Basics in Inorganic Chemistry
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Lecture - 07
Coordination Chemistry: 18 Electron Rule, VBT

Two topics whatever we have seen so far is based on different metals, right. We have seen, of course in periodic table every element is there in that, last topic which was the extraction there we particularly see the metal complexes or you know ores in different oxide form, 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 the they are d block element and they have either full filled or half half filled or you know partially filled d orbitals.

And thereby their chemistry is usually something what is called very exciting compared to all others, ok.

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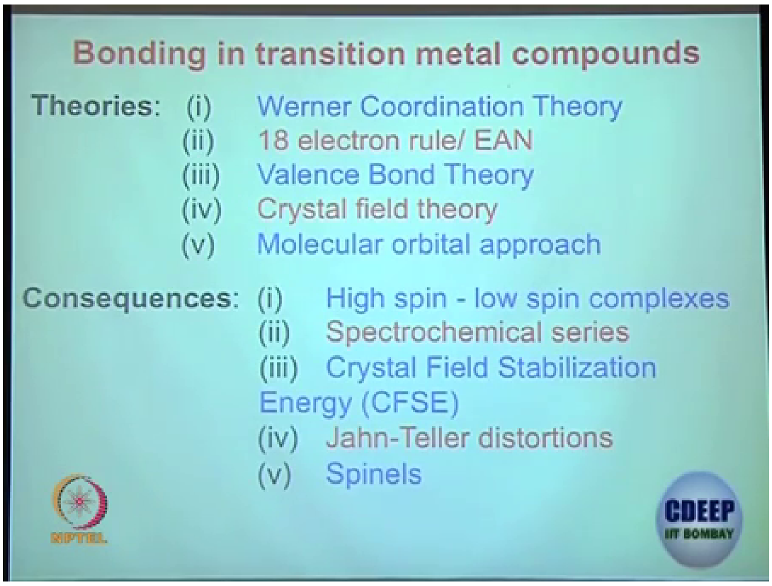

Bonding in transition metal compounds

Theories: (i) Werner Coordination Theory
(ii) 18 electron rule/ EAN
(iii) Valence Bond Theory
(iv) Crystal field theory
(v) Molecular orbital approach

Consequences: (i) High spin - low spin complexes
(ii) Spectrochemical series
(iii) Crystal Field Stabilization Energy (CFSE)
(iv) Jahn-Teller distortions
(v) Spinels

So, chemistry of transition metals we will be discussing. In this we will be particularly focusing on these theories, ok; 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 distortions and finally, about the spinels. So, these are roughly the topic I am going to cover today, ok.

I will start with Werner coordination theory, ok. I would like to take you let us say more than really you know 100, 120, 30 years back what chemist was thinking. That time of course, right now we see the book books are well written because 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 in that perspective. If you are looking at, right now you may not be able to appreciate the importance of this contribution Werner coordination theory you have to really look back at least 150 years or so.

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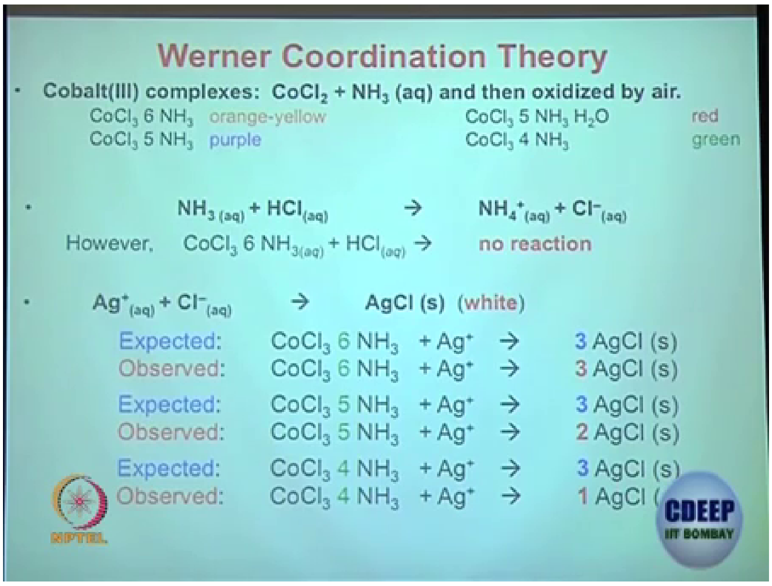

Werner Coordination Theory

- Cobalt(III) complexes: $CoCl_2 + NH_3$ (aq) and then oxidized by air.

$CoCl_3$ 6 NH_3 orange-yellow
$CoCl_3$ 5 NH_3 purple
$CoCl_3$ 5 NH_3 H_2O red
$CoCl_3$ 4 NH_3 green

- $NH_{3\,(aq)} + HCl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$

However, $CoCl_3\ 6\ NH_{3(aq)} + HCl_{(aq)} \rightarrow$ no reaction

- $Ag^+{}_{(aq)} + Cl^-{}_{(aq)} \rightarrow AgCl\ (s)$ (white)

Expected: $CoCl_3\ 6\ NH_3 + Ag^+ \rightarrow 3\ AgCl\ (s)$
Observed: $CoCl_3\ 6\ NH_3 + Ag^+ \rightarrow 3\ AgCl\ (s)$

Expected: $CoCl_3\ 5\ NH_3 + Ag^+ \rightarrow 3\ AgCl\ (s)$
Observed: $CoCl_3\ 5\ NH_3 + Ag^+ \rightarrow 2\ AgCl\ (s)$

Expected: $CoCl_3\ 4\ NH_3 + Ag^+ \rightarrow 3\ AgCl\ (s)$
Observed: $CoCl_3\ 4\ NH_3 + Ag^+ \rightarrow 1\ AgCl$ (

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 importance information although were there, but then it can H not be explained, ok.

So, for example: over here one of the 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 starting material depending on the reaction condition how much ammonia you give, how much heat you give, what solvent you use, let say a 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, ok. This is where Werner came in. He tried to first time give an explanation what might be happening in there, why from same starting material we are trying we are getting different compounds or what type of compounds they are, ok.

So, of course, that time lot of things were not really established X-ray crystallography, spectroscopic, other techniques were not simply there, ok. 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, ok. 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, ok.

Now, if you look at this reaction cobalt chloride plus HCl, simply there is no reaction, ok. If ammonia was just there as if like just 3 ammonia with HCl you are expected to get this reaction, but with these complexes none of these 4 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, right. So, it is not just ammonia gas sitting in the complex, it is something has happened. Again, I am talking about 150 years old you know discovery.

Now, what they try 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 orange yellow one let us say and they try to add silver. Now, you can quantify how much silver chloride is formed. They have quantified that 3 equivalent of silver chloride is formed. So, all the 3 chloride are accessible for silver class, ok.

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 is forming, although 3 chlorides are there, only 2 chlorides are accessible that is how you can clearly see between first and let us say second compound you already having some sort of discrimination. 3 chlorides are accessible only 2 chlorides are accessible, ok. Now, if keep on doing it for other compound. What you learn is let us say for example, this one you can get only one silver chloride, one equivalent, ok, for the first one it has 3, then 2, this 1 and so on.

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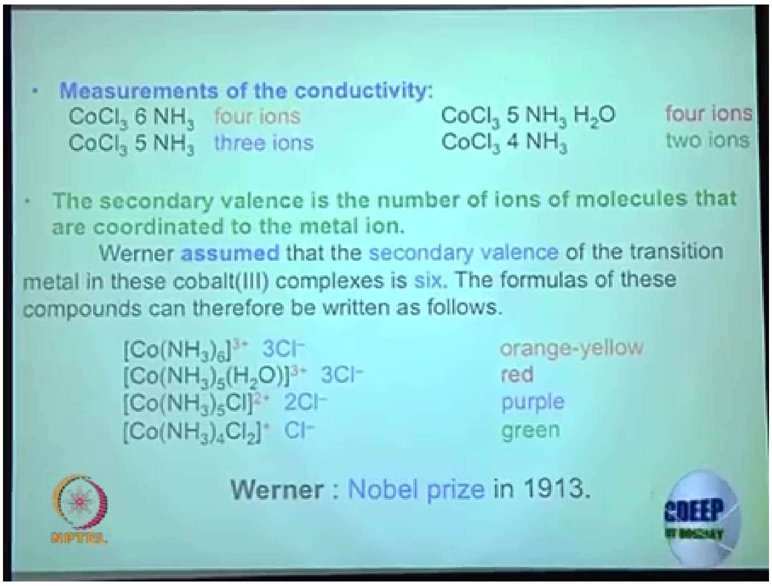

- **Measurements of the conductivity:**

$CoCl_3$ 6 NH_3	four ions	$CoCl_3$ 5 NH_3 H_2O	four ions
$CoCl_3$ 5 NH_3	three ions	$CoCl_3$ 4 NH_3	two ions

- **The secondary valence is the number of ions of molecules that are coordinated to the metal ion.**

Werner **assumed** that the secondary valence of the transition metal in these cobalt(III) complexes is six. The formulas of these compounds can therefore be written as follows.

$[Co(NH_3)_6]^{3+}$ $3Cl^-$	orange-yellow
$[Co(NH_3)_5(H_2O)]^{3+}$ $3Cl^-$	red
$[Co(NH_3)_5Cl]^{2+}$ $2Cl^-$	purple
$[Co(NH_3)_4Cl_2]^+$ Cl^-	green

Werner : Nobel prize in 1913.

And, then what you do is you try to do the conductivity measurement. Conductivity measurement tells you how many ions are there, how many cation how many simply how many ions are there. For the first case they found 4 ions, 3 ions, 4 ions and 2 ions. So, how many ions are present in that colored species you can kind of count, ok. So, conductivity measurement gives you that.

Now, this is where the brilliance I think the you know 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 is 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 1 chloride is accessible; that means, 2 chlorides are with bound with the metal center I mean this is actually a revolutionary thought when almost nothing was known. So, of course, you can say Nobel Prize in 1913 of course, our grandparents and great grandparent's time. But it is it is really really a classic you know understanding or classic idea theory that kind of I would say redefine 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 you know 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 2 ion, 1 cation and 1 anion, so two ions conductivity measurement will give you 2 ions, this one 2 anions and 1 cation whole thing is 1 cation, right.

So, it is 3 ion. All those things now, you look back the simple experiment now can be x you know kind of explained by this of course, that guy deserve 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 bend anything, ok.

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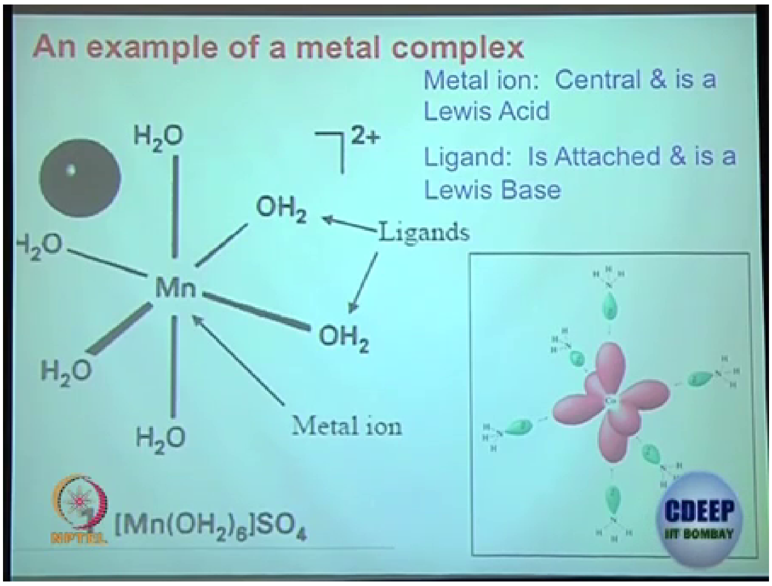

An example of a metal complex

Metal ion: Central & is a Lewis Acid

Ligand: Is Attached & is a Lewis Base

$[Mn(OH_2)_6]SO_4$

Now, so that is what a metal complex should looks like then like what Werner tried to say. You have a metal center ligands this ligand, 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 charge are there they will neutralize it, right just like in the last place. Let us say over here cobalt is 3 plus, but 2 chlorides are there, so cobalt over all this ion is 1 plus, ok.

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, ok. The Lewis acid is the one which is the metal at the center, very simple, right. 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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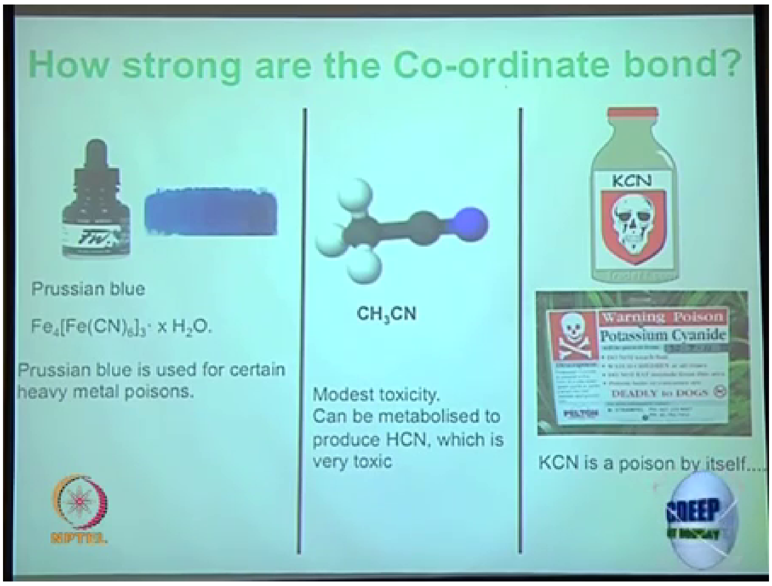

How strong are the Co-ordinate bond?

Prussian blue

$Fe_4[Fe(CN)_6]_3 \cdot x\ H_2O$.

Prussian blue is used for certain heavy metal poisons.

CH_3CN

Modest toxicity.
Can be metabolised to produce HCN, which is very toxic

KCN is a poison by itself....

So, how strong are this coordinate bond? Something like potassium cyanide. You know that this is a ionic compound, ok. Now, it is very deadly poisonous, all of you, never ever even try to taste 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 thing may or may not be that much water soluble. So, that is 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, end of the course we will see that they can bind with the iron center with the porphyrin ring known as the hymn 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 iron center. Those binding sites are getting occupied by these guys. Carbon monoxide, cyano how they are getting bound, how strong is their binding these sort of information we might we will be able to tell you at the end of the class, ok. Not this class and end of the course.

Now, when you take acetonitrile this is a solvent, ok. 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 a cyano, this is also cyano, but things are completely different. It is still toxic, but not as toxic as these. Of course, you know that Prussian blue which is widely used, right.

Of course, none of these are friendly chemical, I would see, I would say except water do not expect anything to be friendly, neutrally. You use acetone for removing the nail polish or anything erasing those are bad things 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 takes time, ok.

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 you know consume, that is going to cause something, if not today maybe 10 years down the line. See some sometimes some poison works over the long time.

So, Napoleon Bonaparte for example, is believed to be believed to be murdered by arsenic poison, ok. So, and not over so, every I mean I am forgetting the exact story. Every day let us say with the meal or whatever he was 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 death sometime. I mean not only these there are there are even painting, some of the painting uses some of the deadly chemicals which a lot of lot of things are there.

Even let us say you know in car garage you see in the movie, right 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 its painful. It is not painful, but it is in movies at least they show, right. All 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, ok, 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 abuse the chemical, specifically not to other human being or other living things it is bad you know. Sometime people have idea to kill a tree with some chemical; those are the bad ideas, ok. And you fight with someone you see lot of stories here and there. So, do not abuse chemical, let me go forward.

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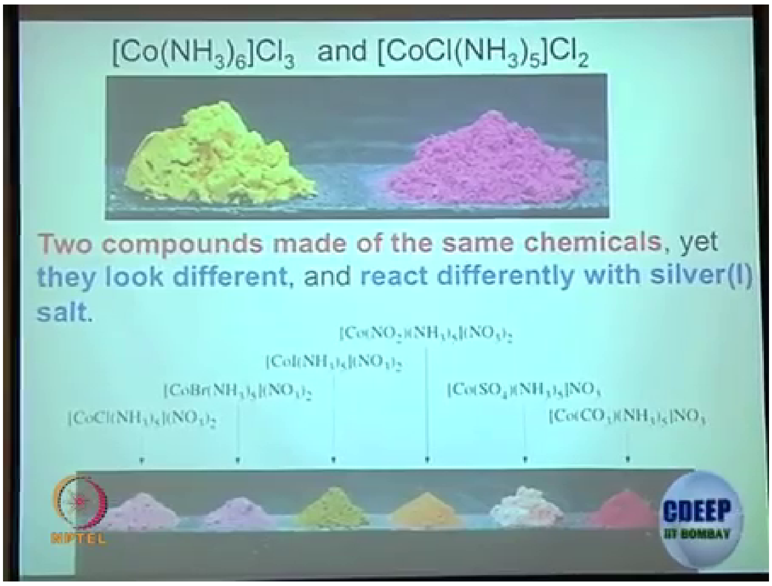

$[Co(NH_3)_6]Cl_3$ and $[CoCl(NH_3)_5]Cl_2$

Two compounds made of the same chemicals, yet they look different, and react differently with silver(I) salt.

So, for example, these the same thing what I 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, right.

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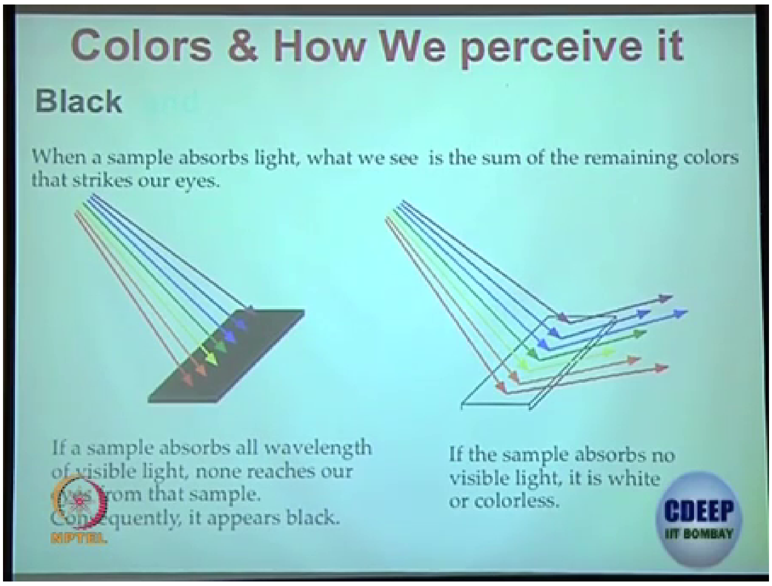

Colors & How We perceive it

Black

When a sample absorbs light, what we see is the sum of the remaining colors that strikes our eyes.

If a sample absorbs all wavelength of visible light, none reaches our eyes from that sample. Consequently, it appears black.

If the sample absorbs no visible light, it is white or colorless.

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 going that species is going to be black in color, if nothing is absorbed that is going to be white in color for example, and you know sometime there is a of course, there is a complimentary color then you know 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. See this sort of you know complementarity you are familiar with it is. Of course, you are not going to ask any question for this course, but just know how the color appears in different things, ok.

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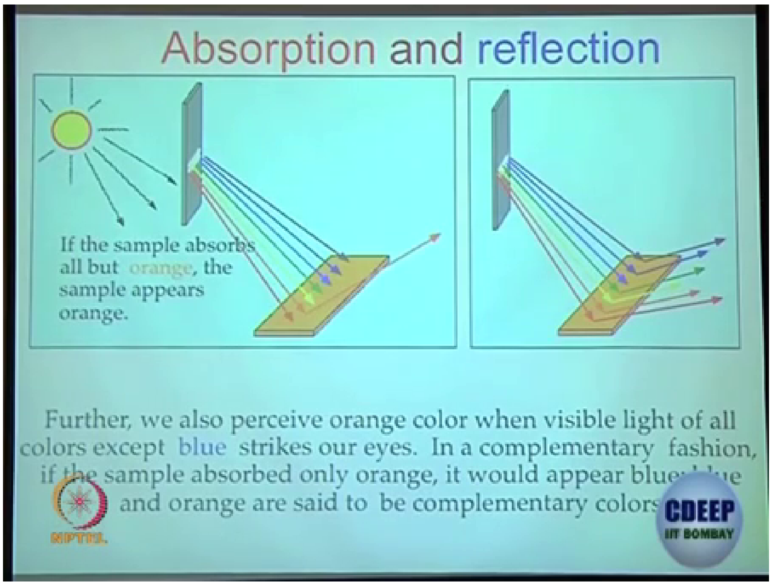

Absorption and reflection

If the sample absorbs all but orange, the sample appears orange.

Further, we also perceive orange color when visible light of all colors except blue strikes our eyes. In a complementary fashion, if the sample absorbed only orange, it would appear blue; blue and orange are said to be complementary colors.

Say everything else is consumed except orange, so we see orange and you know 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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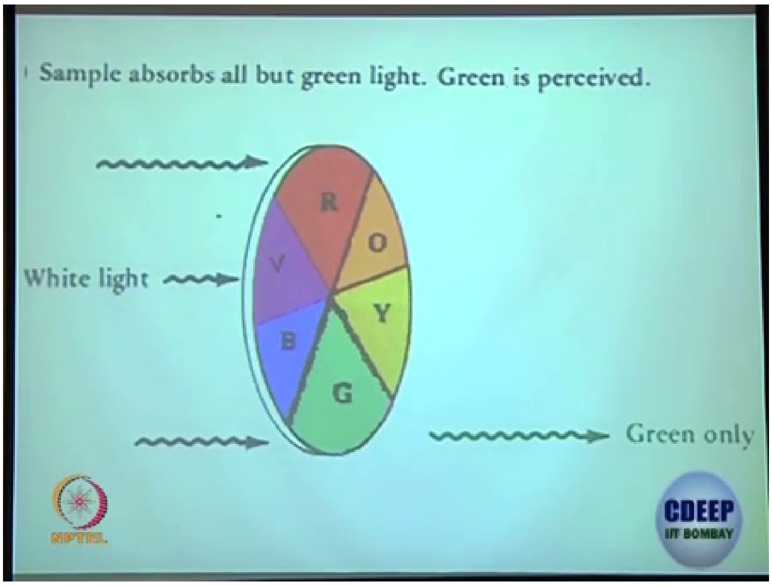

Sample absorbs all but green light. Green is perceived.

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

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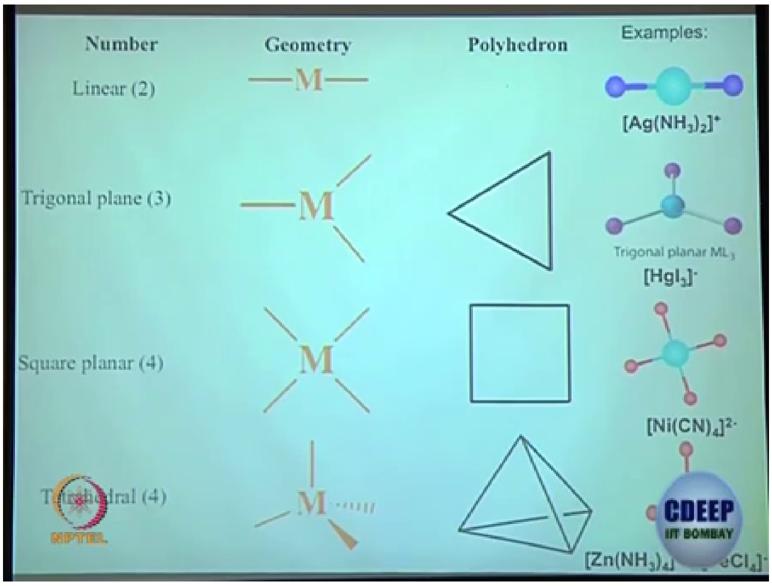

Number	Geometry	Polyhedron	Examples:
Linear (2)			$[Ag(NH_3)_2]^+$
Trigonal plane (3)			Trigonal planar ML_3 $[HgI_3]^-$
Square planar (4)			$[Ni(CN)_4]^{2-}$
Tetrahedral (4)			$[Zn(NH_3)_4]$ $eCl_4]^-$

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 also can be coming from here, ok. So, you should be familiar with the structure or basically their geometry, ok. So, this is a linear when the metal is at the center and two ligands are there usually they will you know they will have a linear coordination. One example is given here, ok. 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 planar complex. For example, mercury triiodide, ok.

Over here nickel tetra cyanide you can have a square planar geometry you can see. So, nice it is like perfect, almost perfect geometry. Now, tetrahedral you know of course, you know C H 4 is tetrahedral you know, but with the metal complex something like iron tetra chloride is tetrahedral, zinc tetra ammonium species is tetrahedral and so. There are lot of tetrahedral complexes as well.

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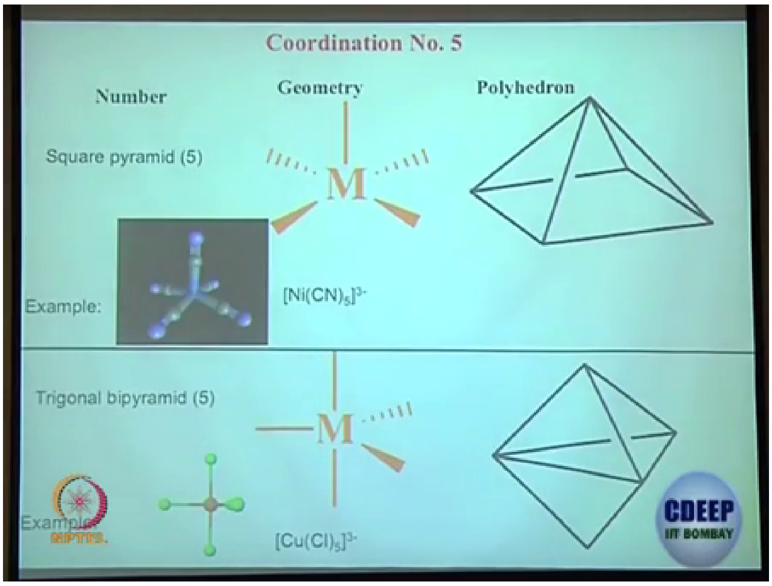

Coordination No. 5

Number	Geometry	Polyhedron
Square pyramid (5)		
Example:	$[Ni(CN)_5]^{3-}$	
Trigonal bipyramid (5)		
Example:	$[Cu(Cl)_5]^{3-}$	

We have 5 coordination nickel tetra nickel penta cyanide. So, nickel is in the middle 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, right. 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 looks like should look like. This is trigonal bipyramidal. So, there is a plane between these 3 and then one in the axial one in the sorry, two in the axial on top sorry. One in the equatorial position sorry axial position as it is shown here sorry.

Student: (Refer Time: 19:23).

Those sort of explanation will be coming. This is where different, different theories has come up, ok. 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 the next class it will be cleared. That is part of the discussion, ok.

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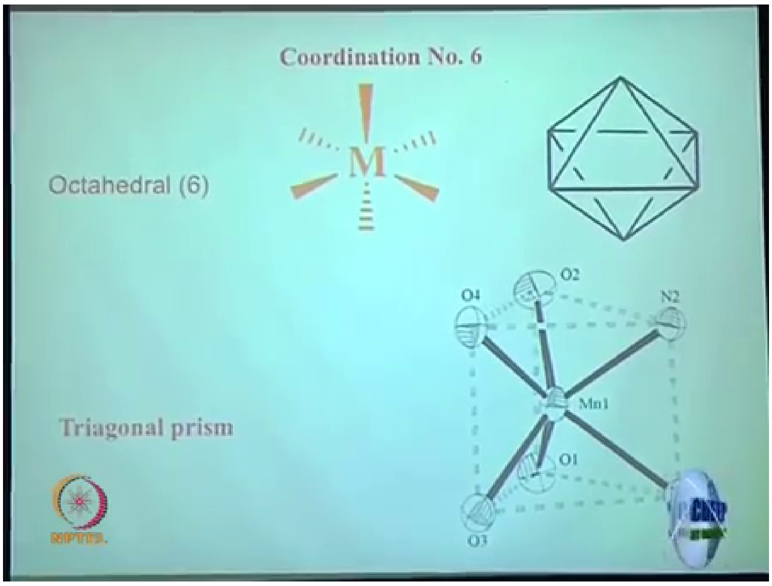

Coordination No. 6

Octahedral (6)

Triagonal prism

So, there are other compounds these are this is a manganese you know hexa or 1 2 3 4 5 6 yeah, manganese hexa oxo complex or M NO 6 complex. Octahedral can be you know as you say know what octahedral is this is the basal plane or the 4 of these are in the same plane these this is axial that is axial, so something like this.

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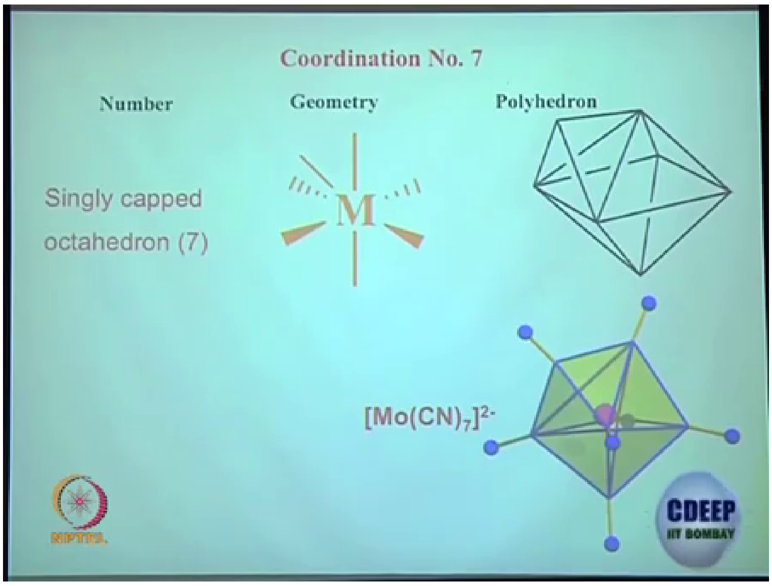

Coordination No. 7

Number

Geometry

Polyhedron

Singly capped octahedron (7)

$[Mo(CN)_7]^{2-}$

So, you know these coordination number 7, you look at these it should be clear. If it is not clear please do come back, ok. There are pentagonal bipyramidal as it is shown in here and shown. Up to this, I think you should be remembering coordination number 8, ok.

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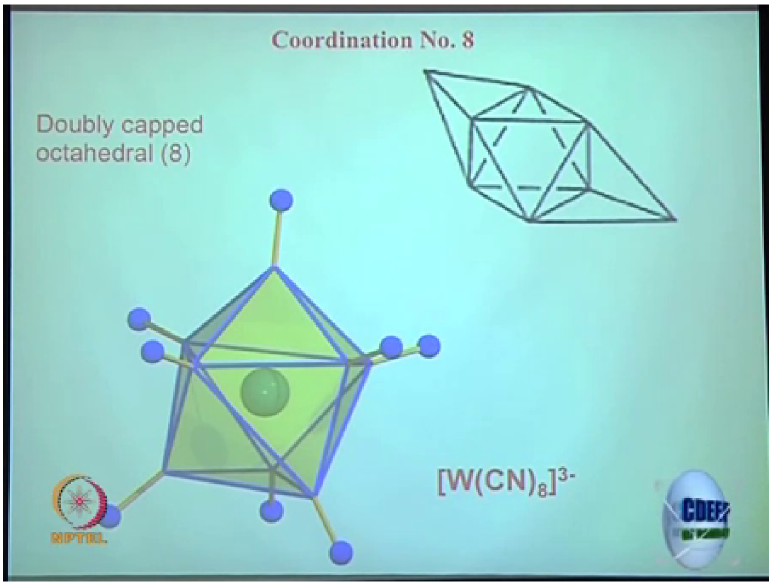

Coordination No. 8

Doubly capped octahedral (8)

$[W(CN)_8]^{3-}$

So, metal center is always at the middle and then different ligands are no over there surrounding the metal center and thereby giving different geometry, ok.

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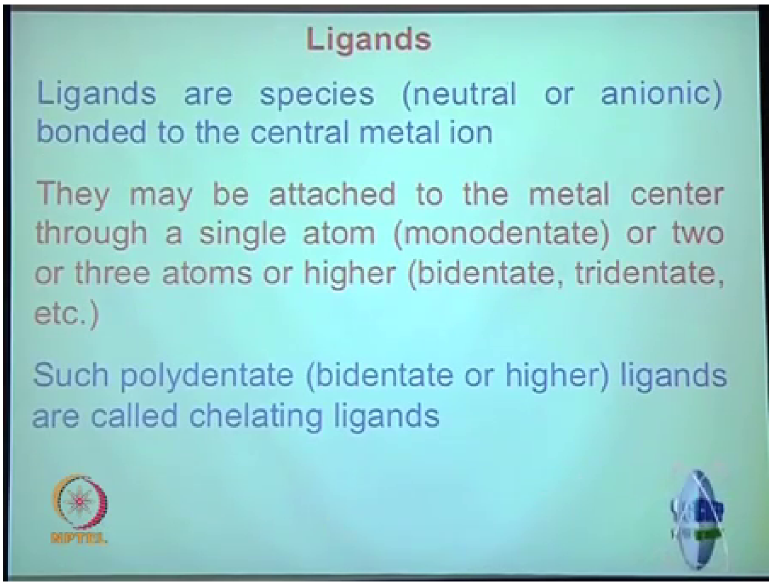

Ligands

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

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

Such polydentate (bidentate or higher) ligands 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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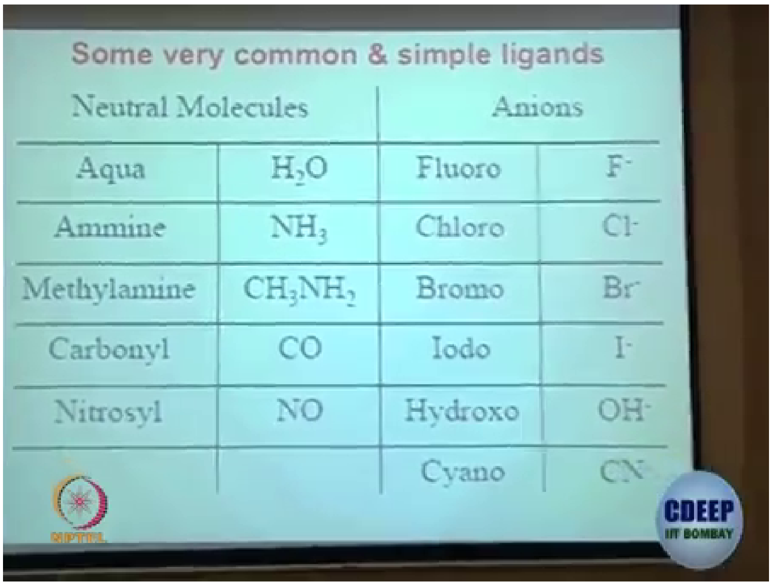

Some very common & simple ligands

Neutral Molecules		Anions	
Aqua	H_2O	Fluoro	F^-
Ammine	NH_3	Chloro	Cl^-
Methylamine	CH_3NH_2	Bromo	Br^-
Carbonyl	CO	Iodo	I^-
Nitrosyl	NO	Hydroxo	OH^-
		Cyano	CN^-

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, right. 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, O H, O minus, O 2 minus or alkoxide RO minus, any let us say C H 3 O methanol, like methoxide C H 3 O.

Anything that has hetero atom anything that is negatively charged can bind with the metal center those are the one is that going to be the ligand, ok. 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 C O. Carbon monoxide has an that with the lone pair with the carbon, it gives to the metal and also it can have the back donation from the metal, ok.

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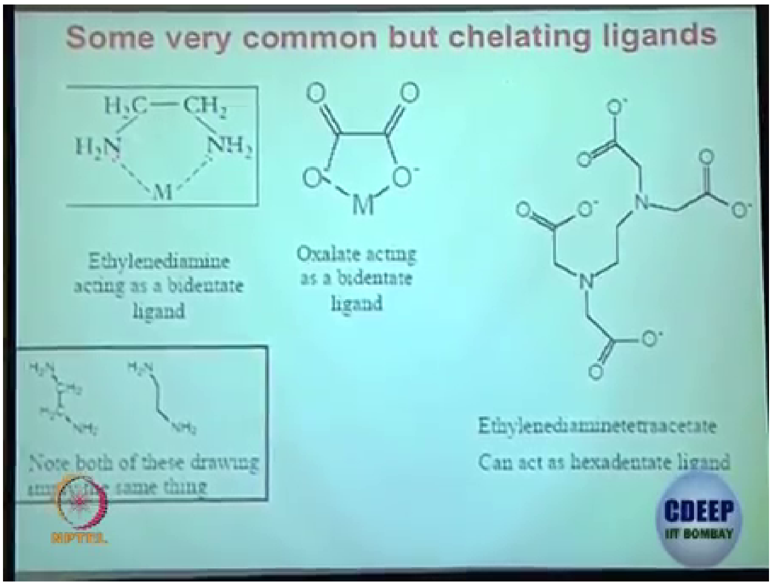

Some very common but chelating ligands

Ethylenediamine acting as a bidentate ligand

Oxalate acting as a bidentate ligand

Note both of these drawing imply the same thing

Ethylenediaminetetraacetate Can act as hexadentate ligand

So, there are different type of ligand as you know. Those are monodentate ligand in this slide whatever you have seen there are bidentate ligand. So, as you see the ligand itself is this part it is coordinated with the metal center at two points, ok. So,. So, what we try to see actually is something like a 5 or 6 membered ring formation which is going to be thermodynamically stable, ok. All of you can see it. So, I hope most of you can see.

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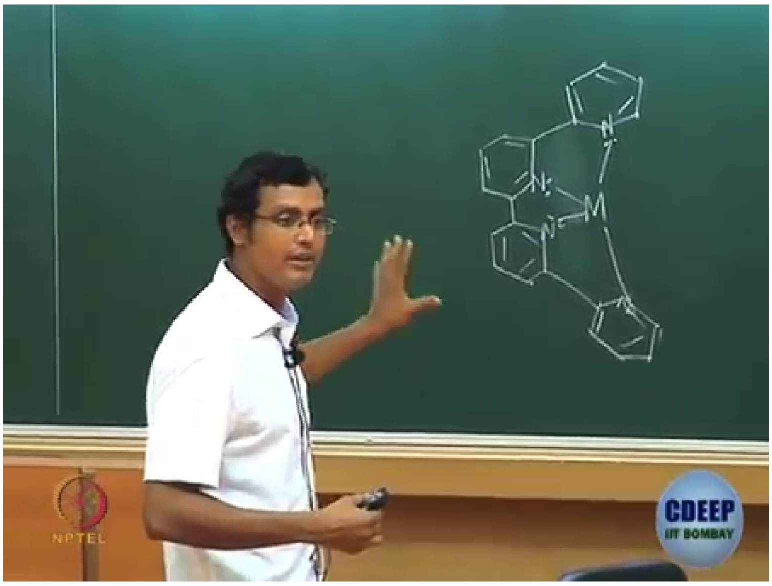

See this is the metal center, the coordinating atom, coordinating atom two coordinations are there or two coordinating atoms are there, right. So, these are the donation, lone pair is donating . Overall you see 1 2 3 4 5, it is a 5 membered ring formation which is going to stabilize it, the metal. It is like a killator it is just like you are going to hold it. You hold you are holding by one hand it is not going to be that strong monodentate ligand in the last slide, right.

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 man, but something it is a very big rope and tied together at a point it is not going to be stable compared to if you have a 5 or 6 member or 7 membered ring those are going to be more stable, 5 to 7 membered rings are usually more stable, right.

So, for your bidentate ligand, usually you see 5 to 6 membered ring formation. This is ethylene diamine forming 1 2 3 4 5, 5 membered ring. Oxalate binding with the metal center with two oxide or O minus in a 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 the EDTA coordination with the metal will be extremely strong that is actually is used in 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 stripping off. It will just pull off because the coordination is so strong, 5 coordination of course, sorry.

Student: (Refer Time: 25:18).

Sorry, 1 2 3 4 5 6 sorry, 6 coordination that is right, 6 coordination, ok. So, it is it is going to be a multi-dented. So, that is why the multi-density has the almost truly multi-dentisity increases you will have a very strong binding, right. EDTA is yeah sorry 6 coordinates.

Now of course, you can have tri-dentate, 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, tetra pyridine. 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 we will discuss today, ok.

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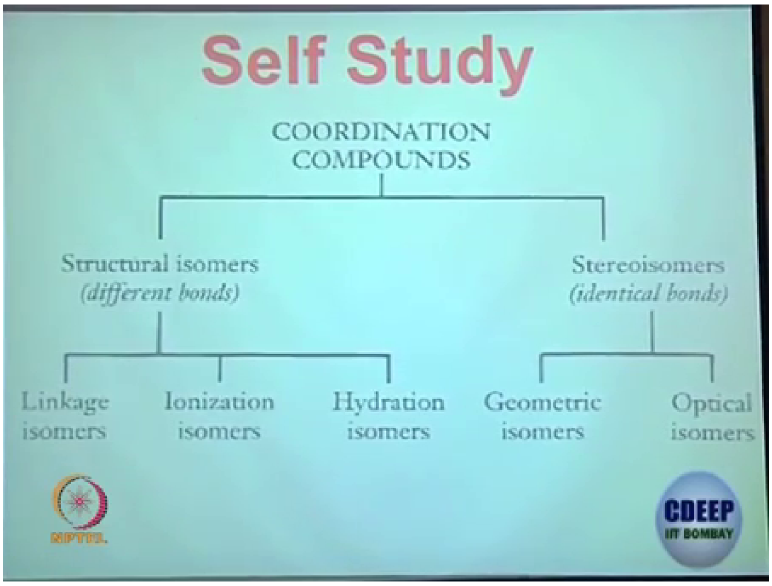

Self Study

COORDINATION COMPOUNDS

Structural isomers *(different bonds)*

Stereoisomers *(identical bonds)*

Linkage isomers

Ionization isomers

Hydration isomers

Geometric isomers

Optical isomers

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 mark question, on isomerism.

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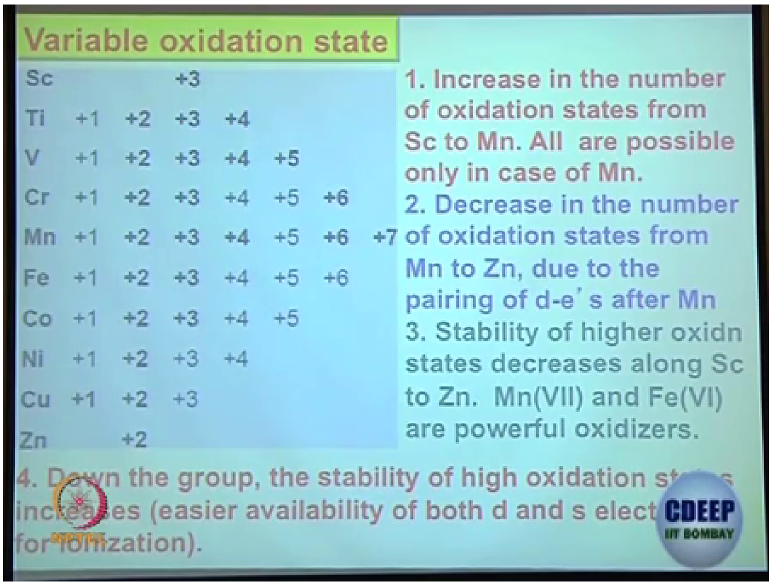

Variable oxidation state

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 number of oxidation states from Sc to Mn. All are possible only in case of Mn.
2. Decrease in the number of oxidation states from Mn to Zn, due to the pairing of d-e's after Mn
3. Stability of higher oxidn states decreases along Sc to Zn. Mn(VII) and Fe(VI) are powerful oxidizers.
4. Down the group, the stability of high oxidation states increases (easier availability of both d and s elect for ionization).

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, ok. 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 informations are also given here over here.

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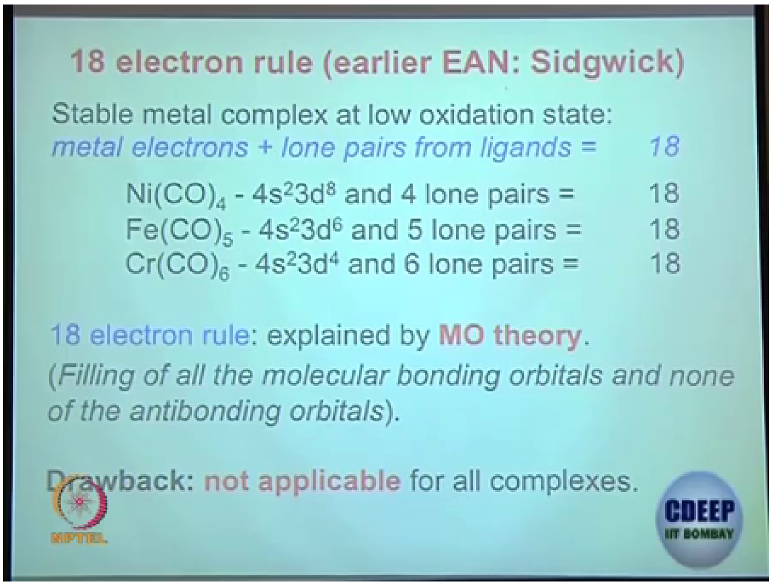

18 electron rule (earlier EAN: Sidgwick)

Stable metal complex at low oxidation state:

metal electrons + lone pairs from ligands = 18

$Ni(CO)_4$ - $4s^2 3d^8$ and 4 lone pairs = 18

$Fe(CO)_5$ - $4s^2 3d^6$ and 5 lone pairs = 18

$Cr(CO)_6$ - $4s^2 3d^4$ and 6 lone pairs = 18

18 electron rule: explained by **MO theory**.

(*Filling of all the molecular bonding orbitals and none of the antibonding orbitals*).

Drawback: not applicable for all complexes.

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 they say that what happens you know chemists are working. A lot of different theory is going to come, but if it is going to test the success then it has to be a good on, it has to explain a lot of things of course, no theory is going to be self-such or you know 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 scientist figure out that there is a rule which maybe 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 ion 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?

Student: (Refer Time: 29:29).

d 6, d 6 system, ok. So, d 7 s 2 are total 9 electrons valence electrons and 3 goes out, d 6. Now, the rule says 18 each ammonia can give you two electrons, ok. So, how many you need? 12 more electrons, so 6 ammonia. So, cobalt 3 plus we 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 question definitely comes within 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, 15 I mean 12, all species 12 electron species are stable. You know these some of these species you can get it rock stable in the air even, nothing happens to it, ok.

So, it is not the ultimate rule, but I would say it is very good percentage of the complexes you see can follow this rule or you can explain the complex formation by following this rule that it simply is the 18 electron rule. So, you should be able to count the electron based on based on this 18 electron rule or what happens to that. So, you again read up nickel tetra carbonyl. Nickel is what? H to 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 oxyo will give you 10 iron is 8, so 18 electron. Chromium hexa carbonyl 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, ok. Valence electron of the metal and the donor each donor should give you the two electrons anyway. Usually, but there are exceptions like nitric oxide; we just do not perhaps need to go into that much, ok.

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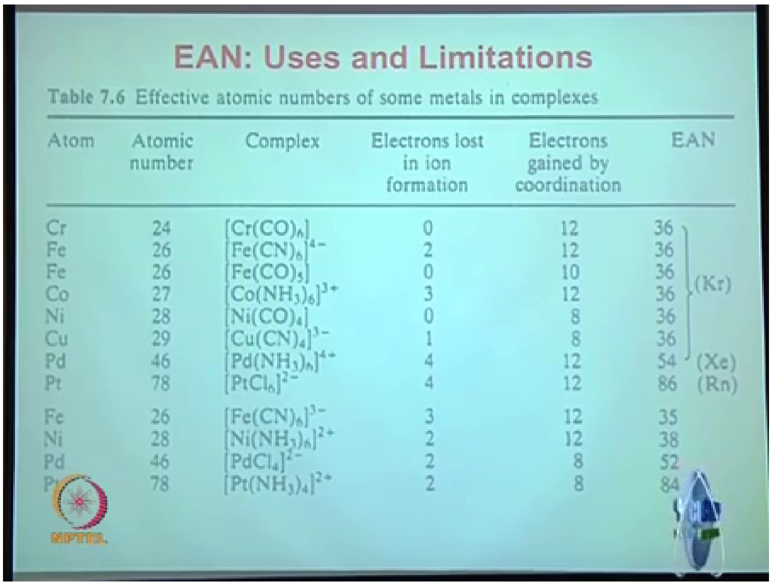

EAN: Uses and Limitations

Table 7.6 Effective atomic numbers of some metals in complexes

Atom	Atomic number	Complex	Electrons lost in ion formation	Electrons gained by coordination	EAN	
Cr	24	$[Cr(CO)_6]$	0	12	36	(Kr)
Fe	26	$[Fe(CN)_6]^{4-}$	2	12	36	
Fe	26	$[Fe(CO)_5]$	0	10	36	
Co	27	$[Co(NH_3)_6]^{3+}$	3	12	36	
Ni	28	$[Ni(CO)_4]$	0	8	36	
Cu	29	$[Cu(CN)_4]^{3-}$	1	8	36	
Pd	46	$[Pd(NH_3)_6]^{4+}$	4	12	54	(Xe)
Pt	78	$[PtCl_6]^{2-}$	4	12	86	(Rn)
Fe	26	$[Fe(CN)_6]^{3-}$	3	12	35	
Ni	28	$[Ni(NH_3)_6]^{2+}$	2	12	38	
Pd	46	$[PdCl_4]^{2-}$	2	8	52	
P	78	$[Pt(NH_3)_4]^{2+}$	2	8	84	

Now, in the other way around sometime what you can say is the effective atomic number wise. So, what we have so far taken for the metal is just a 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, if you look at s 2 p 6 d 10 that is how it is 18, right. 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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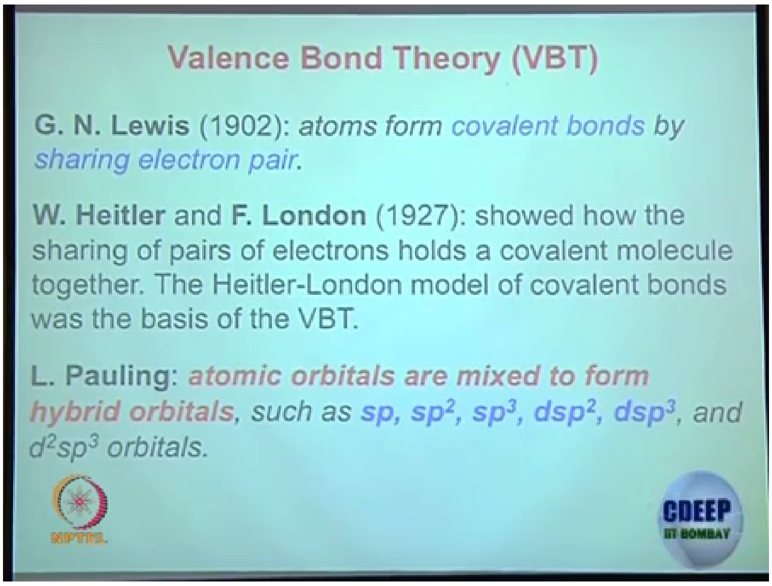

Valence Bond Theory (VBT)

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

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

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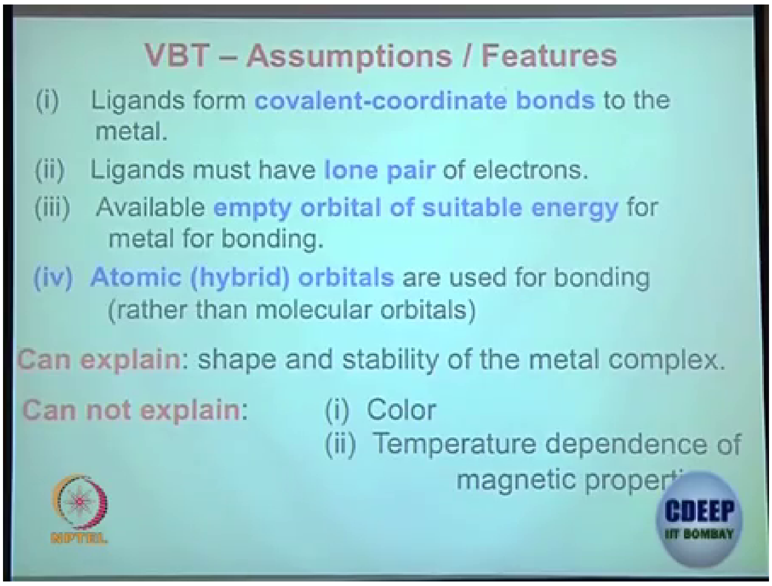

VBT – Assumptions / Features

(i) Ligands form **covalent-coordinate bonds** to the metal.

(ii) Ligands must have **lone pair** of electrons.

(iii) Available **empty orbital of suitable energy** for 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 of magnetic propert

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, ok. 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 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 is orbital metallic orbital. Specially, let us say if you are talking about 3 valence or sorry principal quantum number 3, you have 3 s, 3 p, 3 d, not all of them are going to be completely fill out for most of the cases. So, 3 s, 3 p, 3 d specifically 3 d and 3 p these are available for binding with the ligand.

So, ligand can give their two 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 vacant. Of course, if it is filled 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 sublevel up, ok. Now, that is where those after formation we will get the coordination bond, ok.

Now, the moment 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 shape it is? I was showing you know linear, square planar or not square planar linear let us say or you know 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 you know the color information about color and temperature dependence of magnetic properties which will be discussing, color and temperature dependent.

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, yeah 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 deeper sense. This is the limitation. Of course, what happens in 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 you know 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, ok.

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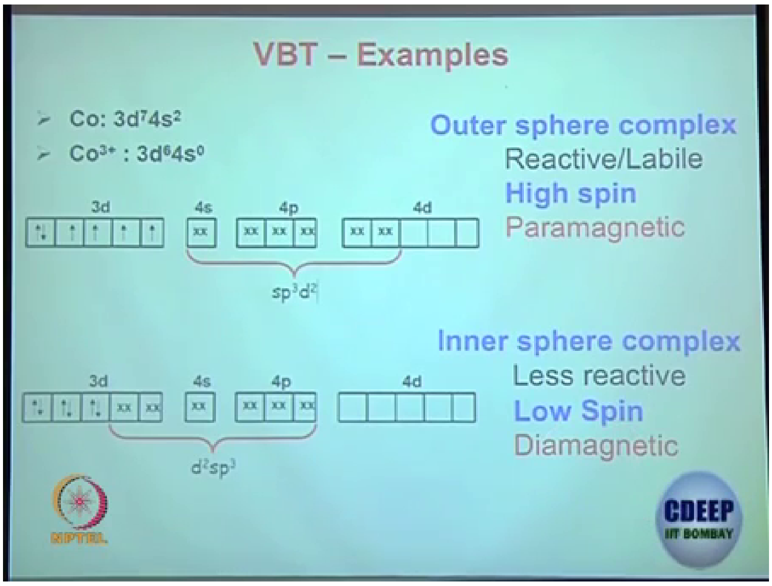

VBT – Examples

- Co: 3d^{7}4s^2
- Co^{3+} : 3d^{6}4s^0

Outer sphere complex
Reactive/Labile
High spin
Paramagnetic

Inner sphere complex
Less reactive
Low Spin
Diamagnetic

Let me look at it. So, you have seen it something like this cobalt. Cobalt is d 7 h 2 cobalt 3 plus will be 3 d 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 4 s, 4 p and 4 d 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 they are going to be a problem. It has to be somewhat close orbital where ligand can interact, ok. So, these orbitals are available, you have 6 of the ligands 1 2 3 4 5 6. So, the hybridization is going to be s p 3 d 2, you have seen how the name has come s p 3 d 2, ok.

Now, you look at other consumer possible. This is going to be the high spin situation where spins are maximum, right. Here 4 unpaired electrons are there. There could be another scenario when you can have all these electrons pair up and you can have two of the d, 1 s and

3 of the p involved in compound or complex formation or coordination bond formation, ok. So, this scenario will be called d 2 s p 3, you have studied it before most likely, right.

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