Bioinorganic Chemistry
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 32
Tungsten Enzymes – IV

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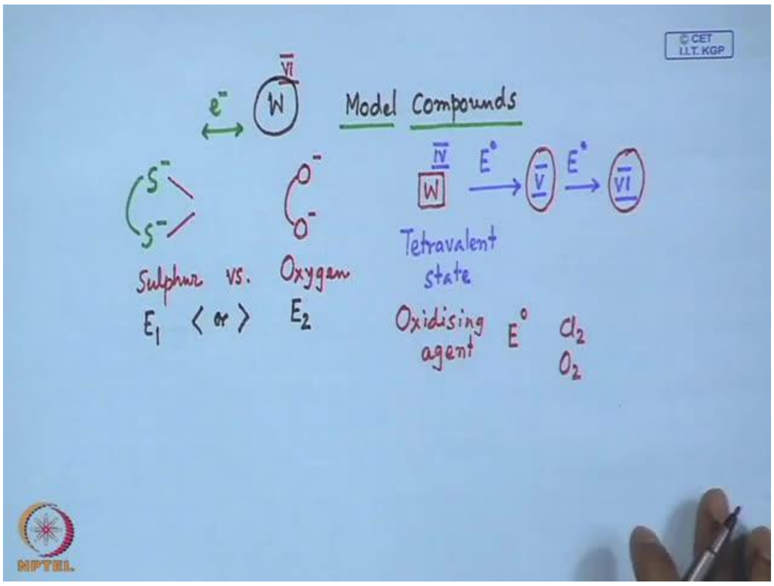

Hello, Good morning everybody. So, we will still with the tungsten enzymes, because we are started one important thing on tungsten is the corresponding model compounds. How these model compounds can help us in understanding the actual reaction based on the metal center that is taking place in all these tungsten containing enzymes. So, one important aspect what we have discovered so far, related to all these tungsten bearing synthetic molecules as well as the metalloenzymes of that these are responsible for typical electron transfer reactions. So, when these electron transfer reactions are taking place, and we are just simply changing the corresponding oxidation states on the tungsten, and how the corresponding ligand system, which is sulphur based and the tungstoterene unit, where we have two negative charges on the thiol backbone.

In stabilizing this high oxidation state when we can consider that tungsten is present in plus 6 oxidation states, which is the most known, one where the highest possible oxidation state of tungsten is residing. The affective Charles transfer from the sulphur, which is bigger because this amount of Charles transfer from sulphur anions, the thiolate anions will be definitely bigger than the corresponding transfer from the oxygen atom.

So, we can just simply compare that donor ability of sulphur verses oxygen in these systems. So, one very important thing what we can study is that, whatever model compound we make on these two ligand say based on tungsten, which can lead us to some formation whether we should be able to oxidize this tungsten center, if this center is present in the lower oxidation state that means the tetravalent state.

So, if we have the tetravalent state and if we go for the corresponding oxidation to pentavalent state and the hexavalent state and if we can measure the corresponding E 0 values of these two steps. That means how easily and how quickly we can oxidize the tungsten center from the tetravalent state to pentavalent to hexavalent state. So, if we just compare these E 0 values and if we can compare these that means, if these values for one particular type of molecules are E 1 and another type is E 2.

Then by simply comparing these two values either E 1 can be less than E 2 or E 1 can be greater than E 2 these are the two situations, we cannot have any situation where E 1 is equal to E 2. So, the effective Charles transfer from the sulphur bearing ligands, we can compare with that of the Charles transfer from the oxygen bearing ligands. So, if we find that this particular oxidation potential, E 0 value for oxidation is less than that of for the corresponding species surrounded by the oxygen bearing ligand. We can simply say that the compound sulphur environment can be easily oxidized compared to those in oxygen environment.

So, if we take the corresponding oxidizing agent, because for this sort of electron transfer based on this thing that means, this is the reduction on the other hand if we can have the oxidation on the tetravalent state like these, we need some oxidizing agent. So, these oxidizing agent will immediately tell us because all the non-oxidizing agents, that means the corresponding redox potential value E 0 values for all the different oxidizing agents, starting from chlorine gas, oxygen gas and all other things. So, how we can choose the corresponding oxidizing agents by knowing the corresponding E 1 values and E 1 0 or E 2 0 values for the corresponding tungsten compound, can tell us how easily we can oxidize this center to the corresponding pentavalent state or the hexavalent state.

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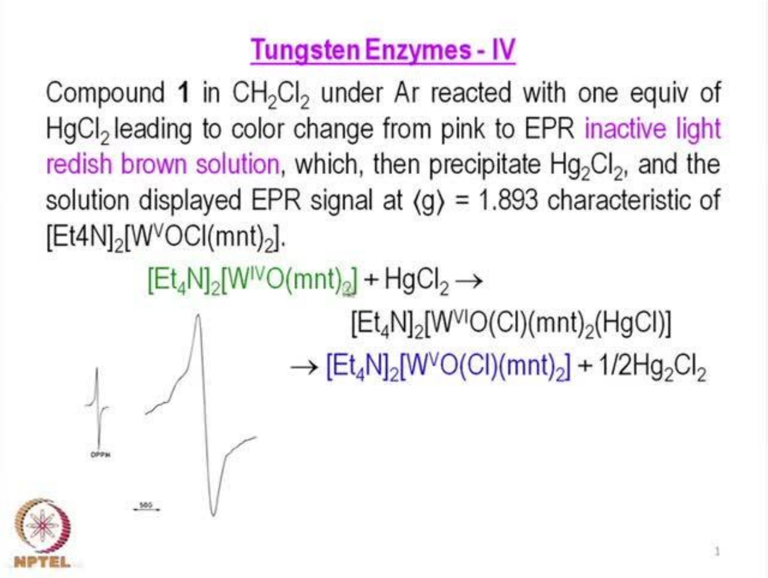

Tungsten Enzymes - IV

Compound **1** in CH_2Cl_2 under Ar reacted with one equiv of $HgCl_2$ leading to color change from pink to EPR inactive light redish brown solution, which, then precipitate Hg_2Cl_2, and the solution displayed EPR signal at ⟨g⟩ = 1.893 characteristic of $[Et4N]_2[W^{V}OCl(mnt)_2]$.

$$[Et_4N]_2[W^{IV}O(mnt)_2] + HgCl_2 \rightarrow [Et_4N]_2[W^{VI}O(Cl)(mnt)_2(HgCl)]$$

$$\rightarrow [Et_4N]_2[W^{V}O(Cl)(mnt)_2] + 1/2Hg_2Cl_2$$

So, one such situation you can encounter the example we have taken from the last time that, one is the maleonitriledithiolate based ligand we have taken. This is basically what you have seen that, this is basically sulphur bearing ligand. So, dithiol in type of ligand you have the back bone with double bound and two sulphur in the negative charge. So, this maleonitriledithiolate type of ligand, when it is stabilizing the tungsten? When you have the corresponding tetravalent state?

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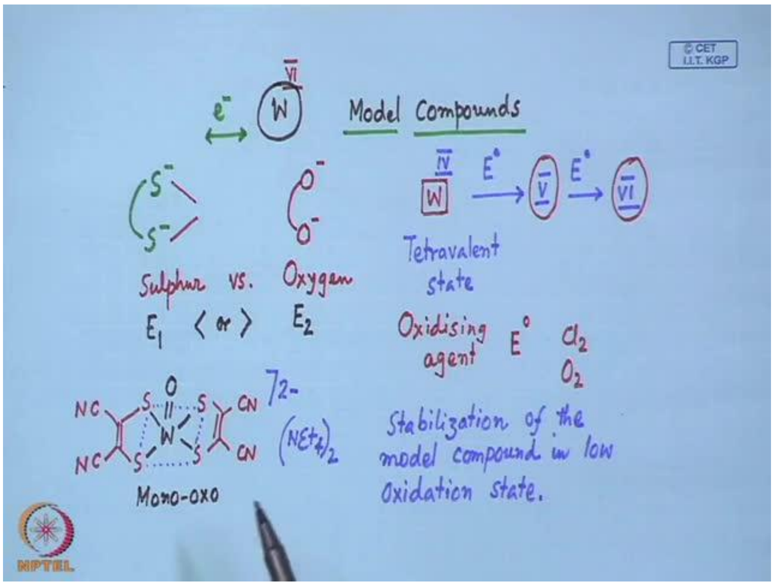

Model Compounds

Tetravalent state

Oxidising agent E° Cl_2 O_2

Stabilization of the model compound in low oxidation state.

So, this one, so we just take the system on this maleonitriledithiolate, these are the C N groups. So, you have two ligands and we have the tungsten. Depending upon the starting metallic salt what we have used for the preparation of this compound, if we get this as the corresponding only mono-oxo species, which is in a typical square pyramidal geometry. So, this geometry, this is the basic square plane and we have the square pyramidal geometry and four of these sulphur anions providing 4 negative charge and this oxygen is also providing 2 negative charge. So, 4 plus 2, 6 negative charges are there and tungsten in plus 4 oxidation state will give us, then overall 2 negative charge on the complex anions. So, it can be stabilized by the corresponding ammonium salt, which is tetraethylammonium salt. So, the question is that, how we get this particular one in the plus 4 oxidation state?

So, that means the stabilization of the species, of the model compound in low oxidation state. So, in this low oxidation state it can be achieved. If we have a corresponding mono oxo compound the compound is therefore, the simple mono oxo compound. So, if we take this compound that means in that plus 4 oxidation state the mono-oxo maleonitriledithiolate compound of tungsten, which is soluble in dichloromethane, the solvent is dichloromethane. Two exclude the presence of Ar, that means we do not want to take any chance that Ar is the oxidizing agent and following oxidation by Ar the oxidizes species can also be different and it can transfer oxygen, which removes the oxygen present by argon environment. So, on the argon environment it reacts basically with one equivalent of mercuric chloride.

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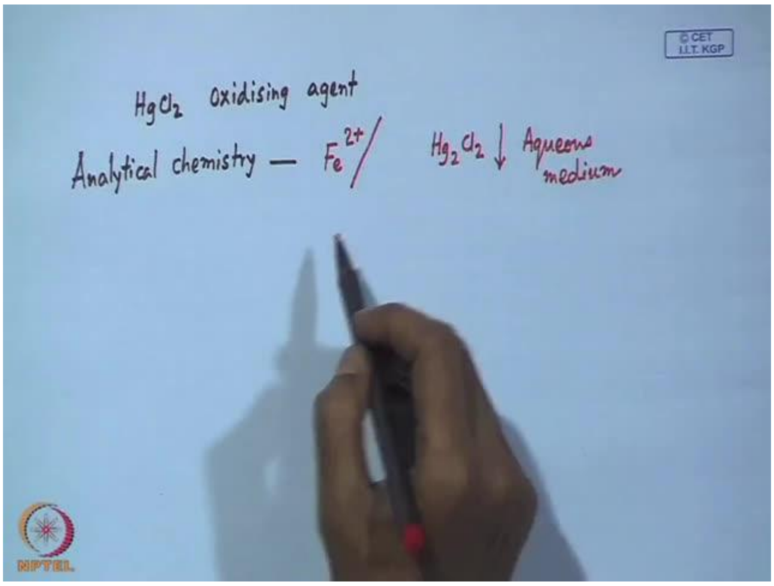

So, Some idea from the corresponding E 0 value of mercury chloride, so that mercury chloride what I told last day, that if we are utilizing mercury chloride as our oxidizing agent it has several advantages, like the way we use mercury chloride solutions in analytical chemistry. So, what we did there in analytical chemistry, this mercury required is a very useful reagent for oxidizing any particular one, that means any center which can be F e 2 plus, so this can be oxidized by this mercury chloride. So, for this ferrous ion or any other one this mercury can be a very good oxidizing agent. So, this particular one because this mercury required do settle between its other reduced form, which is mercurous chloride.

So, when mercurous chloride is forming it has less solubility even in some organic solvent medium, which is less soluble in aqueous medium. So, it is less soluble in aqueous medium, mercurous chloride immediately precipitates out from there. So, when we use this mercuric chloride from there, the color of the solution immediately changes from pink to some EPR inactive light reddish brown solution. So, the color changes there, one is there when we have this corresponding compound that means this one which is formed immediately. So, due to the color change nothing is happening which can be sensed by EPR spectral measurements.

So, EPR is a very sensitive instrument for measuring the corresponding spectrum where we can measure the spectrum by knowing that whether there is any change in oxidation state on that tungsten. So, if the tungsten center goes from plus 4 to plus 5, then only we can detect the presence of tungsten five, that means the pentavalent state of tungsten in the medium by knowing the corresponding spectrum, the corresponding EPR spectrum of the species in solution. But what is happening there the color changes taking place from pink to reddish brown solution. So, pink was not EPR active, reddish brown solution was also not EPR active. But what happens at the same time after some time mercurous chloride gets precipitated and the solution then started displaying one EPR signal at g is equal to 1.893.

So, these are very characteristic values depending upon the corresponding magnetic field. So, if we have the magnetic field and corresponding absorption is taking place like this, this is the typical EPR spectrum for that solution. We basically measure the corresponding g value, how we measure this corresponding g value at 1.893 is that how much this one this particular one, that means this is the corresponding field that means the magnetic field is 3200 that gouse for diphenylpicrylhydrazyl radical. So, diphenylpicrylhydrazyl radical shows corresponding signal at around 3200 gouse and with respect to that value, where this particular one is appearing. So, compared to these, because this field is known at this corresponding zee value 2.0034 is also known.

So, based on that value on DPPH, we can determine the corresponding g value for this signal. It is a very simple technique so, that simply comparing with the reference material the reference sample for EPR spectrum for reference sample is the corresponding DPPH. And with respect to DPPH will find out the field and from the field we can calculate the corresponding g value which is therefore, characteristic for the species based on tungsten five.

So, how this tungsten five it is forming the solution, what we have done we have done the reaction of the tetravalent maleonitriledithiolate compound of tungsten with mercury chloride. So, immediately what is happening there this particular mercuric chloride is transferring one of its chloride and to the tungsten side, which is very important and this one basically…

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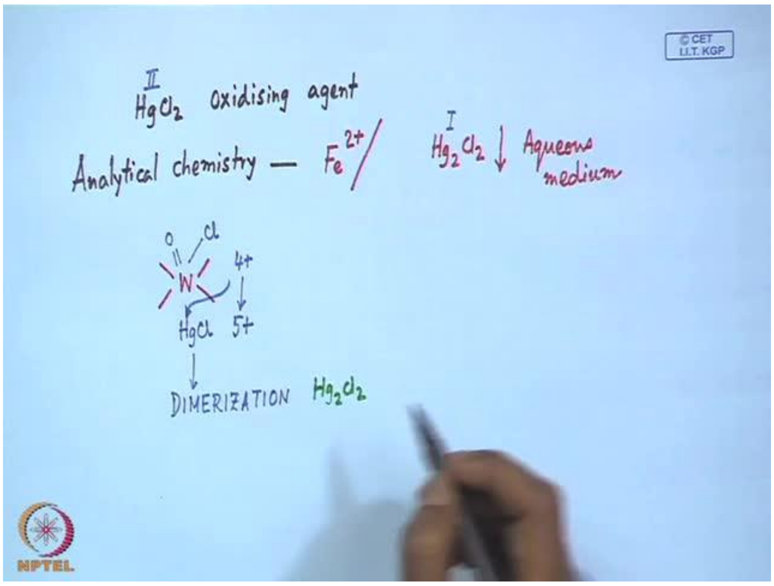

So, you have this tungsten side as, we have these two ligand groups attached to the tungsten and then we have this oxo species 1 and we have the transfer of this C l and loosely bound Hg Cl is there. So, this particular one Hg Cl, so transferring one chloride ion this mercury is in plus 2 oxidation state, but this mercury is in plus 1 oxidation state. So, if the electron transfer is taking place to the mercury it can be reduced to mercurous species. So, when chloride is transferring, so one more electron transfer is taking place, that means this tungsten site which was in the plus 4. So, it is 4 plus it can go simply to 5 plus, that means one electron it can transfer to the tungsten mercury site.

So, mercury center which one was in the plus 2 oxidation state will be reduced to plus 1 and this can dimarize, so this HgCl will dimarize, so dimerization can take place. Therefore, that dimerization will lead to the formation of H g 2 c l 2. So, thing is that when this radius brown solution is forming. So, this particular species when mercurous chloride is still attached to the tungsten site and this particular one, basically when we consider that is this immediate formation of this tungsten, which is in the plus 6 oxidation state.

So, that means if we just go for this to plus 6 also, which is a two electron transfer process. So, this is going for plus 5 still we have one charge, which is taking care of by this particular mercurous chloride species derived from the mercuric chloride. So, due to that basically is electron transfer will now take place over here, so this is tungsten six and this corresponding mercury center. So, if electron transfer is now taking place, because this still mercury chloride that means Hg Cl plus, this is plus, this is one positive charge is there still.

So, due to that electron transfer this one go for dimerization and mercurous chloride getting precipitated from the system and we end up with something where we have the tungsten center is again reduced back to a pentavalent state. So, this is an unique example for stabilizing the tungsten in the plus 5 oxidation state by using a very simple reagent which is nothing but mercury chloride. So, mercury chloride is basically the responsible for oxidation of this tungsten compound in plus 4 oxidation state, 2 tungsten five through some intermediate which is tungsten six, when Hg Cl is attached to this tungsten six and whose color was radish brown.

Since, the starting tetravalent as well as this intermediate hexavalent both of them are the EPR inactive, we do not get any EPR signal for the pink solution as well as for this radish brown solution. But what we get when after the precipitation of mercurous chloride the solution gets turbid and we can filter it out and the turbidity goes away. The clear solution if we can take for again the EPR spectral measurement we find the same signal, which was earlier we were finding after the precipitation of mercurous squared in the reaction medium. That this particular species is definitely responsible for the corresponding EPR spectrum in plus 5 oxidation state.

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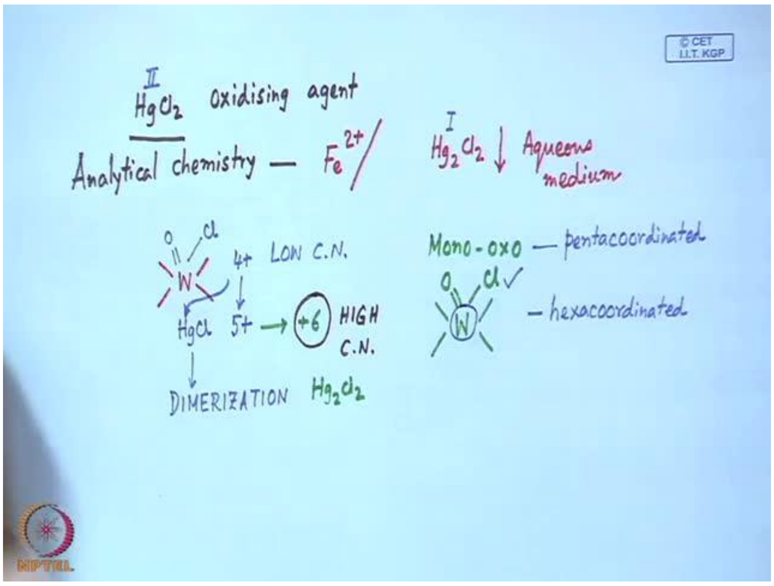

So, what is happening there basically, when we have in case of the mono oxo species, we have one oxo site, one oxo center on the tungsten, but during this particular one when we go for this particular oxidation. So, what is happening therefore, that tungsten center with two ligands, we have a double bound o and one c l. So, this is some kind of again something we all know as the corresponding oxidation of the center and one more ligand addition. Because this is when we have this mono-oxo one, on this mono oxo compound was penta coordinated penta coordinated and when we go for oxidation plus addition of one ligand. This is the new ligand which has come to attach to the tungsten site and the system goes from penta coordinated 1 to hexa coordinated system, with the addition of chloride anions a new ligand.

So, what we find that as we go for the lower oxidation state for tungsten in the tetravalent one, we have here basically low coordination number for the 4 plus. But when we take out the electron, we oxidize the center through pentavalent to hexavalent. Then the electron demand for the plus 6 oxidation state has changed and it is more electron greedy through the donation of new ligands. So, we have at this situation we have the corresponding possible high coordination number for an hexa coordinated species.

So, is very simple we can consider we can go for oxidation as well as the addition of new ligand, which something we call it in case of catalysis is there it is the oxidative addition reaction. So, we go for the corresponding oxidation we allow the corresponding expansion of coordination number and then we introduce the corresponding chloride anion there. So, this particular chloride transfer from mercury chloride is a very simple and very unique reaction, where it changes the oxidation state as well as we expand the coordination number around this tungsten ion. So, this is very useful and effective information for the catalysis.

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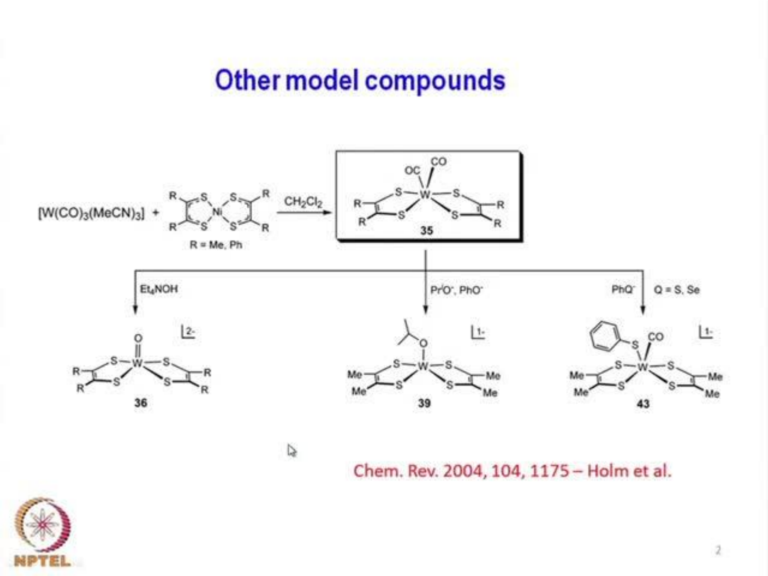

Other model compounds

Chem. Rev. 2004, 104, 1175 – Holm et al.

So, what is happening there? that means if we just consider the other model compounds, where we just simply want to have a reaction, because this sort of diethylene ligands are well known. So, this sort of this again this diethylene type of ligand, so is these are s minus and s minus ligand. So, these are very simple also if we have the corresponding quenoxilelediethile ligand. So, quenoxilelediethile if we have a quinoxaline backbone, this is also very simple reaction for there. So, quenoxilelediethile, so this is type of ligand and it gives very useful compound with nickel. So, nickel when reactory this sort of ligand gives a bisculate and that bisculate it basically is square planer one.

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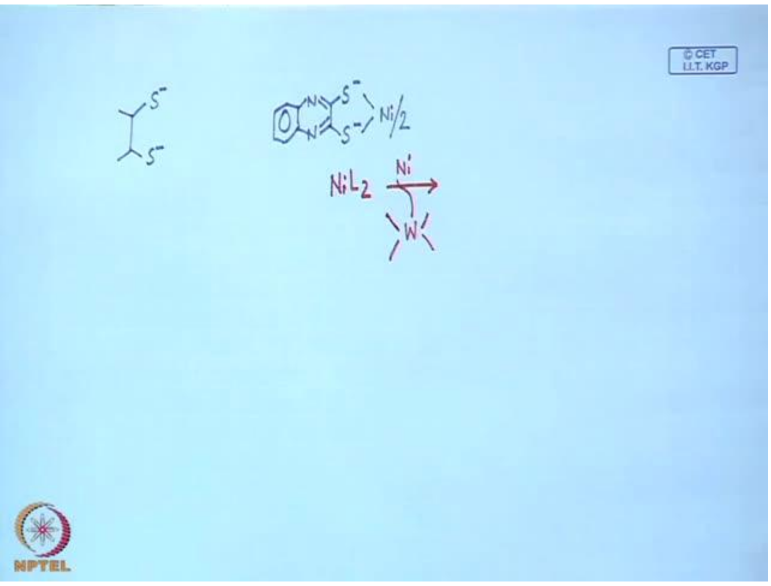

So, when we have this particular, sometimes we can generate this diethyl ligand in c 2 in solution the reactive species, which is giving rise to this particular quenoxilelediethile type of thing, is also used for making the corresponding template reaction for nickel. So, NiL 2 compound, which can be very easily make. Now, the metal ions metathesis reaction that means, we substitute this particular that means nickel will be substituted by tungsten. So, hoping that in that particular environment when these two sulphur ligand are there. So, nickel will be simply replaced by that tungsten and we immediately get the corresponding species as tungsten with these two ligands, which were originally attached to the nickel site.

But we can also go for using a corresponding carbonic compound of tungsten because, like molybdenum, like chromium tungsten also give rise to very useful carbonyl compounds, including the tungsten hexacarbonyl species, where tungsten is surrounded by 6 carbon mono oxide molecules. Once such intermediate species is there, which is stabilized by 3 acetonitrile ligand as well as 3 carbon mono oxide ligands. To stabilize a tungsten in hexacoordinated form and in same dichloromethane solvent, which is a very useful solvent for reactions of these type of model compound.

We react with this particular nickel compound where R can be methyl methyl, phenyl phenyl, bithylene type of ligand. So, what is happening there? That the loosely bound acetonitrile molecules, which is basically present over there, so these loosely bound acetonitrile molecule. So, these all three acetonitrile solvent molecules, acetonitrile is a very useful solvent molecule also. So, all three acetonitrile as well as one carbon monoxide molecule goes away, giving rise to one particular highly distorted type of hexacoordinated species for tungsten. Where we have two carbonyl molecule still attached to this particular tungsten species.

So, what we basically find there that whenever we get these that means this was basically tungsten in the 0 oxidation state, which undergoes oxidation as we remove these particular carbonyl as well as the acetonitrile molecules and we have the corresponding stabilization from the sulphur unit. So, these sulphur units basically go for the stabilization for the tungsten charge on it. We get a simple compound of that where we have the basic code the metalloenzyme type, tungsten enzyme type basic code bound to four sulphur groups. This was basically our idea wherever, we make this molecule, which should be the model compound of the tungsten enzyme we have these four groups which should be bound to 4 sulphur atoms.

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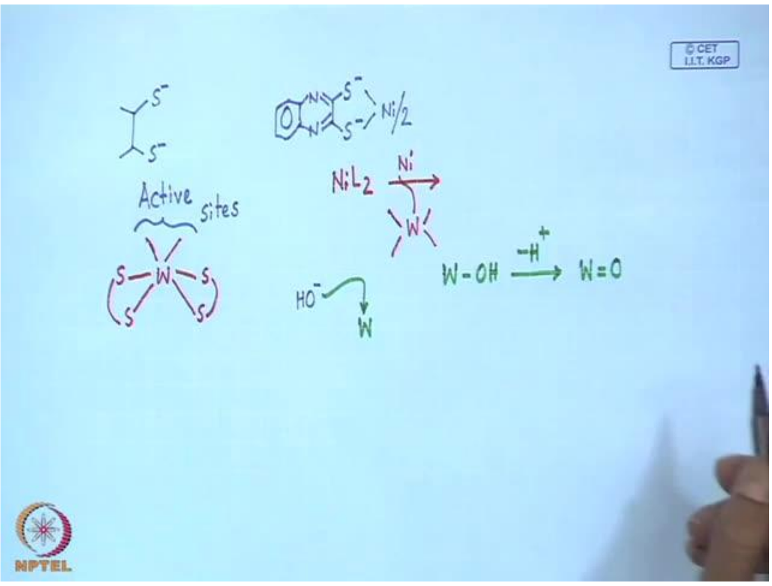

So, when these four sulphur groups are bound to this tungsten, we have two carbonyl functions. So, how these carbonyl functions that means, these are therefore, our catalytically active sites. So, wherever we go for these type of reactions on the model compound, we see that these are the corresponding active sites. So, on tungsten we have two other positions, which are nothing but our active sites for catalytic reactions. So, these two sites are very important to have. So, through these reactions with tungsten carbonyl starting material we have to carbonyl groups on these two positions.

So, next we can see that corresponding reactivity pattern, how these two carbonyl groups, when they are bound to four sulphur bearing ligands? How they are reacting with different reagents? Which can give us some idea that whether we can retain some of these carbonyl functions or we can just completely remove these carbonyl groups? That means whether these carbonyl dioxide, monoxide ligands can be retained their or can be kicked out. So, the same tungsten when reactive with tetraethylammonium hydroxide. So, when it is reacting with simple base, this is very strong base though compared to sodium hydroxide or potassium hydroxide the tetraethylammonium ion based base. The tetraethylammonium hydroxide immediately provides the corresponding OH minus group to this tungsten site.

It immediately cleaves these two carbonyl groups or carbon monoxide molecules are going away from tungsten and a double bound is forming there between oxygen and tungsten. So, what is happening there, when we provide these HO minus as the corresponding salt of tetraethylammonium ion to the tungsten site, so these two tungsten site was attached to two carbonyl functions. So, this can go and occupy that particular position and during that occupancy intermediate state is forming where tungsten is coordinating with the hydroxide ions. So, W OH is forming from that site and which then in the next step go for deprotonation and that deprotonation would lead to the tungsten oxygen double bond species.

So, we get this particular tungsten double bond O species and the corresponding oxidation state is also not changing much, we have two negative charge on it. Because, this 4 sulphur is providing 4 negative charge and oxygen is providing 2 negative charge, all together we had 6 negative charge, which is balanced by the tetravalent tungsten giving rise to an overall anionic charge 2 minus on the anionic complex of tungsten. So, this is one sort of reactivity with respect to a strong base, but if we go for the reactions with alkoxide ions instead of hydroxide ions. So, if we use the corresponding salts of phenol or the corresponding salt of isopropyl alcohol. So, isopropyl alcohols just simply go and bind with this particular tungsten site as the corresponding alkoxide group.

Since, this is terically crowded it will not allow to go for attaching the corresponding six positions, because the starting compound is hexacoordinated. But the resulting compound is penta coordinated with the removal of both the two carbon monoxide molecule with the introduction or the attachment of this alkoxide anion. So, way the hydroxide anions is reacting which is giving rise to double bond tungsten species, which is five coordinated and still if we can have a single bonded tungsten oxygen bond to that of our alkoxide group. We still get a penta coordinated species, which is similar to that of the species number 36, both 36 and 39 are almost similar type of species forming over there.

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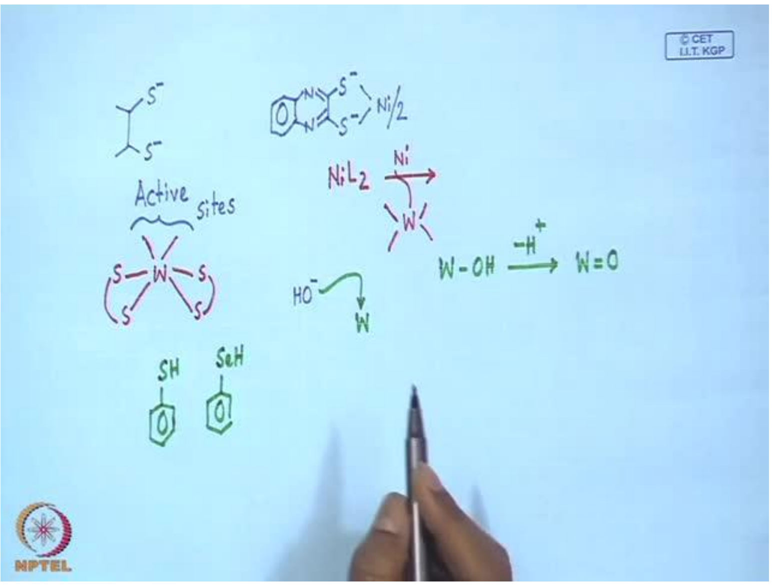

But in case of sulphur the reactivity is little bit different, if we just simply thiophenol anion, sileno anion corresponding PHS or PHFE minus species, which we get this is a SH is thiophenol and SEH is the corresponding selenophenol, SEH when both of them are anion. So, the sulphur the reactivity of this sulphur bearing incoming nucleophiles, how they are reacting with these dicarbonyl compound 35 can be tested. But interestingly the codes of the reaction is little bit different to that of our reaction with hydroxide ion or dylcocsite ion. Is that one carbon monoxide can be retained with the introduction of one thiophenol unit by the replacement of the first carbon monoxide molecule.

So, the product is still hexacoordinated where one carbon monoxide molecule is still present and the tungsten in a S 5 environment. So, this is highly sulphur dominating environment, where five sulphur groups are present around tungsten and in that situation tungsten can still maintain its bond with that of a carbon monoxide molecule. So, Charleston such that this particular sulphur is unlike this one, it is not removing the corresponding carbon monoxide molecule form the tungsten. So, the reactivity pattern and so, how the catalytic cycle is going on, that can be tasted if we just simply go for the corresponding reactions with hydroxide ion, alkoxide ion or the thiophenol anion.

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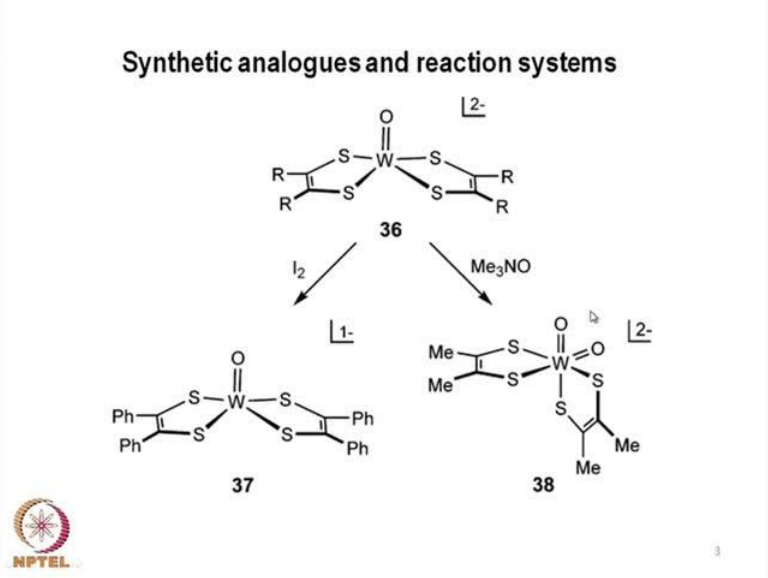

Synthetic analogues and reaction systems

In one more example and the corresponding reaction system can be tested on these that means when we have the dioxin molecule, mono-oxo molecule that means when we have that corresponding species as 36, which is forming from 35 by the reaction with tetraethyl ammonium hydroxide. So, how this species, that means again it is like that of our enzyme type mono-oxo species. So, this how this mono oxo species can be reacted, because this particular one is in that tetravalent states. So, the way we just now seen that how the corresponding compound the model compound in tetravalent state can react with mercury chloride.

So, we have done this one for testing the corresponding reaction of this 36 with that of iodine. Instead of corresponding oxidation with chlorine or any other mercury chloride type of thing which, just can go for simply iodine oxidation. This iodine oxidation, this is basically the 36 compound is in the plus 4 oxidation state and which is simply going for one electron oxidation only giving rise to the corresponding tungsten compound in the pentavalent state. So, it will have one less negative charge on the ionic part of the compound.

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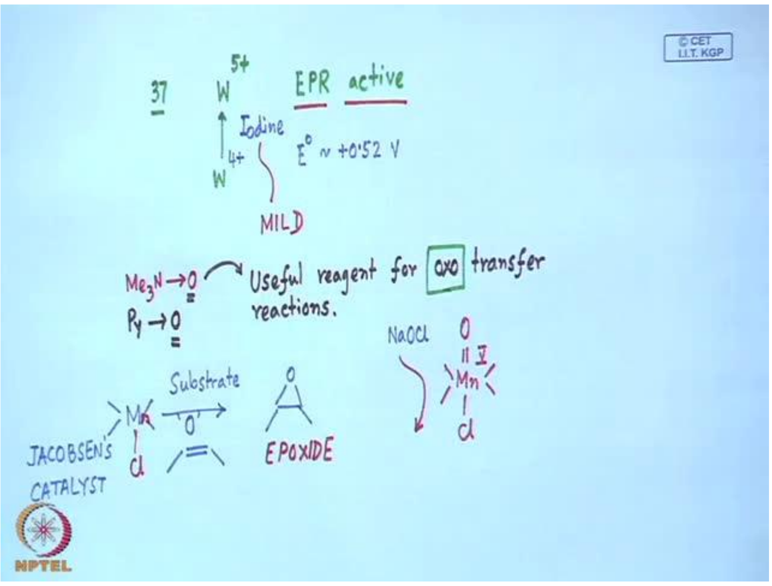

So, 37 is therefore, the corresponding pentavalent compound, so this 37 is bearing tungsten in the pentavalent state, it would be therefore, EPR active. So, just by simply doing this reaction that means, we should be able to oxidize some of these compounds particularly the biological compounds, the enzymes the tungsten enzymes. We can go for the corresponding oxidation of this tungsten 4 plus to tungsten 5 plus by simple oxidation with iodine. So, iodine oxidation can be available, because we know that the corresponding E 0 value of the tungsten is close to plus 0.524. So, it is a very low potential oxidizing agent compared to chlorine or bromine.

So, this low potential oxidizing agent is also suitable for oxidizing tungsten from plus 4 oxidation state to plus 5 oxidation state. So, we see that in this particular case what we have utilized is a very mild oxidizing agent. So, this oxidizing agent is a mild one and we should be able to generate one particular EPR active species that means this particular cycle of reactions, most of the time goes to the pentavalent oxidizing state of tungsten. One more reaction, this is the corresponding redox transfer reaction on the left. So, the change from 36 to 37 is basically the corresponding electron transfer reaction, whether it should be able to oxidize this tungsten site from tetravalent to that pentavalent state. And on the right what we get that the conversion of 36 to 38 with the use of some oxo transfer reagent, which is trimethylamine n oxide.

So, any three n is well known to us is a trimethylamine species and which is reacting hydrogen peroxide or any other oxygen donor agent to give trimethylamine n oxide. The way we get pyridine with reaction with hydrogen peroxide can give pyridine n oxide, so this n oxide molecule are very useful reagent for oxo transfer. So, they are useful reagent for oxo transfer reactions. So, we can transfer these oxygen atoms very nicely to any other system, which is well known for any study, because we all know that the formation of these oxo groups are very useful in catalysis in any other industrial catalysis as well as biological catalysis

If we have any metals center and if we see that some substrate is reacting over there and that particular substrate if we seen that this particular substrate has a double bond. If we just manipulate on some reagent which is an oxo transfer reagent, whether we should be able to go for the corresponding approxide formation. That means, the metal center is there that is of well known Jacobsen’s catalyst based on manganese and there one more useful reagent is that simple inorganic compound sodium hypochlorite.

So, if sodium hypochlorite is given and in this Jacobsen’s catalyst, is a silent type of ligand that means its four positions are blocked. Initially the manganese compound what is forming is basically M N, metal is M N. We have initially the manganese in the trivalent oxidation state is a five coordinated one and through the reaction with Na O Cl it basically gives manganese which is not very stable, but in plus 5 oxidation state. So, that particular catalytically active species is responsible for the transfer of these oxygen to this alkene compound. So, it can be styrene or it can be any other compound bearing double bond, which can be very easily go for the corresponding epoxide formation.

So, the epoxidation reaction, this epoxide reaction is basically catalyzing through these oxo transfer agent. So, these basically all reagents are known as the corresponding good oxo transfer reagents and if we can go for this any oxo transfer reaction. On this particular tungsten model compound number 36 what will happen, whether this particular tungsten site can accommodate further oxo group that means, we know that the tungsten center can go for like molybdenum that both mono-oxo species as well as dioxo species. So, in this particular one only there is a change in orientation of the corresponding positioning of these ligands.

So, we have a roughly square pyramidal five coordinated tungsten compound in the tetravalent state and through the simple transfer of this oxide anion, this oxo transfer reagent reaction from trimethylamine n oxide reagent, just simply go for the corresponding hexacoordinated compound. And tungsten goes from plus 4 to plus 6 oxidation state and these two oxo groups, basically take the positions they are cis Dioxo compounds. So, these two oxygen positions are cis, is not that this oxygen will go and attack this tungsten from the opposite side of the existing tungsten oxygen bond.

So, instead of that the reorganization of this bidentate ligand, so this bidentate ligand is basically pushed from this side to that side and this oxo group is attacking from there. So, when the oxo group is attacking the tungsten side form this side, these two ligands are basically pushed down and one of the soluble position is taking the corresponding transposition with that of the existing oxygen atom. And we get some reorganized form that means the hexacoordinated species as the corresponding hexavalent compounds.

So, what we get if we have a catalytically active or the catalytically proactive species on tungsten base, which is the compound number 36. We can go for the electron transfer in, what is happening after simple electron transfer? What is happening after electron transfer followed by ligand transfer also? And which is some other kind of oxidative addition reaction, which is different from that we have seen just now for the chloride. In case of Cl minus the oxidation state was changing from plus 4 to plus 5, but in this particular case due to oxo transfer the oxidation state on tungsten is changing from plus 4 to plus 6.

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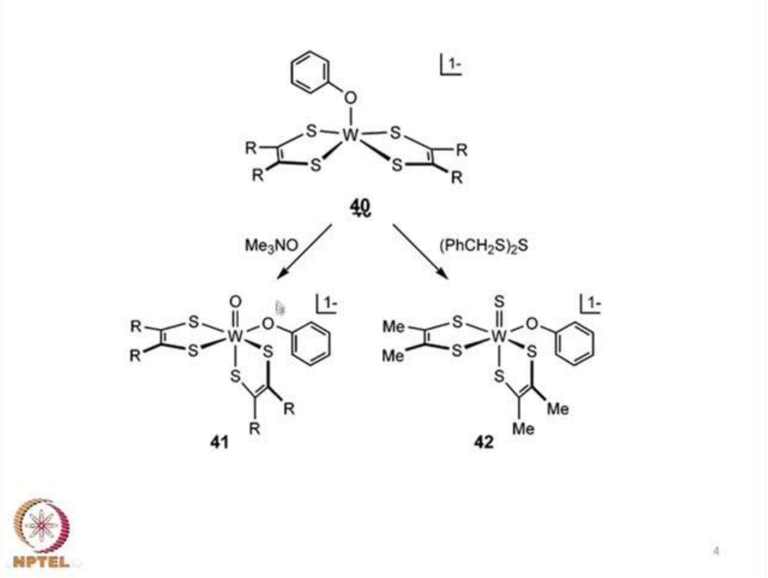

So, these reactions also can be examined for the other compound which was 40 that means, when the phenoxide ion like that of alkoxide anion, which is penta coordinated one is reacting with that of our other reagents. So, when these basically like that of trimethylamine n oxide reaction. So, for the trimethylamine n oxide reaction it goes to these two positions. Similarly, when this trimethylamine n oxide is reacting with compound number 40, what is happening there that this particular one can nicely accommodated oxo group. This oxo group is now straight away forming the corresponding species what was present from this oxo compound.

So, this is basically the compound number 40 is our non oxo compound and these non oxo compound is basically reacting with the oxo source or some oxo transfer reagent. Immediately forming the oxo compound and is again an hexacoordinated compound, but one oxo and one phenoxo. So, oxido, phenoxido compound like that of our dioxido compound. So, the dioxo compound what we have seen just now that which is hexacoordinated and two cis positions are occupied by two oxygen atoms of the dioxo groups.

Similarly, here one of the group is occupied by this oxo function, which is the incoming of oxo group from the tetraethylammonium n oxide and this particular phenoxido group is little bit go for some adjustments. So, coordination environment adjustment is taking place and which is now occupying the trans position of this sulphur of this sulphur. So, trans position of this sulphur, this oxygen is basically moved from here to there while giving space for accommodating this oxido group, which is coming from tetraethylammonium n oxide. But when we go for the corresponding oxo transfer reagent, we can also go for the some reactions where we can have the sulphite transfer reagents.

So, which is nothing but another type of groups is the trisulphide type of molecule. So, which is trisulphide is a polysulphide are well known for providing sulphur as S 2 minus. So, this is your tri sulphite reagent for that based on benzyl thiol. So, this can vary easily provide sulphite anion to that system and interestingly we all know that the sulphite groups when we use the sulphite groups as the reagent in group analysis and analytical chemistry.

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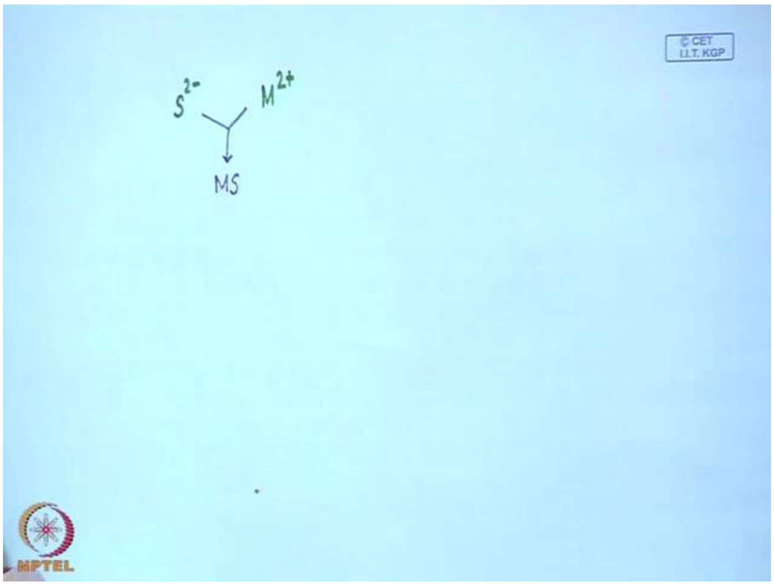

We all know that S 2 minus when it is available, it can react with many metals salts in plus 2 oxidation state like, iron, like copper and they go for their corresponding precipitation, as M S metal sulphites. Metal sulpoginites are precipitated out from the medium and group analysis is we can go for that. But here what is happening that if you just provide S 2 minus on compound number 40 whether we can take out this sulphur as tungsten as tungsten sulphite is not possible because, tungsten already in plus 4 oxidation states. So, W S 2 is also not forming through the reaction of this reagent.

So, metal ion transfer or the corresponding metathesis reaction based on the removal of the tungsten, from this relating environment is not possible with the use of this sulphur transfer reagent. What is happening in state? Like that of oxo transfer reaction the same reaction is taking place that means the reactivity of sulphur as sulphite ion or oxygen as oxide anion, both are of similar. Because, this particular position is occupied by sulphur, what was occupied by oxygen in compound number 41? So, M A again this reorganization of this phenoxide anion is taking place and sulphur is simply sitting over there as making the sulphur double bond with that of our tungsten center.

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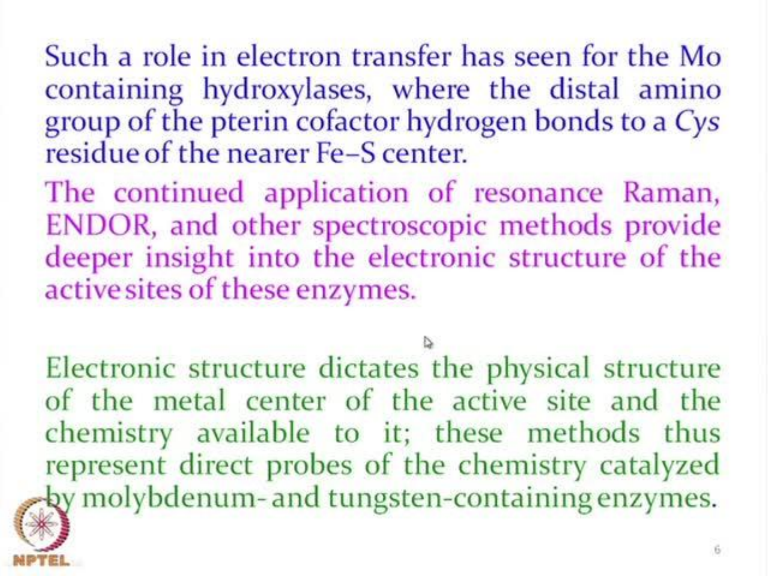

Such a role in electron transfer has seen for the Mo containing hydroxylases, where the distal amino group of the pterin cofactor hydrogen bonds to a *Cys* residue of the nearer Fe–S center.

The continued application of resonance Raman, ENDOR, and other spectroscopic methods provide deeper insight into the electronic structure of the active sites of these enzymes.

Electronic structure dictates the physical structure of the metal center of the active site and the chemistry available to it; these methods thus represent direct probes of the chemistry catalyzed by molybdenum- and tungsten-containing enzymes.

So, what we see that the electron transfer reactions are taking place on all this molybdenum containing different hydroxylases, where we have the Cys residue are present near to iron sulphur centers. So, several techniques like Raman Endor and other spectroscopic methods also provide good information’s for the electronic structure of these active sides of these enzymes.

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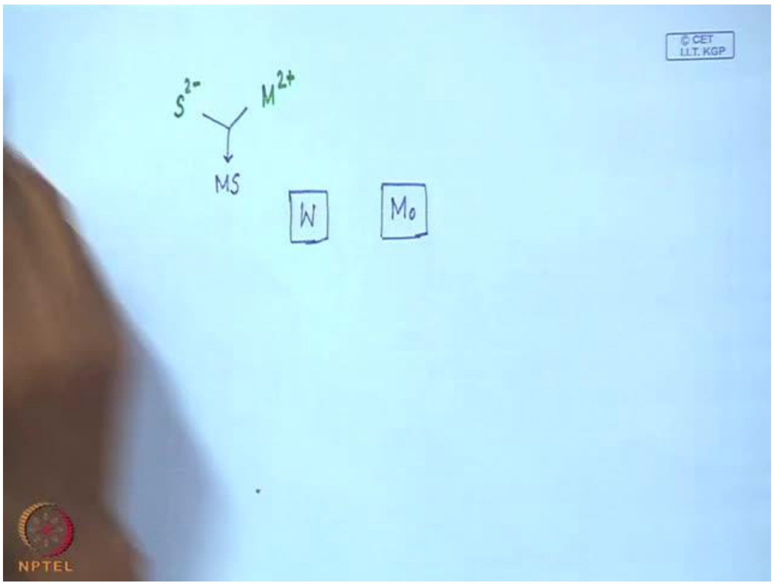

So, whether we have a tungsten site or a molybdenum site? So, we just follow the different spectroscopic techniques to establish, what are the different oxidation states? What are their corresponding coordination environments? And how these metal centers are reacting with all these different groups? So, to know the corresponding nature of these active sites, so electronic structure determination is very important, which can inform us about the physical structure of the metal center of the active site and the corresponding chemistry available on it with respect to electron transfer.

But redox reactivity we can see and how the new groups are coming and attaching to the metal center for ligand substitution or ligand addition reaction. So, for all these reactions based on the molybdenum and tungsten containing enzymes the difference spectroscopic methods are therefore, very much useful to know the corresponding chemistry, which is being catalyzed by these metal centers.

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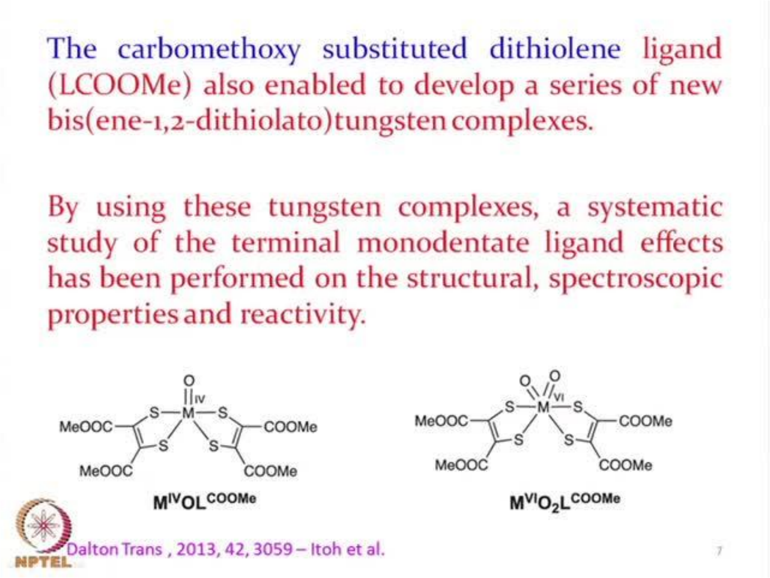

The carbomethoxy substituted dithiolene ligand (LCOOMe) also enabled to develop a series of new bis(ene-1,2-dithiolato)tungsten complexes.

By using these tungsten complexes, a systematic study of the terminal monodentate ligand effects has been performed on the structural, spectroscopic properties and reactivity.

$M^{IV}OL^{COOMe}$ $M^{VI}O_2L^{COOMe}$

Dalton Trans , 2013, 42, 3059 – Itoh et al.

So, this particular one can also be very nicely established in a very recent work, which has been just published, where this dithiolene group of molecules can be changed to that of your corresponding group of molecules like carbomethoxy substations. So, what should be the effect of the COO, any group with respect to the CN group?

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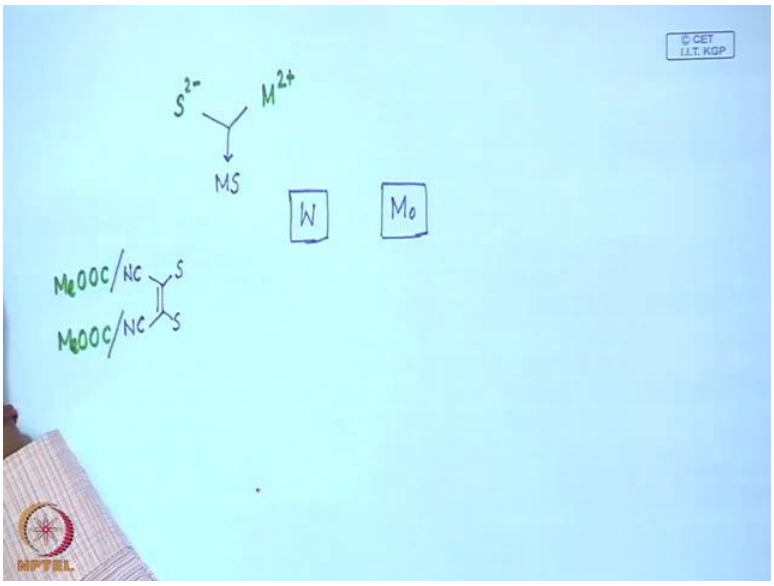

So, what we just change here, this say, one change for the ligand system is that we have the dithiol unit on in back bone, double bone, back bone and maleonitriledithiolate we have checked earlier for the different molecule compounds. So, these can be compared with other substituted version, which is the corresponding ester function instead of the cyanide function, which is COOMe, how these groups are basically reacting to give the corresponding model compounds. So, the carbomethoxy substituted dithiolene ligand, which is abbreviated as L COOMe, COOMe is the substitution for the cyanide function.

These also very nicely give both mono-oxo as well as the di oxo compound and these synthetic compounds can also be studied for their corresponding properties related to their structure the spectroscopic signature. And the different properties and reactivates related to the different tungsten enzymes, because this can also be studied for the corresponding molybdenum enzymes. Systematic study like that of our previous system can also be studied here also for the mono-oxo compound in plus 4 oxidation state. And the di oxo compound in plus 6 state, but only thing why this ligand modifications we are doing that the electronic structure on these ligands are different.

These can donate modular electron to the metal site and E 0 values would therefore, be modified and how the mode electron push from the ligand site, which is not possible to be study the biological counter part of this ligand. The molybdenum pterin or the tungstotrin units which cannot be modified, but for the synthetic molecules we can modify the ligand back bone and we see how the environment for the electronic structure change can give rise to the other type of reactivity pattern on these centers.

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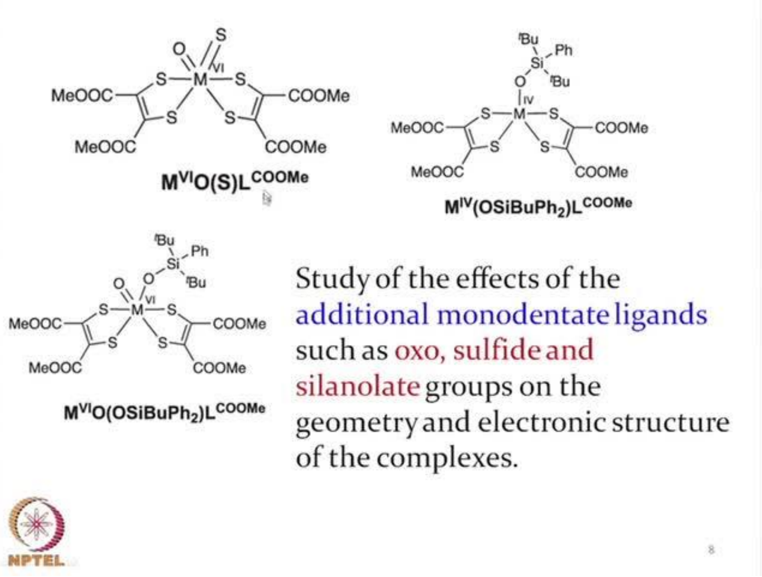

$M^{VI}O(S)L^{COOMe}$

$M^{IV}(OSiBuPh_2)L^{COOMe}$

$M^{VI}O(OSiBuPh_2)L^{COOMe}$

Study of the effects of the additional monodentate ligands such as oxo, sulfide and silanolate groups on the geometry and electronic structure of the complexes.

So, this particular case that means when we get for the corresponding mono-oxo and dioxo compounds. So, this ligand L COOMe can also stabilize this corresponding one, as the corresponding oxo compound, dioxo compound and one is also important is the corresponding hybrid one the oxo sulfide species. Then other silanol also silanol can also go for this oxygen transfer to this center and this oxo silanol species can also be formed over there.

So, addition and electron transfer reactions based on these different mono dented ligand and some is forming double bond and some are forming single bond, can give the exact geometry and electronic structure of these complexes. Because theoretically we can also calculate the corresponding electronics of these complex, how the electronic structure can be useful for different enzymatic reactions that can be studied with these model compounds.

Thank you.