Bioinorganic Chemistry
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Lecture - 19
Nickel Enzymes III

Hello, so we are talking about those.

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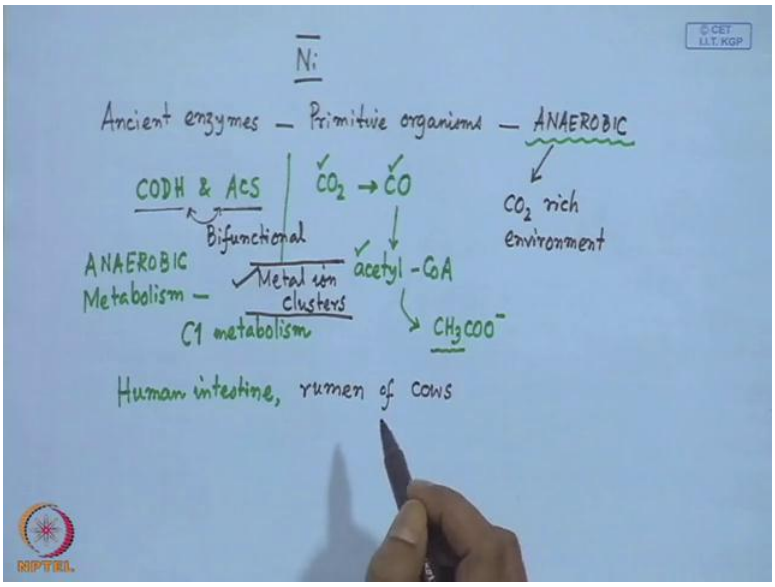

Enzymes on nickel and this were basically some ancient enzymes with call them also because in some cases this are very much useful for the primitive organisms so those primitive organisms. They basically relay on or live on some an aerobic atmosphere that means it is basically a C O 2 rich environment, so for that what we see, here that both carbon monoxide the hydrogen is and acetyl C O enzyme scythes. Both are responsible for reduction of C O 2 to C O and that C O is subsequently transformed into acetyl C O enzyme a.

So, this basically are very important thing particularly when our environment is an aerobic, so we are not talking anything related to dioxygen environment. So, for that reasons we can also considered all this reactions as an aerobic metabolism and some times since we are talking or we are conceal rings one carbon center.

That means weather it is from the carbon monoxide or carbon dioxide or the acetyl function because this acetyl function can ultimately used for the removal of or the formation of acetate anion an iron in the system. So, apart from that when we have only the methyl function attach

to that we also considered this as C 1 metabolism that is an aerobic metabolism is also can be considered as C 1 metabolism. So, all this primitive enzymes which were sometimes present in our system also in human intestine when we do not considered the presence of dioxygen molecule for degradation of any small pieces or any small molecule or most of the time it is present in rumen of cows.

So, they basically do very interesting reactions and for this we considered this to as sometimes both of them are functioning together. That means we are talking something the accumulation carbon dioxide or carbon monoxide for the formation of acetic or acetyl C O enzyme A, we considered this two when they are couple together we considered them as some by functional enzyme also. This can also be considered as bi functional and from here we are just simply interested to know what type of metals centers or the metal ion clusters are present.

So, from an in organic chemistry form of view you just basically focusing or attention on the metallian clusters. So, the biology is level some of this clusters as one C cluster and some of this a cluster and if we can find out how many metals present there then we try to find out the what type to reactivity can give on those metal centers.

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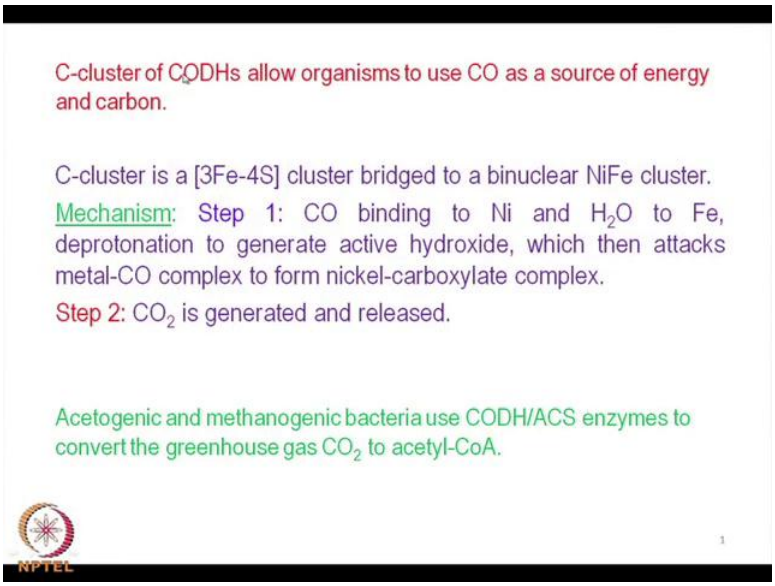

So, the C cluster which is present in C O D H, the carbon monoxide deydrogen is allowed organisms to use carbon monoxide as a sources of energy and carbon, so that is the metabolism anaerobic metabolism is therefore dependent on the use of carbon monoxide or

carbon dioxide. So, this use basically use for the sources for the energy and carbon and sometimes will find that all this transformations, because there are also related to some electron transfer as well as proton transfer because what we have seen is the case of the hydrogen diseases.

The reaction of hydrogen diseases that they are proton coupled electron transfers, so when we see something that the only hydrogen atom or some copper proton electron copper transfer is taking place to are also able to see synthesis at the particular point some a type of molecules. So, our basic goal to know this system related to this iron and the nickel cluster which is already seen in the case of hydrogen diseases. So, this particular C clusters is very simple that is C clusters is present in C O D H and we have seen earlier that this is A cluster of 3 iron 4 sulfur cluster, so what we know that from the ferredoxin type of molecule.

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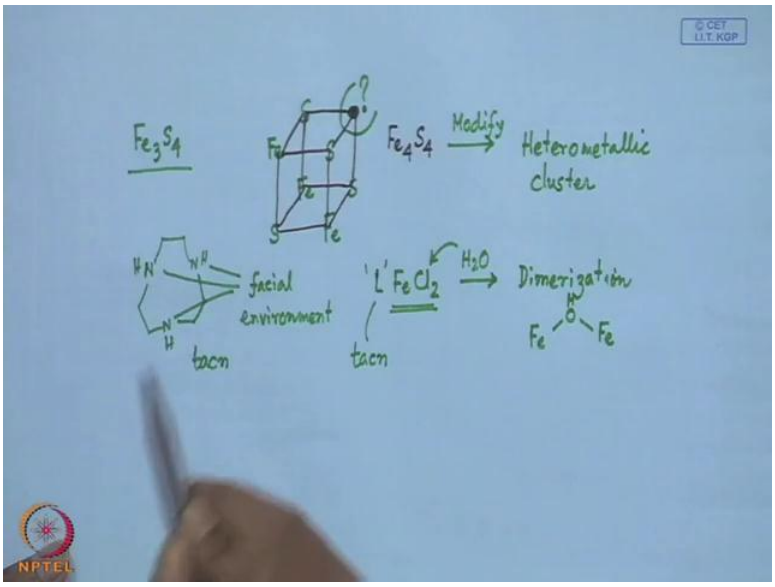

When we have certain cube like, so very simply write this motive we have F e 4 S 4 and in this particular case when we have F e 4 S 4 and, here we see that what we are getting something that is F e 3 S 4, so we basically creates some vacancy over here. So, if this iron position, so other one is also iron position this is also is your iron position and that is also our iron position and these are all in organic sulfur in the sulfur itself. So, this we all know from the basic structure of ferredoxin molecule four iron ferredoxin molecule, so if we considered because here we are simply modifying the cluster.

So, F e 4 S 4 cluster, so we modify that cluster such that we can put some other metal center to get a hetero aromatic cluster. So, if we bring some metal center here within the cluster motif you will find that till you have three organic sulfur atoms available to bind this particular metal center if it is a nickel is nickel is coming over there. So, you have basically 3 sulfur groups and they are when they are sharing what vertex cubes there are, basically this position all these 3 sulfur are disposition.

So, basically we can think of something were we know that a ligand like triaza cycla nonane is known in which is also a very unique 1 to give you a facial environment. So, this is also giving you some facial environment, so this particular part, so what we do basically gets that one particular face providing 3 sulfur atom which can go and bind to your the incoming metal center which can be your nickel. So, this is like this one, so when you have this one facial environment for triaza cycla nonane known is in which is l considered as l which say is coordinating to iron and the simplest possible salt is l F e C l 2 using take in t a c n as a triaza cycla nonane.

So, this is also your t a c n, so this particular information also give ours some important clue that this immediately can, so for dimerization how this if F e C l bounds a very weak, a very week one for hydrolytic reactions. So, if we can go for a if it is reacting some water presence of water it is also getting hydrolyzed, so this particular unit can very easily gives us something following deport nation of water molecules from this coordinated water. So, water will kick out the chloride function attach to the iron center, so basically you get in the simplest possible motive which is hydroxide base diron spices that is the simple thing is that when you bind in one particular face.

You have one metal center and some loosely bound groups a nickel chloride you are giving, so nickel chloride immediately coming here, but on for the headalitic reaction. But, it can bind to some other metal center or any other cluster the demarcations of cluster is also possible through this vertices, but the simplest possible or the most critical one how you generate the each one, so this cluster will immediately take off another position which is your metal center. So, this C cluster is, now have that is you have three iron and four sulfur present within the cluster and that is this two a binuclear N i F e cluster, so what I am you just telling that when you some vacancy over here.

So, you get one position that position can be occupied by another incoming metal center like another nickel or some other already ligand bond iron sit, but if you a already you have a like hydrogenise type of a N i F e cluster. So, that particular cluster can also we put with that of other existing cluster, so that structure will find, so our basically interactive know what type of structure you have and how they are reacting. So, for this all this reactions you when you get some position as nickel within the cluster, so the nickel will have very high infinity for binding to carbon mono dioxide like your nickel tetra carbon formation or any other catalytic reaction related to carbon.

Any organic metallic reaction related to that, based on the carbon or any carbon hydroxide diseases, so binding of carbon monoxide diseases to nickel and water to iron. So, if it is involving some iron and if you can generate some active hydroxide function from the deprotonation of water molecule this water molecule is water molecule which is bound to your iron center. Which can give a lies to deprotonation and its generated the hydroxide and that particular hydroxide iron can attack our this particular assembly the nickel attack to carbon monoxide hydroxide so in C O 2 generated.

The hydroxide can attack your metal carbon monoxide complex to give lies to nickel carboxylate type of diseases. So, same type of reactivity pattern we can have in some other points were you can converse in C a C S that C O is converted to C O C S 3 and that will be released at the corresponding carboxylate function. So, in the second step your carbon dioxide is generated and released, so it is the inter conversions C O and C O 2, but when we go that means this particular by functional enzymes function that means we take one part is C O D H type which is isolated C O D H.

But, the other part is A C S type, so if you have one particular part which is C cluster, so this C cluster is also be present in this particular one that means all acetogenic and methanogenic bacteria. That means they are able to produce acetyl functions or acetyl that means some important organic functions were required to go for acetylation or they can go for production of methyl. So, there are some bacterial things methanogenic bacteria are there which can produce large amount of power that green house gas. So, we are talking about consumption of one green house gas carbon monoxide and carbon dioxide, but at the same time if the methanogenic bacteria are active will produce another green house gas which is our methyl.

So, in that particular case or this this two the enzymes convert the green house gas C O 2 to acetyl C O a. So, this basically one particular path way there C O 2 or C O can we converted to acetyl C O a and in another case. So, another group of molecules which are again dependent on nickel which will be utilized for some points that were that the nickel center will be attach to your methyl function. That means that methyl C O bilamin and that methyl cobalamin type of nickel function can take up 1 hydrogen and produce in your corresponding methyl molecule.

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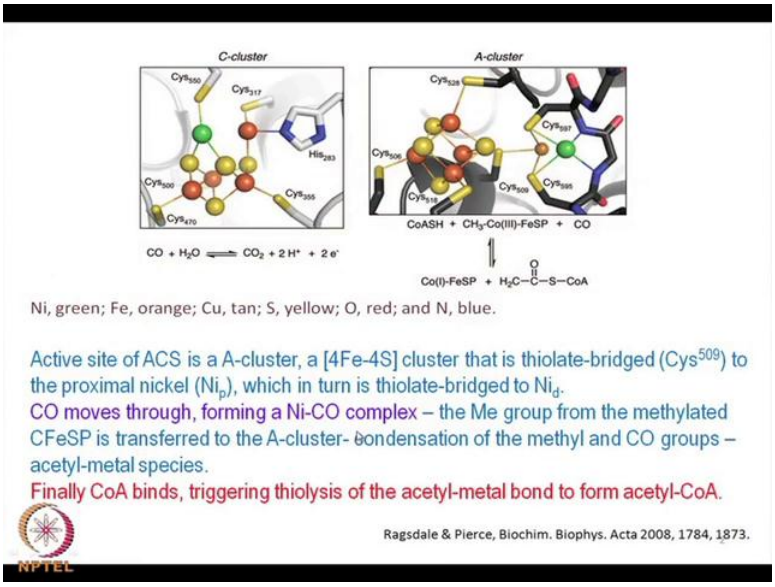

So, this particular structure what we seeing for the last class that you have the same thing that you have created some vacancy this is basically your cluster original F e 4, F e 4 cluster you generated some vacancy. So, once you generate the vacancy you can have 3 sulfur groups on F s which is available to bind your nickel side. Sometimes this particular assembly with that of your other protein parts can react and go for this particular reaction which we have already discuss in the C cluster.

But, now will see that what is the corresponding function if you have A cluster, so the detail are the other part of the that means that came that cluster, this particular things we see. But, this is the thing what we have from the corresponding protein structure, so this particular active site which is involving your A cluster. So, in A C S only A C S not coupled in C O D H you have the A cluster, so we just talking about two cluster nothing else one is C cluster and

one is A cluster. So, if you are asked to compare that this particular C cluster or the A cluster with that of other known clusters which are in present in biology.

So, one such is that your corresponding ferredoxin then some other groups of clusters like that in molybdenum is present nitrogen in diseases. So, in this particular case you have no such removal or the modification of the corresponding cube in type of geometry that means 4 F e 4 S sulfur cluster is present and you have some thiolate bridged. That means the system received from 509 that system residue 509 is available and that 509 system residue this residue. So, this particular system residue is coming and that is basically utilized for taking of, now not only a single nickel, but 2 nickel center, one is N i p and another is N i d, N i p is nothing but your nickel center.

Which is very close or closed to that particular iron cluster which is the proximal nickel and d is your distal nickel, so these could have some different functions that when you being not only a single nickel. But, another nickel and we are talking about some reaction were to have this methyl group, methyl group is there which is attach to some particular center and you have the carbon monoxide. So, what you immediately think that you are one such nickel center is utilized for carbon monoxide binding and another center is utilized or a providing that particular methyl group then this two are coupled together and forming your acetyl function.

So, acetyl C o A, so acetyl is C o A generation nothing but your individual reactivity for the metal centers for the reactants like carbon monoxide and the methyl function. So, positioning on this two nickel groups, so one is there and another is there, so if you have the system reduce not only this 509 this is C y s 509 this is C y s 595 this is 97. So, this is they are pretty close 95 and 97 and this is the different side is 528 so when this system is residues that means 509 is coming into the picture.

So, it is basically attaching to your this nickel center to the cluster, so not in the organic sulfide group which is responsible because in the earlier this particular case the C cluster in organic sulfur is coordinating to your nickel center. Now, your C y s 10 sulfur is responsible for not only coordination, but also for the bridging, so you have for this coordination for the proximal nickel means N i p and for another thiolate bridged nickel which is your corresponding distil nickel. So, again in the same passion for the C O D H or carbon monoxide is moves through the protein turn in basically, so long distance it can moves.

So, gas can move a long distance then when it is approaching your nickel site it can form the corresponding carbon monoxide complex and the methyl group which is coming from other side which is the corresponding iron base the iron base sulfur protein. But, coronate structure is there also another ring is also present, so methyl group is available from other center that methyl group is attach to your mono carbon dioxide giving again at the end point also you are generating acetyl matalan spices. So, whatever you have your metal center is utilized for trapping mono carbon dioxide another metal center is utilized for trapping for methyl function and ultimately the during conversion like is very simple catalytic pauses S.

So, all the catalytic pauses S is involved in oxygen addition redacted elimination that your carbon monoxide attach to the metal center is getting transformed to your acetyl function. So, finally what we are producing finally this particular C O enzyme A basically binds to your acetyl entry triggering the thiolysis of the acetyl metal bond to form the acetyl C o A because acetyl C o A you have the all the time this sulfur again you have the thiolysis. So, this thiolysis all the time the thiolysis giving you some reaction based on nickel that is why the coordination chemistry related to nickel and sulfur is very interesting.

So, in organic sulfur is utilizing for nickel binding your system sulfur is utilizing for nickel coordination and then finally, your acetyl which is also bound to your metal center giving your acetyl C o A. But, acetyl C o A this is 3 C O, so this H C o is attach to your C o A through sulfur, so sulfur and some important role and if you talk about because the stabilization of this thiolate or the sulfate is not so easy. Even in the laboratory scale the preparations of nickel thiolate complex are not so easy because the thiolate nickel is strongly oxidizing it can reduce oxidize the thiolate center and itself reduce to nickel 1.

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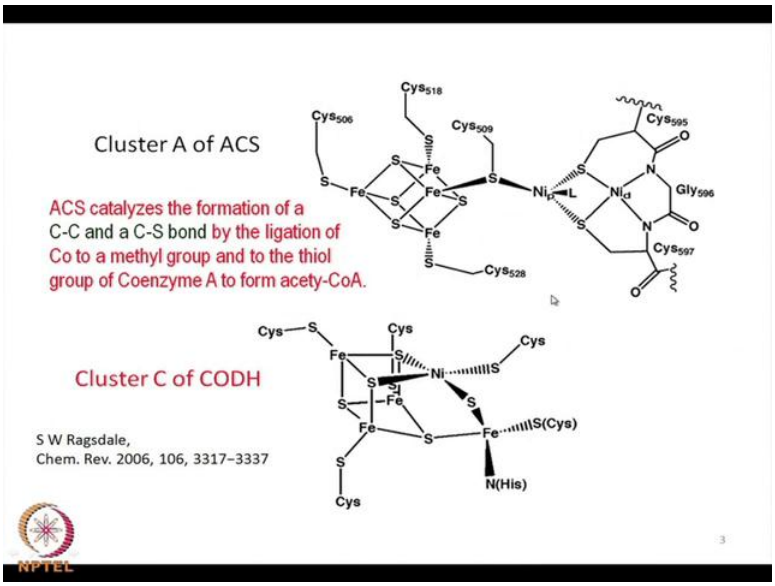

So, here also now we see that typical drawing which is you can have this is available when this camera were because this taken from the camera because all this information and literature are this not available some standard different books. So, it is directly taken from the camera preference, so this is you cluster C, now you can have camera were because all this protein structures you cannot write in tour answer book. But, this you should able to write nicely, so you see that how much the distortion is taking place that is very important that you have the regular cube structure we call it as very regular cube in structure.

But, all this distances are not same because you have the non bonding sulfur, sulfur distance which will be different from the non bonding that means the diagonal F e F e distance. So, you have you cannot have a regular square which should be destroyed in some points, so when you create some vacancy that means this position this site that means creating the vacancy that means one iron center is removed.

That is also well known in iron sulfur protein also you have studied that also the real case cluster, so real case cluster because occasionally they produce in all some catalytic reaction the F e 3 S 4 cluster. So, F e 4 S 4 cluster is responsible for generating our F e 3 S 4 cluster, so this are still that is original system sulfur coordinating like your ferredoxin types of molecules, so you find that. So, much similarity with that of our ferredoxin type of molecules, so when we take out this particular group that means when you take out this iron

what we taking out we are taking this system sulfur also because if you recall F e 3 S 4 structure this iron is attach over here iron was there.

Here, that iron is bound to this organic sulfur this in organic sulfur and this in organic sulfur and this particular iron was tetrahedral geometry since all F e 3 S 4 molecule all iron environment are tetrahedral. But, in this particular case when you take out, so these particular systems sulfur the original sulfur system present in the F e 3 S 4. So, it is moving away, so if some mechanism is there have that means you can move out this system sulfur to some distance, so there is something and you can have something related to that type of organic sulfur.

So, this is also in organic sulfur, so if you can have some supply in organic sulfur and the system sulfur is little bit going away from the cluster you generate the vacancy and that vacancy can be taken up by your nickel site and this will definitely be a distorted one forget about the presence. This second iron the first one when you have the F e 3 unit you put the nickel and how much distortion can be there how much distortion can take place on the cluster structure. That you can also see because this will definitely be a distorted structure because whatever nickel we putting over here with has complete different coordination geometry because earlier we are trying to replace the iron site which is the tutorial 1.

But, now we are putting the nickel and nickel have a preference particularly in a sulfur environment like what we know that the tetra sign in nickel also depending upon the strength of this ligand which is coordinating to your nickel center. So, this nickel center those you can have the corresponding environment like that of your iron that it can also go for tutorial geometry, but it is not preferring that put tutorial geometry instead it will go for a square plan geometry so when you have square plan geometry. So, you definitely have some distortion within the cluster which cluster the cluster is, now instead of F e 4 now it is N i F e 3.

So, you should also be able to tell or write the corresponding distortion on the N i F e 3 cluster and how much is different from the corresponding regular F e 4 structure or F e 4 clusters which is present in ferredoxin molecule. So, is one solved of distortion what we are getting replacement of on iron center by nickel and the second level of distortion is coming when we breaking the second iron site over in here. The second iron site is over is bring over here and it is already bound to A 1 system residue and one in this residue, so this 2 nitrogen

and sulfur is basically behaving like a bidented motive by dented protein liked in motive which is available for iron coordination.

This sulfur which was already present with that of your F e 4 S 4 units is available for coordination not to this nickel. So, this sulfur not available for coordination to this nickel because for the regular geometry we thought we could thought if it is a tetrahedral one this sulfur will go and bin into this nickel simple. But, it is not happening because already you have a planer arrangement and this sulfur is not available for this iron, so this geometry. So, you have, now from this cluster structure that what type of coordination you can have, so basically on this corresponding F e 4 S 4 structure what we are putting.

We are putting that is why we makes that statement that within that F e 4 S 4 cluster we have created one vacancy then we putting one by nuclear N i iron motive like your hydrogen is more motive. So, nickel iron motive which is sulfur bridge which we are putting or attaching to the existing structure which has been creating on vacancy by removing one iron site, so once you put this one. So, this a typically square planer one, but this is not a square planer one it will telling to words a titrated hedral geometry, so this iron will have a different geometry.

So, it is already bridge with the sulfur to your nickel center and, now it is attracting this sulfur, so it is a M u 3 sulfur, so it is providing connectivity. So, this iron is basically providing connectivity in one end it is attaching to cluster and another end is attaching through that nickel center. So, if we can considered that some electrons and proton supplier is given by your cluster structure you have the nickel site and you have the iron site also that the statement already we mate that because this iron site which is again a lower coordinated one which is a four coordinated site. So, it can go for another coordination, for five another coordination, for six similarly this nickel site which is a square planer one can go for fifth coordination and the sixth coordination.

So, that is why you have a low coordination site we have a generated low coordination site and the entire thing the enter C cluster is C O D H or else remember that it is in a proteins environment. So, it is not in that that is a not in some other group, so other molecules are available, so there are plenty of water molecules are available. So, in all the cases were we see that if you have the bear nickel center available in any nickel salt when you dissolve in water it will immediately attract six water molecules to give you regular extorter geometry.

But, in this particular case if we this two have something catalytic activity based on this nickel site your protein environment is such that that it will not go for any kind of coordination from the typical site before catalysis. So, during catalysis it can for binding the mono carbon dioxide or the acetyl function, but before the catalysis cycle starts that means the restrings states in the restrings states is nickel could be kept or should be preserved in square planer environment. So, your protein environment should be such that and also your coordination environment because is a strictly square planer one, so your protein environment will block this position for coming water molecules closed to the nickel center to give you a panda coordinated or extra coordinated spices.

Best on this site nickel site attach to this clusters, so this is the C cluster solely 1 or another if you think of starting from your ferredoxin molecule it should be able to draw the structure. It should be able to justify the position and little bit you can except that what type of catalysis of when we are talking about carbon monoxide the hydrogen is weather the carbon monoxide can go and bin to a any of the nickel site and go for the transformation. But, for the A cluster which is a completely different one and which is there a side by side because we are putting this together because side by side we can compare this two clusters at the same time so here the F e 4 S 4 cluster is intact.

So, F e 4 S 4 cluster we are not destroying, here this system sulfur we have taken out and that system sulfur is utilized for for the nickel coordinating here this system sulfur for this 509 still recall the number is in the protein structure what we are identify. So, this system residue 509 which is already attach to iron, so this particular one can, now function as a very bridging a useful bridging interaction were this proximal nickel site.

So, if you have a cluster structure forgets about the right path because this particular is one ferredoxin molecule. So, we are studying is well know this F e 4 ferredoxin molecule were all the 4 iron sits attach to system diseases and we are elaborating that particular cluster from one iron site. So, all this system residue system residue this one and that one, so all are the three system residue if we think all this system residue in terms of simple thiolate coordination. So, that thiolate coordination immediately can give some idea that this thiolate sulfur this thiolate sulfur that thiolate sulfur can also be useful for bridging interaction.

But, you should have some vacancy over here, so with in the big protein structure because we are focusing the attention on the cluster only on the metal side. So, vacancy available vacancy

your available vacancy site is such that only this iron can allow the bridging through its originally coordinated sulfur resistive. So, you have some amount of vacancy over here this particular position only and this sulfur this system sulfur will start interacting with your proximal nickel and what about your distal nickel. So, your distal nickel is already there are and which is already bond to your both the two nitrogen sits from the polyp toil change, so these are the a might nitrogen's.

So, this is the glycine residues and two other end you have the system residues, so this glysis the type of type is glysis. So, this type type is basically providing a bindted motive through this two nitrogen atoms, so which is similar that of your, is particular cluster C were you have this sulfur and nitrogen one from N residue and another from the system sulfur. So, this your by dinted motive, so you have the same by dinted motive and, here the bridging groups for this two sulfur is coming from the cluster another is organic sulfur.

But, now you have some extra sulfur the system residue one more system residue another system residue from this completing on the distal nickel a tetra coordinated environment. So, on the both two ends, so this are well known coordinated motive that another is from the in organic sulfur. But, now you have some extra sulfur the system residues one more system residues and another system residues from this is completing on the distal nickel a tetra coordinated environment. So, on the both two ends, so this are well known coordinate motive that means you have something if you have not only the system sulfur residues which can be attach to your iron site.

That attach to system residues bound to your cluster molecule can some interaction, so bind some other metal center such that it can function as a very good bridging unit such that hedrometalic can starts. You have some metal on the F e 4 cluster unit and this on the right hand side, this right is also interesting motive because if you just block this one this two sulfur. If you could bleach it which is a very good micro cyclic ligand, so the part of micro cyclic ligand and most cases like this of your trip yap types. So, this trip yap types when we can have if they provide some groups some like 2 nitrogen and 2 sulfur, so basically it is a N 2 S 2 a cyclic this parts is only a cyclic, so rest is cyclic.

So, N 2 S 2 groups are available and this sulfur groups they are thiolate sulfur if you make the S are, S are or S methyl or s methyl this will not be available for any bridging functions. So, that gives us to large number of coordination of compound also also out of chemistry well

known before discovered of this molecules, so this are the very recent identification. So, but once you know the typical coordination chemistry related to this micro cyclic motive because immediately can have some time during the structure solution of the protein can immediate difficult you whether this is S or S methyl.

So, immediately since the nickel will identified first because all the heavy atoms, so all the metal center, so identified first so when you identified nickel. So, this two nickel center you can immediately find out even if you do not solve the structure because large number of extra structure people have solve. So, for this this thing to get a accurate structure, so accurate bond distance and all, so when you determine this two nickel positions or find out the nickel position this to position nickel distances are less. So, this a basically N 2 S 2 diamond structure both of them are I S T by the thiolate sulfur, so this are the very short distance, so immediately that will tell you no other interaction is coming from like your other l group that means other mono rented ligand it will be only this by this 2 sulfur.

So, during the catalysis, so what you have you have not only, so this iron site is not instead of iron here you have, now one nickel sits, so both of them are, now nickel. So, during the formation of this acetyl function will get something that is this two are very common all the time the C C bound formation. That means it is a simple one that is acetyl group function the attack of the mono carbon dioxide to your methyl group and the C S 1 formation when your sulfur or thiolate of the C O enzyme is attaching to your acetyl function.

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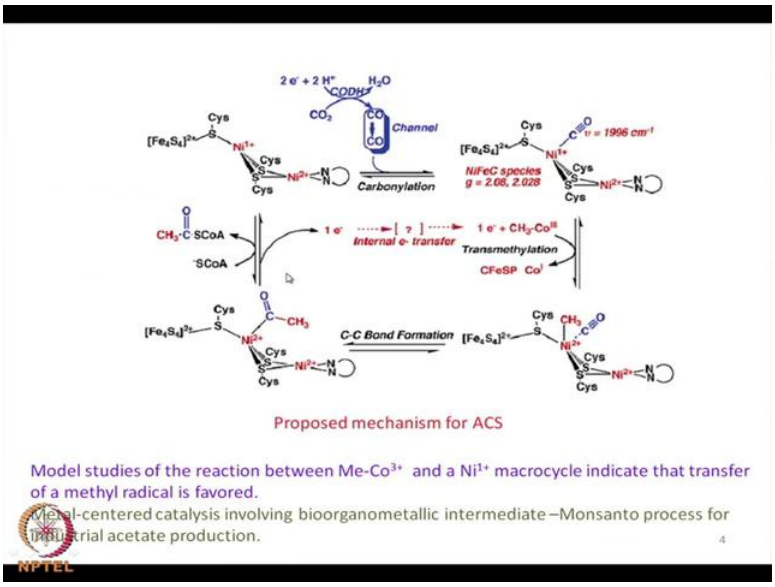

So, this can be a little bit complicated one but once you realized the structure so this is now we are simply focusing your attention on the metal center because the metal centers available are metal center responsible for this catalysis. So, how the positioning, so basically is very complex of your metal complex, so in terms of metal complex is very complex architecture one end you have the cluster unit. But, that cluster unit is required for holding this nickel and this nickel site what we can have this in the low coordination site because already what we have shown in the previous cluster you have l.

So, one loosely bound A l is there, so when l is present this nickel the proximal nickel is in its preferred coordination geometry. The coordination N is number 4 otherwise it can simply go away to living behind your nickel in try coordinated form, so when there are low coordination. So, immediately you can think of that like in a copper center also the copper or nickel in low coordination number is 2 or 3 you can go down that means you can reduced particular site is easily to nickel 1. So, when this low coordinating sits that means already this by two system sulfur residues and, so it is typically in sulfur environment.

So, typically sulfur environment and what we find this particular case that means in this particular case you go for this and if you have and if you do not get the corresponding electron transfer to that particular site. So, this particular nickel site is even is forming or immediately reacting with a nickel in bible in states it will immediately go for reduction because you have typically system sulfur residues which can provide huge amount of charge in residue to the metal site. So, this particular in case of copper also because what you can have if you allow to reacts with any nickel salt then if your nickel 2 plus salt is oxidizing in nature.

It can immediately go for oxidation of system sulfur or the thiolate sulfur to give you disulfide your by product by disulfide and your metal center will be reduced in the cluster of oxidation states if you are enable to generate nickel in 0 oxidation states. So, always will have the tendency because even if you do not have the nickel in the bible in states, but if you have the thiolate coordination. So, thoil groups there are basically the sacrificial group they they the thiolate groups insert will destroy and that thiolate functions will destroy that that destruction will give a some important thing that this will be reduced to nickel 1.

Why we are taking about the formation of nickel 1 and this particular one that means the proximal nickel 1 means that means proximal nickel. So, this proximal nickel is our catalytic

site which in the low coordination its coordination number is 3 compared to your distal nickel which is your nickel 2 plus because it is already in nitrogen environment it is not that it is a in all sulfur environment. So, if you compare the coordination environment to this two this nickel site will be available for this particular reaction which is coupled for C O D H. So, what we are talking over here is the center which is available the cluster available on the S C S.

This particular part is depended on C O D H because carbon monoxide is dihyrogen diseases use there are and which is giving us that institute generated carbon monoxide because we do not have mono carbon dioxide there we have only carbon dioxide. So, during this conversion C O D H is active and that CODH is reacting with your carbon dioxide forming your mono dioxide and that is why in the previous slide where I have shown you that you wrote also that there is a channel and through that channel your movement of this gas is taking place.

So, the gas molecules are moving through the biological channel or the protein channel and they are basically going and approaching to the nickel site. So, this immediately in the low oxidation states you have and this immediately goes for the attachment of carbon monoxide, so for the walk for several years people are trying to identify to this things. But, initially we know the activity the catalysis we know that means the identified that this particular enzyme and the other enzyme contain iron they contains nickel also.

When you identify that nickel center is present and is responsible for your C O D H is activity or ACS activity, so immediately people are trying to look at that weather because they have the previous knowledge several and more than 100 years knowledge of nickel tetra carbonyl. So, that particular informer they can have the nickel can bind in the 0 oxidation states in nickel tetra carbonyl. So, carbon monoxide can interact with our nickel, so is the nickel carbonyl spices can be generated so we the people take the help of spectra opitecnic is a very useful spectra opitecnic is our earlier.

So, ftir is useful because when this particular part that means when this particular center is the C O D H is generated carbon monoxide and this carbon monoxide is in the free state in the gassy state. So, if we are able to take this particular sample so gas sample can also be analysis in a different cell holder for I R, so gas can be analyze so this C O has a different stretching frequency have a compare to the C O which is bound to your nickel 1. So, mono

villain nickel is bound which has a characteristic nineteen 1996 centimeter in that frequencies that immediately tells us that you have a carbon monoxide bound to your nickel site.

But, the embay equity by the nickel site weather it is a bible an nickel or mono bible nickel because your nearby nickel site is bible end. So, that embay equity should have, so what you can do you can do, now the E P R spectra, so E P R spectra for this nickel this is your 3 in ironed system and this is also your three ironed system both are E P R active. But, in one particular case you have bound carbon monoxide in another case it is not, so if you side by side compare this 2 E P R spectra for this particular case spices and that will find that this have some cathartics.

The correspondent the nickel spectra for G vales of 2.08 and 2.08, so is basically when 2 zeros are available we call it as a exile distorted spectra, so basically is axially distorted. So, is one axially distortion and excel distortion the other is one your rhombic distortion three axis distortion, so all the three different xyz are different, so if you can have 3 G values. So, depending upon seniority or the environment of the system you can have and this particular value is very much characteristic which is for your nickel class 1 states and bound mono carbon dioxide.

So, you have this particular mono carbon dioxide, so we are happy to have a system your nickel is bound to a mono carbon dioxide and, now we have to provide your methyl group. So, anything related to that that means Trans metallization reaction if it based on methyl cobalamin function, so your methyl cobalamin is, so any C O word three sides cobalamin is trialing caballed and that caballed particular so your methyl group is here. So, basically there are providing the methyl group, so they are providing methyl function to your nickel site, so innately because still there is about the function of this two sits that means.

So, whether this one site is responsible for carbon monoxide binding people proposed also that the other nickel site is responsible for binding of methyl group. But, it is not that because this is a simple by dented bible in nickel site in N 2 S 2 environment, so it will not, so any kind of activity that binding of methyl functions to eat. So, this nickel site it when it bins it is transferring this particular methyl functions from that C O bind center and you get that particular methyl nickel function. So, it is very viler one immediately after this mono violent nickel site which is E P R active in this particular case can established corresponding

oxidation states of the nickel for this any electron transfer because you have this in the bible and states both the 2 iron bible and states and there are E P R in active.

So, these particular spices in the catalytic cyclist will be E P R in active, so most of this types for biology catholic cycle we real on only the I R spectra, but also E P R. But, initially we should be able to identify which particular spices is E P R active and whether that spices is giving rise to the generation of your corresponding product that means how the product is generating from they are, so this E P R active. So, when you react this one with your methyl cobalamin some spices is generating which will be E P R in active.

So, very simple one people have tried all this model and all this reactions from there is basically based on the model study even you can do also because even we can have three useful thing that the vitamin B 2 l the molding of vitamin B 2 l is very easy to do you can take d m g dimethyl glax. So, two of the dimethyl glax can bound to A any combined centers, so it is basically giving the influent binding and that influent binding is very much similar to your coring binding, so cobial twice d m g complex.

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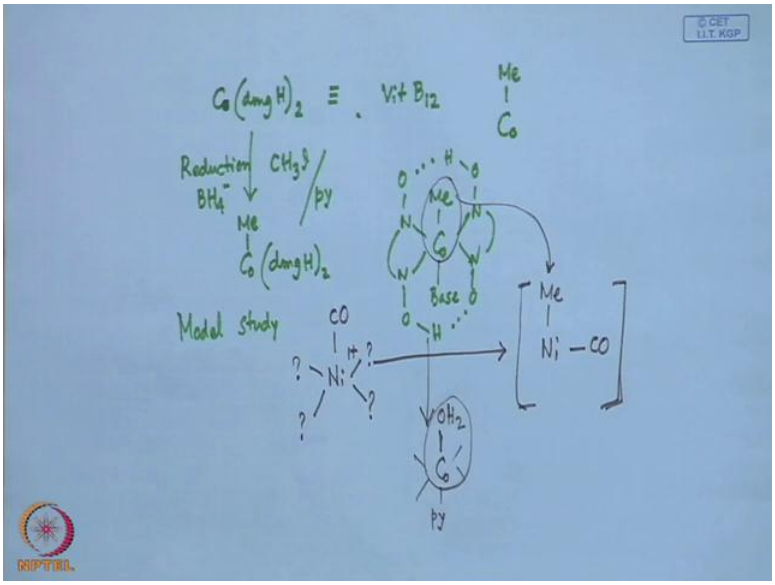

So, that cobial d m g d m g has 2 proton, so one is going for deprotonation, so this is very much similar to that of our vitamin B 12. So, if you have the vitamin B 12 where you have the covalent center and we are talking about the binding of the methyl group on the covalent center. So, this particular one is also is a very simple reaction on the covalent d m g H that what you have to do you have to go for reduction reduction reaction from there are sometime

sodium borohydrade is fine and some sources for methyl. So, this will generate found to methyl very easy to make in laboratory people I have tried I think, so this cobbled which is bound to two d m g is, so d m g is organisms functions.

So, you have the methyl function and some time we need for the very useful reaction on this cobbled center for attachment of methyl we required some base, so for that reason simple use perdition so this is base is now your perdition. So, this since if the reacting pattern is like this, so models studies can be make because in the laboratory you can make, so what we just basically. So, for this thought of model studies that you make this and our challenges for that is you have already a nickel mono villain nickel bound to a mono carbon dioxide and we want to supply that that nickel C O any.

So, this particular, this was the information we know that the nickel catalyses reactions, so if you able to have some other type of particular environment like that of caballed environment some useful are good ligand in environment. You can make such that you are able stabilizes nickel in the mono violent states and you just go for the corresponding mono carbon dioxide compound, so you will analysis by recording the is spectra then you use this. So, as the source of your methyl function then weather model compound also you are able to transfer this particular nickel carbon in compound or nickel carbon mono oxide compound the nickel carbonyl compound can be transformed.

This it can be a Trans have some Trans, some existing this is not be stable one immediately it can go for the corresponding acetyl function. So, this particular attachment, so this you just see that weather because what you are getting you are transferring this over here, so whatever you are living behind with this compound which will be the corresponding cobbled ago compound. So, what you are getting from there are that means there are, now you identify that some tetra scope tecnic or any other indicial tecnic you have identify that instead of you your come unit.

Now, you have the cobbled A C O unit cobbled water unit and then that methyl group is move to your nickel site. So, that immediately form the information what we can have that the reaction model that is that the reaction is between methyl coalmine and nickel 1 plus any micro cycle. Now, so the nickel is there, so this particular nickel is protein stabilizing this particular nickel site, but here any kinds of micro cycle also do the same reactions. So, like your system sulfur because the last molecule what will see in the next stage that nickel in a

micro cyclic environment can also be established in the lower oxidation states is not that whatever micro cyclic compound you make that all be stabilized in the nickel cluster in plus 2 oxidation states it can be stabilized in class 1 oxidation states.

So, if you have a nickel micro cycle which can also tell us that you can transferred this methyl radical from this particular caballed function or the cobbled center to the nickel center. So, at this point because both the in radiance and the both the separate the methyl separate and the carbon mono oxide function were attaching to the nickel. So, is very similar to that some catalytic pauses like the monsoon to the process the acid preparation or the acidic synthesis is the industrial prepare what we see.

But, that time the industrial thing is known, but this particular detail information about the biological thing was not known. But, nature is doing in the same passion the same metal center is utilizing or holding this two and at this point you have the C C bound foundation on the nickel. So, that is why you can think of something that nickel based catalysis and you can think of since it is coming out from the biology is the bio organic spices. So, bio organic metal intermediate is there, so protein is also doing the same function over here, but we are utilizing for big industrial process that means the catalysis process.

So, the simple is thing that like your using Palladian or other metal center rhodium and all the will thing and catalysis and all, so you have the center generated the center is reduced an you attach this two groups. Now, this particular one you have the corresponding cc bound formation and after this C C bound formation, but you can have your have this this is the depotonated acetyl C O enzyme is originated is S H. So, at this point it is S H is depotonated 1, so depotonated is C O enzyme A is reacting with this one at taking up this acetyl function to give you acetyl C O enzyme A.

So, at this point what we are giving you this we are getting C C bound formations and here you have the cc bound cc bound formations. So, this are the two basic steps that means at one point you are generating the C C bound and another point you are generating the C S bound. So, once it is giving, so you are just going back that is so what basically we lions from this particular thing that you have the metal center catalysis and it is involving your bio organic metallic intermediates this are the basic things.

Thank you.