Advanced Transition Metal Chemistry – Valence Bond Theory

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Lecture – 12
Valence Bond Theory (VBT)

Hello everyone, once again welcome you all to MSB lecture series on advanced transition metal chemistry. This is the 12th lecture in the series. In my previous lecture, I had initiated discussion on valence bond theory and I did discuss about various hybridization concepts and also with respect to transition metal compounds. I discussed selected electronic configuration such as a d^7, d^8 and I showed how one can form different type of complexes and one can explain the bonding using valence bond theory. So, now let me continue from where I had stopped.

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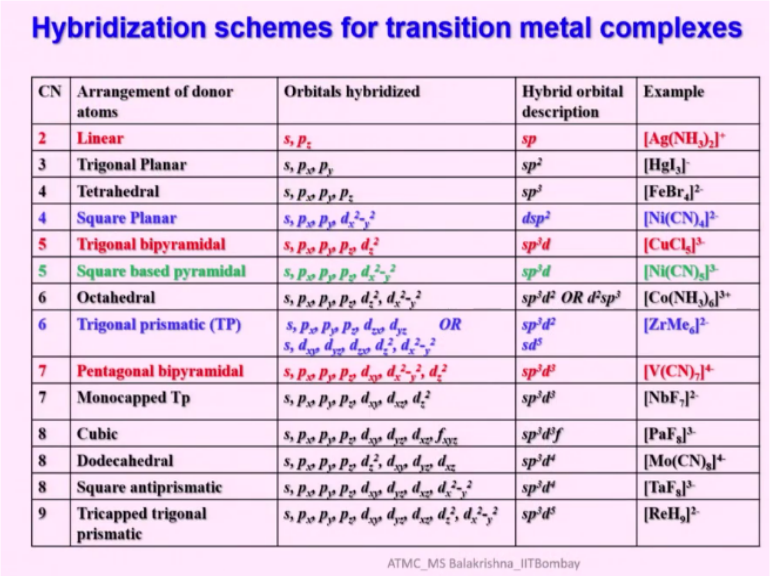

Hybridization schemes for transition metal complexes

CN	Arrangement of donor atoms	Orbitals hybridized	Hybrid orbital description	Example
2	Linear	s, p_z	sp	$[Ag(NH_3)_2]^+$
3	Trigonal Planar	s, p_x, p_y	sp^2	$[HgI_3]^-$
4	Tetrahedral	s, p_x, p_y, p_z	sp^3	$[FeBr_4]^{2-}$
4	Square Planar	$s, p_x, p_y, d_{x^2-y^2}$	dsp^2	$[Ni(CN)_4]^{2-}$
5	Trigonal bipyramidal	$s, p_x, p_y, p_z, d_{z^2}$	sp^3d	$[CuCl_5]^{3-}$
5	Square based pyramidal	$s, p_x, p_y, p_z, d_{x^2-y^2}$	sp^3d	$[Ni(CN)_5]^{3-}$
6	Octahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{x^2-y^2}$	sp^3d^2 OR d^2sp^3	$[Co(NH_3)_6]^{3+}$
6	Trigonal prismatic (TP)	$s, p_x, p_y, p_z, d_{zx}, d_{yz}$ OR $s, d_{xy}, d_{yz}, d_{zx}, d_{z^2}, d_{x^2-y^2}$	sp^3d^2 sd^5	$[ZrMe_6]^{2-}$
7	Pentagonal bipyramidal	$s, p_x, p_y, p_z, d_{xy}, d_{x^2-y^2}, d_{z^2}$	sp^3d^3	$[V(CN)_7]^{4-}$
7	Monocapped Tp	$s, p_x, p_y, p_z, d_{xy}, d_{xz}, d_{z^2}$	sp^3d^3	$[NbF_7]^{2-}$
8	Cubic	$s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{xz}, f_{xyz}$	sp^3d^3f	$[PaF_8]^{3-}$
8	Dodecahedral	$s, p_x, p_y, p_z, d_{z^2}, d_{xy}, d_{yz}, d_{xz}$	sp^3d^4	$[Mo(CN)_8]^{4-}$
8	Square antiprismatic	$s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}$	sp^3d^4	$[TaF_8]^{3-}$
9	Tricapped trigonal prismatic	$s, p_x, p_y, p_z, d_{xy}, d_{yz}, d_{xz}, d_{z^2}, d_{x^2-y^2}$	sp^3d^5	$[ReH_9]^{2-}$

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You can see the table I have given here. I have covered almost all hybridization you come across for transition metal complexes having different ligands and also having different geometries and hence different hybridization, they have used. Look into the first one, here arrangement for donor atoms or ligands is linear with respect to central metal atom, and when the coordination number 2 is there, invariably we use *sp* hybridization, example diamine silver complex.

Next trigonal planar with coordination number 3, here example I have given is $[HgI_3]^-$ with sp^2 hybridization. And of course, tetrahedral, you are all know that we use the sp^3 hybrid orbitals. We have several examples, just I have given one of the examples here, tetrabromoferrate. Then square planar, most of the d^8 metal complexes invariably show square planar geometry along with d^7s^2 system with +1 oxidation state.

For example, rhodium and iridium along with nickel, palladium and platinum, that is square planar, the hybrid orbitals we are using is dsp^2. Under trigonal bipyramidal the hybridization is sp^3d. I have given one example of copper here, and you should remember, for example, when we move to square based pyramid, again we are using sp^3d, that means we should be able to differentiate between the *d*-orbitals that are involved in these two hybridizations.

If you look into trigonal bipyramidal, we have two ligands in the axial position, so we need to use d_{z^2} orbital and hence here the hybridization of sp^3d involves d_{z^2}, whereas in case of square based pyramidal, four ligands are in the plane, so we need to use orbitals that are oriented in the plane or along the plane. So, that is the reason we use here $d_{x^2-y^2}$. So, hybridization is same, but the *d*-orbitals are different in these two cases, that one should remember.

And of course, in case of octahedral, we are using sp^3d^2 for outer orbital complexes or d^2sp^3 for inner orbital complexes. Just I have given one example of hexammine cobalt. We have numerous examples for both the cases, inner orbital, as well as outer orbital complexes. When we go to coordination number 6, we come across another important geometry that is trigonal prismatic and here also the hybridization is essentially the same sp^3d^2, but the orbits we are taking among *d* are different.

One such example is, we can take s, p_x, p_y, p_z and then d_{xz} and d_{yz} are taken here, not d_{z^2} and $d_{x^2-y^2}$,we prefer, in case of octahedral complexes, but when the early metal exists in their highest possible oxidation state, we can as well consider inner *d*-orbitals instead of taking *p*-orbitals and hence many trigonal prismatic complexes utilize all *d*-orbitals along with s to have a hybridization of sd^5, instead of sp^3d^2.

And this is true with metals in their high-valent state, especially metals having d^1, d^2, d^3 electronic configurations. And then when we have coordination number 7, we have pentagonal bipyramidal geometry. So, in this case since we need 7 orbitals, we are using additional one more orbital from d, here it is a d_{xy}, $d_{x^2-y^2}$ and d_{z^2} along with *s*- and 3*p*-orbitals.

Example, I have shown here, sp^3d^3, pentagonal bipyramidal. But when we have 7 coordination, we can also have another geometry that is called capped or monocapped octahedral geometry. So, in this case also sp^3d^3 is there, but the orbitals are different, you can see here. In the same way when coordination number 8 is there, we come across three different types of geometries. One is cubic, one is dodecahedral, one is square antiprismatic.

In case of cubic, we use the sp^3d^3f , that comes to *f*-block complexes. And then in case of dodecahedral coordination number is 8, we are using sp^3d^4. Here we are using sp^3d^4 and then I have listed all: d_{z^2} and d_{xy}, d_{yz}, and d_{xz} are used in dodecahedral geometry. When we have square antiprismatic geometry again sp^3d^4, and here except for d_{z^2} all *d*-orbitals are employed in this hybridization scheme.

And the example is this [octafluorotantalate]$^{3-}$ = $[TaF_8]^{3-}$, and then the last one with coordination number 9, the most symmetric geometry you can think of for coordination number 9 is tricapped trigonalprismatic and here, this is an example, where all valence orbitals have been utilized in arriving at a hybrid scheme having the composition sp^3d^5. This is sp^3d^5 hybridization, example is $[ReH_9]^{2-}$.

Here 9 metal to hydrogen bonds are there and this is one of the rare examples of homoleptic hydrides having as many as 9 metal two hydrogen (M—H) bonds and this has tricapped trigonal prismatic geometry. So, now to make you familiar with some of these geometries, I should show you; it becomes very clear, and then you should be able to distinguish between trigonal prismatic and octahedral geometries and what are the difference between them.

(Video Starts: 07:29) So, if you can see here, this is trigonal prismatic geometry. You can see this one, this is the triangular prismatic geometry, and now I have octahedral geometry here. And then: is there any alternate name for octahedral geometry? Yes, this is trigonal prismatic and this is trigonal antiprism. If it is trigonal prism, this is trigonal antiprism. So, then how they are related? It is very simple. You take this one and if you see these two triangular faces, they look eclipsed, right.

They, look at, eclipsed here and whereas if you look into this one, if you just try to see this triangular face and this triangular face, they look like staggered. That means, this is a triangular antiprism, staggered one, and where we have eclipsed one, this is trigonal prism. But is it possible to convert? Yes, just see keep this one and turn this face something like this and then you have to connect this one with three more sticks, then you can get octahedral geometry.

So, this is the relationship between trigonal prism and trigonal antiprism or octahedral. So, now this is octahedral and then you go back and see them eclipsed, this is trigonal prism. You take this trigonal prism and make one of the face staggered and you can visualize octahedral geometry. **(Video Ends: 09:06)** There should not be any confusion between these two geometries.

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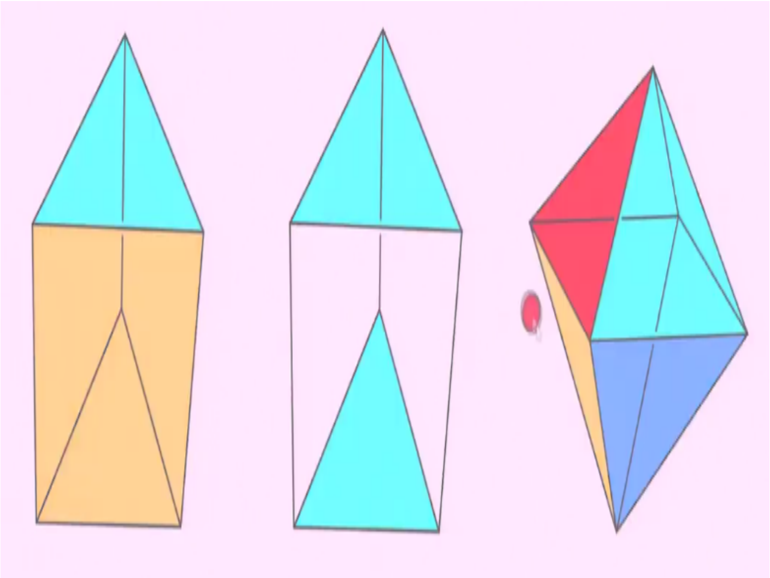

I have shown those things here. So, this is trigonal prism. You can see the relationship of these two triangles there on same side. That means if you just bring it towards the screen, then what happens they will be eclipsed, whereas here you can see, you take any two, and they are staggered.

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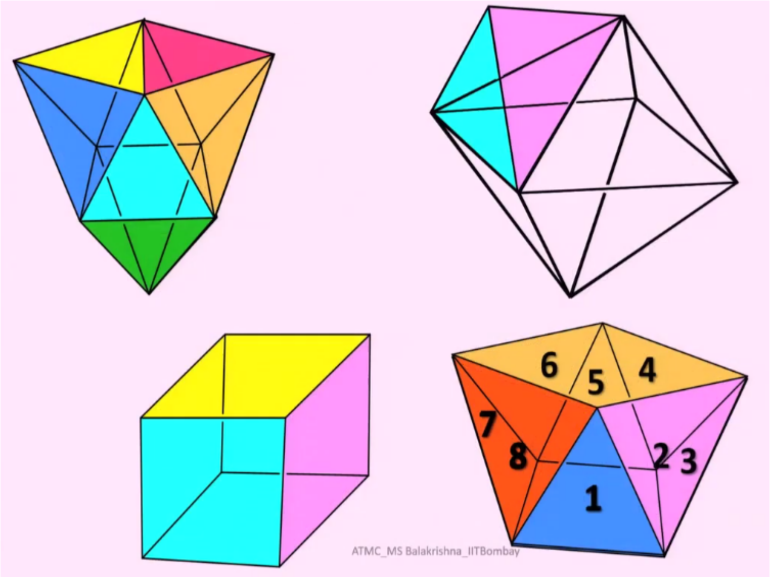

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Similarly, we can compare this tricapped trigonal antiprismatic geometry. I mentioned in case of $[ReH_9]^{2-}$ for coordination number 9. You consider this one, you can see here, we have 1, 2, 3, 4, 5, 6; 6 vertices are there and then on each of rectangular faces if you put one more vertex and then connect it with four bonds, then this will be monocapped and then if you put one more here and connect it with four bonds this will be by bicapped trigonal prism.

And then, one you put here, and make bonds with here, then this becomes tricapped trigonal antiprism. This is what the geometry adapted by $[ReH_9]^{2-}$to accommodate 9 hydrogen atoms surrounding rhenium atom. You can see this one. This is monocapped and this is bicapped and this is tricapped trigonal prism and you can distinguish these three new vertices added. So, total vertices are 9, so this is tricapped trigonal prism.

And similarly, you can take for coordination number 7 octahedral is there and besides pentagonal bipyramidal, another possibility is monocapped octahedral geometry. So, you consider one of these faces and add one more vertex and connect it with the three more bonds then that becomes monocapped, look something like this, you can now distinguish the seventh vertex coming here. This is monocapped octahedral.

And this is cube now, the same thing, the cube is there and in the cube you take the square then turn it so that both of them are not eclipsed. So, you take this yellow face and rotate it so that this will be staggered that means vertex will be pointing here, turn it, so something like this. So, now connect them in this, one each square you, put one more so that you will end up with two equilateral triangles.

And on four sides you will end up with two equilateral triangles so that you will be having 8 equilateral triangles and then you have two square faces. This is called square antiprism. Sometime coordination number 9 one can also have monocapped square antiprism, sometimes you can also have another one below, so that you can have bicapped square antiprism. So, this is for coordination by 10, this is the most common one.

In some cases, coordination number 9, instead of adopting this one, they can also adopt this geometry having monocapping on square antiprism. It is bicapped here on these square faces, then it becomes bicapped square antiprism; even I have an example here. You can see this is, how it looks like. **(Video Starts: 12:27**) So, this is one face, and this is another face, and they are staggered to each other.

When they are staggered to each other, you can clearly see these eight faces here, eight equilateral triangles. So, you can count them, there are eight. **(Video Ends: 12:46)** So, this is all about, I wanted to tell you about the geometrical difference between various polyhedra.

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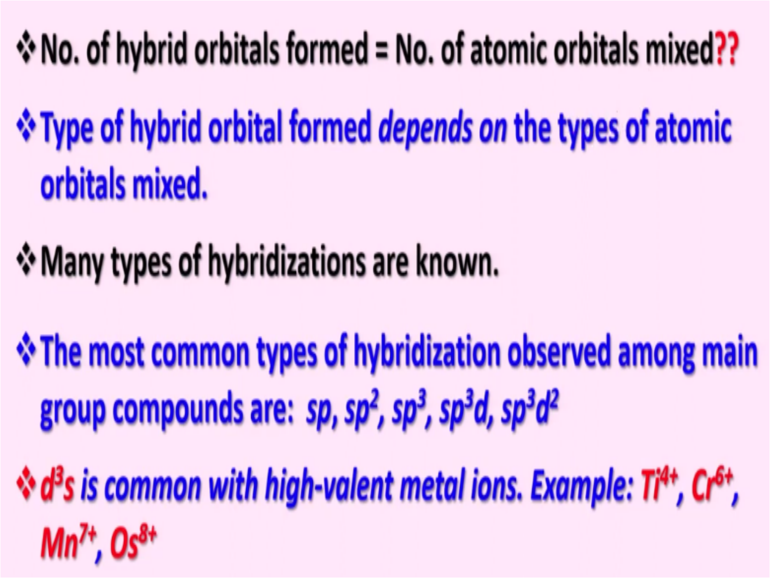

- ❖ No. of hybrid orbitals formed = No. of atomic orbitals mixed??
- ❖ Type of hybrid orbital formed *depends on* the types of atomic orbitals mixed.
- ❖ Many types of hybridizations are known.
- ❖ The most common types of hybridization observed among main group compounds are: *sp*, sp^2, sp^3, sp^3d, sp^3d^2
- ❖ d^3s is common with high-valent metal ions. Example: Ti^{4+}, Cr^{6+}, Mn^{7+}, Os^{8+}

So, in the beginning I made a statement: number of hybrid orbitals formed is equal to the number of atomic orbitals mixed. Is it really true or is there any exception? I shall tell you in a couple of minutes the answer for this one. And then, the type of hybrid orbitals formed depend on the types of atomic orbitals mixed that is absolutely correct, no issues. And many types of hybridizations are known, you saw, all possible hybridizations I mentioned.

And one more thing you should remember, when we have octahedral geometry with metals in their high valence state especially with early metals, it is not just sp^3 hybridization. You should remember one more thing when we talk about tetrahedral complexes of early transition metals or metals in the highest possible oxidation states not necessarily they utilize sp^3 hybrid orbitals.

Sometimes they also utilize all the d orbitals thus the showing d^3s hybridization that is quite common with high valent metal ions, example titanium tetrachloride: if you take titanium, it is not sp^3 hybridization environment, but it is utilizing d^3s . And similarly, if you take potassium dichromate, chromium is using d^3s because this is inner d-orbitals and it is essentially using 3*d* and 4*s*. So, it should be d^3s .

And, similarly in $KMnO_4$, manganese utilizes d^3s and in osmium tetroxide, osmium is in +8 oxidation state, this also utilizes d^3s while forming osmium tetroxide. However, the most common types of hybridization observed among main group elements are *sp*, sp^2, sp^3, sp^3d, sp^3d^2 or in some cases d^2sp^3. I put a question mark here you can see number of hybrid orbitals formed is equal to the number of atomic orbitals mixed. It is not true, there is an exception here, that is, what I want to show you here.

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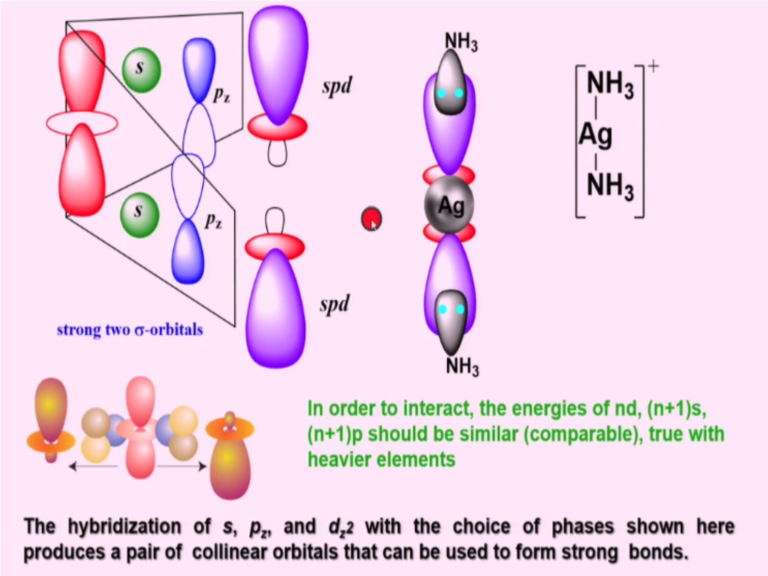

In order to interact, the energies of nd, (n+1)s, (n+1)p should be similar (comparable), true with heavier elements

The hybridization of s, p_z, and d_{z^2} with the choice of phases shown here produces a pair of collinear orbitals that can be used to form strong bonds.

Look into this one. Here, we come across two to *spd* hybrid orbitals. That means three orbitals are involved one p_z, one *s*, and one d_z^2, but still we are ending up with only two hybrid orbitals, *spd* oriented opposite to each other in this direction. So, these empty orbitals can take readily from ligands to establish a linear molecule. The example is diamine silver plus complex, $[Ag(NH_3)_2]^+$. So, how that happen?

The hybridization of p_z, s, $d_z{}^2$ with the choice of phases as shown here; produces a pair of collinear orbitals that can be used to form strong bonds. In order to form strong sigma-bonds, some metal ions utilize this kind of hybridization, very rare ones. You can see now, so these two *spd* hybrid articles are oriented in this direction. Now if two ammonia ligands are coming, they donate a pair of electrons to these empty orbitals to form strong diamine silver complex. This is the complex, here.

And in order to interact, the energies of the nd that is 4d and n+1s (5s) and 5p should be similar, true with heavier elements. So, energy should be very comparable. And if you go for heavier elements, the energy difference is marginal and remarkably decreases, as a result, as the size increases, they diffuse into each other because of this one what happens, in order to strengthen metal to ligand bond, they utilize this kind of hybridization. In fact, molecular orbital theory also suggested significant mixing of *s*, *p* and *d* orbitals in this complex.

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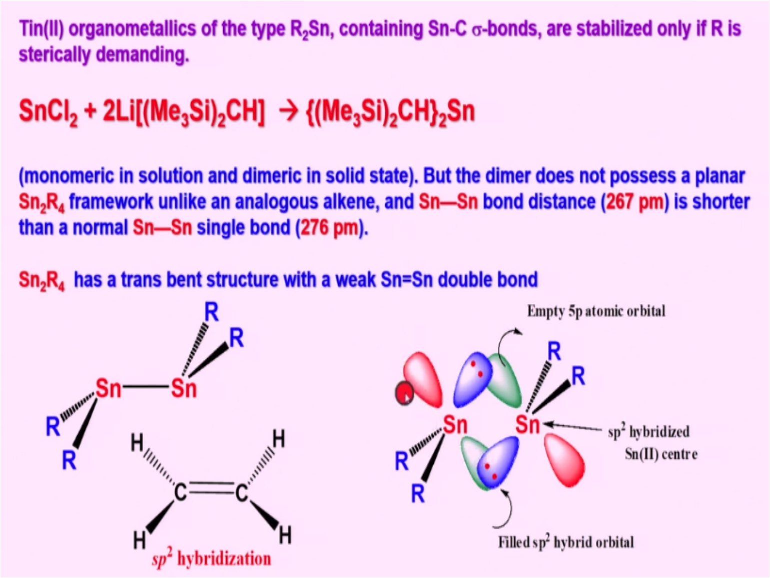

Tin(II) organometallics of the type R_2Sn, containing Sn-C σ-bonds, are stabilized only if R is sterically demanding.

$SnCl_2 + 2Li[(Me_3Si)_2CH] \rightarrow \{(Me_3Si)_2CH\}_2Sn$

(monomeric in solution and dimeric in solid state). But the dimer does not possess a planar Sn_2R_4 framework unlike an analogous alkene, and Sn—Sn bond distance (267 pm) is shorter than a normal Sn—Sn single bond (276 pm).

Sn_2R_4 has a trans bent structure with a weak Sn=Sn double bond

Now, I will show you another interesting hybridization, looks very similar to ethylene, but how they utilize in a different way to facilitate metal to metal multiple bonding especially in case of main group elements. So, tin 2 (Sn^{2+}) organometallics of the type, two Sn with bulky organic ligands, containing tin to carbon sigma bonds, are stabilized, only, if R is sterically demanding.

That means in order to stabilize elements in their low valence state you have to have bulky groups they will give umbrella protection. One such example I have shown here when you react $SnCl_2$ with very bulky ligands such as this one, it forms di-coordinated tin compound and then this is monomeric in solution, but dimeric in solid state. But the dimer does not possess a planar Sn_2R_4 framework very similar to ethylene.

Ethylene molecule is planar you can see, simply something like this, it is something like this. In contrast, this tin dimer has a different structure. And another interesting thing is the Sn-Sn bond distance is 267 picometre, this is shorter than a normal single bond having a distance of 276 picometre. That means is slightly shorter, but that is good enough to evoke a multiple bond character.

That means this has some multiple bond character between two tin atoms and then thus Sn_2R_4 this dimer has a trans bent structure with a weak tin-tin double bond. Now using hybridization concept, is it possible to explain this trans bend structure? If it is a planar structure like ethylene, no issues, simply you can say, it is sp^2 hybridization and there sp^3 are there on carbon, $2sp^2$ hybrid orbitals are utilized.

Three sp^2 hybrid orbitals are there on carbon and two sp^2 are utilized in making two CH bonds and one for CC bond from each CH_2 fragment. Now what happens, but the structure is something like this. And in case of ethylene, we have something like this, so no issues with this one, sp^2 can very easily explain the bonding here. But if you see here, what would happen? Similar to carbon it also undergoes sp^2 hybridization here.

But in this case what happens? One of the *p*-orbitals is left unutilized, but not left with an electron, but empty and now we have three sp^2 hybrid orbitals are there, and two sp^2 have one electron each. whereas the third sp^2 has two electrons, so that we have one p-orbital without having any electron. So, now they orient in this fashion in order to see this kind of Lewis acid base type of bond formation.

Now, this acts as a Lewis acid and now this acts as a Lewis base. And similarly, this empty *p*-orbital on this tin acts as a Lewis acid, whereas this filled sp^2 orbital acts as a Lewis base. So, in order to facilitate this kind of overlapping, this orientation has to be in this fashion. It is not like this, it should be something like this. When they rotate like this, what happens? Empty *p*-orbital on this tin atom will be aligned towards this one so that they can have overlapping.

So now, we have two electrons here, and two electrons here, it is not really a strong pi-bond, it is not a sigma-bond either, but it is intermediate between that one. We have still 4 electrons between two tin-tin atoms, but because of this kind of overlapping, what happens? They do not really represent too strong bonds, whereas they are relatively weak. Nevertheless, they add some multiple bond character and hence the Sn-Sn bond distance decreases to 267 from 276.

And now, you can see very interesting sp^2 hybridization. And in fact, if you look into multiply bonded compounds of main group elements, whether you take arsenic-arsenic, bismuth-bismuth, even lead-lead or silicon-silicon in all these cases this is what exactly happens, this kind of sp^2 hybridization takes place. And in order to facilitate this kind of overlapping, they have to take this kind of alignment, as a result they have a bent structure. So, that means successfully you can explain this trans bent structure using this hybridization concept.

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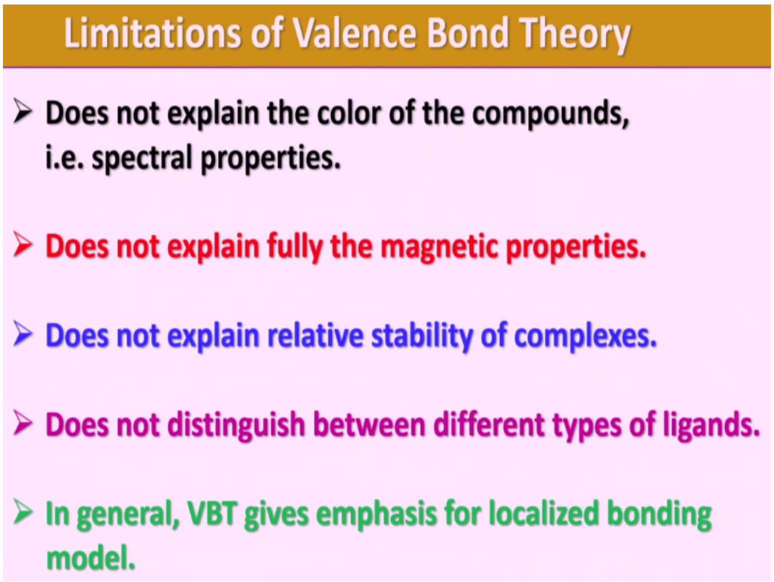

Limitations of Valence Bond Theory

- Does not explain the color of the compounds, i.e. spectral properties.
- Does not explain fully the magnetic properties.
- Does not explain relative stability of complexes.
- Does not distinguish between different types of ligands.
- In general, VBT gives emphasis for localized bonding model.

And what are the limitations of valence bond theory? When we talk about limitations; the limitations are more or less confined to its utility among coordination compounds. That means it does not explain the colour of the compounds, that is spectral properties. Does not explain fully the magnetic properties, especially the temperature dependent magnetic properties and also it gives emphasis for spin only values.

When you go for 4*d* and 5*d*, most of the metal ions do not obey experimentally determined values. Experimentally determined values are always different from theoretical values calculated from spin only and valence bond theory does not explain these things. And does not explain relative stability of complexes. Once you have coordination number 4, it can depict whether tetrahedral or square planar, but relative stability of complexes with the different ligands; answer does not come from valence bond theory.

That means it does not explain about strong field ligands and weak field ligands. Does not distinguish between different types of ligands, it does not distinguish as far as valence bond theory is concerned, whether you take cyanide, whether you take carbon monoxide, whether you take triphenylphosphine, ammonia it is just a ligand having a pair of electrons that is coming towards the metal, that is it.

In general, VBT gives emphasis for localized bonding model. Again what happens? It will try to confine a pair of electrons between the two atoms through overlapping, that means if there is some delocalization, there is no answer from valence bond theory. So, these limitations are sufficient to look for a better bonding concept to explain various aspects related to metal complexes, that is where crystal field theory made its entry into coordination compounds.

So, in my next lecture, I shall tell you more about crystal field theory with an interesting background to this crystal field theory as well. With this, have an excellent time reading chemistry.