Circular Dichroism and Mossbauer Spectroscopy for Chemists

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Lecture – 10
Chirality and point group – III tutorial

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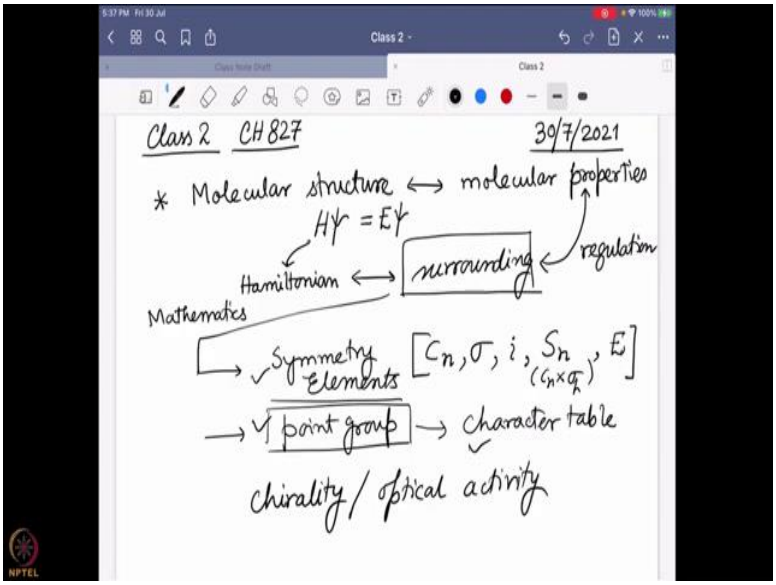

So, in the previous class we are discussing one of the important topic is, how the molecular structure and molecular properties are interconnected. And for that we find out that this originally Schrödinger equation $H\psi = E\psi$ can be used as one of the starting point. Where we can actually use it to find out how it is actually happening? H is represented by the Hamiltonian and which typically defines the surrounding of an electron that we are actually mostly looking into and try to find out his wave function, its energy and other properties.

So, over there, when we talk about this this H or Hamiltonian we found that is connected to the surrounding and that actually has a huge role to play during the regulation of this molecular properties. So, if we want to understand how the surrounding is playing a huge role. We have to define it or understand it properly. And we found that we can understand it with the help of mathematics.

With the help of mathematics, we can understand and we can use symmetry elements. Because, the symmetry elements can define how we can actually project the electron in different orientation? And how its relation with the other existing atoms and molecules. So then we also find out there are different molecules billions of them but we can all define them with the help of only five symmetry elements, five different kinds of symmetry elements.

First is proper axis of rotation then there is the plane of reflection then there is centre of inversion or centre of symmetry, the centre of reflection. Then we have S_n which is the improper axis of rotation, where you do a C_n followed by a σ_h operation. And at the end operation E

the identity operator. The importance of the identity operator will come again when professor Leela will teach you.

But the system is that in this identity operator is required to ensure this symmetry elements can have a particular relation in between them. We can actually club them or assemble them such that you actually form a group and that is which is known as the point group. So, this point group suggests that each of the molecules can be defined in respect of what are the different symmetry elements present.

And if you have different symmetry elements, there is a particular relation also connected among them. For example, as we were saying earlier, if you have C_n axis of rotation, where n is your principal axis. That means n is the highest number possible, at that time if you have a number of C_2's perpendicular to that you have to have a number of C_2's. You cannot have n-1 or n+1 or any other number.

Either you have n number of C_2's or nothing perpendicular to it. If you have σ_v plus, in a molecule where the principle acceleration is C_n you have to have n number of σ_v's or nothing. So, this kind of interesting relations exist between them because they are actually following the simple laws of mathematics. And when we combine them together, we find they can be termed as point groups and each of the point group can be defined in terms of called character table.

And if I can find out what is the point group of a molecule which is a pretty straightforward method that we have discussed in the earlier class. You just have to ask a few questions to the molecule with the answer of yes or no? And after a few questionnaires, you can end up what will be the point group of the molecule. Then look into the character table of that particular point group.

This is very similar to the periodic table which is already available in the internet which has been prepared well ahead by the mathematician. Just look into that and from there you can define different characteristics of a molecule. Whether it is spectroscopic interactions, whether it is a bonding interaction, all these things you can connect back to the character table and the point group.

So, in that thing in our mind we figure it out that yes, the symmetry elements, the point group, the character table are the important factors. And if I want to define a molecule, I need to find out what is the point group and from there I can comment on different molecular properties. So, one of the molecular properties that we are more interested in is known as the chirality or optical activity. And last class we try to figure it out.

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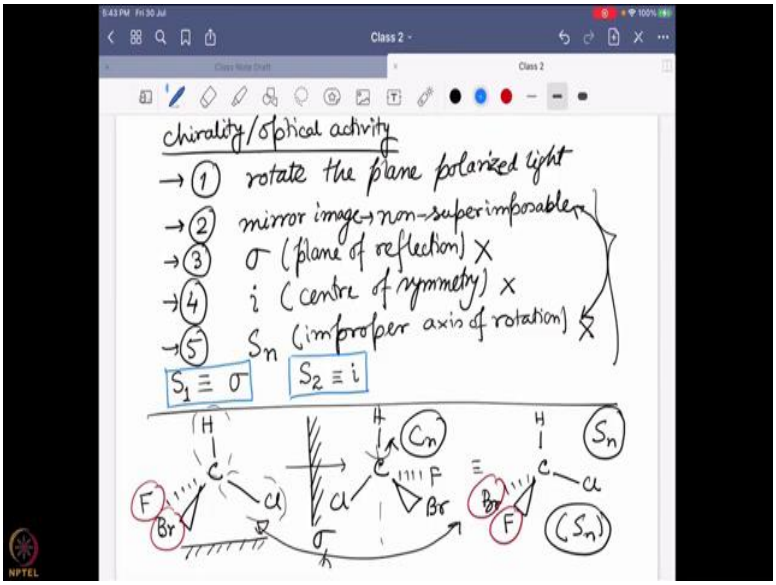

What is chirality? Or what is the optical activity? And if I remember correctly, we have five different definitions come out of it. So, I'm again writing them one by one. So, chirality is such that a molecule which can rotate the plane polarized light. We will come into that a little bit later probably next class. What is a plane polarized light. So that that is, will be defined by a chirality.

If it is a chiral molecule, it will rotate. If it is a chiral molecule then it is not. Second definition we have that take the mirror image of a molecule and see if it is super imposable or not. If it is non-super imposable, it is chiral molecule. If it is super imposable that that means it is a chiral. Super impossible means that is going to match exactly what your starting molecule is. The third definition we have found that your molecule cannot have any plane of reflection.

It should not have anything. The fourth definition was that your molecule should not have a centre of symmetry. And the last definition was your molecule should not contain any improper axis of rotation. So, these are the five definition we found that can define whether my molecule is chiral or not. So, one of the other way I actually try to define that all these particular systems, specially the last four are actually interconnected among them.

To exemplify that we actually took the example of this particular chiral molecule. This is nothing but carbon connected with four different groups. And what we found that first take the mirror image. So that means we are following the definition two, to find out how it is actually done. And we found this molecule looks like this and then we try to rotate it along this C H axis to ensure that it looks as close as singular to the original molecule.

But this chlorides and the C H bonds on the plane and on the right hand side of the molecule. And we did that and when we rotate, we found everything is same but the fluorine and bromine these two systems actually exchange place. So that is why it is not anymore super imposable. So, these two molecules are non-super imposable. So, we said that this is nothing but a chiral molecule.

And then we try to find out when you are taking the mirror image over here this particular function. It is nothing but a sigma reflection, a

plane of reflection and then when you try to rotate it and try to see how it is super imposable or not. Because that is what we typically do even without understanding or even with a comprehending that we are actually nothing but doing a rotation.

When we try to find the mirror image it is super impossible or not. So, over here we are trying to do different C_n operations. So, you are doing a sigma operation, we are doing a C_n operation. So, basically, you are doing a S_n operation. And some of you might argue that this plane of reflection might not be in the perpendicular to the C_n axis we are doing but we learned that it does not matter.

A molecule can have only one particular reflection. So, outside the molecule if you want to put a plane of reflection and take a reflection plane does not matter where you put it, you are going to find the same reflection. It is kind of you are looking at a mirror does not matter. How do you look into the mirror? You are going to find the reflection of yourself only. No other person will show up on the other side.

So, similarly no matter which particular way you put the mirror if you are looking at a particular molecule, the reflection would be the that particular molecule. And it can be only one particular reflection. So, in that respect we can say over there. What we are doing is C_n and sigma h. We can say so, we are doing a S_n operation. And that means these two systems if it is super imposable or not of the mirror image and the S n is nothing but the same.

And similarly, we can found that if my S_n, the n is 1 that means I am doing a C_1. That means leave the molecule as it is and do not leave doing a sigma plane. That means S_1 is going to be equivalent to sigma. So that defines chiral number three that a molecule cannot have a sigma plane. Because, basically it is having a S_1. Similarly, if you do some mathematics you can find the S_2 is nothing but centre of symmetry.

So, similarly, it defines the chiral number four. If you have a S_2 system or a centre of symmetry, you also cannot have a chiral molecule because the mirror image will be very similar to super impossible to the original molecule. So, with that respect, we can figure it out this all these four chirals 2, 3, 4, 5 there are nothing but the same thing defined in different ways.

So, from there we find out that what we need to find that whether the molecule having S_n or not. Now, finding an S_n might not be that easy. So, what we are going to do for that?

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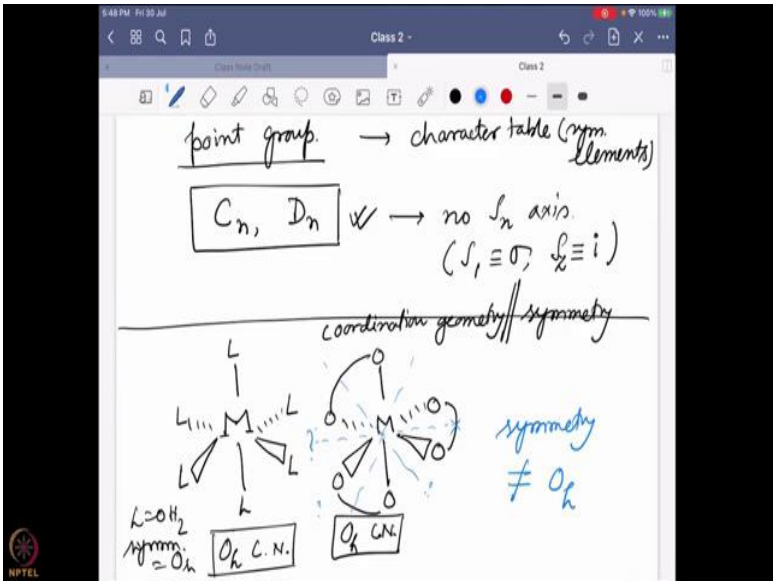

We are going to find out the point group of the molecule. And as we know from the point group, I can look into the character table and in the character table all the possible symmetry elements are already given. And over there I have to just glance it and to see if there is any S_n axis present there or not. And by S_n, I mean also sigma and i because, they are variations of S_1 and S_2.

And what we found there are only two different point groups present in the world which does not have any of these S_n symmetry elements. And those are C_n and D_n point groups. These are the two point groups have no S_n axis and by no S_n axis, I also include S_1 equivalent to sigma and S_2 equivalent to i. So, this is something we have to remember. So, what we need to know is to find out the point group and figure it out, if it belongs to C_n or D_n.

If it belongs to C_n and D_n your molecule will be chiral. If it is not, it is achiral a simple that and again, we look into that how to find out the point group of a molecule very easy ask a few question to the molecule and they will reveal what is the point group of molecule. So that is how we are actually generally find out. What is the point group of the molecule and whether it is a chiral or not? So, as it is inorganic special cast and even the name is actually inorganic complexes.

So, I am giving you an example and this example I am giving a general example same metal is there which is actually coordinated in a octahedral geometry. So, now over here there are two important things. Coordination geometry and the other term is symmetry. They are not the same thing. Coordination geometry means how many bonds it has? What is the geometry it is having? So, if it has six bonds and this particular geometry we say it is a octahedral coordination geometry or octahedral coordination.

But does not mean that it is actually an octahedral symmetry because if you want to have operator symmetry you have to have six equivalent ligands connect to it, such a way that you go any direction through the centre of the molecule you are going to find a same thing. So, this molecule if you have six same ligand say, this L ligand is nothing but water molecule. Then, yes your molecule is not only octahedral geometry but its symmetries also octahedral. Okay

So, over here the symmetry is also octahedral. But now say I took the same molecule with octahedral geometry but instead of water I have oxygen's over there and the oxygen's are nothing but coming from the carboxylate oxygen. So, it is a oxalate group. Two carboxylate group come to each other and over there now say they are connected. Now, once they get connected like this, also the geometry is octahedral coordination geometry but the symmetry is not octahedral, Why?

Because, over here just see if, I see at this seat at this particular point and go through this molecule. I do not find a linker over here is missing. Similarly over here, the linker is missing. Similarly over here, the linker is missing. So, although the coordination geometries octahedral the symmetry over here is not an octahedral one. Okay So, be very careful when you define the difference between octahedral coordination geometry and octahedral point group symmetry there are two different things. Okay

So, now what is the point group of this particular molecule then? So, let us take another deep look into it.

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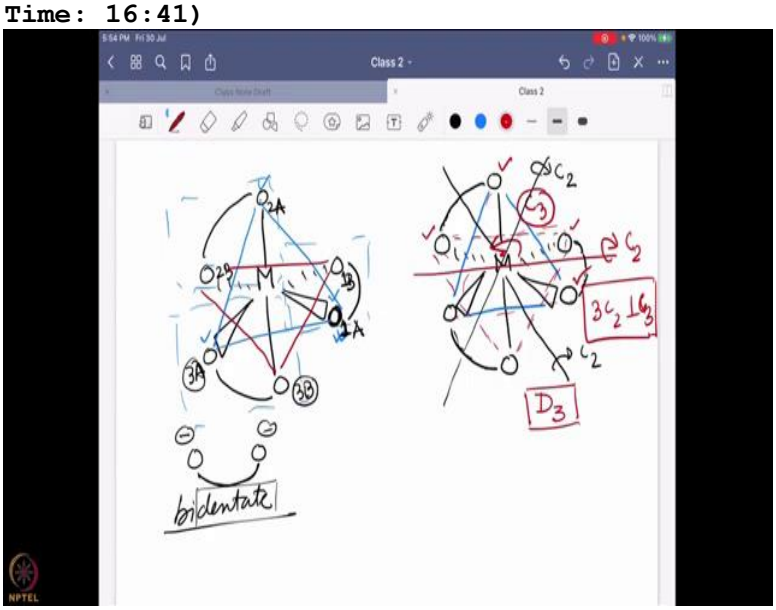

So, over here what is the point group of this molecule? So, again it is not a junior level class. I'm not wasting my time to find out exactly where the different symmetry elements are? So, I'm just giving you the answer. So, this molecule has the highest symmetric axis of rotation present over here is C_3 and where is the C_3 present? To look into that what I am going to do look into this ligand little bit carefully.

So, this ligand which is nothing but a auxiliate ligand to negative which has outside ligand and connected by a carbon-carbon linker. So, this particular linker when it is present over here, you can see that two particular binding spot for the same ligand. But we call them as bidentate ligand. This term dentate comes from the denticity that means how many times it is biting the metal? It is fighting two times and over there, they are connected to that and now see take a look into each of the ligand.

There are three such ligand right one over here, one over here and one over here. And each of them has two pair of metal oxygen bonding. And if you look carefully one of them, you can say towards you one on them

is actually backwards to. Take example of this one, this system over here say I'm writing O_1 and O_1, see it is O_{1A} this is O_{1B}. You can say that O_{1A} is actually towards you.

Because, this wedge bond means above the plane of the paper and the dotted bond means it is behind the page of the paper. So that means 1A is towards you, 1B is backward. Similarly over here, if I say it is 2A it is 2B. You can say 2A is on the plane of the paper, 2B is on the backside. So that means again 2A is towards you, 2B is on the back side. Over here say, it is 3A and 3B.

You can say the 3A is above the plane of the paper, 3B is on the plane of the paper. So, relatively we can say that the 3A is towards you, 3B is backward. So, each of them has two sets of metal oxygen bond. One of them is toward you, one of them is backward to you. Now, connect all of them which is above the plane of the paper. So, this one, this one and this one and connect those which are actually back side of the paper.

So, let me probably put a different colour to differentiate it out. Now, If I draw the molecule one more time and now what I'm doing drawing the linker in a dotted line. So that you can see the triangles properly. So, one triangle is this one above the plane of the paper. One triangle is backwards. Now, if you rotate the system through over here, a C_3, 120 degree rotation. Because, you see it is a triangle over here. right

Forming over here, another triangle forming over here so, there are two triangle oppositely oriented sitting there. So, if you rotate that you will see a similar structure, exactly similar structure you will find. And that is going to give you the same structure. So, there is the C_3 is present. So, for an example, If I rotate it, this particular system is going to go over here. This particular oxygen is going to go over there.

And this connection is also moving in the same direction. Then you can figure it out. This is the C_3 axis. Now, if you have a C_3 axis, obviously I'm not going to it is not linear, not special group. So, if it is a C_3 axis, the next question will ask to it whether it belongs to D or C point groups? For having to for for the D or dihedral point groups, you have to have C_2's perpendicular to the C_3 and if you have C_2 you have to have 3 or nothing and there is present C_2's over here through this oxygen oxygen connector.

If you rotate at 180 degree, you can see you are going to get the same thing. And as I said, if one is present because the principal axis C_3, the other two should be present and would be in a very similar position. So, those will be over here going through this oxygen oxygen bonds. So, you have C_3 and you have $3C_2$ perpendicular to C_3. And there is no other symmetry elements present there other than obviously central symmetry uh sorry, the identity factor E the rest of them are not there.

So, it is belong to a point group D_3. And that is why this molecule is going to the chiral molecule. So, what you now need to do? Is either say directly here. It is going to be chiral or you can also do that same operation that we actually learned from our beginners that take a mirror image and see try to see if it is super imposable to its original structure or not.

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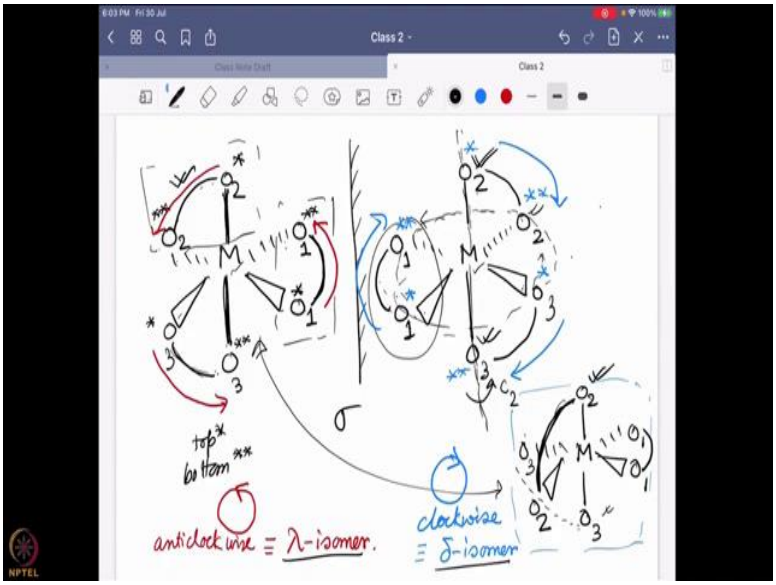

So, let us try that. So, here is this one, here is this one, here is this one and then over here, I am taking the sigma for the mirror image. So, first draw the molecule will draw the connector later because coordination (23:37). So, the coordination geometry is going to be octahedral. So, over here then draw the oxygen first and then at the end we will draw the connectors. Because that is the only thing it is changing.

So, over here, this is the connector and I'm writing O_1,O_1 to understand it better. So, they come over here. So that will be the connector say this is O_2, O_2. So that will be over here and over here. So, there will be this connector and obviously the O_3, O_3 will be somewhere around here. So, now this molecule, is it super imposable or not? So, again after the sigma orientation, may not be that easy to understand.

So, we have to try to rotate in such a way that it actually matches to its original structure as much as possible. So, what is the original structure metal in the centre that is tipped. But over here see these two oxygens which is one above the plane, one below the plane which is on the right hand side. Now, it comes on the left hand side. So, let us put this one on the right hand side, how we can do that if we rotate that over here 180 degree.

And if we do that what we are going to get is the following. We can first draw the oxygen's that is going to be same. So, if I rotate it over here 180 degree, these two oxygen system will come on the right hand side. That is my O_1, O_1. Now, if I rotate it 180 degree, the O_2 on the top one is not going to change its position because that is sitting on the axis of rotation. But this O_2 this go to is going to change and come to this side, 180 degree rotation.

So, it will come to the forward side. So, this is the O_2. So, now their connection is such like this and obviously, the last of the O_3's will be connected from the bottom but just imagine how to do that. So, this is the O_3 over here. That is going to be same position. This O_3 which is in forward move 180 degree and go to the backward side. So, now you can see these two molecules, although the oxygen's are almost in the similar positions.

But their connectors are not because over here you can see this O_2,O_2 connector is kind of on the back side. Now, it is come to the forward. Similarly, this O_3,O_3 is kind of in the forward side. Now, it goes to the backward side. So that is why these molecules are not super impossible. Obviously, this molecule is going to be chiral molecule. And that we have find out earlier when we said this is a point group of D_3.

Now, the nomenclature of this kind of inorganic molecules, how to do that? It is again very simple what we have to find out again the connectivity between the same ligand molecule. Because, the ligand molecules are bidentate at this condition, we have to find it out each of the end of the same bidentate molecule, how they are connected? Because, each molecule has one top side and one bottom side.

The top side, I'm putting a star and bottom side I'm putting a double star. So, this is the star double star for this particular ligand. For this two, you can say this is the top and this is on the backward relatively. And over here, this is the top and this is on the backward side. Okay With respect to on the plane of the paper you have drawn, this is wedge bond top, this is dotted bond bottom, this is solid bond that means on the plane of the paper.

This is dot in bond that means backward side. Similarly, this is wedge and these on the plane of the paper. So, this even it is plane of the paper. It is relatively backward compared to this one. Now, you look into them and try to find out which direction you are moving from going to top to bottom. So, over here I am moving this direction, over there I am moving this direction, moving this direction.

You can see all of them are moving in the similar direction. So, if it is moving in the similar direction then try to find out what is the overall rotation? You can see it is a rotation on the anti-clockwise or lever rotator. And this particular system with anti-clockwise rotation it is known as the lambda isomer. On the other hand side, if you look into this particular molecule over here.

Now, you can see this is the top, this is the bottom, this is the top, this is the bottom, this is the top, this is the bottom and now which direction it is moving now? All of them you can see it is moving on the right hand direction. So, it is a clockwise movement and clockwise movement and this is actually known as the delta isomer. So generally, for this thing to understand which is lambda, which is delta and lambda. So, try to put the molecule in such a way that will be easier for you.

For example, if you get this particular orientation, this is the same molecule but it may be a little bit difficult to get out the delta, lambda. So, try to put in this particular orientation. So that at least you can find which is top, and which is bottom very easily. And then try to figure it out. And with respect to that you can find out which is the lambda. And which is the delta isomer. And over here this molecule is called delta and lambda isomer.

No matter whether the C_2 axis is present there or not? So, over there the C_2 axis are present because both end of the ligand is same over here. They may not be the case, If both the ends are not same. For example, you are using one end, amine and one end carboxylate. Then the

molecule is the ligand is still bidentate but not symmetry. And in that case, if you put a molecule with this particular ligand three of them and then you can still find a molecule very simple similarly looking but you might be losing the C_2 over there.

So that molecule will belong to a C_3 point group. So, be very careful when you look into this kind of multi-dented inorganic molecules which are actually optically active, very careful which point group it belongs to and how to find out their nomenclature delta or lambda isomer. okay So, any question till this time? Say, anyone have any question? So, over here, so far, we have gone through that optical activity is important and optical activity does exist even in a inorganic molecule.

Even the coordination geometry is not a chiral geometry and if it has bidentate ligands three of them. If it is coordinated, it can produce a optically active or chiral complex. And now we know how to do that how to find its point group? How to find this the nomenclature of the different enantiomer? So, this delta and lambda isomer obviously, they are enantiomer very similar to D or L isomer that you find out from the organic chemistry.