Coordination Chemistry
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Lecture - 14
Coordination Equilibria – II

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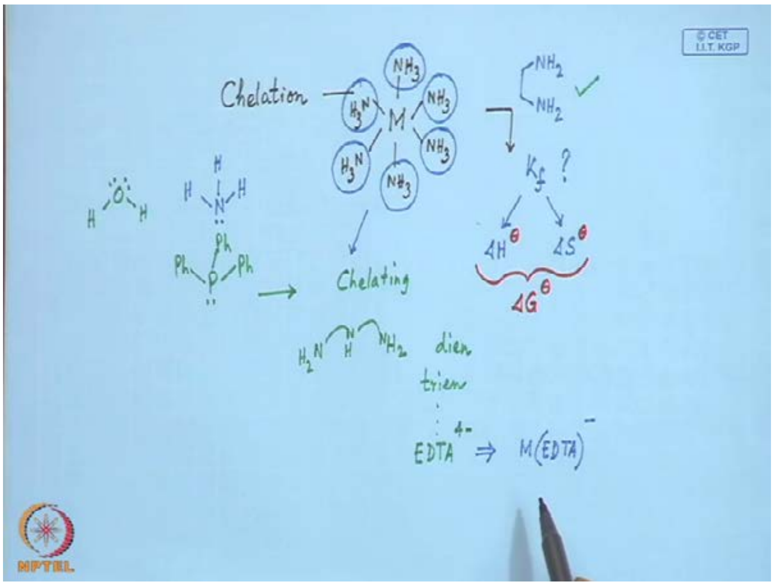

Good evening. So, we are just seeing how the chelation is operating to a particular metal complex, say centre M which is bound to so many amine groups, say and if in the reaction we just allow it to react with ethylenediamine. So, what is happening to its K values and if we just consider that these K values can have two determining factors; one is the corresponding enthalpy term and another is the corresponding entropy term. So, how these two values, the entropy term and the enthalpy term can balance the corresponding values for the delta G 0, such that we can consider that the reaction is spontaneous and the reaction is moving from left to right, because we will be discussing something where we just go on changing the nature of the chelating ligand, because monitoring the substitution of this monodentate groups by some other monodentate groups has some effect.

But it is not always very much encouraging to study the corresponding complex equilibria by replacing all the 6 monodentate ligands by some other monodentate group. Only thing that if we can have some arrangement where these ammonia groups with two electrons as lone pair binding to the metal centre is changed with a steric bulk related to the first spin groups P Ph 3 which is also bound to the metal centre. And the property of the metal centre is greatly changed or greatly enhanced towards some catalytic activity, then only we can consider the corresponding binding of the metal centre by replacing the water molecules bound water molecules by ammonia and ammonia by phosphine and that we will see that how the nature of these monodentate ligands can enhance and can contribute to the reactivity pattern of the corresponding metal complexes, but here we see that the corresponding ligands.

So, when we use a bidentate ligand we get some values for these thermodynamic parameters; from measurement of those values we can say something that the contribution is either entropy control or enthalpy control. So, if we move from ethylenediamine to any other tridentate ligand, say by changing the corresponding values of the arms; that means diethylenetriamine or triethylenetetramine or at the end we have the EDTA, EDTA in anionic form; that means the EDTA 4 minus. So where we see that, since we are talking about the binding of these metal ions particular those where octahedral centre is generated and if we get to use for single step complexes and reactions; so, we do not care about the intermediate binding of one after another of these monodentate groups.

But instead we can consider a single step coordination of the ethylenediaminetetraacetic acid to the metal centre. So, in a single step it can form the M EDTA complex and the binding constant for that would be very high. It will have both the corresponding enthalpy contribution as well as the entropy contribution for the formation of this M EDTA complex. So, this metal EDTA complex how nicely or how quickly we can form to trap these metal ions from the system that we will see how we can use.

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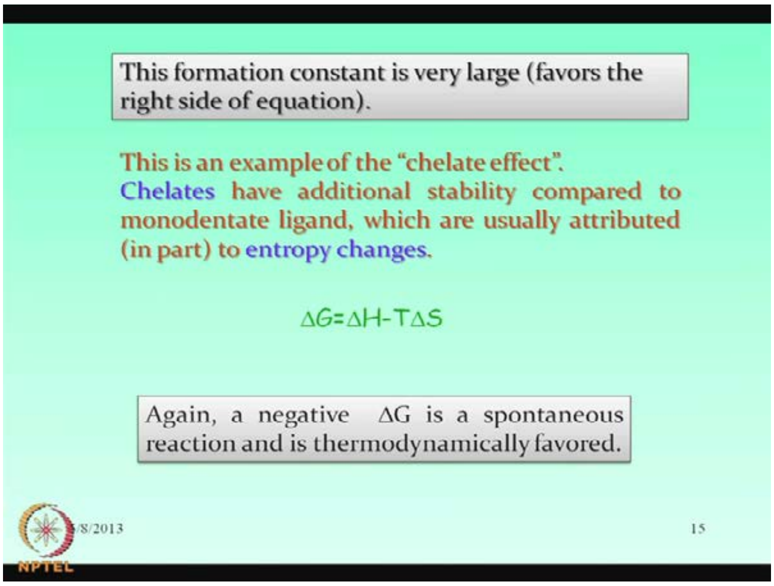

This formation constant is very large (favors the right side of equation).

This is an example of the “chelate effect”. Chelates have additional stability compared to monodentate ligand, which are usually attributed (in part) to entropy changes.

$\Delta G = \Delta H - T\Delta S$

Again, a negative ΔG is a spontaneous reaction and is thermodynamically favored.

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So, these thermodynamic parameters are definitely helping us to favor some of these reactions particularly the formation of these groups. So when the formation constant is very large, we can consider that it favors the formation of the complexes and it immediately goes from the left hand side to the right hand side very quickly. So, we see the tremendous effect of the chelation and we consider them as the corresponding chelate effect, because they have some additional stability which can be compared with the corresponding binding of the monodentate ligands, such as simple water molecules or simple aqua complex which are forming over there and can be considered as due to the effect of the corresponding parameter as the entropy term. So, delta G is well known corresponding relationship for the delta H minus T delta S.

And a negative delta G is obviously giving us some idea that the corresponding complexes and reaction is spontaneous and thermodynamically favored. So, we are not bringing at this particular point, the corresponding aspect which is also controlling and which is also contributing the coordination equilibria is the corresponding kinetic term; how quickly or how fast they are forming in a particular reaction. That we will deal with some other classes where we will be talking about the kinetic aspect of the complex formation and that kinetic aspects are also very important in studying the corresponding reaction mechanism in all these complexes.

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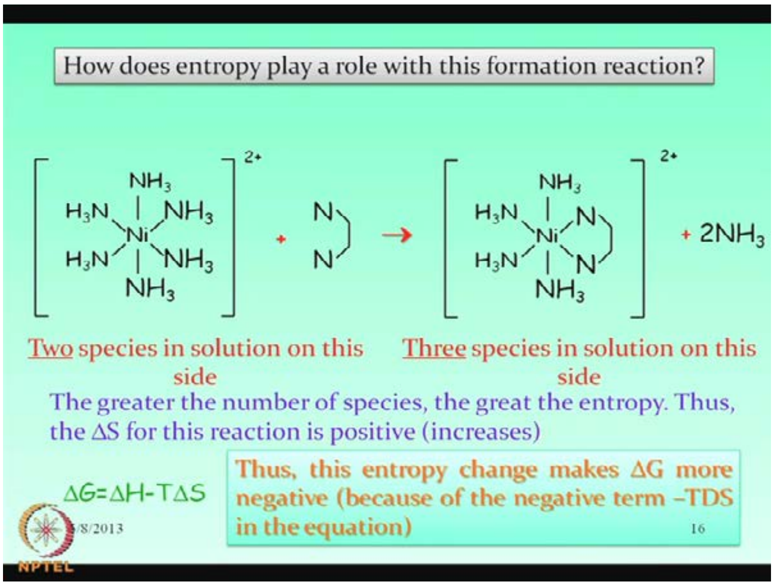

How does entropy play a role with this formation reaction?

Two species in solution on this side

Three species in solution on this side

The greater the number of species, the great the entropy. Thus, the ΔS for this reaction is positive (increases)

$\Delta G = \Delta H - T\Delta S$

Thus, this entropy change makes ΔG more negative (because of the negative term –TDS in the equation)

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So, it would be thermodynamically favored and the delta G can give us some idea about how they are thermodynamically favored. So, initial formation of one chelate ring therefore gives us some idea that the entropy is playing the important role to the formation of these complexes, because in this particular case, we are talking about the reaction of the hexamine complex with that of the ethylenediamine. And we are considering that one species is already the corresponding complex species, which is dicationic also is reacting with the neutral ethylenediamine molecule.

So, we are not considering anything related to some electrostatic interaction between the cationic species and some anionic species or any other hydrogen bonding interactions or any other non-covalent interactions are operating between these two species. But only driving force is that we are talking in terms of two individual species present in the solution during the reaction; that means on the left hand side and after the reaction one particular ethylenediamine coordination can remove two ammonia molecules. So, 2 ammonia molecules are removing from the medium and when in a single step the tris-chelate is forming, we will see that six ammonia molecules will be removing there. So, altogether we have large number of species forming in the solution and we will have a. definite entropy contribution for the chelate formation.

So, that is true when three ethylenediamine molecules are reacting with this hexamine compound or this hexamine compound is reacting with EDTA molecule also. So, the hexadentate EDTA molecule immediately takes away the complex as the corresponding unique species as the single species by the removal of all the bound ammonia molecules. So, that is why whenever we have the multidentate ligands coordinating to the metal centre and if it is the corresponding aqua complex, we will see that large number of water molecules are surrounding over the molecule and when the ligand is directly binding to the metal ion, all the bound water molecules will be removed in a single step and large number of species will be available for a reaction which we see that and in the right hand side we have large number of species.

So, definitely we will have contribution from the entropy term. Because the greater the number of species, the greater will be the entropy contribution for the delta G value. Thus delta S for this reaction is positive; that means delta S value is changing due to the change in the number of species from left to right. So for the reaction, the negative T delta S, this is the delta; this T delta is in the equation is therefore is a negative term. So, the positive value of the delta T will contribute towards the value for the delta G and the delta G is negative and we will have the corresponding contribution for the negative delta G value for a spontaneous reaction.

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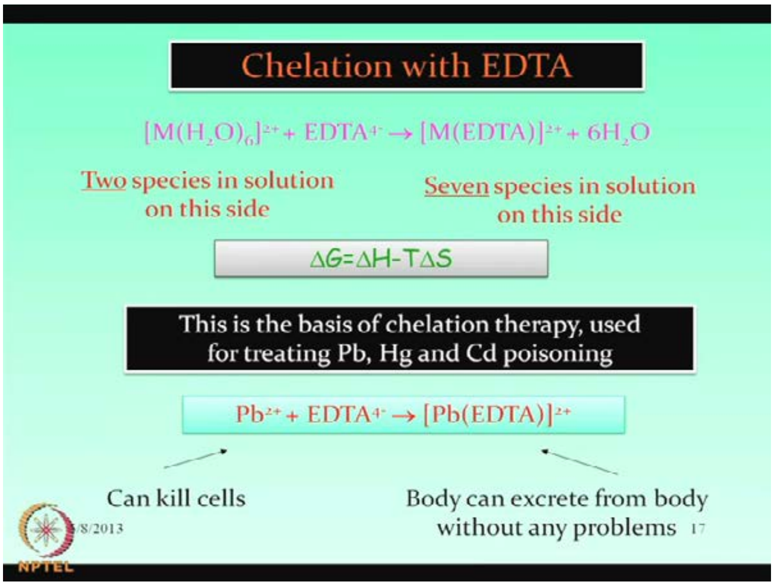

Chelation with EDTA

$[M(H_2O)_6]^{2+} + EDTA^{4-} \rightarrow [M(EDTA)]^{2+} + 6H_2O$

Two species in solution on this side

Seven species in solution on this side

$\Delta G = \Delta H - T\Delta S$

This is the basis of chelation therapy, used for treating Pb, Hg and Cd poisoning

$Pb^{2+} + EDTA^{4-} \rightarrow [Pb(EDTA)]^{2+}$

Can kill cells

Body can excrete from body without any problems

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So, we have the example for the corresponding chelation with ethylenediaminetetraacetic acid and EDTA in the deprotonated form; four acetic acid groups attached to the EDTA molecule can give rise to the tetraanionic form and in all cases. So, all transition metal ions and other main group elements also they immediately go and bind in this form; whether the metal centre is favoring a corresponding octahedral geometry or not but EDTA can bind through it some of its important donor groups like nitrogen and oxygen to the metal centre removing all the water molecules which were bond to the metal ions from here.

So, in this particular case two species from the left will contribute seven species in solution towards right. So again the delta G value if we consider, this will contribute more for the entropy thing. So, that will give rise to the corresponding delta G value higher and this delta G value will also definitely contribute towards the corresponding formation constant. So, formation constant for the metal EDTA complexes would be higher. So, this particular thing is a very good condition for the chelation therapy. So, therapy is dependent on the chelation metal ion chelation. If we are considering something in our body related to the binding of the metal ion by a unique ligand system which is EDTA. So, EDTA can trap any metal centre nicely and remove from our body from the environment from any other system. So, these are the some examples of some harmful metal ions like lead, like mercury, and like cadmium.

So, they are also industrially polluting metal centre. So mercury, lead, and cadmium can pollute the corresponding water in the environment and it can be also some industrial effluent. So, lead is utilized very much in the industry from paint and all other cases; mercury is utilized for several other cases like electrochemical cells, mercury cells and all and cadmium is required for the battery making thing. So, they are highly polluting our environment in the water level in the water system. So if we want to purify that water, we have to trap the metal ion from the solution state because they are in the cationic form most of the cases, not in the free metal form and immediately we can use EDTA to bind these metal ions. And lead will bind EDTA from the corresponding lead EDTA complex and this particular lead which we know that this is harmful to our body also, because it can kill some important cells in our body.

But this particular lead EDTA complex when it is forming, it can be removed from our body; so, body can excrete this from our system. Without any problem we can remove this from our body. Similarly if we can have some iron overload in our body; so, iron overload can also be counteracted by the use of EDTA. In case of thalassemia patients, the blood transfusion is required to the patient. So, large amount of blood is given to the patient. So, blood containing iron is getting loaded in the body for the patient. So, we have to take out this extra iron which is not utilized for the blood synthesis in the patient’s body. So, that iron can also be taken out by the use of EDTA. So, the EDTA utilized there can be a very good medicinal thing and the chelation therapy would be useful for the binding of all these metal ions.

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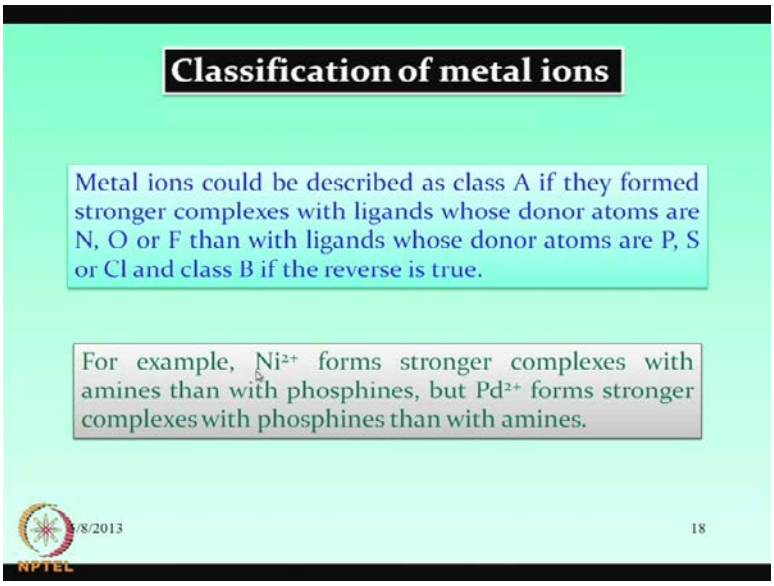

Classification of metal ions

Metal ions could be described as class A if they formed stronger complexes with ligands whose donor atoms are N, O or F than with ligands whose donor atoms are P, S or Cl and class B if the reverse is true.

For example, Ni^{2+} forms stronger complexes with amines than with phosphines, but Pd^{2+} forms stronger complexes with phosphines than with amines.

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So now going from these ligand systems, how they are contributing to the equilibrium of metal and the ligand system; now we just move on to the classification of the different metal ions for their type of binding potential. So, metal ions could be described as class A type. So, among the all the metal ions starting from the transition metal ions to the main group metal ions and the lanthanides and the actinides will have one particular class and that class is labeled as A only if they form good bonds with the nitrogen, oxygen, and fluorine donor atoms.

So, they can form stronger complexes if the ligand system has nitrogen, oxygen, and fluorine. Then the other system; that means other types of ligands whose donor atoms are bigger; that means phosphorus, sulphur, and chlorine compared to nitrogen, oxygen, and fluorine. So, compared to nitrogen if we use phosphorus, compared to oxygen if we use sulphur, and compared to fluorine if we use chlorine, we get another class of metal ions which have a different preference for the metal ion binding and we call them as class B metal ions.

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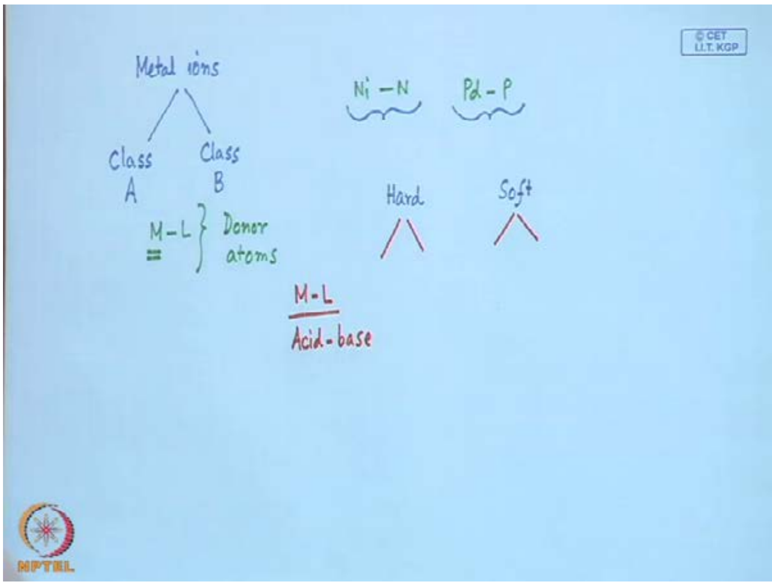

So, all these metal ions can be classified as class A and class B. How? By looking at the corresponding combination of metal with the ligand; so metal is there; so, depending upon their choices for coordination to this particular donor atom. So, the donor atoms are important. So, if it has some immediate preference for these donor atoms, we get the class A type; if the other types are favored the other group donor atoms are favored, we get the class B type of metal ions. So, we find that when we are talking in terms of the corresponding nickel, the first transition series element the 3 d element nickel 2 plus and it immediately forms stronger complexes with amines.

So far from our studies on these classes, we have seen that nickel has a corresponding nickel salts and nickel chloride or nickel nitrate which is forming and which is available as the corresponding hexaco compound is immediately reacting with the ammonia molecules and the corresponding hexamine complexes are forming very easily. But they are not so easily forming the corresponding phosphine complexes, say, triethylene and phosphine or some other phosphine substituted by different r groups, but going down from nickel 2 plus to palladium 2 plus; that means from 3 d element to 4 d element, we have some choice to know that palladium 2 plus can form stronger complexes with phosphine than amine.

So, we should have some preference for the formation of nickel nitrogen bond and palladium phosphorus bond. So, we will see that depending upon the environment what we are getting from the metal complexes or some biological molecules or some catalyst; that means the nickel nitrogen assembly is preferred. Similarly palladium phosphine assembly is preferred for their stability as well as sometime their reactivity to some other reactions. So, nickel will be preferring all nitrogen donor ligands and palladium will be preferring the phosphorus related ligands. So, we just propose some theory which is well known by HSAB theory, hard and soft acid-base theory.

So, hard and soft acid-base theory will talk us something related to two cases; that means we can have a situation where something will be calling as hard and something will be denoting as soft. So, when we talk about the corresponding complexation reaction; that means the metal-ligand complexation reaction will have both hard metal centre and the ligand can be characterized also hard ligand. Similarly in case of soft system we can have the soft metal centre; that means the soft acid and the soft ligand system; that means the soft base. So, M L reactions what we know now that it can also be considered as the corresponding acid-base reaction because metal ions can be considered as the corresponding acids and ligands can be considered as the corresponding bases.

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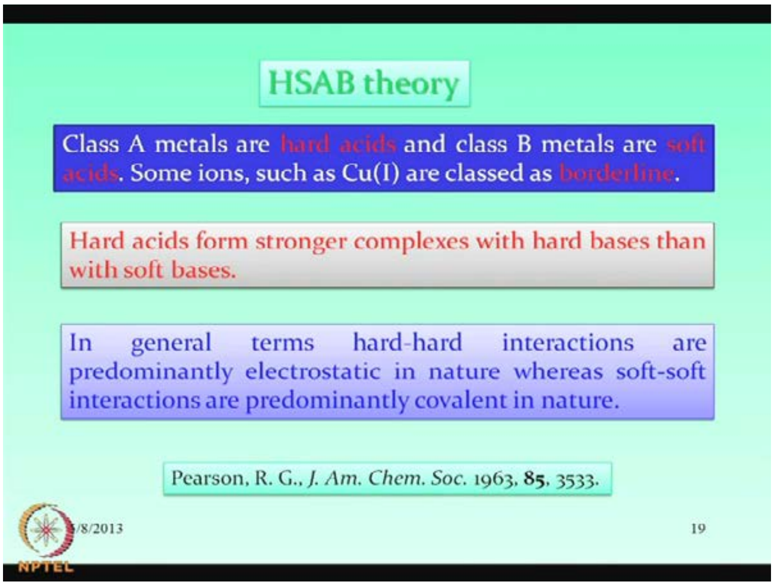

HSAB theory

Class A metals are hard acids and class B metals are soft acids. Some ions, such as Cu(I) are classed as borderline.

Hard acids form stronger complexes with hard bases than with soft bases.

In general terms hard-hard interactions are predominantly electrostatic in nature whereas soft-soft interactions are predominantly covalent in nature.

Pearson, R. G., *J. Am. Chem. Soc.* 1963, **85**, 3533.

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So, this theory what it tells us that we have classified class A and class B such as nickel and palladium. So, class A metals or metal ions are hard acids and class B metals or metal ions are soft acids. So, first category is for H; that means the hard acids and the second category is the S acids. So, such example we can have the copper in lower oxidation state; that means the copper one, it can be classified as a borderline. So, it is neither hard nor soft it is the borderline case because it can have the duel affinity that it can bind both nitrogen as well as phosphorus which are well known as hard base and the soft base ligand system or the donor atoms. So, hard acids form stronger complexes with hard bases than with soft bases. So, hard acids will have only preference for hard bases.

The general terms for the hard-hard interactions, so we will be considering all these metal-ligand complexation reaction as either hard-hard reactions or soft-soft interactions. So, that will be very much easy to identify that what type of metal will prefer what type of ligand if we can classify these in terms of the corresponding interactions as hard-hard interactions and soft-soft interactions. So, hard-hard interactions are predominantly electrostatic in nature; that means we can have higher oxidation states on the metal centre and high charge density on the ligand centre and small atom on the ligand system. So, which should be mostly electrostatic in nature and soft-soft interactions are predominantly covalent in nature. So, if we consider other cases also; that means the non-covalent interactions in metal complexes. So, metal when reacting with the ligand system we have the electrostatic interactions first.

Then at some points also we can have the covalent interactions also. And then if we proceed further for the interaction like hydrogen bonding interactions or say other non-covalent interactions like hydrophobic interactions or Van der Waals interactions, we will see that these interactions would be of different types which we cannot classify as hard-hard interactions or soft-soft interactions. So, starting from purely electrostatic interactions to covalent interactions, we can have some other interactions as well. So, all these things; that means, it is a famous paper in Journal of American Chemical society 1963 by Ralf G Pearson. He proposed first that thing and categorized the metal ions first as two different types as hard and soft.

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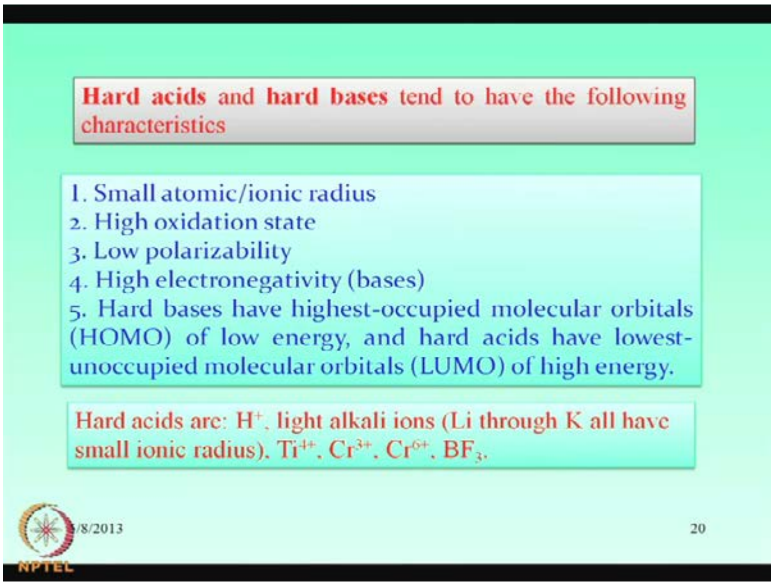

Hard acids and **hard bases** tend to have the following characteristics

1. Small atomic/ionic radius
2. High oxidation state
3. Low polarizability
4. High electronegativity (bases)
5. Hard bases have highest-occupied molecular orbitals (HOMO) of low energy, and hard acids have lowest-unoccupied molecular orbitals (LUMO) of high energy.

Hard acids are: H^+, light alkali ions (Li through K all have small ionic radius), Ti^{4+}, Cr^{3+}, Cr^{6+}, BF_3.

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So, when we consider the corresponding coordination of the bases it will be very easy to identify that the hard acids and hard bases how we can characterize them; that means they have the corresponding characteristic properties that both hard acids and hard base can have small atomic and ionic radius; that means if the oxidation state is high; that means if they have high oxidation state, the size is small and ionic radii is also small.

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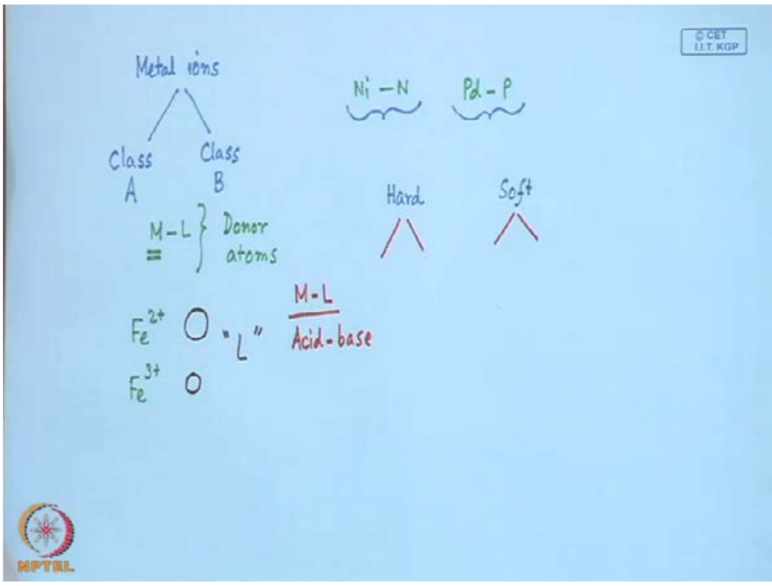

So, if we just simply go from Fe 2 plus to Fe 3 plus. So, oxidation state is changing; we are going from a lower oxidation state to a higher oxidation state and the size of this species is changing. So, this will have a bigger ionic radius and this will have a smaller ionic radius. So, the radius will tell us that the type of interaction between this metal centre with the ligand system; the available ligand system what we can have in our hand would be more electrostatic type. More electrostatic type is already we have presumed that more electrostatic type interaction would be between hard-hard interactions. So if the ligand is of hard type, the ferric ion will react and will favor the corresponding interaction for the M L bond formation rather than the ferrous ion.

It can have low polarizability; once the size is small, the polarizability of the atom or the ion is also less. So, smaller atoms and smaller ions will not go for polarization of the charge; that means, the charge separation at one side it is positively charged and at the other side it is negatively charged and which can also be controlled by the Fajan's rule as we all know. So hard bases, the ligands which we are considering as the corresponding hard bases have the corresponding HOMO, the highest-occupied molecule orbital of low energy and how does it have lowest unoccupied molecule orbital of high energy. So, the energy parity for these two is different. So, the hard base will have the corresponding HOMO of low energy; that means they are in the lower lying level.

So, they can donate the electron density efficiently to the metal ion and the metal ion will have the corresponding hard acids have the lowest unoccupied molecule orbital. So, this is also the lowest one. So, this ligand will have the highest one and this one. So, we have the corresponding matching HOMO and LUMO for the metal and the ligand. So, hard acids are the examples of the most important; hard acid is a very small one is the proton.

So, H plus is the well known hard acid and with respect to the H plus we can think of the comparison of all other reactions or all other metal-ligand formation and the lighter alkali metal ions lithium to potassium, then titanium; if we consider the titanium from the first tension series, the titanium in the tetravalent state which is easy to get also, chromium in the trivalent state not in the bivalent state, chromium also in the hexavalent state and for the molecule like BF 3 also. So, for BF 3 molecule we can have some good base like ammonia which can interact with BF 3 forming the BF 3 ammonia molecule as the corresponding complex.

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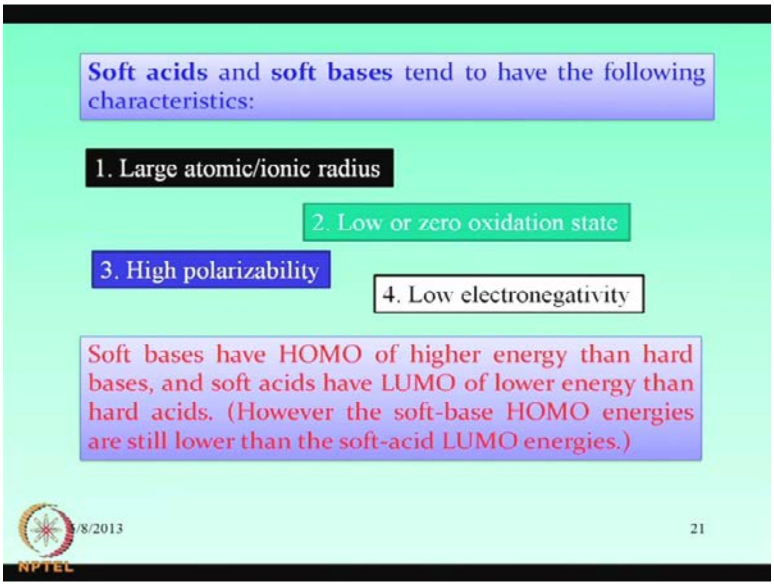

Soft acids and **soft bases** tend to have the following characteristics:

1. Large atomic/ionic radius

2. Low or zero oxidation state

3. High polarizability

4. Low electronegativity

Soft bases have HOMO of higher energy than hard bases, and soft acids have LUMO of lower energy than hard acids. (However the soft-base HOMO energies are still lower than the soft-acid LUMO energies.)

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Similarly the soft acids and soft bases tend to have the corresponding characteristics which we can also level together, which we are not leveling differently; that means one for acid and one for base, but they are altogether can have large atomic and ionic radius. So, they are all of bigger size; both the metal as well as the ligand, they can be of low or zero oxidation state.

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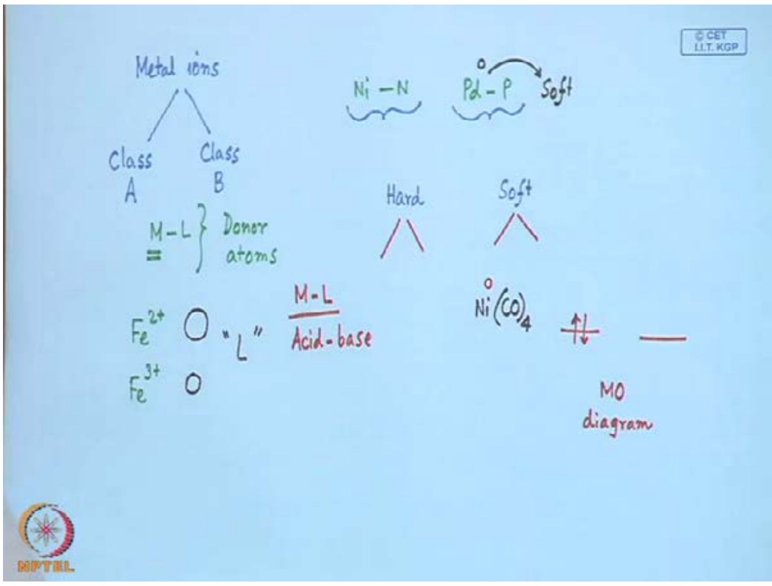

So, if a metal centre is there; that means if the palladium is available and if this palladium is in zero oxidation state or this palladium is in the plus one oxidation state. So when the oxidation state is zero, it will definitely be soft in nature. So, not only palladium which is bigger in size in plus two oxidation states, but the oxidation state control is also there. As we reduce the centre from palladium 2 plus to palladium 0, we are making the centre more softer and it will definitely prefer more coordination with the phosphorus type of ligand rather than the nitrogen type of ligand when the oxidation state is reduced from 2 to 0. So it will have low or zero oxidation state, both will be soft; that means if it is acid; that means the metal ion, we can have the low or zero oxidation state.

Similarly the bases; that mean the corresponding donor atom which is utilized for the corresponding base, then high polarizability; that means the bigger size of the atom or the ion compared to oxygen if we have the sulphur donation, so that sulphur donation can be considered as soft donation because it has bigger size and it has high polarizability. It can polarize its corresponding charge from two parts; one can be positively charged and other can be negatively charged with delta plus and delta minus polarizability which is not very hard. And it can have low electronegativity; that means it is not preferring electron much when they are shared with other atoms. So, these four types or four characteristic features can level a particular centre as a soft centre or soft acid centre or a soft base centre.

Similarly the organization of the corresponding level of the molecular orbital because these all will be talking again in terms of the corresponding binding when we will talk about the corresponding bonding features, say, when we will be talking about the corresponding bonding of say very simple molecule like tetracarbonyl nickel. So, this tetracarbonyl nickel basically we just see that nickel is binding with four carbon monoxide molecules with nickel in zero oxidation state and both the nickel and the carbon monoxide molecule the corresponding levels for the molecular orbital. So, the molecular orbital diagram basically will be useful to us.

So, molecular orbital diagram we can have and depending upon the donation and the acceptance whether this particular metal centre is responsible for donation. So, we can have the matching orbital and we have the field levels here and we have the MT level over here. Then only this particular electron density can be donated to the MT level and we can have some interaction between the metal centre and the ligand. Similarly if we can have two other matched levels where the field ligand level can be donated to the MT metal level, we can have also a different type of bonding in synergistic manner and we can have the multiple bonds between the nickel and the carbon centre. So, we see that the soft bases what we have seen in case of the hard definition.

Thus bases have HOMO of higher energy than hard bases and soft bases have LUMO of lower energy than hard acids. So, the corresponding ordering of the HOMO and LUMO energy level, if we theoretically calculate all these levels, the HOMO level and the LUMO level for the meta and the ligand. Then we should be able to tell about the corresponding softness and hardness of the metal centre as well as the ligand centre. So, however the soft-base HOMO energies are still lower than the soft-acid LUMO energies. So, the corresponding energies will definitely tell us whether it is in the higher part or whether it is in the higher side or in the lower side that a particular system can function as a hard acid or hard base or a soft acid or a soft base.

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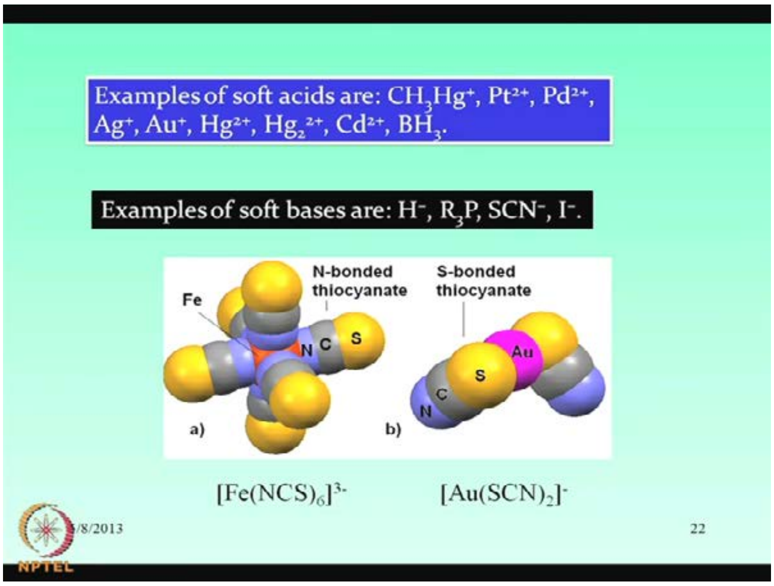

Examples of soft acids are: CH_3Hg^+, Pt^{2+}, Pd^{2+}, Ag^+, Au^+, Hg^{2+}, Hg_2^{2+}, Cd^{2+}, BH_3.

Examples of soft bases are: H^-, R_3P, SCN^-, I^-.

$[Fe(NCS)_6]^{3-}$ $[Au(SCN)_2]^-$

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So, the example for the different soft acids would be the methyl mercury species, then the platinum 2 plus, the palladium 2 plus; since as already we have seen the palladium 2 plus in the bivalent state, we can go and bind to the corresponding phosphorus centre only instead of the nitrogen centre which is hard, then silver, then gold; all are in the monovalent state, then mercury 2 plus also little bit in the softer side, then mercurous ion, cadmium 2 plus, and BH 3 not BF 3; BF 3 was hard, but BH 3 is soft. So, what we see that when we have the mercury-mercury bond and the charge is not much, the mercurous ion which is Ag 2 2 plus is also of soft nature. Similarly this CH 3 Mg, the methyl mercury species which is a very useful organometallic component, how it can react with the corresponding other anions, say, ligands that is also very important to know.

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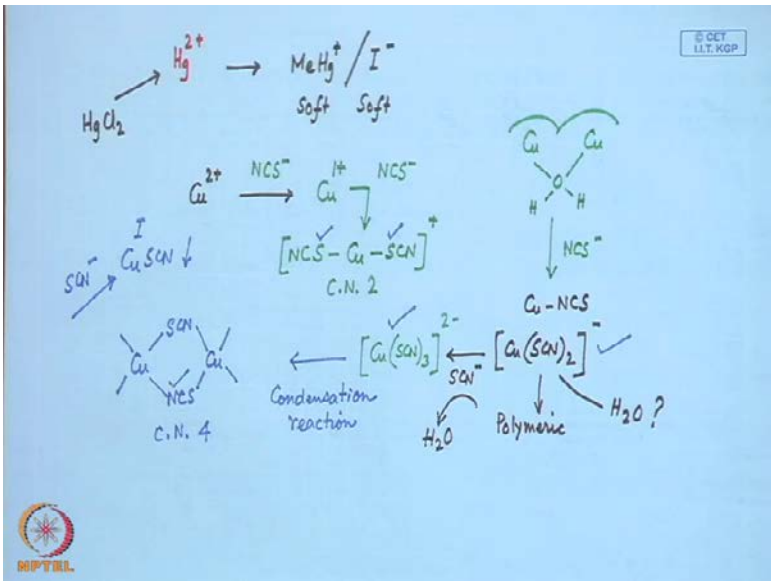

So, if we have the mercury as Hg 2 plus and this we all know how mercuric ion can bind because we know that this mercuric ion is present in mercuric chloride. But if we can get from there the corresponding methyl mercury species and which would be soft and it will definitely prefer the corresponding soft anion, say, I minus compared to F minus. So, once we can utilize for some metal centre where the centre is converted to a soft type. So, it will definitely attract the corresponding anion whether we are talking it in terms of the corresponding complex formation or binding, it can only prefer the corresponding soft counterpart as its ligand to bind. Similarly the gold and the silver ion can also bind in the similar fashion towards the corresponding species as the corresponding soft acids. And the soft bases are as we already told you that the corresponding phosphine, the prosperous base ligand the corresponding phosphine would be there, then hydride ion which is the soft base. So, the H minus would be the soft base to the ligand system.

So, all hydrido ligands can give us the corresponding soft ligand for the reaction, then thiocyanate anion. So, the sulphur end basically; the sulphur end is softer compared to the nitrogen end. So, when thiocyanate anoin is binding through sulphur it is soft and then I minus what we have seen just now for binding with methyl mercury anion. So, these two binding is very easy to monitor. So if we have methyl mercury, it will bind with iodide. Similarly if we have silver ion, it will just prefer for binding to I minus rather than F minus. So, this is some situation what we get for the corresponding molecules where the centre is like this; that if we have the iron centre and which is basically going for binding to thiocyanate and iron is present in the ferric state which is a very useful test for the corresponding red blood coloration and the identification of iron in solution by addition of sodium or ammonium thiocyanate to the medium.

And it immediately gives the octahedral complex if we use the corresponding stoichiometric proportion; that means 1 is to 6. Stoichiometry if we utilized for reaction with ferric ion, it will just bind through six sides of an octahedral geometry and all these groups basically are bind through nitrogen’s only. So, it is not that some of them are binding to the iron centre through nitrogen and some of them are binding through sulphur. This is because the ferric centre what was present is already hard in nature. So, when the ferric centre is first binding to the thiocyanate as NCS to nitrogen; that means one iron nitrogen bond is formed and the combination; that means from one side, it is hard-hard combination. The ferric and the nitrogen from the thiocyanate side is hard-hard combination. So, that hard-hard combination is not changing the corresponding character of the iron towards the soft side. It was rather as hard and it still remains as hard when it is binding to at least one thiocyanate through its nitrogen.

So, as more and more thiocyanate groups are binding to the ferric side, it is not changing its affinity for binding to some other soft side. So, it was hard; it will remain as hard and it will bind also the hard centres until it is binding all six thiocyanate anions through nitrogen donor points around the iron side. But what happens if we just simply go for gold and when we see that the gold is there and this gold which is present as Au plus; this particular species, this Au plus. So, when we have the Au plus which is a soft acid. So if it is a soft acid, it will definitely bind to the corresponding centre through sulphur because the sulphur end of thiocyanate is soft.

So, the sulphur end of the thiocyanate will be attracted to the gold and here instead of some straight binding of this thiocyanate groups, we can have some angular binding to the gold side; so, the gold in plus 1 oxidation state. Similarly in this list we do not have the copper. But if we have copper which was present as cupric ion and if this cupric ion is utilized for reaction with NCS minus, we find that this particular case that copper can be reduced to copper one plus and that copper one plus can bind to NCS minus and once we have this; that means when it is in the plus two oxidation state, it will have some choice for binding through nitrogen or sulphur. But if we are able to reduce it to copper 1 plus, like gold it will again bind through sulphur only forming the corresponding species as this.

So, this is the usual thing when we see that if we have a copper compound or say dicopper compound and if some position is occupied there by water molecule and if we react it with NCS minus, it not only replace this water molecules but also it can take out this copper as Cu NCS species and the internal electron transfer can take place, copper can be reduced and thiocyanate as you do halogen can be oxidized giving rise to this particular species as Cu SCN whole 2 minus and this species is very interesting species because it can also condense together and we can have some polymeric product out of the condensation of this particular species. So, like this gold we can have also the corresponding copper. So, immediately by these categories we can have the classification of the metal ions as well as the ligands for binding to the different ligand system.

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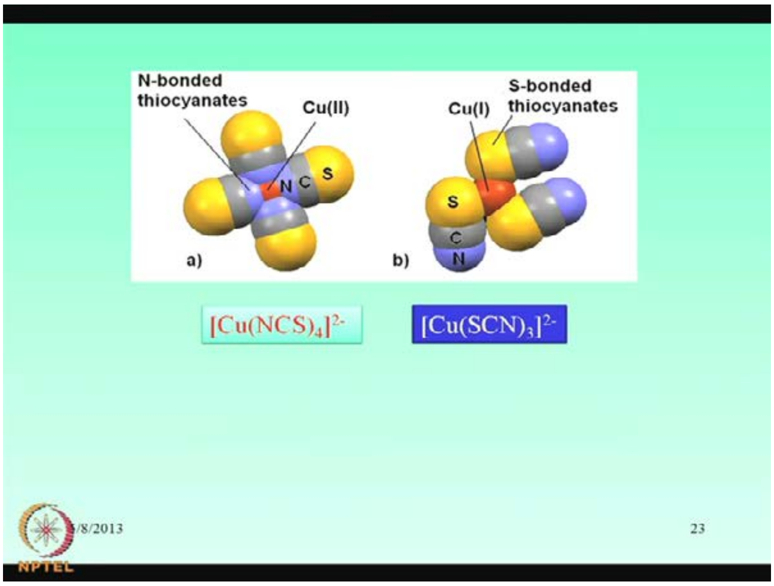

$[Cu(NCS)_4]^{2-}$ $[Cu(SCN)_3]^{2-}$

So, just now what we have seen also that the copper binding for this copper when we can have the cupric copper, it can bind through nitrogen and four such NCS groups can surround the corresponding copper species. Similarly if we have copper one the way we have just seen that the copper can bind to two thiocyanate groups. Similarly it can bind also three thiocyanate groups to give a species like Cu SCN whole 3 2 minus. So, this particular thing is also interesting. So, when the reaction of copper with thiocyanate can take place and we have these ideas that this particular species as well as whole 3 2 minus can also form. Because if like mercury or like gold or like silver, if copper is not remaining in this situation; that means with a coordination number of two, it can have a corresponding coordinated water molecule.

So, if we have the corresponding coordinated water molecule. So, the coordination number of three can be fulfilled over there and if that species is there, then we just have the corresponding ligand substitution reaction for the removal of this water molecule by thiocyanate giving rise to this species. And once this species is forming over there, this can also go for condensation reaction for basically bridging species. So, different types of bridging can be formed by changing the corresponding pattern for the coordination number. So, coordination number is enhanced from three to four as well as the different types of arrangement for the loop formation it can also take place and different types of these arrangements can take place from there.

Because the initial starting compound what we can have the situation that the copper which is already present as the copper one is not always true that this particular species that this one when it is there; that means both of them are through sulphur, one of them can also be through nitrogen; that means whenever we have the corresponding thing which we prepare in the laboratory for corresponding analysis of the copper as copper thiocyanate as white precipitate. And that white precipitate can go rise to corresponding immediate formation of the copper one and the thiocyanate species and that can take up more and more of these thiocyanate anions to give this species or give that species. So if one of these species is bound to sulphur, the second one can reach can go for the corresponding coordination through nitrogen. So, the nitrogen coordination is also there; otherwise we do not have the corresponding bridging environment. So, this is other possibility of sulphur bounded thiocyanates to the copper centre which is soft and the copper centre in cuprous oxidation state is also soft.

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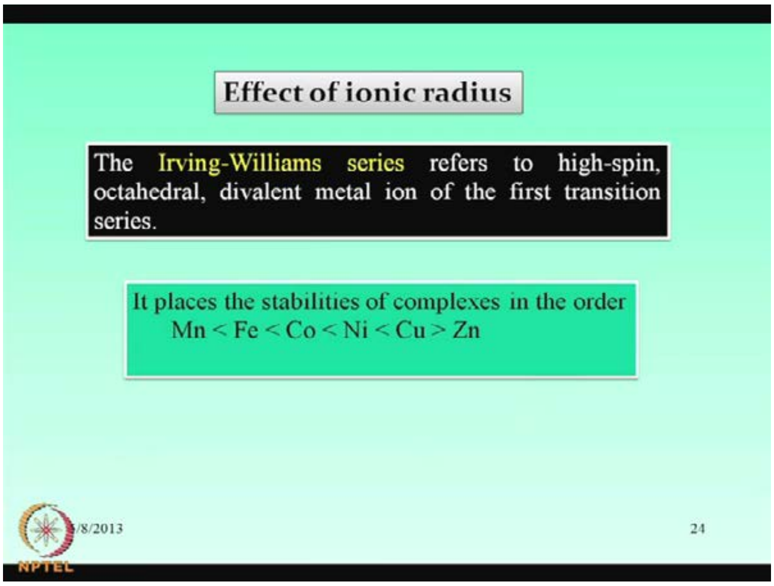

Effect of ionic radius

The **Irving-Williams series** refers to high-spin, octahedral, divalent metal ion of the first transition series.

It places the stabilities of complexes in the order
Mn < Fe < Co < Ni < Cu > Zn

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Then effect of ionic radius can be considered in a series of these metal ions which can be considered or known as Irving-William series. It refers to the high-spin octahedral, divalent metal ions of the first transition series. So, when you talk about the first transition series elements, starting from manganese to zinc, we see that for high-spin octahedral compound of these have some different type of stability order from manganese to iron to cobalt to nickel to copper; it is related to the corresponding gain in the substitution of the water molecule by the incoming ligands, as well as the corresponding crystal field stabilization energy. That we will introduce in our future classes that how we calculate the corresponding crystal field stabilization energy to correlate the corresponding stabilities of these complexes. So, CFSC values can have some role to play with the stability of these corresponding complexes.

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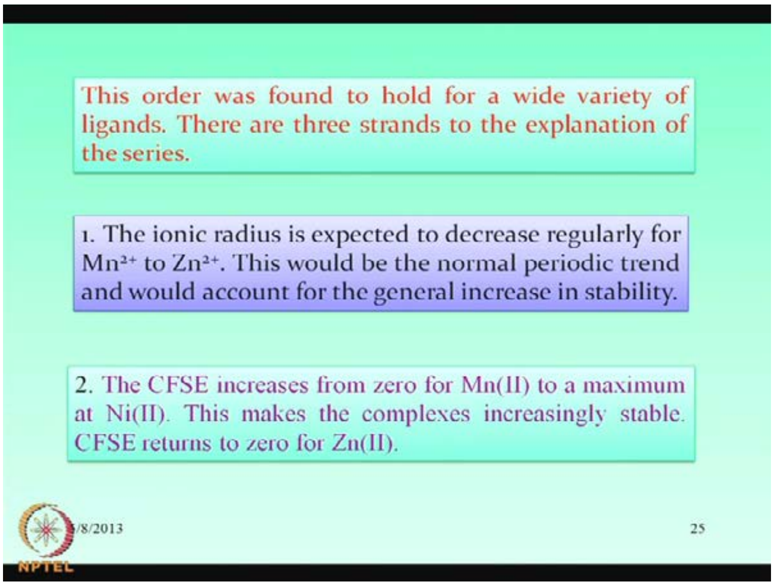

This order was found to hold for a wide variety of ligands. There are three strands to the explanation of the series.

1. The ionic radius is expected to decrease regularly for Mn^{2+} to Zn^{2+}. This would be the normal periodic trend and would account for the general increase in stability.

2. The CFSE increases from zero for Mn(II) to a maximum at Ni(II). This makes the complexes increasingly stable. CFSE returns to zero for Zn(II).

Wide variety of ligands when we are talking about, three strands of explanation in the series we can have; the ionic radius is expected to decrease regularly from manganese to zinc; that is why we get the order which is a normal periodic chain and would account for the general increase in stability of the system. This is the crystal field stabilization energy which also increases from manganese to nickel; that is why the chain goes from directly from manganese to nickel which will make the complexes increasingly stable and CFSE returns to zero for zinc. So, that is why from manganese it is rising up to nickel it is reaching and when nickel is in the maximum value and then it is dropping zero to zinc.

So, the coordination equilibria what we are studying in this class is that it has some contribution from the crystal field stabilization also in the solution state. Because the crystal field stabilization energy will also be controlling the bonding pattern, will also control the corresponding magnetic properties of all these. But in the solution, the very basic reaction when the metal is added to the ligand system, the very basic reaction, the very basic metal-ligand bond formation is also controlled by the formation of the corresponding complexes. And if we are able to find out the corresponding crystal field which is true definitely as in the solid state like that of our crystals and we can have also some stabilization like the entropy stabilization of the complexes; we can have also the corresponding crystal field stabilization.

Because we have some energy gain and that energy gain will be considered as the corresponding crystal field stabilization energy for the contribution what we see that how it is moving from manganese to the nickel. So, when you talk about the zinc, it will not have any preference. But if we compare with the other metal ions of the series, we can talk about the position of the zinc with respect to their corresponding stabilization as well as the stability.

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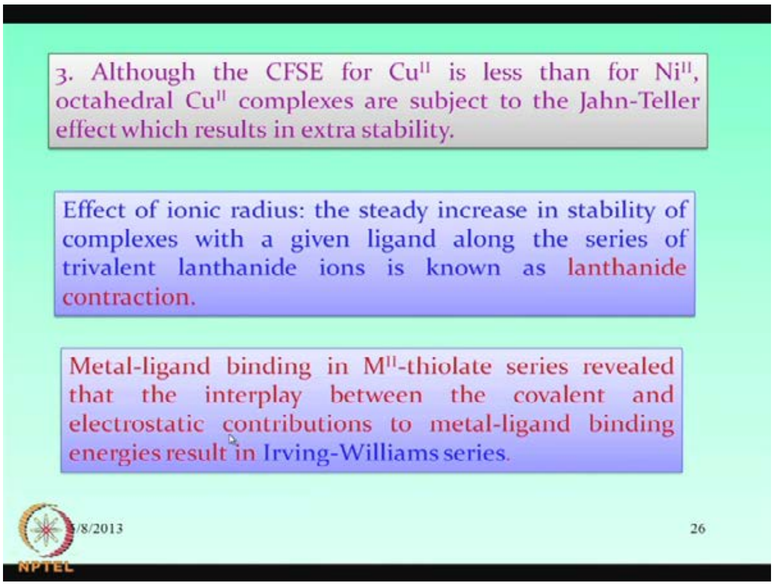

3. Although the CFSE for Cu^{II} is less than for Ni^{II}, octahedral Cu^{II} complexes are subject to the Jahn-Teller effect which results in extra stability.

Effect of ionic radius: the steady increase in stability of complexes with a given ligand along the series of trivalent lanthanide ions is known as lanthanide contraction.

Metal-ligand binding in M^{II}-thiolate series revealed that the interplay between the covalent and electrostatic contributions to metal-ligand binding energies result in Irving-Williams series.

The CFSE of copper 2 is less than that of the zinc two in the octahedral copper 2 complexes, but they all undergo Jahn-Teller distortion which results in extra stability because it will not have some preference to go for the octahedral coordination. It has low CFSE value, but due to Jahn-Teller effect it gains some extra stability to the system. The ionic radius effect is also applicable to the elements in the lanthanide series. The steady increase in the stability of the complexes with the given ligand, one particular ligand is given which is binding to the lanthanides along with the series of trivalent lanthanides is known as the corresponding lanthanide contraction as we move from one end to the other like that of the movement of manganese to zinc.

Similarly for all the lanthanide elements if we move from one side to the other, we have the corresponding lanthanide contraction. And the metal-ligand binding in the metal 2 dithiolate series also follow the corresponding this series because of the covalent and electrostatic contributions are interplaying between the metal-ligand bonding and the corresponding energies for the metal-ligand bond formation.

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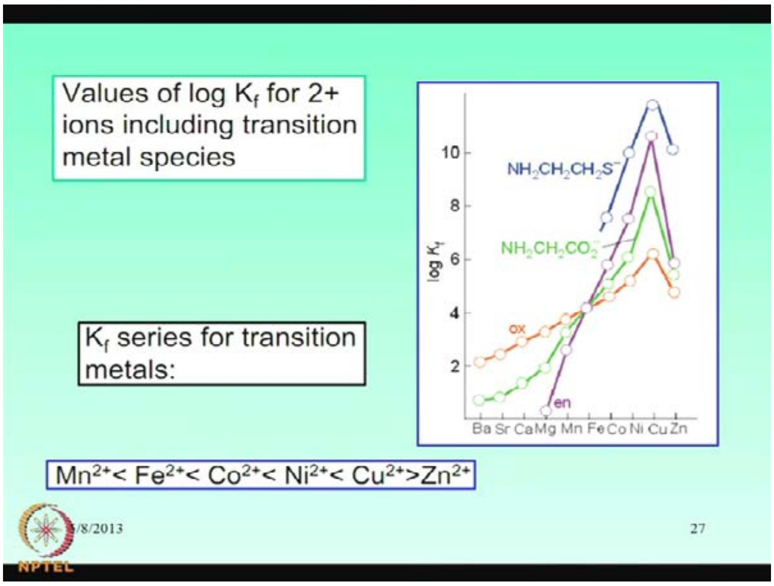

Values of log K_f for 2+ ions including transition metal species

K_f series for transition metals:

$Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$

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So, if we just simply plot the thing what we are talking for all these classes that the K values the formation constants for the different ligands like ethylenediamine, oxalic acid, glycine, and the corresponding sulphur analog for the NH 2 CH 2 S minus. So, we are just steadily increasing from manganese to corresponding nickel or copper and it is dropping basically in zinc. So, K f series for the transition metal ions are basically following the series from Mn 2 plus to iron to cobalt to nickel to copper and then it is dropping to zinc 2 plus.

So, the formation is constant. So, any ligand if we take the neutral ligand, if we take the dinegative ligand, if we take nitrogen-oxygen bearing ligand, if we take the nitrogen-sulphur bearing ligand; they follow this trend which is confirming the corresponding nature of the metal ion and the nature of the metal ion along with the CFSE will basically control this particular order; that we will see also in our future class when we will be talking about the determination of the corresponding CFSE values.

Thank you very much.