Bioinorganic Chemistry
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Lecture - 22
Molybdenum Enzymes-I

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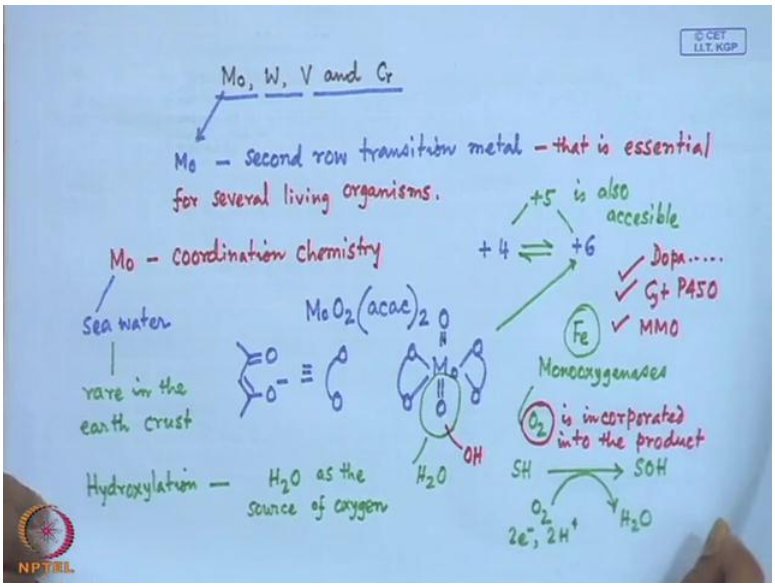

Welcome, so in next of our few classes we will discuss the in corresponding enzymes of several metal ions such as molybdenum tungsten vanadium and chromium these are different compare to what we have discussed so far. Today we will just focus our attention on this particular one that means the molybdenum which we all know that it is the second row transition metal, second row transition metal that is essential for several living organisms.

This particular one can do what we will see particularly from the molentunum cortisone chemistry if we know little bit of that because this particular metal ion most abundant and sometimes very much found in sea water. It has given corresponding complexes in two most stable oxidation states one is plus 4 and another is plus 6, so well know metal complex of molybdenum we all know that M o O 2 species having if we have acetyl afiton a c a c we call acetyl action at ligand which is nothing but your this one. So, when it is bound to that is if you have the molybdenum compound, so these two ligands this is basically your O donal ligand which will found this O and that O and you have the corresponding dioxo compound.

So, this molentunum dioxo compound which is immediately tells us that it can be stabilized in plus 6 of the state, so if we can go for a two electron transfer from that compound we will get are we will stabilize this corresponding molybdenum compound. Molybdenum presents in the biological system because this one if it is abundant in sea water, but are rare in the earth crust in the earth crust. So, if we can go for settling between these two oxidization states of plus 4 and plus 6 and obviously we can remove one of the oxo part.

So, that can be stabilized if it can go for binding to water we can say that it can be stabilized to plus 4 oxidation states intermediate one which is plus 5 sometimes between the catalytic cycles is also accessible. So, we can have these T oxidation states and what we are going to look is that one such interestingly x n what we have been studied for iron chemistry that hydroxylation. But, this sort of oxidation is different compared to other hydroxylting reactions because water we leave here as the source of oxygen. If we at all go for any kind of such hydroxyl reaction because in the different mono oxygenizes, what we have seen in case of iron chemistry that we had mono oxygenizes.

In those mono oxygenizes instead of water molecule we have used O 2 as our source for oxygen say this O 2 is basically oxilating our species such as, if we had the substrate what we have seen already earlier. Then that substrate can be hydroxlated to S O H and that of substrate utilizing water forming H 2 O, so water than 2 electrons and 2 protons. So, side by side while we talk about all these molecules we will compare what we have seen in case of iron chemistry. What we basically expect when we change the metal center from the iron to molybdenum because this particular one is different because this oxygen from O 2 is incorporated within the substrate or into the product.

So, this mono oxygenizes what we have seen in case of topamin beta mono oxygenizes than cytochrom P 450, so all we have studied earlier. But, we should be able to compare one another this is topamin hydroxlases and than methane mono oxygenizes all are utilizing oxygen from the air or any other oxygen source. But, in this particular case you will be utilizing water molecule as a source of oxygen, so that means water can able to give you.

That means, if we can go for the attachment of the water to the molybdenum center of at some point it is possible to attach the age group to the molybdenum center or ultimately the oxydo group or oxydo ligand center. So, these all are inter changeable once you have the water molecule that you expect that the some point you can generate the molybdenum oxo

compound. This is on the molybdenum center or the corresponding hydroxide spaces, so these particular classes of molecules we call them as molybdenum hydroxylases.

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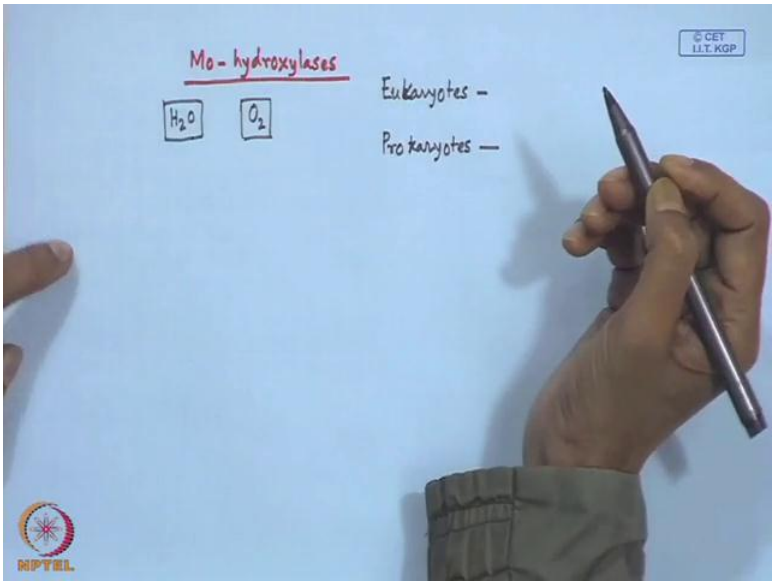

So, these molybdenum hydroxylases which are therefore different from iron mono oxygenizes and they are basically responsible for the corresponding introduction of o g e function of any carbon. One more interesting thing is that they are basically operating on different Eukaryotes and Prokaryotes, Eukaryotes and Prokaryotes because in case of iron corresponding transfer radiated by iron we have the impartment. We have the atmosphere which is dominated by O 2 that means you have aerobic impartment in case of molybdenum oxygen supply is less. We have the water corresponding molecule and that water molecule is responsible for the corresponding hydroxyls reactions.

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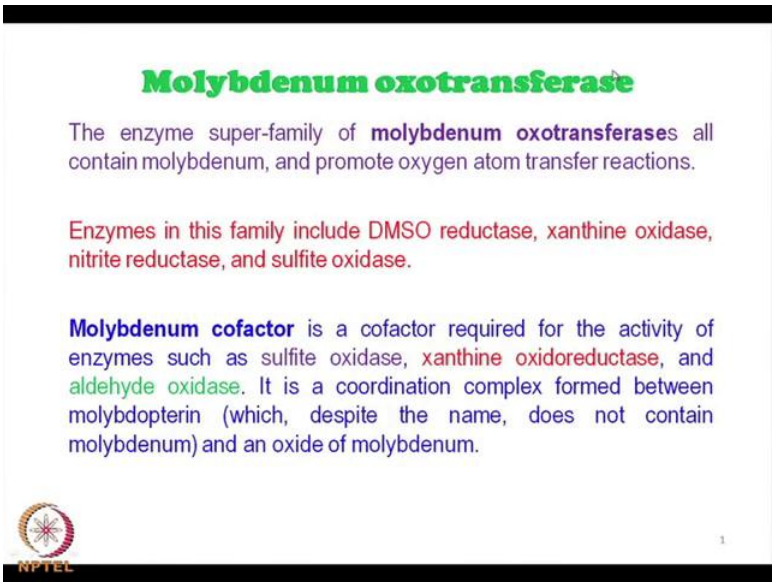

So, one such example is that we call considered molybdenum oxotransferase, so molybdenum oxotransferase the name immediately will tell you that, if you have the molybdenum and the corresponding molybdenum compound and, that oxo can be generated from the water molecule or the hydroxide function. So, you have the corresponding molecule molybdenum oxospecies and that molybdenum oxospecies can go and transfer to any other substrate for these oxotransferase.

If they basically super family of oxotransferase all contain molybdenum and promote oxygen atom transfer reaction. But, interestingly at that point you should know that these oxygen transfer basically taking from the water molecule, so there is large number of molecules present and we will see two or three examples for that. One of them is dimethail sulpaoxide deductive xanthine oxidase nitrate reductance and sulfite oxidase, so all these things what you see that basically what we are talking about nothing but only the transfer of oxygen.

So, if we are able to transfer these oxygen what we are unable to do without the help of these enzymes that means from the water molecules itself, so if you have this dimethail sulfite how you can go further corresponding transfer of dimethail sulfone and than dimethail sulfoxides. So, how you transfer that oxygen on this sulfur because we all know all these are easy to get particularly when you have the dimethail molecules. Even the simple hydrogen peroxide can transfer one such oxygen to the center than xanthine oxidase is also the corresponding

oxotransfer reaction on the xanthine molecule and nitrate reeducates is a inter confession between nitrate and nitrate.

So, always we are talking something related to all transfer the oxygen atom from water molecule through molybdenum nitrogen center to the carbon center or the corresponding sulfur center in the fight an ion. That means sulfite to sulfate inter conversion is also possible with the help of these molybdenum oxotransfer. So, we consider them as co factor because this cofactor is required for the activity of the enzymes such as sulfite oxidase xanthine we call it oxidase or oxido reductase because the reaction is reversible one.

One other example can also be aldehyde oxidase, so aldehydes molecules can also be oxidize because you can transfer that oxygen to your compound center of aldehyde. So, it is corresponding we call it as a coordination complex basically because you have the definite ligand system which is bound to the metal center and we get it as a molybdopterin molecule and that molybdopterin molecule is does not contain any molybdenum. So, that is why we call it as a molybdenum cofactor and oxide molybdenum in one point you have the oxide of molybdenum and another co factor is required.

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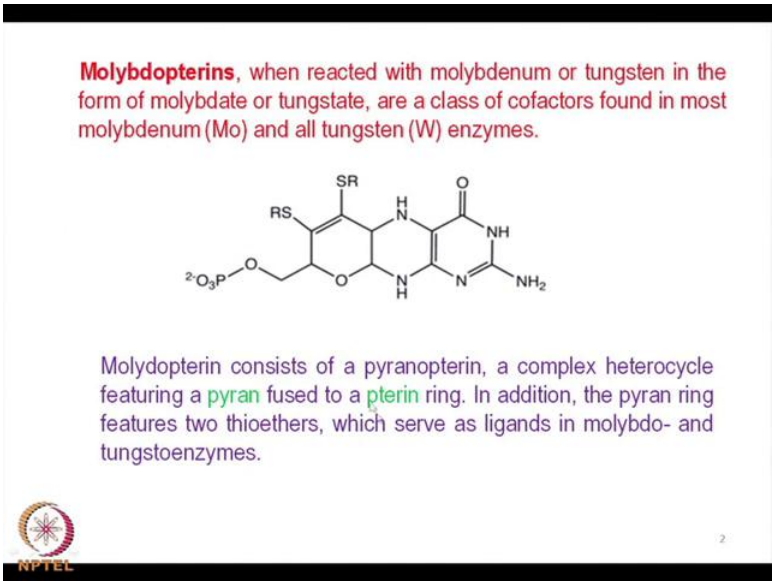

So, what is that, so this is your molybdenum factor, so this particular part is derived from some other thing that how it is derived well as you see that this is without molybdenum. But, since it can catch up molybdenum nicely we call it as a molybdoterimes when reactive molybdenum or tungsten because little bit we will see about the tungsten also because you

know that the chromium molybdenum and constant they have the similarity. If molybdenum can give rise to such species or such compound we expect that tungsten also will give all these molecules, so form a molybdate or tungstate.

So, basically not another molybdenum because molybdenum always have some acenity for the corresponding formation of the molybdenum species this is very difficult to get molybdenum compound without your oxo center. So, always go for the corresponding species as the molybdnate and the tungstate are class of co factor is found in molybdenum and all tungstate enzymes. So, this is basically we call it as molecule terin and it is basically the one such co factor and when we see the entire molecule we always try to find what we want the groups basically present which can go and bind to the molybdenum center these are the two sulfur you see that this particular part.

This particular part is basically suitable because this parts of S S and the other A S sometimes it is very difficult to identify what are these R groups whether these R groups are hydrogen are any such alkyl function all alkyl group. But, the positioning of these two sulfur atoms immediately tells that this can be a very good by dented ligand like that oxo molybdenum actile acetone compound. So, you need always a bidented ligand system whether it is based on oxygen bidented ligand or sulfur sulfur biegented ligand is molecto molean terri molecule is basically functioning is a whole big molecule.

But, only this particular part will go and attach to the molybdenum center and it is behaving like a bidented ligand. So, these biegented ligands go for the functioning of the corresponding enzyme function or whether the zentine oxidize alfhate oxidize type of reactivity. So, it is consisting of a pyrancpterin complex hydro cycling feature a pyran this is the pyran part this is the pyran part it used to a pattering ring, so basically in the biological system they are bio synthesed. So, in biological system we generate N C 2 we are generating the species and this pyran ring is important because on the pyran ring we have the disulfur function which can be utilized for molybdenum coordination.

So, this pyran ring therefore features two thioethers which serve as ligand in molybdo and tungsteoenzyem. So, why we call it as a molecule terrain part of this this teria N part is other part and the terrain part sometimes we call it as a pyrano terrain ring also. So, the pyrano ring where you have the alfer groups attached to it and those two sulfur groups are basically utilized or molybdenum coordination. So, what basically we get from there is a typical

system is a molecule are nothing but, a useful ligand system is a dithoil ligand, so that of your ethane dithoil what we can have a, is a diethane ligand and which can be generated into.

So, in the biological system can be biosynthesized and interestingly all other rules basically your nitrogen oxygen and all other parts of these groups they are having also potential donor groups functions. But, those groups are not utilized for molybdenum coordination only these two sulfur groups have higher affinity for molecule bounding and this particular part is responsible for molybdenum coordination. So, that we get from this particular one ring fuse to the other and the entire molecule is responsible for coordination to your molybdenum system.

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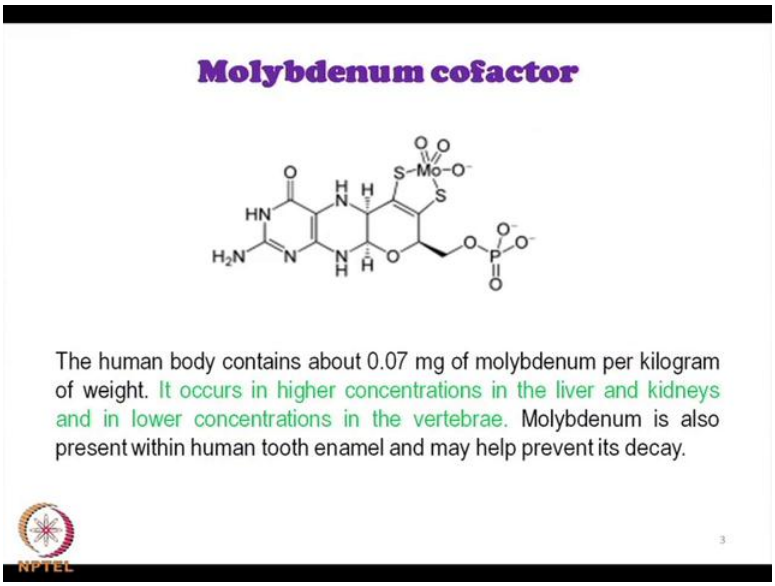

So this particular when it bound to the molybdenum you see molecules you have this, so this basically giving a bidented coordination form these through these sulfur atoms and these two sulfur groups are bound to hydrogen. They can remove very nicely depending upon the P h of the medium, so there can be controlled the hyalite function close to hyalite groups are bound to our hyalite function center. This molybdenum dioxo center molybdenum dioxo group very useful and this particular case we see molybdenum can move from a coordination number of 6 to a coordination number 5.

So, what we all know that any magnetic function like on palladium and that palladium can have a coordination number of 4 and it can go up to a number of 6 also. Here, also molybdenum when it is not in the higher possible oxidation state, but in this particular case

you have these two functions in the S minus and the S minus and the molybdenum dioxo form and this can be some other loosely bound group from the system. So, our human body contains this much amount of molybdenum catcher ate function activities are slowly we are going to know all these things.

So, per kilogram body weight we have only 0.07 milligram of molybdenum and mostly it is available in liver and kidneys and it is in the lower concentration of the vertebrate. Molybdenum is also present in human tooth enamel and may help to prevent decay also because in the solid forms molybdenum form it is little bit it is present within that of your tooth enamel.

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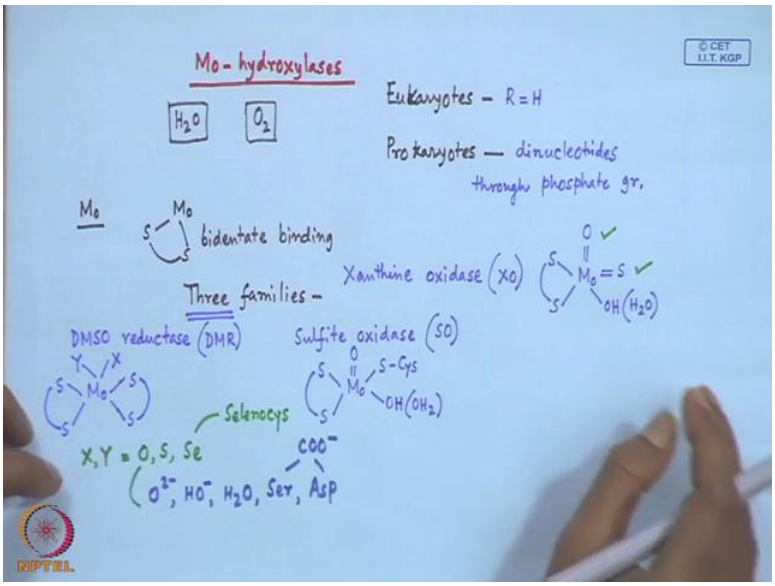

So, when we have this molybdenum and when we identify that this particular molybdenum is at least bound to a diethyl system, so it is a bidented coordination bidented binding from organic ligand part is available. So, basically we will talk in such groups are molecules are 3 families which are cathartically active and these 3 families your first one is basically that of your xanthine oxidase which we consider as X O. That we have in the molybdenum center and is not only sometime bound to your oxoform, but it also from the sulfite function it can be present and which is also present and you have that from the molybdenum to terrine part the sulfur part.

This can settle between hydroxide function and water function, so once you supply the extra proton to function water molecule and it is very easy to remove that from the molybdenum

center because always we know that the water center which is present to any metal center is very loosely bound you can substitute that water by some other group. So, this is xanthine oxidase we can have the sulfite oxidase which we can abbreviate as S O and this basically has a molybdenum oxo center than some sulfur center from tenin sulfur the other one is O age or water.

Obviously, the other two are double sulfur that and that terrain unit, this terrain unit basically fixing the molybdenum system and that particular one is very much useful to go for the different karyotes and prokaryotes. In the particular molecule what we have seen that you have a terminal fasted group this terminal phosphate group is very important and sometimes there are other substitution basically because if we consider this O as O R. So, this phosphate terminal this phosphate terminal can be armed depending upon these different substitution this R can be your age, so in different U corrodes R will be age only basically free phosphoric acid of attachment.

But, in case of different attachment different case of bacteria such as in prokaryotes that have the different R groups, the R groups can be the different nucleotides also you can attach through these phosphate groups. So, these nucleotides that means the different bases and they are corresponding mono phosphate units the cyto sin mono phosphate adenine mono phosphate the govanin mono phosphate and all these we know one phosphate group is ready available. So, you have the molybdenum center and then the corresponding pyran terrain unit and that pyran unit is used for attachment of the molecule. But, phosphate group can also play some important rule to attach the different nucleotides are in a simple phosphate unit.

So, in these karyotes the R group on that phosphate is basically on the age and, in case of the different prokaryotes you have the nucleotides or such as dinuclotides. So, these groups basically can be attached to the molybdenum center how these dinucleartides are attached through phosphates through the phosphate group. So, we are talking about these such families one is xanthine oxidase and sulfide oxidize and other one is D M S O reductance which is abbreviated as D M R. So, in this particular case, so the corresponding coordination measurements are basically different, so here we are attaching all 6 positions.

So, these are common to all other that means these are sulfur sulfur coordination from here and on the 2, so on the other two sides also like our acetyne molecule from the both the two sides sulfur sulfur binding from that terrain unit and you have y and x. So, these groups are

different, so theses what are these y and x functions x and y functions can be oxygen sulfur that we have seen in these two cases oxygen and sulfur. Here, also oxygen and sulfur and sometimes it can be helinium also because we know that there are selenocistin.

So, from the selenocistin we can have selenium group from where are they and these oxygen also it can vary a lot already we have seen it can be your oxido it can be your hydroxide or it can be water. So, you can have O 2 minus these oxygen it can be H O minus it can be water and above these three have the free mine acids also me time the ceriman residue the carboxyl function of the mine acid and aspartic acid also. These two available found also structural also that they are they critical attached corresponding acid function that means these two are basically going for oxygen for C O minus units, so these C O minus units are coming from there.

So, these two groups are basically completely different from when we think of some selenium unit sulfur unit, but otherwise they are very much similar to that of your dioxo molybdenum acetyl acetone unit. So, you have two bidented molecules from these bidented groups are attaching to the molybdenum center. But, the reactivity pattern of these three families of molecules are comparing to the different because attachment of these bidented groups.

Two such bidented groups are basically stabilizing this particular center much more because you have these two side which are reactive. But, compare to this particular one these two centers are coordinated only one side you have the fix co ordination from the sulfur units. But, you have the three groups from the other three sides you can go for the change or the hydroxylation reaction or other reactions based on molybdenum.

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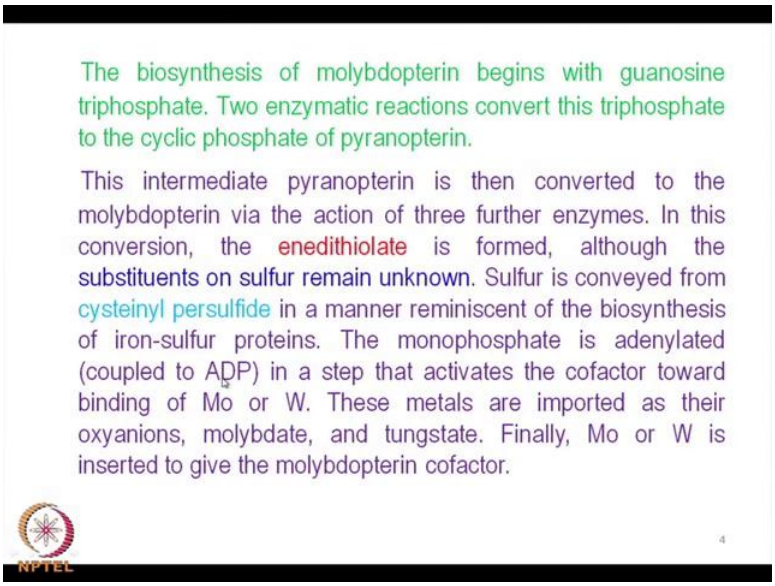

So, these particular biosynthetic part it we should know that the, we have the molybdenum terrain unit is begins with one guanosin tri phosphate structurally how we will see that how you can have the guanosin tri phosphate. For this bio synthesis we have how you get the molybdenum is in the molybdenum center is responsible for giving some enzymatic function but, initially they are generation of molybdenum terrine is also reacting. So, two enzymatic reactions basically convert this type of phosphate to cyclic phosphate of pyran terrine, so guanosin basically your source for the nitrogen bearing part of the molecule molecule is your guano sine.

So, initially you have guanosin tri phosphate and that guanosin tri phosphate is giving you a corresponded cyclic form phosphate terrine. So, if that cyclic phosphate terrine is lost we will end up with the guanosin terrine part, so this intermediate part which is your pyran and terrine converted to your molybdenum terrine by the 3. Further, enzymes is just a, remember of enzymes of action of these enzymes if we can know that all these enzymatic actions is in the generation of is particular center is sustained that.

Here, you required enzymes for the conversion that means the phosphate conversion and after that how you get that molybdenum to terrine part that you know without molybdenum ligand part. So, they are also basically seen further enzymes are utilized and in ditrilate you should recall it to have a double bound. So, you have a double bound in dithalim part, so you have a double bound part and have the ditrilate, so what we are generating on the system you are

generating ad in the ditrilate part because if this particular part is saturated one you have much more flexible by dented liagen.

But, when you have the double bond this much more rigid and the planner structure is conserve when it is going to bind your molybdenum. So, that is why it has some different role compare to enedithiolate, so you have all the ethane diethyl is available in the laboratory you can utilize ethane diethyl to go for molybdenum coordination and you will get the corresponding molybdenum compound. So, although this substituent sulfur remain unknown that the time to tell you that what are the R groups the R groups is developed unable to identify because during the processing this R groups is not available, this is only the molybdenum sulfur centers available.

So, what are the original R groups whether that they are the only hydrogen oxide of molecule is not known so sulfur is compared from cystinin part for sulfide. So, any cystin based molecule is there and it is inciting to if we can generate some for sulfide system. This for sulfide system we all know in a double bound or tribal bound it can go for the attachment to the corresponding organic backbone, so this basically is very much similar to our synthesis of our iron proteins because the sulfur is giving there. The cystin sulfur is available for the binding to your perdoxian molecule, so the monofoxian is monophospahte is adenylated in a step that activates the cofactor to the binding of molybdenum and tungsten.

So, this is particular ligand is available to you and is basically activating the system for co ordination and when these metals are available they are not in the free form they are oxoanase. That means they are in the molybdenum form and the testate form and when they are in the molybdenum form or tungstate form they go a bind to the molybdenum terrine factor. So, inside we adjust generating this molybdenum terin cofactor than little bit we can modify through those sulfur because the sulfurs are required you do not able to utilize the oxygen and the nitrogen for molybdenum coordination.

That is why this like that of your iron sulfur coordination chemistry and the plaster chemistry the molybdenum sulfur chemistry is also very important. So, that molybdenum sulfur chemistry plays an important role because whenever you attach sulfur atoms in the thylate form it can give there corresponding reaction related to your molybdenum center.

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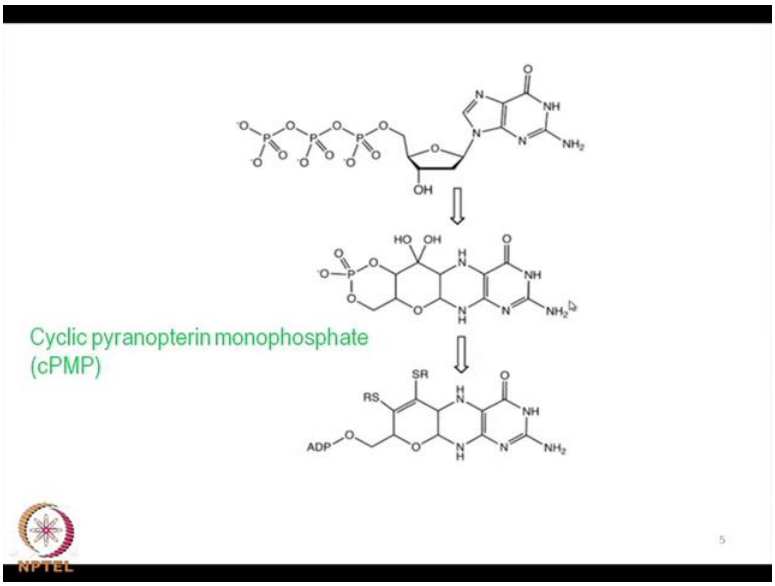

So, this basically what we are getting, so this is what we are getting guanosin tri phosphate, so what we have in your hand, so basically somebody ask you that how you convert the phosphate to molybdenum terin. So, that is very simple to convert enzymatic conversion you should know how the molecule is getting transferred because these are very recent knowledge for ask that how this particular part. So, this is there, so you have the sugar unit and the tri phosphate unit, so this basically giving you the cyclic pyranopterin monophosphate c P M P. So, these abbreviations are all nowadays very much important because sometimes we find some reaction we find or c P M P dependent reaction.

So, it is nothing but cyclic pyranopterin monophosphate, so you see that because it is basically the typical conversion for the monophosphate to diphosphate and triphosphate also A T P A M P and A D P type of conversion. So, phosphate groups are getting hydrolyzed and you have the sugar unit and that sugar unit basically utilized for these corresponding to giving you that the pyranos unit. So, this pyrons ring is formed from this particular sugar unit and this pyrons scope then you have these two positions are available you see that one is coming from the cyclic phosphate part.

So, you have these two average available groups or available points which are there, which are there for corresponding conversion to in diethyl unit. So, this enzymatic function though it is very difficult make a laboratory, so the enzymatic reaction will push us to give something where this particular part is getting modified through the insertion of two sulfur atoms. So,

that it can be a very good ligand with a part which is derived from guanosin molecule, so this bio semantic path way will tell you how we can go or which is basically we call it depending upon your demand because you need a diterial ligand.

That diethyl ligand generating because initially identified that initially we identify the molybdenum center for the molybdenum is required for all these enzymatic reaction and that we identified first. Then we try to identify the immediate environment around molybdenum what I have seen just asked that depending upon the different enzymes what are the molecules molybdenum environment. Then we will have identified the ligand part and these ligand part is also very much important how it can be generated that means people will also able to trace that the different enzymatic step whether you required two enzymes in one state or three enzymes in other safe.

You require corresponding groups as the cystinin part sulfide you requirement of the cystinin sulfur for sulfide how the sulfur is attached to the synthesis. We call the sulfur attachment to the biological system is very much similar to that of your R n sulfur protein formation, so this basically give you the ultimately we can say and we can try to draw the structure that this is the ultimate ligand structure which can go and bind to your molybdenum center. So, this basically reactions are the hole is dependent on the c P M P molecule and that c m P M P molecule is generated.

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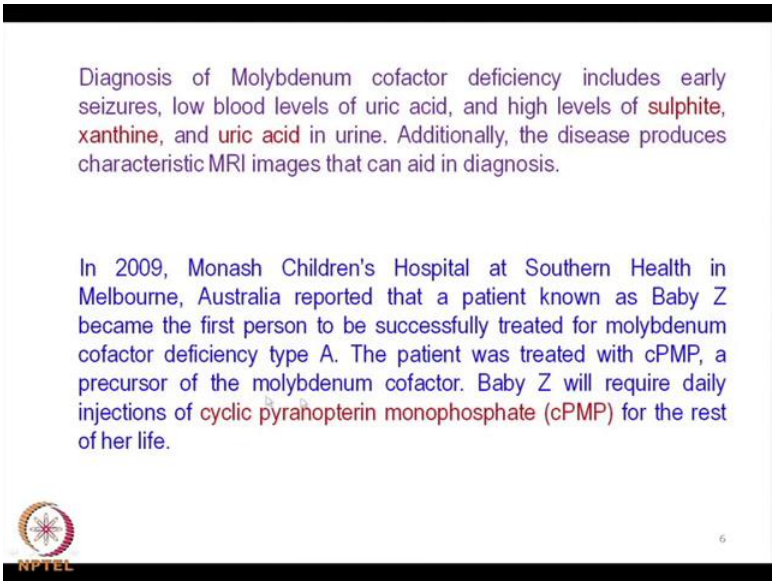

In C 2 atom from the particular molecule which is dependent on the molybdenum, so how these things are very much important because once we identify the molybdenum is essential and its corresponding cofactor is also. So, deficiency also give rise to some problems to us, so the deficiency of the molybdenum cofactor the early seizures low blood levels of uric acid and high levels of sulphate, xanthine and uric acid in urine. So, if you can go some corresponding assimilation reaction where we get the corresponding nuclear base the formation of uric acid, so that we will see in case of xanthine oxidize case that the corresponding concentration of uric acid.

So, uric acid constrictions vary from one particular part to the other that means your nutrition for all these nucleotides are not right. So, you have some problem, so it can go for some disease and that disease can be diagnosed by emerigation, images and which can help you for the proper diagnosis. So, this is one such examples and I am just sighting out example because how people are doing is the only recent example is only 2009 people have identified that is c P M P.

So, well known for this family and this doctor basic ligand that this particular c P M P concentration, so if we have this in our body, so in Monash children hospital people have identified in Australia that is one baby is treated with molybdenum cofactor deficiency type A. We know we consider all about your iron deficiency and all other things what are deficient to us because these are very important, so they have identified very nicely that they have molybdenum cofactor deficiency not molybdenum deficiency. So, not metal iron deficiency not iron deficiency, but the corresponding heme deficiency when we consider that sometime we call that you are deficient in hemoglobin.

But, whether you are deficient in iron or whether deficient in the globing part or the heme part that is very important. So, this molybdenum cofactor what is that molybdenum cofactor is without molybdenum cofactor the other part the other organic part S they have identified that this that particular may be efficient in molybdenum cofactor. One particular type they have identified that level type A and how you get the corresponding relayed they are deficient in this particular one. So, they are unable to produce the corresponding ligand which can bind your molybdenum center, so you supply it externally that is why they have been treated by the c P M P molecule.

So, these, all these nuclear base type molecule the sugar based molecule all you can make in the level of laboratory. So, if the baby is deficient only important thing or the challenging part of this particular type experiment is that you try to identify weather that particular patient or the baby is deficient in molybdenum or the corresponding cofactor. So, cofactor deficiency is very important to know, so that particular thing is very consulting that people can afford in Australia also we cannot afford they required daily injection of c, c P M P for the rest of her life.

So, that is very important but they can try even if they can survive that baby for say 10 years or 15 years, so this is basically research finding and they know it that it is not the molybdenum, but your ligand part. So, that is why there are also very much interested to know the biosynthetic part of the corresponding synthesis of the ligand because I, we do not know, because we know the degradation of the heme part and the formation of the hem part, but we do not know much about all these particular possess when it is related to your molybdenum center.

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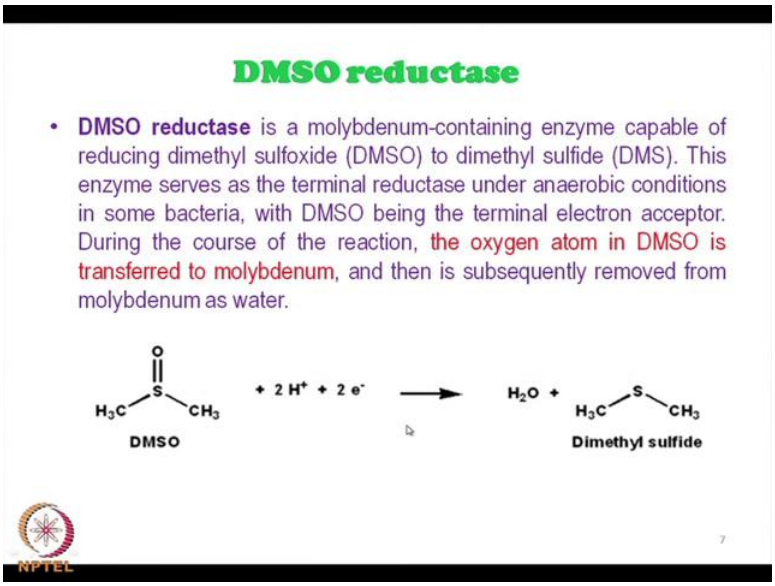

So, one one by one we will just see, so from the first one is your D M S O reductase, so three families we have identified is that.

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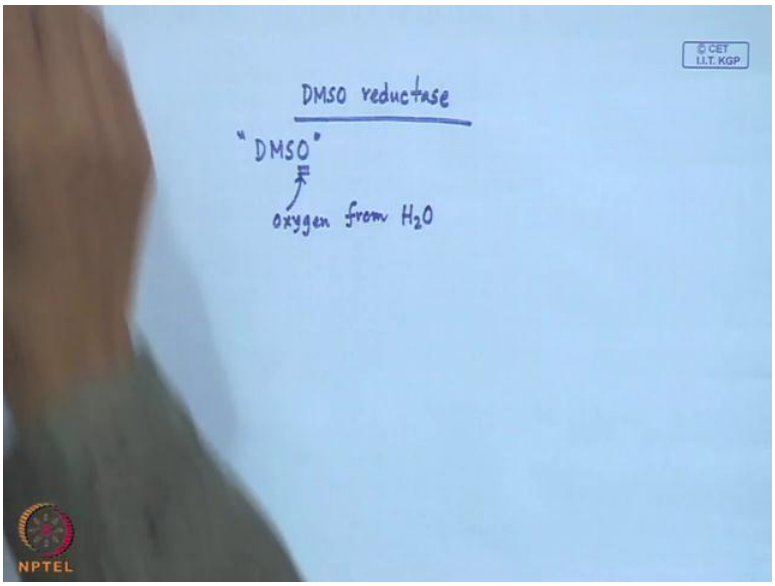

Your D M S O reductase, so in these D M S O reductase how we get this corresponding formation of D M S O molecule through the supply of these oxygen from basically water molecule. So, again is the molybdenum containing enzyme capable of reducing your dimethyl sulfide or sulfoxides, so if you can have the corresponding dimethyl sulfide. So, you can reduce the from dimethyl sulfoxide to dimethyl sulfide or sometime if we are able to get its corresponding dimethyl sulfone S O 2 is the corresponding sulfone form.

So, basically what we are removing these all oxygen we are removing these oxygen, so if it is molybdenum base also if it is a molybdenum base center is available, which is part of 1 oxo center. So, this D M S O can confer that molybdenum center to its corresponding molybdenum dioxo form, so that is basically its tribal reaction. So, is A terminal reduction under anaerobic condition in you do not require dioxygen and that also immediate details are that dioxygen from A R or tioxygen from from any other source these not required for this type of reaction.

So, this basically D M S O being that terminal electron accepters to these D M S O molecule is accepting 2 electron and 2 proton. So, any such reaction changing any biological fraction changes sometime we require there should be some useful groups or some useful mechanism vary its substrate is available which can we functioning there as a very good electron accepter. So, during the course of the reaction the oxygen atom in D M S O is transfer to

molybdenum that is the basic idea that how you transfer this oxygen form D M S O to the molybdenum center.

So, that molybdenum center definitely should not be in the corresponding form that means it is not a corresponding oxo form or the dioxo form, so what we have seen in case of its corresponding molybdenum active sides just. Now, we have seen the corresponding molybdenum active side of D M D O reductase is that it has no oxo or the dioxo form. So, this particular form immediately it will have some bigger affinity means the corresponding these two ligands because this is the D M S O reductance have 2 ligands in all two other cases you have only one particular diethyl group or diethyl ligand system attaching to the molybdenum.

So, you have this molybdenum center which is in the plasic oxidation state and this oxo and this Syrian oxygen. So, these two are your x and y just now what I have told you where you are having the particular D M S O center is based on something where you have 2 diethyl unit like 2 actile action groups and two of these groups are x and y. So, one x is your oxo and another is your Cyrene oxygen, so this particular one and that immediately while you are supplying electron and proton basically these oxido function can be converted to hydroxide and then to water molecule.

So, this specific basically giving rise to you that corresponding or corresponding water molecule, when you transfer these 2 electrons to the molybdenum center, converting this molybdenum 6 to molybdenum 4. So, that is why this molybdenum center is settling between plus 4 and plus 6 of oxidation states and 2 electron state is therefore established. So, immediately what we see that whether you are going from plus 6 to plus 4 state or a plus 4 state to plus 6 state because this particular one like that of your palladium in different catalytic system. When palladium in plus 4 oxidation state we all know that it will be in a hexa coordinated environment, so is basically oxidative addition.

In other case we get the reductive elimination when you go for the retrace of the, of the same molybdenum center we go for reductive elimination that is why you are moving from a hexa coordinated system to a penta coordinated system. So, this penta coordinated system is very useful therefore, so when we basically reduce the system that means from molybdenum plus 6 to we are going to molybdenum plus 4, here supplying electron that means you can do also electro chemically. Suppose you do cyclic boltametry and you take this particular molecule

and the corresponding cyclic bolt among the gram will tell you that whatever species you are generating after reduction because this you are going for a chemical reduction.

But, electro chemical reduction is also possible and you are supplying two electron and if you do the same electron chemistry in some protic medium not in pure acidonitile or pure diechlo methlyn. But, in some medium where you have the proton that means that the aqua medium also because the removal of these oxo function you require this proton, that means the protonation is required for the removal of these oxido function as hydroxide and ultimately as the water. So, this hexa coordinated system species is going back to a penta coordinated one the cyclic voltrametric trace will immediately tell you that these particular environment.

These two coordination environment are different because this particular one is not going for only electron transfer, but some other group transfer because this group is not they are this group is not resent over there. So, this oxido function not they are also considered as some group transfer oxidation reductance reduction. So, once you reduce it, so once you reduce it your oxo reductase function is going anywhere getting some penta coordinated one that means on the other hand you are able to generate some molybdenum species species in low oxidation state.

Like that of your palladium centre or some other catalyc center in the 0 oxidation state also you can go for its corresponding reaction dimethyl sulfoxide. So, dimethyl sulfoxide can nicely transfer this oxygen to your molybdenum center these blue oxygen atoms is immediately transferring to the molybdenum center because what we get some time that water molecule can give rise to corresponding molybdenum atom, oxo compound. Some hydrogen peroxide also available going for this, but if you utilize this particular one you do have accidently some time covered all these things routinely.

Followed all these things because why we are bringing the question of measurement in the form of electro chemical measurement or cyclic voltmeter because this particular species is a useful solvent because most of the time when you go for studying molybdenum compound, electro chemical measurement. If the corresponding compound is not soluble in diclode methlyn if it is not solvable aceto nitrate or even in D M F we try dimethyl sulfoxide, so dimethyl sulfoxide is a routine solvent for all these sort of measurement.

But, remember we should remember very nicely that this particular one that is not reacting with the compound of this type if it is reacting we will end up with the some dimethyl sulfide.

You get able to identify the corresponding dimethyl sulfide from the medium it has some typical smell also and from the solvent medium you can recover dimethyl sulfide which can also establish that during catalytic cyclic involving electro chemistry also. Cyclic voltmeter also you can generate some amount of dimethyl sulfide from your solvent which is your dimethail oxide.

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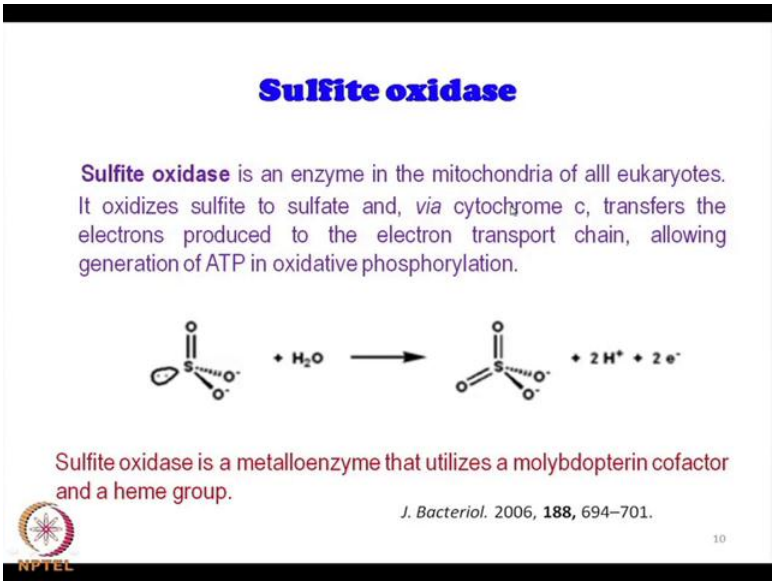

So, that is why related to that is very important, so next day because today we are not able to cover this one also the second one that sulfide oxide we will study. So, in this particular case is enzymes, so definitely again like that of our dimethyl sulfoxide thing that means you can transfer these oxygen sulfide to sulfate and what we all know because these are very useful biological system. They are very mild system and sometime we get to know that they are going via some cytochrome C which basically your source of electrons because we are not using some any other chemical reducing agent or the electrodes system for this electron transfer.

This transfers electrons produced to the electron transport chain, so we all know that cytochrome C, cytochrome C oxidase all they are present in cytochrome electron transfer chain so if at some point we required so many electrons. That means we require 2 electrons to activate the molybdenum center and that activation for the molybdenum center is useful for the oxidation of the sulfite to sulfate unit. So, at that same time like since we all know that the

corresponding electro potential that how much free energy you transfer from there, so basically we can also allow the generation of the corresponding A T P.

So, phosphate transfer potential is useful, so phosphate transfer potential if it is available for this electron transfer of reaction of conversion of sulfite to sulphate at the same time as a byproduct definitely. So, as a byproduct we should be able to produce some amount of A T P molecules, so basically we are very much getting some useful molecules like A T P during the corresponding oxidation of sulfite to sulfide. So, it is again molybdenum is depended an enzyme and the same molybdo terin cofactor is utilized for the conversion of this reaction.

Now, which is not there case of dimethyl sulfoxide type of operation or using molybdenum enzyme that him group is required where is heme group that is also a molic system also a reaction where it is depended on cytochrome C since it is cytochrome C depended. Therefore, the corresponding sulfite oxidase should also be depended on your heme group that means this is depended on two such metalo enzymes, one metalo enzymes is involving molybdenum and other part is involving your iron centre. That means iron hem which is present in cytochrome c molecule is also involve for sulfite oxidase so you can have the detail information from this reference for this molecule.

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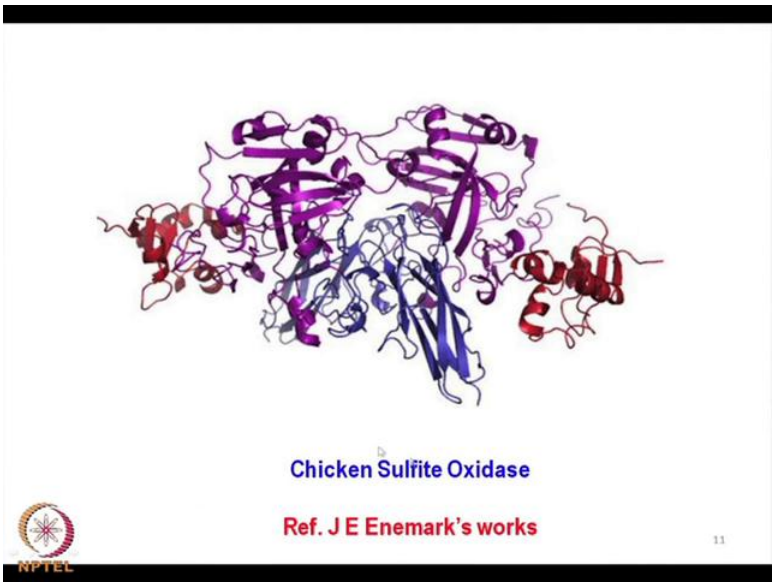

So, little bit I will just carry on next day also that this is the whole complicated molecule and this person is well known for on this molybdenum sulfur chemistry John E Enemark, so even if you go for his site I have taken it from his site basically his homepage. So, you will get this

particular information that this they have the corresponding protein structure for the enter molecule. When they crystallize this particular thing because what we have seen that, during the determination of this all enter protein structure and the protein structure solutions are sometime very different without metal centre.

So, we should be very happy if you have a metal centre over there that means solving the structure of only the corresponding ligand part without metal centre is sometimes difficult because because the scattering factor is related to the heavy metal or the heavy centre. One particular technique is well known that the heavy atom method, so we are lucky enough if you have a corresponding metal centre within the protein structure is very easy to crystallize it.

Crystallize it is helping your crystallizing process because until and unless you do not get the good crystal you do not have the corresponding protein structure. In this particular case what we will see that during this conversion basically is not that particular metal centre is available in the metal centre are there definitely depending on the molybdenum and iron. But, this particular anion when it is forming for the sulfite function and it is converting to sulfate and that sulfate is basically trapped inside.

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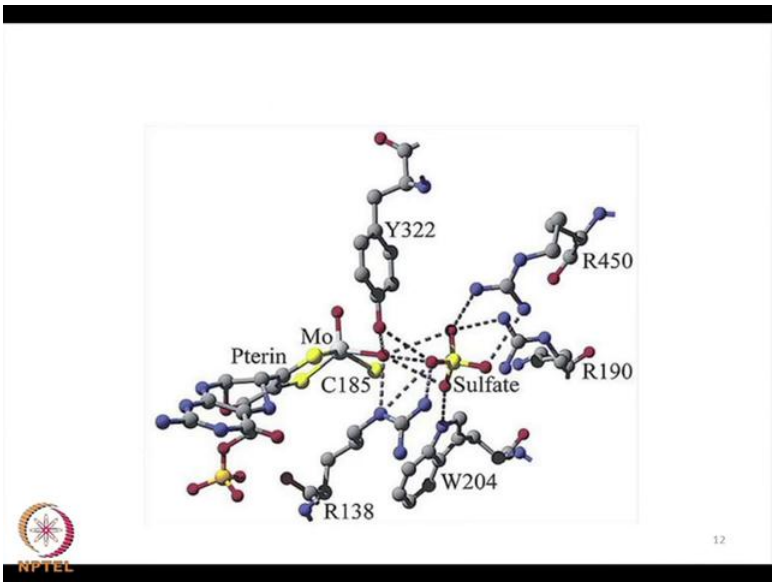

So, sometimes we call will just do not worry for that will come back again when this particular one, so you see that the product that means sulfite has been converted to the sulfate and that is being trapped within the system. So, this particular system is very easy or you can

characterize it, I can crystallize it and identify the molybdenum centre as well as the sulfate centre very nicely. So, this is basically system, because we have studying so much about the corresponding anion recognition, all these things. So, now anion which is produced from the system through the oxidation of sulfate is now being trapped within the molecule itself, so molybdenum centre is there and sulfate what is formed is getting trapped.

Thank you.