Bioinorganic Chemistry
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Lecture - 20
Nickel Enzymes-IV

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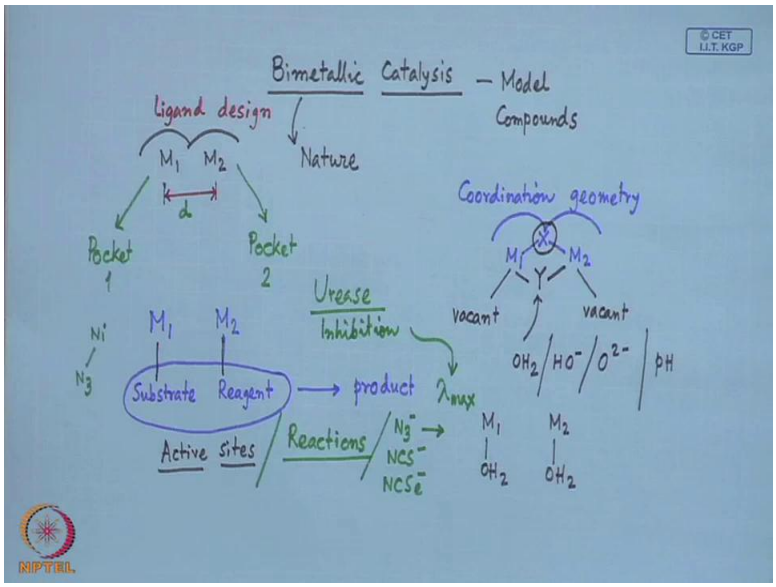

Hello, so today, we will continue those nickel enzymes and today, will see first that some of the model compounds in their involvement in say Bimetallic Catalysis. So, is a very well known term now a days, that what do you mean that if you have 2 metal centers. And basically, while we study all these informations that any particular motive whether it is a biological motive or synthetically prepared molecule, the two metal centers are present. So, whatever informations we are getting. So, nature is giving that inspiration to know that particular thing and one important aspect for that catalysis would be that how you place 2 metal centers it can be a 2 iron center or it can be a 2 nickel center. Because today, we will see, some molecules, synthetic molecules where 2 nickel centers are present.

So, this basically involves the ligand design, which is the most important part of this particular study that ligand design that means, what particular type of ligand, you can have and you get basically 2 distinct pockets and biological system also the protein gives that particular pocket. So, this is basically, your pocket 1 and another is your pocket 2 and how you can fix this particular distance, because while you go for this particular type

of catalysis and always we basically think that one particular site that means, the metal 1 and metal 2. So, this particular site is basically, holding your substrate if we are talking simple ureas activity. So, urea should go and bind that particular site.

And the other site, which will be you reagent that means, the nucleophile, it can be your water molecule or it can be your hydroxide anion. And then we get something that this particular thing that means, the reagent and substrate will react giving you your product. So, that is the idea that why we take these 2 metal centers in a particular system. So, these 2 metals centers that means, their coordination geometry will play an important role that what type of ligand you should take and what are the connectivity's. So, if we can have one single connectivity that means, we put X over here.

So, one pocket which is elaborated around X and another pocket which is elaborated to on the other side and if we get M 1 here and M 2 here and this particular group is utilized for bridgingum. So, this is basically a single point attachment; so singly bridged binuclear systems; so X is there. So, singly bridged attachment if you have then you can tell something related to your distance. So, it is say D 1 then in the next case that means, you can have sometime you can bring the second group that also can go for the bridging. And when you have a situation like this in X and Y both are involved for bridging, you can decrease the corresponding distance between M 1 and M 2 and remembered that whenever, we bind this thing always you should have some vacant positions.

So, designing this thing we always required some positions which should be vacant. So, these 2 vacant site can be utilized for substrate binding and the second site for reagent binding. And if X there and X is part of the ligand during the ligand design, if you think that X should be there and based on that X you get the corresponding binuclear compound and this one which is coming from outside. If this X, we call it has a endogenous one which is coming from the ligand system then Y is exogenous that means some small group like sometime will find a labial group is also find water molecule. So, it can be water based, why it is water based? Because, X is there and some other donor points if it is available for binding M 1 and M 2 you have some other positions available which can either be occupied by monodented water molecule. But if this M 1 and M 2 are close enough, you get a bridging water molecule or a hydroxide group or a oxido function. And depending upon that, that means, depending upon their protonation level and the PH of the medium. We can move from here to here or here to water molecule

and interestingly when you make these and if it goes for some kind of loose binding o on M 1 and M 2 will find that if this water bridge clips you get 2 water molecules, which are bound to the system in monodented fashion.

So, if you get ultimately this arrangement this is also suitable for your substrate binding and reagent binding, because these water molecule can be substituted by your incoming substrate molecule. And these water molecule, if water is not required something else is required for attacking your substrate has reagent or has some useful group which will attack your substrate. So, these 2 water molecules will be there. So, what is this X? How this X can be modified? And how this X can change the different distances? So, we will see this in some model compound that means, synthetic compounds, what we can make in the laboratory. So, what we have seen that.

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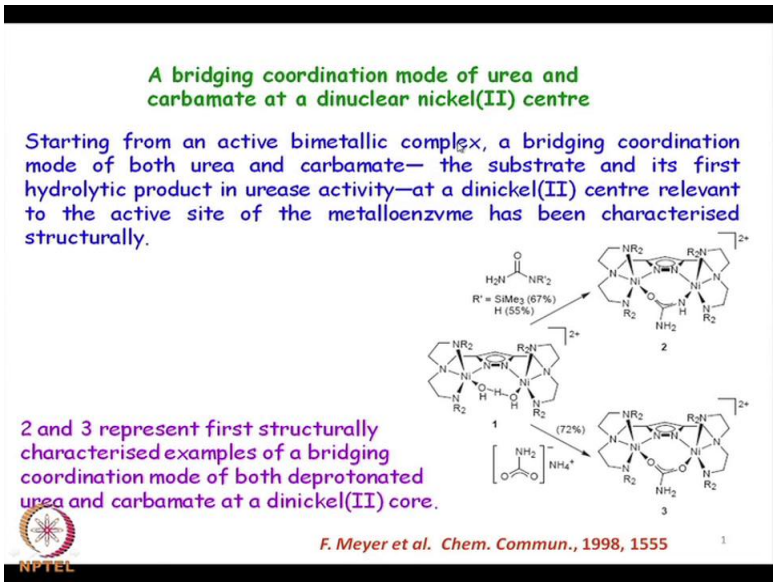

That the bridging coordination mode of urea when we are taking about urease molecule. So, this is one such motive do not worry about the complex structure for that. So, if you have this N 1 and N 2, what we need, we need 1 pocket for binding the first nickel and another pocket for binding the second nickel and this particular one. So, this is the endogenouss bridging unit which is based on perazol. So, perazol group is utilized for holding this nickel and that nickel through it is N N bridging mode. So, N N bridging mode on the perazol and this perazol group you have other tridentated groups you can make on the other sides. So, these 3, this nitrogen and this nitrogen can give you a facial

capping on the other side of the nickel at this particular nitrogen is giving you the fourth coordination.

So, you have 3 from this capping part and, 3 from the other side. So, you have 4 coordinated nickel and this side and another 4 coordinated nickel on the other side. So, these 2 nickel centers, when they are coordinately saturated, you get a penta coordinated species. And you have something which is nothing but since you have some vacancy some positions it is sometime it only based by hydroxide group or is a dimmer of hydroxide and water molecule. So, water molecule. So, is a basically water hydroxo plaster is there utilizing for your binding the nickel groups. So, this bridging coordination mode of urea and carbamate that people have identified in this paper that the groups which are responsible for binding a dinickel site because model studies gives us all this informations related to the urease activity.

So, we get a bimetallic complex and using a reaction where you have the dinickel celial urea this are, are time is tri methyl celieal function. So, basically is that you get the corresponding urea binding in this form and you have N H in the deprotonated form. So, it is not the pure substrates as urea but, the binding mode people are tried to identify it, that this can be your substrate molecule which is binding. So, you have that nice gravity that means the nice vacant positions where you can displace this water and hydroxide groups by your substituted urea molecule. So, which therefore, can be your relevant part for the active site of metalloenzyme in urease molecule. So, this is the typical reaction condition where you get and you will find that you have something that you get the corresponding species that the nickel nickel distance is important.

So, these molecules, people have prepared it and then structurally characterize. So, this particular this nickel nickel distance will tell you. Whether, this nickel nickel distance for compound 1 is suitable for bridging hydrox function or a hydroxide water group for longer distance of nickel nickel. Because, you have here when it replaced by these groups you have a bridging unit, which is a 3 atom bridging unit like that of our acetate function. So, when acetate group bridges to nickel center through oxygen carbon oxygen like your copper acetate. You have reasonably bigger distance compare to a single atom bridging, compare to bridging by a hydroxide function and ethoxide function or single oxygen of acetate group. So, this distance is reasonably big enough because, we get in

the second reaction where ammonium carbamate is used. So, directly the hydrolyzed product of this urea hydrolyzed product which is forming there.

We just utilize they have utilized it because, whether your urea that ammonium carbamate is going there and is binding these 2 nickel sites. So, they are basically prepared and structurally characterized. And in one case that means, this bridging unit you can have large number of this what I am just told you, that you have this exogenous function. An exogenous function, when you the nearby second metal that means, this bimetallic system or the bi metallic complex what we can have that is not that you have 2 such groups that means, 2 urea molecules or 2 water molecules are coordinating to each nickel site in monodentated fashion. So, your distance will always attract because, this particular site will be remain vacant, if you have water coordination and only that urea molecule is binding the first nickel in monodentated fashion, that is not happening there. and this in the second case also.

So, these thing this particular core, you look at the core basically. So, this if you consider these 2 nitrogen and this is the 3 atom bridging unit oxygen carbon oxygen. So, 3 plus 2 5 plus 2 from the perazol unit. So, is a 7 membereded ring. So, these 7 membereded ring; obiviously, will tell you that immediately, while looking at the bridging units which are utilized for bridging. You can immediately say that this nickel, nickel distance is bigger enough, compare to some bridging what will see in some few other examples, that this can be your phenol based also. Because, in earlier systems in other systems, we know that this can be your phenol that means, the phenol oxygen can be utilized to hold 2 nickel sites. So, when you have one single atom here another single atom here and 2 nickel. So, that basically N 2 O 2 core that is also possible to have, where you have the shortest nickel nickel distance.

So, these things if you get the corresponding structure and all these and the positioning these 2 nickel centers. You can characterize something related to your magnetic interactions also, that people do for the magnetic interactions where these nickel 2 sites are present. So, you have the deprotonated urea and carbamate which nicely binds to 2 nickel sites.

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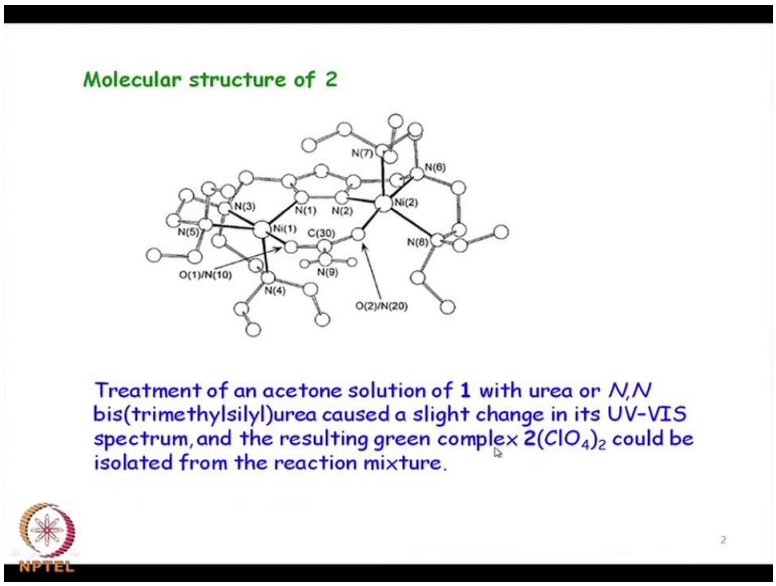

So, this particular structure basically in the acetone solution of 1 urea and this trimethylsilyl urea. So, is substituted version of urea and the monitoring can also be possible is not that you have the structure and you determine the structure then only you will able to tell; whether, you get the corresponding substitution by urea or the carbamate group, but if you simply notice the corresponding change in the UV visible spectrum that means, there is a slight change in the corresponding color of the green compound. Because, this nickel you have the strong dd band for the nickel 2 because, both the 2 centers we are not talking anything related to the nickel in other oxidization state that means, nickel in plus 1 or nickel in plus 3. Here, basically will get nickel in plus 2.

So, the dd transition will be predominating and you have the green compound of this and when it is reacting with the incoming group that means, the exogenous function any exogenous function. So, any exogenous group will coordinate. So, you get something that means, your corresponding ordering for the dealers are modifying and there is a slight change in all these lambda max values. So, if you have a spectro watometer and if you monitor the corresponding dd transaction bands will see that several there is little bit change for that due to this short of coordination.

So, the positioning of nickel to nickel sites is respect to this perazol unit, this your perazol unit and the corresponding binding of this groups can also tell us something related to that of your corresponding sites that means, when we have this M 1 and M 2,

we get this substrate sites and the reagent binding sites. These are your basically, we call them as active sites. So, what is there that means whether, your active site is vacant or they are binding to water molecule, or they are utilizing some other donor groups because the availability of these active sites are very much important for their reactivity of the enzymatic site. So, the reactions for those active sites is important. So, if these are not available that means the vacant sites are not available and if they are water bound or the bridge groups, if they are occupied by some strong groups, say N 3 minus or thiocyanate or silinocyanate etcetera.

So, addition of these groups like what we just have seen that the binding of urea and the binding of the carbamate groups changes your corresponding pattern in UV visible spectrum. So, the corresponding lambda max values for the binding of these groups individually or separately, that can also be studied nicely and if they are bound strongly because, we are talking in terms of the binding of urea and it is transform form as carbamate, but when azitesis binding to this sites either the substrate site or the reagent site and if they make some strong nickel nitrogen bound so, nickel and then azite.

So, if they are making some strong bounds to that and basically this particular catalytic site will lose their catalytic activity because, you cannot remove the azite from the system. So, that particular activity that means, if we are thinking of some activity related urease activity. So, that activity will be inhibited. So, inhibition study that catalytic inhibition study can also be dump by looking at some of these exogenous useful groups, that exogenous groups which are coming there and binding to the nickel site by simply looking at your corresponding lambda max values. So, that gives us not only the substrate binding or it is transform product, but also some kind of inhibition. If it is possible to achieve there at the active site that can also be studied.

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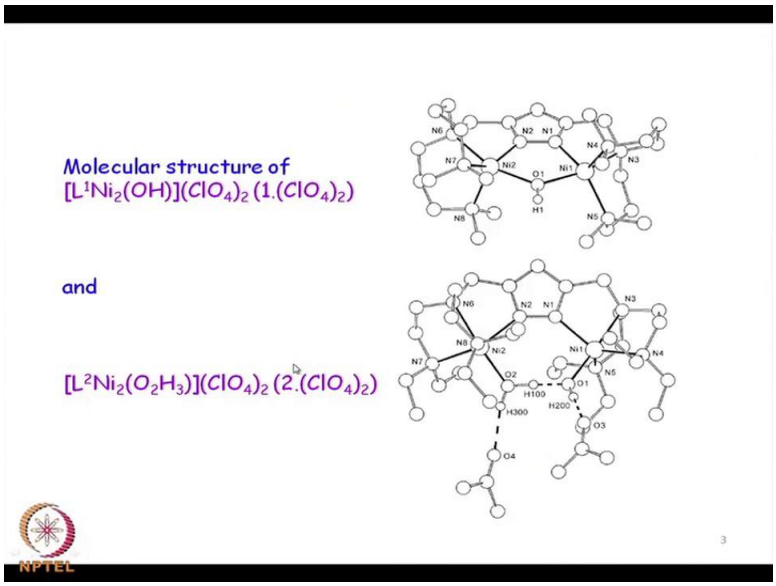

So, these other 2 example is a basically, the same molecule where you can have this hydroxide groups. So, in this particular case where you see that a bigger unit was present where you have this water molecule. This water is there and you have the hydroxide function. So, this particular unit so, basically what is happening there that individually this particular perazol motive is so important, but you have the corresponding 2 bounds. Because, whatever coordination geometry your achieving on the nickel site is important, if it is penta coordinated one you should think of what type of penta coordinated geometry your getting around nickel 1 and around nickel 2 because, it is a simple penta coordinated one. You can have a geometry of square pyramidal 1 or a trigonal bipyramidal one. A nickel have a square pyramidal and bipyramidal geometry then which particular bound is available, if you have all the positions are there.

So, which particular bound is available for binding this lose water molecule that you should think of. So, whether, it is typically in this direction or it will be some of angular direction. So, basically just what we have seen that you can have 2 nickel sites and the possibility is also there the 2 of these sites can be occupied by 2 water molecules, here this water molecule has undergone deputation only. So, this is your hydroxido site bridge function and this is your water molecule and you see if you bring any substrate molecule like that of your urea that urea will immediately replace first what the water molecule. So, it will, you will have a urea bound water molecule there and in the second nickel site is having some hydroxide group.

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So, this metal bound hydroxide group will then immediately attack your urea molecule. So, urea carbon will be attacked by your hydroxide function. So, the flexibility of this particular backbone, because a protein structure, what we can have in nature. In the biology, what we get the proteins structure is so much flexible. That the flexibility of this system will say something that you can have some sometime will find the depending upon a 1 particular form the particular enzyme have different forms depending upon some protonation level that means, 1 particular site is protonated and another site is deprotonated. You have the corresponding interaction that means, the bound is typical parallel this 2 bound that means, it is moredent groups which is attaching nickel 1 and nickel 2 are almost parallel then you have 1 parallel water coordination to this site and another parallel water coordination to that site.

In that case you can have the individual water molecules attaching to this site and attaching to that site will not form any kind of this hydrogen bounding interactions when they are angular because, basically we find this o distance. So, when they are in hydrogen bounding distance. So, they are in hydrogen bounding distance then only it forms some hydrogen bounding interaction and that is basically, governed by the typical endogenous backbone of the ligand that means, perazol backbone if the perazol backbone is controlling because, the most favored geometry for that is that the one site this other site you have a perazol unit that means, you have NN bridging from thisside NN bridging. So, what you except you except from the other side you will have also a NN type of O type of bridging that is either you can have a symmetrical 6 membered ring, 6 membered core ring is formed involving 2 nickel sites.

So, what will now see that how you change this particular perazol backbone that means, this bridging unit is. So, important and while talking this all this model compounds you have to have this particular primary coordination site which is very important; otherwise, you cannot bind 2 nickel sites like that of your proteins structure because of protein has a very huge system and you have the already pre made that cavity and other cavity and those 2 cavities basically, bringing 2 nickel sites close to each other. But here you need the basic support from this parent unit either it is a phenol unit or a perazol unit. And you can have atleast one coordination site out this has this nitrogen and 1 site has that nitrogen.

Otherwise, if you have a simple perazol unit like perazol, imidazol and all these nitrogen bearing hydro cycles. If you do not force has that means, if you do not have such type of gelatin arm like this, this is the NN gelatin arm of this perazol elaborated ligand and this is another NN gelating arm on the other site. So, if you do not have this gelate arm it will not hold the first nickel similarly, it will not hold the second nickel by the simple perazol unit. So, if some supporting system is there then only perazol can bind to these 2 nickel sites as bridging unit; otherwise, perazol can be happy and can stay has a monodentity unit to this particular sites.

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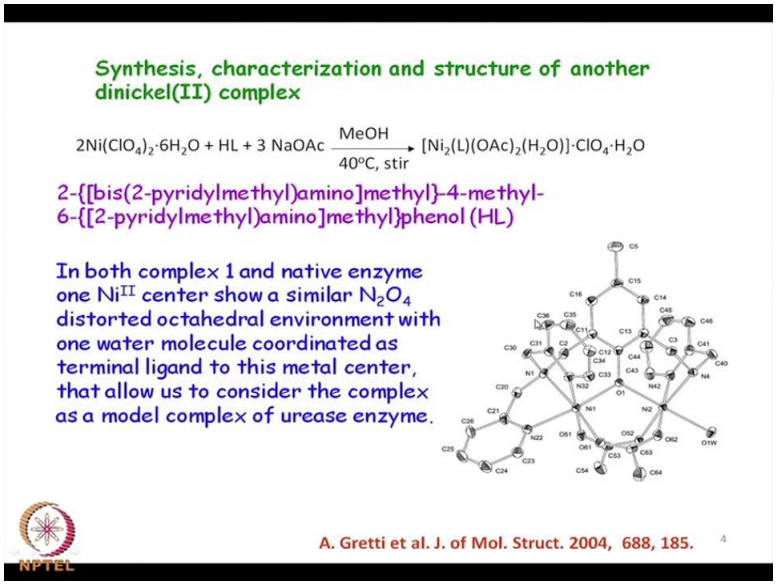

So, this, this is second example where you just take the elaboration that means, how large number of any bimetallic site. This is some I am giving setting some of these examples, where you can have a particular unit that means, whenever we talk that any bimetallic catalysis or bimetallic units are required, that you have to bring 2 metals centers not more than that atleast 2.

So, the very basic minimum number of metal centers you required for this sort of catalysis is, is a very simple thing is like perazol you now take the phenol unit. So, the same thing the phenol unit and from these 2 ortho positions, you elaborate this group and again you bring one nitrogen here. So, it is elaborated through this nitrogen and it is elaborated through this nitrogen also. So, including this nitrogen and this phenol ring, you have the corresponding size of this ring. So, you have the 6 membered ring. So, this

is a 6 membered ring and on the other side also you have the 6 membered ring. So, that 6 membered ring will be there.

So, that is the give you the corresponding stability rendered on the nickel 1 and nickel 2. So, is very simple to make it also because, if you have 2 atleast 2 substitutions on these positions on the phenol units and the 2 position and the six positions. So, this is the whole name of this ligand based on phenol and you have the ligand and very simple salt that any salt from that your periodic table you can have. So, it is one example is that for the dinickel compound in 2, 2 plus 2 oxidization state because, we are talking about phenol. When it is based on phenol you do not expect that you will be able to stabilize nickel in the lower oxidization state. So, this a already you have the charge and phenol is well known to stabilize the nickel in the most normal oxidization state of nickel say plus 2. So, you are providing something that means, you will you are giving nickel percolate over here. So, is the most suitable salt because, the percolate groups you can remove very easily then give this ligand.

So, not the nitrogen, but you elaborate further, because these are the 2 other pyridyl units so, these 2 pyridyl units so, if you consider on the left hand side this nitrogen, this nitrogen and this nitrogen. So, look at the molecular structure how you read is not that you should be a very expert coordination chemist. You look at the nitrogens available which are binding to the nickel site because, the protein substrates are coming like this the histidine chain all the aminoacids side chains are coming like to bind the nickel site. So, you have these 3 nitrogen. So, how we make these elaboration this that this is basically, a part of the pyridyl ring. This is also a part of pyridyl ring and this nitrogen is aliphatic nitrogen which is directly attached to your phenol unit. So, what you can have, if you do not go for this all this complex system that individually, we can, we make basically, this tridentated ligand all the time you can mak so, if you have this pyridyl based system.

So, 2 pyridyl groups you can have. So, if you take any pyridyl where you have the in ortho position you have the amen function. So, so in any pyridyl, you have in the ortho positions. So, methyl amen function and you take the second pyridyl ring has your pyridyl 2 aldehyde, I mean get the corresponding ship base. So, a simple ship base you will get and that ship base will be a tridenatated ship base. So, this nitrogen the second nitrogen and the third nitrogen. So, if you have the tridentated ligand and if you reduce

the tridentated ligand and next step of this making, this molecule is that how you put the tridentated ligand to the phenol unit. So, simple course of reaction is the simple manic reaction is possible or if you can have CH 2 Br substitution on these 2 positions.

So, that immediately react with the reduced form of these that means, you have the NH function and you attach this part to this group. So, the similar arrangement for the other side, but you have something, because this particular example will give you not only when you force this particular system because, you react with nickel percolate the ligand and sodium acetate. Why you are not using something, because sometime the solubility and the crystallization is. So, important because, you cannot use nickel acetate for that reaction. So, initially we do the reaction with percolated then externally you are adding sodium acetate because, initially what you are looking for that this positions which what are occupied by these 2 acetate groups, these are your acetate groups. So, initially when you react with percolate, nickel percolate those will occupied loosely either by the percolated anions or by water molecules.

So, these will be the loosely attached groups over there and in this particular case, you have the pocket. So, the nickel center in both the cases it is similar, but instead of getting this particular parts. So, on the left hand side so, this structure on the left hand side you have a tridentated part from this nitrogen, this nitrogen and that nitrogen, but on the right hand side you see is a different one. So, we make something. So, this particular binutated ligand is some example where these 2 pockets are different is not a symmetrical binucleating ligand. So, protein structures are also sometime like this that means, your available histidine groups and all these groups are not matching in number for the left site of the cavity then your right side. So, if you take something that means, you on the right hand side you do not allow a tridentated ligand to bind, but, also a give a bindentated one.

So, you will have only 2 nitrogen’s available from the right hand side. So, 1 site is available which is nicely occupied by simple water molecule. So, that is why this water in the formula it is there this water molecule. This water molecule is there on the right hand side. So, what basically, we getting from here that is the same dinickel compound and this can also be considered as a model complex for urease activity because, this acetate functions. The next step, what you will able to do is that you remove this acetate groups. So, if you just loosely go for some bisalt or some weak acid you protonate this

acetate function and acetate functions will go simply leaving behind the corresponding acid as again percolated and you react with the urease molecule urea molecule and the water or the hydroxide function those will be occupied by these groups, but other interesting aspect This is the chance that I can tell you here immediately because, We will not study all these things because, the much more complex system in the ezymatic function is a hetero binuclear system.

So, some hydrolytic enzymes like purple acid phosphatase type of thing or what we have seen in case of superoxide dismutases that you have a center which is superoxide dismutases are copper based system an one, one particular site is occupied by zinc also. So, that is a copper zinc system and if you go for purple acid phosphatases, which is a iron zinc system. So, you have a pocket, where you will find from this molecule basically, if you do not prepare any such molecule, but if you look at the structure nicely for this molecule e immediately, you can think that high can replace this particular point by changing the metal salt for the reaction as iron, iron will go inside nicely in presence of substituting this particular nickel sites.

So, iron will sit nicely over here and this particular site is also suitable for binding zinc and when zinc is binding over there the most preferred coordination number for zinc is 4 and 5. So, it is this water molecule will go, will not go there and it will be closely your square pyramidal geometry. So, if zinc is sitting over here, you get a system where you have a square pyramidal geometry for the zinc and you have the octahedral geometry for the iron. So, that sort of things so, you generate some asymmetry within the binucleating ligand and you will able to make any compound like, you can put iron on the left pocket and zinc on the right pocket. And you have the bridging unit, because you can modify these groups because, when we talk for the simple urease molecule and that urease molecule, we are talking about some hydrolytic reaction.

So, when we talk about some ester hydrolysis so, phosphate ester hydrolysis so, those group of molecules are the similar type of molecule, those are phosphatases. So, one such example I just giving will call it as a PAP, the purple acetate phosphatase. So, that purple acetate phosphatase is also similar where one site like that of superoxide dismutase is basically, zinc is present and if zinc is involved there and iron is involved there and we are not going for any kind of Redox reaction is a hydrolytic reactions zinc is fine. So, any water bound or hydroxide bind group on zinc is useful for hydrolyzing

your substrate molecule, which is your phosphateseter. So, phosphatester will be hydrolyzed over there and will remain like your acetate function their corresponding phosphoric acid substitute. Phosphoric will remain there and which will be bound to your metal center. So, this gives us some idea that how you go for some model compound for dinickel system model compound for hydro bimetallic system like copper zinc or iron zinc system.

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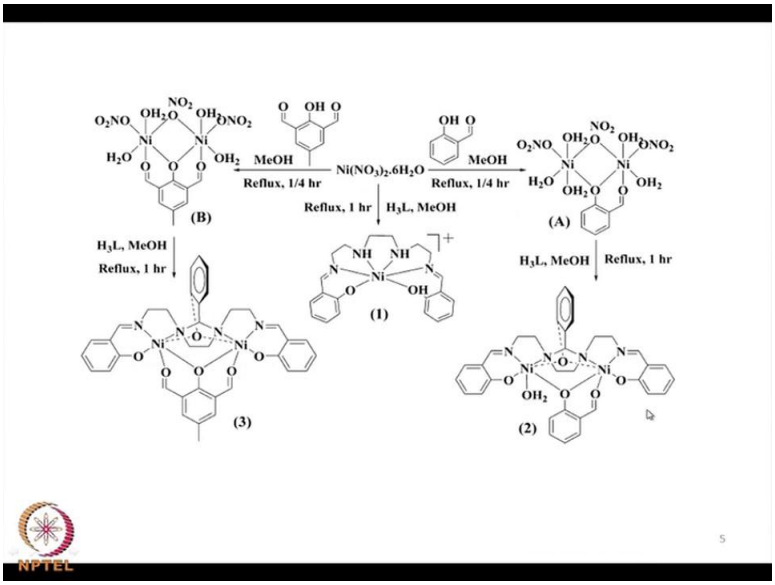

So, one such example simple example that we can go for this type of thing that when we are handling this molecules, we are talking that means, we are handling something related to our nickel salt. So, we just go for some group, where you have the nickel nitrate as a salt and this is another example of a binucleating ligand and is very simple ligand you can make with a long chain, amen ligand which is nothing but your is a well-known one is triethylenetetramine. So, if you have a triethylenetetramine, this 4 nitrogen's are coming from triethylenetetramine backbone. So, very simple way if you react triethylenetetramine with salicylaldehyde.

So, on 2 ends you have the salicylaldehyde has a ship based, but here because of the availability of the 2 adjacent NH functions you can make some imidazole ring also. So, once your able to make someimidazole ring on the adjacent nitrogen you basically, compartmentalized this hexadentated ligand into 2 form. So, this is basically, your backbone that means, like that of your perazol unit or phenol unit. So, this phenol unit

which is attached to your imidazole ring can go for bridging to nickel site. So, you have some group, but what when giving this example because, your ligand is not very much strong because in city you can make when you add is a very simple reaction even anybody can make in the laboratory that you have to take the triethylenetetramine and salicyaldehyde.

So, that ligand, if you can have and that gives large number of reactivity pattern for that when you react. So, one particular reaction condition. So, this gives us some idea that why this reaction conditions are important, how you get that we do not know whether you will get a compound like 3 or a compound like 2 or a compound like 1. So, in 1 sort one example is giving you that you can get that when you react it directly with this particular imidazolidin based by nucleatic ligand. This is the ligand which is written as H 3 L you have 3 protons on these 3 phenol groups then this the second and the third. So, when it is reacting with these your getting some mono nuclear compound so that means, you must have a very good backbone.

The stability of the backbone which we are talking about say a perazole backbone or your phenol backbone. The stability of the backbone is important, but in this particular case you have the substitute imidazolidinring and that substitute imidazolidinring is not. So, stable is different from your imidazole ring is imidazolidin which is a reduced form of imidazole and which we make from diamin andaldehyde. So, diaminandaldehyde immediately gives us imidazolidin ring. So that imidazolidin ring is also very much sustable for hydrolysis reaction. So, in 1 sort what we are getting that in urease reactivity, the nickel center which is bound some water molecule or some hydroxide group is responsible for the hydrolysis of urea, but in this particular case if your ligand is not. So, stable and nickel is present and you are doing all these reactions are in aqueous methanolic medium.

We are not maintaining any dry condition or some not atmosphere. So, methanol is there. So, water molecule is also there. So, water is interacting. So, because this 6 water molecules for the nickel nitrides starting nickel mines, you have plenty of water molecules already present. So, those water molecules already they are. So, nickel bound water molecules remember it. So, you have nickel bound water molecule and when we are along with to react with your ligand. So, nickel bound water molecule is your reagent now, which is your catalyst can be is a reagent for hydrolyzing your imidazolidin

backbone, a similar to that of your urease activity. So, it is hydrolyzing the imidazolidin backbone leaving behind that means, this particular phenol unit that means, the salicyaldehyde group simply, when go for this reaction your salicyaldehyde group will go away. So, it just simply removing from there.

So, originally if you have this ligand because, you see this ligand. So, here you have the intact this particular part, you have this intact part. This on the left hand side what you have you have 2 nitrogen and 2 oxygen, because these oxygen is your phenol bridging unit. So, the you have the N 2 O 4 pocket on the left and on the right hand side also you have N 2 O 4 pocket, but when this particular group is going away that means, removing one salicyaldehyde molecule from the system, your ending with a simple hexadentated ligand. So, this is a typical hexodentated N 4 O 2 ligand and nickel will be nicely coordinating to all 6 donor groups and giving a corresponding complex. But this thing is that the situation is depending upon the condition of the that and you are not adding some strong base because, in most these cases when we talk about the coordination of phenol to any metal salt or any phenol substrate you are using and in presence of the metal salt, if you do not put appropriate base, a simple triethylaminenene.

So, giving some appropriate base is very important; otherwise, you do not gets the corresponding deprotonation of the phenol unit. Here we have, directly reacting this because basically, your refluxing in menthol for 1 hour for with this ligand giving you some compound already, you have the nitride groups present. You see this compound which has been isolated has good crystal when you have crystallize it in the single crystals also from the parent solution. So, this compound is crystallizing has a monocationic compound not a neutral compound because, you have these 2 positions already, if they go for deprotonation you get a corresponding neutral compound. But this particular O H you see like that nickel has some affinity for binding water molecule it has some affinity for binding hydroxide function. Similarly, in this particular molecule a simple mono nuclear nickel compound, but it gives.

In this particular case you have the deprotonated phenol oxygen you have a salt nickel oxygen bound, but this nickel oxygen bound is long enough because, you have coordinated phenol group. So, this particular nickel will also gives us some information that this nickel is coming out form the medium, where you have both the 2 phenol units in different protonation level, one is in deprotonated form another in the protonated form.

So, what basically we see that if you the nickel nitrate and if you use this particular type of ligand, which is a very fragile ligand you can call. It is fragile ligand because, it is getting hydrolyzed is not. So, stable that that means, your backbone is not. So, stable it is not retaining nicely. So, backbone can go away for any kind of nickel based hydrolyzed reaction. So, what you think of that if you use in a reverse way that when we are talking about in all these biological system, all this enzymatic nickel system, that if you have this particular phenol based dialdehyde 2 sticks diformyl phenol proposition is also substituted by methyl group.

So, this particular unit, what we just talking about the generation of this ligand, or any ligand in protein chain also, if they are elaborated based on tyrosineresidue. So, tyrosine amino acid residue why this tyrosine is so important in all this sort of interactions with the metal salt? Why this tyrosine residues in some point giving rise to the periodical for the galactose oxidase activity and all these. So, binding of this phenol unit is important, because if you do not have these groups that means, this aldyhyade functions if you do not have is very difficult to go for corresponding binding of this phenol unit.

Phenol can bind to any single metal salt in monodentated fashion only, but you have some groups like that simple aldehyde functions. So, you get this that means, if you have on the other one side that means, this particular unit on the right side, this is your salicyaldehyde. So, will see that, we are doing all these reactions because, the well-known corresponding bidentated O type of ligand is we all know that is acetyl acetone, acetyl acetone. So, salicyaldehyde is also behaving in same fashion that is simple salicyaldehyde can be a very good bidentated ligand will come there actually. So, right now, if have you see that elaboration on the both side of the phenol unit if in the form of that that phenol ring or you bring these 2 groups from the protein chain.

If you are able to bring these 2 protein chain of a group from the protein chain from histidine residue or any other residue so, you can put one metal here and you can put another metal. So, that basically gives us. So, whatever you react with the nickel nitrate with that of your this particular dialdehyde you get some particular motive like this. So, in this particular environment that means, that nickel nitrate salt. So, nickel nitrate salt is giving you a particular unit which is binuclear team. So, very simples thing that means, you have any simple such ligand anything you can think of, anything you can make and you can allow it to react. So, always you think of that whatever, this type of unit you

allow it to react with any simple metal salt nickel nitrate nickel percolateor anything you always think of distress motive that means, you are forcing your phenol unit to bridge these 2 nickel sites. So, then you have in your hand these same ligand H 3 L. So, when you allow it to react with asite because, this particular unit based a very, very readily you can isolate it and when this exogenous group is present, you do not find any kind of hydrolysis.

So, if the condition is same in presence of this group the same ligand in methanol reflux for 1 hour. So, condition is same, but, you aregetting 2 different compound 1 and 3. So, the presence of your supporting unit that means, you can consider this now has your exogenous group so, exogenous bridging unit. So, anything like your azide function your thioycyanide or hydroxide function. You can consider as a exogenous unit because this particular part is not part of your ligand unit, your ligand unit is this one above. So, this particular. So, it is basically a motive. So, in solution what we are getting in solution you basically, you can have some motive because, you can have all these loosely bound nitrate groups water molecules and all these are all loosely bound thing.

So, on this dialdeyhede platform, you can have a dinuclear entity is a dinickel complex you can make in the solution, and above that particular system because, you think of some catalyst environment you can go for some catalytic reaction. So, if you are thinking or if you can talking about something related to a nickel catalysis. So, you take the nickel salt you put something some support mechanisms that where you some exogenous ligand which can support these 2 nickel sites and you get this. So, this particular thing is forming that is why you are able to stabilize this particular unit and is a symmetrical one. So, in our previous example where we have seen that you can have an symmetricalbinucleatic ligand, but, but this ligand is a symmetrical one. So, both the 2 pockets are same, but, if you change and what you are reacting your exogenous ligand is also symmetrical, which is forming phenol aldehyde group and phenol carbonil function.

For this nickel has well has this nickel, but if you same thing that means, elaboration of this ligand that, if you get this one with dialdehyde we should get it with monoaldehydelike salicyaldehyde. So, when we react with salicyaldehyde the starting compound what is forming in the solution and you get this particular one. And in this particular case, you see we are forcing because, this particular sort of motive is not easily available in the system. Where your functioning as a bridging unit and again whatever,

we are discussing so far about the positioning of these 2 nickel sites are important. And these 2 positioning of these nickel sites as important otherwise, you can have this particular unit, if these nickel 2 are little bit different if the distance is beyond 3.8, 3.9. You get this nickel is bound to 2 water molecule this nickel and on the right hand side, you have only bidentated salicyaldehyde, what you except. But since, the nickel nickel distance is salt you start some interaction with this phenol unit and this phenol group is utilizing for bridging between these 2 nickel and one such group.

So, your exogenous group is not that all different salt of exogenous group can bind a dinickel motive symmetrically. So, is a asymmetric binding. So, exogenous group asymmetrically bound to these 2 nickel sites and if you think of something related to that particular type, what we are getting for dinickel system that this can be your substrate. We are talking about something binding of urea, but instead of urea, what you can have in your hand is now a carbonil function which is coming from the salicyaldehyde and this carbonil group is nicely coordinating to your nickel site. And the second site is having some your nucleophile that means the water molecule. So, this is the situation where you can have the reagent in your hand that means, the water is bound to one nickel site. And your substrate or carbonil function which is similar to that of your urea coordination is attached to your second center. So, from a simple ligand system you can have three different types of molecules, which can give rise some information some understanding about your urea's activity.

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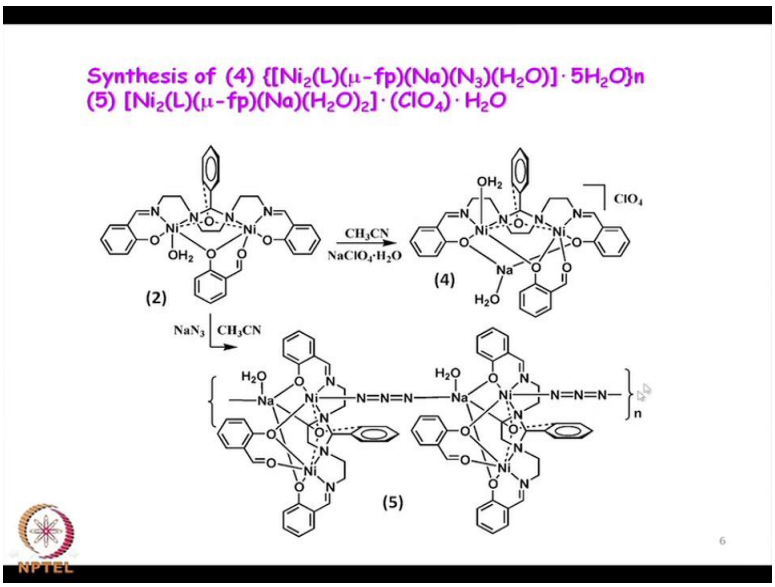

And if you go for a further reaction that means, when you talk about something that means, if you have a ligand system, and that ligand system is in your hand and that ligand system is utilized for a nice dinickel systems. So, this is your dinickel system and salicyaldehyde is utilized for bridging these two nickel sites, but this particular unit when we talk in terms of the corresponding reactivity pattern. So, these complexes these binuclear nickel complexes are very much reactive in. So, the reactivity pattern, these are two such examples that if you go for what we are talking just now, that if you are allowing to react with sodium azide.

So, this compound to whether, you can substitute this corresponding position that means, whether, your water molecule, this particular group was attached to your water molecule is occupying by your azide function that means, what we are talking in terms of the corresponding poisoning or innovation of the catalytic site. So, that we should know how good they are for reacting some exogenous groups like azide or thioycyanide or any other hydroxide function. So, when you allow it to react with this azide function. So, they are substituting this water molecule, and this salicyaldehyde function is still remains, it is not going away, but interestingly we get some different architecture. So, sometimes in solution chemistry and in the biological system, when we study all these biological sites, this particular groups are very difficult to understand that when you have you this particular unit.

So, the reactivity pattern for these so, if you have. So, when you are utilizing this sodium azide is not that in biological system you are providing both together that means, your providing the cation and you are providing the anion together. So, when you are providing in a synthetic molecule. So, that is why the synthetic chemistry is so important and you get something that means how your anion is entering into the system and how your cation is entering into the system. And if you because, everything is now in front of you and you know the entire structure, only thing that you have to justify the reaction. We are justifying the reaction, why it is happening, if something is given to you the ligand is given to you should be able to tell that, why it is binding this fashion and why it is simply transforming for a very simple reaction with that of your sodium azide.

So, before talking in terms of these, you just simply go for another sodium salt which is your sodium percolate. So, this compound, you see the reactivity pattern because, if we can recall the thing that this particular compound is definitely we have identified this

compound is not a neutral compound, because all the time what type of compound you are getting; whether, a cationic compound and neutral compound because, when we talk in terms of interaction with some other biological staff say simple interaction with DNA molecule which is anionic. So, if you have some cationic unit and that cationic unit nicely goes into the DNA site. So, the cationic will have a typical interaction for that, but those are much more complex interaction that is very difficult to identify or understand sometime.

But before that if you have a corresponding cationic compound in your hand. So, definitely we are we have not able to understand that thing, but initially when they are reacting because if you can monitor the corresponding reaction kinetic initial all the 4 nitrogenase the nitrogenase are all neutral in nature. So, all the 4 nitrogenase are available to bind your nickel site then your phenol groups because, they are all protonated. So, they will have some weak reactivity pattern for the nickel site. So, they are reacting with your nickel site. So, this particular system is there that means, if you provide that means, if your able because this particular thing if you just simply go for potential metric acid based titration based on that, you will be able to deprotonat this hydrogen and you will get the neutral compound. So, deprotonation will be possible when you have the phenol bound to the nickel site because, you have this particulars is much more acetic compared to your 3 phenol.

Your PK value for this is less compare to your typical phenol what we know for the isolated molecule. So, this is your neutral compound and that neutral compound, when you allow it to react with say sodium percolate. So, instead of going for some protonation because, you have not provided any proton source to the system we have provided instead a cation and this particular cation. So, this thing that means, it basically, this binuclear nickel site because all the time when we talk in terms of the biological system. You have large number of this cation species, when we talk about the corresponding sodium palm or the potassium palm in the biological system in 1 cell. So, you have plenty of sodium site, but when we in terms of the corresponding nickel site and which is bound to the phenol unit.

So, some groups are still available. So, you see in this particular synthetic compound what we can characterize it and we can solve the structure for it is typical identification. So, ultimate identification for excess structure determination is possible. So, if you have

some already phenol groups, which is bound to the nickel site is available there. This sodium is go for coordination like that of your typical thyether binding. So, crown ether well known, you all know. So, the crown ether type of coordination we all know. So, if you can have a 3 oxygen atoms in a cyclic crown ether type of arrangement it nicely binds your sodium or the potassium ion.

So that sort of situation, if you are able to give with that of your dinickel compound because, you have 1 2 3, these 3 oxygens, 3 oxygens. If you see the corresponding structure for these will find they are positions nicely over there that means, this 2 3 oxygen atoms are closely disposed like that of your corresponding cyclic crown ether, 3 oxygen crown ether, we know that of your treiger cycler nonan type of thing the try oxsa cylononin. So, tryoxsa cylononin, if you can have. So, if you available 3 oxygen which is well known to bind your sodium site, but in this particular case, this oxygen is already utilized for is bridging groups to these 2 nickel. So, this oxygen is not available for binding your sodium site and this 2 terminal oxygen groups only can bind your sodium and sodium is also attracting 1 water molecule.

So, your neutral compound your forcing it to again, a cationic compound, but not providing any protonation on the phenol groups, but putting some sodium into the system. So, what in this fashion this is the another avenue that gives us some idea that how you immediately convert a corresponding neutral compound, neutral binuclear or, a dinickel compound you can immediately convert it to a corresponding cationic compound. If you put sodium within it and you have the corresponding typical anion outside that. So, if you get that particular thing and if you have already this thing then is what is happening there instead of percolated, if you have azide function. So, in this percolate compound, you have water bound to it. So, this loosely bound water will be immediately replaced by your azide function. So, depending upon your corresponding position and all these thing and we all the time you can think of that azide coordination can replace your salicyaldehyde molecule, but it is not that see is very delicate molecule.

And so many things are there because, the whole dinuclear compound is already present over there and that dinuclear compound you do not find any ligand exchange reaction, where salicyaldehyde group is not knowing aways, alicyaldehyde group is because, it is bridged cumchillation is there. So, it is strongly hold holding the molecule and azide function replacing this water molecule and you have a different type of thing that means,

this azide in the other nitrogen is close to this sodium. So, sodium is now involved for bridging. So, is a basically coordination polymer 1 di chain is forming and that chain is forming is very unlike unit, that when you supply both the sodium an azide. Azide is coming and occupying the sodium site and already, through this reaction we have seen that sodium can bound. So, this is binding through ligand oxygen end only. So, basically we are decorating the molecule by putting sodium on the 2 oxygen.

So, these are basically, binding on the oxygeners, because this sodium is again a metal center cannot interact with the nickel. So, already you have the sodium. So, this particular azide function is bridging your sodium and nickel is not that your getting. So, everything can be broken and you can have a bridging unit between 2 nickel sites, but it is not holding is a very delicate molecule in that passion. So, you are getting some chain and this particular chain is propagating getting. So, you have binuclear motive here you have binuclear motive here and you are propagating getting that chain, through nickel azide sodium and nickel azide sodium.

Thank you.