Advanced Transition Metal Chemistry – Inorganic Reaction Mechanisms

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Lecture – 50
Substitution Reactions in Octahedral Complexes; Stereochemistry of Products

Hello everyone. Once again, I shall welcome you all to MSB lecture series on transition metal chemistry. This is 50th lecture in the series, only 10 more are left. In my previous lecture at the end started discussion about the stereochemical consequences of substitution reaction and how even Werner contributed for understanding of the different isomers that can be formed if we consider optical isomers or geometrical isomers.

And once after substitution is over whether we can get cis compound, cis gives cis or trans or we get a mixture of isomers or what would happen, if we consider optical isomers, all these were studied based on cobalt(III) complexes because cobalt(III) complexes as I mentioned they undergo substitution reactions very slowly. As a result, with simple devices, one can measure rate constant, in that context cobalt(III) complexes and their chemistry look to be very vital in understanding reaction mechanism.

Still, we use the same data started during Werner's time to explain substitution reactions in square planar complexes, although, lot of people have contributed much later. So, now let us continue from where I had stopped. I was discussing about how important it is to see the entering ligand and the leaving ligand positions and what direction entering ligand you set in the second coordination sphere to come to the first coordination sphere during substitution reaction.

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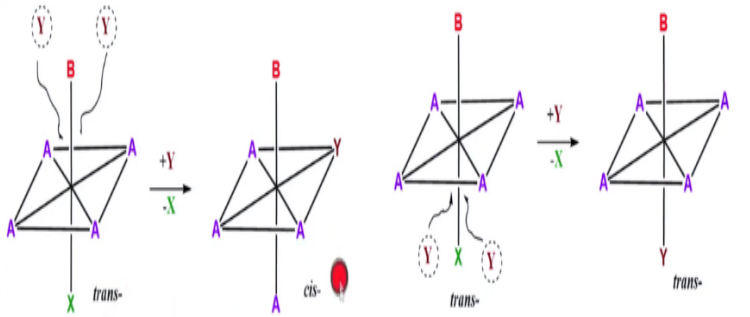

Substitution where the entering group Y in the second coordination sphere is opposite to the leaving group X.

Substitution where the entering group Y in the second coordination sphere is adjacent to the leaving group X.

Let us consider these two cases here. I have considered a trans compound here, in the plane we have 4 ligands A and we have X, X is the leaving, so in all cases in future X denoted ligand is the leaving ligand and then B will define the isomer's conformation, so now this is a trans compound. So, now when we start substitution reaction in the second coordination sphere Y has an option of entering in a position opposite to the leaving group, in that case what happens, simply it comes here.

Once when it enters either here or here what happens, one of the A groups would occupy the position vacated by X and then the cis compound would result. You can see here, it can go any of this, then you will be having a cis relationship between B and Y, hence it is called cis compound. The trans compound would give cis compound, if the entering group is in the opposite side of leaving group.

On the other hand, let us consider the same trans compound and if the entering ligand is in the same position or very near by the leaving group in that case what happens, there is no net change in the conformation, a trans compound would give a trans component. So, that means substitution where the entering group Y in the second coordination sphere is opposite to the leaving group, trans would give cis.

On the other hand, substitution, where the entering group Y in the second coordination sphere is adjacent to the leaving group, then trans compound would give a trans compound. So, this kind of analysis seems okay for reactions that yield primarily only one isomer. If there are no

preferred orientation of the entering group in the second coordination sphere, would give a mixture of isomers.

If it has a preferential orientation, that may be governed by sometimes the type of ligands we have in the surrounding and also the type of ligand coming, and also the bulkiness and steric and all those things matters. So, in that case, what happens we would get a mixture of isomers. Werner during that time concluded that as there is no way to predict the orientation of the entering group in the second sphere, it is not possible to anticipate the stereochemical change that would take place during substitution, this was his conclusion.

However, with modern spectroscopic and spectrophotometric evidences and also analytical instruments many we have at our disposal, so prediction of stereochemical changes may not be very difficult. In homogeneous catalysis, of course, you must be knowing people use directing groups and these directing groups play a major role in generating or synthesizing organic compounds or performing desired organic transformations.

So now keeping in mind that an octahedral complex have an option of forming the product via dissociative pathway S_N^1 mechanism or displacement pathway S_N^2 mechanism also known as associative pathway.

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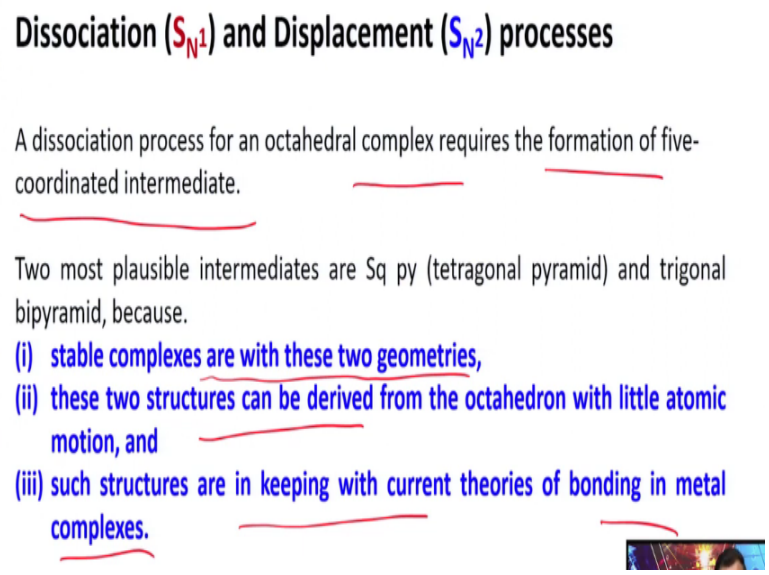

So, that means dissociative process for an octahedral complex requires the formation of five coordinated intermediate, we should remember. The ligand goes, what happens, now we will be left with 5 ligands. When you have 5 ligands it can assume one of the two well-known

geometries that is square pyramidal geometry or tetragonal pyramid, and other one is more common one, trigonal bipyramidal geometry.

Why when coordination number 5 is there, all complexes in the intermediate have preference for these two geometries is, stable complexes are known with these two geometries and we have plenty of complexes among coordination compounds having both square pyramidal geometry, in some cases and also trigonal bipyramidal geometries. So, that means the most preferred geometries are square pyramidal or tetragonal pyramid, and trigonal pyramidal geometries.

So, these two structures can be derived from the octahedron with little atomic motion that is another important aspect. When we derive another geometry from the existing geometry, we have to do movement of atoms or ligands with octahedral going to square pyramidal or trigonal bipyramidal, with little atomic motion we can generate these two low coordination geometries and also such structures are in keeping with current theories of bonding in metal complexes.

And further we also have evidence through experiments that these two are the preferred geometries and also even the stereochemical consequences and after performing some reaction of isolating various optical or geometrical isomers that can also tell you about the geometries. Which geometry it has opted during the substitution reaction or which intermediate it has opted and hence we can also get information about mechanistic pathways, whether it is dissociative or associative.

Let us consider the reaction of cis or trans again MA_4BX through a squared pyramid intermediate, now it can take place without rearrangement because Y enters the position vacated by X. So, that means basically what happens **(Video Starts: 07:19)** what we have is; so these four are A and this is B and this is X and now what would happen is, if I take out this one generate a square pyramid.

You generate a square perimeter like this now, this is blank and now here Y enters the position vacated by X. This assumption makes perfect sense and the central metal atom is easily accessible at this position and the formation of new octahedral complex requires no additional atomic motion. This just goes and another one comes. So, this is what exactly

happens in case of square pyramid. I take out this one and then it comes back, X goes and Y comes.

As per valence bond theory, if we consider valence bond theory, the hybridization that utilized by octahedral complex is d^2sp^3, if it is inner orbital complex, inner sphere complex. In that case what happens, one of the d^2sp^3 is empty now without electrons, because the leaving ligand has departed, now it is projected outward. It is something like this, it is projected outward in this direction.

This is suitable for maximum overlap with the orbital with a pair of electrons coming from the entering ligand. If the entering ligand is coming with a pair of electrons and this is already empty and this is projected out, this empty d^2sp^3, so immediately electrons can be donated and a metal to ligand bond can be established. So, as for crystal field theory, nucleophilic attack at this position is favoured because of low electron density.

Even if you go with crystal field theory, this is a nucleophilic we are telling, so in that case what happens since here electron density is less this is the ideal position for nucleophilic attack. **(Video Ends: 09:03)**

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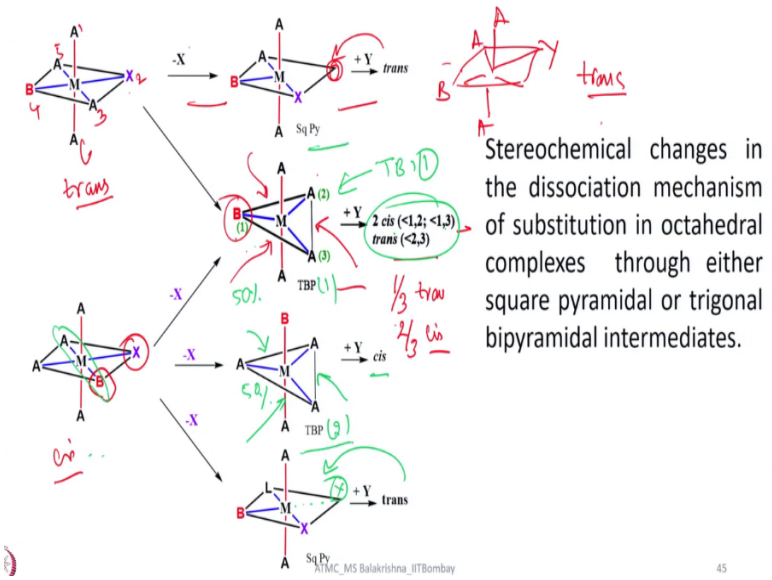

So, now let us just look into the stereochemical changes that one can see in a dissociative mechanism. In a dissociative mechanism as I mentioned earlier, we can think of two possible geometries one is square pyramidal geometry and other one is trigonal bipyramidal geometry.

So, here we can see in this case, initially let us say the chances are 50-50. Let us assume the chances are 50-50 for forming square pyramid as well as TBP.

When it forms square pyramidal geometry, so this X departs and this position is vacant now and next Y is coming here and this is established here. This compound comes back here. So Y comes here and this is B and this is A. So, what we get is a trans compound. So that is what I have shown here. And then on the other hand, it can also assume trigonal bipyramidal geometry, in that case you should know how to number 1, 2, 3, 4, 5, 6 and be consistent when you are labelling them.

You start with the axial top one and then go to the plane 2, 3, 4, 5 and then 6 and keep this numbering constant when you generate intermediates that is important. So, now with this one what you can do is you go for trigonal bipyramidal geometry. So now so B is sitting here, when B is sitting here. So, Y should attack, Y can attack from different positions. For example, it can come from here or it can also come from 1, 3 here.

When it comes and when it reverts back to octahedral geometry, so this Y will be cis with respect to B. So in this case, what happens, in two cases, when it approaches from 1, 2 and 1, 3 so we end up getting cis isomer. On the other hand, if the entering ligand Y comes from here, what would happen is, the relationship of B with respect to Y would be always trans, so we end up with trans.

That means if it take trigonal bipyramidal geometry, what we are getting is one-third trans isomer and two-third cis isomer. This is your about trans compound, we are considered here. Now let us look into the cis isomer. Let us consider cis isomer. In case of cis isomer, again we can think of square pyramid intermediate, again trans is straightforward.

Now what happens, X is departed from here. When X is departed Y comes here and then we get a trans compound, trans compound would be there, but when we go for trigonal bipyramidal now we have two options there. What are those two options? B can be apical or B can be equatorial. So, B can be apical and this one can be apical or this can be equatorial. That means we have two options, the chances of formation of these two trigonal bipyramidal intermediates is 50%.

And this is 50% together and this is of course overall if I consider this 25-25% and this is 50%, because if I consider both are 50-50, of course at the end when we get the different isomers, we should be able to tell whether it really followed this method or not. So, now when it goes from this method, this isomer, now you can see here again 1, 2 and 1, 3 positions you can get, whereas in case of 2,3 you get, so this holds good again for cis, with this TBP, this you can call TBP 1 and this is TBP 2.

In this case, Y we have put it now and now we have three positions. It can come here, it can come here and it can come here. So, no matter from which direction it comes, we get cis only. So, now you should be able to calculate the total ratio of what kind of isomers we are getting and what is the ratio of cis to trans with cis and also trans, it is up to you now to once again repeat this exercise and try to say we are taking 100% of this molecule.

In terms of percentage, you should be able to write how much percentage of cis we got, how much percentage of trans we got when we start with a cis octahedral complex and also when we start with a trans octahedral compound, involving both square pyramidal geometry as well as trigonal bipyramidal geometry. In case of cis, two trigonal bipyramidal geometries are involved along with square pyramid whereas in case of trans what would happen, only one trigonal bipyramidal isomer is involved and one square pyramid that you should remember.

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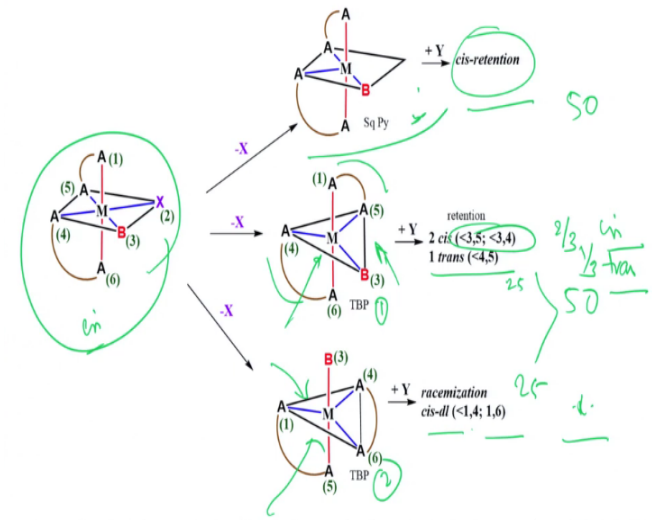

Stereochemical changes in the dissociation mechanism of substitution reaction of *d*-cis-[M(AA)$_2$BX] with Y through either square pyramidal or trigonal bipyramidal intermediates.

Let us look into optically active compound to see the consequences of substitution reaction on optical activity. For this one best would be to choose a simple ethylenediamine complex of this type, cis ethylenediamine complex and of course one B and the X can be anything, one is

water, one is chlorine or one is bromine, one is chlorine, anything, they should be different, they are different then it exhibits optical activity.

So, then you can think of optical isomerism in these compounds when you do substitution reaction. Now we will consider like this. So, again it is very straightforward, for that one I have chosen something like this. **(Video Starts: 14:50)** This is one ethylenediamine and I have another ethylenediamine something like this. So now you can see, this looks like ethylenediamine compound and these two are the ligands and this is B and this is X.

So, now what would happen is X departs here, if the X departs and this position is vacant, not much one can do it, Y can easily enter and this is the site where it can establish a bond with the metal and substitution reaction will be completed. In this case, what happens the cis compound we start with, cis is there. So, cis would give, cis means retention you can see. On the other hand, when we think of trigonal bipyramidal geometry, so we get something like this.

Let us assume this is B and now what would happen is positions I have already numbered, you can see here, positions already I have numbered here and here. Let us look into the position from which Y is entering. So, Y can enter from 3, 5. It can enter from 3, 5 here or it can enter from 3, 4 so here, so you enter from here. Here it can enter or here it can enter, in both the cases what happens here it can enter and then here it can enter, in both the cases what we get is cis product.

On the other hand, if it enters from 4 and 5 position, 4 and 4 position is somewhere here. So, now if it enters from here, what would happen you get a trans isomer, so that means with this one. So, now we will see with the other one, again as I said these two possibilities are 25-25% and this is also fifty. So total this is 50% and if this is 50% let us assume, in this case this is 25, TBP 2 and TBP 1 is 25%.

Just I am giving a hint for you to calculate the percentage of cis and trans isomers or retention or isomerization in this reaction, this is how we should see. And if I say exclusively, it undergoes substitution reaction involving only TBP then you can ignore this one. Just ignore this one and focus on these two in case of cis, and when you go to the trans there will be only one TBP and one square pyramid that is in case of non-optical other geometrical isomers.

Now with other one, what would happens is this is something like this we are considering, in this case we have positions 1, 4 and 1, 6. When it enters from 1,4 here, and 1, 6 here in both cases what happens racemization happens we get a mixture. It appears very statistical, but it makes sense. It makes sense and if you happen to be a research scholar or if you are doing M. Sc. Project, certainly you can go for some of these complexes and you can examine what kind of isomers you are getting, this is a wonderful experiment to look into it and analyse whether these assumptions, whatever we are making with possibilities having two different geometries are something good or not. So, in this case, again so what would you get is in case of optically active compounds is square pyramid, retention would be there, no changes.

On the other hand, when it undergoes substitution through two intermediates of TBP, TBP 1 TBP2, we get to two isomers 2/3 and 1/3 trans we are getting here, and here we are getting racemization. So, now if you think it is 100%, you can segregate and write in terms of percentage what is it, how much percentage retention is there and how much percentage cis is there, how much trans is there and how much racemization is there? So that you can make yourself familiar.

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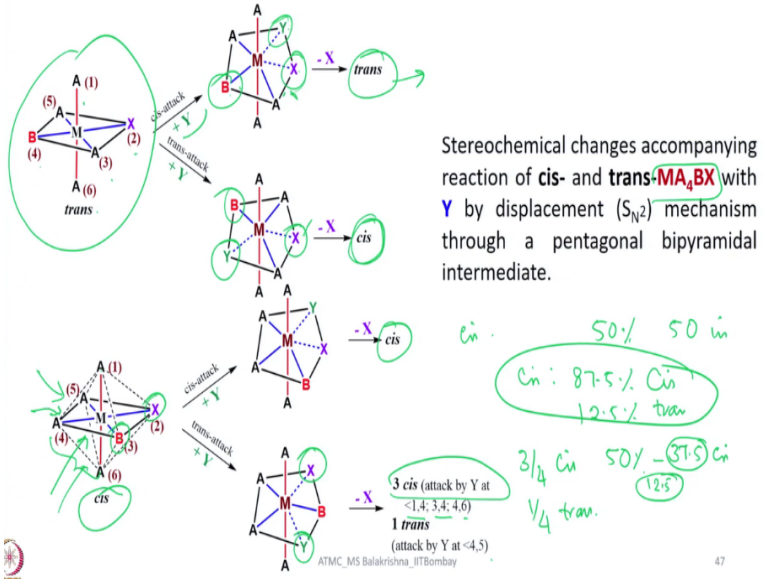

Now this is about dissociative pathway. So, dissociative pathway I told you we can consider both cis complexes, trans complexes and also optical isomers and involving both square pyramidal geometry and trigonal bipyramidal geometry. If the substitution reaction follows associative pathway or displacement method, in that case we have to consider an intermediate having coordination number 7.

And the best and ideal symmetric geometry one can think of for the intermediate with coordination number 7 is pentagonal bipyramidal. And here now let us look into the stereochemical changes accompanying the reaction of cis and trans MA_4BX with Y as entering ligand involving S_N^2 mechanism through a pentagonal bipyramidal intermediate. So, for this one again, you had to label this way.

As I mentioned first, you label the starting top axial 1 as 1, then come to the plane 2, 3, 4, 5 and then go to that lower axial one 6, remember this one. And now here what happens we call cis attack and trans attack, very similar to what we saw in the beginning. Cis attack means, it will come to a position close to the leaving group, trans attack means it goes to a position opposite to the leaving group, you should remember or it can also be called as a front attack and back attack.

In case of cis attack, what would happen Y comes here and, of course here the rate determining step is formation of entering ligand to metal bond. So, in this case what would happen is we get an intermediate here, cis attack what happens, it comes very close to the leaving group, you can see either come here or it can come here, it does not matter both are same. And then when X departs, it will revert back to octahedral geometry.

And we get the trans compound because this is with respect to this one we are taking. So, now B,X were trans, now B,Y are going to be trans, so we get a trans product. I mean both are equally possible when you are performing substitution reaction and if it follows S_N^2 mechanism involving pentagonal bipyramidal geometry, 50% chances for cis attack and 50% chance for trans attack, because here there is no preferred orientation of the entering group in the second coordination sphere that we should remember.

So, in that context, we should consider both of them equally probable geometries intermediates, and now in that trans attack what would happen is it comes to a position trans to the leaving group here. When it comes to the trans leaving group, it has to be cis with respect to the B here. In that case, what happens, once X is eliminated and then when it reverts back to octahedral geometry, the relationship between B and Y would be cis.

So, we end up getting cis product here, this is with respect to trans. Let us consider the cis compound here. In case of cis complex, we are referring to these two, cis and again equal possibility is there for cis attack, and trans attack. In the cis attack, what would happen is, it will come here, absolutely very clear cis would give a cis, but in case of trans attack we can see a different product is coming here.

You can see here, I have marked here in case of cis what are the positions it can attack which is mutual cis disposition with respect to the leaving group here. So, for example if it comes at a position 1, 4 you can see here 1, 4 is this one, if it comes here 1, 4 and 3, 4 and then 4, 6. The 3,4 is this one and 4, 6 is this one here. In all these three positions, when Y is entering its disposition would be cis with respect to B, as a result what happens we get three cis isomers.

On the other hand, in the trans attack if it attacks from 4, 5 position, 4, 5 position is this one, 4, 5 position if you see between these two where it is entering, as a result what happens it will be trans disposed with respect to B, we get trans compound. So, that means here also we are getting 3/4 cis and then 1/4 trans. And then here what we got is here everything cis here.

So, that means if it is 50 and this also 50, I will tell you how to calculate the ratio, this is 50%, this is 50% and then 50 is cis now here and in this one 50 divided by 4, 50 divided by 4 is this is 12.5. That means this will be 12.5 and then that will be 37.5 I would say will be cis. So, that means in this one, the cis can give 87.5 cis and then 12.5 trans. So, considering 50% possibility of cis attack and 50% possibility of trans attack.

Again, I am telling you this is with normal monodentate ligands, if you have some bidentate ligand some of the positions are blocked for the entering ligands, as a result what happens it will be having now minimum orientations or preferred orientations to do cis attack or trans attacks. It is very interesting. You take tridentate ligand, you take bidentate ligand and also take some time tetradentate ligand.

In that case how many isomers we can get, very interesting, you can go with different ligands and also sometimes bulky ligands and try to establish the stereochemical changes that accompanies these kind of substitution reactions, keep working on those things and problems also one can look for in standard textbooks that deals with reaction mechanism. With this, let me stop this lecture.

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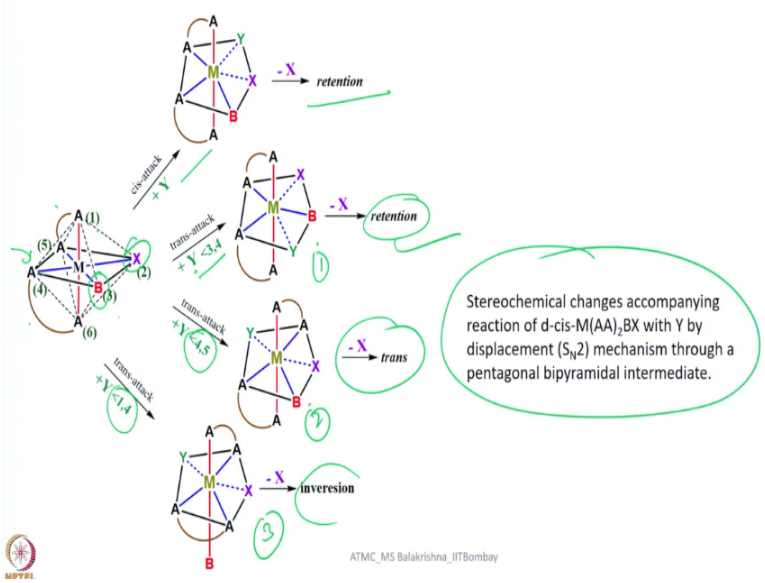

Before I conclude let me go with one optically active isomer using displacement method here. So now again, you can see in this case a typical complex, whatever I considered in dissociative method. I am also considering here, say ethylenediamine and this is something two different monodentate ligands. So, in that case, again cis attack is there, cis attack, retention will be there because cis comes and end up with a cis product.

And the trans what happens again retention will be there in case of trans attack, in the other one here you come across three different possibilities, you should remember. In case of optical isomer, as I mentioned we have three options here. This is 1 and this is 2 and this is 3. Of course, these combined together I wrote and I showed you, whereas here I have just divided them for better understanding.

So, in each position I have, there also I could have written that many because there showing the position would be very easy and that is the reason, I did not do it in case of trigonal bipyramidal geometries, whereas here it is a little bit not straightforward that is the reason I have shown here. So, trans attack can happen in three different things, with three different relative positions of B and X and ethylenediamine one is retention.

And when it attacks from 4 and 5, here trans compound is formed, so optical activity is lost and then in this case what happens, inversion happens when it attacks from 1, 4 position; 1, 4 position here. In that case what would happen is inversion happens. That means we know

now what kind of stereochemical changes that accompanies when we start with an optically active compound like this through displacement or associative mechanism.

So, with this I conclude this discussion of stereochemical consequences of substitution reactions in octahedral complexes. And in my next lecture, let me talk about electron transfer reactions or redox reactions.