Bioinorganic Chemistry
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Lecture - 35
Vanadium Enzymes - III

Very good morning to everybody, so still we are with the vanadium, how the metal is responsible for different kinds of reactions in biology that we will see.

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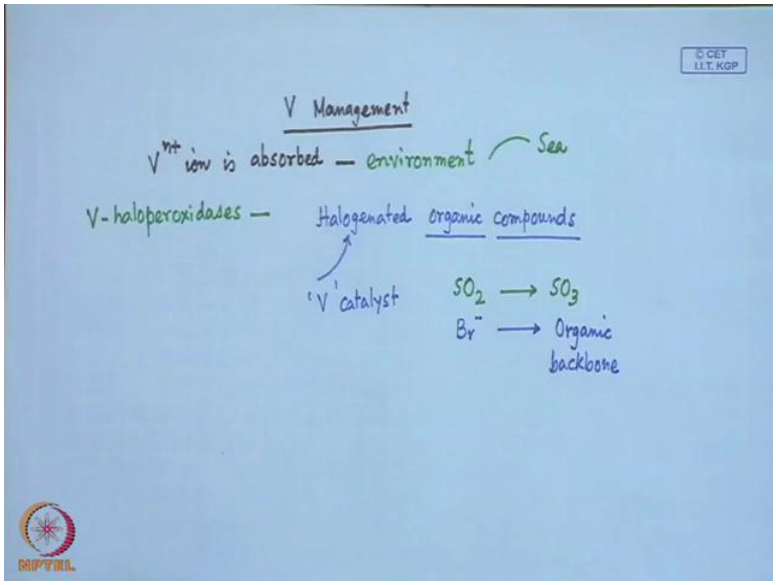

And interestingly the vanadium management in the biology is important, because we are discussing something where this vanadium in some oxidation state in ionic form is basically absorbed by the living system and that absorption which is dependent on the environment.

So, how the environment is responsible, if the environment is typically the marine organism's for the sea. Then will find how the sea water not only containing vanadium, but also some other important species other important chemical species, which can be managed by this particular center which can sometime behave as a very good catalytic center.

So, today we will just follow the vanadium enzymes part III, because we are one after another we are continuing for these different type of enzymes; one important enzymes for that system is the vanadium based different haloperoxidases. And those we have seen

that is a very important reaction, because most of the organic compounds that we all know that there are some halogenated organic compounds have some useful properties, halogenated organic compounds and if this particular one; that means, how we can halogenate a particular organic basic mighty that can be seen, so like that of the metal ion; that means, the vanadium.

So, this vanadium center can act as a very good catalyst as we all know that V 2 O 5 is also a very good useful industrial catalyst for the preparation of sulphuric acid by the contact process where V 2 O 5 is the right catalyst. So, not only manipulative when you have studied the tungsten, when we have studied the molybdenum sensor system. Now, this vanadium system is also not only useful for transferring the oxo center because in the contact process sulphuric acid preparation, we basically go for the conversion of SO 2 to SO 3. But now one more important thing one important chemical reactivity pattern can be shown by the vanadium compound is that, we can handle some of these halides like bromide chlorides or iodides for the incorporation this bromine within the organic backbone.

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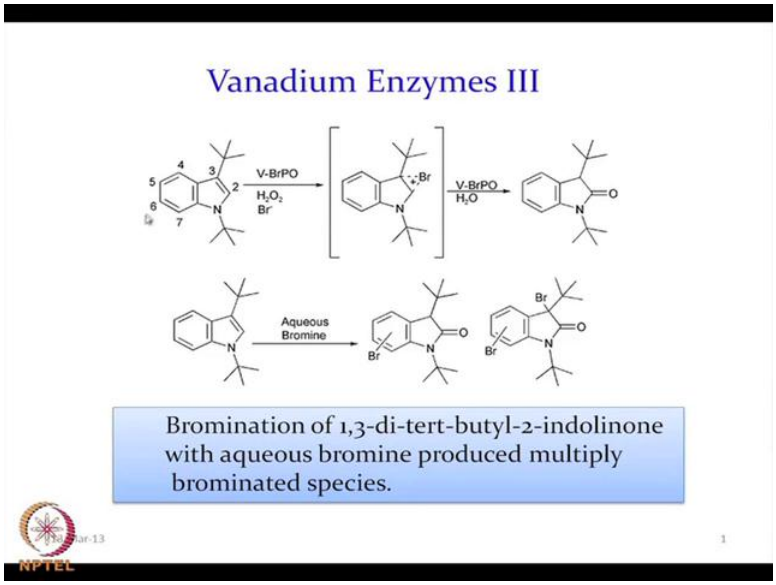

So, people have tried for different reactions for the direct incorporation of this bromide ion in some large and complex and sometimes medicinal important molecules. So, this is one such example, if we can have highly substituted one this carbon is substituted by a terceributile group. This nitrogen is also substituted by terceributile group, that means,

this carbon does not have any hydrogen is nitrogen also does not have any hydrogen for bromination reaction. So, if we want to have some other positions, where the available CH bonds are there and we expect that some kind of bromination selectively on those carbon atoms.

So, if we get that particular product then those molecules like our marine natural products can also be useful medicinally, they can have some pharmaceutical importance and we can use them as drugs or medicines. So, very simple reaction has been tried with this particular substrate with that of our vanadium bromoperoxidase. So, this is the living enzymes. So, the enzyme has been taken in presence of hydrogen peroxide and bromide ion.

So, the basic idea behind this thing that what we have studied last time or the previous class that we are able to form some bromonium ion by the enzymes the hydrogen peroxide and the bromide ion. So, if bromonium ion is available over there and is interacting through this particular double bond this C C double bond between carbon number 2 and carbon number 3. So, if it starts interacting with this particular double bond which is much more reactive compared to the other double bonds which are resonance stabilized within the benzene ring.

So, what do we expect that we expect that there should be some bromination reaction on this particular carbon. But instead of that we go for this particular bormoperoxidase vanadium containing bromoperoxidase is responsible for typical oxo transfer reaction what we see basically for the different different types of oxygen insertion reactions in the organic backbone. So, like that of our molybdenum compounds or that of our tungsten compounds what we see in this particular case same reaction is happening instead of the corresponding intermediate based on the bromonium ion that.

This oxygen of this particular water molecule which is there in the reaction medium is getting activated by the bromoperoxidase enzyme and that particular enzyme is therefore, going for the corresponding oxo transfer reaction from the phenadyl ions. So, phenadyl ions is forming over there and that phenadyl oxygen is getting transferred to this particular carbon center to give you the corresponding oxygen transfer on the substrate molecule.

So, what we were expecting that we should have some kind of bromination reaction on this particular substrate, but that we are not getting instead of that, we are getting some carbonyl function on the backbone on the five membered ring on the right hand side of the substrate. So, this can also be encountered, if we instead of using the enzyme we can use the aqueous bromine solution.

How the same substrate behave towards the aqueous bromine solution, how the bromination reaction can take place. Whether that particular reaction can selectively go for bromination in some of this carbon atom, because these nitrogen and this carbon is sterically crowded and substituted nicely; we do not have any hydrogen atom available for substitution by the bromine atom.

So, this basically give two major products one is for the bromination at this particular carbon, which is already substituted and as well as the ring bromination and other one only ring bromination. So, we basically get multiple bromination reactions so we do not get any reaction, where the selectivity can be seen. So, this particular reaction with aqueous bromine is less selective and gets you multiple products and the bromination reaction for a particular region cannot be chosen.

So, this particular direct reaction with aqueous bromine is not very useful one compared to the corresponding bromination reaction using the bromoperoxidase molecule. So, bromination reaction what we have seen here is that one three di tert butyl one indolinone with aqueous bromine can produce multiple brominated species. What we expect we still expect that if we can make some modification in the reaction medium that we can avoid this particular carbonyl group insertion in the molecule, we can expect some amount of bromination within the some other substrate or this type of substrate with some modification within the backbone.

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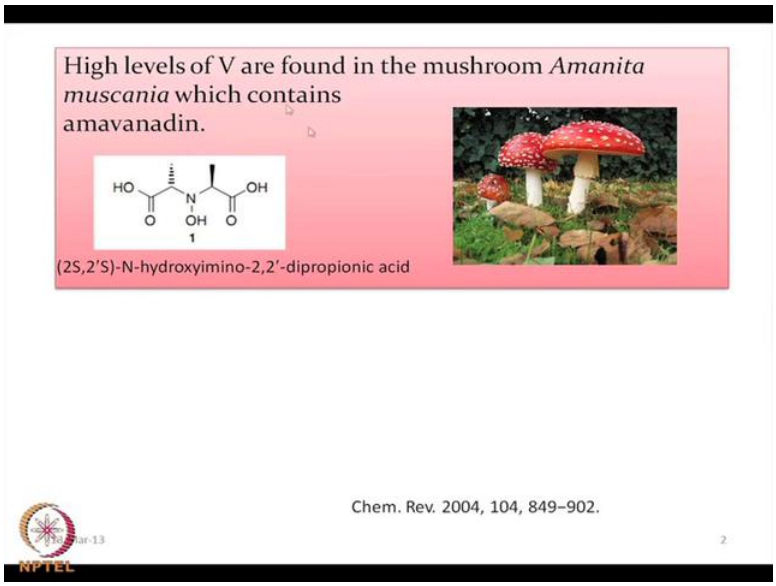

So, in the next part what we will see that a typical system in the marine organisms, where we will see that high levels of vanadium we found in the mushrooms. So, the mushrooms are also can have bromine, so one such variety and one such category has been identified in amanita muscania which contains amavanadin. So, we can have some selecting ligand like that of our siderophore.

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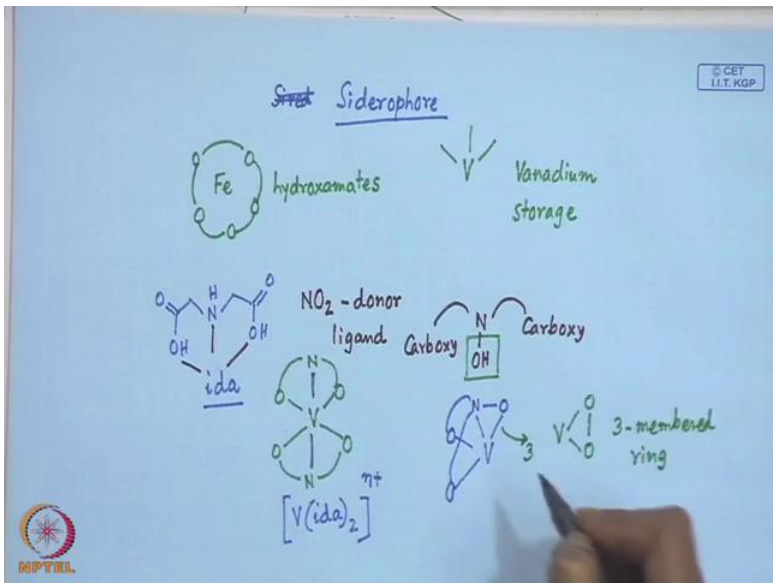

So, this is basically a siderophore type of molecule siderophore, so is basically a siderophore type molecule where we have seen the different siderophores; that iron

center was there. And the oxygen based macrocyclicgeleting ligands are available and basically those are hydroxamate based and those hydroxamate based geleting ligands can bind iron nicely for storing iron for biological requirement.

So, hydroxamates are there for binding iron within some macro cyclic kelet ring. Similarly if we want to bind this vanadium, so what type of ligand we should use to bind vanadium in the biological system. That means, we are talking something which we can consider it as the vanadium storage molecules, vanadium storage system. So, how it can store basically, because we can have some free vanadium ion and what are the typical ligand system that we basically get for the corresponding vanadium binding.

So, if we have this carboxy enduring dichropunic acid base ligand which is 2 S 2 S 2 in hydroxyl amino two two phrine di propunic acid. So, in hydroxyl amino which is very much similar to that of our amino di acetic acid because amino di acetic acid we all know is a very standard ligand system, which is ida amino di acetic acid. So, basically this particular one is a very useful N O 2 type ligand. So, nitrogen donor one nitrogen donor and two oxygen donor N O 2 donor ligand.

And one such ligand can bind one vanadium through this oxygen through this oxygen and this nitrogen. So, similar to that only difference in this particular case is that nitrogen, now we have that in O H group. So, we have this the carboxy end and on the left also, we have the carboxy. So, what is the difference between this amino di acetic acid and this N hydroxi amino. So, N hydroxi amino this is the difference is only N hydroxi amino. So, how this particular N O H group compared to the N O H can function towards the binding of the vanadium ion that we can see. So, if we have this vanadium center for this amino di acetic acid.

So, this particular one, so this is the nitrogen one this is the oxygen and this is the oxygen, similarly on this side we have nitrogen oxygen and nitrogen. So, very standard and very regular octahedral coordination can be seen, if we use this ida ligand for vanadium binding and two such ida molecule can bind vanadium and depending on the vanadium oxidation state. We can have that overall charge in plus on the molecule on the typical isolated molecule. So, whether it is cationic we should provide some anions to crystallize it from the solution.

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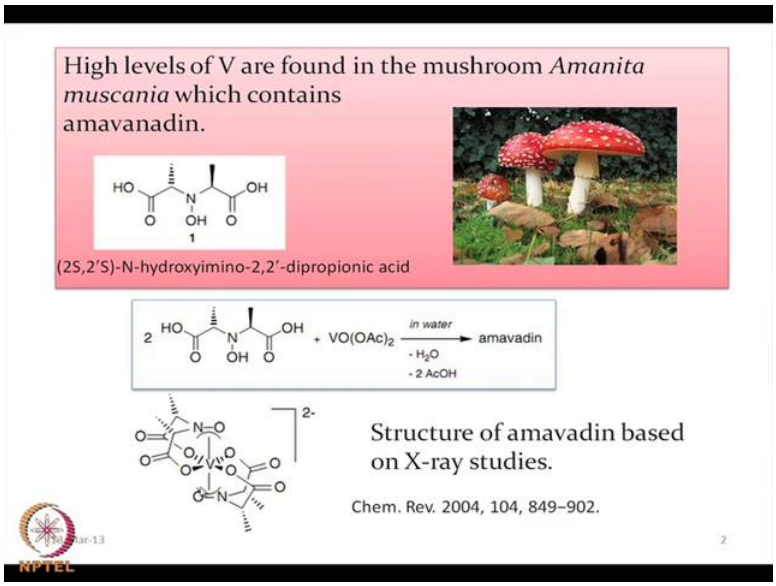

So, when we have the N O H function in it and how this amavanadin can bind in the mushroom to take up vanadium from the molecule. But the reactivity for this what people have studied afterward because synthetically this particular one can be made in the laboratory; and when we react with V O vanadyl acetate anion in water. So, vanadyl acetate can in water giving rise to removal of one water molecule and one acetic acid giving rise to amavanadin.

So, in the same way what we have seen just now that for amino di acetic acid, where N O H group isnot present only the n h function is present and two such molecule can bind to the vanadium center to give this particular type of octahedral compound as amavanadin. So, amavanadin will be very useful molecule, because this low molecular weight ligands can be available in this mushrooms and vanadium can be stored nicely over there.

So, in this particular form what we see that this vanadium can form four such binding positions like these of the carboxylic O H O H group, so four such groups are there. And these N O functions this N O functions can function or bind differently where, when we have the amino function we direct binding for these nitrogen to the vanadium this nitrogen to the vanadium, but when N hydroxin N hydroxi amino function is available what we find that this vanadium is basically pointing towards the nitrogen oxygen bond. That means, it is forming a triangular kelet ring where both nitrogen and oxygens are

bound to the vanadium center which is very much similar to that of our binding of peroxide anion to the vanadium center.

So, this sort of three membered ring already we have seen is possible for peroxide binding to the vanadium center in bromo peroxidase in chloroperoxidases in other peroxidase molecules. So, here also since this nitrogen was known that in case of this amino di acetate binding this nitrogen is there. And we see that this nitrogen to the vanadium molecule and this sort of binding if they are not in the facial form that can be also in the meridional form. So, one face of the octahedron, so vanadium is there. So, we basically this two are we can have and we have two of these one such ligands, so this ligand nitrogen and ligand oxygen.

And this basically giving the carboxiend of this and this is another carboxiend of this giving rise to the binding of this particular half of the molecule. So, this V N O binding is V N O binding is very much similar to that of our vanadium peroxide binding, what we have seen in case of bromo peroxidases or other. Same type of synthetic molecules that these three membered ring is possible. So, when binding of these N hydroxo ligand is in the same fashion and when we have this tridented binding like this and we have the o. So, this particular o giving rise this particular depotonationand, we have this particular three memembred ring, so these also a three membered ring for stabilization of this particular ring.

So, this binding and these coordinations also are very important and we basically get the corresponding thing form x ray structure determination. So, structure of the amavanadin molecule can be identified through single crystal x ray structure determination. And we find that the typical coordination because if we consider all the binding positions; that means, this nitrogen this oxygen and four oxygen in the plane; and on the other side this nitrogen and this oxygen. So, all together eight atoms eight atoms from two such ligands are involved in trapping vanadium in the mushroom molecule. So, what we see that this sort of thing when it is forming and mostly vanadium storage is important and also the electron transfer behavior.

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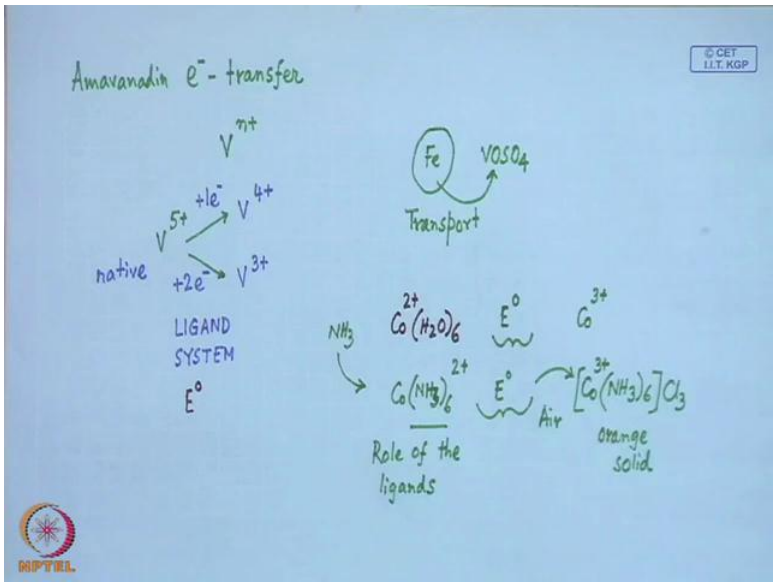

So, this amavanadin molecule can function as a very good electron transfer molecule, it can show one electron transfer; that means, whatever vanadium center we have in the amavanadin. So, is in plus, so it can donate one electron to the system or any other molecule or it can except one electron for any other reducing agent. So, both way you can only go for changing one oxidation state once step oxidation state, so that is why we consider it as a one electron redox mediator.

So, only it can go for a single electron transfer from the system and the ligand what is present there in hydroxydicarboxy ligand is very stable towards hydrolysis that is why it is not releasing vanadium. So, easily because if the ligand is hydrolyzing very easily only we are ending with some aquavanadyl compound, but this particular ligand is not undergoing any kind of hydrolysis reaction. So, they are very stable and we can trap vanadium very nicely within this molecule. And also we can see that if we take the laboratory available molecule like vanadyl sulphate instead of vanadyl acetate, what has been prepared from the vanadium molecule has been found to interfere with the siderophore mediated iron transporting bacteria and plant.

Just now we were discussing that iron center is there and we can have some siderophore ligand to trap this vanadium sorry iron and this siderophore ligand system is well suited; that means, the cavity size is such that it can trap iron. Similarly, when we can use if we use vanadyl sulphate for the system and if the same ligand is available for trapping

vanadium as well as vanadyl ion then basically this particular one in different bacteria and plants the availability of this particular salt is only hampered the corresponding iron transport. So, iron transport mediated by siderophore molecules can be disturbed by the presence of vanadylsulphate why because this particular vanadyl ion or the vanadium in mono oxo form can go and.

Nicely substitute the iron bound to the siderophore ligand and it cannot help or it cannot go for the transfer or transport of iron from one side to the other. So, in both bacteria and plant is vanadylsulphate interference tells us that vanadium in a similar fashion like that of our iron can be bound to the siderophore type of ligation and we also see that when vanadium is taken up as vanadium 5 from sea water. So, in the pentavalent oxidation state it is initially trapped by the ligand and inside the cell what we see that when they are getting stabilized it is not the plus 5 oxidation state it is some reduced form of this metal ion; that means, the plus 3 or plus 4 oxidation state is getting stabilized in aqueous medium.

So, how we get that, so from vanadium 5 we have to get the two other species which are vanadium 4 plus; that means, we should go for one electron reduction or vanadium 3 plus where we have to go for a corresponding 2 electron reduction. So, there should be some available reducing agents which can reduce directly that vanadium available in the sea water in plus 5 oxidation state.

So, this is the native metal ion which is directly available from the sea water by the ligand system. So, you have the ligand system the siderophore type ligand system and this particular ligand system when you all know that when this particular ligand is going to bind the vanadium 5 basically we can manipulate the E 0 value and immediately after binding the reduction potential is going down, and it can be reduced nicely by some biological reducing agents to vanadium 4 plus or vanadium 3 plus.

The same thing what we know in the laboratory chemistry that if cobalt two ion is present that means the any cobalt salt cobalt two chloride is present, and which we dissolve it in water when you dissolve it in water it basically binds 6 water molecules. And these 6 water molecules give a typical coordination environment which has a characteristic E 0 value for the oxidation reaction to cobalt three plus and if the magnitude of these E 0 values is quite considerable. We cannot get the cobalt three

compound of the hexaco environment; that means, the hexa co cobalt three plus is not, so easily made.

But, if we just simply add some ammonia aqueous ammonia within the system which immediately replaces all 6 water molecules by 6 ammonia molecules. And as a result our coordination environment is getting changed from O 6 environment to an N 6 environment. And now the corresponding E 0 values for this particular species drops down, and we easily oxidize this particular compound to cobalt three plus; and we know that air is only sufficient for that oxidation.

So, the oxygen molecule present in air can oxidize this particular species which is not possible to oxidize this one to give us corresponding hexamine cobalt three compound which can be isolated as the corresponding chloride salt as a beautiful orange solid. So, the importance of the ligand, so this is the ligand, so ligand is playing some important role in manipulating the corresponding E 0 values. So, the role of the ligands used to binding the metal ion.

So, role of the ligands and therefore, important and in the same way if we have the ligand system which can reduce the corresponding E 0 values for that reduction reaction from the vanadium 5 to vanadium 4 and vanadium 5 to vanadium 3 play. We can easily reduce these two and we can stabilize this particular oxidation state the reduced form of this state metal ion can be stabilized in that particular ligand environment and that can be stored nicely.

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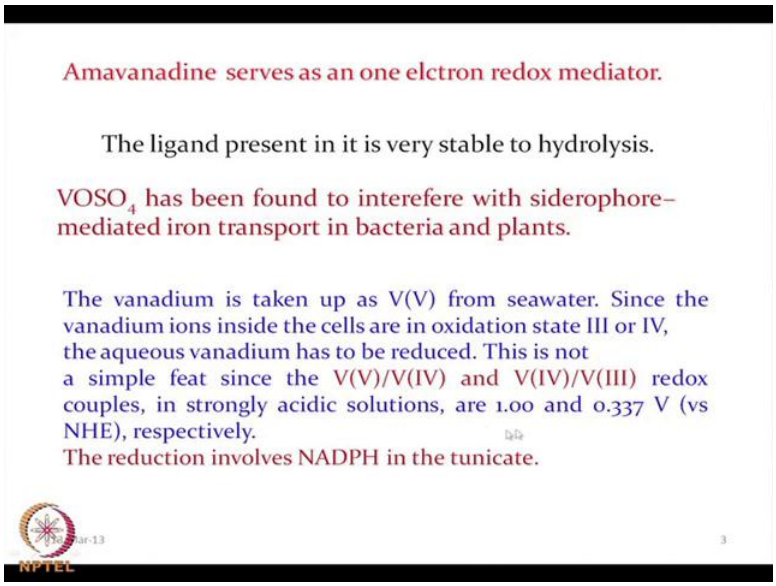

So, if we consider only the vanadium aquousion like that of our cobalt system, that for the reduction reaction for vanadium 5 to vanadium 4 and vanadium 4 to vanadium 3 is not so easy to have it. Because the strongly acidic medium at very low p H value say p H 1 or 2 these redox couple for these corresponding reduction reactions are 1.00 and 0.337 volt, but its normal hydrogen electrode.

So, these potential are pretty positive so whatever biological reducing agent available to us like NADPH or FADPH. So, these are not useful to reduce this particular aqueous vanadium ion. So, aqueous vanadium ions like that of our cobalt ions what we are seeing just now are not so easily reduced back to a particular reduced form where we can stabilize this particular metal ion in that particular oxidation state.

So, when ligand comes into the picture and it binds to the vanadium center the E 0 vale is getting reduced and we can use NADPH nicotinamide adenine dinucleotide NADPH as the useful biological reducing agent or biological reducten. And in all these tunicates and all other system where vanadium is stored this particular vanadium center can be reduced to either vanadium 4 or vanadium 3 and they are stored over there very much.

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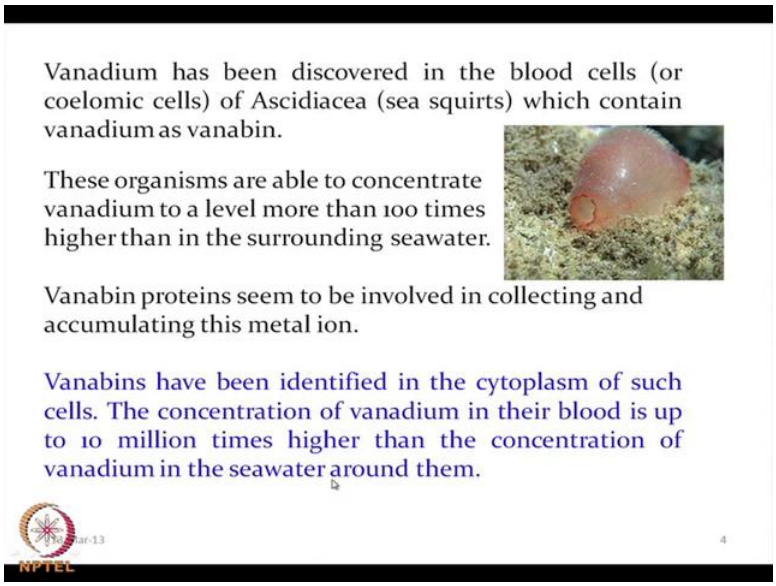

So, this particular one as well as this amavanadine is also some other molecule other biological systems like the sea squirts and coelomic cells in the blood cells of this. So, ascidiiacea which contains also vanadium like amavanadine. But this time the molecule is stored as vanibin, so these vanabin molecule which available again from the sea level. So, the sea squirts which are there can bind and can trap vanadium over there. And these are the benezens basically are available to concentrate vanadium at a level more than hundred times higher that the surrounding sea water. So, in sea water we have some available concentration of vanadium.

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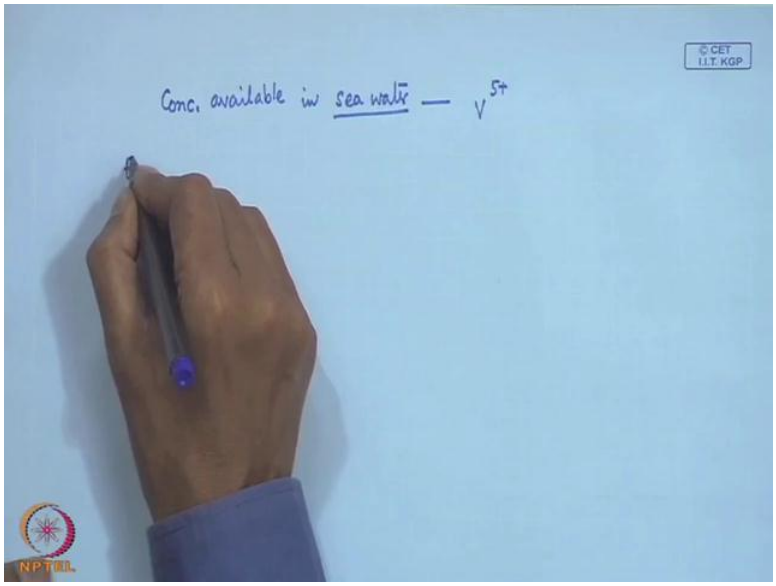

So, you can consider the concentration available in sea water is some concentration vanadium say vanadium 5 plus. And the ligand is available which binds this particular one and then transfer to this particular marine organisms and this transfer of these marine organisms for this particular one is also changing the corresponding concentrations within the living organisms; because this particular concentration what is available in sea water is pretty less.

But, due to this accumulation of this vanadium by the ligand system available there we can increase the concentration level in all these organisms which is much higher than the available concentration in the sea water. So, sometimes hundred and sometimes more than 100 times concentration or enrichment vanadium enrichment, we can call it from the sea water can be achieved by all these organisms through noise binding of vanadium by some useful groups. So, in this particular case these are the vanabin proteins and these vanabin proteins are therefore, responsible for binding the vanadium ion transferring the vanadium ion to the system, and then finally accumulating that particular molecule to the living organism.

So, it is this particular protein system, which is required for collecting and accumulating this metal ion. So, it is not only binding the metal ion it in the bound form it basically collects the metal ion and ultimately it is in their system accumulating the metal ion. So, we get higher level of concentration for the vanadium in their body.

So, vanabins can be identified in the cytoplasm of such cells. So, if we can like amavanadine we can identify vanabins and some time it can go up to 10 million times higher than the concentration of vanadium what is found in the sea water around them. So, basically it is concentrating within their living system and we are getting more concentrated vanadium in the living organisms related to these all sea squirts.

So, if we see that vanadium is thus essential for ascidians and tunicates and they are stored in a highly acidified vacuoles of certain blood cell types. So, if their blood cells are responsible for generating some vacuoles and those vacuoles can be termed as corresponding vanadocytes like lymphocytes or any other biological systems which is having some affinity for vanadium ion we can call them as the typical vanadocytes. So, vacuoles can be formed and those vacuoles can be utilized for binding the vanadium ion and can be storing the corresponding vanadium into the system.

So, vanadium 5 which is present in the sea water thus can be reduced already we have seen in these two oxidation stage. And can be stored in the soluble form within the very base acetic vacuoles because these vacuoles are very acidic and in acidic condition what we see that the electron transfer behavior already several times I told you that the E 0 values for the reduction potential the standard reduction potentials for these systems.

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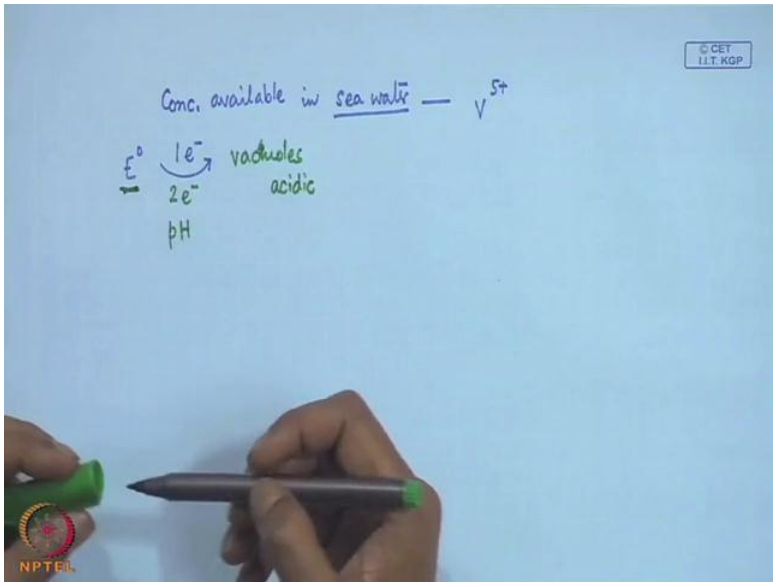

So, we just go for the corresponding electron transfer, whether it is a single electron transfer or a double electron transfer also in some condition, where p H there is some important role for the corresponding reduction reaction, so if the vacuoles, so if the vacuoles, so vacuoles are there and which are highly acidic in nature. So, the corresponding E 0 values what is that available for this reduction reaction must be well matched to that of our biological reducing agent. So, we find that the corresponding observation that whether your E 0 value is less or more in acidic medium compared to

the basic medium that is also responsible for storing the corresponding vanadium in these bodies.

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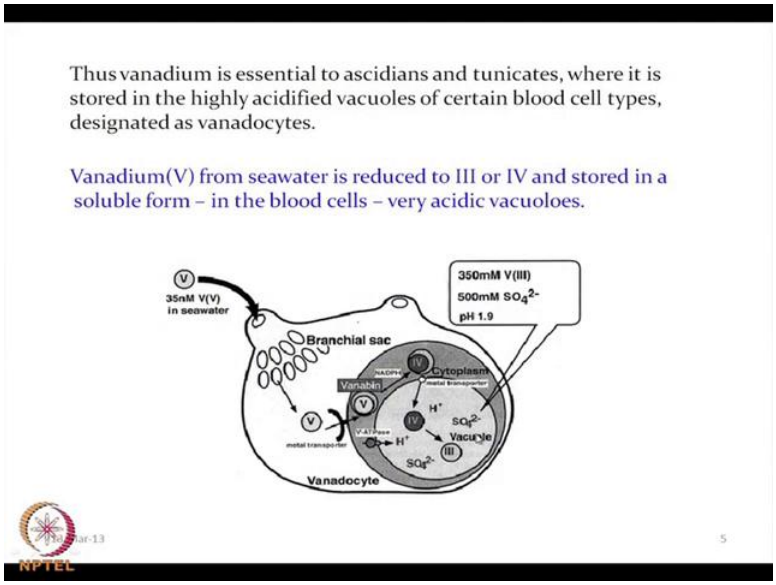

So, this is a typical form where in the living site what we see that the cytoplasm is there and vanadium in the highest possible oxidation state in this particular case vanadium 5 plus in sea water and is entering through some points in the membrane. And branchial sac's are also there, so these are basically trapping this particular vanadium and these vanadium in plus 5 oxidation state this is the oxidation state and they are known as metal transporter and the entire area, we call it as the corresponding vanadocyte. And when it is crossing this particular barrier in the cytoplasm, this can be stored in the vanabin.

And initially the vanabin the ligand the corresponding ligand which is being supplied to binding the vanadium 5 initially binds these vanadium in the pentavalent state. And NADPH is available and NADPH is there which is reducing this vanadium center from vanadium 5 to vanadium 4. Though for the entrance of this particular cytoplasm barrier, we need one metal transporter. So, sometimes we call this particularly regions as the receptor sites.

So, this particular region can function as a gate, which allows the vanadium to enter within this cytoplasm as vanadium 5 plus and this 5 plus oxidation state is immediately reduced to vanadium 4 plus. So, there will be some difference between the character of

the vanadium in plus 5 oxidation state and vanadium in plus 4 oxidation state as well as their size the ionic radia is also different.

So, in this particular case the gate is allowing vanadium to enter into the system in plus 5 oxidation state. But here for this particular cytoplasm this is the cytoplasm area and when it is pushing that particular vanadium within the vacuole which is highly acidic in nature. We need another metal transporter to transfer for vanadium specifically in plus 4 oxidation state; that means, the tetravalent vanadium can only be transferred through this point by a different type of metal transporter, which is different for transferring this vanadium in the pentavalent oxidation state. And it is going within the vacuole as vanadium 4 and why this particular region why inside the vacuole is highly acidic that can also be justified.

Because, several a t p ages the first part ages the a t p also has some phosphate groups phosphate ester groups are there is a tri phosphate ester, and that tri phosphate ester in a t p molecule can take part in the hydrolysis reaction, and there are some a t p ages molecule which are vanadium dependent. So, vanadium can play some important role for the hydrolysis of these a t p molecules and phosphate groups are being released and this particular case basically sometimes this protons are utilized for the hydrolysis reaction which can be considered as the acidic hydrolysis or some time bases are required if the O H functions is developed or can be obtained from the water molecule itself.

So, which can be considered as the base induced hydrolysis reaction or base induced a t p age reaction where base is utilized and the vanadium a t p is molecule can release more number of protons to the system and for charged balancing or the charge neutralization some amount of anions are also available. So, sulphate anions can be available over there, so the vanabin in the bound form or vanadium which is supplying or providing the vanadium in the plus 4 and sometime some of the vanadium can be reduced to vanadium in the trivalent state.

So, basically what we can consider over here, we have the ligand environment or ligand encapsulation, but still from the charge balancing or the availability of the anions is in the system. We see that the sulphate ions can store this particular vanadium as vanadium sulphate in either plus 4 oxidation state or plus 3 oxidation state. And we can go for a corresponding enrichment of the vanadium; that means, the vanadium concentration can

go up nicely from 32 nanomoler solution which was vanadium 5 in sea water. And within these particular vacuole it can go up to 350 milimoler of vanadium 3.

So, thing is that the system is getting reduced and more and more number of vanadium ions in the lower oxidation state either in the vanadium 4 or vanadium 3 can be accumulated at a p H of 1.9. So, you see this is a highly acidic p H, where this particular thing is stabilized and this particular concentration of sulphate anion within the vacuole is in the range of 500 mili molar.

So, this particular one is also well matching to that of the vanadium accumulated concentration it is 500 mili molar and this is 350 mili molar. So, they are well matched as if the vanabin is transferring the entire vanadium they are and that this vanadium is storing there as the corresponding vanadium sulphate where the vanadium is present in trivalent oxidation stage. So, this is basically the entire mechanism for the transfer of vanadium from the sea water with two within the aqueous system where vanadium is getting reduced and is stored in a very high concentration.

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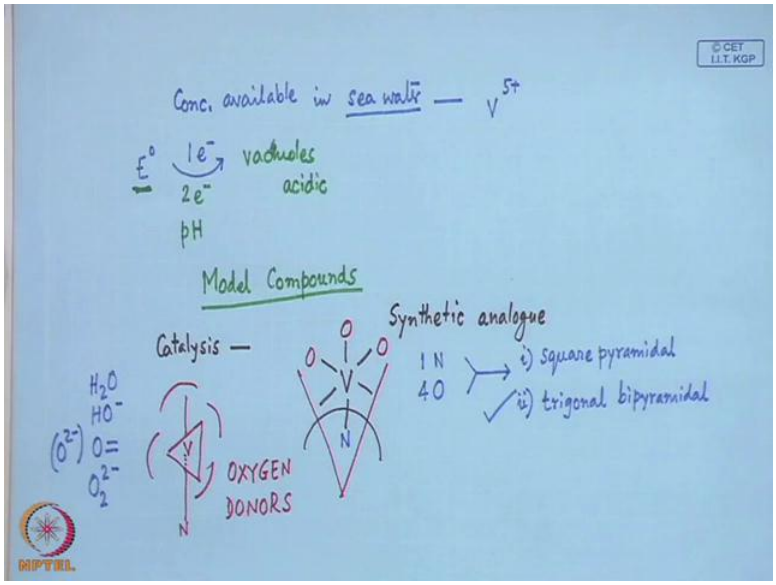

So, in the next particular part what we see that how we can have the model compounds how the model compounds can be prepared to see their corresponding activity what we see in the biological system; that means, the model compounds how they are taking part in the catalysis reaction. So, one such is the corresponding modeling where we find that

the haloperoxidase is what we have identified that these haloperoxidases we have seen earlier that they are very much vanadend dependent.

So, if we have these haloperoxidases as the corresponding vanadate is getting trapped within these heloperoxidases. So, what we see that the corresponding structural models we can have for vanadium 5 complexes for a particular donor sets. So, if we can get the corresponding model compound or the synthetic analog. So, synthetic analog can we have, so we already know the corresponding vanadium coordination environment; that means, the what are the donor groups present in vanadium heloperoxidases.

So, based on that basically based on that information we can chose that one nitrogen donor atom, and 4 oxygen donor atoms can be sufficient to model a corresponding vanadium center as a environment which can be either a 5 coordinated geometry suitable for square pyramidal or trigonal bi pyramidal geometry. So, two geometries we can have once we can have a corresponding ligand system based on one nitrogen center and 4 oxygen center for square pyramidal square pyramidal and trigonal bi pyramidal geometries.

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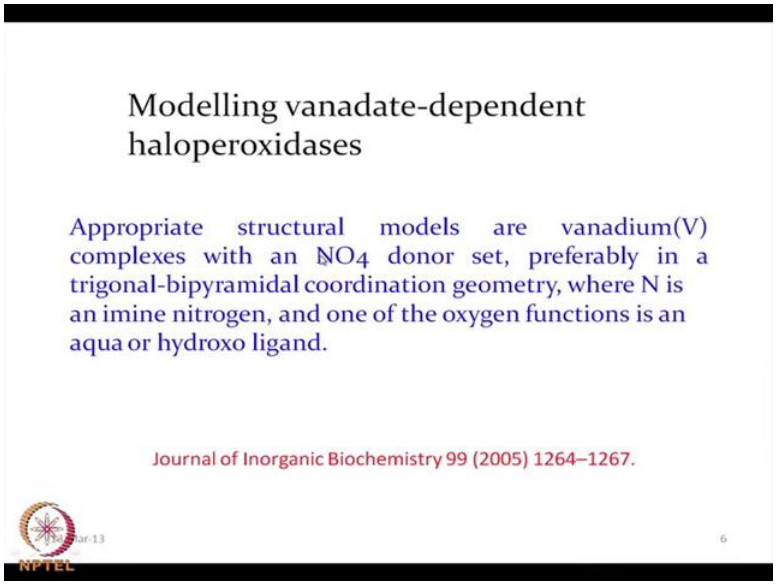

So, situation is such that when we have this vanadium 5 complexes in this particular donor side. And what we have seen in the actual reactivity for these heloperoxidase system that the corresponding preference for the coordination geometry is for a trigonal bi pyramidal one. And we have seen that the epical side if we blog this particular epical

side by one of the nitrogen atom that is the hysterin nitrogen atom was present in the enzyme molecule, and that hysterine nitrogen attaching from the epical side of the trigonal bi pyramidal geometry.

So, in this particular case if we chose the ligand system in such a way that the available nitrogen the single nitrogen for this 5 donor atoms is coming as the corresponding imine nitrogen function, because the imine based ligand systems are known as the corresponding sick basis. And we know that all sick basis are very easily we can make from the reaction with that of one amine nitrogen with that of our aldehyde or keton.

So, one imine nitrogen can be dedicated to make the corresponding model compound of the vanadium. And all other four positions we can takeup by the oxygen functions because we have seen that surrounding this vanadium if we can have one nitrogen from the epical side when the environment is not octahedral, but when the environment is trigonal bi pyramidal this one the second one. So, once this particular side is blocked by nitrogen the all other remaining positions what is there? So, all other positions, so they are all based on the oxygen.

So, we are happy to make that thing that we can get this thing like an one ice cream cone basically and this particular one because this is not the triangular plane which is occupying the corresponding trigonal plane. So, trigoanl plane is like this and we have this trigonal bi pyramidal geometry like this vanadium is sitting nicely over there. So, nitrogen is there, so within this cone. So, whatever we can have above these nitrogen. So, this this all this positions, so they are all our oxygen donors.

So, that is the most important thing and it is most beautiful thing is that that we have to do all these things based on only one single nitrogen and the remaining positions can be all oxygen. Because we can have several of these oxygen donors available they can be from water molecule they can be from the potonation of the water molecule as the hydroxide anion. Or they can be directly forming bond with the vanadium as the oxo bond; that means, they are O 2 minus they are basically O two minus and sometimes when in the actual catalytic cycle we have the corresponding binding of the peroxide anions.

So, we see that 1, 2, 3, 4; four different types of oxygen donor atoms can be available to bind to the vanadium center. So, initially if we go for the making the corresponding

synthetic molecule or the model compound based on these. So, only we have to concentrate our attention and we have to focus our attention for making the system with one single nitrogen, the rest can be all by the oxygen functions.

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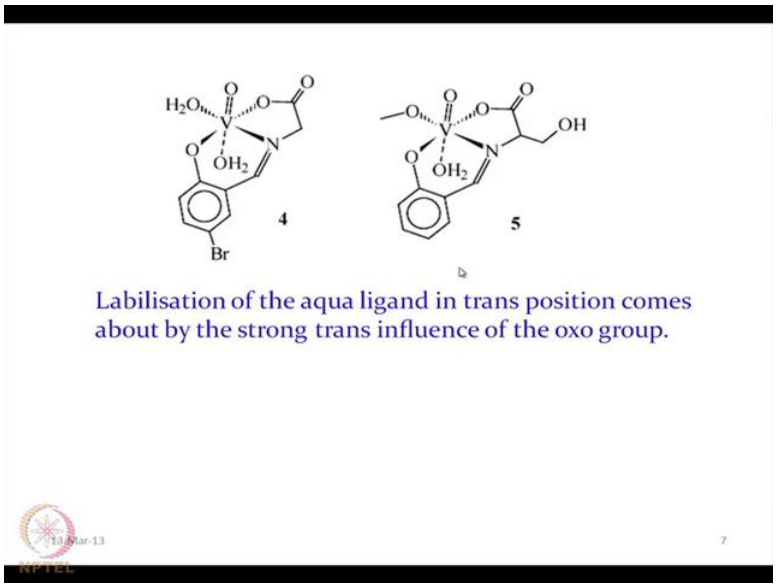

So, what we get from there one such example two such examples basically that we have these two synthetic molecules we can make. One is basically the corresponding sileceldehyde bond substituted sileceldehyde molecule, where you have this is the aldehyde function which is attached to that of our glycine part this is the NH 2 function of the amine acid glycine which is little bit biogenic therefore, in nature since we are handling amino acid, so this amino acid with that of our sileceldehyde molecule giving a very good tridented in O 2 type ligand.

So, when it is reacting with vanadium center it is forming a tridented capping within this particular plane this is the meridonal plane. So, these NO 2 ligands binding this meridonal plane and other three positions are occupied by two water molecules and one oxo oxygen. Similarly, in this other case in the second case also if we have a different type of ligand with plus substitution on the seleceldehyde ring; that means, it is not bromo substituted one it is the simple seleceldehyde ligand.

And we have some other groups like that amino acid derivative with alcohol part pentent over here whether we can have some preference of binding through this oxygen of the carboxy end; or the hydroxyl group from the alcohol and that can also be checked and

similarly here also we have again NO 2 tridented binding one is the oxo binding one is the water molecule. And instead of this water molecule we have now alcocxite binding this is our it can be ethyl or it can be methyl, so our O minus is directly bound to the vanadium center. So, this two molecules can be synthesized and can also be structurally characterized for looking at the corresponding nature of this NO 2 ligand.

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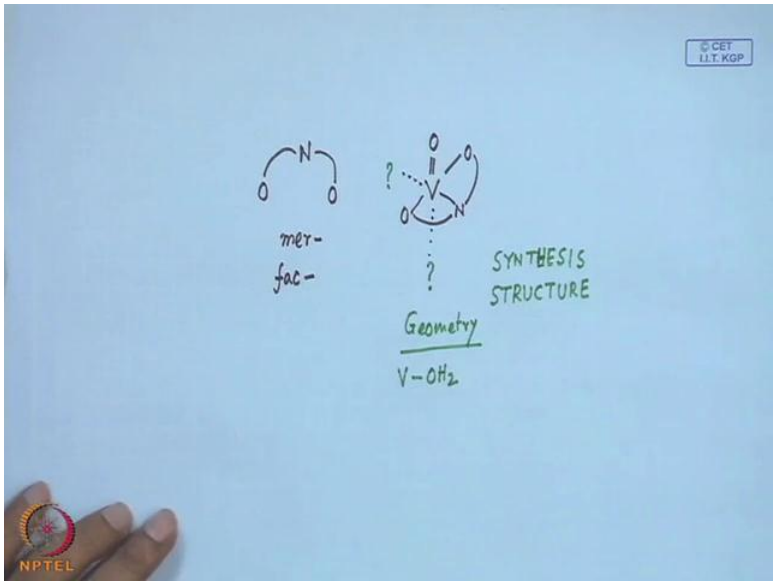

So, we have this N O and O ligand, so whether this particular ligand is binding in the meridonal fashion or facial fashion which is very important; because we can have the vanadium site when we fix it as the vanadium oxo bond. So, we can have these three positions which are occupied by these; that means, this nitrogen, this oxygen and these oxygen, so this is the binding.

So, we can think of the corresponding occupancy of these positions, so how the other groups are coming and binding through these positions. So, we can go for synthesis we can go for the synthesis and we can go for the corresponding structure. So, once we determine the structure basically why we do the structure, because we want to know the corresponding bond distances corresponding angles and finally, the geometry of the overall molecule.

So, the geometry basically tells us that what sort of bond we have if we just consider the corresponding only vanadium water bond. So, the corresponding binding of these aqua ligand if it is there and which is trans to this oxo function. It can have some trans effect

or trans labilizing effect or from the oxo groups; that means, it can labilize this water molecules which is trans to this particular water molecule bound to this vanadium, and can remove very nicely for binding the peroxide or any other incoming group to this particular site. That means, we basically enhance the reactivity pattern which is trans to these oxo groups of the vanadium center. So, the next day will see how the different bond distances the information for the different bond distances can help us to understand the detail catalytic picture of these vanadium centers.

Thank you very much.