Advanced Transition Metal Chemistry – Crystal Field Theory
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Lecture – 16
Crystal Field Theory (CFT)

Hello everyone, welcome to MSB lecture series on advanced transition metal chemistry. In my previous lecture, I discussed about the impact of ligand field on the energy of various d orbitals to make you familiar in writing crystal field splitting diagrams for various geometries, let me continue from where I had stopped. Again, I did mention about how similarities one can initiate in case of tetrahedral as well as cubic crystal field splitting and having the same splitting pattern. Let us look into more examples now.

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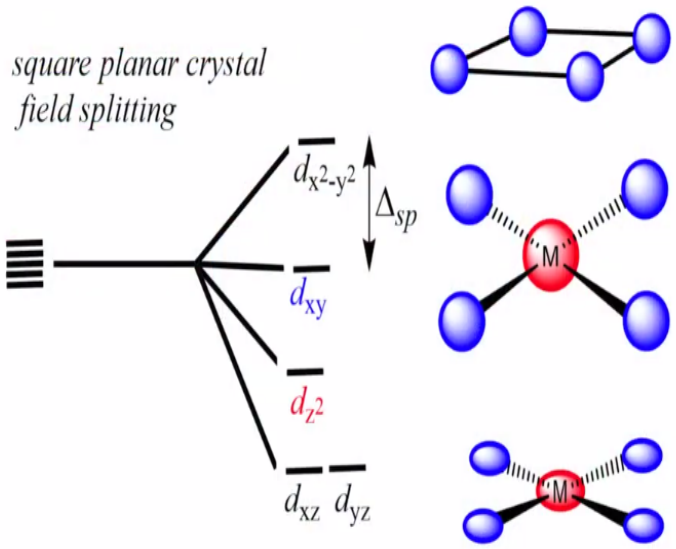

First, let us look into the square planar crystal field splitting that you are all familiar and, also, I showed in my previous lecture how they split. You can see here 4 ligands are in the plane and if you assume molecule is sitting with z-axis perpendicular to the plane of the molecule, that means molecule is spaced along the xy plane so that we have 4 ligands approaching along the x, – x and y, – y direction and no ligands are approaching along z direction.

As a result, what happens? Any orbital that is oriented in the z direction or in z associated planes, their energy will be low and hence d_z^2 and d_{xz} and d_{yz} have relatively low energy, but on the other hand, 4 ligands are coming along the xy plane as a result, $d_{x^2-y^2}$ will be having

higher energy and then d_{xy} has partial overlapping and it has little lower energy compared to the $d_{x^2-y^2}$ and this is the typical crystal field splitting diagram for square planar complexes here.

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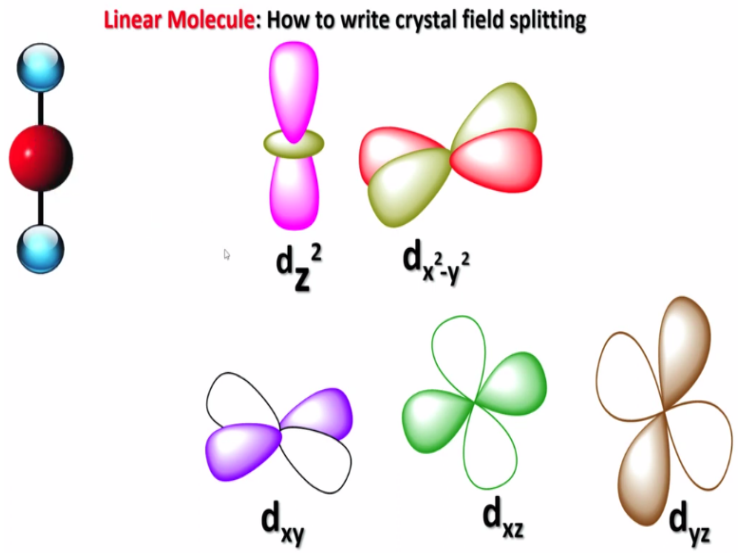

So, now, let us look into an interesting geometry that is linear geometry. Linear geometry, I did mention about few examples, diamine silver complex. And also, I did explain about how valence bond theory explains in a very unusual way taking 3 orbitals and making two *spd* orbital through the mixing of d_z^2, s and p_z orbitals. Let us look into the splitting diagram using crystal field theory to understand the relative energies of the orbitals.

And let us assume the linear molecule we are considering is placed along z axis. So, something like this. This is a linear molecule and metal centre is coordinated to two ligands in a linear fashion. As usual, we have to now write the crystal field splitting for which we have to understand the orientation of these five orbitals with respect to this linear geometry that we have given for this ML_2 molecule.

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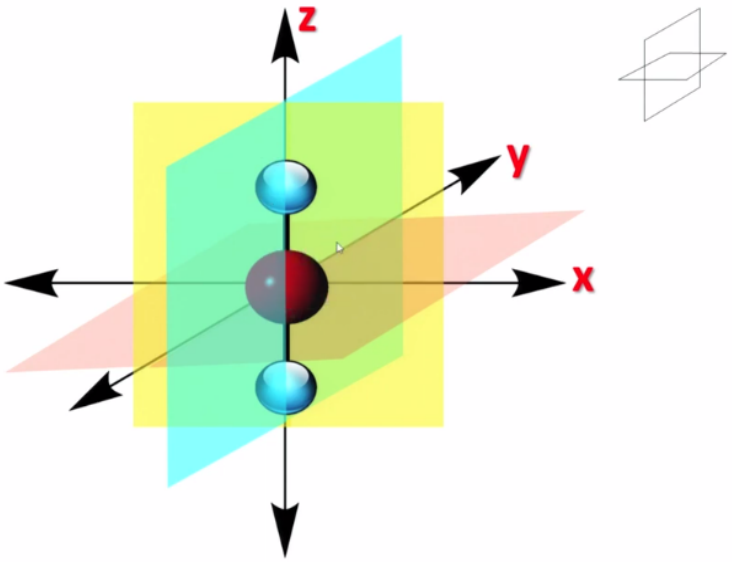

And to begin with simply write Cartesian coordinates and identify 3 planes here; xy plane, xz plane and yz plane here. Now, I place like this. Now, I have to see the consequence of replacing this one in this fashion on various d orbitals.

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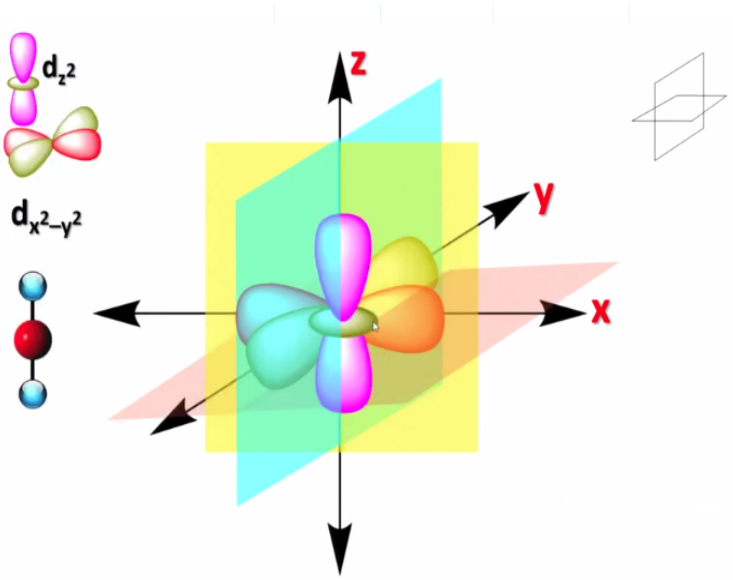

This is $d_{x^2-y^2}$. And then this is d_{z^2}, of course it is greatly affected because these two ligands are also coming in the same direction.

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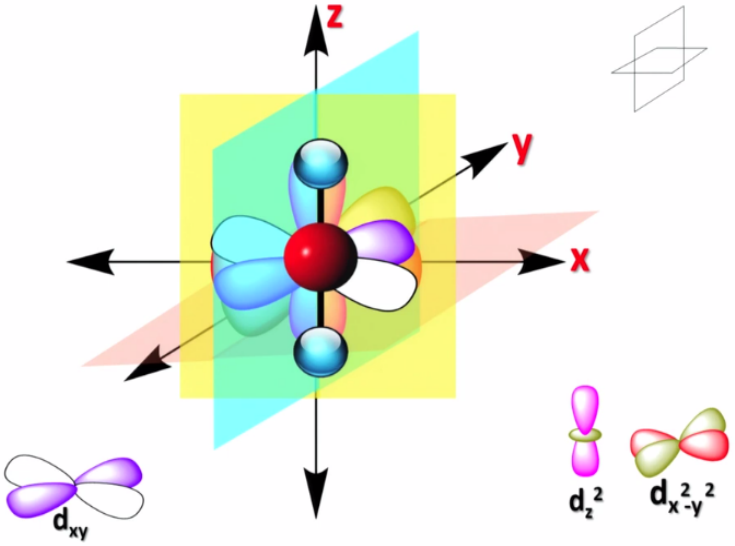

And then we have d_{xy} orbital and then again to make you familiar to give stress upon your understanding, I put again linear molecule here.

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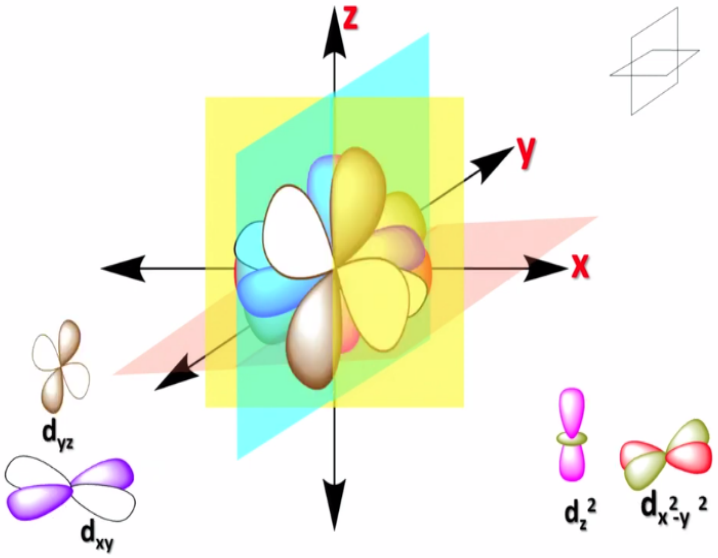

And I will take it out and add d_{xz} and d_{xy} is already added, d_{yz} I have added.

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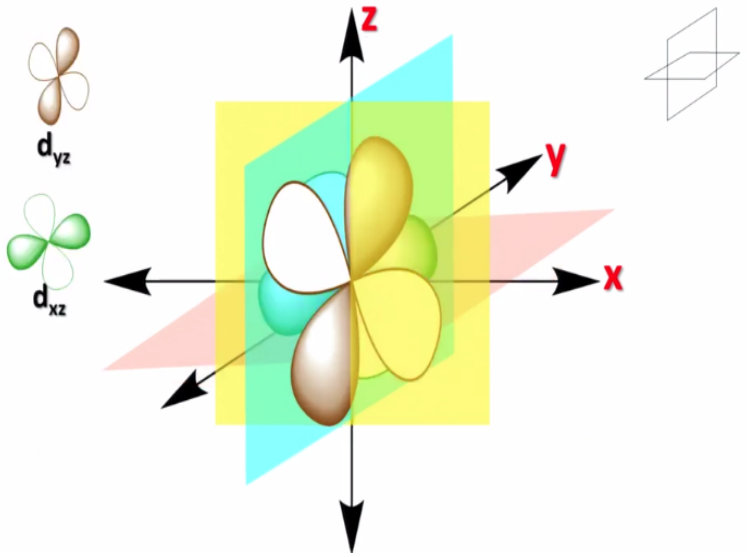

And I have added d_{xz}. Now, we should try to write the relative energies of *d*-orbitals under the influence of linear crystal field.

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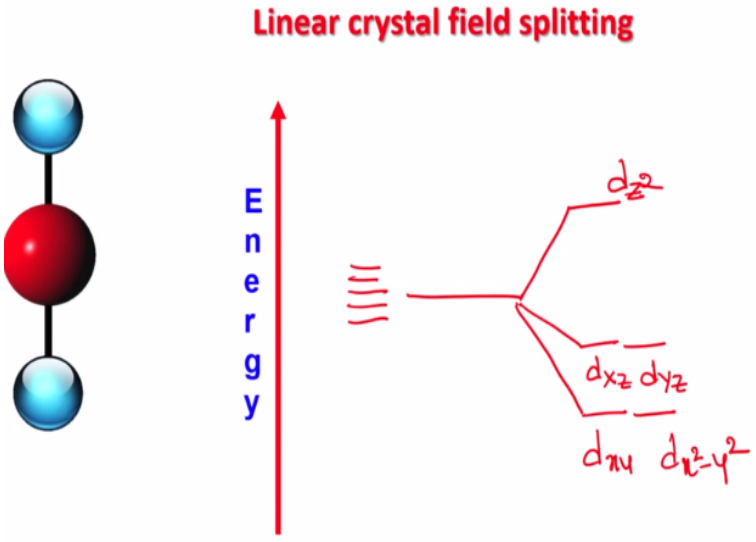

Let us consider, these five d-orbitals. Obviously, you should know which one is here because this is d_z^2, the molecule is in this direction. And now the second one will be d_{xz} and d_{yz} and the least energetic ones are d_{xy} and $d_{x^2-y^2}$. So, this is for linear crystal field splitting. So it is very easy, is that right?

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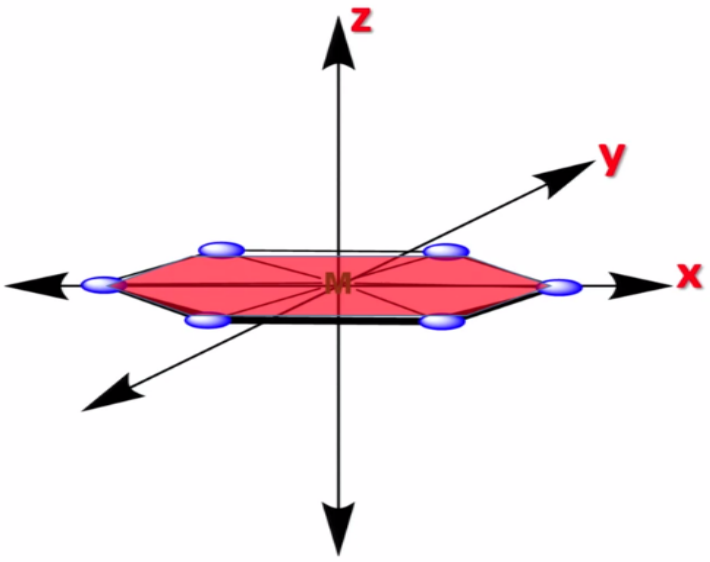

So, now another interesting one, hexagonal planar geometry. And if you recall Werner's coordination theory, he prepared a series of octahedral complexes having different compositions, like MA_6 and MAB_5 and MA_2B_4 and MA_3B_3 to identify which geometries would give you isomers and accordingly he tried to isolate as many isomers as possible and later he concluded with that important experimental work that for coordination number 6, the most preferred geometry would be octahedral.

And have you come across any examples of transition metal complexes having hexagonal planar geometry? It is very difficult because you have to put lot of stress on orbitals to orient in this fashion by distorting their original positions and that really makes unstable, as a result we do not come across examples for hexagonal planar geometry, especially when coordination number 6 is there. The most preferred geometry is octahedral and the alternate one we have at our disposal is trigonal prismatic geometry.

But nevertheless, let us try to look into it and find out whether any example is there or not in the literature. This is hexagonal planar. So, as usual I place Cartesian coordinates and look into relative positions of various orbitals. Here to understand the impact of them on the 6 ligands approaching in this xy plane, you can see the six directions in which 6 ligands are approaching the metal to establish ML_6 having hexagonal planar geometry. It appears like imaginary, but later you will be surprised to see result in the literature.

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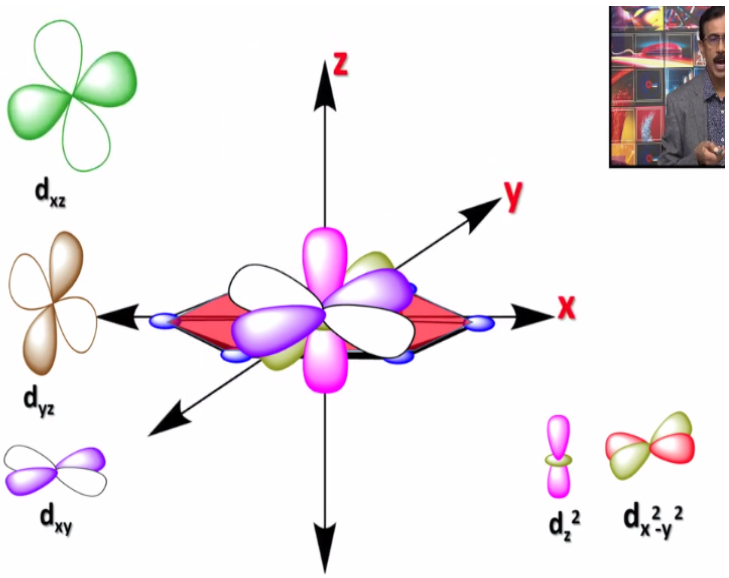

So, this is how I have placed some orbitals here; you can see which are the orbitals I have placed here. I have placed $d_{x^2-y^2}$, d_z^2 and d_{xy}. Now, I should place again Cartesian coordinates and add xz and yz here. So, that means if you go back here, you can see that since 6 ligands are in the plane, the 6 ligands are in the xy plane, whatever the orbitals that are present in the xy plane will be affected more.

And once again if you see here d_{xy} has maximum overlap with the direction of approach of 6 ligands compared to $d_{x^2-y^2}$. As a result, here the energy of d_{xy} will be much higher compared to $d_{x^2-y^2}$. Next comes d_z^2, we do not have anything and same things in case of d_{xz} and d_{yz}.

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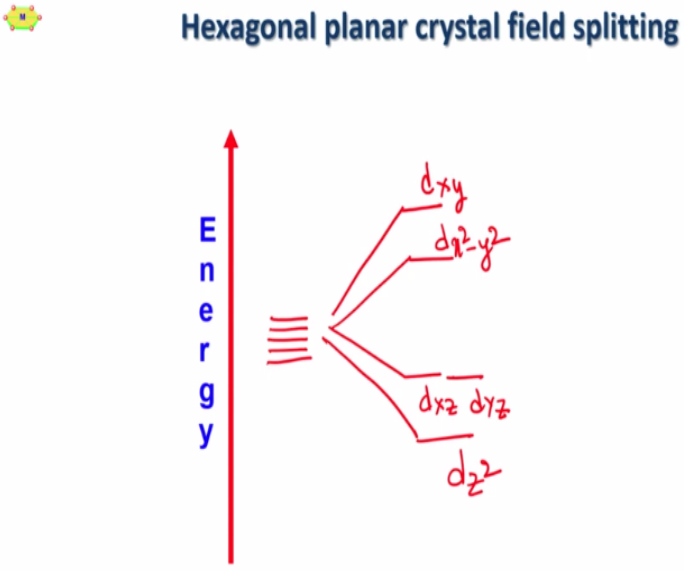

So that, writing the crystal field splitting diagram for hexagonal planar geometry would be very easy. Once again consider 5 d orbitals and then here it splits into four levels. Now, I

have shown four levels out of each third one from top or second one from bottom is doubly degenerate. And as I mentioned, d_{xy} has maximum overlapping with direction of four ligands when they are approaching along the xy plane.

So d_{xy} will be much higher in energy. The next one is $d_{x^2-y^2}$. Next what we have is d_{xz} and d_{yz} and the least energetic one is the d_{z^2}. So, this is how one should be able to write crystal field spitting for hexagonal planar molecule, if at all if it exists among coordination compounds of 3d, 4d or 5d. It is very easy, is that right? So now, I give a list of several geometries, I am going to discuss one or two more.

But nevertheless, you should make an attempt to write crystal field splitting diagrams for all geometries that I showed or you can look into various polyhedra and also you make an attempt to write crystal field splitting diagram for them.

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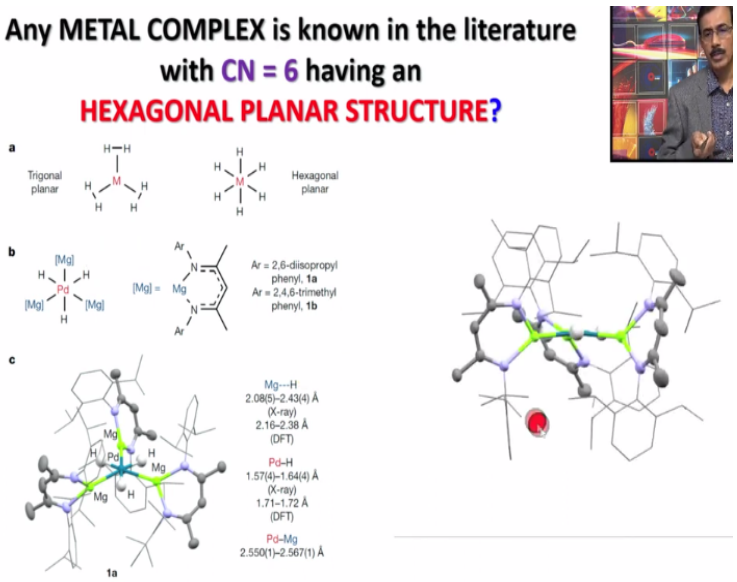

The question is any metal complex is known in the literature with coordination number 6 having a hexagonal planar structure? Yes, there was a paper appeared in Nature in 2019 that after palladium complex having hexagonal planar geometry. So, this is the molecule shown here, you can clearly see palladium is coordinated to 6 ligands, three hydrides are there and three magnesium moieties are there and here magnesium is attached to a ligand called NacNac.

And this ligand is derived by reacting with very bulky primary amines with acetylacetonate and these ligands have been extensively used in various aspects of both main group chemistry

and transition metal chemistry. And here one interesting thing is they have made a magnesium complex, this is mono anionic. So, magnesium still has one electron to donate and now three such bulky groups are attached to palladium in this fashion and in between three hydrogen atoms are there.

And then if I ask you to identify the oxidation state of palladium and oxidation state of palladium in this molecule comes to be "zero" because three anionic hydrides are there and three cations are there, eventually they cancel and the Palladium is d^{10} system and now all 6 ligands are according to covalent method, one electron they are donating this is a d^{10}, 16 electron complex and this is how the structure looks like. You can see here how the entire metal coordination sphere looks planar here.

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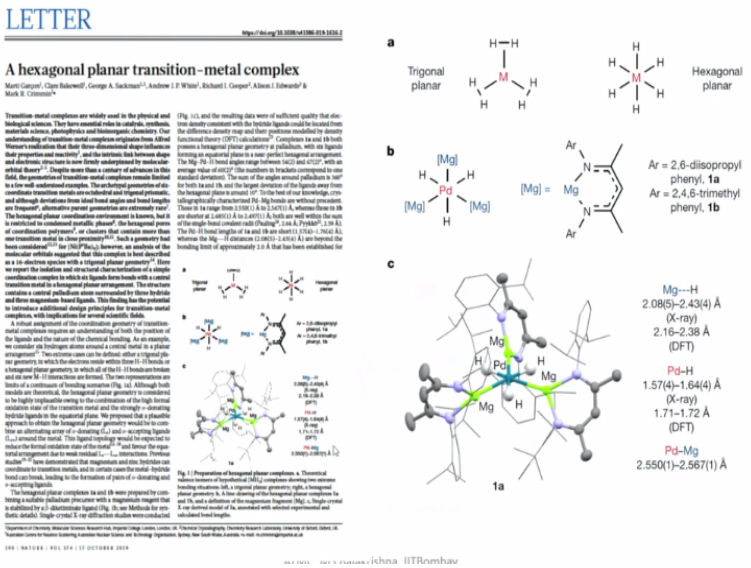
LETTER

A hexagonal planar transition-metal complex

Trigonal planar

Hexagonal planar

Ar = 2,6-diisopropyl phenyl, **1a**
Ar = 2,4,6-trimethyl phenyl, **1b**

Mg···H
2.08(5)–2.43(4) Å
(X-ray)
2.16–2.38 Å
(DFT)

Pd–H
1.57(4)–1.64(4) Å
(X-ray)
1.71–1.72 Å
(DFT)

Pd–Mg
2.550(1)–2.567(1) Å

1a

This came in Nature in 2019.

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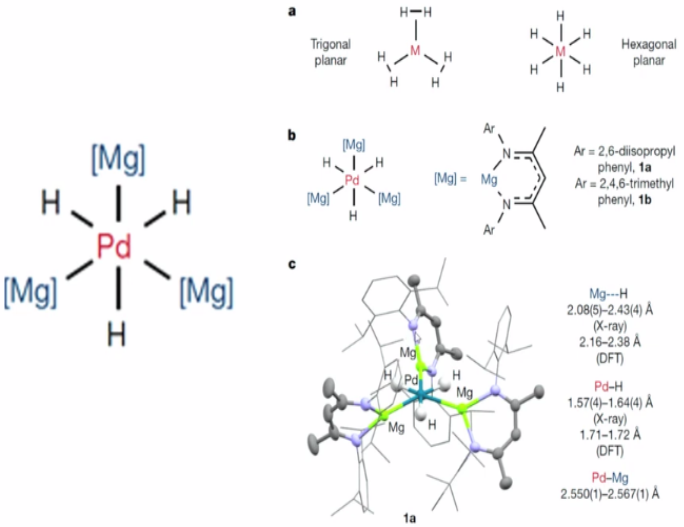

Mark R. Crimmin and co-workers, Nature _2019_574,390-393

This is the only example, we have, to show that this very unusual geometry is also quite possible with transition metals. It is very interesting and it is a surprise result here.

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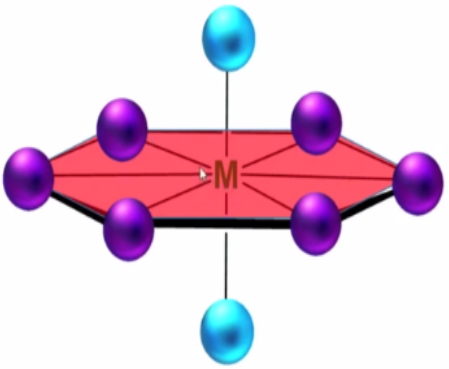
Hexagonal Bipyramidal Crystal Field Splitting



So, now, let us look into hexagonal bipyramidal crystal field splitting. In my previous slide I showed you about writing crystal field splitting diagram to hexagonal planar. Now, let us see how to write the similar crystal field splitting for hexagonal bipyramidal geometry. Here only the difference between the previous one, hexagonal planar and hexagonal bipyramidal, is we have two more ligands approaching along z direction.

So, that means they have an impact on d_z^2 orbital and probably energy of that one is elevated in contrast to what we came across in case of hexagonal planar, that is going to be only the difference or anything else we shall see. So, this is the typical hexagonal bipyramidal

molecule and the metal is at the centre. To distinguish between axial and the planar, I have given different colours for the ligands, it does not matter if it is homoleptic or heterolytic.

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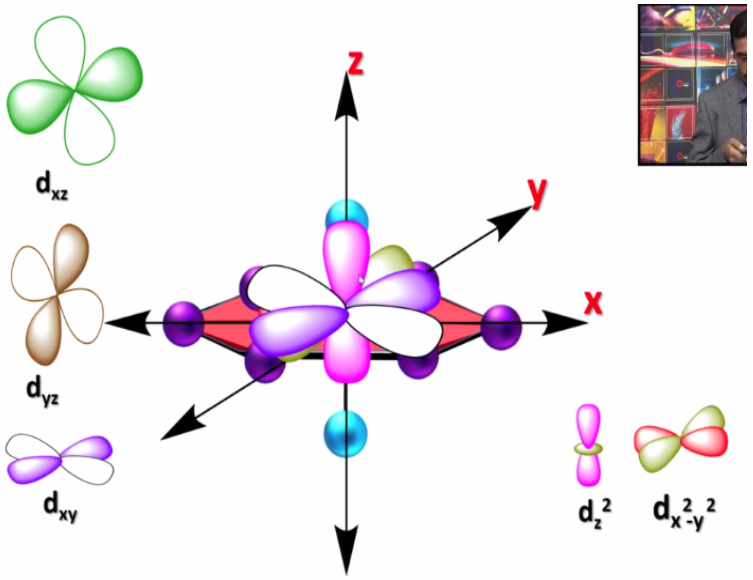

Now, again consider these five d orbitals and place Cartesian coordinates and place this molecule here and place one, you can see now the impact on d_z^2 and then you can also see the impact of $d_{x^2-y^2}$ and then d_{xy}. The impacts are very similar to what we saw in previous example of hexagonal planar except the influence of d_z^2, rest would remain same.

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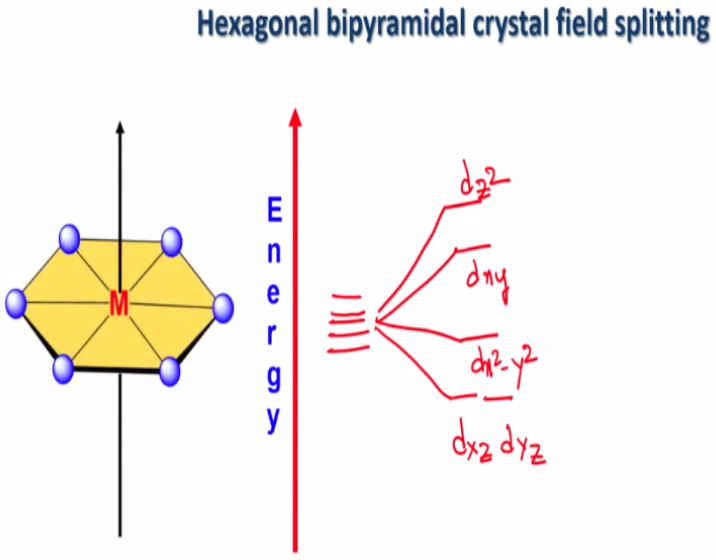

So, now let me write crystal field splitting diagram for this one. So, five are there here, So, now I have written for energy levels with the least energetic one is a doubly degenerate, obviously you can make out which is this one. The orbitals that are least affected when you visualize hexagonal bipyramidal molecule are d_{xz} and d_{yz}. And the maximum affected orbital

is d_z^2 because two ligands are coming in the same direction, so this is the d_z^2. And as usual d_{xy} will be having maximum overlapping with 4 ligands in the plane.

As a result, this is d_{xy}. The one left is without any problem one should be able to write. What is this one, this is $d_{x^2-y^2}$. So, this is how hexagonal bipyramidal crystal field splitting can be drawn in this fashion to show the relative energies of various orbitals. Hope you have understood, how to write in a simple way Cartesian coordinates and then putting the geometry at the centre, and then try to paste the ligands to understand their influence and writing the appropriate crystal field splitting diagrams.

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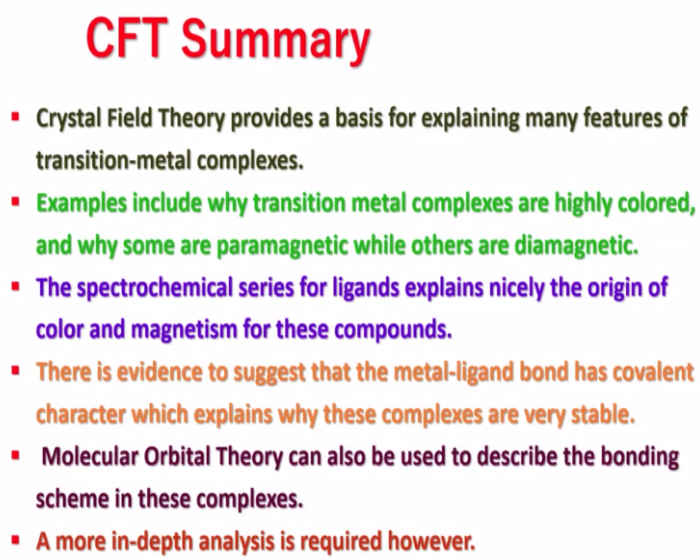

So, let me summarize now crystal field theory. Crystal field theory provides a basis for explaining many features of transition metal complexes, that you saw in my last two lectures. And the examples include, why transition metal complexes are highly coloured and why some are paramagnetic while others are diamagnetic, so that information about magnetism also comes. The spectrochemical series for ligands explains nicely the origin of colour and magnetism for these compounds.

And there is evidence to suggest that the metal-ligand bond has covalent character which explains why these complexes are very stable. And of course, I did not really mention about that nephelauxetic effect, that is coming under ligand field theory, I am going to start that one. And molecular orbital theory can also be used to describe the bonding scheme in these complexes.

To understand better about the significance of the ligand field one should go for either ligand field theory or I would say molecular orbital theory. Nevertheless, ligand field theory and molecular orbital theory are almost the same. A more in-depth analysis is required however to understand all aspects using molecular orbital theory as it involves tedious calculations. So, let me stop today and begin my next lecture on molecular orbital theory. Until then have an excellent time reading chemistry.