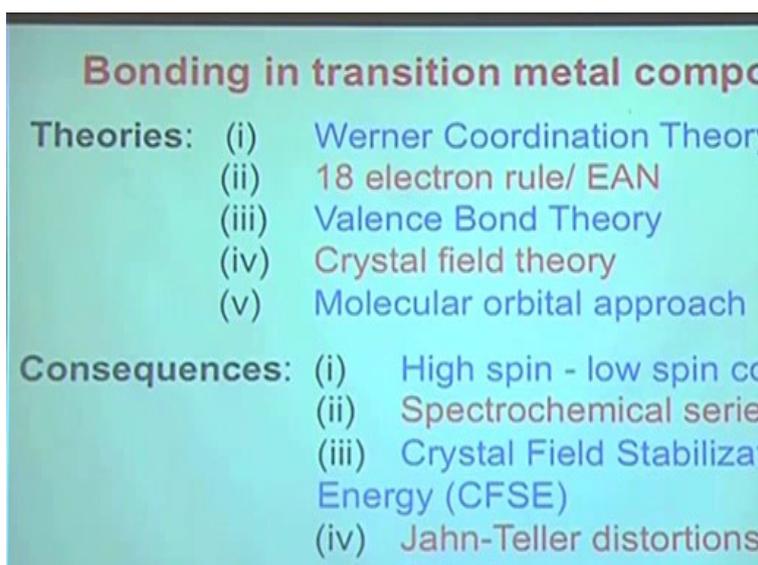


Concepts of Chemistry for Engineering
Professor. Debabrata Maiti
Indian Institute of Technology, Bombay
Lecture No. 29
Coordination Chemistry: 18 electron rule and VBT

Two topics whatever we have seen so far is based on different metals. We have seen, of course, in periodic table every element is there. In the last topic which was the extraction there we particularly see them metal complexes or ores in different oxide forms, sulfide forms and so on. In this one particularly we are going to discuss about the transition metals and transition metals only, because they do have d, they are D block element and they have either fulfill or half filled or partially filled d orbitals. And thereby, their chemistry is usually something what is called very exciting compared to all others. So, chemistry of transition metals we will be discussing.

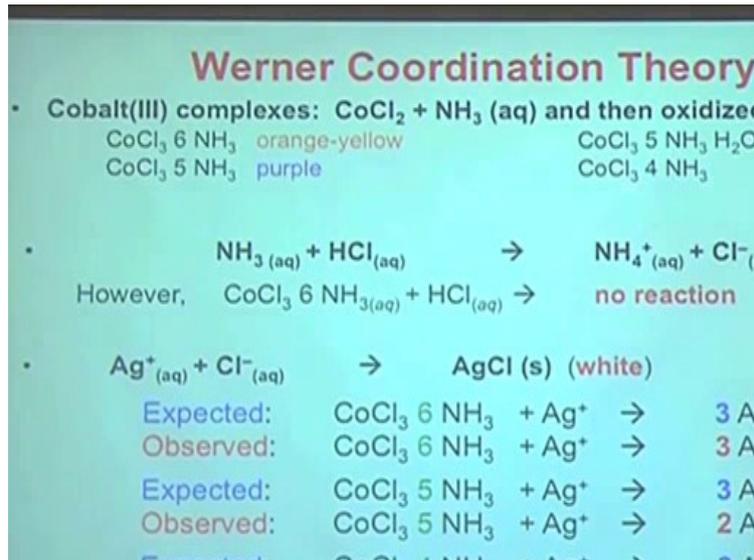
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In this we will be particularly focusing on these theories; Werner coordination theory, 18 electron rule, valence bond theory, crystal field theory, not too much perhaps on molecular orbital approach. Also, we are expected to learn high spin low spin complexes, spectrochemical series, crystal field stabilization energy, Jahn-Teller distortion, and finally, about the spinels. So, these are roughly the topic I am going to cover today. I will start with Werner coordination theory.

I would like to take you let us say more than really 100, 120, 130 years back what chemists was thinking. That time, of course, right now, we see the books are all written, because a lot of studies has already been done over the last 100 years, 150 years. If you just look back, forget that there was almost very little understanding at somewhat like 150 years back.

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In that perspective, if you are looking at, right now you may not be able to appreciate the importance of this contribution Warner coordination theory, you have to really look back at least 150 years or so. What that time was known very simply is different complex can be formed, but how they are forming, what they are forming, what type of compounds they are, and why the colors are coming, shows, these important information although were there, but then it cannot be explained.

So, for example, over here one of the instance where we see cobalt chloride reacting with ammonia under aerobic condition, what we are seeing essentially is cobalt chloro or cobalt chloride with different equivalent of ammonia can be incorporated from same static material depending on the reaction condition, how much ammonia you give, how much heat you give, what solvent you use.

Let us say, lot of different parameters are there, but the starting material remains same. What people have observed is you can form different color complex. That time what it is forming people did not know. They all knew that different species are forming based on their color. This

is where Werner came in. He tried to first time give an explanation of what might be happening in there. Why from same starting material, we are getting different compounds or what type of compounds they are.

So, of course, that time a lot of things were not really established. X-ray crystallography, spectroscopic other techniques were not simply there. So, all people perhaps can rely on is whatever is known before and based on that come up with some sort of theory. That is what we are trying to say. So, what was known before is ammonia and HCl can react to give ammonium chloride. What they are found that these compound, they do not know what type of compounds are they, but they know that they are different color and different equivalent of ammonia is there.

Now, if you look at this reaction, cobalt chloride plus HCl, simply, there is no reaction. If ammonia was just there as if like just free ammonia with HCl you are expected to get this reaction. But with these complexes, none of these four complexes, for example, did give ammonium chloride. So, it is definitely not, the ammonia is definitely not present in free form. That is the first conclusion. So, it is not just ammonia gas sitting in the complex. It is something has happened. Again, I am talking about 150 years old discovery.

Now, for what they tried to do? This is a known reaction which is known for long, silver plus if you add to a chloride solution, you will get silver chloride white precipitate which is something I guess, right now, you are very familiar with or have done some experiment. So, what they have done is they have taken the first compound orangey yellow one, let us say, and they tried to add silver. Now, you can quantify how much silver chloride is formed. They have quantified that three equivalent of silver chloride is formed. So, all the 3 chloride are accessible for silver plus.

Now, they have done the same experiment, let us say, with this one, purple one. And they found that with silver plus only 2 equivalent of silver chloride in forming. Although 3 chlorides are there, only 2 chlorides are accessible. That is how you can clearly see between first and let us say a second compound you already having some sort of discrimination. 3 chlorides are accessible, only 2 chlorides are accessible. Now, you keep on doing it for other compound what do you learn is, let us say, for example, this one, you can get only 1 silver chloride, one equivalent. For the first one it has 3, then 2, this one and so on.

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• **Measurements of the conductivity:**
CoCl₃ 6 NH₃ four ions
CoCl₃ 5 NH₃ three ions
CoCl₃ 5 NH₃ H₂O four ions
CoCl₃ 4 NH₃ two ions

• The secondary valence is the number of ions of molecule are coordinated to the metal ion.
Werner assumed that the secondary valence of the metal in these cobalt(III) complexes is six. The formulas of compounds can therefore be written as follows.

[Co(NH ₃) ₆] ³⁺ 3Cl ⁻	orange-yellow
[Co(NH ₃) ₅ (H ₂ O)] ³⁺ 3Cl ⁻	red
[Co(NH ₃) ₅ Cl] ²⁺ 2Cl ⁻	purple
[Co(NH ₃) ₄ Cl ₂] ⁺ Cl ⁻	green

And then what you do is you try to do the conductivity measurements. Conductivity measurement tells you how many ions are there, how many, simply how many ions are there. For the first case, they found four ions, three ions, four ions and two ions. So, how many ions are present in that colored species you can kind of count. So, conductivity measurement gives you that.

Now, this is where the brilliance, I think, the, when nothing is known from out of almost a black box, this guy Werner come up with some theory. And that is what very simply what you know kind of a coordination compound or the secondary coordination sphere. What he is trying to say is, there is a metal in the center and these ligands, so called let us say chloride, ammonia, they are coordinated with the metal center.

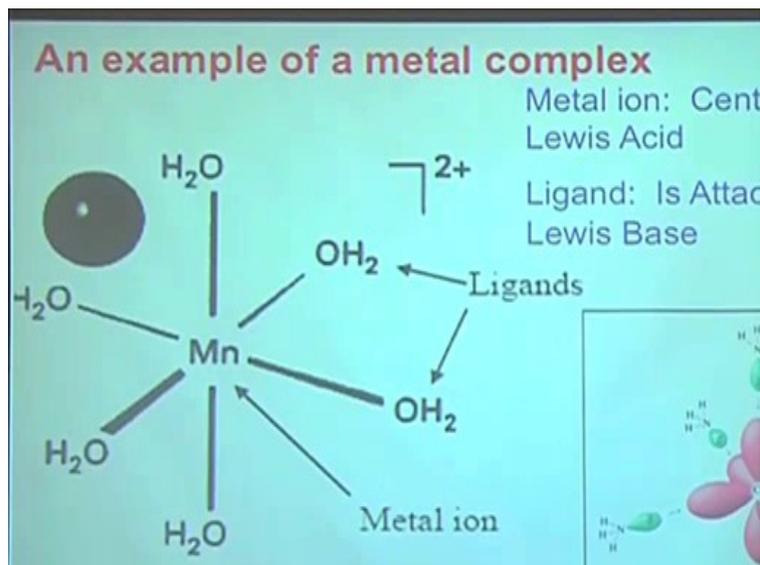
That is the first coordination sphere, and the outside, whatever else is left that will be outside, those are accessible. The one which are with the metal complex, those are kind of not accessible. Let us say, when you are seeing 3 chloride, if only one chloride is accessible that means 2 chlorides are bound with the metal center. I mean, this is actually a revolutionary thought when almost nothing was known.

So, of course, you can see Nobel Prize in 1913, of course, our grandparents and great grandparents time, but it is really, really a classic understanding or classic idea, theory that kind of, I would say, redefined the whole understanding. People did not have any idea what the

complex is, how it forms and so on. So, if you now try to look back, everything falls into place, all those conductivity study, all those silver experiments silver nitrate or silver whatever salt experiment, so 3 chloride can be precipitated, 3 chloride can be precipitated, 2 chloride can be precipitated, 1 chloride can be precipitated, because those are not directly bound with the metal center.

On the other hand, if you look at this is two anion one cation and one anion, so two ions, conductivity measurement will give you two ions. This one two anions and one cation, whole thing is one cation. So, it is 3 ion all those things. Now, you look back the simple experiment now can be kind of explained by this, of course, that guy deserved the Nobel Prize, no doubt back in then. Of course, now, you try to come up with something like this, it is not going to dent anything.

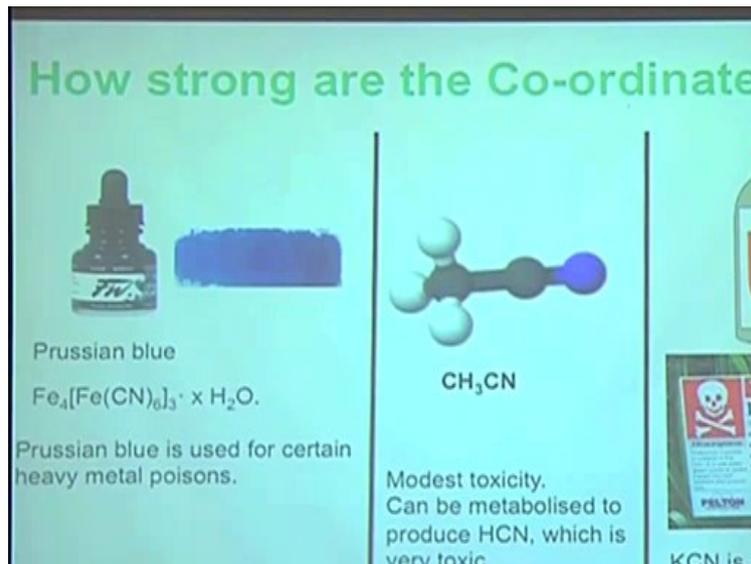
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Now, so that is what a metal complex should look like then, like what Werner tried to say. You have a metal center, ligands. These ligands could be same ligand, different ligand, combination of different things, but it should be coordinating. So, this is the main coordination sphere. So, 2 plus means overall this whole thing is having 2 plus. So, manganese could be 6 plus, but if some negative charges are, they are they will neutralize it, just like in the last place, let us say over here. Cobalt is 3 plus, but 2 chlorides are there. So, cobalt, overall this iron is 1 plus.

Now, you know what is metal ion, what is ligand, the basis, the explanation or the definition is given. Ligand is the one which is attached and usually it is a Lewis base. The Lewis acid is the one which is the metal at the center, very simple. So, you can look at this pictorial diagram which kind of showed how perhaps these ligands are bound with metal orbitals, which I will be coming again in later slide.

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So, how strong are this coordinate bond, something like potassium cyanide. You know that this is a ionic compound. Now, it is very deadly poisonous. All of you knew. Never ever even try to test it. I mean, it is a bad idea. And the problem is it is water soluble. That is why it is so dangerous. Lot of things, it is not like potassium cyanide is the only bad things known, but it is water soluble. Lot of bad things may or may not be that much water soluble. So, that is how let us say living organism may not be affected too much, but potassium cyanide is one of the bad ones.

Carbon monoxide gas is again another bad one. All these hopefully we will be able to learn at the end of the course. We will see that they can bind with the ion center with the porphyrin ring known as the haem center. And thereby they can prevent the oxygen binding which we are inhaling. This oxygen is going in our body and is getting bound with the porphyrin ion center. Those binding sites are getting occupied by these guys, carbon monoxide, cyano, how they are

getting bound, how strong is their binding, this sort of information we might we will be able to tell you at the end of the class. Not this class, end of the course.

Now, when you take acetonitrile this is a solvent. See, this is how that, of course, this is not a friendly element, but you can see this is by having a covalent bond changes a lot of things. This is also cyano, this is also cyano, but things are completely different. It is still toxic, but not as toxic as this. Of course, you know that Prussian blue, which is widely used. Of course, none of these are friendly chemical. I would say except what are, do not expect anything to be friendly, literally.

You use acetone for removing the nail polish or anything erasing, those are bad thing like erasing board and other things, those are bad. Anything else pretty much. Benzene you end up drinking, you are dead. I am sure. I mean, not immediately, it will take some time. So, none of the chemical, I would say, is friendly, or maybe sodium chloride, but not from the lab but at home. That is fine.

But do not ever try to experiment with any chemicals without knowing their properties first of all and do not consume, do not touch physically, do not smell directly or do not definitely do not consume. That is going to cause something. If not today, maybe 10 years down the line. See, sometimes some poison works over the long time. So, Napoleon Bonaparte, for example, is believed to be murder by arsenic poison. So, not over, so every, I mean, I am forgetting the exact story.

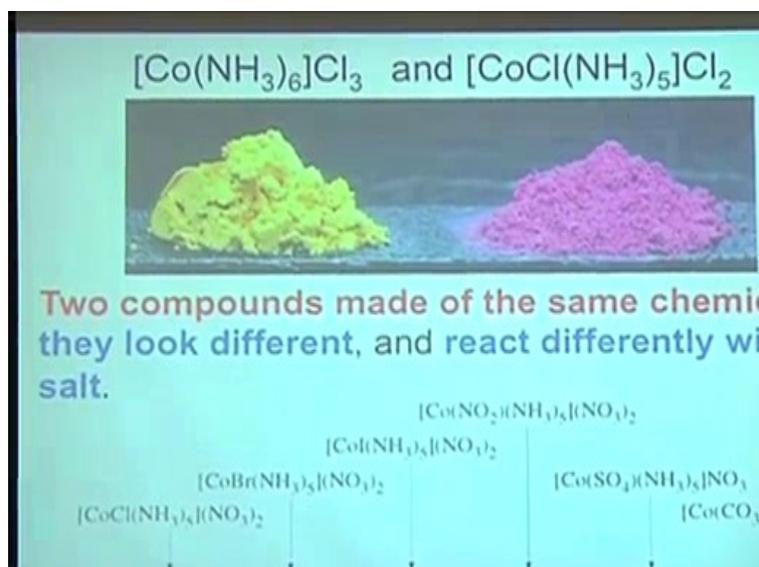
Every day, let us say, with the meal or whatever you are consuming some amount of arsenic was given to him by the loved ones, I do not know who. And over time he had consumed enough arsenic. Of course, arsenic is going to and those are painful deaths sometime. I mean, not only these, there are even painting, some of the painting uses some of the deadly chemicals, which, a lot of a lot of things are there.

Even let us say in car garage you see in the movie, you go in a confined space in a small room with the car on, you keep the car on that is one of the way to do suicide. You should not follow. It is painful, it is not painful, but it is in movies at least they show. That is I would say less painful. So, it is a small garage. Everything is closed. You put your car on. Slowly carbon monoxide get generated enough to kill you. Let us say by the overnight someone can be killed.

But of course with the type of murder we are seeing nowadays in the news, I do not think I need to make you aware of what bad things can happen.

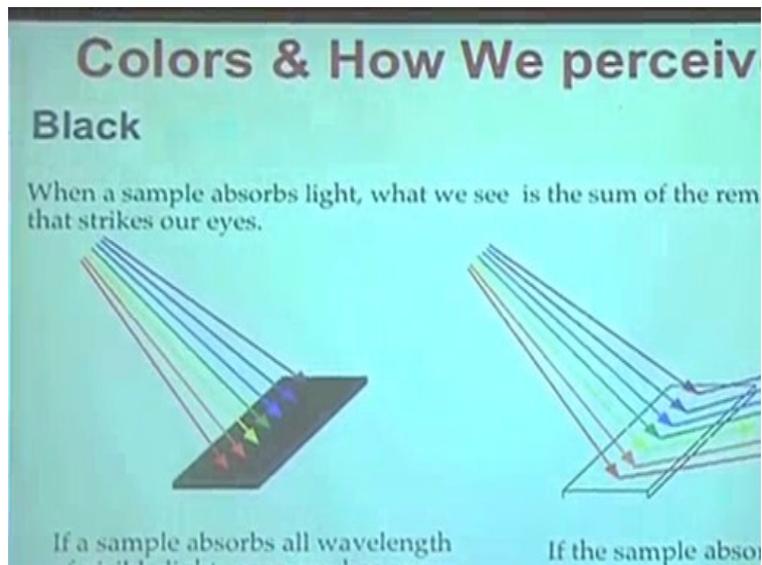
Anyway, you should, the main point I am trying to bring to you is simply chemicals are dangerous. Please do not play with chemical and do not abused the chemical specifically not to other human being or other living things. It is bad. Sometimes people have idea to kill a tree with some chemical. Those are the bad ideas. And you fight with someone, you see a lot of stories here and there. So, do not abuse chemical. Let me go forward.

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So, for example, the same thing what was showing, see how different the color could be depending on the where the anions are or how the compositions are. It is exactly same compound. If you see formula-wise cobalt 3 chloride and 6 ammonia, but completely different color, thereby completely different compound, same formula, but completely different compound and giving completely different colors.

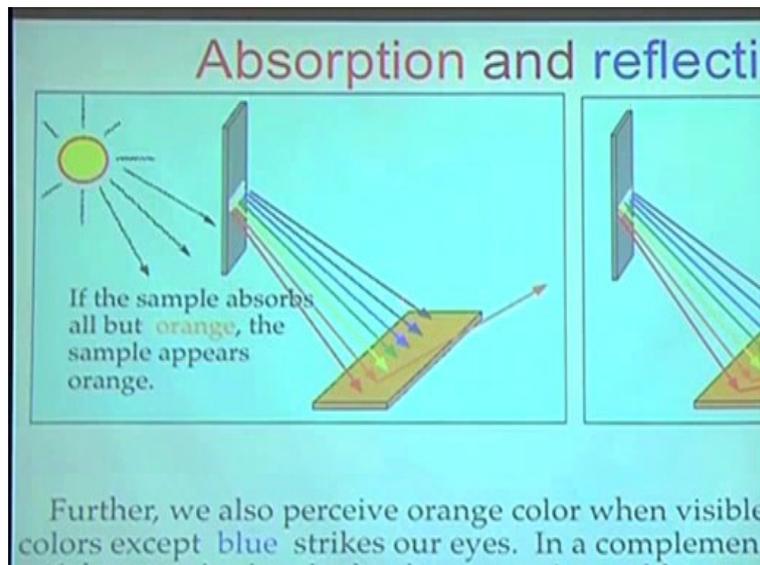
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Of course, in physics, you have learned how the color we perceive and how what happens, why you see this is white, something is black, something is orange, something is blue, you just try to refresh your memory from that perspective. So, very briefly, if all the colors are consumed or absorbed by some compound or some species that you are, that species is going to be black in color. If nothing is absorbed, that is going to be white in color for example.

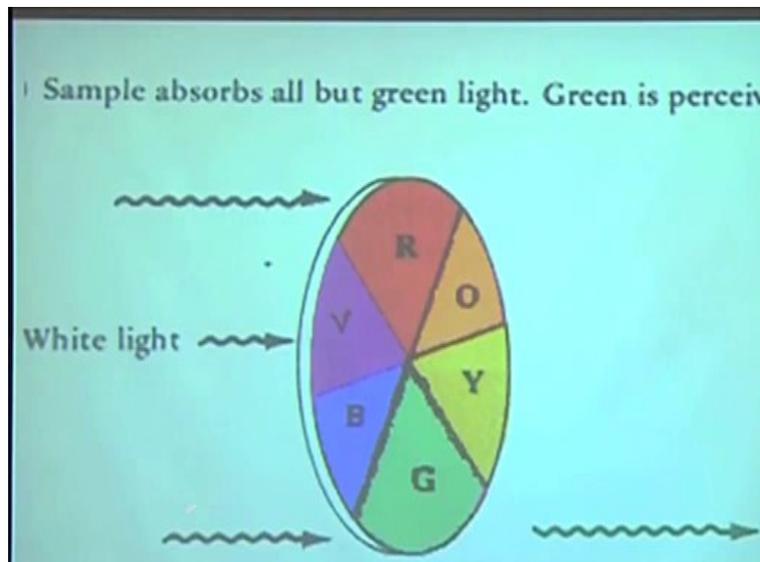
And sometimes there is a, of course, there is a complimentary color, then let us say, for example, if blue is just absorbed by some species, all you are going to see is orange. If orange is absorbed by some species, all you are going to see is blue. So, this sort of complementarity you are familiar with. It is, of course, we are not going to ask any question for this course, but just know how the color appears in different things.

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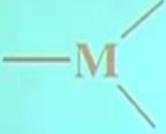
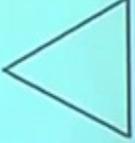
So, everything else is consumed except orange. So, we see orange and everything else did not get consumed only blue gets consumed. So, we see orange and so this sort of complementarity is there.

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So, for example, over here, we tried to show that sample absorbs all but green light. Everything else is absorbed except green light. So, you see green. These are pretty fundamental stuff you have studied before.

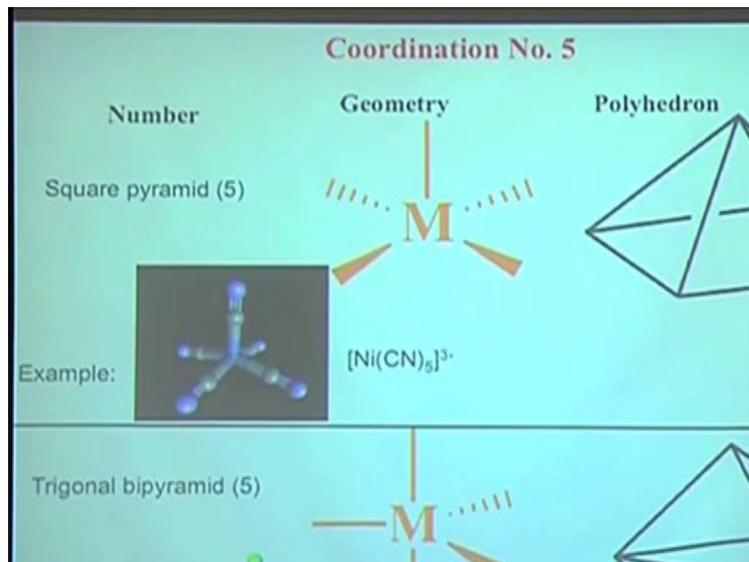
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Number	Geometry	Polyhedron
Linear (2)		
Trigonal plane (3)		
Square planar (4)		

Now, this is something I have discussed before in the first topic. I will take you just through this in a minute, but I guess one question or so can be coming from here. So, you should be familiar with the structure or basically their geometric. So, this is a linear when the metal is at the center and two ligands are there usually they will have a linear coordination. One example is given here. You have a metal and 3 ligands. 3 ligands could be separate, 3 different ligands or 3 same ligands, does not matter. You usually have a trigonal or planar complex, for example, mercury triiodide.

Over here nickel tetracyanide, you can have a square planar geometry. You see so nice. It is like perfect, almost perfect geometry. Now, tetrahedral, of course, CH_4 is tetrahedral, but with the metal complex something like iron tetrachloride is tetrahedral, zinc tetra ammonium species is tetrahedral. There are lot of tetrahedral complexes as well.

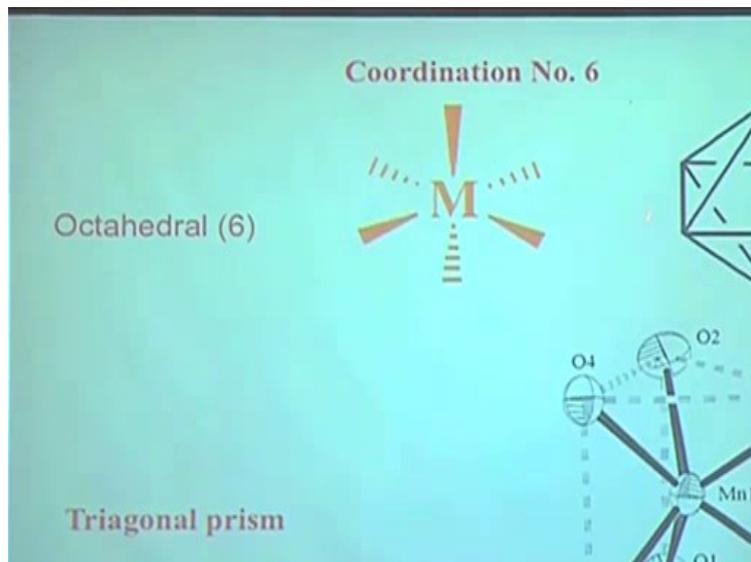
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We have 5 coordination nickel pentacyanide so nickel is in the middle, cyano, cyano, cyano, cyano, nickel is in the middle cyano, cyano, cyano, cyano. So, it is overall a square pyramidal geometry around the metal center or in this case nickel center. So, these are one example. I think it is better to kind of, I do not know, I should not say memorize. You should kind of visualize how the metal complex should look like.

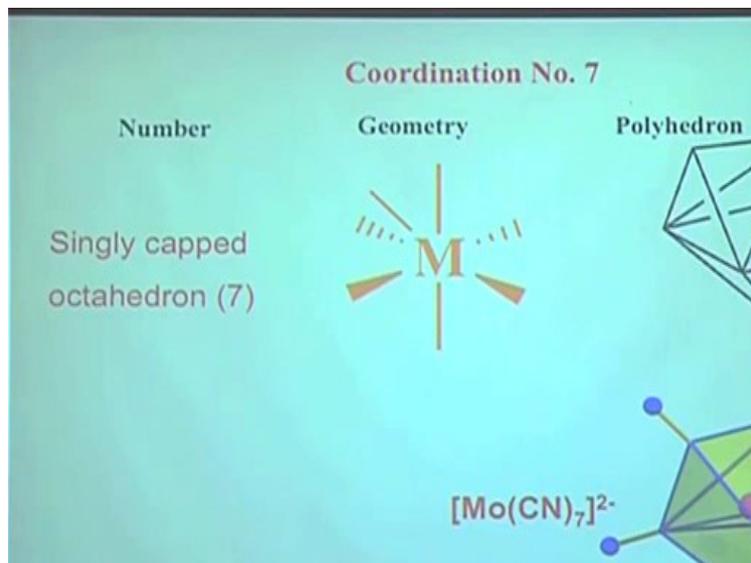
This is trigonal bipyramidal. So, there is a plane between these three and then one in the axial, one in the, two in the axial on top, one in the equatorial position, axial position as it is shown here. Those sort of explanation will be coming. This is where different theories had come up. We are slowly getting into that. At the end of the class it might be clear. If it is not today clear maybe hopefully definitely in the next class it will be clear. That is part of the discussion.

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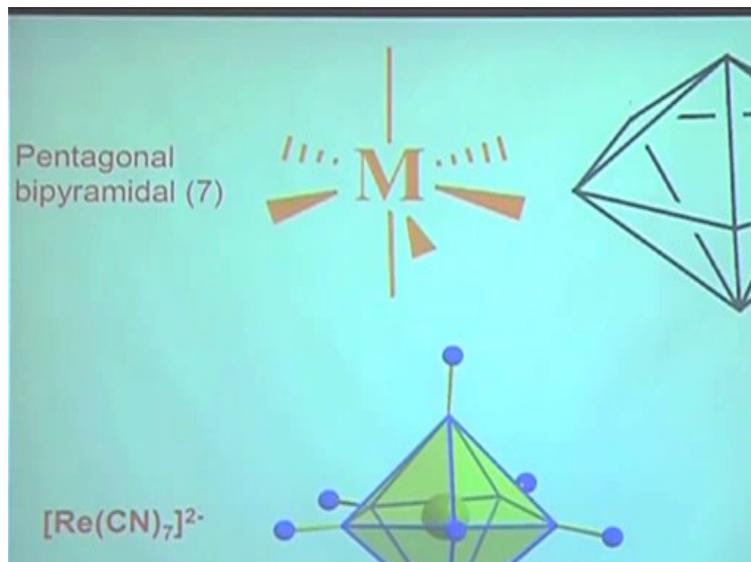
So, there are other compounds. These are, this is a manganese hexa 1, 2, 3, 4, 5, 6, manganese hexa-oxo complex or MnO_6 complex. Octahedral can be, as you know what octahedral is, this is the basal plane or the four of these are in the same plane. This is axial that is axial so something like this. So, you know these.

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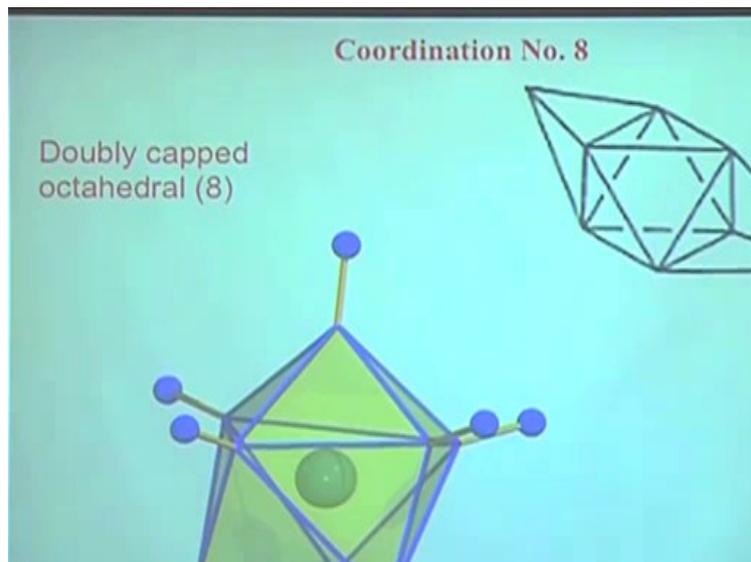
Coordination number 7, you look at these, it should be clear. If it is not clear please do come back.

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There are pentagonal bipyramidal as it is shown in here and shown up to this.

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I think you should be remembering coordination number 8. So, metal center is always at the middle and then different ligands are over there surrounding the metal center and thereby giving different geometry.

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Ligands

Ligands are species (neutral or anionic) bonded to the central metal ion

They may be attached to the metal through a single atom (monodentate) or three atoms or higher (bidentate, tridentate, etc.)

Such polydentate (bidentate or higher) are called chelating ligands

Now, of course, I am not going to get to the definition of ligands. It is there for you if you want to read about it.

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Some very common & simple ligands

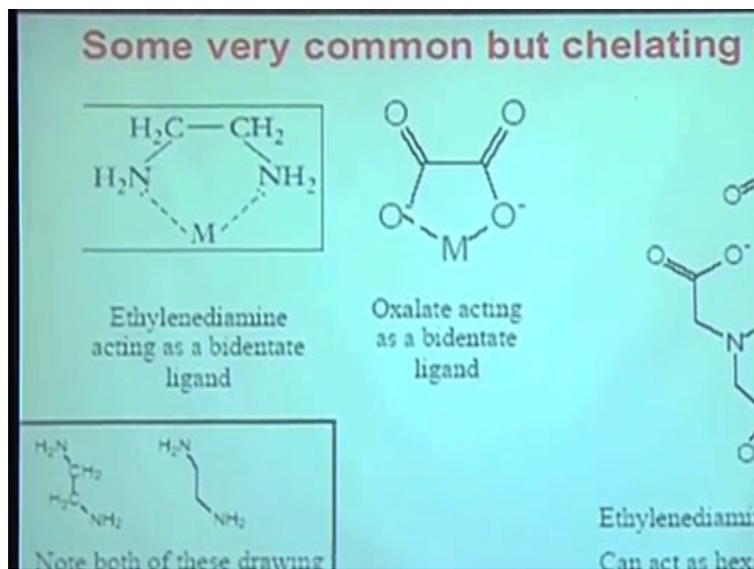
Neutral Molecules		Anionic
Aqua	H ₂ O	Fluoro
Ammine	NH ₃	Chloro
Methylamine	CH ₃ NH ₂	Bromo
Carbonyl	CO	Iodo
Nitrosyl	NO	Hydroxo

But what are the ligands? The usual ligands as we already have discussed chloride, ammonia, water, fluoride, bromide, cyanide, whatever can coordinate with the metal center. Usually it is a negatively charged species or it has a lone pair, hetero atom, nitrogen is a hetero atom, oxygen is a hetero atom, sulfur is a hetero atom. So, any species with these, sulfur let us say thiol SH or alkyl sulfide like RS minus, OH, O minus, O₂ minus or alkoxide RO minus, any let us say

CH₃O, methanol like methoxide CH₃O, anything that has hetero atom, anything that is negatively charged can bind with the metal center those are the one that going to be the ligand.

Some of the ligand just binds with the metal center, just donates. Actually some of the ligand can extract out even electron from or back donation as we see, let us say, CO. Carbon monoxide has that with the lone pair with the carbon it gives to the metal and also it can have the back donation from the metal. So, there are different types of ligand as you know. Those are monodentate ligand in this slide whatever you have seen.

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There are bidentate ligand. So, as you see the ligand itself is this part. It is coordinated with the metal center at two points. So, what we try to see actually is something like a 5 or 6 membered ring formation which is going to be thermodynamically stable. All of you can see it. So, I hope most of you can see. See, this is the metal center, the coordinating atom, coordinating atom, two coordinations are there or two coordinating atoms are there. So, these are the donation. Lone pair is donating, donating.

Overall, you see, 1, 2, 3, 4, 5 it is a 5 membered ring formation, which is going to stabilize it, the metal complex. It is like a chelator. It is just like you are going to hold it. You are holding by one hand is not going to be that strong monodentate ligand in the last slide. These are one of which are going to hold it by one hand. And these are the one which is going to hold the metal center with two hands.

And if it is, if the ring is too big, of course, if a very long, I do not know, I mean, not a band, but something it is a very big rope and tied together at a point is not going to be stable compared to if you have a 5 or 6 membered or 7 membered ring those are going to be more stable. 5 to 7 membered rings are usually more stable. So, for your bidentate ligand usually you see 5 to 5 membered ring formation.

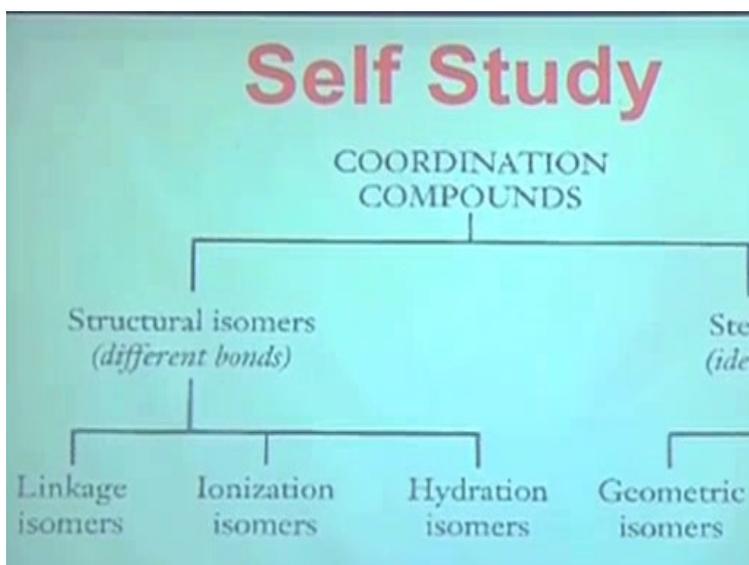
This is ethylenediamine forming 1, 2, 3, 4, 5, 5 membered ring. Oxalate binding with the metal center with two oxide or O minus the 5 membered ring 1, 2, 3, 4. This one will also give you 5 membered ring. Now, this is what going to bind with 1, 2, 3, 4, 5. It is a penta coordinated ligand. Here it is a bidentate ligand. It is going to bind with the two ends. Now, the EDTA will bind 1, 2, 3, 4, 5, 5 centers. So, you expect that EDTA coordination with the metal will be extremely strong. That is actually is used in a lot of cases.

When you have no idea how to do, you just add EDTA, for example, I mean chemistry sense, it will extract out the metal center. It is almost like dripping off. It will just pull off, because the coordination is so strong, 5 coordination. Of course, 1, 2, 3, 4, 5, 6; 6 coordination, that is right, 6 coordination. So, it is going to be multidentate. So, that is why the multi-denticity, as the almost truly multi-denticity increases, you will have a very strong binding. EDTA is 6 coordination.

Now, of course, you can have tridentate. This is bidentate. If you add, for example, over here another pyridine this is called terpy, you can have terpyridine. Of course, you can add perhaps it

is may not be that extremely stable, but it is stable very good tetrapyridine. So, you can have more and more. See in all these cases we are having 5 membered ring formation which is essential. This is called chelation, chelating. You are holding it together. And thereby you are going to have a very, very good ligand that will hold metal center very tightly. Of course, this tight binding, strong binding, weak binding we will come back again, high spin, low spin perspective we will discuss today.

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Self study I will not discuss. This is the isomerism part. I think in the model you have, you are given enough information on it. So, you just study about the isomerization in these coordination complexes what type of. Maybe I think one question usually expected from this part, maybe one more question on isomerism.

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Variable oxidation state						
Sc					+3	
Ti	+1	+2	+3	+4		
V	+1	+2	+3	+4	+5	
Cr	+1	+2	+3	+4	+5	+6
Mn	+1	+2	+3	+4	+5	+6 +7
Fe	+1	+2	+3	+4	+5	+6
Co	+1	+2	+3	+4	+5	
Ni	+1	+2	+3	+4		
Cu	+1	+2	+3			
Zn		+2				

1. Increase in the of oxidation stat
Sc to Mn. All are only in case of M
2. Decrease in th
of oxidation stat
Mn to Zn, due to pairing of d-e' s
3. Stability of hig
states decrease
to Zn. Mn(VII) an
are powerful oxi

Now, variable oxidation state we briefly discussed in the first class. So, understand why variable oxidation state exists and which are the one some of the informations are given here. So, as you can see from scandium to manganese, let us say, this variable oxidation state increases and up to 7 it goes and after that it decreases further. If you go down in the periodic table, you will see higher oxidation state gets stabilized more often. These are the things you have studied before. Refresh your memory again and information are also given here, over here.

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18 electron rule (earlier EAN: Sidg

Stable metal complex at low oxidation state:
metal electrons + lone pairs from ligands =

$\text{Ni}(\text{CO})_4 - 4s^23d^8$ and 4 lone pairs =
 $\text{Fe}(\text{CO})_5 - 4s^23d^6$ and 5 lone pairs =
 $\text{Cr}(\text{CO})_6 - 4s^23d^4$ and 6 lone pairs =

18 electron rule: explained by **MO theory**.
(Filling of all the molecular bonding orbitals of the antibonding orbitals).

Now, in terms of theory, we have discussed Werner coordination theory. It is a simple theory 1913 Nobel Prize, let us say, we understand by now, at least. Next theory which came up or which was, that see that what happens chemists are working, a lot of different theories going to come. But if it is going to taste the success, then it has to be a good one. It has to explain a lot of things.

Of course, no theory is going to be self searched or no theory is going to explain everything correctly, but as long as it can explain quite a good number of things that theory remains with the scientist in the book. One such theory is 18 electron rule. Again, this is a rule, empirical rule. It is not like God given rule, and compound followed.

Compounds are there, then scientists figure out that there is a rule which may be looks like 18 electron rule. What is it? Simply it tells you those ligand metal coordination when you do as we were showing, if it is forming a 18 electron, valence electron, total count is going to be 18 electron, then it is going to be a stable complex.

In other way around, so let us say you have a metal, whatever cobalt, how many ammonia you will add with cobalt. You keep on adding, whether you add one ammonia or two ammonia, I mean, let us say you take cobalt, salt and you add ammonia or cobalt iron, let us say you have taken and you add ammonia, excess ammonia, a lot of ammonia you have added, so up to how many ammonia one particular cobalt center will have, one ammonia, two ammonia, you keep on counting.

Let us say this is where cobalt 3 plus, cobalt 3 plus means it is a d6 system. So, d7 s2 or total 9 electrons, valence electrons and three goes out d6. Now, the rule says 18. Each ammonia can give you 2 electrons. So, how many you need, 12 more electrons. So, six ammonia. So, cobalt 3 plus will have hexa ammonia species or ammonia ligand. It is not 1, not 2, not 7, not 9, not 10. So, what do you see for a large variety of complexes, you will be able to understand the formation of those species by keeping 18 electron rule in mind.

But the next caution definitely comes within it, it is not going to be universal. It is not like if it is not 18 electron, it is not going to form, it is not. There are up to 16, 14, 12 all species, 12 electron species are stable. These, some of these species you can get it rocks table in air even. Nothing happens to it. So, it is not the ultimate rule. But I would say it is a very good percentage of the

complexes you see can follow this rule or you can explain the complex formation by following this rule that is simply is the 18 electron rule. So, you should be able to count the electron based on this 18 electron rule or what happens to that.

So, you can read up nickel tetracarbonyl, nickel is what $s^2 d^8$, so 10 of them, carbonyl is 2, carbon will give 2 electrons to the nickel, so 2 plus 8, 10 and 4 going to be 18. Same is here. 5 of CO will give you 10, iron is 8, so 18 electron. Chromium hexacarbonyl it is same. So, any complex you try to look at you should be able to count. Is this clear to everyone? You should be able to count the electrons.

Valence electron of the metal and the donor, each donor should give you the 2 electrons, anyway, usually, but there are exceptions like nitric oxide. We just do not perhaps need to go into that much.

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EAN: Uses and Limitations

Table 7.6 Effective atomic numbers of some metals in complexes

Atom	Atomic number	Complex	Electrons lost in ion formation	Electrons gained by coordination
Cr	24	$[\text{Cr}(\text{CO})_6]$	0	12
Fe	26	$[\text{Fe}(\text{CN})_6]^{4-}$	2	12
Fe	26	$[\text{Fe}(\text{CO})_5]$	0	10
Co	27	$[\text{Co}(\text{NH}_3)_6]^{3+}$	3	12
Ni	28	$[\text{Ni}(\text{CO})_4]$	0	8
Cu	29	$[\text{Cu}(\text{CN})_4]^{3-}$	1	8
Pd	46	$[\text{Pd}(\text{NH}_3)_6]^{4+}$	4	12
Pt	78	$[\text{PtCl}_6]^{2-}$	4	12
Fe	26	$[\text{Fe}(\text{CN})_6]^{3-}$	3	12
Ni	28	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	2	12
Pt	46	$[\text{PtCl}_4]^{2-}$	2	8

Now, in the other way around sometime what you can say is that effective atomic number-wise. So, what we have so far taken for the metal is just the valence electron, instead of valence electron if you take the total electron, all electrons present, for example, chromium, chromium has 24 electrons and the carbonyl, 6 of them 12, 12 plus 24 it is going to be 36. These are going to be the nearest noble gas configuration. Of course, that makes sense and that is what nothing but 18 electron rule is.

So, it is if you look at $s^2 p^6 d^{10}$ that is how it is 18, $s^2 p^6 d^{10}$, 10 plus 6 plus 2, 18. That is why the 18 electron rule is. But it is also other way to look at it effective atomic number rule. Forget it.

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Valence Bond Theory (VBT)

G. N. Lewis (1902): *atoms form covalent bonds by sharing electron pairs.*

W. Heitler and F. London (1927): showed how sharing of pairs of electrons holds a covalent bond together. The Heitler-London model of covalent bonding was the basis of the VBT.

L. Pauling: *atomic orbitals are mixed to form hybrid orbitals, such as sp , sp^2 , sp^3 , dsp^2 , d^2sp^3 orbitals.*

Now, I am going to valence bond theory and then next topic will be crystal field theory. Of course, I think some of you or most of you know all these things, but I will keep on adding something new that may not be learned before, may not have learned before, you may not have learned before. So, valence bond theory I will not get into the definition. See those are for study purpose, you study. I will just explain what it is.

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VBT – Assumptions / Features

- (i) Ligands form **covalent-coordinate bonds** to metal.
- (ii) Ligands must have **lone pair** of electrons.
- (iii) Available **empty orbital of suitable energy** on metal for bonding.
- (iv) **Atomic (hybrid) orbitals** are used for bonding (rather than molecular orbitals)

Can explain: shape and stability of the metal complex

Can not explain: (i) Color
(ii) Temperature dependence

So, by valence bond theory, we try to see the metal complex formation. We have a ligand. We assume that these are ligand metal covalent bond formation. We have discussed what covalent bond, what ionic bond and so on. So, you know also. Usually it is a covalent coordinate bond. Ligands should have a lone pair. These are the assumption. If it does not fit, you cannot perhaps talk about this, valence bond theory.

Empty orbitals, there should be available empty orbitals for the metal centers. We will come in a minute how, what atomic orbital we are talking about. And after ligand donation, we are talking about a hybrid orbital. So, you know that metal is there, there is orbital, metallic orbital, especially, let us say, if you are talking about 3 valence, principal quantum number 3, you have 3s, 3p, 3d, not all of them are going to be completely filled out for most of the cases. So, 3s, 3p, 3d, specifically 3d and 3p these are available for binding with the ligand.

So, ligand can give their 2 electrons into those orbital, atomic orbitals. So, this is what valence bond theory is. Ligand lone pairs or those electrons can be donated into those p or d orbital let us say or up to s orbital as well if it is happened, of course, if it is failed you cannot. Each of them can have, let us say, s can have total 2, p can have 6, d can have 10, of course, there is sub-level up. Now, that is where those, after formation, we will get the coordination bond.

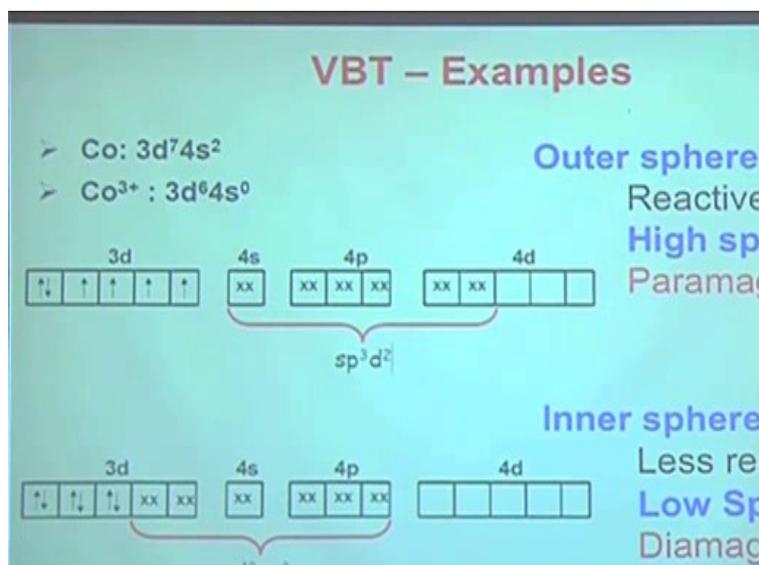
Now, the moment we will give you the examples it will be more clear. But what we are trying to say is the positive things about this approach is you can understand the shape and stability of the

complex. What safe it is. I was showing you linear, square planar, not square planar, linear, let us say, or trigonal so on, different shape you can say. But geometry usually it will be little difficult for most of the cases. Definitely you cannot get the color, information about color and temperature dependence of magnetic properties which we will be discussing color and temperature dependence.

So, although you can get the coordination, what type of coordination it is, hybridization as well and most likely you can also tell the shape or let us say linear, trigonal, square pyramidal, tetrahedral and so on. But more than that you will not be able to say, you cannot be able to get deep. You cannot understand in a deeper sense. This is the limitation. Of course, what happens is slowly theories has evolved.

Since all the information we cannot explain by this valence bond theory, next step which people accepted is the crystal field theory. But this development of crystal field and valence bond theory has occurred quite simultaneously, almost simultaneously. Still, we teach this valence bond theory, because it is so easy to understand. It is the first thing you kind of remember. Let me look at it.

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So, you have seen something like this, cobalt. Cobalt is d^7, s^2 . Cobalt 3 plus will be $3d^6$. So, those d^6 are going to be occupied over here 2, 1, 1, 1, 1, 6 electrons gone. What you left up with is 4s, 4p and 4d orbitals. So, those orbitals are having suitable energy that is important, suitable

energy so that ligand electron can be donated. If those orbital energy are too high or too low, then there going to be a problem. It has to be somewhat close orbital where ligand can interact. So, these orbitals are available. You have 6 of the ligands 1, 2, 3, 4, 5, 6. So, the hybridization is going to be sp^3d^2 . You have seen how the name has come sp^3d^2 .

Now, you look at other confirmer possible. This is going to be the high spin situation, where spins are maximum. Here 4 unpaired electrons are there. There could be another scenario when you can have all these electrons paired up and you can have two of the d, 1s and three of the p involved in compound or complex formation or coordination bond formation. So, this scenario will be called d^2sp^3 . You have studied it before most likely.

Now, of course, this is the one which we are saying that it is an outer sphere complex. It is going to be, the ligands are going to be labile, this is a high spin complex, because the spin you see is 4 unpaired electron and here we do not have any unpaired electron, so this is going to be paramagnetic. Over here is the inner sphere complex. You say these are less reactive, low spin and diamagnetic. Diamagnetic means no unpaired electron in the complex, low spin, spin is minimized. This is high spin. This is less reactive and inner sphere complex.