Coordination Chemistry
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Lecture - 2
Definition

Good evening everybody. So today, we will continue our discussions, what is going on coordination chemistry, and today we will just basically specify our attention on the definition.

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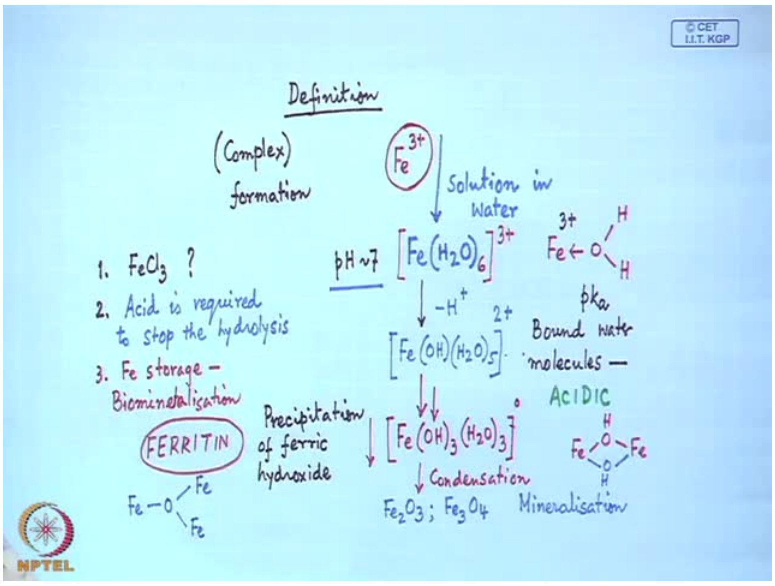

So, how we can define a particular complex? When we have seen in our last class that complex formation rather is playing some important role from materials to the live processes and the central part of it is a typical metal centre. What we have seen that it can be a ferric ion; so how we consider that coordination chemistry can be developed around a particular metal ion, and first of that thing which will be mostly devoted to the solution of any such metal salt. This is a very simple and basic question, what we can ask to anybody, but the answer of that question is not so simple, because whenever we have the solution in water… So, what we find that, what is happening there in water?

And from the idea of forming not only 1 iron oxygen bond, but 6 iron oxygen bond like this, and where we can have first sphere of attraction. This is forming from one such lone pair of electron available on the water molecule. So, we have six such these thing and over all charge on this, but this is a very standard and very well known; and also a very complex question, related to the complex chemistry is that whether this particular species, which will consider as the hexa aqua ferric ion, will exist in a solution of water at neutral p H, say p H 7.

And some more complex thing can happen afterwards, if this water when coordinated to iron center and this iron is in plus 3 oxidation state, and it is sharing. That means the electron density from this particular oxygen is pushed towards the vacant orbital of iron and the p k a basically, the p k a of this O H is changing. And this particular p k a value is such that, it is going to towards some position, where we can consider that this bound water molecules. These bound water molecules, to ferric ion are acidic. So, if they are acidic what will happen? That we can expect some amount of release of the proton, so if we consider that 1 of the proton will be released from 1 such F e O H to bond, so we will get at least, F e O H bond.

That means instead of aqua coordination, we have the hydroxido coordination. And remaining 5 H 2 O will be there as water molecule, and we have release of 1 proton, so charged been utilized at one point, so this will be 2 plus. So, if this particular situation continues for removal of more number of H plus, that means removal of more protons at one particular stage, where we have, so we have two step of those proton releases. We have F e O H whole 3 H 2 O whole 3 as a neutral species and which basically we can consider as the precipitation of ferric hydroxide.

So, this particular condition, we will call as precipitation of ferric hydroxide. So, this basically tells us some important thing that, when we go for the dissolution of ferric chloride salt. So, whether the dissolution of ferric chloride in a solution where water is present at p H 7 is possible or not? Because if this particular removal of proton is taking place, will end up with not a solution of ferric chloride, what a solution of ferric hydroxide. So, what is happening therefore, that hydrolysis of this particular complex, so hydrolysis of these aqua complex is taking place and we are not getting a typical ferric chloride solution in a step.

So, to get a typical ferric chloride solution, we should add that means the, hydrolysis of water molecule bound to the iron center, the ferric center can be prevented, if we add few drops of dilute acid. So, acid is required to stop the hydrolysis, so that is there. And in a next step what we get, that during the precipitation of ferric hydroxide what we all know, that some amount of this during removal of more water and condensation. That means if at this particular point condensation can take place between these ferric hydroxide with bound water molecules and iron iron bond. That means if we can have something where F e O H F e network is forming, and will end up with species like F e 2 O 3 or F e 3 O 4.

So, ferric hydride or any other such type of mineral like systems or the molecules can be formed there and we can consider this step as mineralization. So, in our body also in any system, wherever we are talking the dissolution of iron, iron in the system, iron in the living system also. And if iron is ultimately stored, so iron storage is possible in our body, when we get iron from the food material. And if iron intake is surplus, which is not immediately required completely for the production of hemoglobin and mioglobin molecules, access iron can be stored in this fashion and the mineralization can take place, and this particular process will call it as bio mineralization. And one such important molecule in our body is there, which is the ferritin molecule.

So, whatever iron we have in living system or in any other reaction chemistry also and the, if we cannot control the p H and the p H is at certain point, and iron is not in the solution, which is not utilised for the synthesis of hemoglobin and mioglobin molecule, but can be stored as ferritin, where more and more this F e O H O H type of binding. Sometime we can have when 1 hydroxide group is attached to 2 iron center. This particular O H, can have again a different p k value compared to the hydroxido ion, which is not bound to the iron centre and it can also go for dissociation of proton making this hydroxido ion to oxido ion.

So, when it is forming oxido ion, so the code can also be formed from a new hydroxido and new oxido bridge network. This is a mineral like network, which can be formed in ferritin molecule. So, what we see from this particular ss making solution.

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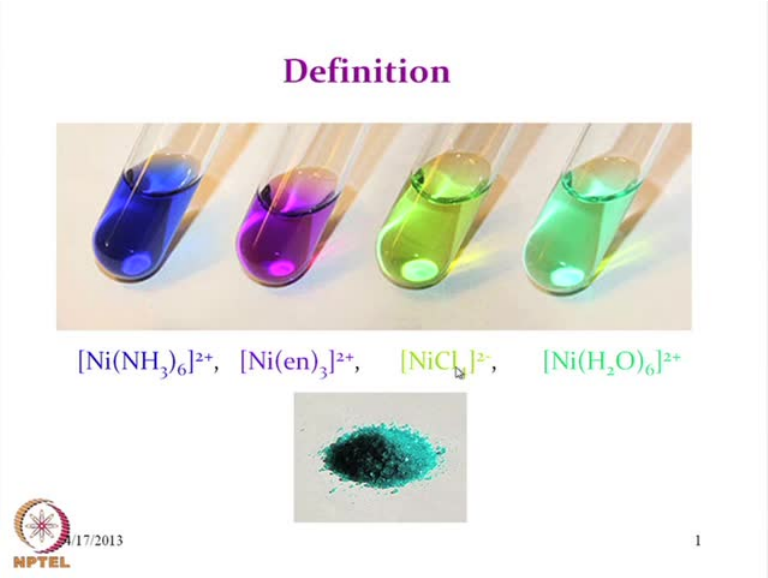

Definition

$[Ni(NH_3)_6]^{2+}$, $[Ni(en)_3]^{2+}$, $[NiCl_4]^{2-}$, $[Ni(H_2O)_6]^{2+}$

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So, what we have? We have certain amount of any salt, so this is a typical salt and if the nature of this salt, we know it can be a nickel salt. So, if this salt is in our hand and we try to make some solutions like, that of our making iron solution. So, when we take this particular salt, so it is not a typical iron salt or copper salt or any other metal salt, but it is colored. So, colored salts we all know what is particular salt can be colored, it cannot be potassium chloride, it cannot be sodium chloride, so definitely it is a typical salt, which can give rise to the colored to our system.

And when we simply dissolve it in water, like dissolution of ferric chloride, it is also not ferric chloride, the colored also tells us that this is not ferric chloride also. So, if we just try to dissolve it in water, immediately we get a typical solution and the solution has a characteristic color. If we are able to analyze the color of this species, we should be able to tell what is forming over there inside this particular test tube. So, this is basically a nickel salt, so nickel sulphate or nickel chloride is there in our hand and when we dissolve it in water, it gives like iron the hexa aqua nickels chloride or sulphate.

So, if it is a nickel chloride, it gives hexa aqua nickel chloride salt as a complex or if it is a nickel sulphate, we will also end up with hexa aqua nickel sulphate complex. So, simple taking any salt in a test tube and addition of water can give rise to our coordination complex. So, complexation is so easy to have but we sometime forget to write in this particular fashion, when we are considering that nickel is doing some central role in some catalytic reaction, in some other biological reaction, that the first species what is forming over there is the hexa aqua nickel 2 plus.

And this particular thing that means the color change is nothing but from this particular complex, we can have this complex, we can have this complex and we can have this complex. So, when we add nickel hexa aqua and some H C l to it or some potassium chloride so that means supply of C L minus.

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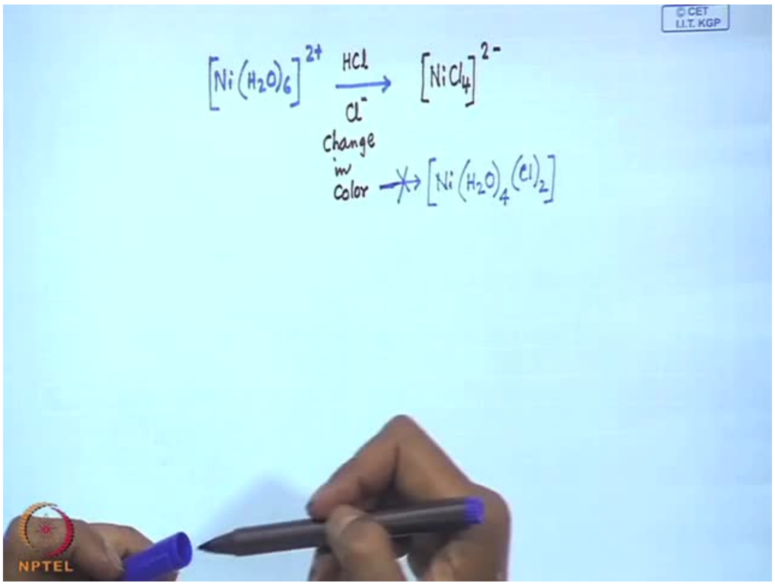

So, if we have hexa aqua nickel 2 plus cat ion has the corresponding complex and we add simple H C l is also sufficient. So, H C l is providing the ligand as C L minus and the nature of this particular ligand is only giving rise to 4 C L minus groups around the nickel centre. We get the corresponding tetra chloro complex. So, the substitution of these, by this chloride anion is possible and we get some one particular geometry to the other particular geometry. It is very easy to make also, is not only true for nickel, but it is also true for the cobalt or many other metal ions, where supply of these C L minus to any water solution of the salt, can give rise to the corresponding tetra chloro complex.

And one interesting aspect of this is that, the color of the species will immediately change from the original color. So, the associated reaction condition can be monitored by looking at the change in color for the reaction. Why the change in the color is taking place? Because the C L minus is one after another substituting, all 6 water molecules around this nickel centre and also we are not getting any such species in this particular case, where we have 4 water molecules and 2 are the substituted one that means this one. So, in this particular condition, in this very simple condition we are not getting any complex of this type, but the 4 C L minus can substitute 6 water molecules together, though in a stepwise manner, but the ultimate product of the reaction will only be the tetra chloro complex, not this tetra aqua di chloro species.

So, this particular s species is forming from a one particular typical color of this is that green, to a olive green color. Similarly, if we add ammonia to this water complex, this aqua complex we get the blue coloration. It is also true when we add copper sulphate solution and ammonia, we get also a royal blue color due to the formation of tetra amine complex of copper. Similarly, here also addition of ammonia molecules will replace all the 6 water molecules coordinated to the nickel centre by changing its color from green to blue. And another interesting reaction is also this another different type of ligand, will also go for characterizing and defining those ligands also. This is a typical ligand abbreviated as ethylene diamine, it is unlike this ammonia this is diamine form and is organic ligand.

So, organic ethylene diamine ligand when bound to the nickel centre by replacing 6 water molecules, will give rise to the formation of another species another complex species, where three such ligands are required to fulfill its first coordination sphere, and the color is changing to violet. So, once we know this four reactions starting from the dissolution of solid, nickel, salt, we can get this particular one. If we look at all the 4 colors, we should be able to tell the 4 different colors nicely. And if we can measure the corresponding electronic spectrum that we will see, that the most important condition, most physical characterization for knowing the complex formation is by measuring the corresponding electronic spectra of these solutions.

So, by knowing these color basically and it is corresponding electronic spectra and we will slowly expose to that for knowing the corresponding lambda maximum. That means the electronic absorption spectra and the corresponding co-efficient of absorption the molar absorptivity. All will tell us that what type of electronic transition is take place, for changing one color to the other. Right now, we should keep in our mind that, the different colors basically and we should be able to know what particular type of complex is forming, within the solution. So, we should know the four colors and we should know the four complexes forming over there.

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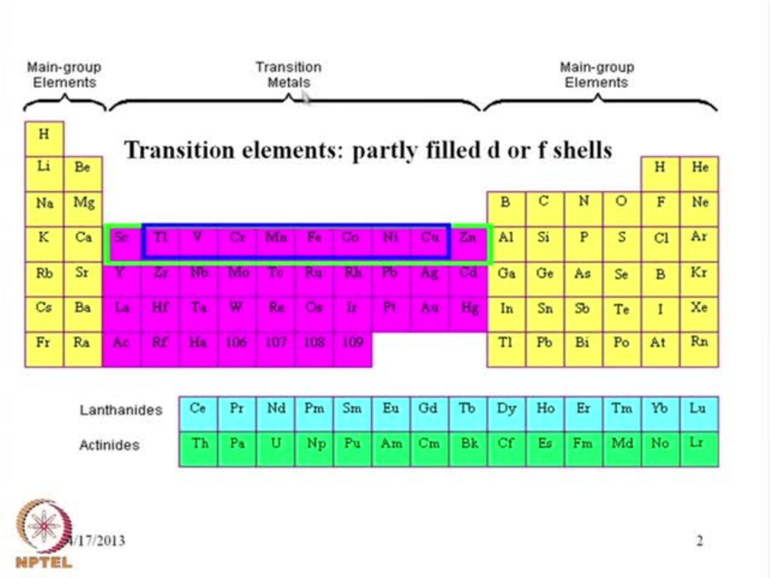

Transition elements: partly filled d or f shells

H																	
Li	Be															H	He
Na	Mg											B	C	N	O	F	Ne
K	Ca	Sc	Tl	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Al	Si	P	S	Cl	Ar
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pb	Ag	Cd	Ga	Ge	As	Se	B	Kr
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	In	Sn	Sb	Te	I	Xe
Fr	Ra	Ac	Rf	Ha	106	107	108	109				Tl	Pb	Bi	Po	At	Rn

Lanthanides	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinides	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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So, why we are talking all this things related to some of this species? So, we will have the entire periodic table and for this particular class, that means the coordination chemistry classes we will just focus our attention on the first series of this transition metals. And we have just started our discussion in this second class of iron of nickel and little bit of copper. So what are they? They are the transition metal ions and they have some typical electronic configurations. Due to that particular electronic configurations, we have certain number of unpaired electrons present in say bivalent nickel or trivalent iron or bivalent or tetravalent manganese.

Those electrons are responsible for their color, even for the very simple species, what is forming in water. And if we consider this entire series from this one, this is not T l, this is titanium. Titanium to copper, so this titanium to copper series will consider as the first transition series elements, or 3 d metal ions. So, when they are responsible for complexation, we will consider as the 3 d metal complexes and the next series from zirconium to silver we will consider them as the 4 d metal complexes, and from hafnium to gold, we can consider them as the 3 d metal complexes.

We will write now, we will take out all these green colored green bordered, this metal ions like scandium and zinc yttrium and cadmium and lanthanum and mercury because in particular oxidation state, this candium as well as this zinc, will not have any unpaired electron, so that by definition we cannot consider them in this ionic form. That means in some oxidation state, bivalent or trivalent as containing unpaired electrons in the d levels or the d orbital’s.

So, basic definition we can consider for these transition elements, which are responsible for the formation of metal complexes are that they should have partly filled d or f shells. So, when these are f shells, we are considering these as the corresponding lanthanides. That means cerium to lutetium, but when we have the d elements we consider them as the transition metals.

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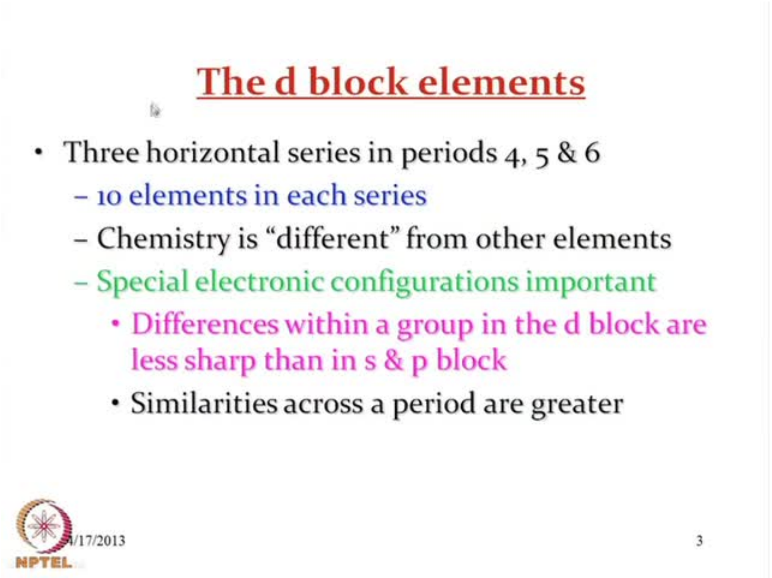

The d block elements

- Three horizontal series in periods 4, 5 & 6
  - 10 elements in each series
  - Chemistry is “different” from other elements
  - Special electronic configurations important
    - Differences within a group in the d block are less sharp than in s & p block
    - Similarities across a period are greater

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So, how we can define the d block elements? So, we have like this 3 d, 4 d and 5 d and they are basically positioned at 4, 5 and 6 series of periods. So, this is first, this is second, this is third, therefore, this line, this horizontal line belongs to forth period, this is fifth period and the sixth period. So, fourth, fifth and sixth periods will be considered as the corresponding elements of this particular block. Each series has 10 elements because we have 5 d orbital’s and the 5 d levels we are talking about.

When 5 d levels are filled by 2 electrons each, 5 into 2 that means, 10 electrons will be there and as a result we can have 10 elements in one particular series. And their chemistry is different from the other elements, so that is very important to know that, whenever we talk about their chemistry that means when we consider about the chemistry of manganese.

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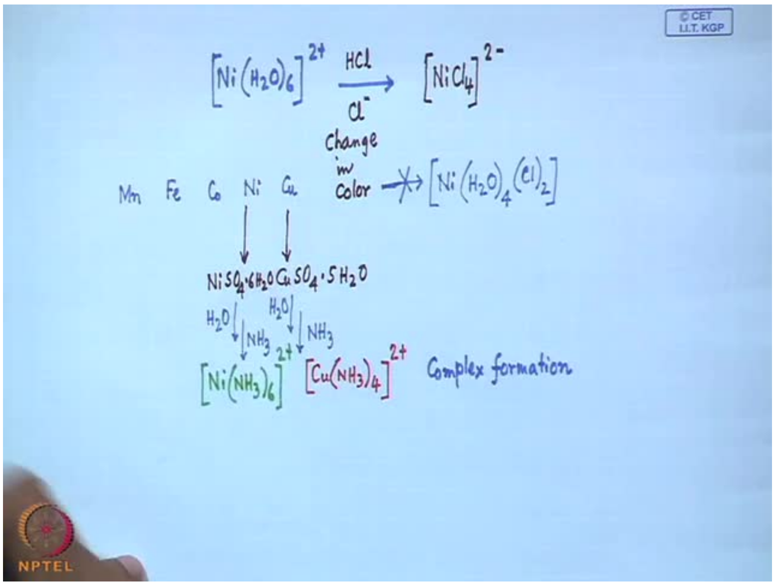

If we consider the adjacent element as iron, then the next adjacent is cobalt, so manganese, iron, cobalt, nickel and copper. So, what we can see that their chemistry is completely different. So, if we have certain sorts of these metals, that means salt of manganese, salt of iron, salt of cobalt, salt of nickel and salt of copper. And if we just consider the simple metal salts, that means if we just consider that we have a metal salt like copper sulphate, and another metal salt just now we have discussed as 6 molecules of water crystallization.

So, when we are dissolving in water, we have seen just now dissolving in water and that means, water will first coordinate with them and then addition of ammonia. Here also water first, then ammonia, what will happen there? Therefore, that this nickel will form the hexa amine complex and this adjacent one, that means the copper will form tetra amine complex. So, they are the adjacent elements, their salts are almost similar, but when they are reacting with water followed by ammonia as ligands. Their ultimate products are different. One is forming hexa amine, another is forming tetra amine complex and their colors are also little bit different.

So, in terms of only the complex formation, so the complex formation ability are different. So, depending upon the nature of the metal ion that means the copper is behaving differently with respect to this particular nickel, though they are two adjacent transition metal ions. So, their chemistry is therefore different. So, in terms of the complexes in reaction they form different complexes, related to the metal ion special electronic configurations are important and differences within a group in the d block are less sharp than in the s and p block.

So, within one particular group, the character for the metal ions are not very much different because we are going from one particular system, that means d 1 to d 2 to d 3 to d 4 to d 5, we are getting this particular configurations, within the filling up of only the d blocks, corresponding orbital’s. Similarities across a period are greater, so across the period there similarities, there complexation reaction, their other reactivity of the metal complexes are very much.

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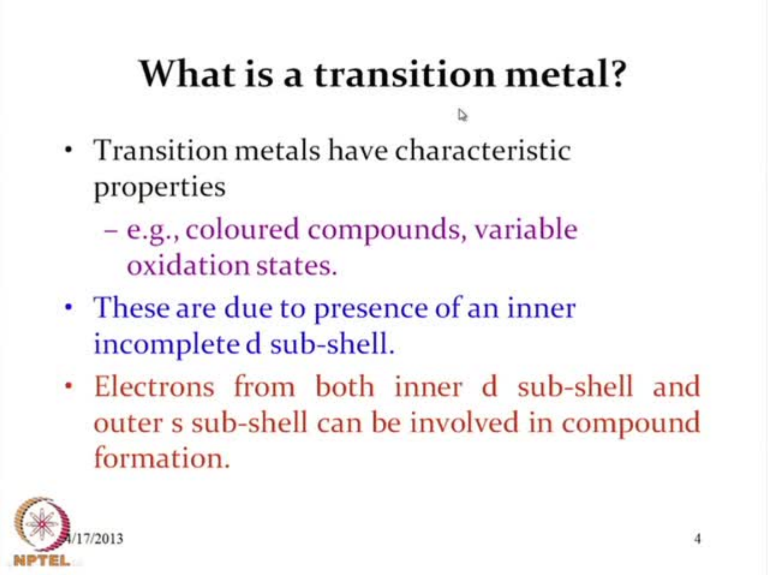

What is a transition metal?

- Transition metals have characteristic properties
  - e.g., coloured compounds, variable oxidation states.
- These are due to presence of an inner incomplete d sub-shell.
- Electrons from both inner d sub-shell and outer s sub-shell can be involved in compound formation.

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So, why this transition metal ions have been chosen to get the corresponding metal complexes because they have some unique properties? First we have a already seen that when you dissolve it in water molecule, they always produce a colored solution. And also, sometimes they give rise the variable oxidation states, which is very important.

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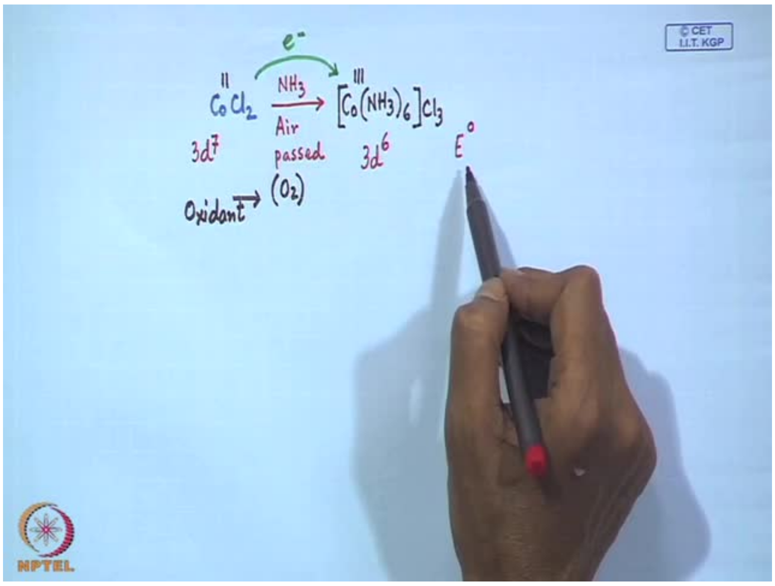

That means whenever we have certain metal centre, that in our previous class what we have seen, that if we have cobaltus chloride as a solid, cobalt chloride solid is in our hand and if we just dissolve it in water and then ammonia is added and air is passed. That means bubbling of air within the solution will result, what? Will result a typical metal complex and the complex is nothing but hexa amine cobalt 3 chloride. So, what we have basically? We have this particular one, where cobalt is present in plus 2 oxidation state, but this complex is forming a corresponding compound, which is in the trivalent state.

So, what we see their dissolution of any such chloride salt like nickel chloride, ferric chloride and copper chloride, this will give you immediately during the dissolution in water as the corresponding aqua complex. And when in presence of ammonia, that means we put ammonia we change the surrounding of this particular environment from water to ammonia, and we pass air. Air pass is nothing but we just passing oxygen present in air, which is a typical oxidant. So, these oxidant is responsible for the oxidation of cobalt 2, cobalt 3 and this is much more stable because, we will not be able to get the corresponding bivalent version of this complex.

So, the variable valiancy that means in one case, the aqua complex is stabilized in particular water environment and another case the amine complex, is stabilized in the trivalent oxidation state. So, we get the variable oxidation state, that means plus 2, that means the cobaltous state and the plus 3, the cobaltic state can be achieved by simple manipulation. And we can also study a very important reaction related to these variable oxidation state that means the electron transfer reaction. The corresponding electron transfer reaction is also very important. So, we get the variable oxidation states within these metal complexes.

Why we get such thing? That means the colored compounds as well as a variable oxidation states, because we can have the presence of inner incomplete d sub shells. So, when we have a typical electronic configuration, that means the cobalt in 3 d 7, so we have the cobalt 2 where we have 3 d 7 electronic configuration and cobalt 3 is 3 d 6. So, we have 5 d orbital’s, and in the first case the d orbital’s can have 7 electrons and in other case the d orbital’s can have 6 electrons. But, the maximum capacity of d electrons to be present within the 5 orbital’s are 10, so the occupancy in this form that means at d 7 level it is partly filled. So, partly filled d orbital’s can be oxidized to a configuration where it is d 6 because if this particular configuration can have some extra stability.

So, oxidation is possible from cobalt 2 to cobalt 3 and for this particular oxidation the corresponding standard electro potential is also to be known us. So, not only the change in the oxidation state, the variable oxidation states availability for metal complexes, but also we can measure the corresponding susceptibility, the thermodynamic reaction drive. Drive for the oxidation reaction can also be monitored, can also be measured, for the measurement of the different e g o values of these complexes, which can ultimately give you certain things, where we can consider the electron transfer behavior in any metal bearing system. So, metal is the central part, where we can consider the electron transfer. So, electrons from both inner d sub shell and outer s sub shell can be involved in compound formation.

So, during the compound formation if the s sub shell electrons are available, it can form bonds, where we can have the corresponding complexes of say nickel in 0 oxidation state. So, s sub shell can be utilized for the involvement of the compound formation like tetra carbonyl nickel, where carbon monoxide is the ligand, which is forming with the nickel in 0 oxidation state or the other d sub shell electrons where oxidation has been taken place and the 2 s electron has been lost, for the formation of nickel in plus 2 oxidation state.

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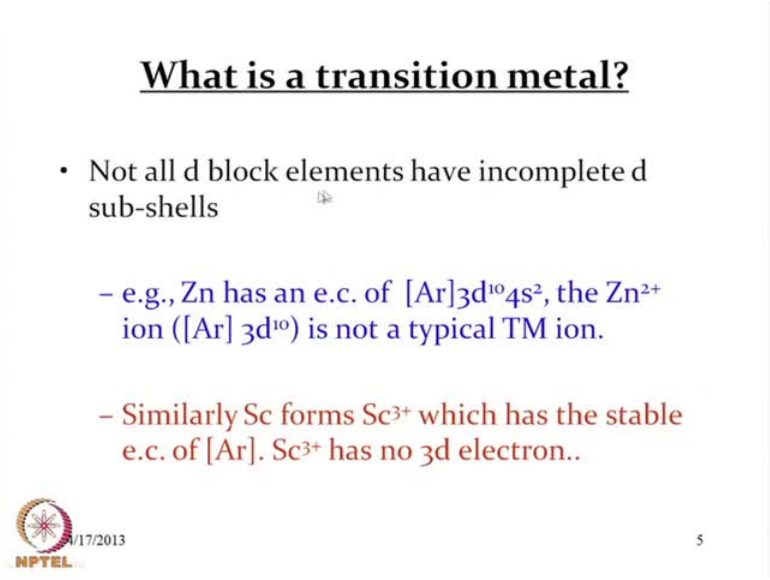

What is a transition metal?

- Not all d block elements have incomplete d sub-shells
  - e.g., Zn has an e.c. of $[Ar]3d^{10}4s^2$, the Zn^{2+} ion ($[Ar]\,3d^{10}$) is not a typical TM ion.
  - Similarly Sc forms Sc^{3+} which has the stable e.c. of [Ar]. Sc^{3+} has no 3d electron..

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So, not that all d block elements are incomplete, d shell sub shell that is why we have excluded scandium and zinc from the list because zinc has an electronic configuration of argon 3 d 10. It has not having some incomplete d level, that is why we are not considering zinc in plus 2 oxidation state, that means bivalent zinc as a typical transition metal ion. At the same time, scandium in the trivalent state also as only electronic configuration of argon, so it is has argon like electronic configuration, it has no d electron, so anything related to d electron property that means the complex formation, the color of the compounds, the variable oxidation state. The magnetic movement, will also not be associated with zinc as well as scandium. So, from the left of the series and on the right of the series we can exclude zinc and scandium.

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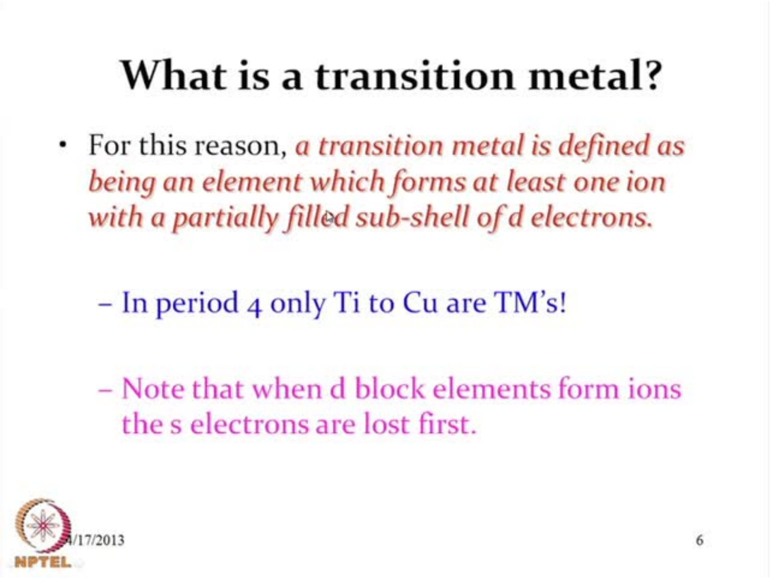

What is a transition metal?

- For this reason, *a transition metal is defined as being an element which forms at least one ion with a partially filled sub-shell of d electrons.*
  - In period 4 only Ti to Cu are TM's!
  - Note that when d block elements form ions the s electrons are lost first.

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So, a transition metal what can be defined as an element, which forms at least 1 ion with a partially filled sub shell of d electrons. That means at least it can have one oxidation state like that of our copper.

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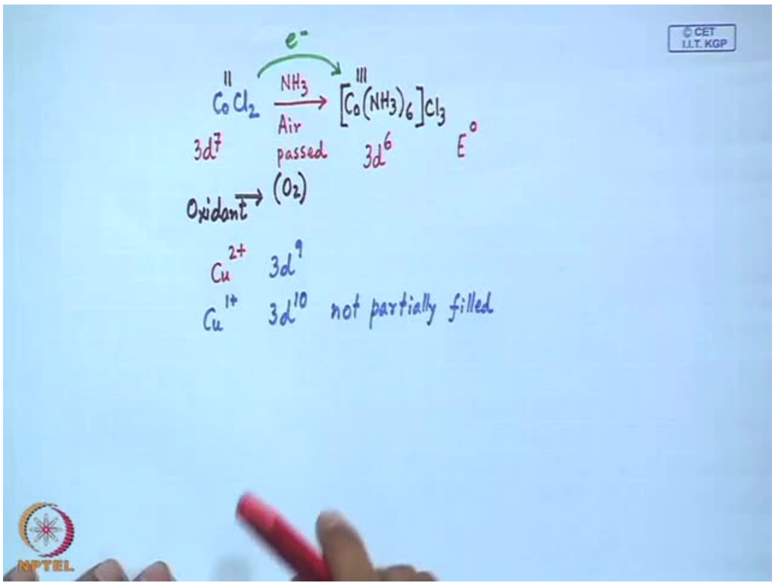

When we have copper in bivalent oxidation state, what we see that the corresponding electronic configuration is 3 d 9, so at least 1 oxidation state is available for the formation of a species like 3 d 9. We can consider that copper as a transition metal ion because it has partially filled d level. But if we have the copper in cupper state, which has an electronic configuration similar to that of our zinc 2 plus, which is not partially filled. So, it cannot consider, this particular species immediately based on the number of electrons present in the d level as a transition metal electron configuration because it is filled.

So, at least if we can have one oxidation state which has a partly filled d level, we can consider this as the transition metal. So, in period four only titanium to copper at… Therefore, we can consider as the transition metal ions. And when we are forming the corresponding ion the s electrons having lower in energy, so for the bivalent species formation, the s electrons are lost first, then the d block electrons starting losing from the system.

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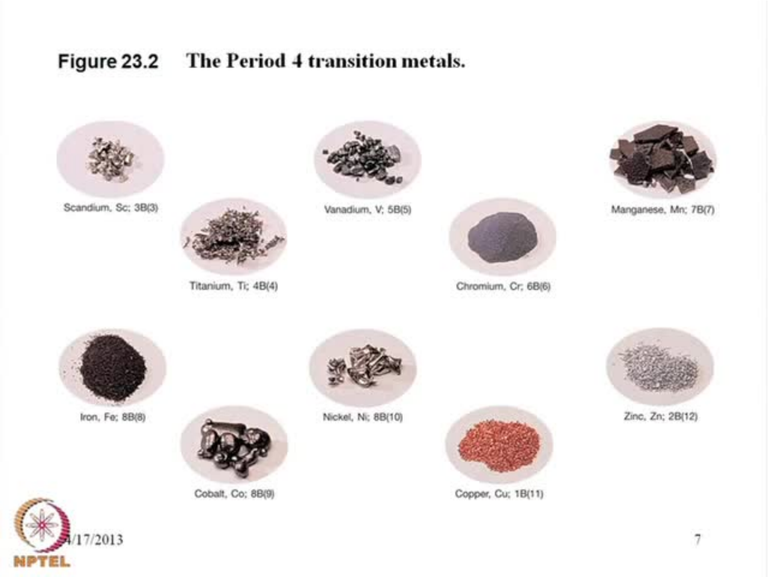

Figure 23.2 **The Period 4 transition metals.**

So, if we just simply look at the corresponding nature of the metals, which is very important. So, from scandium to titanium to vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, so all 10 elements of the first series, what we are discussing is there. For the formation of the corresponding ionic form that means trivalent scandium and bivalent zinc, we do not have any electronic configuration, where d electrons are present. In this particular case and all the d electrons are filled in the bivalent zinc case. So, we will not consider in the ionic form within the list of transition metals. So, from titanium to vanadium, we have the different forms of these granules of these metals, but when they are forming their corresponding salts, which are very important. So, instead of titanium, if we just talk about the corresponding salt that means the titanium chloride.

Instead of talking in terms of the corresponding nickel, we can talk in terms of the corresponding salt as nickel chloride or nickel sulphate. Similarly, cobalt chloride or cobalt sulphate, so what is happening there? How we make these salts nicely from these individual corresponding metal in this corresponding elemental form is that when we dissolve these these metals, that means the copper. If the copper is reacted with nitric acid and depending upon the different condition of these acid, whether it is concentrated or dilute, hot or cold we have the corresponding reactions of the different path ways, but ultimately what we will be getting from their is the, copper 2 nitrate salt.

So, once we have the copper two nitrate salt we can crystallize it also from the medium and we can get the corresponding crystalline copper nitrate salts. And in then next step is… Therefore, we can dissolve this copper nitrate salt in water, where we find that dissolution of copper nitrate in water is responsible for the formation of the corresponding complex, as the tetra aqua copper 2 nitrate. So, all 4 water molecules will come, which coordinate to the copper centre. And the nitrate as the anion which is forming with that particular salt is coming from the nitric acid, will present in the outer coordination sphere, that means second sphere of attraction of the corresponding metal complex.

So, these are the list for the corresponding metal salts and if we go from those metal salts to the corresponding metal compounds that will see how they are forming, but before that if we just simply look at one more example, where, how the color can give some idea to us.

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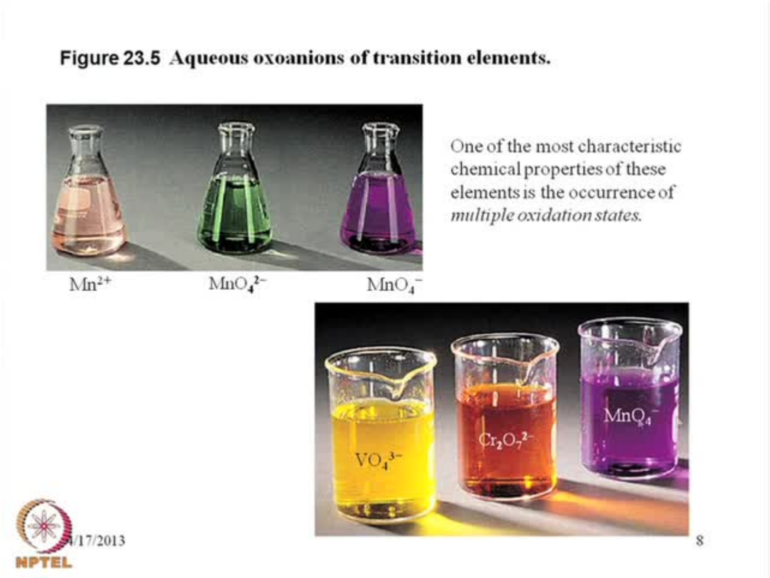

Figure 23.5 **Aqueous oxoanions of transition elements.**

One of the most characteristic chemical properties of these elements is the occurrence of *multiple oxidation states.*

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And if we can have, so here is that, is the complex species in some different form and which we often encounter. That means the aqueous oxo anions of transition elements, so when we have the manganese chloride, the manganese salt present or manganous sulphate and manganous sulphate when dissolve in in water, we get a very light pink solution. And when these are oxidised to manganate or to permanganate, the color is changing from pink to green, light pink to green and then again to dark pink. So, this particular color change is basically due to the formation of the permanganate anion, so it is in plus 2 oxidation state. It is in plus 6 oxidation state and it is in plus 7 oxidation state.

So, as we change the corresponding oxidation states, we are also changing the corresponding energy required for the corresponding absorption of radiation, to see the solution colored in its corresponding complimentary form. Similar thing is also known for the corresponding solution of venadate, when venadate is dissolved in in water sodium venadate or ammonium venadate. Similarly, dichromate and permanganate, this is the permanganate, the same permanganate is giving a different solution colored to us.

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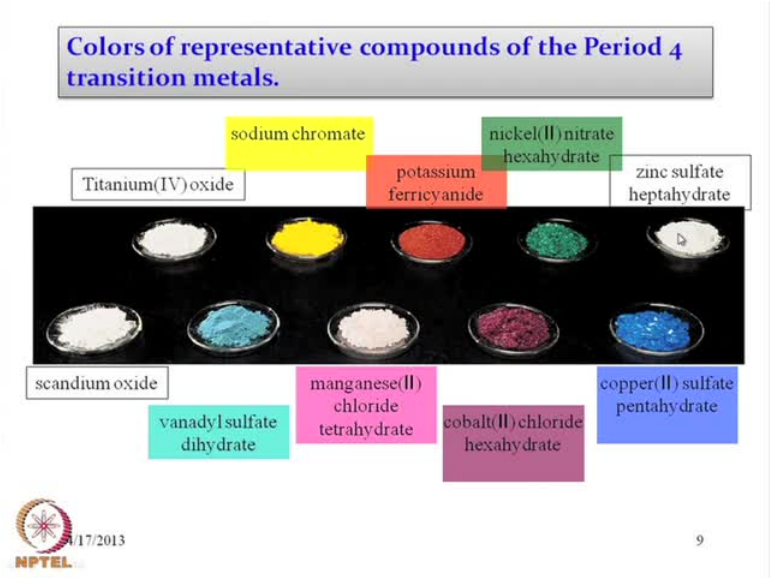

Colors of representative compounds of the Period 4 transition metals.

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So, what we see that the different compounds from the different metal salts and we have seen the nature of these typical compounds. And what we see here in this particular slide, that we have seen earlier, the different condition or the nature of the different metals when we go for the corresponding salts and some of the salts can be simple oxide only. So, scandium oxide which is typically white in color and this particular scandium oxide in this particular form, they are not giving any typical color, but is (( )). Some time they are very light in color.

Similarly, titanium 4 oxide T i O 2, the root root I. So, titanium 4 plus, which will also not have any characteristic color to that, but when we go for the corresponding chromium or vanadium salt. This is vanadis sulphate, di hydrate which is colored sodium chromate is also colored. Then manganese two chloride manganese 2 chloride, tetra hydrate which is has a very light color light pink in color, light purple in color in solution. So, this color is very difficult to see when we dissolve in in water. Then is strongly colored species like potassium ferrous cyanide, cobalt chloride, nickel 2 hexa hydrate. What we have just seen the dissolution of the corresponding nickel salt, and the addition of some other reagents to change the corresponding color.

This is copper 2 sulphate penta hydrate, when we dissolve it in water and add ammonia, we get a different color and zinc to sulphate hecta hydrate, which has no color, which is colorless, which is out of the list of the transition metals.

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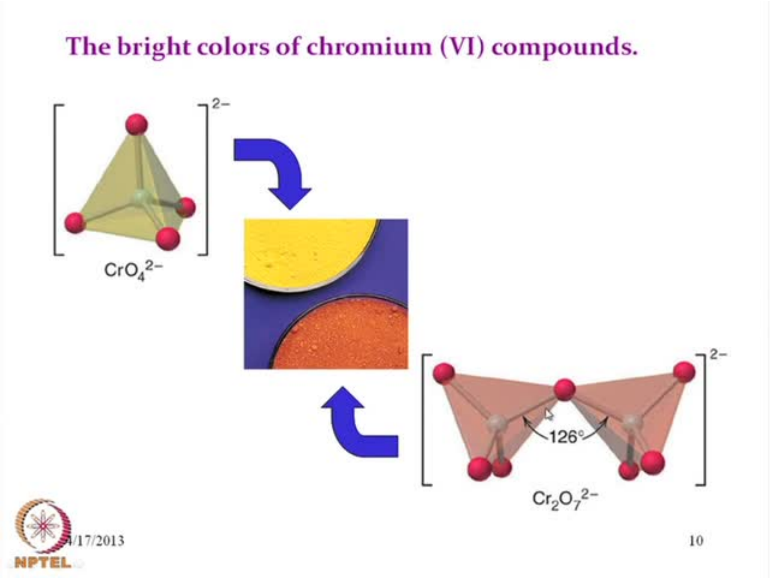

The bright colors of chromium (VI) compounds.

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So, this particular bright colors we get for these two species also. That means this is the chromate and chromate is typically bright yellow in color and these were originally, initially when we do not know. The all other colored species we use these as very good pigment. Similarly, this is dichromate this is very useful, analytical reagent for oxidation reaction because is a very strong oxidizing reagent. This is the mild oxidizing agent and interestingly this binding of this chromium with 4 oxide anions O 2 minus, giving rise to some species, which is C r O 4 2 minus and you have 4 chromium oxygen bonds.

So, these oxide anions basically forming the corresponding complexation reaction with that of our chromium and chromium is in plus 6 oxidation state, and this plus 6 oxidation state basically is stabilized only in a environment, where 4 such oxide anions are present. But in some acid based reaction this two chromate anions in acidic condition can condense to form the dichromate anion and this dichromate anion is still a strong oxidizing agent. But with the removal of one water molecule in presence of two protons, we have a situation where two tetrahedral unit.

This is the tetrahedral fagment of chromate, 2 tetrahedral fagments are attached to each other. And this is a typical example is a very basic example where we see that a complex coordination anion is forms, oxo-anions is formed, where we have a species of binuclear motif. That means two chromium centers are present over there.

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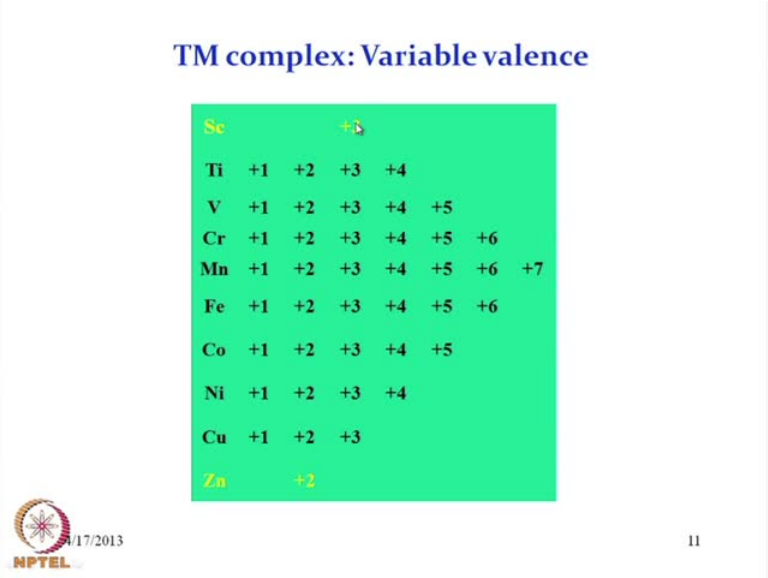

TM complex: Variable valence

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					

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So, if we just down the most of these oxidation states that means what are the possible oxidation states and what we can deal. So, it is a very big list for that. When we have this manganese, so manganese can have all possible oxidation states. That means the possible oxidation states if we can achieve by means of given some environment on the metal centre, we can consider that we can have a situation where variable balance is possible. And manganese can be stabilized from plus 1, plus 2, plus 3 to plus 7 oxidation state.

What we have just seen that, manganese in manganous plus 2 chloride, can be oxidized to manganate anion through some intermediate of M n O 2, which we get in pyrolusite in nature. Nature is providing this particular manganese as the pyrolusite the mineral in plus 4 oxidation state and ultimately to the most oxidized form like chromate and dichromate as permanganate. Similarly, chromium can go up to plus 6 oxidation state. In all these highest possible oxidation states, that means titanium in 4 plus vanadium in plus 5, chromium in plus 6 and manganese is plus 6, 6 we do not have any number of unpaired electron in the d levels.

That means the d levels are empty and we are having a situation where we can consider them as a d 0 system. But still that d 0 system can have a complex species because some strong electron donating anions are attached to them. They basically feed up with some electron density to the empty orbital’s of the metal centers. So, that is why though, this is highest possible oxidation states are possible to achieve. Similarly, iron in some condition is very uncommon to reach up to an oxidation state of plus 6. In case of cobalt, we can go to up to plus 5.

So, again is a very symmetrical arrangement, from here titanium to manganese at plus 7 and then again go down to nickel and copper to plus 3 oxidation state. These 2 in yellow color we are excluding from the list of transition metal ions, as plus 3 in the case of scandium and zinc in plus 2 oxidation state, where we have also no unpaired electron.

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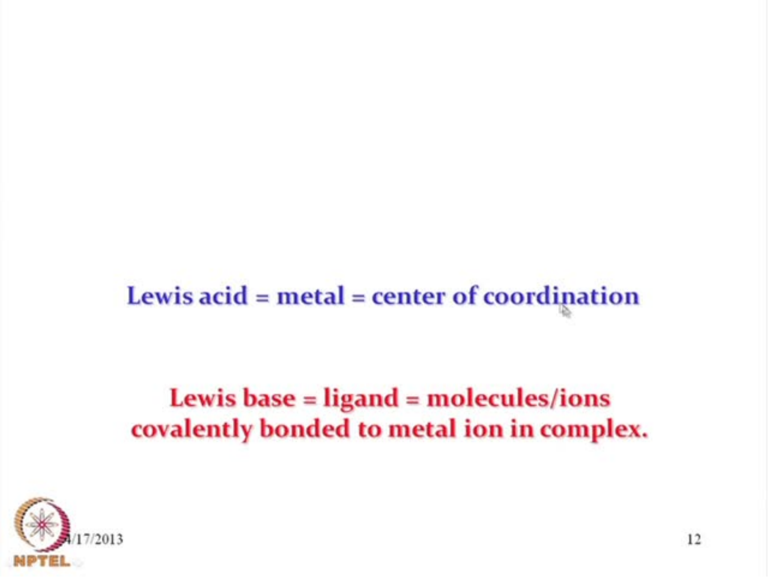

Lewis acid = metal = center of coordination

Lewis base = ligand = molecules/ions
covalently bonded to metal ion in complex.

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So, in any oxidation state we cannot have a d 1 at least electronic configuration. So, during the formation of these corresponding complexes, if we consider the Lewis acid as the metal centre, which is our center of coordination…

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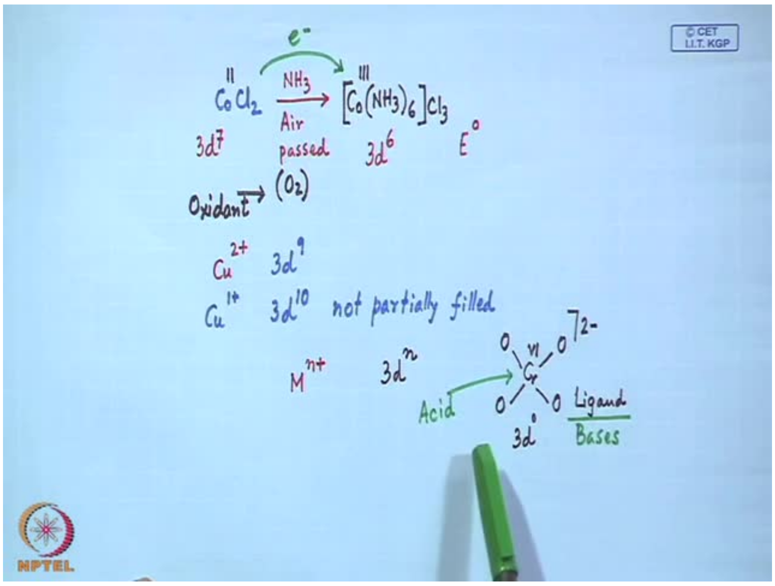

So, if we have M n plus and if it can have at least 1 unpaired electron or few unpaired electrons and if it belongs to the first transition series, with an electronic configuration of say 3 d n and it is already having some positive charge in it. So, it is basically an electron greedy, so this particular centre can function as a Lewis acid. So, the centre for forming the corresponding coordination bond or the coordination complex, they are always Lewis acid. And is surrounded by some amount of bases, when the base is the water molecule we have the corresponding aqua complex.

And these bases that means these particular water molecules we consider as ligands, they can be simple molecules like water or ions like hydroxide ions or oxide ions, covalently bonded to the metal ion in the complex. So, just now we have seen that, if we have the chromate, the tetrahedral chromate complex, where O, O, O, O 4 oxide anions are there. And overall we have a charge of 2 minus because we have a centre of chromium as in the plus 6 oxidation state. So, this is a 3 d 0 situation, we do not have any electron in it, but these are highly charged. These O minus oxide anions, so these oxide anions are now functioning as good ligand.

And these ligands are basically our bases, so they put electron density to the corresponding acidic centre. So, the centre, the metal ion centre is acidic in nature and the bases will push the electron density to the centre and as a result, we have the strong chromium oxygen bond. And these particular bonds can stabilize this particular species, so all these oxo anions are therefore, stabilized in this particular fashion. So, next day we will see how we can change? How we can define other ligands also, and how they are going to bind to the metal center and change the corresponding property of the transition metal ion?

Thank you very much.