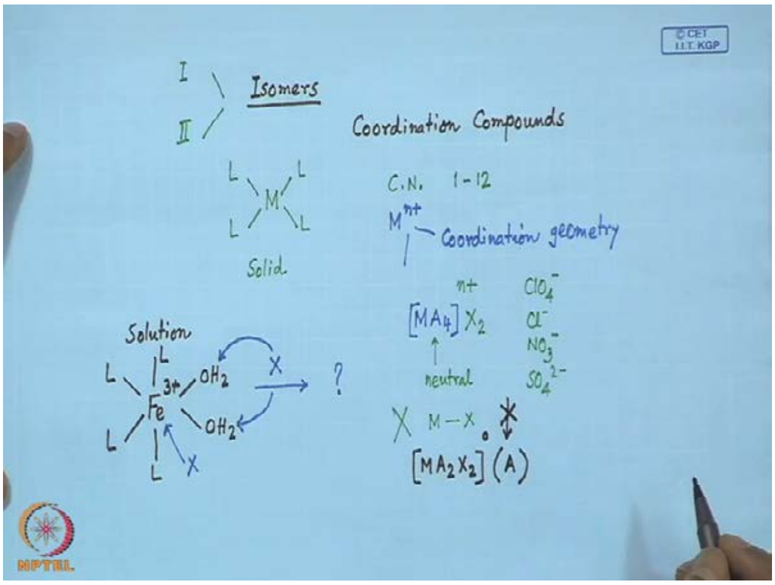
Coordination Chemistry
Prof. Debashis Ray
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 11
Isomerism – I

(Refer Slide Time: 00:28)



Good evening everybody. Today, we will start about the different isomers, what we can have while talking about the different coordination compounds. So, we can have different types of coordination compounds, and we all know now that the central part of a particular complex is the corresponding metal ion, and this particular metal ion is bound to different ligands. So, this binding by different ligands to the middle center can give rise to different types of compounds. And while talking about the different coordination numbers, starting from say 1 to 12, what we have seen that we can have different arrangements of this ligands, around the metal ion.

So, now we will see what type of arrangements we can have. If within the same chemical formula or same chemical composition, we can have different spatial positioning of the different ligand system that give rise to one particular isomer; and in a different arrangement we can have separate isomer. So, we can have isomer one and isomer two, due to the different positioning of this ligands, around the middle center.

So, we will see, first starting from the entire coordination compounds that what we know about the isomerism in coordination compounds. So, this is a very broad field, where large number of coordination compounds we are talking about. So, not only the coordination compounds, but sometimes a simple corresponding coordination, environmental coordination entity in solution.

So, this particular system, what we can have; this we can isolate in the solid state as a corresponding solid compound. But in the solution phase also we can have say, a particular middle center like iron, what is present in our blood also; that it is interacting with some donor groups which can be of biological origin also. So, one ligand is coming over here, the second ligand is coming over here; then we see that when no ligand is present around this particular ferric iron center, we can have only the water molecules; this can be L, the fourth one can also be L.

So, this when basically going to react with some other new groups say x, so how this particular x can replace this water molecule, or this x can replace the water molecule or some other new arrangement can take place where the x can directly attack the particular middle center; that we can see through the different types of arrangements around the middle center, but always we see that depending upon the metal ion, what M n plus we can have, we have the corresponding preference for a particular coordination geometry.

So, if we know the corresponding coordination geometry for a particular metal ligand system, or a particular metal ligand arrangement, then only we can talk about that, if these two positions are different; that means, occupying x by substituting these water molecules, or x can substitute anyone of these L groups, can give rise to a different product system, at least in the solution; at least this interaction can take place in the solution phase.

So, what we see that, when we have the different isomers from these coordination compounds, by definition this would all have the same formula; that means, same metal ions, same ligands and some other groups are present, but the different atom arrangement. And particularly in this case that this in case of the coordination compounds, we will be talking about the corresponding arrangement which is different for the different ligands. So, we can have constitutional or structural isomers, or stereo isomer’s, the stereo chemistry for these 2 isomers; if they are different we can have a different stereoisomer compared to the other.

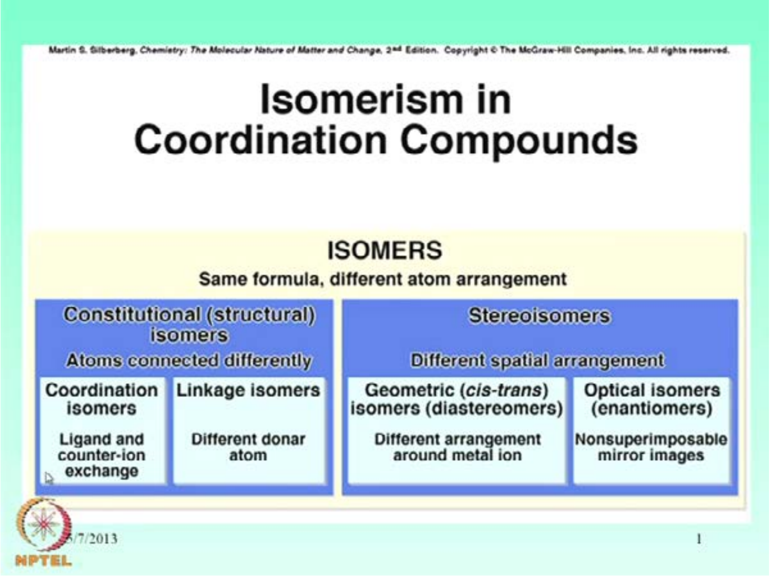
So, in the first case, when the atoms are connected differently, that means, different atom arrangement, how we can see, so we get the coordination isomers. And the coordination isomers has the very basic definition that it is related to the formation of the coordination compound itself; that when ligand and the counter-ion basically do exchange, we get the corresponding coordination isomers.

So, if we have M A 4 species, which is present over there; that means, all 4 ligands which are there can be a instead of L; that means, it can be a tetrahedral or it can be a square planar geometry. But if still these A groups are say, neutral. So, we have the corresponding cationic complex, and we need some counter anion; and, these counter anions can be say perchlorate, can be chloride, can be nitrate, can be sulphate, and all these.

So, if x is chloride or nitrate, that means, mono negative or perchlorate, then it is 2 if n is equal to 2; that means, they are present. This particular thing, that means, x is always outside the coordination sphere, and we do not have any corresponding M x bond. So, M x bond is not there; that means, n is not forming any kind of bond with the x atom; only it is forming 4 M A bonds to the ligands which are A.

Now, if we see that, if some different type of arrangement is possible; that means, M A 2 x 2, if it is possible and if a are neutral, we cannot have A outside. So, outside A is not possible. So, we will have a compound, which have the internal charge compensation, and M A 2 x 2 is forming. So, these interchange between the coordination sphere and the outside of the coordination sphere by the anions or some other groups can lead to the corresponding coordination isomers, where ligand and counter anion can exchange.

(Refer Slide Time: 09:07)



Martin S. Silberberg, *Chemistry: The Molecular Nature of Matter and Change*, 2nd Edition. Copyright © The McGraw-Hill Companies, Inc. All rights reserved.

Isomerism in Coordination Compounds

ISOMERS

Same formula, different atom arrangement

- Constitutional (structural) isomers
  - Atoms connected differently
  - Coordination isomers: Ligand and counter-ion exchange
  - Linkage isomers: Different donar atom
- Stereoisomers
  - Different spatial arrangement
  - Geometric (*cis-trans*) isomers (diastereomers): Different arrangement around metal ion
  - Optical isomers (enantiomers): Nonsuperimposable mirror images

/7/2013

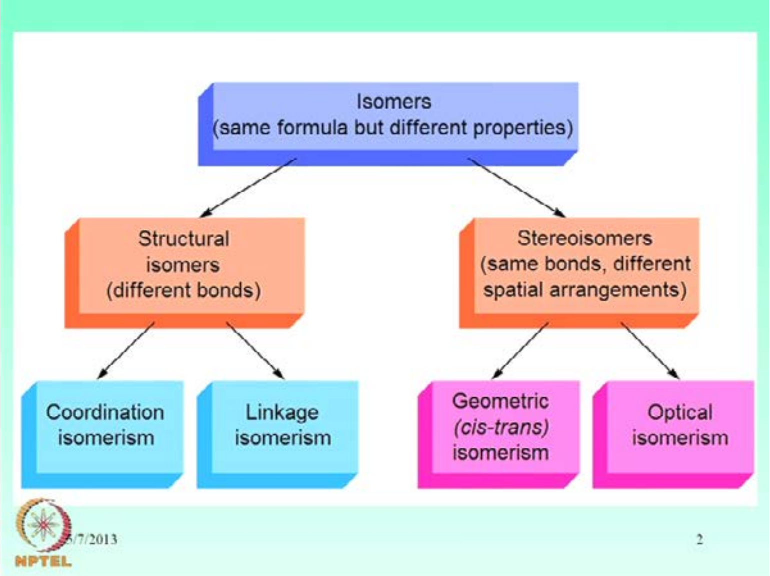
In the second case; so the constitutional or structural isomers are of 2 types: one is the coordination isomer, another is the linkage isomer. And in case of linkage isomer we have different donor atoms which are bound to the middle center.

So, at least we should have a corresponding ligand system, which is made up of more than one donor atom; it can be nitrate, it can be nitrite, it can be thiocyanates. So, when the thiocyanate is there, we know that S C N minus is the corresponding thiocyanate anion; and, that thiocyanate anion, when it can bind to the middle center through sulphur or through nitrogen. So, it can have 2 different types of linkages that give rise to the corresponding linkage isomerism.

Similarly, when the spatial arrangement, that means, the stereochemistry of the complexes are different, due to the different spatial arrangement of the metal ligand system, we get one of them as the geometric isomer and other as the optical isomer. In case of geometric isomerism, we call them as disastereo isomer’s; they do not have any relationship with optical activity; they only based on the cis-trans isomerism. And cis and trans isomerism as of we all know now that, the different arrangements of the 2 similar types of ligands or groups can gives rise to either the cis arrangement, or the trans arrangement.

So, the different arrangement around the metal ions will lead to the geometric isomerism. And in case of optical isomers we can develop the corresponding enantiomers; and these enantiomers can show different optical activity, due to the non superimposable nature of the mirror images of the complexes, that we will discuss in detail; that, how the super imposable and non superimposable cases of the mirror images of the complexes are responsible for the development of optical isomerism.

(Refer Slide Time: 11:30)



Isomers
(same formula but different properties)

Structural
isomers
(different bonds)

Stereoisomers
(same bonds, different
spatial arrangements)

Coordination
isomerism

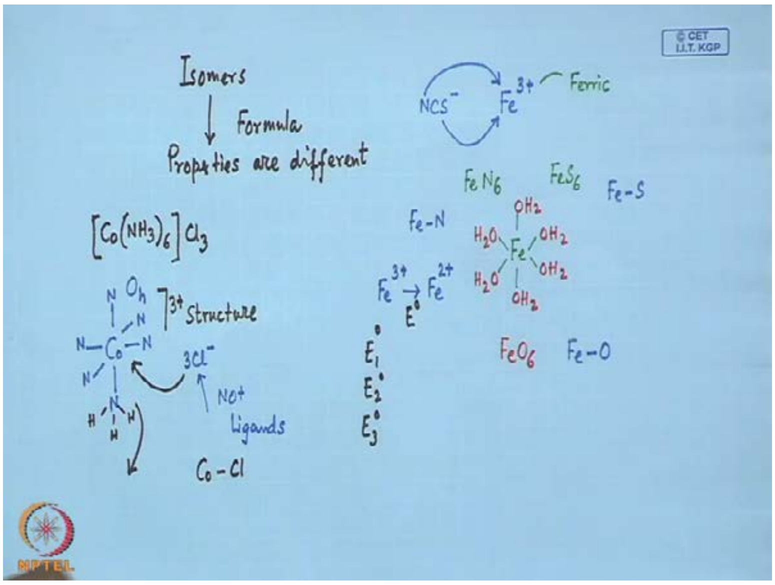
Linkage
isomerism

Geometric
(cis-trans)
isomerism

Optical
isomerism

So, basically what we see that, when we have the isomers, we can have the same formula but different properties, which is very important to know that is why we are studying the corresponding isomerism in our hand.

(Refer Slide Time: 11:48)



So, the isomers which we can have the formula is same, but the properties are different. So, that is a very important point to consider; that, if we can have this very simple coordination isomerism say that, we are talking about NCS minus. So, this anion, and we talking the corresponding binding of this with say, Fe 3 plus. So, if it is binding through sulphur to the iron center, it can have one type of property; but if it binds to the nitrogen, it can have a different type of property, because corresponding nature of this sulphur donor center and the nitrogen donor centers are too different.

So, how we just consider? So, we just consider this as, how we can consider that they can have the different properties. So, if we have the corresponding system, if they are all bound to the thiocyanate anion; in one case we had a chord and environment of Fe N 6, where all the thiocyanate groups are bound to iron through nitrogen only; and in another case we can have Fe S 6.

So, this basically is a very different type of environment, compared to the environment what we all know; when any ferric center, this is the ferric ion, this is basically the trivalent step the ferric site. And ferric site has some strong affinity to bind to the thiocyanate anion, and it will also have some preference for nitrogen coordination against sulphur coordination. So, if, theoretically we can assume that both these 2 compounds are possible to form; in one case we have a compound which is Fe N 6, in another case the compound is Fe S 6. So, these 2 cases can be delt with, compared to the starting compound where the ferric ion is dissolved in water, which is octahedrally surrounded by 6 water molecules; that means, we have Fe O 6 environment.

So, as we change the environment; that means, the bounding patterns are important and bonding patterns are getting changed. Here we can have iron sulphur bonds; if all of them are bound through sulphur then we can have 6 such iron sulphur bonds. In this particular case we have iron nitrogen bonds; and here we have iron oxygen bonds.

So, as we all know that the corresponding properties directly related to the nature of the bond. The way the oxygen is forming bond with iron is different compare to the nitrogen bonding and the sulphur bonding. So, immediately, what we can measure in the solution, we are not going to isolate the compound in the solid state, but in the solution phase we just simply can think of and can talk about, because that is a very important property for electron transfer behavior.

So, if we just can able to monitor the corresponding reduction; that means, the reduction of the ferric center to the feiras center; that means, one electron reduction if we can consider; and, if we can measure experimentally the corresponding E 0 values for the reduction, the half way potential, either through some electrochemical measurement such as polarography or cyclic voltammetry. If we are able to measure the corresponding E 0 value, then we will find that in all these cases, that means, as we change, as we move from one particular coordination environment to the other, the E 0 values are changing. So, we can have E 1 0, we can have E 2 0, or we can have E 3 0, which are very much characteristic to 3 different types of species which are forming in the solution, and the different ligand arrangement around the ferric center.

So, we have definitely a different property related to the isomeric form, because we have the different bonds for the structural isomers; and, we can have the coordination isomerism; that means, one particular ligand system is coming directly attaching to the middle center; they should have going outside the coordination sphere, that means, going to the second sphere of attraction. Similarly, for linkage also it is different, and as we have just discussed that the same bond but different spatial arrangement can lead to cis-trans isomerism or optical isomerism.

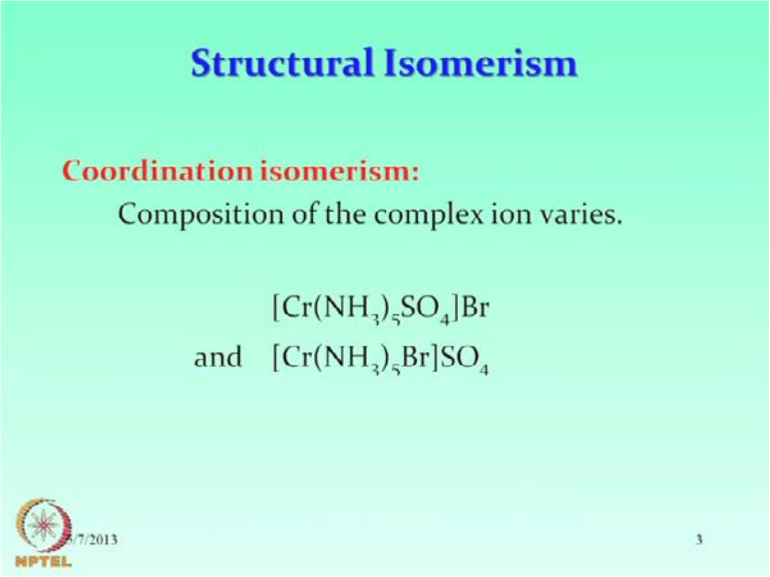
So, first we will just talk about the structures. So, the structural isomerism has a starting point that how we get the corresponding structure of the 3 dimensional molecule, which is a coordination compound.

So, if we just get the corresponding hexamine compound or cobalt, and if it is made from the corresponding chloride salt of cobalt in presence of ammonia, you get this compound. And you all know that is a very useful compound as a beautiful colored compound, which is orange red in color, and which is octahedral in geometry; that means, we have the cobalt center. And this cobalt center is connected to 6 nitrogen atoms of the ammonia molecules. So, for knowing the corresponding structure, that means, we determine the corresponding structure by, as a crystallography.

So, the determination of structure is important, because whatever we are talking about the different arrangements of these groups, we can consider that how these groups are forming, when we get this, that means, when we get this compound which is trivalent, related to the charge, what is there on the cobalt center and Cl minus. So, this Cl minus are not ligands in this particular case; and, we determine the corresponding structure when octahedral, corresponding octahedral coordination around the cobalt center is fulfilled by 6 amine molecules, and the chloride groups are outside the coordination sphere.

Now, if these amine groups which are neutral in nature, so we have this three ammonia molecules, then if one after another this Cl minus groups can enter into the coordination sphere, and these ammonia groups can go out from the coordination sphere, we can have the different arrangements where less number of cobalt nitrogen bonds will be present, and less number of ammonia molecules will be surrounding the cobalt center. And we have the corresponding chlorides which were present the coordination sphere, can come and attack to the corresponding cobalt center forming cobalt chlorine bonds. So, new cobalt chlorine bonds will be forming there, as we get one isomer to the other.

(Refer Slide Time: 20:53)



Structural Isomerism

Coordination isomerism:

Composition of the complex ion varies.

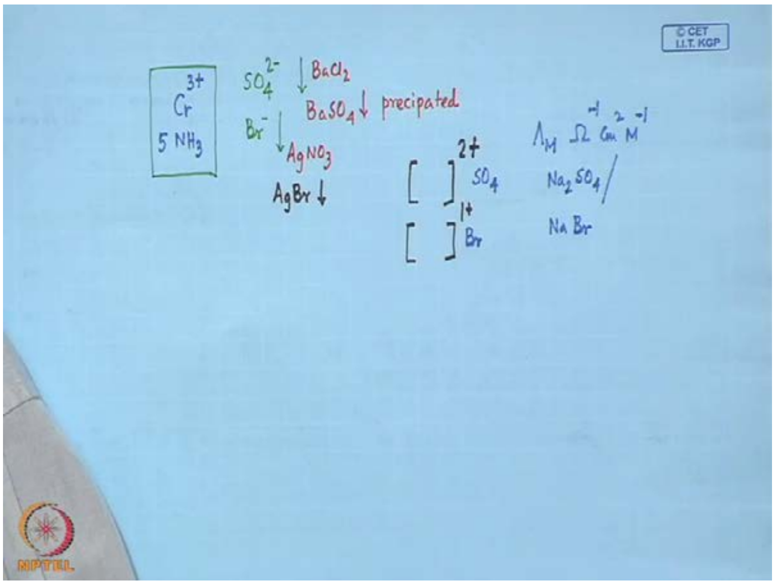
$[Cr(NH_3)_5SO_4]Br$

and $[Cr(NH_3)_5Br]SO_4$

So, this particular isomerism, starting from the coordination isomerism, is the composition of the complex ion varies, which is very important; that when the species which is entering like that of your Cl minus substituting the ammonia molecule, the basic composition of the complex ion is changed.

So, if we have the corresponding chromium compound, which is bound to 5 amine molecule and 1 sulphate and 1 bromine outside the coordination sphere, we get one particular type of compound, where chromium center is bound to 5 ammonia molecules and 1 oxygen of the sulphate group, and Br is outside the coordination sphere. But in the second case, if we can get the corresponding compound as the binding of same number of ammonia molecules, but Br is coming inside the coordination sphere and SO 4 is going out; that means, here instead of chromium oxygen bond from the sulphate, we have the chromium Br bond. And that particular thing will tell us that, the basic composition of the coordination sphere which is there; that means, the composition of the complex ion which is written in the square bracket is different. And if we just go for the corresponding analysis also, we will find that this analysis basically varies with that of the second species. So, how that analysis can vary and that analysis can give us some information related to the presence of these groups.

(Refer Slide Time: 22:41)



So, what we are not changing; that we are not changing the chromium center which is trivalent chromium, and 5 NH 3 groups. So, these are non-variant; these are fixed. So, the analysis, so for the chromium analysis and the NH 3 analysis will not be changing much. But what will be changing there is, the presence of SO 4 2 minus, and presence of Br minus, within the coordination sphere or outside the coordination sphere.

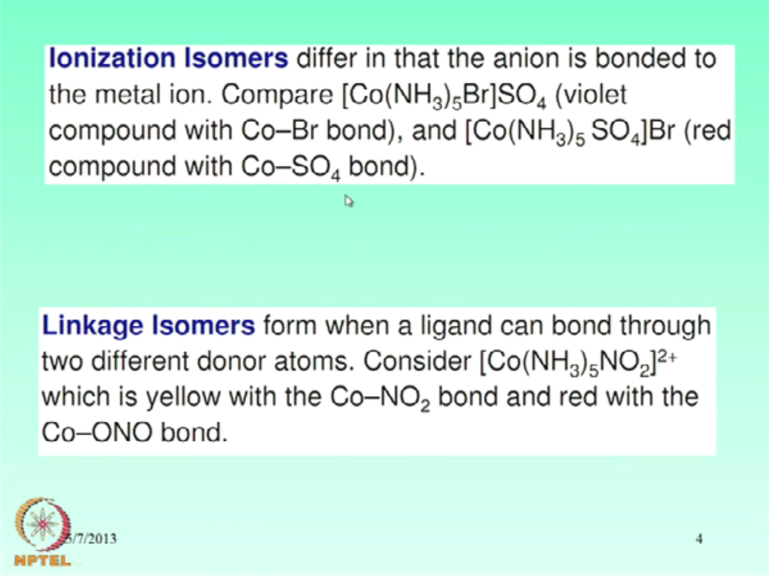
So, if they are outside the coordination sphere that can be very easily identified; if these are present outside the coordination sphere, so that will just simply behave as sodium sulphate as the ionic salt, so is the complex salt of sulphate. And if we add barium chloride, barium sulphate will be precipitated, which is not possible when Br minus is outside the coordination sphere; that means, sulphate is inside binding to the chromium center, in that particular case barium sulphate will not be precipitated.

So, if Br minus is present in the outside coordination sphere, and if we just simply add silver nitrate to the medium, we will be able to see, we will be able to detect the corresponding separation of silver bromide from the medium, which immediately established that Br minus is present as outside the coordination sphere, and which can be separated by addition of silver nitrate like that of the sodium bromide reaction with silver nitrate. And another physical characterization for this compound would be such that when Br is present inside, we have the overall charge on the complex is 2 plus; that means, Br is utilizing that 3 plus charge and the chromium center; but when sulphate is present inside we have a charge of 1 plus. So, that is why, when Br is inside, we have the corresponding sulphate salt, I mean, sulphate is inside we have the Br salt.

So, these 2 are very much can be identified by measuring the corresponding solution electrical conductivity, which is determined in terms of ohm inverse centimeter square, and mole inverse. So, this particular we saw a different type of electrolyte behavior, like that of our, which is equivalent to that of our Na 2 SO 4, or other bivalent cationic salt of sulphate; and this will behave as sodium bromide.

So, solution electrical conductivity can also differentiate; and other physical properties related to that of the presence of this sodium sulphate type of salt, or sodium bromide type of salt, can distinguish these 2 compounds nicely. So, we can establish that some coordination isomerism can take place over there, though the entire composition of the salts would be same.

(Refer Slide Time: 26:37)



Ionization Isomers differ in that the anion is bonded to the metal ion. Compare $[Co(NH_3)_5Br]SO_4$ (violet compound with Co–Br bond), and $[Co(NH_3)_5 SO_4]Br$ (red compound with Co–SO_4 bond).

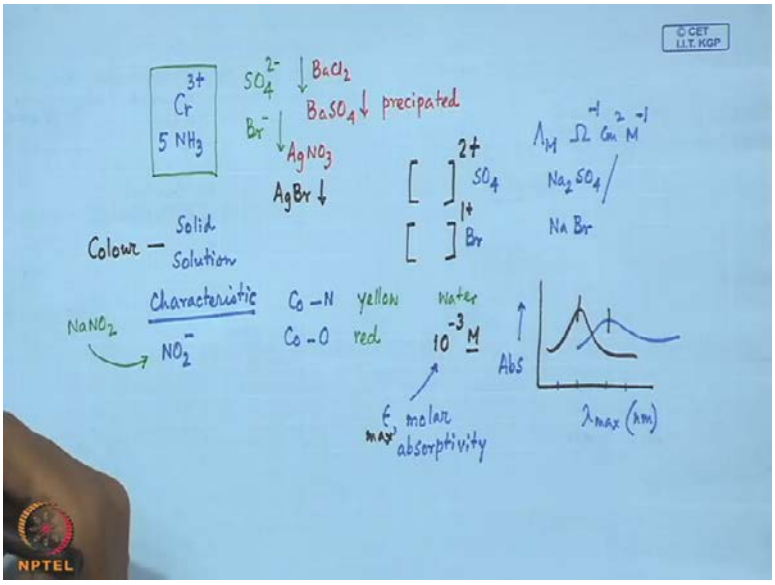
Linkage Isomers form when a ligand can bond through two different donor atoms. Consider $[Co(NH_3)_5NO_2]^{2+}$ which is yellow with the Co–NO_2 bond and red with the Co–ONO bond.

5/7/2013

So, ionization isomers are also possible, and which are differ in that the anion is bonded to the metal ion. Compare to this Co NH 3 in the another example, where cobalt is taken with 5 ammonia molecules and 1 Br, and sulphate which is violet in color with a cobalt bromine bond. But the second compound, where sulphate is inside the coordination sphere, the compound color is red, where we have the cobalt sulphate bond; that means, cobalt oxygen of the sulphate group. So, this particular case; that means, outside the coordination sphere and inside the coordination sphere can give rise to the corresponding ionization isomers.

But the second category of this type of isomerism, we can have for the linkage isomers, when the ligand can form bond through 2 different donor atoms. That means, if this donor atom we are considering; that means, the binding of the nitride group, the binding of the nitrite group if we can monitor to a corresponding compound, which is similar to that of the formation of hexamine cobalt 3 chloride. So, when nitrite is bound to the cobalt center, and we get the corresponding binding through this particular nitrogen atom; that means the cobalt nitrogen bond is forming, and the color of the compound will be yellow. But if the bond is taking place through oxygen of the nitrite group, we get a different colored compound which is red in color.

(Refer Slide Time: 28:23)



So, color is very much important; that means, the color of the compound in the solid state as well as in the solution. So, both, in the solid state as well as in solution, is very much characteristic for the identification of the nature of the compound what we can have.

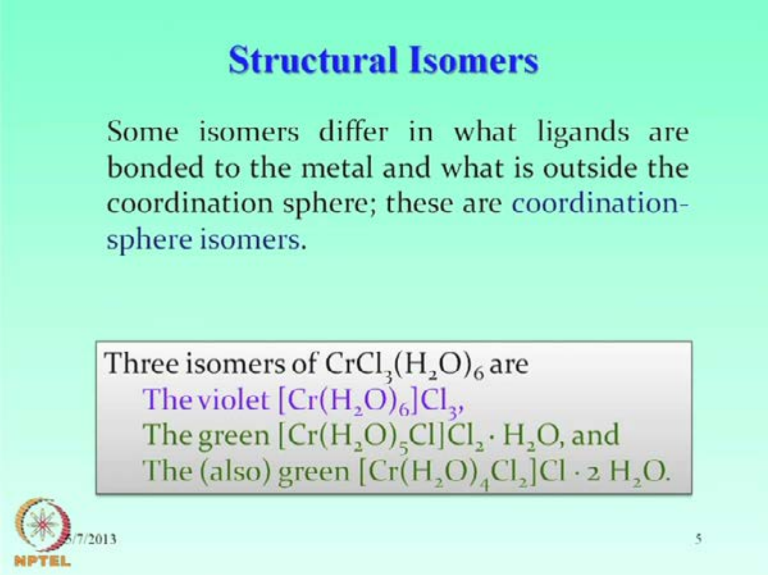
So, if we are just talking about some linkage isomer, where we have the cobalt nitrogen bond, or in other case we have the cobalt oxygen bond, for the binding of the nitrite ion. Because the nitrite binding is also very easy to monitor and easy to see, because the corresponding salt we can use for the nitrite coordination is simple sodium nitrite, which is available in the solid state, and which is highly soluble in water; and, addition of these can give rise to 2 different types of species, where nitride group can function as a very good ligand.

So, when it is binding through the nitrogen atom, it have a color of yellow; when it is binding through oxygen, it can have a color of red. So, these compounds are mostly also soluble in water. So, if we can have the corresponding solution in water, and if we are able to make a solution of say 10 to the power minus 3 molar; that means, a millimolar solution if we can make out of these compounds in a volume of solution, then we can monitor the corresponding electronic absorption; that we will talk in detail afterwards when we will be talking about the spectroscopy of these compounds. But initially, if we can just see that, these 2 compounds will have the different absorption bands: one for the yellow compound, and another for the red compound.

So, these, the nature of these curves will also be different; and this is the corresponding skill in nanometer; that means, the wavelength which is lambda max in nanometer; and this is the corresponding absorbance, and when this absorbance is known and we know the corresponding concentration, one particular property we can dictate there; and we can report that particular property is the corresponding epsilon, the molar absorptivity, the molar absorptivity we can monitor. So, these particular 2 compounds, even in the solution we can say the corresponding 2 characteristic values: one is the corresponding epsilon value, and the corresponding lambda max value. So, whenever you report this particular lambda max, for one particular compound, and another lambda max for the other compound, we will also report the corresponding epsilon max; that means, the corresponding molar absorptivity at this particular wavelength; and with the second case also, the corresponding epsilon value at this particular maximum absorption value.

So, these 2 values can definitely characterize, whether we have a compound which is nitrogen bound, or the compound which is bound through oxygen. So, these 2 things can be identified. So, the spectroscopic technique; that means, the measuring the corresponding electronic absorption spectra can find out, can give us the information's to ask that whether we have a nitrogen bond isomer or a oxygen bond isomer, in our hand.

(Refer Slide Time: 32:45)



Structural Isomers

Some isomers differ in what ligands are bonded to the metal and what is outside the coordination sphere; these are coordination-sphere isomers.

Three isomers of $CrCl_3(H_2O)_6$ are
The violet $[Cr(H_2O)_6]Cl_3$,
The green $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, and
The (also) green $[Cr(H_2O)_4Cl_2]Cl \cdot 2\ H_2O$.

/7/2013

Then, further structural isomers what we can see that, when we have some isomers differ in what ligands are bonded to the metal, and what is outside the coordination sphere, these are therefore, coordination isomers. What we are talking about so far is that, how we are changing the corresponding coordination sphere. So, if they are interchanging between the outside and the inside of the coordination sphere, and the same two groups, that means, A is interchanged with B, and B is interchanged with A, we get a coordination sphere isomer from that particular arrangement.

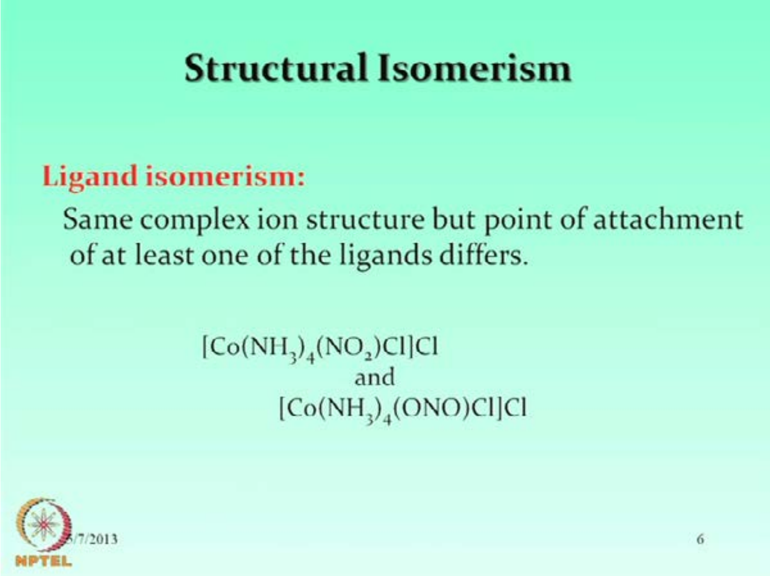
So, one further example we can have is, the 3 isomers of chromium chloride which is bond with 6 water molecules; that means, if we have a salt of chromium chloride with 6 molecules of hydration. So, 6 water molecules of hydration are present in chromic chloride salt, but these salts can have the different nature, depending upon the number of species, that means, number of chloride groups inside and outside the coordination sphere.

So, in the first case, the color of the compound is violet, when we have only the hexaaquachromium 3 species; that means, all 6 water molecules are bond to the chromium center, and chloride groups are outside the coordination sphere, we can measure the corresponding conductivity as one particular type of electrolyte, 1 is to 3 electrolyte type. And we can precipitate out all the 3 chloride anions by reacting with silver nitrate.

But in the second case, we basically see that one of the water molecule is going out from the coordination sphere, which is going from inside to outside, and it is crystallizing at the corresponding water of crystallization for the crystal ion material; and one chloride anion is therefore, going inside the coordination sphere and binding to the chromium center. Similarly, we can have the possibility for second chloride groups go and bind to the chromium center, and that gives rise to another formation. But the water content again is going from here; that means two of the water molecules will be crystallized at 2 water of crystallization.

So, luckily, we can have the same composition for the very simple salt which is chromic chloride hexahydrate. So, the salt itself, what we know that the chromium chloride compound which is present in the reagent bottle in the laboratory, what we see that, that particular compound can present as 3 different isomers which are can be considered, which can be considered as the corresponding coordination sphere isomers. So, one is violet in color, another is green in color, and third is also green in color; and we can have the three different isomers.

(Refer Slide Time: 35:58)



Structural Isomerism

Ligand isomerism:

Same complex ion structure but point of attachment of at least one of the ligands differs.

$[Co(NH_3)_4(NO_2)Cl]Cl$

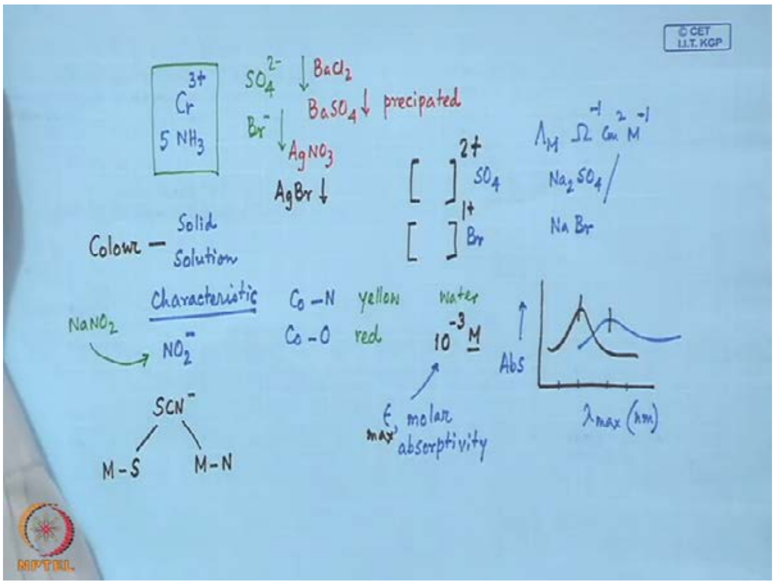
and

$[Co(NH_3)_4(ONO)Cl]Cl$

5/7/2013

So, the next case what we can see is the ligand isomerism; how the same complex we can have the structure, but the point of attachment of atleast one of the ligands is different. If it differs for the connectivity like that of our nitrate and nitrite binding, we get the corresponding ligand isomerism due to the different binding.

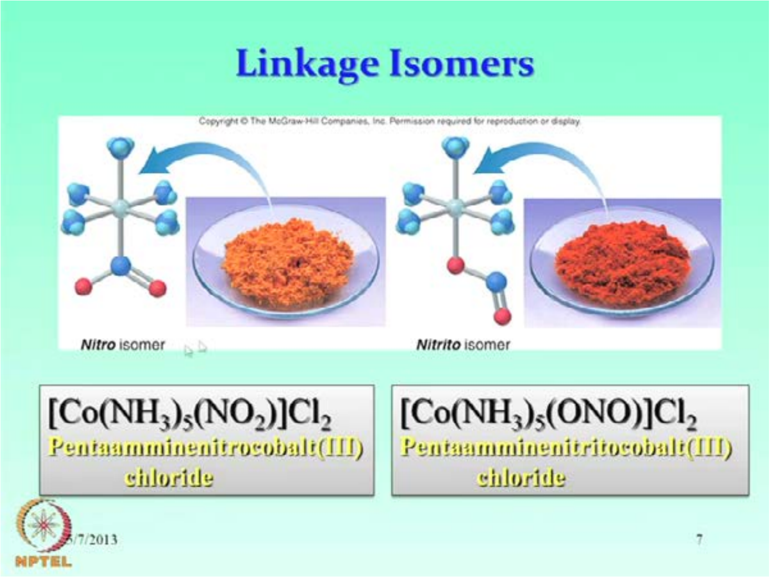
(Refer Slide Time: 36:34)



So, in one case if we have the nitrogen binding, and in another case if we have oxygen binding, we can have 2 different compounds; like that of thiocyanate anion, we can have the corresponding metal sulphur bond if it is attaching through sulphur, and metal nitrogen bond if it is attaching through nitrogen.

So, that basically gives us the example for the corresponding binding for the NO 2 as through nitrogen and through oxygen. And the number of chloride groups attached to the cobalt center are all same; that means, one chloride is inside the coordination sphere and another chloride outside the corresponding coordination sphere, and that will not interchange due to the change of this type of linkage isomerism. It is the isomerism where the binding of this particular cobalt for atleast one ligand system; that means, the different attachment for atleast one type of the ligand which is present in the coordination sphere.

(Refer Slide Time: 37:40)



Linkage Isomers

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

$[Co(NH_3)_5(NO_2)]Cl_2$
Pentaamminenitrocobalt(III) chloride

$[Co(NH_3)_5(ONO)]Cl_2$
Pentaamminenitritocobalt(III) chloride

/7/2013 7

So, that basically giving the different linkage isomerism, and we can have the 2 isomers: one, when it is bond through nitrogen we call it as a nitro isomer, and which is little bit yellowish red in color, which is light red in color; and the second one which is bond through this oxygen of the nitrite group, is the corresponding nitrito isomer.

So, the change in the color of these 2 species, basically also tells us at the same time that the corresponding electronic spectra is getting changed, when we have the cobalt center which is forming with all the corresponding, donor groups are all nitrogen. 5 are coming from the NH 3 groups, these are the NH 3 groups; and one is coming from the NO 2; that means, the coordination sphere is basically Co NH 6; that means, all nitrogen 5 of one type and one of different is using the pentaamminenitrocobalt 3 chloride compound. But in the second case which is having the corresponding binding through oxygen of the NO 2 group which is pentaamminenitrito, the nitrito isomer, pentaamminenitritocobalt 3 chloride.

So, we can just simply level, because of the presence of these 2 different types of attachment of the NO 2 group, we get one as the nitro isomer and another as the nitrito isomer. So, that we can just simply level as the corresponding binding position of one isomer to that of the other; and that basically change the color and some other properties; that means, if we just talk about when we will talk at the solution equilibria; and the reaction mechanisms for this change and for this transitions we will find that one particular group will be strongly bond to the cobalt center compared to the other. So, one isomer will be very readily can be substituted by some other incoming group compared to the other species.

(Refer Slide Time: 39:57)

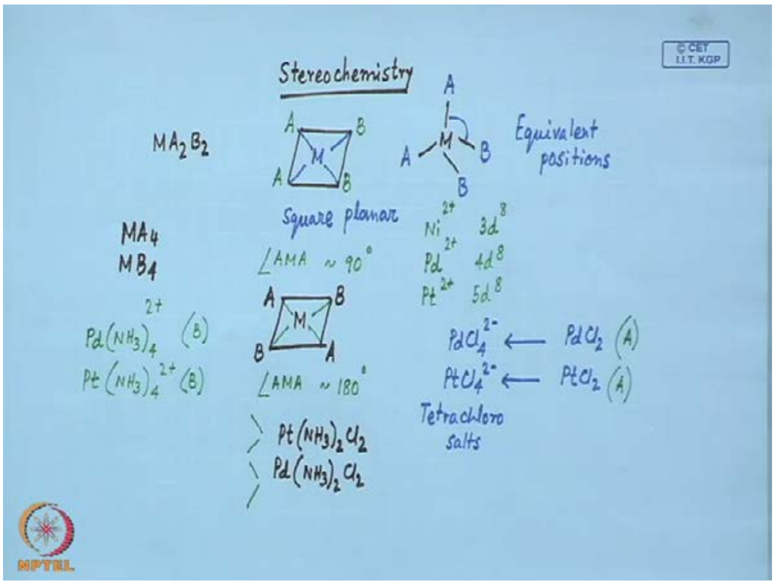
Stereoisomerism 1

- Geometric isomerism (cis-trans):
- Atoms or groups arranged differently spatially relative to metal ion
    - $Pt(NH_3)_2Cl_2$

/7/2013

Then, we will just talk about the corresponding stereoisomerism; that means, how specially, how the stereochemistry can play some important role for the different type of arrangements.

(Refer Slide Time: 40:10)



So, the spatial arrangement, which can be considered as the stereo chemical arrangement; and, just what we have seen that if we can have MA 2 B 2 type compound, that means, 2 of these ligands are of same number; and we just talk about the corresponding geometry as, one as the square planer another as the tetrahedral.

So, if we have a tetrahedral geometry like 2 A and 2 B, and if we interchange these 2 positions we will get the same isomeric form, because all the tetrahedral positions are equivalent. So, we have the equivalent positions. So, we cannot get 2 different types of arrangement, because we have the corresponding ligand metal ligand angle which is close to the tetrahedral angle, and that particular tetrahedral angle will tell that all of them are equivalent to each other, and we cannot have the different type of arrangement.

But specially, if we can arrange in a different way in a square planar geometry, if the geometry is square planar, we get one arrangement as the 4 groups in the plane, where these 2 A groups are on the one side, and B groups are on the other side, and we have an angle of A M A, close to 90 degree, we will have one particular isomeric arrangement. And definitely if we can have a other type of arrangement, where M is there and we interchange the positions of this A and B, now if we put A, 2 A groups diagonally opposite, and 2 B groups also diagonally opposite, and in that particular case we get a corresponding A M A angle which is the characterizing value for these 2 groups, it is close to 180 degree.

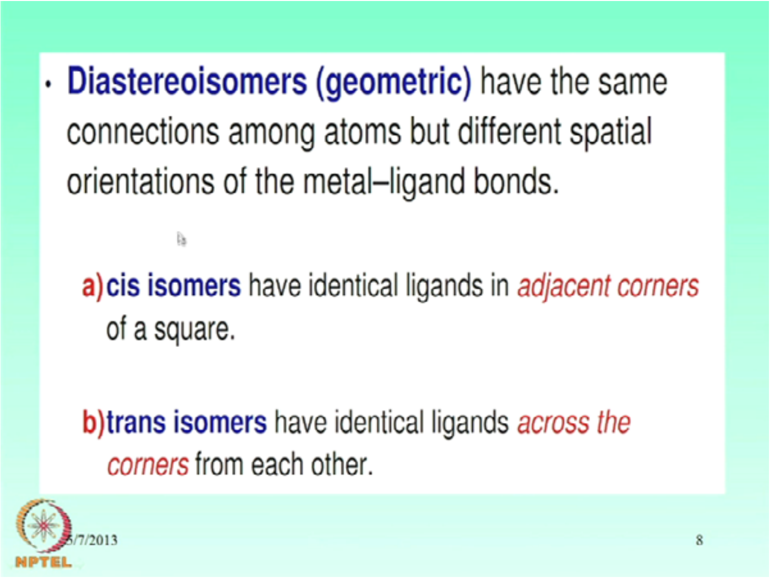
So, this particular spatial arrangements, for these 2 types, basically can give rise to 2 different isomeric arrangements. So, this particular arrangement is very important and very useful to know also, because we can have large number of such compounds which can be prepared from say, palladium or corresponding platinum salts as well as nickel salts. Because these are giving 2 plus oxidation states, 3 d 8 species, 4 d 8 species, and 5 d 8 species. So, initially there we can have the corresponding p d Cl 4 2 minus compound, which can be prepared from simple palladium chloride like nickel chloride. Similarly, we can have tetrachloroplatinate salt from platinum chloride. So, these are the 2 different types of tetrachloro anionic salts.

So, when these salts are there, and the other side also we can just think of that these can also give rise to the corresponding complexes, if we change these by say, other type of ligand. Because this is of one type say A type of ligand, this is also all A. Now, if we introduce B as the corresponding ammonia compound, corresponding ammonia as the ligand. So, if we have or platinum, that means, we are only having B. So, these compounds, so either starting from palladium chloride or platinum chloride to tetrachloroplatinate or palladate, or the corresponding compound with that of our ammonia molecule, we get the corresponding compound as the corresponding simple M A 4 and M B 4 compound. And if some synthetic procedure we can have, such that we can go from this particular species to some intermediate formation of these M A 2, B 2 type of compound; such that we have for platinum we can have M A 2 or M B 2 and then A 2 is the corresponding Cl 2 compound.

Similarly, we can have for the palladium also. So, these are all M A 2 and B 2 type of compound; and therefore, we can have 2 different types of isomeric form one same type of ligands form in 90 degree angle, and in another case same type of ligands can form 180 angle. So, we can have 2 different types of isomers, which are known as the corresponding geometric isomers.

So, in one case, we will be talking this as the cis isomer, in another case we will be talking this as the trans isomer; when the angle is 90 degree we call them as this isomer, and when the angle is 180 degree we call them as the trans isomer. So, this is the example where we have 2 NH 3 groups are attached to the platinum center and 2 chloride groups as the second ligand.

(Refer Slide Time: 47:46)



- **Diastereoisomers (geometric)** have the same connections among atoms but different spatial orientations of the metal–ligand bonds.

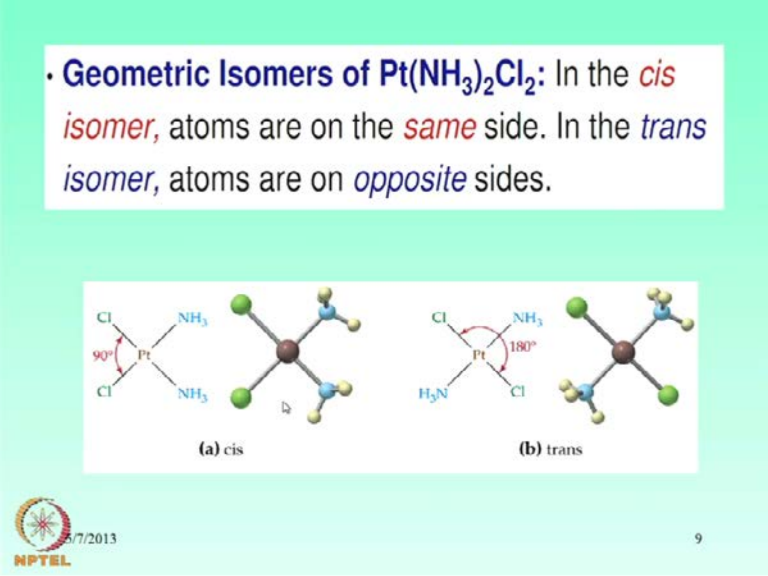
  a) **cis isomers** have identical ligands in *adjacent corners* of a square.

  b) **trans isomers** have identical ligands *across the corners* from each other.

So, we will be generating from cis isomers and trans isomers, we will call them as diastereoisomers. So, these are very important types of molecules. In coordination chemistry we get some compounds as diastereoisomers, that means, they are not related to any kind of optical activity, at the same connections among atoms; that means, among atoms means, that means, the middle atom and the ligand atom. But different spatial orientations related to the metal ligand bonds. Only the metal ligand bonds are different. In case of cis isomers, we have identical ligands in adjacent corners of a square.

So, if we have a particular square arrangement, and adjacent corners not diagonally opposite. Adjacent corners will take off 2 similar ligands or same ligands or identical ligands, then we will be use this particular isomer as the cis isomer. Similarly, in case of trans isomer, the same ligand or the identical ligand will be there, which are diagonally opposite to each other; that means, they are present across the corners from each other. So, when they are diagonally opposite to each other, we will be calling these as the corresponding trans isomer. So, the arrangement is very simple; that means, we can have the 2 one type of compound; that means, one type of ligand; that means, amine ligand or the Cl ligand.

(Refer Slide Time: 49:23)



- **Geometric Isomers of $Pt(NH_3)_2Cl_2$:** In the *cis isomer,* atoms are on the *same* side. In the *trans isomer,* atoms are on *opposite* sides.

(a) cis

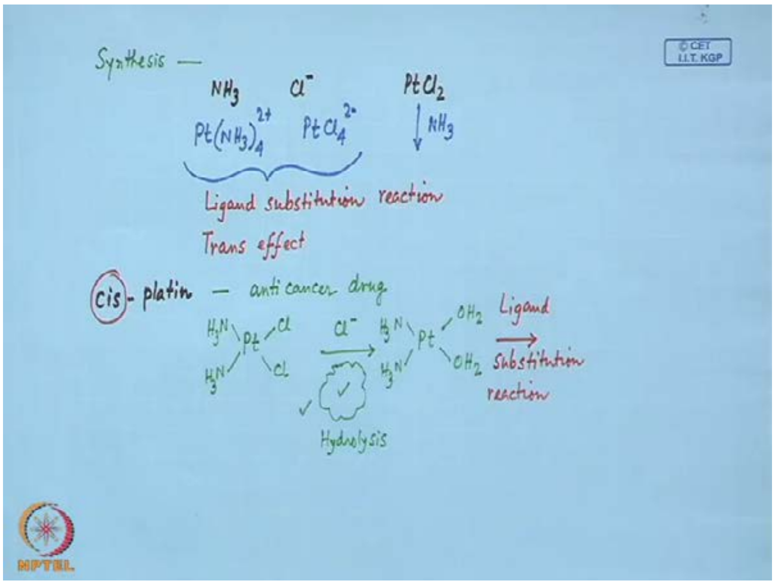
(b) trans

5/7/2013

And in case of cis isomer, the atoms are on the same side; and in case of trans isomer, atoms are on opposite sides. So, this is the case, what we are just seen that, in case of platinum in cis compound, this Cl Pt Cl bond angle is around 90 degree which is this particular one; in another case this particular one is that we have the Cl Pt Cl bond which is 180 degree.

So, these 2 compounds, the composition wise they are all same. But the synthesis of these 2 compounds; that means, the synthesis, we will discuss, separately we will discuss about the synthesis.

(Refer Slide Time: 50:15)



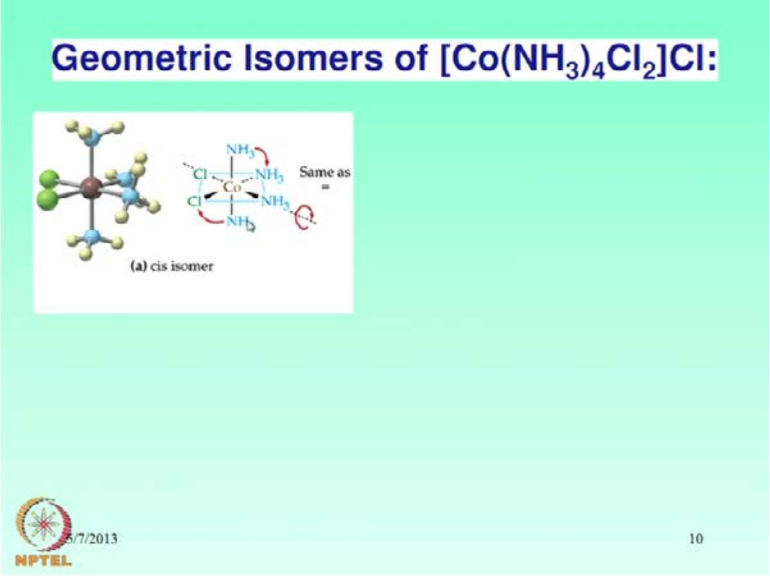
So, synthesis of these 2 compounds should be definitely a challenge for us, because we will be playing with 2 different types of ligand: one is the corresponding NH 3 group, another is the Cl minus. And the thing is that we are starting compound for these 2 as the corresponding chloride salt; that means, the platinum chloride salt we are taking; and we are trying to put this particular ligand. So, whether this particular metal salt can give rise to the reaction with ammonia, or we can have the corresponding 2 compounds of A 4 and B 4 type; that means, that Pt NH 3 whole 4 2 plus, or Pt Cl 4 2 minus, we encounter some kind of corresponding ligands substitution reaction.

So, we will talk in solution chemistry for this as the ligand substitution reaction; and we will see something where the corresponding effect will be consider as the corresponding trans effect. That means, the ligand substitution reaction would be controlled by the corresponding trans labilizing effect of one particular group. If the trans labilizing effect of NH 3 is greater than Cl, then ammonia will labilize the corresponding trans amine group for the entry of the Cl group; and the same is also true, if Cl has more trans labilizing power than NH 3, it will labilize the corresponding trans position for the corresponding substitution. Because this particular molecule which is known as cis-platin is a very useful anticancer drug; and, in that particular case only cis is useful as an anticancer drug, because the positioning of these 2 cis groups around the platinum is important ; that means, in presence of say Cl minus which is there in plenty. That means, the concentration of Cl minus is the deciding factor, when in our body particular a person who is suffering from cancer, is that if we have the corresponding cell; and the cell can have 2 different types of chloride concentration: one is inside the cell, and another is the outside the cell.

So, if there is some concentration difference for that, and if we can go for the corresponding hydrolysis of this particular compound; that means, this particular compound can go for the corresponding hydrolysis. So, this is the hydrolysis reaction. And these hydrolysis can go for some reactions which is dependent on the chloride concentration; when the chloride concentration is less it can go for the corresponding hydrolysis for this, and then it can go for ligand substitution reaction. So, that is the basic activity for this anticancer drug of this only this isomer, which is the corresponding cis isomer. So, it can go and bind for the corresponding nucleo bases, because this platinum water molecule is very labile; and this platinum water bond is very much labile for that and it can go for the ligand substitution reactions with that of the DNA bases can take place from there.

So, these 2 compounds are, therefore, very much useful, when we see that the cis isomer can have different in terms of the corresponding anticancer activity of the cis molecule, where the trans isomer is inactive. Because it has 2 position which are diagonally opposite to each other; and if there is any kind of hydrolysis, it cannot function as a clip; these 2, the 90 degree apart it can function by binding 2 adjacent basis in the DNA molecule.

(Refer Slide Time: 55:55)



Geometric Isomers of $[Co(NH_3)_4Cl_2]Cl$:

(a) cis isomer

5/7/2013

So, what we see, therefore, that in case of octahedral compound, that starting from this square planar compound, if we just go for the corresponding octahedral compound, we will get the corresponding compound as, the corresponding symmetry for this where we have the cis isomer.

So, now, we simply see that this particular cis isomer is little bit different from that of the square planar arrangement, where we just considered this particular square plane, where by definition what we are defining for the platinum compound, that the chlorine, metal chlorine bond should be 90 degree. The same is also true for the octahedral compound where we find that the chlorine cobalt chlorine bond, in this particular octahedral compound, where we have 4 ammonia ligand as well as 2 chloride ligand.

So, chlorine cobalt chlorine bond is 90 degree. So, this particular compound we will be talking as the corresponding cis isomer, due to the position of the 2 chloride groups related to the octahedral cobalt center. So that we will see, how this particular geometric arrangement is possible, which is different from the other arrangement also.

Thank you very much.