Chemical Crystallography
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Lecture - 41
Disorders in Crystal Structures

Welcome back to the course of Crystallography. In the previous couple of lectures we have discussed about handling the data with a couple of software. We have seen how a Bruker software or a Rigaku software can be used to analyze the recorded data and then how one can solved structure and do refinement using Olex 2 and for that you use the cell x for such a solution and refinement.

And then in the previous lecture we discussed about how to understand the intermolecular interactions, how to identify the inter molecular interactions using mercury, how to get some basic molecular parameters, the inter planer angles and all that using mercury and also I have shown you how you can generate the simulated powder x ray diffraction data using mercury for comparison with the experimental data.

So, the data that is simulated from this single crystal data should then be marched or should then the compared with the observed experimental power data on the bulk sample. And if all the peaks match one to one then you know that the bulk sample and the single crystal are one and the same but in it may so happen that, during the crystallization process from different solvents you might have resulted in a different crystalline form which is different from the original powder that was used to grow the single crystal.

So, in that case the powder x ray diffraction data simulated from the single crystal we will not match with the observed powder pattern on the bulk sample and the peak positions will be different, peaking densities will be different and that will be indicate that you have caught at different crystal structure which is called a polymer and you characterize it as polymer a b c or alpha beta gamma whatever.

Polymer (Refer Time: 02:27) is another phenomena which we should discuss in one of the classes to just to brief you that a particular compound is potentially possible to be arranged in 3 dimension in more than 1 different ways to grow a crystalline architecture.

So, a compound which can have a multiple number of crystal structures are called to have polymers or we call them as polymers at means many forms of a particular compound in crystal structure. Today we want to now discuss about the possibility of disorders in crystal structure.

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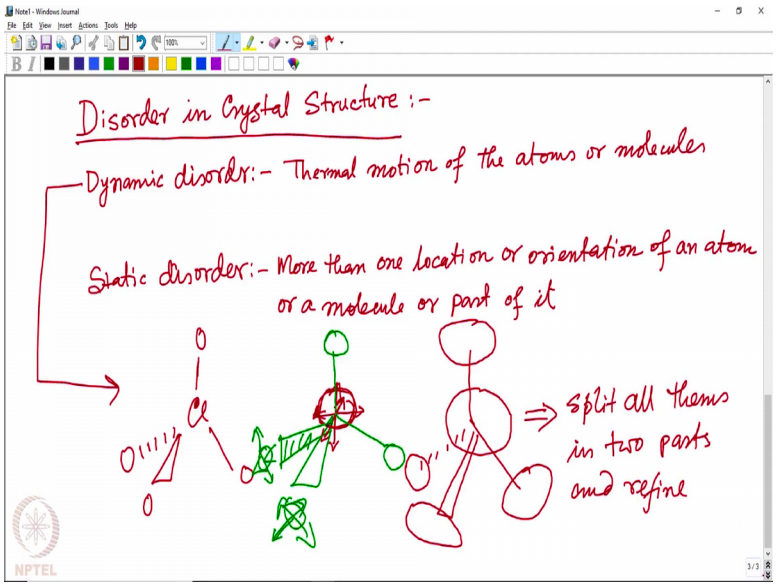

Disorder in crystal structure: What do we mean by disorder? Disorder means the atoms not being fixed at one place. The origin of this disorder could be of 2 types.

One can be a dynamic disorder, the other one can be static disorder. In a dynamic disorder, the main reason for that is the thermal motion of the atoms or molecules. And static disorder means more than one location or orientation of an atom or a molecule or a molecule or part of it. So, this dynamic disorder which is mostly due to temperate effect it so may happen that, we have a part load it anion which is tetrahedral in geometry at room temperature, the chlorine may have a very large thermally leave side which means the chlorine is vibrating in along x y and z.

As a result of that, the oxygen atoms which are connected also are vibrating in all the possible directions with respect to those oxygens as well. So, what we get is over all a picture, which has a very large believe side for chlorine and very very large flat type believe sides for oxygens, which actually form a tetra hydra, but that tetra hydra is highly distorted. One can treat this data by splitting all the atoms in 2 parts.

So, what you do is you split all the atoms in 2 parts and refined, which some constants.

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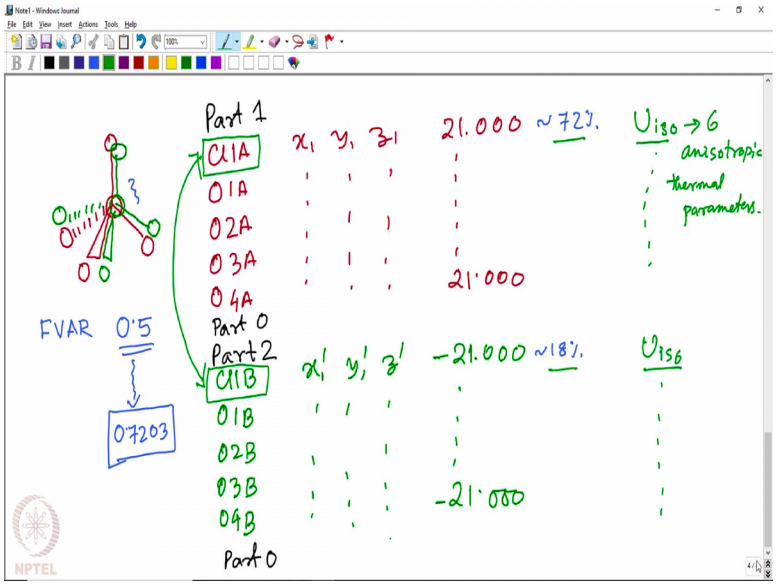

So, when you do that for every split and portion, you have one set of 5 atoms as I am trying to draw. See I am trying them slightly shifted because; it is because they are on a particular thermal motion. So, now, if I have the first set numbered as Cl 1, O1, O2 and O3 and O4, the second part will be numbered as Cl, rather we can number it has Cl 1A, O1A, O2A, O3A and O4A and for the chlorine one again part 2 we write it as 1B, O1B, O2B, O3B and O4B. These are the four oxygens of green molecule and those are the 4 5 for the red molecule.

So, what we have is this is called the part 1 and this is called the part 0, part 2. We end that part 1 with a command part 0 in the ins file you also end this as part 0; which means, the disordered parts are over. Then what you have are the corresponding atomic coordinates x 1, y 1, z 1 and all the atomic coordinates for all of them; similarly, for this you should have x 1 prime, y 1 prime, z 1 prime and all of them will have their corresponding x y z coordinates after splitting. And then we will have a term for occupancy. As I said the occupancy parameter is generally written as 11.00 for 100 percent occupancy.

But in case of this disorder structure, instead of writing it has 11.0, we write it as the first part as 21.000 and we write all those as 21. And then for the second part we write this as

minus 21.000 for all of those. And in this instruction file at the top we will have one line (Refer Time: 10:43) FVAR, FVAR.

So, at that point, we identify to start with us 0.5; that means, this 21 represents fifty percent occupancy, minus 21 represents 50 percent occupancy. When we try refined the structure depending on the actual electron densities at those two sides, this quantity in FVAR we will keep on changing. It may so happen that on doing several rounds of refinement, this FVAR parameter stabilizes down to like 0.7203. Which means this is about 72 percent and this is the remaining which is about 18 percent.

So, this then refines the relative occupancies of 2 different orientations or rather two different locations of those two groups. And then those 2 inions of per chlorate and it refines down to a particular occupancy. And then at the end as usual we will have the isotropic thermal parameter for all of them, which also will be independent parameter and will be refined along with the refinement of occupancy.

So, once with isotropic refinement we have converge to the least square refinement convergence, then one should do anisotropic refinement and get that Uiso to get converted to though 6 anisotropic thermal parameters.

So, this procedure is followed when there is a disorder as I have discussed in case of per chlorate. Actually this method of refinement, the way we talked about it is part 1 and part 2, this is done in case of all kinds of disorder treatments using the cell x, you with in Olex 2 or even if you are using with win g x is another package.

Now if you see that the coordinates of Cl1 and coordinate one a and coordinates of Cl1B are very very similar or their exactly same and also the corresponding thermal parameters for those are also very similar. You can then constrain or restrict that both chlorine 1A and 1B it should have the same location and same thermal parameter. So, to do that one can use two commands simultaneously.

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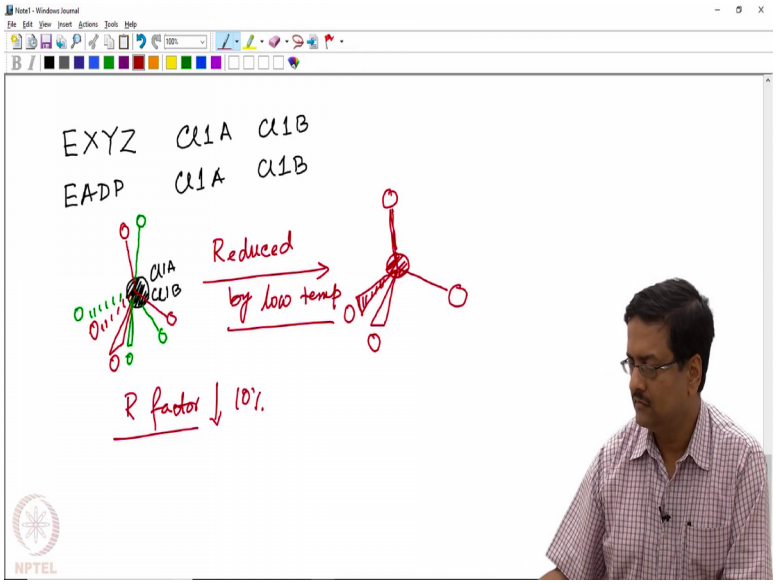

The command is EXYZ which means, the two atoms that we are doing to right have the same XYZ coordinates that is equal XYZ coordinates. So, we write it as EXYZ and then we name those 2 atoms suppose Cl1A and Cl1B, which means they will have same at for coordinates.

Then another command we write as EADP, which means equal atomic displacement parameters and you right Cl1A, as Cl1B. What it do is, it would place both Cl1 and Cl2 that is Cl1A and 1B at same place, which same a thermal parameter. And then I have the other oxygens refined over a set of 4 coordinates. And the refinement would bring your R factor below 10 percent.

So, this type of disorder that we can handle and can then this can be reduced. This can be reduced by doing it at low temperature because, on lowering the temperature, the atomic vibration will reduce So, that the atoms that are present in this particular molecule will have a smaller thermal vibration and as a result they will be more confined towards their nucleus and the disorder will be reduced.

So, this is a dynamic process on increasing the temperature disorder increases, on decreasing the temperature the disorder reduces is called a dynamic disorder. The other type of disorder that one can have is as I already indicated is called static disorder.

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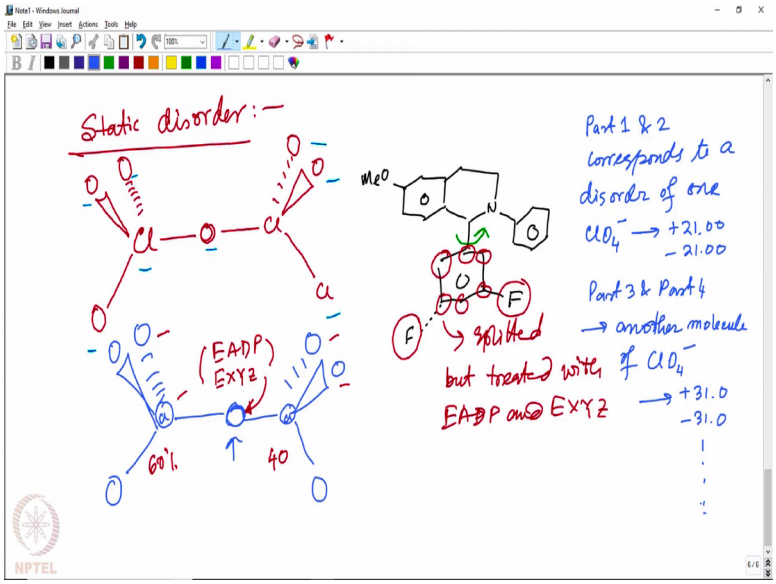

This also can happen with a per chlorate anion or an any such anion as we are discussing with per chlorate let us stick to that.

It may so happen that in the structure at some equivalent position, the per chlorate anion is oriented like this and in another site the same per chlorate is oriented like this. Which means, at some place the per chlorate is oriented like that, 3 oxygens pointing towards left and in another side three oxygens orient like this, but the 2 oxygens which are here they are at same crystallographic location. So, as a result what will happen is that this group we will actually be looking like that. And this 2 different orientation of the per chlorate is not a result of thermal motion. It is an intrinsic disorder that is present in the lattice.

So, the per chlorate anion at different site is oriented in different way. This particular type of disorder cannot be lowered or reduced or a removed by lowering the temperature. So, if you lower the temperature what will maximum happen is the thermal motion of those individual oxygen and chlorine atoms we will reduce, but still you will be able to see that in the asymmetric unit, you have atoms which we gives you feeling that it is like this. So, it actually means that, this middle oxygen it serving the common atom for both sides and these two sides I have different chemical occupancies.

It may so happen that one side is again 60 percent, the other side is 40 percent. So, in that case, the same type of part 1 part 2 kind of a refinement has to be done with appropriate

identification of those atoms and numbering them appropriately. And then we apply the EADP and EXYZ constrains on the central oxygen which is a part of two disordered portions. A similar type of disordered is also seen in many cases. Suppose if you have an atom a molecule like this, the way I am drying it is a derivative of isoquinoline and then you have a fluorine atom here.

It is possible that this molecule has a free rotation about this CC1, which is form C1 to this aromatic ring. And because of that free rotation, the fluorine on that can appear on either side. And it was seen in our levels one example this fluorine is, on one side about 60 percent and the bond is rotated exactly 180 degree making the fluorine on the other side appearing for 50 or 40 percent.

So, 60 and 40 these disorder is not controlled by the cooling because, when the crystal has grown, the molecule has crystallized in such a way that the 60 percent of the molecules have the aromatic ring rotated in this orientation with fluorine towards the left and 40 percent of the molecules I have crystallized with fluorine on this side.

And at room temperature in solid state, this orientation of phenol ring is restricted. So, this rotation is only allowed in solution. So, from room temperature to low temperature, we cannot convert all of them to one direction. So, what we can only do is we lower the temperate; we reduce the thermal vibration of all the atoms in a molecule and then treat those individual atoms as 2 spitted portions.

So, here what will happen is we have 6 carbon atoms, which should be spitted but treated with both EADP and EXYZ commands because, on rotating 1 ring from this orientation to that orientation the carbon atoms have fall in on the same place not at a different places, as a result the coordinates of carbon atoms are same, but the fluorine is changing its orientation from this side to that side. So, that orientation being different the fluorines will not have corresponding EADP or EXYZ.

They will have their own atomic coordinates, should be refined separately using the FVAR command that is the free variable command and doing in it plus 21 and minus 21. In case in one particular crystal structure if you have more than one group of atoms having different types of disorder then the thermal parameters that you encounter or the sorry the occupancy parameters that you encounter, should have numbers continuous. So, suppose if part 1 and 2 corresponds to a disorder of 1 per chlorate group so that,

occupancy should be designated as plus 21.00 and minus 21.00. Then there may be part 3 and part 4 corresponding to another molecule of ClO 4 minus that should be designated as plus 31.0 minus 31.0 and so on.

If you have large number of parts to be disorder large number of anions or part of the cation itself or the part of the original molecule disordered as many disorder sections you have you should keep on going plus 31 minus 31 plus 41 minus 41 and so on and refined them as independent portions which are disordered and are being treated separately. Of course, by doing all these it may so happen that, the number of refinable parameters may increase so much that your data may not support that refinement to happen efficiently and as a result the r factor may get increased.

It may so happen the refinements may not converge and one has to then take a decision up to what 0.1 should actually keep on doing this refinement. If we reach a limit the beyond which we are not able to refined we should stop and get back to our or cans may points suitable for the comments that we can make at that structure refinement part while writing the publication that, this data cannot be further refined using more disordered fragments. At this point I would like to mention one important aspect.

This disorders that we are discussing are treatable disorders using cell x because, these are intrinsic disorders which was incorporated either by temperature effect or by crystallization effect. But there are certain kind of disorders which we have encountered in many crystal structures, which is a random disorder and that random disorder is a result of a thermal shock given to a crystal.

Suppose you have a crystal kept at room temperature, but you are diffractometer equipped with your tri system is running at 100 Kelvin temperature you take the crystal from room temperature mount it, and then directly mounted on the goniometer and put it on the diffractometer. In a fraction of a second, the crystal is cooled from room temperature to 100 k.

This cooling in a fraction of a second results in a peculiar disorder of all the atoms, may be all atoms or some of the atoms which had very different thermal vibrations at a given temperature. So, because of this thermal shock, some molecules may be frozen in a particular orientation, some molecule may frozen in a different orientation, some

molecule may be frozen in a different orientation because of it is very high thermal motion at room temperature and the result is a highly disordered structure at 100 Kelvin.

So, it becomes extremely difficult to treat that kind of disorder and this is random. To avoid such a situation or we always recommend that you take a crystal at room temperature slowly cool the crystal to 100 k so that, you allow all the molecules to slowly reduce their temperature and refined their thermal vibrations and then come to a thermal minima and then fixed at one place at 100 k. Because at room temperature it is possible that different anions at different locations of the unit cell are vibrating in a different manner as a result, they are not only vibrating, they may be slightly rotating also at room temperature.

So, when you try to cool it very slowly, they always reach a state of equilibrium of lowest energy and at a 100 k you may see that the disorder has disappeared, which you might see at room temperature. But then if you suddenly cool a crystal from room temperature to 100 k, in a fraction of a second all those dancing, vibrating, jumping molecules or ions will be frozen at its sudden location and the result will be seen in the isometric unit, which will have the anions or molecules or parts of molecule oriented in different ways, with different types of occupancies and it will become a very very combustion situation to refined those in a given scenario.

Even the data if it is not a good quality data, it will it may not be possible to treat that disorder suitably to reach a lower our factor. That is why, one has to really worry about the data collection procedure, one should be patient and collect the data with as much clear as possible because, you may be collecting a data in 2 to 3 hours time, but if the data is a of not of good quality, then you may we sending spending several hours 10, 15, 20, 30 hours to do this structure solution and final refinements of a poor data.

So, in today's class we have discussed about the treatment of disordered molecules, how to handle this disordered structures using the refinement software. In the next lecture we will try to show you one such disordered structure treatment in reality.