Advanced Transition Metal Chemistry – Valence Bond Theory
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Lecture – 11
Valence Bond Theory (VBT)

Once again, welcome you all to MSB lecture series on advanced transition metal chemistry. This is the 11th lecture in the series of 60 lectures. In my previous lecture, I started discussion on valence bond theory concept and its utility for explaining bonding in coordination chemistry. Today, let me start from where I have stopped.

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Valence Bond Theory

Linus Pauling developed the Hybridisation Theory in 1931

Awarded Nobel prize in 1954 for Scientific Contributions and in 1962 for peace

One of the four individuals to have won two Nobel prizes

Linus Pauling
Born: 28 February 1901
Died: 19 August 1994

We all know that valence bond theory was developed by Linus Pauling using hybridisation concept. And essentially, he started hybridisation theory to explain bonding in methane. In case of methane, he thought that; we have s^2p^2 electronic configuration, what he thought was, first, one electron from *s*-orbital will be promoted to *p*-orbitals and then these three p orbitals would interact with 1*s* orbital of hydrogen to form three bonds having very similar properties.

And the fourth one would interact with one electron left in 2*s* orbital with 1*s* orbital of hydrogen. And then in that case, you are supposed to have two types of bonds, but the studies showed that methane has all the bonds equivalent, as a result the assumption was thought of flawed. And then he thought that, prior to the bond formation between carbon and hydrogen, this s-electron will be promoted to p-orbital.

And then three p-orbitals and s-orbital would combine together to generate a set of four hybrid orbitals having the composition sp^3 and these four sp^3 would interact equally with four hydrogen atoms to have methane molecules with the tetrahedral geometry and later that was extended to all main group compounds and then, they made an attempt to expand that to coordination complexes as well.

So, for his hybridisation theory, he was awarded Nobel Prize in 1954. And then again in 1962, he got another Nobel prize but not for chemistry, but for peace, and he is one of the four individuals to have won two Nobel prizes. The first one being Marie Curie.

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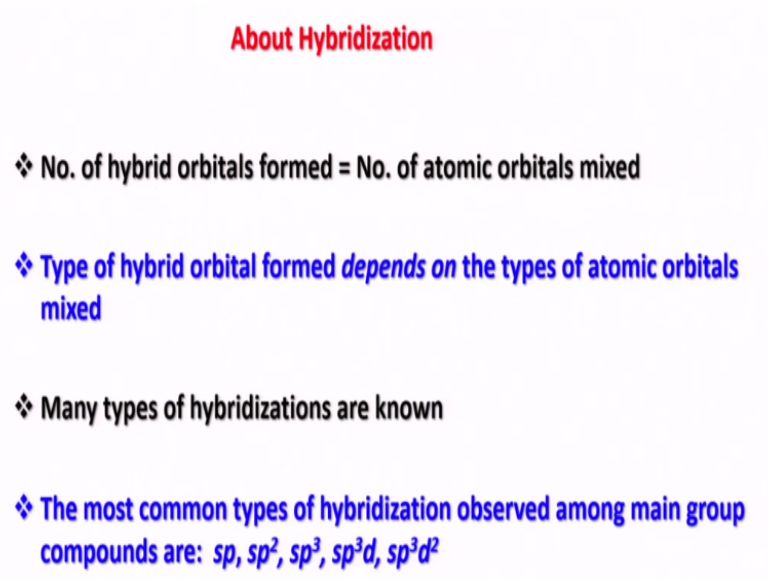

About Hybridization

- ❖ No. of hybrid orbitals formed = No. of atomic orbitals mixed
- ❖ Type of hybrid orbital formed *depends on* the types of atomic orbitals mixed
- ❖ Many types of hybridizations are known
- ❖ The most common types of hybridization observed among main group compounds are: *sp, sp^2, sp^3, sp^3d, sp^3d^2*

So, let us try to understand about hybridization concept. So, according to valence bond theory, the number of hybrid orbitals formed is equal to number of atomic orbitals mixed. For example, if you consider sp^3, we have one *s*-orbital and 3p-orbitals, that results in the formation of four sp^3 hybrid orbitals, that says that, the number of hybrid orbitals formed is equal to the number of atomic orbitals mixed. The type of hybrid orbitals formed depends on the type of atomic orbitals mixed.

As I mentioned, if you take s and 2p then it will be having sp^2 with two-third p property and one-third s property. And many types of hybridization are also known and the most common type of hybridization observed among main group compounds are sp, sp^2, sp^3, sp^3d, sp^3d^2 and of course, we can always debate about sp^3d and sp^3d^2 among main group compounds, but now let us focus on simple compounds to understand the sp, sp^2, sp^3 hybridization before we extend this concept to coordination compounds.

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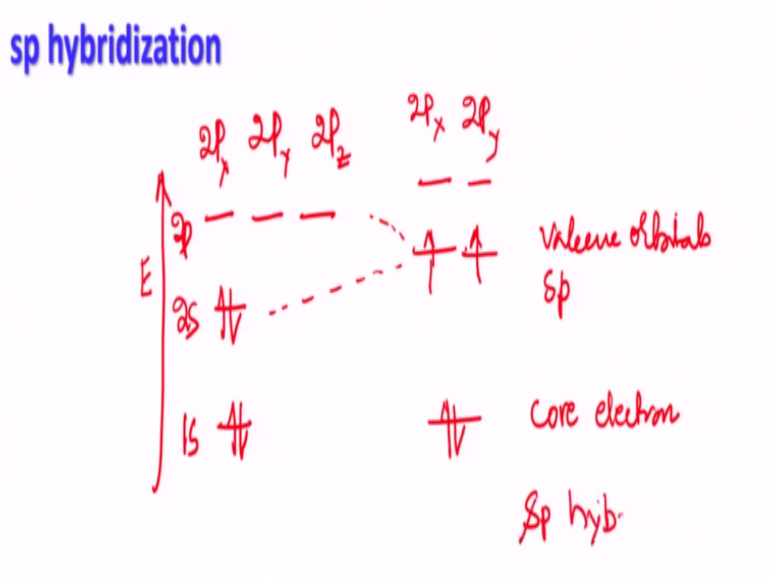

sp hybridization

Now, let us consider *sp* hybridization. Always you should remember to write this one and now let us consider a simple compound having simple electronic configuration having 1s^2 2s^2 and then 2p. So here 2p2s1s. So in 1s we have two electrons. Let us say we have two electrons and here we do not have any electron. Now what would happen is, let us try to mix 2s, two electrons with one of the 2p, preferably p$_z$ in that case.

Let me write two like this, and then other two unitilized ones would remain same. So, then here we have two electrons that means we generated two *sp*^{3} hybrid orbitals having one electron each, they are valence orbitals and *sp*. So, now, what would happen to this one? So, since this is core electrons, does not participate in bonding. So, bonding, we should consider only valence electrons and this we call it as sp hybridization.

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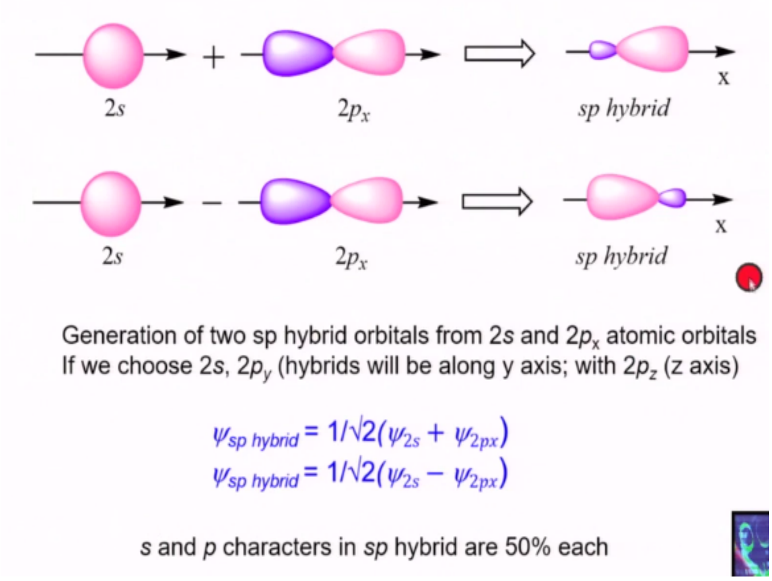

Generation of two sp hybrid orbitals from 2*s* and 2p_x atomic orbitals
If we choose 2*s*, 2p_y (hybrids will be along y axis; with 2p_z (z axis)

$$\psi_{sp\ hybrid} = 1/\sqrt{2}(\psi_{2s} + \psi_{2px})$$
$$\psi_{sp\ hybrid} = 1/\sqrt{2}(\psi_{2s} - \psi_{2px})$$

s and *p* characters in *sp* hybrid are 50% each

And of course, if you are interested in, I have also given here orbital wave functions and here *s*- and *p*-characters in *sp* hybrid are 50% each and this is how you can write wave function. So, here you can see 2s is there and then 2p_x it is combined to generate *sp* hybrid orbitals in the x-direction and similarly another hybrid in x-direction of course with turning exactly opposite to each other and it appears like the two would be looking something like this.

Now, we have sp orbitals disposed at an angle of 180 and now atoms coming should overlap here and overlap here having a linear geometry. The generation of two *sp* hybrid orbitals from 2*s* and 2p_x orbitals are shown and if you choose 2*s* and 2p_y hybrid will be along y-axis and if you choose 2p_z it will be along z-axis.

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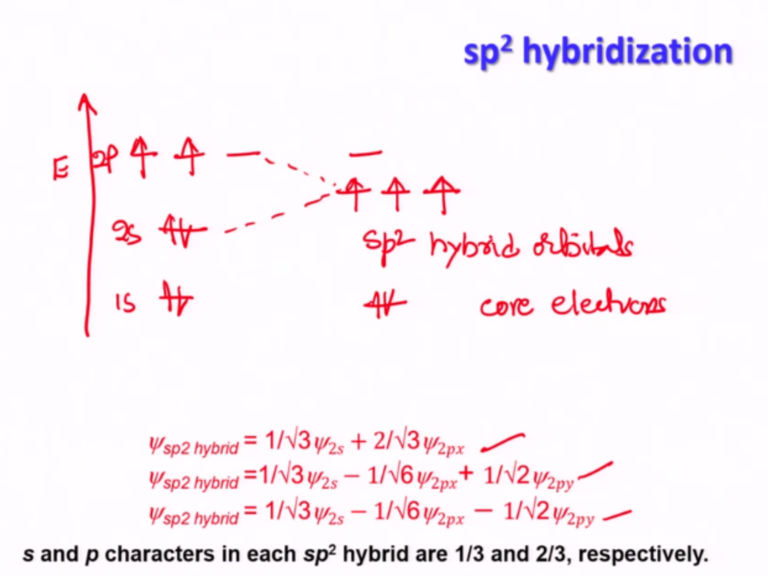

sp^2 hybridization

$$\psi_{sp2\ hybrid} = 1/\sqrt{3}\psi_{2s} + 2/\sqrt{3}\psi_{2px}$$
$$\psi_{sp2\ hybrid} = 1/\sqrt{3}\psi_{2s} - 1/\sqrt{6}\psi_{2px} + 1/\sqrt{2}\psi_{2py}$$
$$\psi_{sp2\ hybrid} = 1/\sqrt{3}\psi_{2s} - 1/\sqrt{6}\psi_{2px} - 1/\sqrt{2}\psi_{2py}$$

***s* and *p* characters in each *sp^2* hybrid are 1/3 and 2/3, respectively.**

Now, consider sp^2 hybridization, this is for sp^2 and let me write here how we can arrive at sp^2 the same way. Again, consider 1s and 2s. We have two electrons here and two electrons here and we have 2p orbitals and what we have is one electron here and one electron here. So, that means we are considering carbon with $2s^22p^2$ electronic configuration. And now, if it undergoes hybridization, there is sp^2 so one will be left.

We have 3 orbitals, 3 sp^2 orbitals are there, having one electron each. And of course, here as usual this core electrons would remain, they do not participate in bonding and one should write like this wave functions for x direction and y direction and z is not used here. So, this is how you should be able to write for sp^2.

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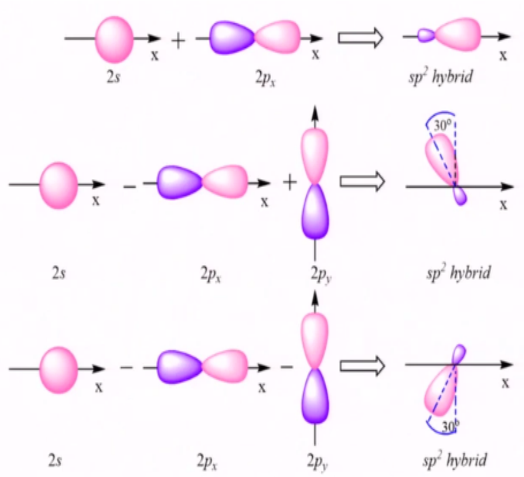

Generation of sp^2 hybrid orbitals from 2s, $2p_x$ and $2p_y$ atomic orbitals (in xy plane)
If we choose: 2s, $2p_x$ and $2p_z$ hybrids would be in xz plane; $2p_z$, $2p_y$ (yz plane)

And here you can see 2s is interacting in $2p_x$ to have an sp^2 hybrid in x-direction. Then what happens, it remains intact in x-direction. Then when 2s is overlapping with the $2p_y$ what happens is initially it is orthogonal, it makes an anticlockwise rotation by 30 degrees to orient in this direction. So that the angle between them is 120. And then when 2s interacts with the $2p_y$ another one, so it can interact in opposite direction with clockwise 30 degrees away from the orthogonality to have 120.

So, basically you will be having something like this with each sp^2 is 120 degrees apart. So of course, here one should be very clear. You can use any of these orbitals to explain, but you should be very clear about the directions and the plane in which you are talking about these molecules are, or you place these orbitals in that plane. So, if you are considering xy atomic carbon, it will be the xy plane.

And if you are considering y and z orbitals, it will be the trigonal planar molecule; will be along the yz plane, or if you are considering x and z so the molecule should be considered kept on xz plane that one should remember.

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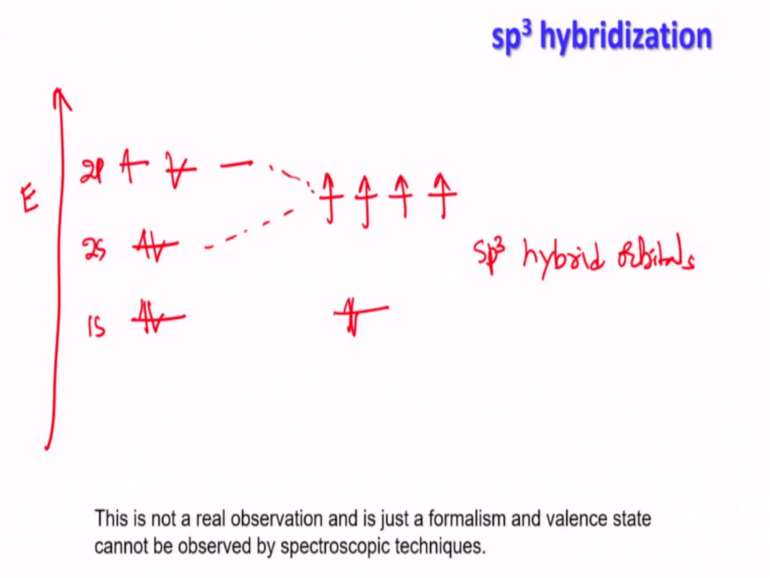

sp^3 hybridization

This is not a real observation and is just a formalism and valence state cannot be observed by spectroscopic techniques.

Now let us consider *sp*^{3} hybridization. Again 1s, 2s and 2p. So, we have two electrons here, two electrons here and two electrons here. And if I am considering *sp*^{3}, what would happen? I have 1, 2, 3 and 4 and now we have one electron each and this remains as it is, core, and we do not have any orbitals left now. So, these are *sp*^{3} hybrid orbitals. This is how we can show *sp*^{3} hybrid orbitals. So, this is not a real observation, it just a formalism and valence state cannot be observed by spectroscopic techniques that one should bear in mind.

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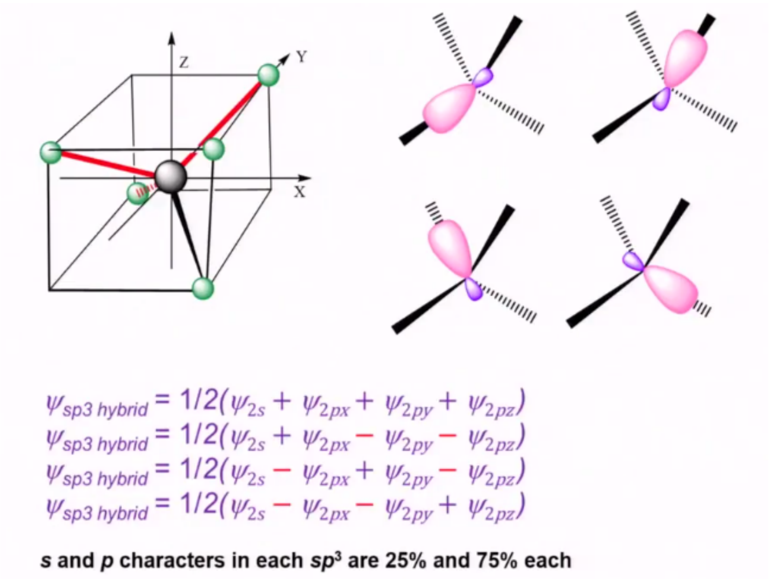

$$\psi_{\text{sp3 hybrid}} = 1/2(\psi_{2s} + \psi_{2px} + \psi_{2py} + \psi_{2pz})$$
$$\psi_{\text{sp3 hybrid}} = 1/2(\psi_{2s} + \psi_{2px} - \psi_{2py} - \psi_{2pz})$$
$$\psi_{\text{sp3 hybrid}} = 1/2(\psi_{2s} - \psi_{2px} + \psi_{2py} - \psi_{2pz})$$
$$\psi_{\text{sp3 hybrid}} = 1/2(\psi_{2s} - \psi_{2px} - \psi_{2py} + \psi_{2pz})$$

***s* and *p* characters in each *sp*^{3} are 25% and 75% each**

And then here the wave functions are written for the four sp^3 hybrid orbitals. Of course, when s is overlapping with p_x, p_y and p_y you know that it is symmetrical So, everything is positive and then with p_x, p_y and it is p_y direction. So, that means, now they are disposed at an angle of 107.8°. This is how these four sp^3 would look like and it is very convenient if you imagine these four orbitals inside a cube.

And if you place the central atom at the centre of a cube and place the ligands on alternate corners, this is how it looks like. There, four peripheral atoms are disposed to four alternate corners of a cube and it makes a perfect tetrahedral geometry. And in this one as I mentioned, s- and p-characteristics are respectively 25% and 75% in each of these orbitals.

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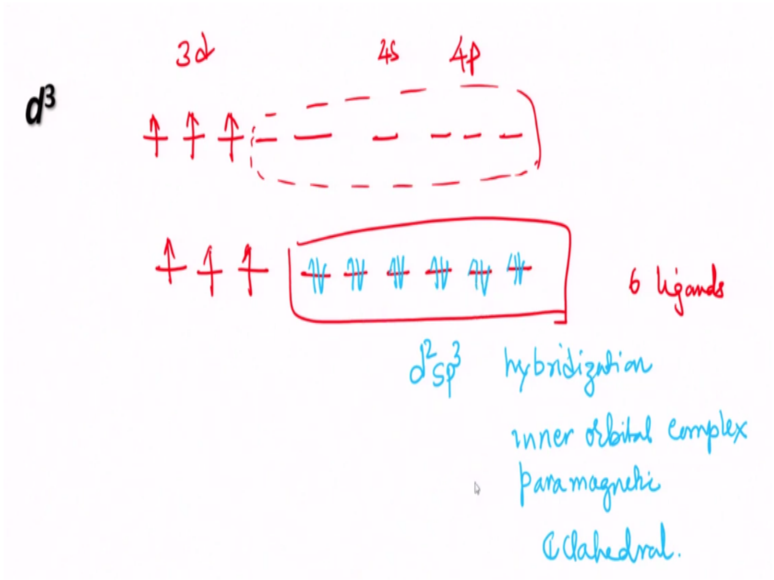

So, let us now extend this valence bond theory to metal complexes. Let us start with d^3 electronic configuration. Let me consider a metal ion having 3 electrons in its d-orbitals. So, now, in this case, what happens? Of course, you should also consider it is 3d, we have to consider 4s and 4p also. This is 4s. If this is 3d, this is 4s and this is 4p. So, in this one what you can do is, if complex is an octahedral compound with coordination number 6.

In order to explain the bonding, we have to go for utilizing all 2 + 1 + 3 = 6 orbitals and 6 orbitals we should use here and this would remain intact. So, now this is the hybridization we are talking about. And here if six ligands are coming with 12 electrons, they will be accommodated something like this. So, since here inner 3d is used for accommodating electrons through hybridization.

So, here two *d* and one *s* and three *p*-orbitals are used, it is d^2sp^3 hybridization. So, you can explain. This is called inner orbital complex and also this is paramagnetic because we have 3 unpaired electrons. So, some of these properties can be explained and the geometry is octahedral. So that means here whether we are considering homoleptic molecule or heterolytic molecules or we have more than one type of ligand, even m a, b, c, d, e, f.

If you consider the six different types of ligands, still the hybridization is d^2sp^3 and still it is an inner orbital complex or still it is paramagnetic and still it is octahedral, but to what extent octahedral geometry is regular or distorted that information does not come from valence bond theory.

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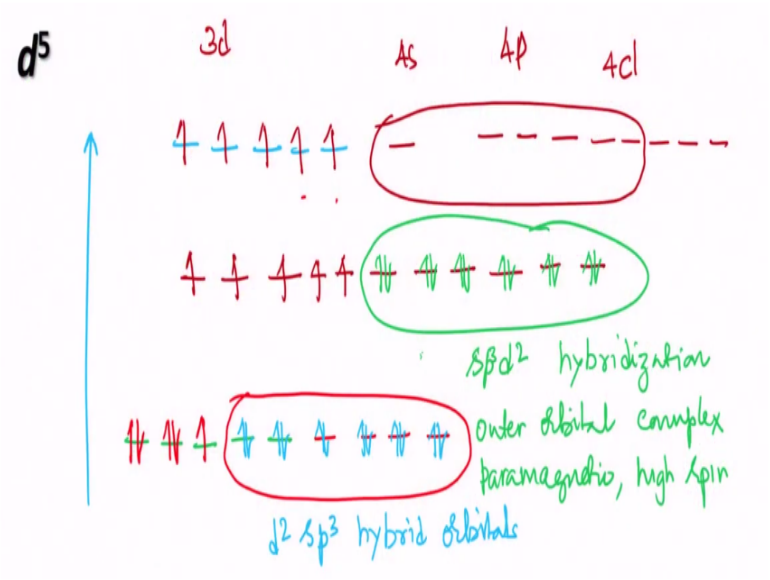

Let us look into d^5 electronic configuration. So we have 5 electrons and of course, if I am considering 3d, I have here 4s and 4p is there. So, now once again if I assume that d^5 metal ion is forming an octahedral complex, then 6 ligands are coming with 12 electrons that has to be accommodated in appropriate metal orbitals. For that one, now, what happens, inner orbitals; we do not have any vacancy.

As a result, what we should do is, we should use 4*d*-orbitals here, and of course 4*d* also we have five and we have to choose two orbitals here and then we can consider this for the bonding. In that case, we have 1, 2, 3, 4, 5, 6 are there and then here, we have 5 as usual, on metal, ligand electrons are accommodated in these 6 six hybrid orbitals. Now, we are using *s*- and *p*- and outer *d*-orbitals.

As a result, what happens in the same sequence, we can write the hybridization as sp^3d^2 hybridization. So, here we have used the outer d-orbitals, as a result, it is called outer orbital complex, still it is paramagnetic. Also, you can call it as high-spin complex. Before we look into d^8 electronic configuration, is any alternate hybridization is possible with this one? If we use strong field again what would happen?

Say, something like this is there, and in this case, what happens, metal electrons from these two will be getting paired here and as a result what happens, two orbitals will be vacant here. So, now again you write 4s and 4p. Now, there is a possibility of utilizing inner d-orbital far hybridization, same thing we shall do it now, something like this, and now we try to accommodate 12-electrons coming from 6 ligands.

Again, we have octahedral geometry and now it is once again d^2sp^3 hybridization So, that means with d^5 electronic configuration, both d^2sp^3 as well as sp^3d^2 hybridization are possible, and how it is possible, valence bond theory does not say. How inner orbital complexes are formed and how high-spin and low-spin are formed, it does not say, but when the electronic configuration is like this, that information comes from magnetic moment.

And once we know the magnetic moment, from that one, one can speculate whether a d^8 or d^5 metal ion would prefer d^2sp^3 or sp^3d^2, that ligand field does not come into picture at all. That means the ligand field strength or the strength of the ligand is not pronounced in valence bond theory.

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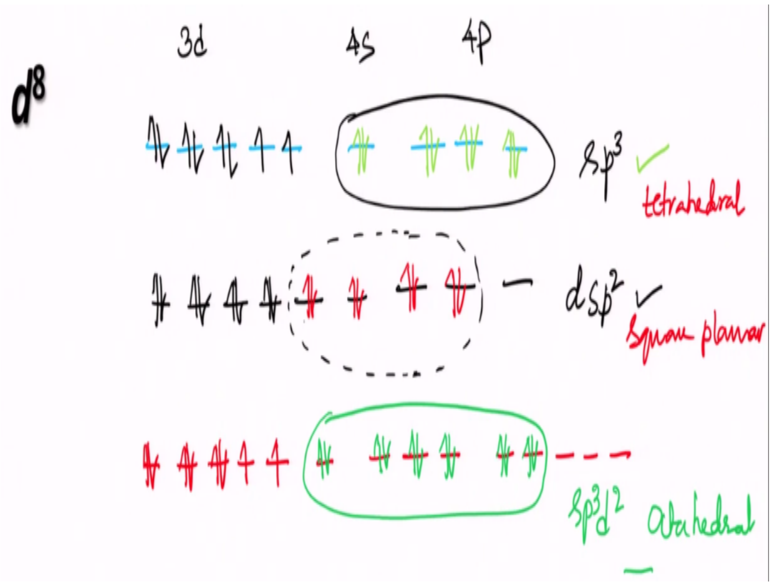

Now, let us look into d^8 electronic configuration. This is 3d, this is 4s, this is 4p. So, consider 1, 2, 3, 4, 5, 6, 7, 8. So, here we have this, electronic configuration is there, now, and in this case what we can do is; since more electrons are there, we assume that metals having more electrons in their *d*-orbitals tends to have lower coordination number. Let us look into first four coordination. In four coordination, without disturbing these electrons, how to make bond, that means, 4s is available, 4p is available.

If the coordination number is 4, we can think of simply sp^3 hybridization. That means ligands coming with the 8 electrons can be accommodated in this fashion. So, that means a d^8 system can have sp^3 hybridization with coordination number 4. And in contrast, so let us consider like this, and this also, if we shall try to pair up, as a result, we will be left with one *d*-orbital. So, now we have 4*p*. Now, one more is there.

Again the strategy is not different, still it prefers 4 coordination number, but inner, when the d-orbital is available as a result what happens, it try to utilize this one in this fashion. So, that means one d-orbital and one s orbital and two p orbitals are utilized. Now if the four ligands are approaching, so *d*- is there and sp^2- is there. That means, these 4 ligands would give you 8 electrons that are accommodated in these four dsp^2 hybrid orbitals.

So, here it is tetrahedral, here it is square planar geometry. But on the other hand, if the metal still prefers to have 6 coordination in that case what would happen? And then we have 4*d* 1, 2, 3, 4, 5. So, in this case what happens, since even if you pair one of the electrons, one orbital alone does not help in making inner orbital complex, if the coordination number is 6. In that case what happens? It will try to go for outer orbital complex.

So, here 12 electrons are accommodated. So, now this if you see, again this is sp^3d^2 and octahedral. So, this explains now the possibility of having different geometries and different coordination number for a given electronic configurations. For d^8 you can have sp^3 tetrahedral arrangement, for d^8 you can have dsp^2 square planar arrangement of the same 4 ligands or if it is ready to accommodate 6 ligands, then it has to be outer orbital complex, with sp^3d^2 hybridization so that it can have octahedral geometry.

So, this kind of information comes from valence bond theory and let us try to extend for some more molecules before we proceed further to take up crystal field theory. Until then have an excellent time reading chemistry.