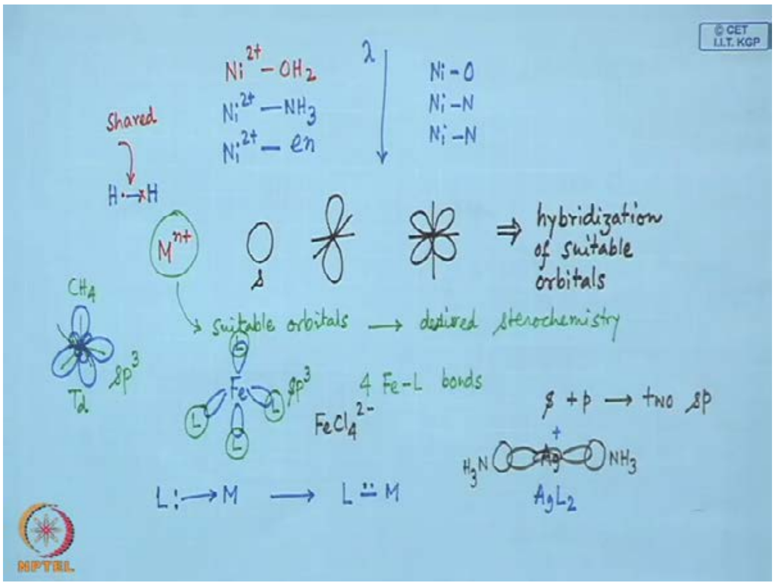

So, how we can modify this interaction of OH2, where water is the ligand then N i 2 plus with ammonia, water is replaced by ammonia, and then the interaction with the bidented chelating ligand, ethylene diamine. So, the colour is changing from one solution to the other, and the interactions related to the corresponding bond which is N i O, N i N and N i N. So, depending upon the corresponding environment for the complex formation and the nature of the bond, how we can consider that when the corresponding octahedral compound is forming, the octahedral complex formation is taking place.

And, how the corresponding electronic transition can take place between u 1 and u 2 which can give rise to the corresponding colour of this particular compound. So, the formation of methane molecule or any other organic compound was first proposed by G. N. Lewis in around 1902. And in there, G. N. Lewis has that idea that the covalent bond can only be formed by sharing of electrons between the 2 atoms.

So, before the advent of the quantum mechanics and any other sophisticated theory, this particular aspect of the formation of the covalent bond in the hydrogen molecule also was proposed. And that particular hydrogen bond formation can be conceived, as if we have one electron from this hydrogen and the second electron from this hydrogen and both these two electrons are shared. So, this was the proposal from G. N. Lewis for the corresponding electron pair sharing between 2 atoms for covalent bond.

But, Walter Heitler and Fritz London, around 1927 showed that this sharing of pairs of electrons holds a covalent molecule together. So, this sharing is very important, and when this sharing is taking place, we can have the entire molecule and we do not have the corresponding atoms separately. So, when we consider the hydrogen molecule, we the definitely have the corresponding hydrogen, hydrogen bond; and the hydrogen molecule has the corresponding hydrogen atoms, they are bounded together. So, that basically gives us the corresponding idea that the electron pairs are localised and those electron pairs are shared between the 2 atoms, and the 2 atoms are being held together for the formation of the corresponding molecule.

Similarly, the formation of the methane molecule as well as the formation of the ML4 species, where we see that one particular ML bond is forming through the sharing of electrons. So, this model which is known as Hitler-London model of covalent bonds was the formal basis of the formation of this corresponding valence bond theory in metal complexes. So, we will consider this as the VBT which is valence bond theory, and these ideas can consider for the corresponding bonding pattern in the metal complexes.

And around 1930, it is Linus Pauling who originally proposed for the different bonds and the nature of the corresponding chemical bond also, where he utilises the hybridisation idea, the concept of hybridisation. So, hybridisation of suitable orbitals, because we all know that whenever we have the metal ion or any other atom, we can have the corresponding orbitals. So, we can have the corresponding s orbital, we can have the corresponding different p orbitals, and different d orbitals. So, these orbitals when they involved in hybridisation; so this idea was (( )) that time for hybridisation. So, hybridisation of suitable orbitals, not all orbitals are being involved for the corresponding hybridisation between these atoms for getting the corresponding bond.

So, if we have a metal ion, and that particular metal ion can have more than one type of orbitals. So, we take only the suitable orbitals, suitable orbitals of the metal ion can go for the corresponding hybridisation, and this particular hybridisation can give rise to the desired stereo chemistry, desired stereo chemistry, because now we all know that when a methane molecule is forming CH4, it has a tetrahedral geometry. So, the sharing of the electron pair for the formation of the 4 C H covalent bonds, will give rise to the corresponding methane molecule as a tetrahedral molecule.

And, the hybridisation is s p 3; that means, one s orbital is mixing with 3 p orbitals giving rise to 4 hybridised orbitals on the carbon atom. So, on the carbon atom, we can have the corresponding hybridised orbitals available. Similarly, for the corresponding hybridisation on the metal centre, if the metal centre is that particular iron centre, and if we can have the similar type of hybridised orbitals what is available for the formation of methane. So, they are available as for the methane.

So, these orbitals like this, on the iron atom is also available there. So, these are the typical s p 3 hybridised orbitals. If we get those hybridised orbitals in a similar fashion, the way we get the corresponding methane molecule, then the ligands with lone pair of electrons will come and overlap with these hybridised orbitals of the metal centre, such that we can have 4 F e L bonds. So, this 4 F e L bonds will be present there within the complex which is F e C L 4 2 minus. So, F e C L 4 2 minus molecule will have 4 such F e L bond, and this is due to the corresponding hybridisation scheme proposed by Linus Pauling.

So, that time he proposed that atomic orbitals form the corresponding atom of the metal ion, mix to form hybrid orbitals; such as, what are the different types of combinations possible. So, these combinations are s p; for mixing of 2 orbitals s and p, giving rise to a linear orientation; and that linear orientation we all know now, that linear orientation means that if we have the s p orbital; that means, mixing s with p giving 2 s p orbitals. So, these 2 s p orbitals, if we consider it is on the silver, silver ion, so this will overlap with the nitrogen atomic orbitals of ammonia molecule giving a linear molecule of A g N H 3 whole 2 plus, this silver is plus. So, like that we have this s p hybridisation for the corresponding A g L 2 molecule.

Similarly, we can have the corresponding s p 2 hybridisation, d s p 3 hybridisation, and the d 2 s p 3 hybridisation for the typical orbital. So, when d 2 s p 3 hybridisation is taking place like s p hybridisation, we are mixing 2 d orbitals, 1 s and 3 p orbitals. So, altogether 2 plus 1 3 plus 3, 6 orbitals we will have. So, why we need 6 orbitals? Because these 6 orbitals are required for the corresponding octahedral stereo chemistry, so if the stereo chemistry is controlled for the formation of the corresponding octahedral compound, we must have 6 hybridised orbitals which are coming from 2 d 1 s and 3 p orbitals.

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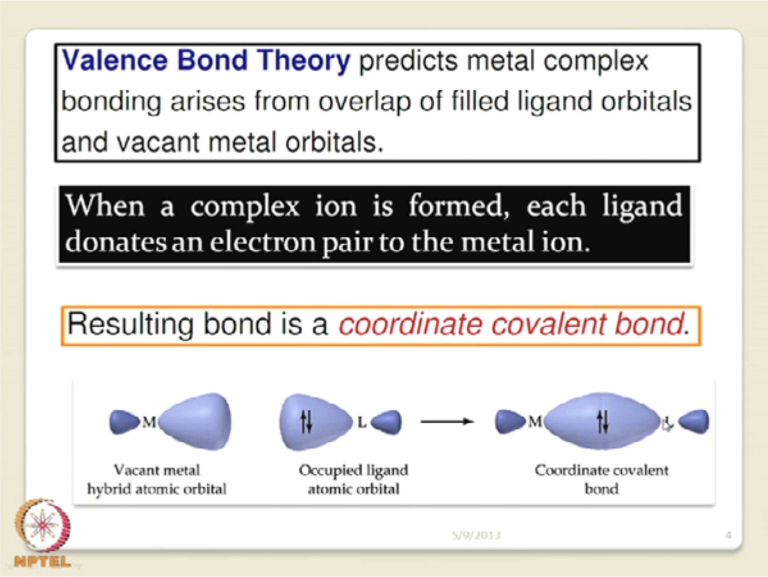

Valence Bond Theory predicts metal complex bonding arises from overlap of filled ligand orbitals and vacant metal orbitals.

When a complex ion is formed, each ligand donates an electron pair to the metal ion.

Resulting bond is a *coordinate covalent bond*.

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So, this valence bond theory therefore, predicts the metal complex bonding which arises from overlap of filled ligand orbitals and vacant metal orbitals. So, these hybridised orbitals, what are forming over there like s p 3, or d 2 s p 3 or s p 3 d 2 type, they are all vacant. So, they are the hybridised vacant metal orbitals. So, we must have first the hybridised vacant metal orbitals, and those hybridised vacant metal orbitals can overlap with the field orbitals of the ligand.

So, ligands can donate the electron pair to the metal orbitals thus forming the corresponding metal ligand bond in a usual way as the coordinate bond, or we can consider this as coordinate covalent bond. So, when a complex ion is formed each ligand donates an electron pair to the metal ion. So, each and every ligand will be utilised for donation of electron pair to the metal ion during the formation of the complex, and we will be getting a corresponding coordinate covalent bond. So, the resulting bond is a coordinate covalent bond.

So, we will be getting a corresponding coordinate bond which is due to the overlap of orbitals of metal and the ligand. So, if we have this vacant metal hybrid atomic orbital; so on M, it can be one of the hybridised orbitals, say s p 3, s p 2, or d 2 s p 3 type of hybridised orbital. So, this is one of the shape of one of the vacant orbital which is utilised for making the corresponding overlap with the ligand orbitals. So, ligand has the corresponding occupied orbital, and the occupied orbital can have the corresponding electron pair in this orbital. So, this M L bond will be forming, and the electron density will be localised between M and L. So, M L bond will look like this and we have the both the electron pair which are coming from the L; the ligand will now be localised between M and L; that means, both the 2 electrons can have now the control by the metal centre as well as the ligand centre, though they are coming entirely from the ligand only.

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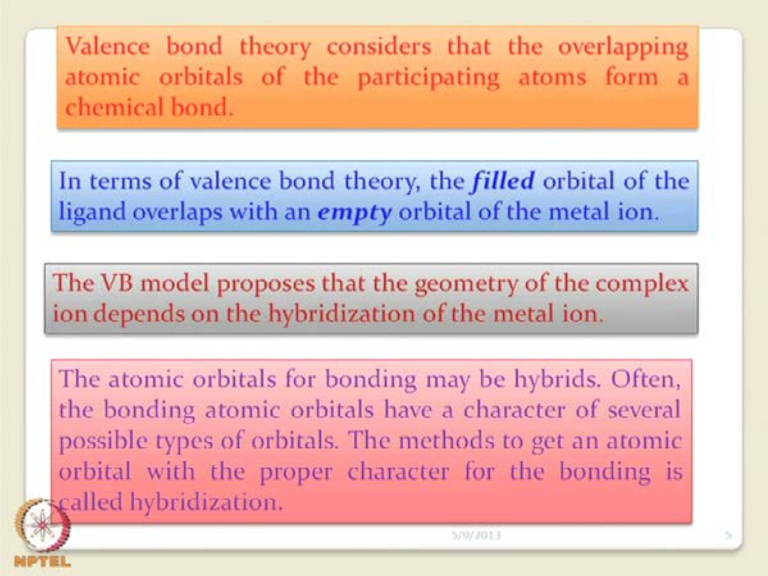

Valence bond theory considers that the overlapping atomic orbitals of the participating atoms form a chemical bond.

In terms of valence bond theory, the ***filled*** orbital of the ligand overlaps with an ***empty*** orbital of the metal ion.

The VB model proposes that the geometry of the complex ion depends on the hybridization of the metal ion.

The atomic orbitals for bonding may be hybrids. Often, the bonding atomic orbitals have a character of several possible types of orbitals. The methods to get an atomic orbital with the proper character for the bonding is called hybridization.

So, this theory therefore, considers that the overlapping atomic orbitals of the participating atoms form a chemical bond. So, how we consider a chemical bond? So, we have the overlap; and 2 atoms that means, the metal ion and the ligand atom are involved. And they are bonded through a chemical bond. And they are engaged in more than one chemical bond to get a corresponding metal complex depending upon their coordination number.

And, in terms of this theory, the filled orbital of the ligand overlaps with an empty orbital of the metal ion. So, this is the idea, and this idea also tells us that the ligand is there, and both the electron pair from the ligand will be donated to M; and once the bond is formed, we just simply write as M L. So, will not consider or will not think of that the both the ligand has been originating from the ligand only, because these 2 electrons will know under control of both the metal as well as the ligand. So, the metal will have the share of this electron, and the ligand will also have the equal share for that electron.

So, the valence bond model proposes that the geometry of the complex ion depends on the hybridisation of the metal ion. So, Linus Pauling proposes the different type of these hybridisations, and depending upon the type of hybridisation whether it is s p 3 or d s p 2, or d 2 s p 2 or d 2 s p 3, we can have the different geometry for the metal complexes. Because the 3 dimensional complex we can have so many geometries possible for all these metal complexes which are not so in number, in case of the corresponding organic chemistry centred on carbon, because in organic chemistry, the carbon centre can have only the tetrahedral geometry.

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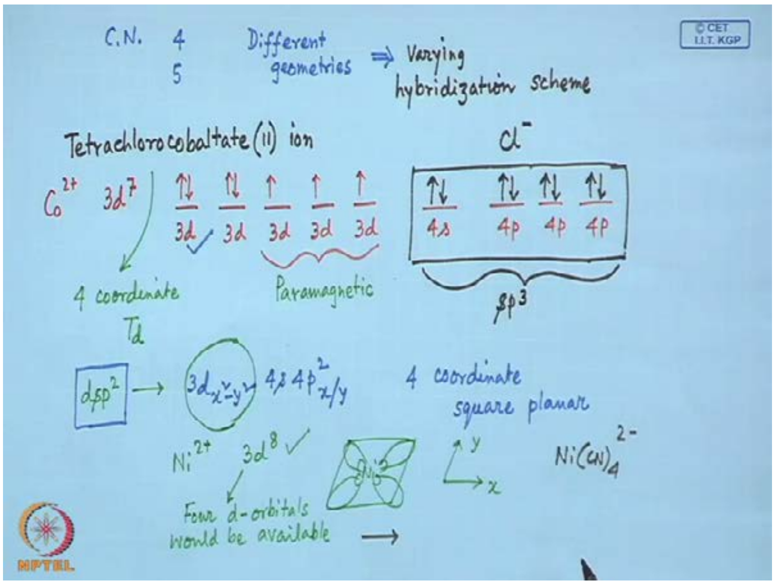

C.N. 4 Different geometries $\Rightarrow$ Varying hybridization scheme

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Tetrachlorocobaltate (II) ion

Cl^-

Co^{2+} $3d^7$

3d 3d 3d 3d 3d

4s 4p 4p 4p

Paramagnetic

sp^3

4 coordinate

Td

$\boxed{dsp^2} \rightarrow 3d_{x^2-y^2}\ 4s\ 4p^2_{x/y}$

4 coordinate square planar

Ni^{2+} $3d^8$ ✓

Four d-orbitals would be available $\rightarrow$

$Ni(CN)_4^{2-}$

But, in case of metal complex where we have seen earlier that depending upon the coordination number say 4 or 5, we can have the different geometries. So, as we have different geometries, we can definitely have the varying hybridisation scheme. So, we must have the hybridisation scheme to accommodate the different number of ligands around the metal centre.

So, the atomic orbitals for bonding may be hybrids; often the binding orbitals have a character of several possible types of orbitals. That methods to get an atomic orbital with the proper character for the bonding is called hybridisation. How we get this? So, this particular methodology, where the different atomic orbitals of the metal centre, say 1 s or 3 p orbitals with proper character; that means, one having s character and 3, 3 having p character are utilised for bonding. So, it is not the pure s, or not the pure p which are being utilised for bonding. Because we need a particular geometrical orientation, the stereo chemistry of the metal complex is different, which cannot be explained by taking the idea that the only the q orbitals are involved in bonding, or only the s orbitals are involved in the bonding, but the hybridised orbitals are involved in this particular type of bonding.

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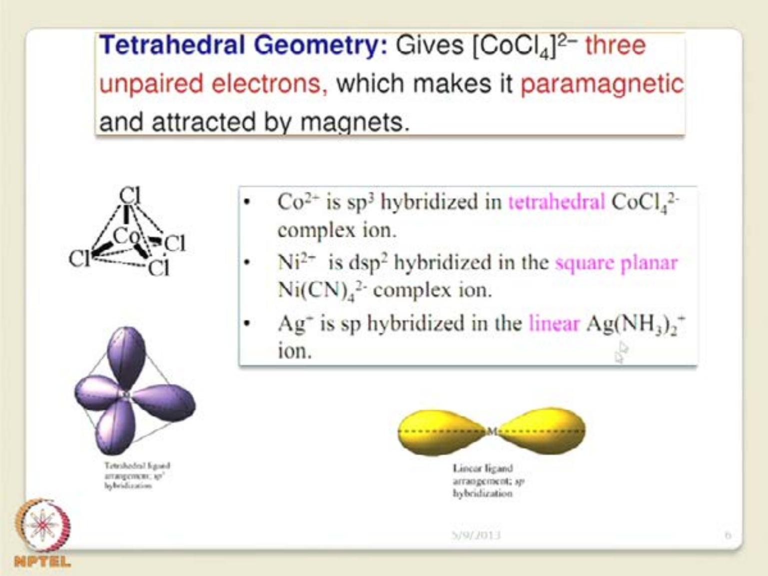

Tetrahedral Geometry: Gives $[CoCl_4]^{2-}$ three unpaired electrons, which makes it paramagnetic and attracted by magnets.

- Co^{2+} is sp^3 hybridized in tetrahedral $CoCl_4^{2-}$ complex ion.
- Ni^{2+} is dsp^2 hybridized in the square planar $Ni(CN)_4^{2-}$ complex ion.
- Ag^+ is sp hybridized in the linear $Ag(NH_3)_2^+$ ion.

Tetrahedral ligand arrangement; sp^3 hybridization

Linear ligand arrangement; sp hybridization

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So, if we see a particular geometry for the tetrahedral complex, like cobalt C l 4 2 minus. So, that number of unpaired electrons, which can have on this particular molecule is important. Because once we make this compound, it can be the corresponding potassium salt, it can be the corresponding ammonium salt, or it can be the corresponding caesium salt as well. So, depending upon the nature of this particular salt, the complex species is CoC142 minus, and it has 3 unpaired electrons.

So, we can have the corresponding unpaired electron on cobalt, which is in plus 2 oxidation state; that means, in electronic configuration is 3 d 7. The 7 unpaired electrons are there, and we are having a geometry of which is related to s p 3, hybridised orbitals. So, all these 7 electrons will be distributed among the 5 levels of the d, and the number of unpaired electrons can be counted from there, considering that this orbitals which are utilised for the formation of this tetrahedral molecule is not connected to the d level, it is only the s level and the p level.

So, this is the corresponding shape of the cobalt tetrachloro cobaltate anion. So, if we have the tetrachloro cobaltate, it is 2, oxidation state is 2. So, tetrachloro cobaltate 2 ion; and it has, since it is cobalt 2 plus, it has corresponding electronic configuration is 3 d 7. So, 5 d orbitals are level available to accommodate the 7 electrons. So, these are 3 d, all 3 d; then 4 s and 4 p. So, if we have the corresponding hybridisation, utilising this s p 3, we will have the corresponding hybridisation like this, where the s p 3 hybridised orbitals they are 4 in number, 4 s p 3 hybridised orbitals will have electron pairs. So, initially they were vacant, and they are coming from the C l minus; the C l minus, 4 such C l minus around the cobalt centre are donated to this particular s p 3 hybridised orbitals.

So, the remaining 7 electrons which were originally present with the cobalt centre; that means, it will have same 3 ion electronic configuration. So, the remaining one; that means, the 7 electrons, these 7 electrons 5; each one is occupying one first, then the paring. So, we have 3 unpaired electron, which is same as that of the corresponding free ion value, that is why we consider the compound as paramagnetic; will be attracted by the magnets also. So, 3 electron paramagnetism can be explained at this particular point, even you consider the corresponding hybridisation scheme.

So, this particular compound will be 4 coordinate and tetrahedron. So, this basically gives us the beautiful hybridisation scheme for the formation of 4 cobalt chlorine bond around cobalt; and we have the tetrahedral ligand arrangement, so this is the tetrahedral geometry; and the cobalt centre will have 1, 2, 3, 4 hybridised orbitals. So, these are the 4 hybridised orbitals, s p 3 hybridised orbitals which are so disposed that they are occupying the corners of a regular tetrahedron.

If we conceive this tetrahedron within a cube symmetry, within a cubic symmetrical arrangement, then alternate corners of the cube will be occupying by the 4 ligands. So, ML4 species; so this chlorine, this chlorine, this chlorine, and that chlorine will be occupying the 4 alternate corners of a regular cube geometry. So, we have 4 hybridised s p 3 orbitals available on the cobalt, and they will overlap with the corresponding field chlorine orbitals for the donation of 2 electrons to these cobalt hybridised orbitals.

Therefore, what we get? We get cobalt 2 plus as s p 3 hybridised molecule in tetrahedral CoCl 4 2 plus complex ion. So, cobalt 2 plus will be there, and will have the tetrahedral geometry; similarly cobalt 2 plus can give series of compounds, so once we know one particular cobalt 2 centre, we should also some idea, have some idea about the other cobalt compound, then plus 2 oxidation state such as tetra thicynate, or cobalt 2 also. So, then you can have the cobalt tetrabromo compound and the cobalt tetra iodo compound, all will be therefore, tetrahedral; and they all will be paramagnetic, and they can have 3 electron paramagnetism, supporting the regular geometry through s p 3 hybridisation.

But what happens if we have the corresponding nickel in plus 2 oxidation state because we know that reaction of nickel 2 plus with C n minus give rise to this particular N i C N 4 2 minus complex species; now the hybridisation scheme is different which is d s p 2. So, this d s p 2 hybridisation for tetracyno nickelate compound is such that which is square planar therefore, that 3 d x square minus y square. So, one of the d level is now utilised for hybridisation; then 4 s is utilised 4 p of 2 ,the 2 of the 4 p levels; that means, x and the y, giving rise to a hybridisation scheme for d s p 2 which is therefore, 4 coordinate again, but is completely different from the tetrahedral geometry which is 4 coordinate, and the geometry is square planar.

So, this particular type of hybridisation scheme allow us something that we have taken out one of the available d orbitals from the free ion electron configuration related to the metal centre. So, if it is N i 2 plus, we all know that it has a next element like cobalt 2 plus. So, it will have 3 d 8 electron configuration; in case of cobalt compound, we are having 5 orbitals available to accommodate 7 electrons. Now, we have utilised one of such d orbitals which are in the x y plane, because the corresponding molecule which are in the x y plane. So, this is the plane which is x and y. So, nickel is sitting over there, and we have 4 hybridised d s p 2 orbitals, 4 hybridised d s p 2 orbitals. So, that is why they are in the x y plane. So, one is out. So, we have the remaining 4 orbitals. So, remaining 4 orbitals are available.

So, 4 d orbitals would be available to accommodate these 8 electrons. So, all the levels would be filled. So, that immediately tells us that the compound which is N i C N whole 4 2 minus, this is a tetracyno nickelate species very easily formed by the addition of cyanide ion to any nickel solution, and it therefore, be diamagnetic. So, this hybridisation scheme also very nicely explain the corresponding magnetic property for the compound tetracyno nickelate.

So, as we have already seen this particular compound we talked about the silver amine complex which should be linear, and since it is linear we should have the introduction of the corresponding s p hybridisation scheme. So, when s p hybridisation is there, we have the linear ligand arrangement; and s p hybridisation will provide 2 orbitals, 2 empty orbitals, hybridised empty orbitals or vacaent orbitals to overlap with the field orbitals of the nitrogen atom of the ammonia; and this side also, another nitrogen atom from the ammonia molecule.

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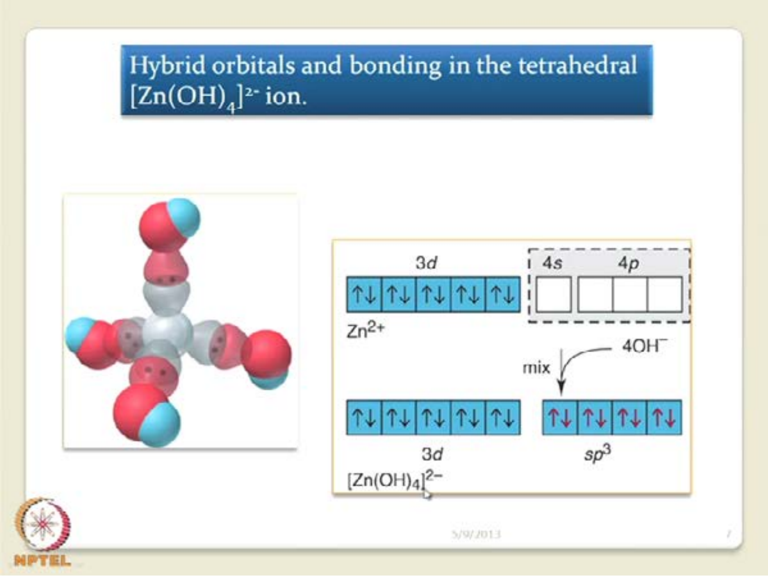

Hybrid orbitals and bonding in the tetrahedral $[Zn(OH)_4]^{2-}$ ion.

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Then, we just, consider what we are just talking about the corresponding tetrachloro, or tetrabromo salt, or the tetrachloro cobaltate. Similar case is happening for tetra hydroxido zinc 2 ion; here we have the zinc centre; and this is the corresponding hybridised orbital, another hybridised, another one, another one. So, is s p 3 hybridised one; and this is the hydroxide o H, this is o H, this is o H, and this is o H then. So, they will again form like tetrachloro cobaltate as the corresponding scheme for the hybridisation.

So, zinc ion which is already in the bivalent state is 3 d 10 electronic configuration, has a 3 d 10 electronic configuration; and this are the vacant levels for s; and 3 p levels are there; these 4 orbitals will mix together, and after mixing we get the 4 hybridised orbitals which are levelled as s p 3; and these 4 hybridised orbitals will next accommodate the 4 electron pairs which are coming from the o H groups. So, this o H groups, o H minus groups basically the hydroxide ions give each of them one lone pair of electrons to be accommodated in the vacant s p 3 orbitals on the zinc centre. So, this is a diamagnetic compound like the free zinc ion; that means, the zinc salt what we can use, the zinc chloride or zinc sulphate, which is also diamagnetic. So, after this type of anionic complex formation, it remains in the corresponding diamagnetic state in z n o H whole 4 2 minus.

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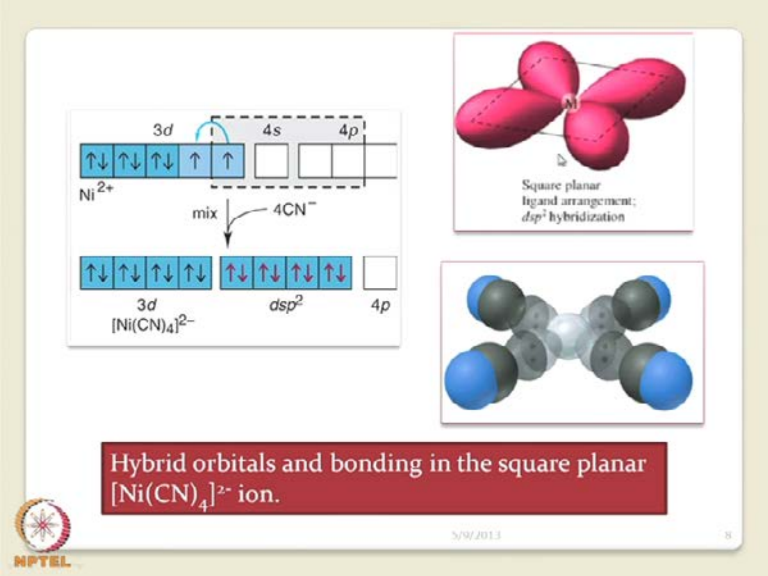

Hybrid orbitals and bonding in the square planar $[Ni(CN)_4]^{2-}$ ion.

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So, this we just have seen that tetracyano nickelate, hybrid orbitals and the bonding in the square planar geometry. So, if we have the corresponding square planar geometry for tetracyano nickelate; and the square plane is like this; and we have one orbital here one orbital, one orbital, and the other orbital in this side. So, they basically give rise to the corresponding tetracyano nickelate species formation.

So, immediately when cyanide ion is reacting with the nickel salt, immediately all the water molecules, because when we are talking this reaction we talk about the corresponding hexa aqua species. So, as we all know the formation of the hexa aqua complex of nickel which is giving hexa amine complex to the reaction with ammonia molecule, or tris ethylene diamine nickel ion, when it is reacting with ethylene diamine.

At the same time, the hexa aqua compound if it reacts with C N minus it gives instead of any octahedral geometry, it gives the square planar configuration. So, we have this particular, that means, only 4 orbitals are available; just now we have described this also; that only 4 orbitals are available to accommodate these electrons. So, initially we have 2 electron paramagnetism on the free nickel centre. So, this paramagnetism form the free ion is no longer available, because we have forcing this particular pairing; that means, this electron is boost to this level, to give rise to 4 vacant levels as d s p 2, which is utilised for the corresponding hybridised orbitals, which are square planar in geometry.

So, these are the 4 hybridised d s p 2 orbitals which are pointed towards the 4 corners of a regular square. And they are next overlapping with the corresponding C N minus groups to give rise to the corresponding tetracyano nickelate molecule. So, this is the state for the 4 coordinate molecule like tetrahedral and square planar.

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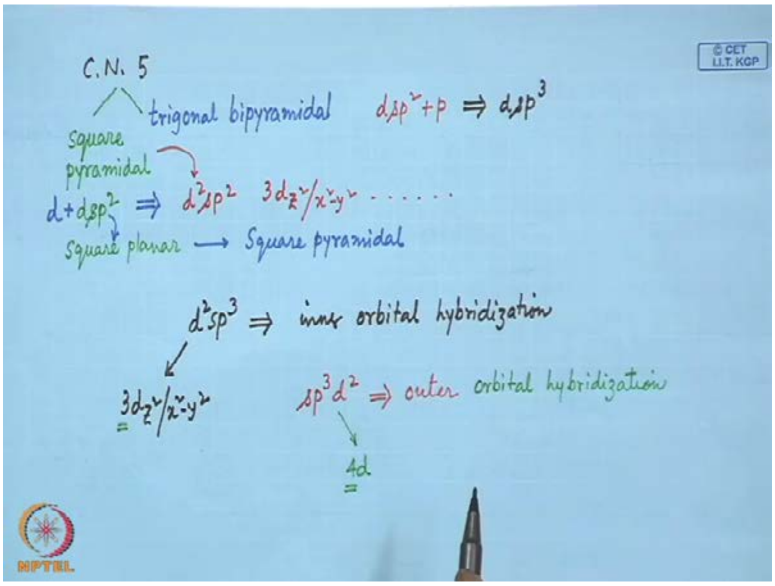

C.N. 5

trigonal bipyramidal $dsp^2 + p \Rightarrow dsp^3$

square pyramidal

$d + dsp^2 \Rightarrow d^2sp^2$ $3d_{z^2}/x^2-y^2$ ......

square planar → Square pyramidal

$d^2sp^3 \Rightarrow$ inner orbital hybridization

$3d_{z^2}/x^2-y^2$

$sp^3d^2 \Rightarrow$ outer orbital hybridization

4d

But, we have discussed so much about the corresponding coordination number of 5. So, in coordination number 5, what we have seen that, we can have 2 different geometries: one is square pyramidal and other is trigonal bipyramidal.

So, in square pyramidal geometry, like that of the square planar compound, we can have the corresponding square pyramidal geometry of hybridisation scheme is d s p 2. For the d s p 2 hybridised scheme, we have already seen for square planar; and we want to move from square planar to this square pyramidal . So, we put now one extra orbital. So, what orbital we will put now? One t orbital. So, this case for the square pyramidal one, because this is for square planar, the d s p 2 for square planar, and when we add one more d level, one more d orbital available for that, for square pyramidal we will have d 2 s p 2 hybridisation. So, in case of d 2 s p 2 hybridisation, we will be utilising one more d apart from the d x square y square, so the new d, which will be 3 d z square. So, we will have 3 d z square as well as 3 d x square y square, and the remaining what we are utilising for d s p 2 square planar geometry.

So, this square planar geometry can be transformed to the square pyramidal one, like this, through the addition of one d. Similarly, this trigonalbipyramidal geometry can be moved from d s p 2, which was there for the square plane arrangement, with the addition of 1 p now. So, for trigonal bipyramidal geometry, we have the corresponding hybridisation scheme as, this as d 2 the trigonal bipyramidal one would be d. Therefore, d s p 3, 1 d, 1 s and 3 p orbitals, so these are the square pyramidal one; and therefore, we get the corresponding two types of hybridisation scheme for the trigonal bipyramidal geometry also.

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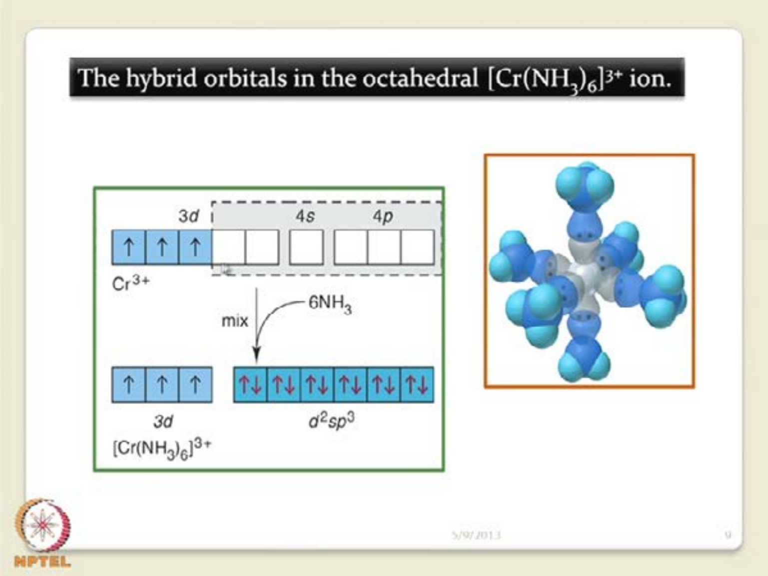

The hybrid orbitals in the octahedral $[Cr(NH_3)_6]^{3+}$ ion.

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Next, we can go for the octahedral geometry; in case of octahedral geometry, what we can have for the hexa amine chromium 3 plus, the hybrid orbitals in this octahedral geometry can have all the 6 directions in the octahedral geometry; all the 6 directions we have the hybridised orbitals. And now the hybridisation scheme is utilising 2 d levels for the scheme and 1 s another 3 p 3. So, s p 3 was known, d s p 3 we know.

So, now, we put one more d from trigonal bipyramidal to octahedral geometry; we will utilise one more d for this octahedral hybridisation scheme which is d 2 s p 3. And we have 3 unpaired electrons in the free ion configuration. So, those 3 are still remaining with that of our compound. So, it shows 3 electron paramagnetism, when we move from octahedral hybridisation for d 2 s p 3. And this is one type of hybridisation where inner d orbitals are utilised. So, we consider this d 2 s p 3 as inner orbitals, inner orbital hybridisation, because the utilised this d levels are 3 d z square and 3 d x square minus y square. So, if we utilise the other d; that means, the 4 d z square and 4 d x square minus y square, then we can have the corresponding hybridisation as the outer orbital hybridisation.

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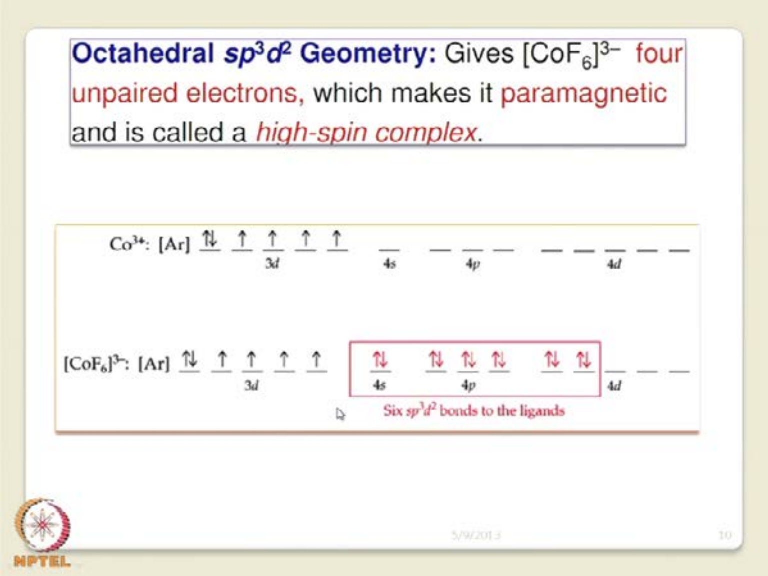

Octahedral *sp^3d^2* Geometry: Gives $[CoF_6]^{3-}$ four unpaired electrons, which makes it paramagnetic and is called a *high-spin complex*.

So, both these 2 are possible. In this particular case, where we have the other one; that means, the s p 3 d 2 hybridisation. And in this s p 3 d 2 hybridisation, which can give corresponding cobalt compound, hexaflorocobaltate having 4 unpaired electrons, because all the d levels are now available for cobalt 3 for accommodating the electrons which makes it paramagnetism and is called as a high spin compound. Because cobalt can have 2 electronic configuration - one is low spin, another is high spin. So, this particular compound, where maximum possible paramagnetism is available; we consider it as a high spin compound.

So, the utilised level is s p and 4 d levels now. So, utilised levels are 4 d z square and 4 d x square minus y square, giving rise to 6 s p 3 d 2 bonds to the ligands. So, these bonds are there; and these bonds are therefore, giving rise to the 6 s p 3 d 2 levels for the typical hybridisation for the hexaflorocobaltate compound. So, this hexaflorocobaltate compound has therefore, 4 unpaired electrons to accommodate giving rise 4 electron paramagnetism.

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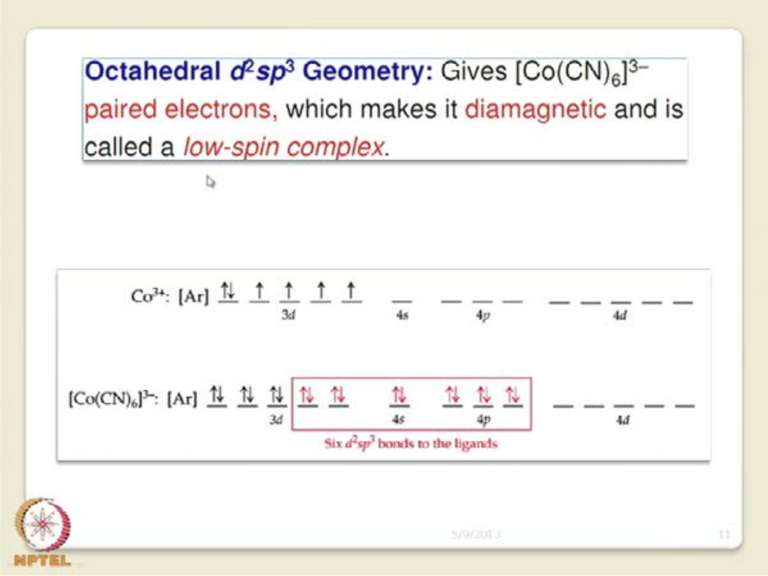

Octahedral d^2sp^3 Geometry: Gives $[Co(CN)_6]^{3-}$ paired electrons, which makes it diamagnetic and is called a *low-spin complex*.

This already we have seen, this is another example for d 2 s p 3 hybridisation, where we can utilise the lower; that means, the inner orbital hybridisation scheme; that means, the lower level of d; that means, the 3 d levels are utilised for hybridisation. So, hexacyanocobaltate can give rise to a species, where all the 6 electrons to be accommodated within the available 3 d levels. So, all of them are paired, and pairing will give rise to a situation where it is a diamagnetic compound; and since the spin value is 0, we can consider them as a low spin compound.

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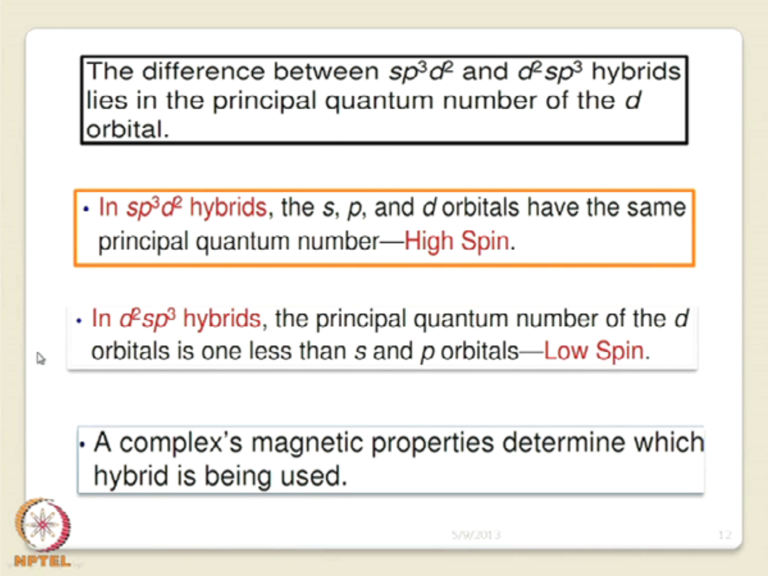

The difference between sp^3d^2 and d^2sp^3 hybrids lies in the principal quantum number of the *d* orbital.

- In sp^3d^2 hybrids, the *s*, *p*, and *d* orbitals have the same principal quantum number—High Spin.

- In d^2sp^3 hybrids, the principal quantum number of the *d* orbitals is one less than *s* and *p* orbitals—Low Spin.

- A complex's magnetic properties determine which hybrid is being used.

So, how we just consider the differences between the s p 3 d 2 and d 2 s p 3 hybrids, is lies in the principle quantum number of the d level. So, what we have seen that, in one case it is d 2 s p 3, in another case it is s p 3 d 2, which is our outer orbital scheme, outer orbital hybridisation scheme; and these are from 4 d levels. So, we are talking something related to the change in the principle quantum number; in one case it is in the 3 d level, in another case it is in the 4 d level. So, we have a change in the corresponding quantum number from 3 to 4.

So, in s p 3 d 2, the s p d orbitals have the same principle quantum number we have the high spin, and when they have the one less than s p; that means, two of them; that means, s and p are of 4 level, 4 level; and one from the 3 level, we get the corresponding low spin configuration. Thus, we find that a complex magnetic properties basically determines which hybrid is being used. So, when we have the magnetic moment high; that means, high spin compound, we utilise the s p 3 d 2 hybridisation; when we get the low spin compound like cobalt compound diamagnetic cobalt which is a 3 d 6 configuration, we utilise the d 2 s p 3 hybridisation scheme.

So, this basically gives us some idea about the corresponding magnetic moment to some extent. And all other properties which is not related to the corresponding idea of the valance bond theory.

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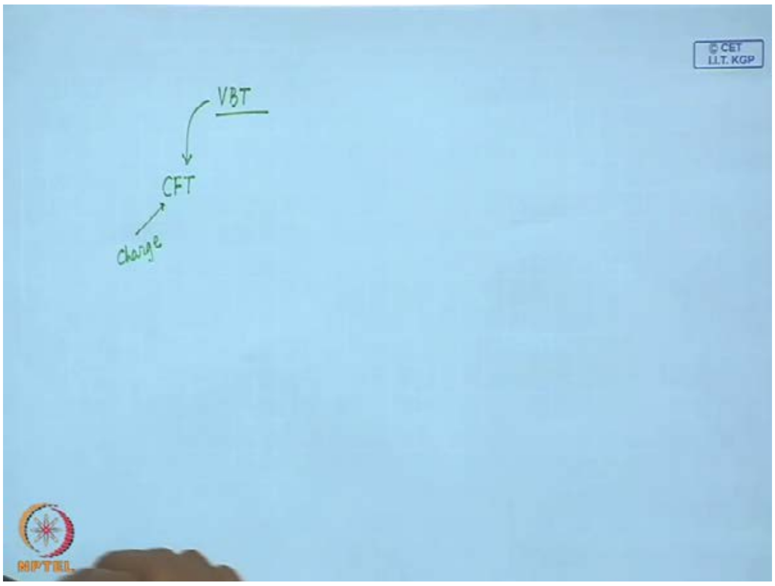

So, what we just see that, in this valance bond theory, what we were discussing that, it can have certain amount of deficiencies as well, which can be rectified in the next theory, what we will be discussing in our next class, which will be crystal field theory, where the idea behind this direct hybridisation of the hybridised orbital and the pure atomic orbital of the ligand will not consider; will consider the ligand as the charges. So, it has the corresponding charge density, whether it is a neutral one or anionic one; and it can compel us for giving some corresponding crystal field splitting pattern, and that gives rise to the corresponding crystal field theory. So, there are definitely some deficiencies that is why we get the corresponding new theory.

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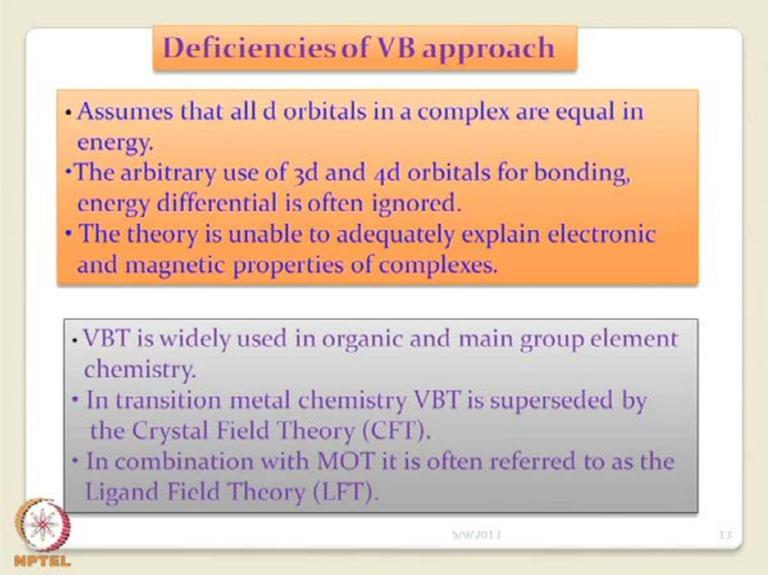

Deficiencies of VB approach

- Assumes that all d orbitals in a complex are equal in energy.
- The arbitrary use of 3d and 4d orbitals for bonding, energy differential is often ignored.
- The theory is unable to adequately explain electronic and magnetic properties of complexes.

- VBT is widely used in organic and main group element chemistry.
- In transition metal chemistry VBT is superseded by the Crystal Field Theory (CFT).
- In combination with MOT it is often referred to as the Ligand Field Theory (LFT).

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And, that particular one, we just consider as the different deficiencies for the valance bond approach. Because it considers all the d orbitals in a complex are equal in energy, but that is not true. Depending upon the corresponding stereo chemistry, the d orbitals facing the ligands differently, because some of them are along the corresponding cartesian axis and some of them are in between; that is why they cannot have, all of them cannot have the equal energy.

And, the arbitrary use of 3 d and 4 d orbitals, just now what we have seen, that in one case as our choice we getting the 3 d level and in another case we are getting as the 4 d level; for fixing the corresponding magnetic moment, in one case as paramagneting and another case as diamagneting, ignoring the corresponding energy difference. The theory is unable to inadequately explain the electronic and magnetic properties of the complexes. So, nicely it cannot explain all the electronic, and all the magnetic properties of the complexes.

And lastly, this is widely used mainly for the organic and main group chemistry, so which is not very much useful for the transition metal complexes. Therefore, in transition metal chemistry, valence bond theory is superseded by the crystal field theory, what we will be discussing in our next class. And after that we will see that, we will introduce the entire compound itself, the whole molecule will be considered in combination with the molecular orbitals. So, when we bring the molecular orbitals, the theory will become known as the corresponding molecular orbital theory, as its often referred to as the ligand field theory. Because the ligand instead of crystal, it is giving the typical field, and which is a combination of molecular orbital theory and crystal field theory, giving rise to the latest theory which is very much useful for explaining all the properties of the metal complexes as the ligand field theory. So, next day we will just discuss about the crystal field theory.

Thank you very much.