Bioinorganic Chemistry
Prof. Debashis Ray
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 15
Electron Transfer in Photosynthesis – II

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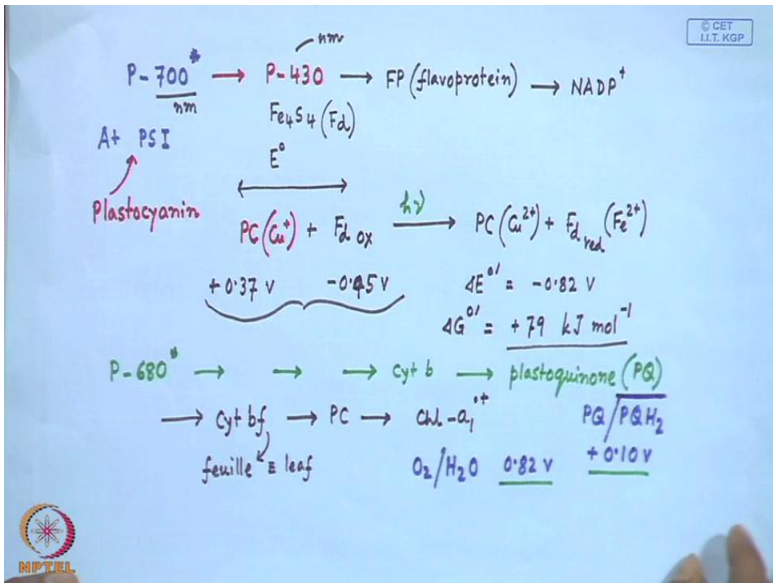

Welcome back. So, we were discussing about those electron transfers following photoexcitation. So, if we had P-700 stared; that means we have the excited species at the photosystem one. So, this particular one is residing at PS 1. So, at PS 1 we get P-700 stared. So, that P-700 stared we have some electron from there and at the next point it is reacting with the ferredoxin what we have shown in the Z-scheme is P-430. It is very interesting to level all this species; P stands for your pigment and this is the corresponding wave length. Because whatever species you are handling; that means where you have this Fe 4 S 4 species as the ferredoxin, and these are very good species we know as electron transfer material. So, we have the corresponding two forms depending upon it is E 0 for the oxidation and the reduction reactions.

And all these iron sulfur proteins or we know that they can expand a very wide range of E 0 values; that is why what we studied earlier also we know that all these ferredoxin type of molecules can be present in photosynthesis, can also be present in respiration. So, depending upon your protein environment around these cluster molecules, you can have the oxidized form where iron centers are present in the ferric form and the reduced form

where the iron centers are present in the reduced form. So, this particular one; that means this Fe 4 S 4 which is our well known ferredoxin molecule and that ferredoxin molecule is coupled with that of your P-700 stared one, and this ferredoxin protein molecule is attached to this one and this particular level which is its corresponding electronic absorption. So, electronic absorption behavior at 430 nanometer for the oxidized form; that means the ferric form of the ferredoxin molecule.

Then it is coupled with some flavoprotein, FP is our flavoprotein. These are all our well known redox mediators because we cannot connect all these directly to the species what we are trying to attach; that means NADP plus. So, it has one particular redox potential value, it has also one redox potential value and between these two we have the intermediate redox mediators which can couple with P-700 star two NADP plus. And at this point when you have PS I and how we studied this also; that means you have one such species; we just studied in our previous two three classes, we read about plastocyanin which are copper proteins. So, blue copper protein is responsible for electron transfer. So, this plastocyanin is taking that electron. So, electron is basically entering in PS I from this plastocyanin. So, plastocyanins in the reduced form can put the electron to PS I and in that particular one when you have this plastocyanin.

So, sometimes we find that whether your corresponding redox couple. So, thermodynamics will tell us whether the reaction of plastocyanin which is a copper based one and if it is copper in reduced form it can react to it the corresponding ferredoxin in oxidized form. So, it can react with ferredoxin in oxidized form. So, this redox couple what we studied earlier also in case of cytochrome chain and cytochrome c oxidases that whenever you have the pair of redox partners you can find out the corresponding changing in e 0 values, the delta e you can find out and the corresponding gives free energy change will tell you whether you reaction is facile or not. So, in this particular case what we find that you have this plastocyanin potential is in the range of 0.37 volt and ferredoxin one is 0.45 volt.

So this gives us that oxidized plastocyanin, PC is your plastocyanin in the oxidized form and ferredoxin in the reduced form which is nothing but Fe 2 plus. So, when they are basically connected we can calculate the delta E difference of these two which is minus 0.82 volt and you can calculate the corresponding delta G 0 prime as plus 79 kilo Joule per mole. So, this particular case; that means whether you have at a particular wave

length, so this is basically this level is your 700 nanometer wave length and from that wave length and from the corresponding values for this, we find that only this much amount of energy change is available for this electron transfer.

So, some processes we can have is a favored processes and some are not favored depending upon these values, but if we just put the radiation the eliminated portion of this can change the particular electron transfer pathways in a different way and that we can also see in case of P-680 as well where you have certain other species connected to that and one of them is cytochrome b, then one such species which is not based on copper but it is a quinone based species which is plastoquinone and the corresponding redox potential is similar to that of your catechol quinone potential and this then clubbed with another cytochrome b type of different version. F is feuille which is a French term for leaf f e u i l l e feuille. So, which is nothing but the French type related to leaf.

So, this are then is also connected to plastocyanin and this is then responsible for generation of chlorophyll a 1 cation radical. So, all these are involved in the different types of electron transfer chain and if we can find out the corresponding values and how this particular, say, plastoquinone because we know the corresponding potential for water and oxygen couple and if this PQ and PQ H 2; that means the quinone form and the catechol form, PQ H 2 is the catechol and if this redox couple is this much and we know the corresponding values for O 2 and H 2 O which is 0.82 volt. So, in this region whether you can have. So, you can differentiate out these two values and you find out the corresponding E 0 and that E 0 we can correlate with that of our h nu, nothing else we are doing.

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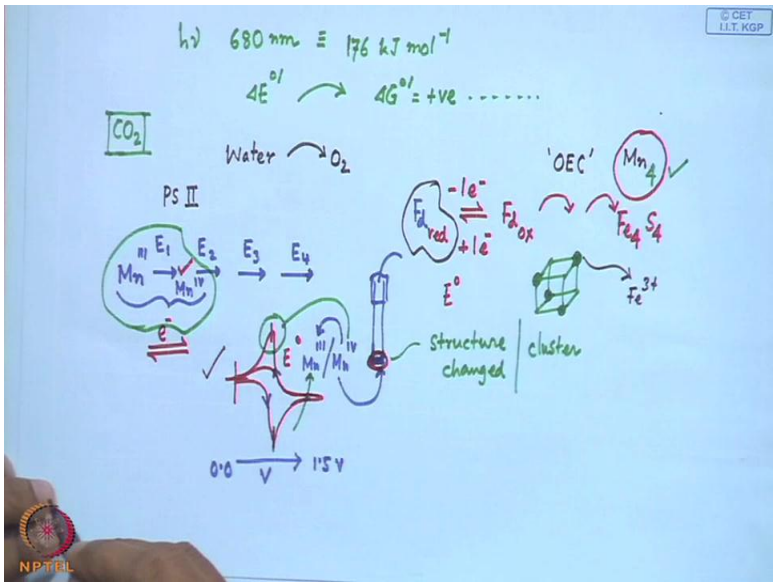

So, h nu for one photosystem is 680 nanometer and another is above 700. So, these are the two values only. So, at this value what we get is 176 kilo Joule and we calculate the corresponding E 0 prime; from there we can calculate the corresponding delta G 0 prime and what is the corresponding value of that kilo Joule per mole, you can find out that in that particular region. So, this typical excitation can give you and you have a corresponding delta G calculated value which will be positive in that particular case. So, these all thermodynamic parameters and all these values will talk us something related to your excitation of magnesium, how we get the electron, how we derive those electrons from those centers and how we can put those electrons to several redox mediators, say, plastocyanin, plastoquinone and all these things.

But what we get that the excitated electron and its chemical energy we have to transfer to our CO2 molecule and which we cannot lose any kind of energy due to molecular vibration as well as florescence. So, the oxidation of this water molecule; that means when we have water in photosystem II we get something what we call also as oxygen evolving center because from water we are getting O 2 molecule. So, it is known as also oxygen evolving center where we can go for typical oxygen evolution and is a 4 one electron state. So, this 4 one electron state is required and your water we are consuming and analysis of metal centers, because it is very easy to know that how people discovered that magnesium is present in chlorophyll and manganese is present in photosystem II. So, it is manganese analysis.

So, any manganese analysis technique it can be a spectroscopic technique also that identification of manganese from its corresponding atomic form will tell us that this is basically tetranuclear manganese. And idea behind knowing the tetranuclear manganese is very simple because we need four electron transfer and in all these cases though we all know that manganese can have the stable oxidation state from plus two to plus seven. So, you can argue that, okay, you can one mononuclear center, you can take out one after another electron for this corresponding oxidation as well as reduction. But in all these cases what you have if you have a mononuclear manganese center and if you can take out one after another electron to go for a change in oxidation state from plus 2 to, say, plus 6 or plus 3 to plus 7, you will encounter with different E 0 values, E 1, E 2, E 3 and E 4.

So, most of the cases where we find that between these two; that mean the first manganese center and its second immediate oxidized form. They are interrelated and we can write the corresponding electron transfer equilibrium in a reversible sign and these electron transfer property should always be reversible; that is why we always rely on something in biological system also the corresponding measurements using cyclic voltammetry; that means whatever you do; that means this is the anodic or the cathodic big potential then you get something which is your E 0; that means whatever you do. So, you can subtle between these two forms, one form and the immediate next one. We are not going from here to here, here to here; otherwise your reversibility will be lost.

So, when we go for these oxidation for one manganese center, say, if it is a manganese three you immediately can convert it to manganese four and whatever E values we get for the corresponding transfer for the manganese three and manganese four. So, what happens there that when we go and when we just oxidize it, then we reverse the codes of its scanning; that means on the electrode surface what you have, you have, say, a platinum electrode. So, platinum is there and is a connected. So, on this electrode surface what you have this manganese and manganese is formed in the plus four. Then you are switching back the corresponding cycle the corresponding direction of the scan. So, this is the current access, this is the voltage access.

So voltage, say, you are scanning from 0.0 volt to, say, 1.5 volt. Now you are scanning back; that means 1.5 volt to you are coming back to 0.0 volt. So, now what is happening? Your manganese four which has been produced from the oxidation of manganese three is

absorbed on this electrode and that is now reduced back. So, this manganese four will be reduced back to manganese three because you are switching back. So, only some little bit difference is there between these two values, but all the manganese four what is forming over there will be reduced back to manganese three. So, the stability or the life span or the life period for this form; that means the oxidized form is important.

So, whatever species you have even if you just talk about the corresponding ferredoxin one in the reduced form and another in the oxidized form because it has a very good co-relation with that of the species what we know and well known species is the Fe 4 ferredoxin molecule the iron sulfur proteins Fe 4 S 4 species. So, it has certain similarity with that manganese four species and there also we get in this particular case we get only one electron transfer. So, it is the oxidation and it is the reduction; not that you are going from a Fe 4 species from one, two, three, all these states because to stay within the reversible domain that whatever you are doing; that means you are just simply oxidizing one particular manganese iron center on the ferredoxin cluster. If you go for oxidizing the other centers as well, your structure will not be stable.

So, you will just break the structure. You can force it because this is electrochemical oxidation; with the help of electrodes you are forcing the oxidation. But biological reducing agents and oxidizing agents are available; it will not provide you the sufficient E 0 value for this second step or for the third step. This is one reason and another reason is that that you have this absorbed species and which is coming back like this manganese four is coming back to manganese three but if this is not stable; that means your manganese four should have certain stability, otherwise it will break; that means its structure can change. It can have a changed structure if it is a cluster, a cube type of structure. Suppose it is a four, means, very easy to put four of this metal centers like this, one here, one here, one here and one here.

So, you have so much connectivity's. Some of these ligands because these other corners are occupied by the ligands either sulfur or in case of Mn 4 we will see by oxygen. So, if they are connected for that then the structure will change and it will not be stable enough to go back to the original position. After this shuttling what you are getting back, you can compare with that of your original structure. So, if it is ferredoxin one after one electron oxidation, you cycle it back, you go for the reduction, you should get back the original

ferredoxin reduced form. Because you are doing that particular electron transfer in solution, you have water; you have some other groups also.

If this has less stability the oxidized form has less stability, it can react with some other water molecule or it can break from their structure and the iron centers, the ferrous ion or ferric ion can leach; that means it can leave your Fe 3 plus from the cluster. So the entity, it should have certain stability that when you switch back to the original position; that means when you reduce it back, the oxidized ferredoxin when it is reduced back, it should produce the same ferredoxin reduced from what you have originally what you have used for the oxidation processes. So, if this is not sufficiently stable what happens, how you know this cyclic voltagram can show you that whatever you are producing on the electrode surface which is absorbed there which is not stable which is not the same species having the same values for this, what will happen after here; that means you are oxidizing it and it is transforming to some other species, you are getting back not with the current value of this position.

So, you will be losing the current value. So, your thing will go away and basically you are getting for this; that means this is for oxidizing this one, but this you are not getting what your suppose to get for the reduction of this manganese four species. So, that is the typical signature whether your structure is unstable whether you are not getting back the same structure. So, if you just go for one step to this, this step to that; that means most of the cases the safest way of thinking this particular arrangement this multicenter arrangement is that, you can have one particular center and four times of that should give you some arrangement.

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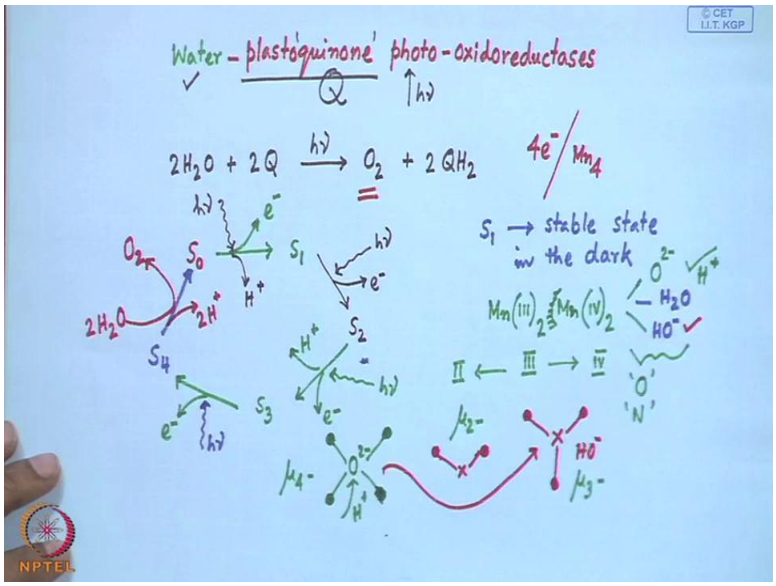

So, this four manganese center which is your water evolving center and this then handling the water and immediately this has attachment for one group which is the plastoquinone; that means the immediate species which is responsible for electron transfer and we are utilizing photon for this. So photo-oxidoreductases, this nomenclature we know already. So, these are very important things and very simple one also because this is nothing but your quinine, this is a big Q, it is a quinone form; plastoquinone is nothing but quinone. So, if you have a catechol quinone conversion. So, the catechol quinone type of species is responsible to interact with water molecule and which is controlled by eradiation and we are looking for some oxidation reduction reaction. So, this is very big name, but what are these though, you have water.

So, from the very beginning of our classes we are just talking about two water molecules and two of this quinone form which is oxidized form the plastoquinone in the oxidized form eradiated giving O 2 plus twice of the catechol form of this. So, this particular one we get but for that particular transfer we need to transfer four electrons. So, like that of your particular metal center where your manganese is there in plus three oxidation state and stepwise you are oxidizing by one electron, then another electron, then third electron and the fourth electron. So, manganese plus three can go up to manganese seven but similarly if you have this particular, so we need the four electron species and we can have arrangement of a tetranuclear manganese complex. So, this tetranuclear manganese complex, so one particular oxidation state we can consider it has S 0 state.

So, s is related to the spin sate. So one oxidation state, then what people have done that you change it to another state. So, you are just leveling; the cluster is your Mn 4 cluster. So, this cluster complex when you get this. So, S 0 to S 1 we get through ejection of electron; that means through oxidation. So through oxidation, at the same time it is also leveraging one proton. So, that we all know that whenever there is electron transfer when some system is getting oxidized it can be your amide backbone also. So, CONH backbone when it is bound to the metal center, if you go for the oxidation of the metal center and the nitrogen is bound to the metal center. But at the same time when you take out the electron from the metal center, the metal center should be electron greedy and that will go for the deprotonation of the amide function. So, your CONH will be CON minus.

So, that can be very readily stabilized in the high oxidation state. So, whatever you have in the system when you go for one electron oxidation, simultaneously you will be losing one proton. It can be from any other bound ligand or it can be from sometime from the bound water molecule or the hydroxide group also. So, this particular thing is activated by because all the states are activated by h nu. So, these are the states like the dark phases and light phases of photosystem II; knowing this particular photosystem II for water oxidation, whether it has to be eliminated or not that we should know. So, at this particular step you put h nu and you get S 1. And in the second step we have other step; that means S 2 and S 2 is again by loss of second electron and it is also triggered by h nu but no proton loss at this step. So this can be differentiated from your S 1, then we have the S 3 step; again one more electron loss and one more proton loss and is also h nu.

This S 3 by simple electron loss can go to S 4. So, this is the step where you get this particular unit. So, you have one, two, three, four, 4 electrons have been lost from the system. So, by doing so; that means by doing or taking the electron one after another, we can move from S 0 to S 4. So, S 0 you can immediately say that this is the super-reduced form of this M 4 complex and this is the super-oxidized form. So, either you put all together the four electrons to the system or you take out four electrons from the system but interestingly among all these 5 species. So, you have 5 species and you can immediately say that this we are talking about four electron transfer. So, four electron transfer plus one starting species; so one starting species plus four electron transfer giving you 5 states. So, 5 of this form and out of this form S 1 is the most stable form.

So, this is the stable form in the dark and this particular one. So, since it is stable it is very easy to identify also this corresponding oxidation state of the manganese and this particular one has been identified as a manganese three four complex, where you have two of the manganese centers in the trivalent state and other two in the tetravalent state; sorry manganese four two. So, it is a mixed balanced species where you have two of the manganese in the plus 3 state and two other in plus 4 oxidation state. So, basically what we are talking about here that the most readily accessible oxidation states what we are talking about here is that it can go from three to four or it can go down from three to two. So by doing so this particular step you get, 2 plus 2 4 electrons, So, this is the simplest possible picture what you can have and in this step when you have this oxidized form.

So, oxidized form basically will liberate two protons from here and this is the step where you get your dioxygen. So, whatever cycle we write over here in this particular state because we are talking about only the photo excitation. You have given photon, you have taken out electron and the protons are coming out. So, this particular S 4 basically collapsing to S 0 when it is reacting with two molecules of water giving you that required dioxygen molecule, so collapsing of that thing to S 0. So, now the challenge is that how we can identify slowly that what are the species. So, manganese is well known. So, manganese is there and we can have the knowledge about this manganese that manganese has corresponding affinity for oxidizes is not a corresponding iron sulfur type of thing.

So, it is very easy to know also once we know the tetranuclear ferredoxin molecule, the four iron ferredoxin molecule; that means you can have these two plus you can have sometime loosely bound water molecules. So, these are basically from oxygen environment and these oxygen environments are further supplemented by the corresponding protein side chains; that mean the carboxyl side chains or histidine side chains. So, these are the other ligating groups and those groups can give you all these values and this particular conversion from water to hydroxido group to hydroxido to oxide group will also be responsible for the elimination of your required number of protons during electron transfer.

So, the very basic assembly for this tetranuclear system what we can see know that once you have this; that means if you just go for a mononuclear to a binuclear system, we all know that you can have some connectivity at least one connectivity to get a binuclear

one and you can have certain connectivity such that if you have a group like this, this oxo or the hydroxido function can do very easily in a mu 3 form hydroxido bridge mu 3 that can give you a trinuclear one and also this O 2 minus. When these are there this O 2 minus if it is bridging four metal centers, you get very quickly a tetranuclear assembly. But for this sort of proton transfer; that means if you have a hydroxido bridging or oxido bridging, this is not a stable structure. Once you can go for protonation, immediately we will lose the entire structure because it is the group; that means the oxido function you have and this is basically the nucleus of the cluster because it is a tetrahedral arrangement.

This oxygen is in tetrahedral geometry and this tetrahedral geometry is basically holding all four metal centers. It can be your 4 manganese also but if you immediately go for protonation. So, one protonation step for this O 2 minus can change this to a hydroxide. This X is nothing but your hydroxide group and its affinity for coordinating four metal centers will be lost. So, it cannot be a mu four ligand; immediately when you go for protonation, it would be a mu 3 ligand. If not a mu 2 one; this is a mu 2 one. So, what is the other alternative formulation what you can have to get this is if you have this dinuclear assembly and if you put another dinuclear assembly close to it. So, that should be our right choice for a tetranuclear assembly and that we all know comparing the corresponding Fe 4 S 4 ferredoxin structure.

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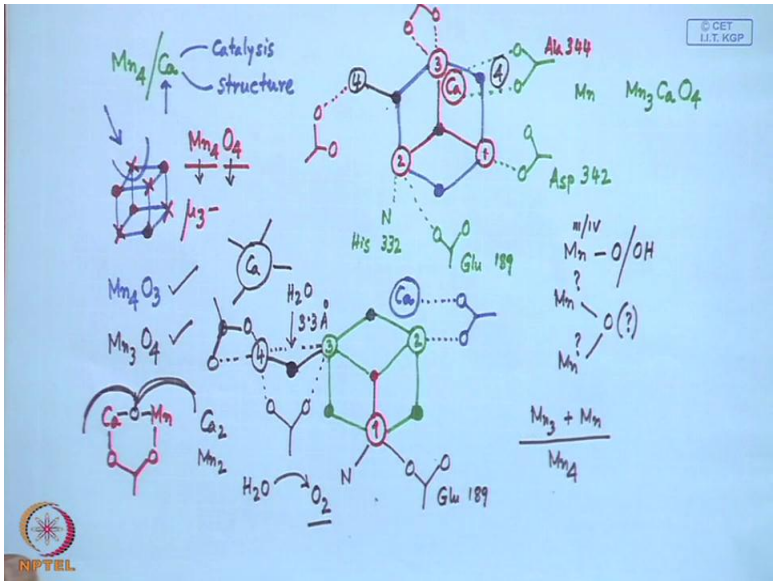

So, that structure we have and not that this Fe 4 you need which can give you a corresponding manganese 4 unit, but also there are certain analysis and that analysis tells us that this particular Mn 4 is there as well as you can have a nearby calcium ion, like the superoxide dismutase or like the magnesium and all these. So, this presence of this calcium it is not a redox active metal ion. So, it will not take part in any kind of electron transfer behavior, but this as always you will find whenever any complicated structure you find either it is synthetic one or is a biological one. So, it has some important role to play in catalysis, how? Because it can have large number of water bound molecules or any other group bound molecules. So, it can provide some activated water molecules instead of free water molecule and also it can contribute to a large extent to the structure of the system; that means if you have a cubic type of structure or cube-like structure, it has something to play with that cubic structure.

So, if we level all the four manganese centers around this one particular central oxido function, this is manganese one, this is manganese two and the third one is manganese three. So, this particular arrangement gives us something that it is not a typical cubic type of arrangement cube-like arrangement but this particular one which is there as a mu three one. So, if we have something; that means the mu three group is there and in a cube type of arrangement if you have all the alternate coordinates are occupied by the metal centers. If it is a four metal unit, it can be your ferredoxin F 4 or this water evolving center Mn 4. So, these are the four metal centers and this other groups these are your bridging groups. It can be your hydroxido group or the oxido group and the nature of these groups are mu 3. All these X groups are binding three metal centers together.

So, when they are occupying the four coordinates of the cube they are in mu 3mode; the binding is in mu 3 mode. So, we have satisfied this particular mode in the mu 3 mode. So, when you have mu 3 mode and in this particular case that if you have a system which is Mn 4 and O 4, forget about the nature of this O, because we get different spectroscopic analysis and x ray structure analysis to some extent. We get this arrangement and we can differentiate only that whether these particular groups are oxygen or sulfur or any halogen group, but sometime we are not able to precisely determine whether this is oxido group or hydroxido group whether this oxygen is attached to a proton or not, that sometimes is very difficult to identify.

So this mu 3 group, so it can be your hydroxido function or it can be your oxido function and this mu 3 group when you are viewing from other direction; that means depending upon these; that means if you have four manganese center and four oxo center, you get the regular cube structure; that means all the eight corners of the cube are occupied. But if you try to have something; that means four manganese are there we know. But if you make it Mn 4 O 3, what will happen? If you make it Mn O 3; that means your one of the vertex is missing, but still you have this cuboidal arrangement. If you take out this vertex and if your another bound distance and bound angle remains same, you will have basically a cuboidal structure; we call those structures as defective cubes or partial cube; we call them as defective cube or partial cube.

So in this arrangement, so we have these groups. So, one of these; that means if you take out this and if you view from here, if you try to view from this direction, you will find that this particular oxygen is like this attaching to manganese one, manganese two and manganese three being this one. So, this is your this one. Then you have another oxygen. So, this side oxygen. So, this I made. So, how you would nicely you can draw you should be able to draw it also very nicely that within hexagonal arrangement. So, this is basically this one because you have all; you have one, two, three, four, 4 bridging atoms, 4 of these oxygen one, two, three, four, 4 these and three metals. So, you have this; four manganese you have and sorry the reverse one, Mn 3 O 4 this one.

So, whether you have taken out this; that means in this particular case you can take out one metal center or you can take out one bridging group. So, you can make it a manganese three system or you can make it a manganese four system with three bridging group. So, this oxygen is there. So, if you find that this one is immediately is only mu two and if it can extent its binding to the other direction, because it is a highly distorted geometry. So, once you start from this particular code structure. So, code structure is a partial Cuban, structure then you have this manganese four and in between, between these things this is not directly connected. You have the calcium close to manganese three. So, what we have in our hand is a Mn 3 from this unit a calcium four oxygen and a distant manganese. So, this is your distinct manganese and this O 2 little bit we should know about the environment. So it is bound to nitrogen of histidine 332, then it is bound to glutamate.

So, only oxygen and nitrogen environment glutamate 189 and this one is bound to another carboxyl function of amino acid is aspartate 342 and since calcium is not a transaction metal ion, sometimes it so happen which is not so common for transaction metal ion that the same carboxyl function like acetate function, what we all know that it is very difficult to go for a corresponding binding of acetate group to copper; acetate group most of the time it can function as a bridging group only. So, these two oxygen when they are utilized for coordination, it should go for two different metal centers, for copper, for copper iron and all but calcium it is loosely bound because both the two bounds are not same, it is loosely bound. So this is alanine, this ala 344 and this again to a carboxyl and nuclear bound and another.

So, this basic arrangement what we can have in our hand that during this transformation when we go for the S 4 state; so electron transfer is taking place from one after another from this manganese, two of them are manganese in the trivalent state and two of them are in tetravalent state, but how this calcium is playing some important role not only for this structural chain but also for a different type of arrangement whether this calcium can go out for another form. So, another form we can get the another structure will see; we will not show all the detailed structure of these; how this particular arrangement can immediately change if we can have this manganese oxygen is here, if we bring down this one over here that basically is taking place. So, change in the structure and within this hexagon we are trying to draw what that positions are changed; that means if you have a cube like structure and all the four positions what are occupied by metal center is now occupied by oxygen; that means their positions are interchanged.

The position of manganese and position of oxygen can change. So, that is a typical structural change for the entire complex. So, this one is connected with this central oxygen and two is now over here and three is here. This is this oxygen. You see that it is not that we are making all these structures in the laboratory but only for one simple electron transfer, the thing has changed from this group to that group where you have now close to that partial cube structure, your calcium is close to number three and it is within the cube structure. Now this same calcium due to that electron transfer has come out to this position. Here is now your calcium which was earlier close to manganese number three.

This was your manganese number three and this two is basically this group which is attached to the other manganese. So, that means this particular group ala 344. So, basically what we are now leveling that your manganese center which was here has moved from here to here. This is the manganese position now. You see this original manganese position is now occupied by the oxygen and oxygen position is now occupied by the manganese. So, that much changes, so basically it is moving. So, if you consider that as a clockwise movement. So if you consider this as a regular hexagon, all the regular hexagon you know has a seismic symmetry. So, you just simply move in a angle of 60 degree; just you move for a angle of sixty degree. But for that the driving force for that is that now two is there and people can identify not only the metal but also these groups; the ala 344 can be identified very nicely.

So, this ala 344 is not moving away much because that is why I pointed out that this is a typical binding typical coordination of the entire carboxyl function to the metal centre which we do not see in case of any metal salt like copper acetate, iron acetate, any metal acetate; the acetate groups are mostly bridging. So, copper acetate is basically a dimer because your acetate groups are bridging two copper centers. So, this is rather a different type of coordination where the entire acetate group is bound only to the calcium and this is not showing any interaction with that available group because you do not have any manganese over here. But if you move one manganese from here to here, you have available manganese over here and this can establish the bridging group. So, you see that is the role of the manganese and as well as the calcium, why calcium is there and calcium is playing something, the role of the calcium what is being played for its structural change.

So, calcium was there which is this acetate coordination. Now calcium and this manganese are now bridged. So, whatever entity we can have; you have a heterodinuclear system, we can consider it as like the superoxide dismutase what we know that it has copper and zinc center; in super oxide dimutases you have copper and zinc center. Now it is a system where you have a acetate bridged calcium manganese compound. It is very difficult to make also if you go for making some synthetic molecule out of these. If you have a binucleating ligand and if you have a binucleating ligand like this having two different pockets, you can have a phenol unit over here and this phenol is

coordinating to calcium and manganese and you are using some salt as the metal salt manganese acetate as the salt, calcium acetate can also be made.

But it is not possible to make this hetero dimetallic system because all the time you will be ending with either a dicalcium compound or a dimanganese compound because your coordination environment for these two if they are symmetrical in nature. So, whatever binucleating system you can have, one particular part should favor manganese coordination and other particular part should favor the calcium coordination. So, that is why this sort of chemistry is pretty difficult to do because if you have a huge database to know that what are the groups which can bind very easily to manganese center and what are the other groups which can favor the calcium binding, then only you can get a simple binuclear compound having calcium in one pocket and manganese in other pocket but here if you have this particular group and is already available, but only thing what is happening over there is the translocation; that means the movement of the metal center, so within the cluster arrangement.

Since you are putting electron you are getting out electron, your structure is getting changed. Why it is getting changed? It is not that you have the oxidation or reduction, you are changing what? You are changing manganese oxygen distance, you are moving from manganese three to manganese four, you are going from one particular case level of protonation to other level of protonation, that also can change the manganese oxygen distance as well as you can change the manganese oxygen manganese angle depending upon your nature of this group whether it is oxido function or hydroxido function as well as the nature of the two oxidation states.

So, these are the other contributing factors which can contribute for the structural change, but the calcium is responsible for binding because it do not have any preference for regular coordination geometry; that is why calcium. If you think that manganese is there or any other transaction metal is there and if they are extra coordinated, immediately we will say no, this can only pay for an octahedral geometry and for octahedral geometry you know this bound distance, bound angle are all fixed. But if you go for a main group element or a non-transaction element like zinc also, it has no crystal field stabilization; it has no special preference for coordination geometry. If you have metal center like this calcium or cadmium, suppose you have calcium, what happens there?

Since it has no such preference for this binding, only the available donor groups from this protein chain or some biological chain; only the available donor groups can come and is such that it can have all sorts of arbitrary coordination. So, this one such arbitrary coordination can make this particular group as a bridging model; that is why you have very distorted one because one bound is short and another bound can be long. Because initially you can think of that this acetate function is coordinating to calcium center in a monodentate fashion because these two bounds are not same. So, it is not a symmetric binding of the acetate group as a bidentate ligand because acetate cannot be a bidentate ligand. It is a forming a 4 membered ring. So, one bound is short and another bound is long which is in the other direction.

So, this calcium can change the structure in a large way. You have this nitrogen coordination; you have this acid coordination from the glutamate group because these groups are not moving. This is still the glutamate 189 but what change is taking place. So, this is one part of change; that means your system is moved from this direction to 60 degree and you have this and this oxygen was mu 3. Now this is not there but what will happen. This manganese number four is there; you will have this manganese, you have this. So, earlier you have this manganese which is connected to a mu 3 oxido function. So it will try to establish, it will try to remain there with the help of some other bridging group. So, this is the part which is very different from the other structure.

So, this particular group which was there on this number four can stabilize your arrangement like this. So, you have this group. So, it is moved but your number four manganese cannot move that much; that is why it is the system where you have Mn 3 plus one manganese which is different from an arrangement where you have a regular cube structure. So, once it is there and you move basically what we are moving. We are moving one manganese over here. So, once you move that manganese. So, this particular new bridging function can take place because you have immediately you can take over water; after deprotonation you can go for hydroxido bridging or further deprotonation you can go for oxido bridging.

So, this particular unit which is a special one which can go for bridging and this particular distance we can measure which is 3.3 angstorm; that means it is tightly bound to the m three unit. It is not that very loosely bound. Earlier we can consider this a dangling one which is the pendant one, this fourth manganese is a dangler; that is why

call it as dangler but when it is forming a firm bridging, it is within this cluster and that basically tells us that how this particular one is responsible for accepting water molecule and it goes for the removal of this O 2. Once you get one group of this and another group of this from the other unit to make O-O bond. So, OO bond formation can take place and these two manganese groups basically can activate this particular oxygen and this particular O 2 unit from there. So, basic idea behind this thing is that how you go for the change in structure during electron transfer.

Thank you.