Bioinorganic Chemistry
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Lecture - 4
Iron storage and Transport-III

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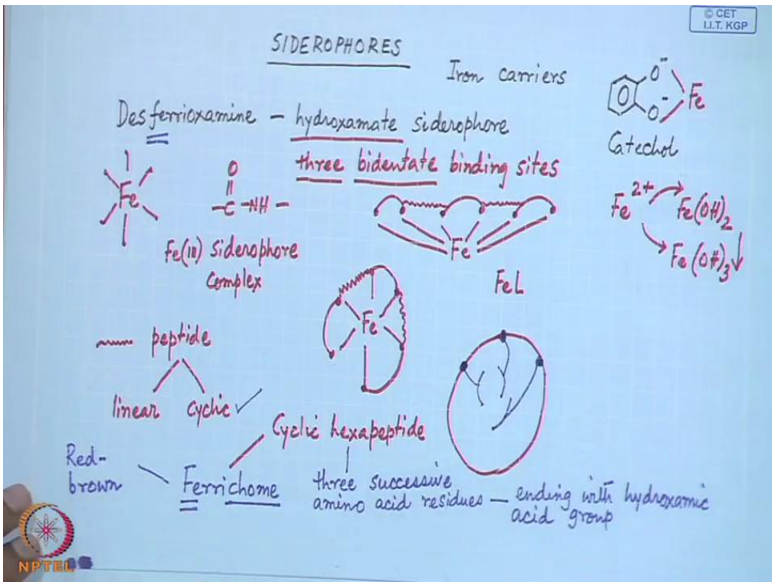

Hello. So, we are still with the siderophores molecules. So, the greek meaning of this siderophores is basically iron carriers and in our last class, what we have seen is one of the pendant function for binding on iron sites by the bacteria or the microorganisms is the catechol unit and today, we will see some of these molecules. One of them is known as desferrioxamine which is nothing but here, we were having a catechol one, but this one would be hydroxamate. So, the iron binding site would be the anacin form of the hydroxamate acid. So, it would be hydroxamate acid bearing siderophore, and definitely is a very good ligand. What we now know is that it can form a tris gillette with iron. So, you can have three bidentated sites. So, the primary requirement for all this siderophore type of molecules is that at least you should have three bidentate binding sites, and if you have a very good backbone and backbone form the protein molecules.

What we see that if these are like this and the most of the cases, we then have a amide linkage as the backbone unit and like the long protein chain, where we find that if we have a long polypeptide backbone and you can have some pendant groups coming from

the histaden or any other group which can be the donor at tones and those donor at tones will be utilized for binding your iron.

Now, this is very important. The three bidentated binding sites and the positioning of these three binding sites are very important because you can argue that you can have six such binding sites in a long polypeptide chain, but that may or may not function as a very good siderophore molecule, but if you have one particular part of the molecule is behaving as a bidentate unit, then another part is also behaving a bidentate part and also, you have a third bidentate part, but from our synthetic molecule because in today's class, we will see some of the synthetic model compounds which are very important because how the nature, how these microorganisms are producing these molecules are also very important to know because historically, when our environment, our earth was slowly reducing in nature, there is shortage of oxygen. We do not have sufficient amount of oxygen.

So, the availability of iron at that time was only the ferrous iron. So, we are not oxidizing ferrous immediately to ferric. What today we see that whatever ferric iron we have, immediately it is oxidized in presence of water and di oxygen molecule to the ferric iron. So, when the earth crust was saturated with iron 2 plus, we just simply get at that time the formation of ferrous hydroxides and this ferrous hydroxide has higher solubility at neutral PAH or near to neutral PAH compared to its oxidized version.

So, when we get atmosphere which is petty oxidizing in nature, we get something which is not ferric hydroxide and the solubility of the ferric hydroxide is less compared to the ferrous hydroxide. So, the iron requirement for all these different micro organisms, the bacteria, the fungi and sometimes for the plants, they provide something. That means some suitable mechanism must be adopted such that you get iron in soluble form which is counter acting against the precipitated form of ferric hydroxide. So, that is why that usable and very interesting gilletting laygy and siderophores are coming into the picture.

Now, if we want to know that this gilletting laygy will give you a corresponding iron complex, so we will have iron three siderophore complex whose formation constant should be pretty high that initially, when the siderophore ligands are available, it can trap the low level of iron available into the living system. So, the low level of iron, whatever iron is available there that immediately bound to those siderophore molecules giving you

the corresponding iron siderophore complex and bacteria is providing some suitable mechanism for that. Now, if you just simply connect these three bidentated parts and if these three bidentated parts can be available for binding the iron site, we get a corresponding Fe l complex.

So, the important thing is now that this position or the relative placement of this donor atoms are very important because we know that when certain part of the legating group having two adjacent donor atoms are binding to any metal centre, say iron, it has some stability which gives you the corresponding gillette effect also. So, if you have a five member ring or a six member ring or sometime a four member ring that gives you the stability. So, already we have seen that you have a catechol binding unit. So, this catechol binding unit when it is forming a complex with iron, we get a five membered ring nicely, so that the same time when we move from the catechol molecule to the hydroxamite molecule, we also know the ring size for the corresponding gillette ring, this ring size is fine. So, we get a complex like this, but if we try to bring the second part; that means, this second bidentated part, so second bidentated part is coming.

So, what should be there as through this zigzag line? So, how far this would be separated such that after binding the first part, the second part will also come close to iron and bind the same iron. It is not that this bidentated part is going to bind a second iron centre. If that happens, what will happen is you have a bi nucleated system, the same laygy and is bridging one iron centre which is Fe 1 and another iron centre Fe 2, but we are not looking for that.

So, the relative disposition of this bidentated site should be such that you can have all three bidentated parts together and you have that connectivity. So, for this hydroxamate siderophore type of molecules, the backbone is known to ours. That means, you have this zigzag part which are the peptide part of the protein chain is the peptide backbone and now, this peptide backbone can be of two types. One can be yours linear type. We know the long chain of the poly dentate ligands. Suppose, you have a very simple exaggedented ligand and we know it has 6 donor groups and that exaggedentated ligand can come and bind to the same metal centre, that may be iron or anything giving you a mono nuclear compound, but if you can have a cyclic one in the same way, we get the micro cyclic ligand, but now the thing is that you have the backbone. So, if you have a

backbone which is a cyclic one and micro cyclic molecules are like that, so on the ring, basically you have certain donor atoms like fluorine, chlorine etcetera.

So, we have certain donor atoms available and those donor atoms are directly attaching to the metal centre, and you get the corresponding metal micro cyclic ligand complex, but in this particular case, if you have this short or sometimes long polypeptide chain, suppose you can have a corresponding hexa peptide site, cyclic hexa peptide. What happens is you have a cyclic hexapeptide and that is giving us the corresponding molecule which is known as Ferri chrome. Chrome means they are all mostly colored because we are talking about Fe 3 plus complex.

So, corresponding iron complex and most of the cases, you have the iron in all the cases. So, this Fe is there in all the molecules Di ferrioxamine ferrichrome. So, they have the corresponding collar which is very similar to that of our iron complex. So, in this particular case, we get a corresponding red brown complex. So, if you have a cyclic hexapeptide and that cyclic hexapeptide can have three successive amino acid residues. What the residues all will end up with the hydroxamite formation.

So, three hydroxamite residues ending with hydroxamic acid group. So, you have here, then one C O N H and then, you have another and then, you have another. So, the other part basically to complete, it has a cyclic hexapeptide. So, other three peptide groups will be attaching there with the corresponding alkyne substitutions. So, this will provide your hydroxamite function, this will provide your hydroxamite function and the third party will also provide you the hydroxamate function. So, this is about a cyclic one. So, if there are two types of this, so one is therefore, your cyclic one and cyclic one is your ferrichrome type and you have the corresponding formation constant which can be definitely different compared to that of your linear type.

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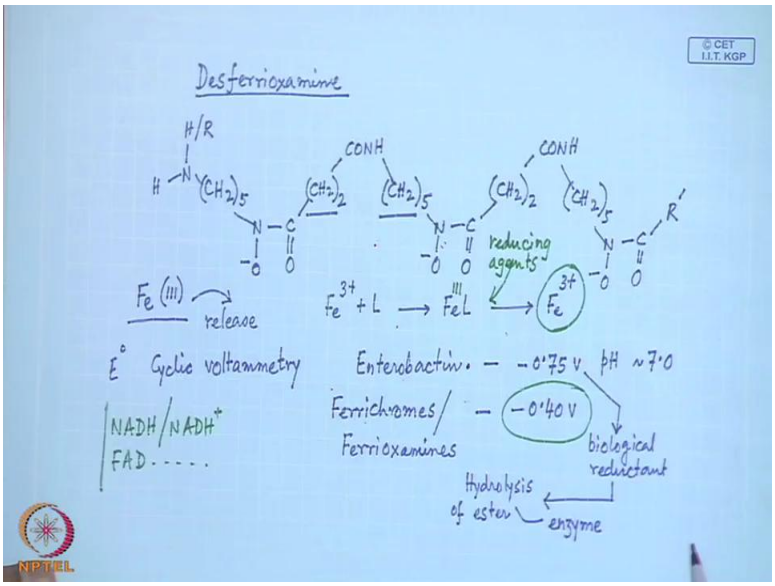

So, what is that linear type then? So, linear type, the same function would be with the backbone. So, one such example is your desferrioxamine molecule which has substitutions. So, this is the basic unit and that particular basic unit basically is repeated. So, you have one bidentated part. It can be H. Both of them can be H or sometimes, this can also be R because there are large number of these type of molecules are available. Some is called desferrioxamine and some is known as desferrioxamine b and so on. So, you have then that C O n H function there and immediately, it is coming as again that C H 2 which is repeated C H 2 whole 5, then O minus. So, 1 2 3.

So, you see the chain length. These chain lengths are very important. So, you have a 5 carbon chain from the one side and 2 carbon chain on other side and then, you can have the mild backbone. So, this is quite far, but for this protein type of molecules and this biological of the living system, the coiling is such that this bidentated part, the second one and the third one all are coming together to bind. The same iron and this particular case. So, when they are getting incorporated into the system, they all are stabilized in the ferric oxidation state, class three oxidation state and they are getting stabilized over there. So, these two particular groups; that means, the hydroxamic acid function and the catechol function, they do control the corresponding release of this iron because we are carrying these irons from one particular part to the other. So, these are very good carrier molecules and unlike our higher organisms, like human being also the transferring molecules are not available. So, the micro organisms cannot make those big molecules

like transferring molecules. So, they can only make the siderophore type of small molecules and those siderophore types of small molecules are utilized for binding iron.

Next problem is that how you can go for the release when you get a corresponding complex? So, if you have a Fe 3 plus plus l, if you give Fe l. Now, the question is how you just get back your Fe 3 plus as the free metal iron. So, one thing is very important that in the enterobactin type of thing wherein the previous class, we have seen that you have an ester type of linkage, so that ester type of linkage if it is getting hydrolyzed, then your iron can be released, but in this particular case, your donor groups are different. So, they are now hydroxamic acid group functions and the corresponding stabilization of these can be determined. That means how strongly they are trapped inside the corresponding metal complex. So, if we can determine the corresponding e 0 values experimentally, say by using cyclic voltammetry, so we will have the corresponding cyclic voltammogram and that cyclic voltammogram can tell us that which particular case the iron can be released easily compared to the other case. So, in case of the catechol type of binding which was our enterobactin, so in case of enterobactin, we can have and the corresponding today's molecules are Ferrichromes or oxamines or ferrioxamines.

So, for these two types of molecules, one is your catechol and another is the hydroxamate one. So, in case of enterobactin, the value is about minus 0.754, say NAHe. Sometime, we measure it with standard calomel electrode or silver chloride electrode, but all the time for the select or chemistry, these are also known as bioelectric chemistry. So, when the proteins we are utilizing and we measure the corresponding redo x potential, so this redo x potential in the most of the cases we measure it at as a corresponding ph values. That means, at a buffered medium. So, all of them are measured close to 7, the physiological PH 7.4 or something like that. So, enterobactin when it is measured, it is giving a minus 0.754, but in case of ferrichromes and desferrioxamine, the value is minus 0.40 volt.

So, by simply looking at these two values, we should know the corresponding mechanism for the iron release. By knowing these values, we just simply predict that which one can be used for easily giving raise to your free iron into the system because bacteria also need iron for their regular survival. So, these molecules are also related to for our bacteria, defense also is as related to your medicine also. So, what we should

know that immediately if we have this, so this is our Fe 3 L compound. So, one way of getting this particular system is that it immediately, if you are able to reduce the compound for that purpose, we know that the corresponding biological reducing agents N A D E H F A D H etcetera.

So, the biologically available reducing agents, so those reducing agents, so what we should know the corresponding E 0 values for N A D H F A D H etcetera. So, what is available in your hand is the laboratory you can have large number of reducing agents you can use. If one is not working, the other you can use and also, for the electro chemistry, the (()) is also there. You set the potential, you oxidize it. You set the potential, you reduce it, but in the biological system, it is pretty complex. You should only have some limited number of reducing agents available and those limited number of reducing agents if they are available and if there potential is matching, they can only reduce any one type of these molecules. So, the value is matching in such a way that it can reduce only the ferrichrome ferrioxamines. So, for getting back the iron form, these molecules is therefore pretty simple that deduction is feasible by all these biological reducing agent, but in case of enterobactin, we cannot get the corresponding deduction.

So, what to do for this? The nature has devised a different mechanism. That means, already I told you that you can go for the corresponding hydrolysis of the ester function and you break the entire molecule. So, in this particular case, so it cannot be reduced by the common biological reductant. So, when the potential is pretty negative, it is 0.75 compared to 0.40. So, we cannot reduce it by biological reductant. So, when we cannot reduce it to Fe 2 plus immediately by using the biological available reducing agent, we should go for the corresponding release of iron for hydrolysis of the ester. So, the possible pathway is your hydrolysis of your ester function. So, you have a cyclic ester function is there. So, for that purpose, we take the help of sometimes for suitable enzyme. So, enzymatic hydrolysis for the different or the typical ester functions. That means, some estereres should be available there and those estereres will break the ester function. That means, you are breaking your ligand.

So, when it is broken; that means, simply the ester function you are breaking, not that you have the catechol function or anything. You are just destroying those functions. So, the bidentated parts remain intact. So, we are not changing the bidentated part. Only they

are possible positioning in the backbone. So, the backbone was your ester backbone. So, if you just break that backbone, stability is lost and it can release nicely the iron sites.

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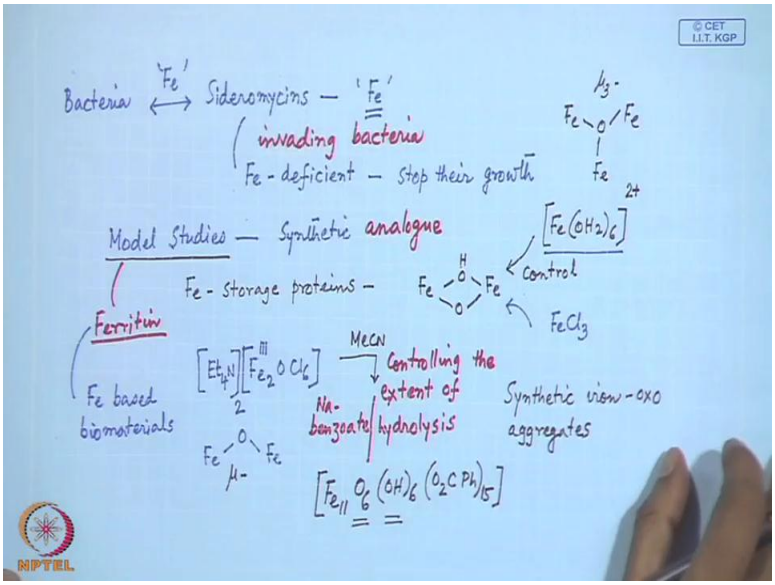

So, for this information, from this information, what we can have is one interesting molecule. We just know that based on siderophores something we call is sideromycins. So, just sideromycins are something which can bind nicely iron. So, when there is a bacterial growth, we are also getting infected by bacteria. So, bacterial infection or some micro organisms is also there, but all these micro organisms now we know that they are depended on iron. So, they will survive on iron. So, if there is a deficiency in iron, those bacterial growth will be retarded, will be stopped. So, some of these molecules; that means the siderophore molecules can be taken. So, some of these siderophore molecules are synthetically there. So, that is why people are studying the model studies.

So, what are these model studies that we should know? So, some synthetic analogue model studies is that some synthetic analogue for these siderophores which can bind nicely the iron which is otherwise available for bacterial growth. So, using those molecules or other is what we will just have the invading bacteria which would be litelyor which can be dead for hours and those invading bacteria, what we should do is we should make them iron deficient. So, if we can make them iron deficient, they will not get iron. So, there will be a competition between the bacteria and these sideromycins. So, they will just compete between these too. So, sideromycin and the micro organisms

or bacteria for iron. So, just you see that the very simple idea that how you just talk, not go for the availability of the iron for the bacterial growth. So, iron deficiency will be created and we can stop their growth. So, growth of the bacterial can be stopped.

So, in this model studies what we will see is that we were just studying in our previous classes, the iron storage proteins and those iron storage proteins. What we have seen earlier that these molecules can give raise to something where one after another, we can have Fe O or O H. So, it can also be like this Fe O H or Fe O Fe system to get this directly from a system which is our simple hexaco one. So, if it is hexaco two plus or three plus. So, oxidation as well as the hydrolysis. So, how we can control the hydrolysis of these that can give us some idea about the formation of model ferritin molecule because these ferrit in molecules are also very much important. Once we can know something about those molecules as the very good iron based materials or bio material.

So, the very simple thing what we can do is that this is your starting material or you can have, say simple hydrolysis of Ferri chloride. So, the choice of the metal salt is very important because depending upon the anons present or anons attached to thatiron centre and how they are getting hydrolyzed on the medium is also very important. So, one such example for that salt people have tried for making unique iron based oxo clusters. So, this particular compound Fe 2 O C l 6. That means, already you can have this e t 4 in it. These are 862 and this is iron 3. So, what you have is this is also easy to make. So, from the starting point, you are just taking the help of a di nuclears metal salt and di nuclear metal salt is allowed to hydrolyze only what happens there. So, to get these important compounds which are useful for these models studies which are synthetic iron oxo aggregates synthetic iron oxo because nature has the protein and that protein can control the corresponding aggregate since within the Ferri tin core.

So, you have the envelope for the protein chain and that envelope is basically allowing one after another. It can control the entry of the iron also, but when we do in the laboratory for a typical model compound for the synthetic iron oxo aggregates, we do not have that control, the protein control that one after another you put iron, you get a monomer, then dimer, a trimer, tetramer, pentamer and so on, but what you can do is that immediately if we take this, so people have studied that this has the solubility. That is why we are taking this salt that tetra ethyalomonium salt of this oxo compound diiron oxo compound. So, you take this in meCn which can go for a corresponding hydrolysis.

So, we can control the hydrolysis. So, controlling the extent of hydrolysis definitely will control the hydrolysis reaction and if we give something, not only this because the supply now that you have oxo already you have water molecule, you have hydroxides, but that will not complete your envelope. So, a protein type of envelope always we need. That means, the coating if you have an iron oxo cluster, so it must be coated with something.

So, what is that coating? So, one useful ligand for that coating for all the metal oxo clusters, all sort of cluster molecules is the corresponding acetate or benzoate group. So, sodium benzoate is given. Now, you can say that you go for the hydrolysis. So, sodium benzoate is given and for that what should be the product? So, we get the product and we analyze first for the iron content and then, the total analysis and then, we go for the structure. So, from this simple reaction if you have a starting material which is Fe O Fe based at least you can think of that it can, if it is going for a dimer formation, the ferritin formation, you know how the chain is forming and the phosphate groups are blocking that chain in the two d layer.

The phosphate groups are responsible for blocking that chain. Now, you have three-dimensional growth also, so that chain, so most of the cases these basic units are defective cubicle unit because you have the oxo or the hydroxo function which are in mu 3 connectivity and those mu 3 connectivity, what I earlier told you that if you have this is one such basic unit Fe O Fe and another fe. That means, this is your oxo hydroxo function in mu 3 mode. So, you have 3.

If this is your oxo hydroxo, so it is attaching one iron, it is attaching to the second iron and it is attaching to the third iron, but the attachment is not in the same plane. It is basically occupying a corner of a cube. So, if a corner of the cube is occupied by the oxo or the hydroxo core, iron will be on the other vertex of the cube. This iron will be other vertex and this iron will be in the other vertex. So, these basic units. It is not that a planer triangular unit is because this particular oxygen either above the plane or below the plane, so that three-dimensional arrays will take you somewhere where you get the molecule. The ultimate product in this particular reaction condition, we get a product which is Fe 11. So, it is Fe 11 O 6 OH whole 6. Then, O2 CpH whole 15. So, immediately you should look at the corresponding charge neutralization that whatever

product you are writing or you are getting is a electro neutral or not whether it is catenic compound. That means certain anons are also there.

So, this particular case, if you just control the corresponding hydrolysis and if you have 11 iron centers in the same fashion, in the synthetic molecule which is your iron oxo cluster molecule. How this cluster is forming? So, somewhere it is starting. So, one iron. Then, if you consider that the two iron centre is there, so the growth of that cluster. So, that growth of that cluster is determined by your 6 hydroxide bridging and 6 oxide bridging. So, not only the oxidation state, you should also consider immediately from the formula that whether this is matching. It is corresponding binding property because you never know that this particular oxo because here it is only this oxo is mu 2. When it is expanding, it is co ordination potential to a mu 31. So, some of these oxo groups can be either mu 2 or mu 3. Similarly, OH is also like that. So, immediately what we go for these formulae of this compound. That means, Fe 11 O 6 and O H whole 6, we should be able to tell that you have 11 iron centers. So, you have mu 3 O 2 minus. How many? They are 6.

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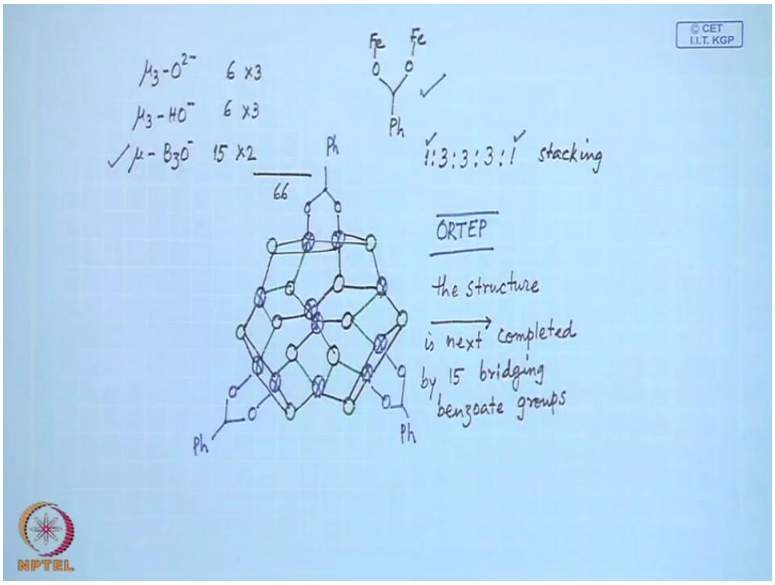

Then, mu 3 H O minus, they are also 6 in number. Then, mu benzoate. Benzoate is bridging, benzoate is like that of your acetate. So, you should know the acetate bridging. So, this is one iron and this is another iron. So, if this is benzoate, so benzoate is also there and 15 such groups are there. So, this is mu 3, this is mu 3 and this is mu 2. So, all

together how much you are getting? 66 for 11 irons. That means all the iron centers are octahydroxination. So, it is not that because most of the time this cluster compound is such that you may not have an octahedral geometry. If the iron site is available for octahedral co ordination, then only you get a corresponding octahedral co ordination. Otherwise, it can be a four co ordinate.

One, it can be five co ordinate because you are not allowing or you are not fulfilling all the six co ordination sites. That means, if your iron site is highly distorted which is not a tetrahedral geometry or which is not a regular penta co ordinate one, that means, a square pin medal or a triangonal bi pin medal one, then it will just force to go for other co ordination geometry.

So, for a quick idea about this how will you draw that? So, it is basically a layer of iron centre. So, one layer containing one iron. That means, it is a capping 1and. Then, you have 3 and then, you have another 3, then you have another 3 and 1. So, this sort of stacking arrangements. So, you have a very simple reaction. Just you are allowing for the hydrolysis and that hydrolysis is giving us a nice molecule which structure wise is also very interesting. So, what will we get there? That means, if you have a central iron, so this iron and at the back. That means, this iron, these two irons are there and then, other two layers you can have these two. This one, this one and this one.

So, these three all are in one layer. This is one in one layer and these two are all in different layers. So, these are basically we get a three-dimensional x structure. So, these have some thermal vibration. So, we call them as the thermal elipe side plots. So, these are the thermal elipe side. From single crystal x structures, we get this entire structure, but what we just want to show you that it has one iron and that iron is basically connected to one such oxo and another oxo. That site and another oxo you have 6 oxo together. So, if the upper one is going for 3 oxo binding, lower one will also go for 3 oxo binding. So, 6 oxo is there. So, all these 6 oxo groups basically are attaching to these two irons. So, one at the top and another at the bottom. Next what will happen is because all these hydroxo and oxo groups are mu 3 in nature, so this particular one will also be binding these two iron making it mu 3.

So, this particular one will also go for this and similarly, this one will also go for. So, all you make them mu 3. This is not so difficult. Once you know the corresponding

composition and all these, so 6 oxo groups are there. They have taken now is your hydroxide functions. So, one hydroxide will be here, second one will be here; third one is here, fourth, fifth and sixth. So, how this will bind them? These are all mu 3 type. So, these hollow spheres are hydroxides. So, this is one connectivity and second one will be this one as well as this one. So, this one will also go for this as well as this and this. You draw all the six hydroxides functions and all the six hydroxide groups are there and you just then, go for completing. So, when it is attaching this iron and this iron and the third one, now you should able to draw or complete it quickly. So, this hydroxide will go one for this, second one for this and third one for this. Similarly, this will go for this one, this and this because these two are pretty close. This is one, this is there and this. So, the whole cage is formed. Now, it is not so difficult.

Now, how will you complete the entire structure? So, the whole structure will be completed by using your benzoate presence. So, the structure is next completed by 15 bridging benzoate groups. So, that connectivity will be pretty complex. So, you should have the locations and we will try to do it. Also, this can be your assignment because one such I can show when you have two adjacent iron.

So, all adjacent irons because this particular binding, this sort of binding is you have to put 15 sash. So, what is happening there? So, you have large number of benzoate functions. So, most of the cases what we know is that very simple copper acetate structure, the acetated group is there and four such acetated groups are utilized for binding two copper centre. So, you can have all these positions will be occupied by these particular benzoate functions. So, 15 such benzoates, you basically get a good sphere. So, what is happening there is the availability of these benzoate function is very useful. So, within the benzoate function, the benzoate groups are there. You are just simply allowing the growth of this iron oxo cluster.

So, if you consider depending upon the size and the corresponding structure of this, if it is in the nanometer size, so you get something which can also be considered as a nano ball type of thing. So, how you control? So, if this reaction is unique for benzoate, it is different for your corresponding acetate is not that you get this particular structure with benzoate. The same thing will get for acetate because the corresponding p k values for the acetate and benzoate is different and you are controlling something what you are controlling the hydrolysis reaction. So, that hydrolysis reaction at the same time can be

controlled by the adjustment of the corresponding p k values of the acetate acid groups what you are using and therefore, binding potential.

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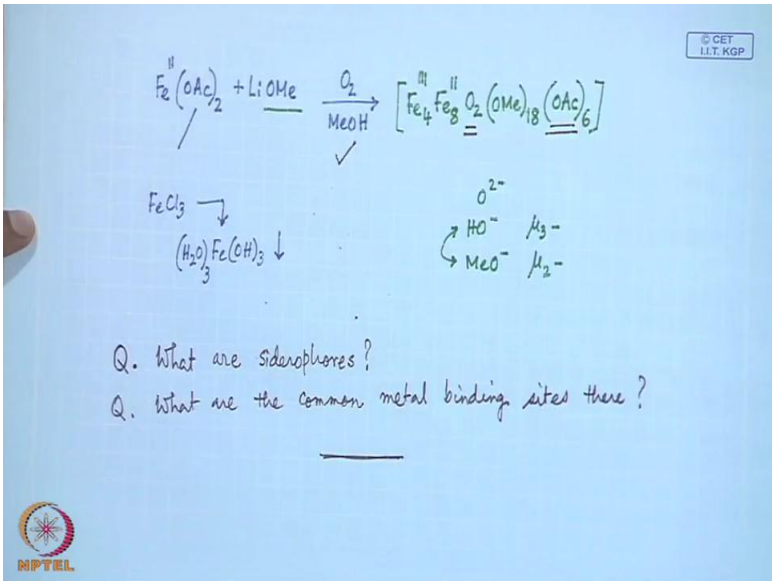

So, if this is a very simple one for that construction and one more example I can give you that for this because these are very useful area of interest for the growth of these iron oxo cluster molecules is that there you were utilizing that dimeric unit Fe O Fe C l 6 molecule. Now, you just simply use ferrous acetate the way that when the biological systems are also utilizing that thing.

So, if we have the ferrous acetate type of thing and we just go for a cluster for that and since, we have taken ferrous acetate, it will be oxidized by the di oxygen present in air. That means, a real oxygen will be utilized for that and for this purpose, the solvent is also important. There we are utilizing acetonital. Now, mytholmin is there. So, solvent the environment and the corresponding starting material. That means, your this acetate is also controlling the reaction. So, the acetate is there because we all know that when we talk most of the time that how the hydrolysis of ferri chloride is taking place to give you the corresponding precipitation of ferric hydroxide, but ferric hydroxide is also not a very simple molecule because you can have if you just simply consider. I will write in this fashion only.

So, all this is coordination sites. So, it will go on condensing and agglomeration will take place, may be where very complex ferric hydroxide structure. That is why ultimately, we

will just go back to the nature. That means, you will end up with the formation of the mineral hematite megatite type of oxo hydroxide clusters we are forming, but we are not getting any discrete unit and so is the polymeric system.

So, making the discrete molecule what biological system is doing for hours for making the ferritin molecule is important. How you control the growth, the size of this? Growth is very important, whether you are getting a cluster type of molecule having iron number is 11 like this or you are getting some species, where iron number is 22 or 34 or 58 such that. So, how you control the environment that is very important. So, the hydrolysis of this ferrous acetate as well as sometime for getting some different type of reaction, we can introduce a different bridging agent or different bridging group. So, this bridging group like that of your O 2 minus, we know O 2 minus is a very good bridging unit and then, H O minus we also know is a very good bridging unit.

Now, you have MEO. So, this will be very much similar to your HO minus, but the difference is that it is only mu 2. Most of the time, it is behaving as a mu 2 bridging, but in other cases, it is this hydroxide can behave as a mu 3 bridging. So, this particular case what we get, you get is that you can think of just not deal with much about the structure that if you have this, it will be a very interesting molecule that ethyl 4 Fe 8 because the establishment of this structure is also very important than less number of oxide bridging O 2 only, but more number of methoxide bridging which are 18 in number and then, the starting acetate groups which are 6 in number.

So, if we just compare now this molecule with the previous one, what information you get? You get that you do not have the hydroxides. You have used a different bridging groups and these two iron. That means you are not completely oxidizing all the iron centers. It is a mixed valiant compound. So, mixed valiant compounds are very important in nature because most of the time when you talk about something, these oxo cluster compounds like that of your manganese is also important. So, when you start from manganese and manganese has also variable oxidation states. So, you will end up with some oxo cluster, oxo hydroxide cluster of manganese, where manganese can have a plus 3 oxidation state. Manganese can have plus 4 oxidation state as well as manganese can have plus 2 oxidation state.

So, this is a mixed variant species, but luckily what we get is most of the cases, it is a neutral compound. So, when you get a big cluster type of arrangement, it is very difficult to get a corresponding compound which is cationic in nature. If it is a cationic one; that means, you have excess charge on the metal centre, but it is not that the depending upon your requirement that way you are getting a neutral compound.

So, depending upon your requirement, your iron centers are getting oxidized because you have started from Fe 2 ferrous iron. So, as your requirement is there only four centers are getting oxidized to the plus 6 state and all others are remaining in the plus 2 oxidation state and you are using less number of oxido bridges, more number of O M E bridges and at the same time, you have the acetate bridges by benzoates, but these acetates are coming from this metal salts. You are not utilizing anything as externally added sodium acetate the way we did it in a previous case by addition of sodium benzoate. So, this thing. So, internally you are supplying all these anions and this particular case what we are getting is the type of bridging groups.

So, numbers of bridging groups are different and you get a mixed valiant compound. So, this simple reaction in the laboratory we can make it all the time that how the typical hydrolysis reaction can be utilized for the growth of these molecules. So, for this type of these things that because all these classes should have some questions. So, I just give you some quick one or two questions. You can have very simple. One is you can just think of and should be able to write that what are siderophores and what are the common metal binding sites available there. That means, you should be able to compare during that case that whether you have the catechol unit and the catechol charge is also important. The hydroxamite unit and the hydroxamite charge and the different E 0 values formed there.

Thank you.