Coordination Chemistry
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Lecture - 3
Classification of Ligands – I

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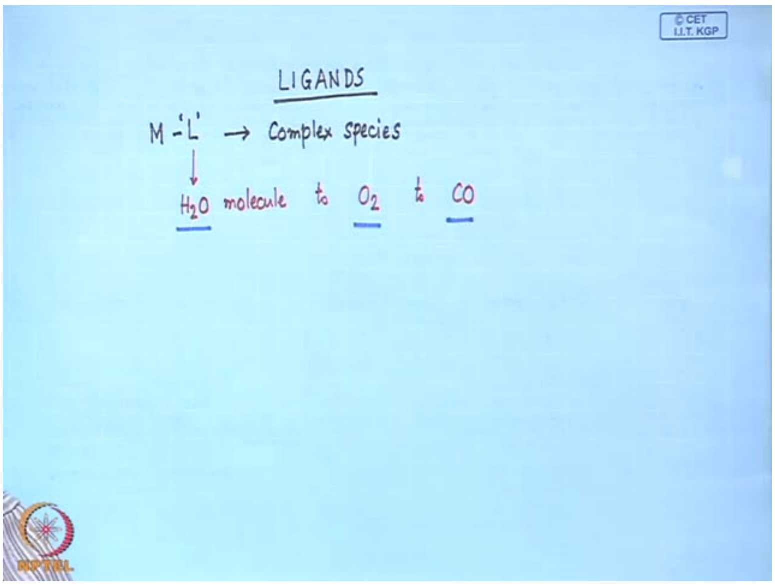

LIGANDS

M -'L' → Complex species

$\downarrow$

H_2O molecule to O_2 to CO

Good evening everybody. So, today we will simply start our discussion on ligands; and in this situation what we have seen so far that if we have metal or anything like metal is present in solution, which can interact with the ligand giving rise to a typical complex species. So, what are these different types of ligands we can have in our hand and which we have seen that it can be the simple water molecule to the gaseous oxygen, to the most toxic gas is carbon monoxide.

So, all these that means if we just simply talk the interaction of the water molecule, the dioxygen molecule or the C O molecule with that of the metal centre and if they interact with the metal centre and can modify the properties of the metal centre as well as their own properties then we can consider that these species are behaving as a ligand when they are surrounding the typical metal species.

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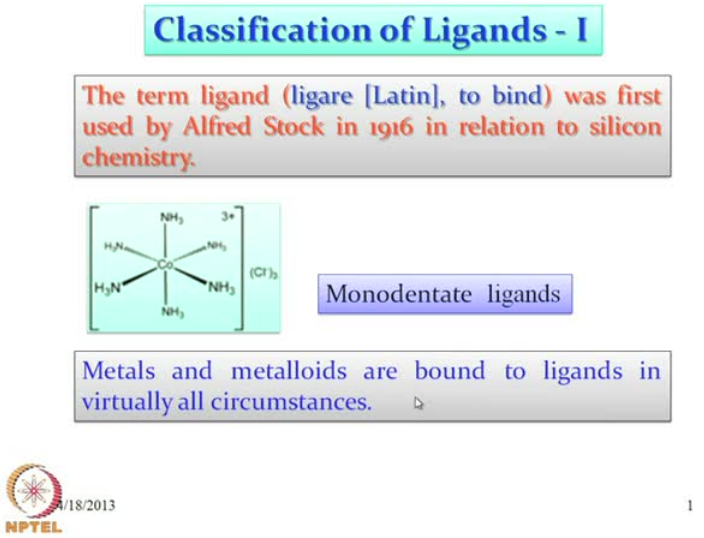

Classification of Ligands - I

The term ligand (ligare [Latin], to bind) was first used by Alfred Stock in 1916 in relation to silicon chemistry.

Monodentate ligands

Metals and metalloids are bound to ligands in virtually all circumstances.

So, in this class we will see about the different classification of the ligands. How we classify most of the ligands depending upon their typical nature of binding to the metal centre. So, historically when people first started talking on these and leveling all these, the term ligand was first introduced in terms of the corresponding binding property of any molecular species or ionic species and it was Alfred Stock who introduced in 1916 in relation to silicon chemistry.

So, silicon is not considered as a typical metal centre, but still we know that that naturally produced different silicates and all other silicon bearing species are there so silicon if we consider is the central element where silicon is interacting with some other species which we can considered as l then these are termed at this time as they are as the typical ligand. So, this we are discussing for the last two classes that if we have the cobalt centre in our hand and initially when cobalt species is present in water we have 6 water molecules surrounding this cobalt and it has a typical geometry that we will discuss shortly that what type of environment we can have.

So, first sphere of attraction what we have seen the first coordination sphere of attraction is made of 6 ammonia molecules surrounding this cobalt centre and if we see from this 3 dimensional figure is a 3 dimensional picture though it is drawn in plane paper, but we see some of the bonds are facing towards the observer and some of the bonds are facing back side of this plane. So, these these two ammonia which is a bold bonds with cobalt nitrogen bold bonds and the ammonia molecules are also bigger in size.

So, they are above the plane of the paper and these two are below the plane and since it is not balancing any charge these ammonia molecules are behaving as a ligand since they are binding the cobalt centre. So, they are basically considered as good ligand and they are only attaching to the cobalt centre from one point that is why they are termed as monodentate ligand and when the full coordination sphere is filled and charge is there 3 plus charge for the cobalt centre which is getting utilized by the presence of 3 chloride anions outside the coordination sphere.

So, what we see that these ligands we can consider as monodentate ligands. So, this is basically one type of classification that what are those monodentate ligands? So, monodentate ligands are those ligands where we have one point of attachment to the metal centre. So, water molecules, these chlorides, these bromides and other halides if they only attaching to the metal centre through one point then they are termed as good monodentate ligands.

So, not only metal, but also metal likes elements like metalloids when they are bound to ligands we see that in virtually all circumstances when metal is in then free form as M N plus or metalloid also there in the free form, they always try to bind the ligands. Even we have seen that when only water molecule is present in the solution in the reaction vessel or in some natural environment in biological systems, these metal centers or metalloid centers will interact with these water molecules.

Also they can interact when the available group is not water molecule, but a dioxygen molecule. So, metal can also interact with the dioxygen molecule and dioxygen molecule can function as a good ligand. Similarly, the toxic carbon monoxide gas which is a gaseous species this can also interact to the metal centre as a monodentate ligand.

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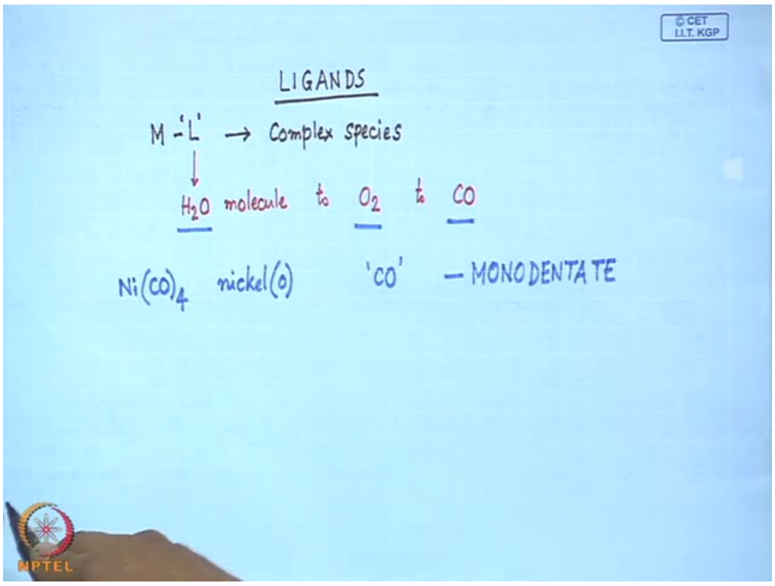

LIGANDS

M -'L' → Complex species

H_2O molecule to O_2 to CO

$Ni(CO)_4$ nickel(0) 'CO' — MONODENTATE

So, what we know that tetra carbonyl nickel species where the nickel is in 0 oxidation state. So, we have nickel in 0 oxidation state and this carbon monoxide gas can also function as a good monodentate ligand. So, starting from water to dioxygen to carbon monoxide all of them can function as a monodentate ligand.

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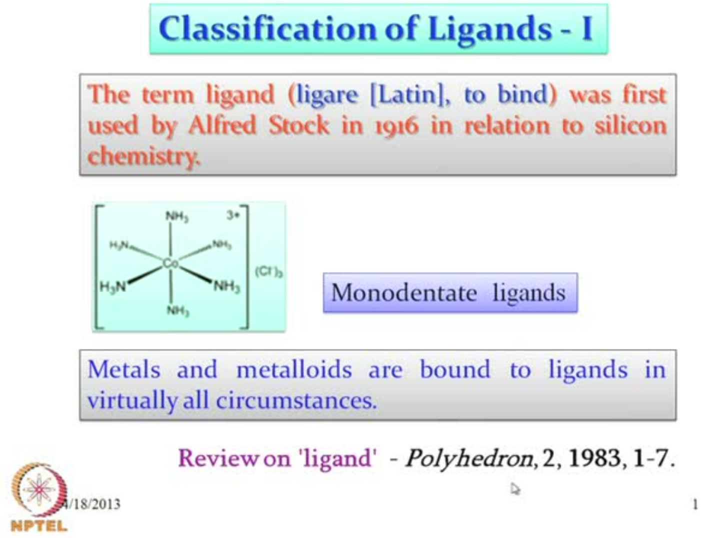

Classification of Ligands - I

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Monodentate ligands

Metals and metalloids are bound to ligands in virtually all circumstances.

Review on 'ligand' - *Polyhedron*, 2, 1983, 1-7.

So, when we see that these are basically also reviewed in this particular reference of polyhedron in of 83 so their all types of ligands have been classified.

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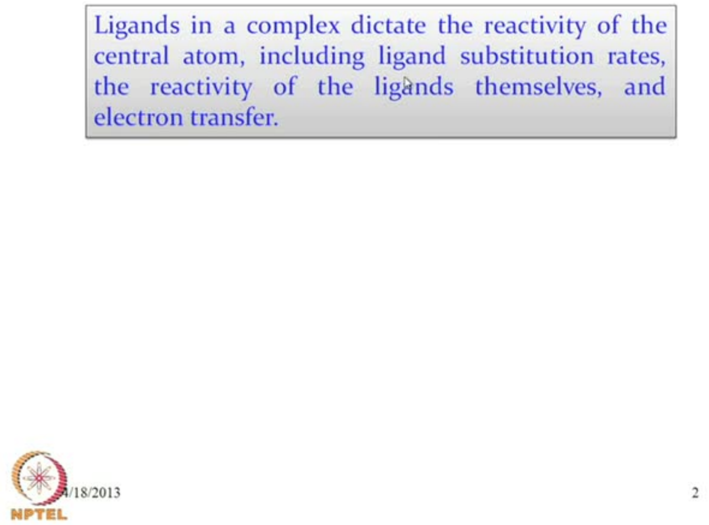

Ligands in a complex dictate the reactivity of the central atom, including ligand substitution rates, the reactivity of the ligands themselves, and electron transfer.

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And we can see that when the ligands are present in the complex what they do, they do basically control the reactivity of the central atom. If the central atom is a metal they will control the reactivity pattern of the central atom. If the reactivity pattern of the corresponding central atom is the metalloid they can also control. So, when one particular ligand centre it can control the reactivity of one metal centre, if it is iron it can control the iron centre in some form, if it is nickel it will control the corresponding reactivity pattern of the nickel centre in a different way. Also it can control the corresponding ligand substitution rates. So, when we consider that one ligand is present with the metal centre it can be substituted by the other ligand.

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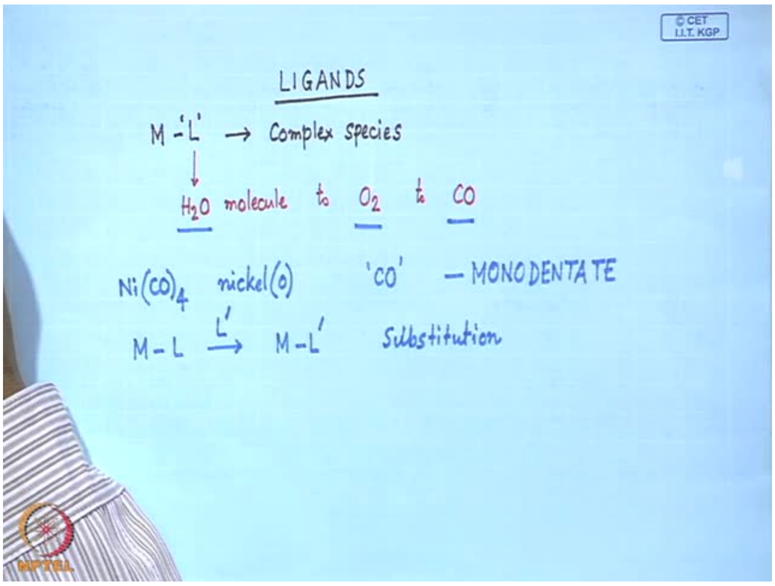

LIGANDS

M-'L' → Complex species

H_2O molecule to O_2 to CO

$Ni(CO)_4$ nickel(0) 'CO' – MONODENTATE

$M-L \xrightarrow{L'} M-L'$ Substitution

So, if we have M L and it can be M L 6 also that means 6 ligands surrounding the metal centre and if this is reacting with M L prime and L is substituted by L prime then we call it as a typical ligand substitution reaction where the ligand L has been substituted by ligand L prime and in both these two cases the nature of the ligand basically what type of ligand we have as L and L prime they will control the corresponding substitution reaction. So, the role of ligand is important for this particular substitution reaction and rate of the substitution reaction is also very important and in some other cases not only the substitution, but also we can talk about the electron transfer which is guided by the nature of the ligand attached to the metal centre.

Then the reactivity of the ligand it is themselves that means when the ligand substitution is taking place we also find that the bound ligand which is present sometime the big molecule, organic molecule is attached to the metal centre and if metal is performing some catalytic role and if we can perform some reaction on this bound ligand we see the reactivity of the ligand that means the reactivity of the organic molecule can also be dependent on the nature of the organic molecule that means the nature of the ligand system as well as the corresponding electron transfer reaction.

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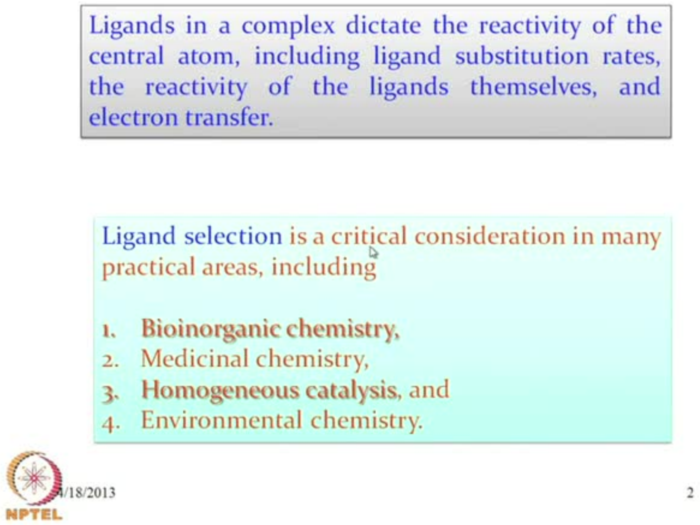

Ligands in a complex dictate the reactivity of the central atom, including ligand substitution rates, the reactivity of the ligands themselves, and electron transfer.

Ligand selection is a critical consideration in many practical areas, including

1. **Bioinorganic chemistry,**
2. Medicinal chemistry,
3. **Homogeneous catalysis**, and
4. Environmental chemistry.

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So, in different areas of this coordination chemistry what type of ligand we are basically selecting is important. It is important or it is critical to consider these when we try to use their choice for practical purposes. So, when we talk in terms of the corresponding bioinorganic chemistry that means the bio-coordination chemistry that means we want to know the corresponding nature of this metal centre what is present in all biologically important molecules.

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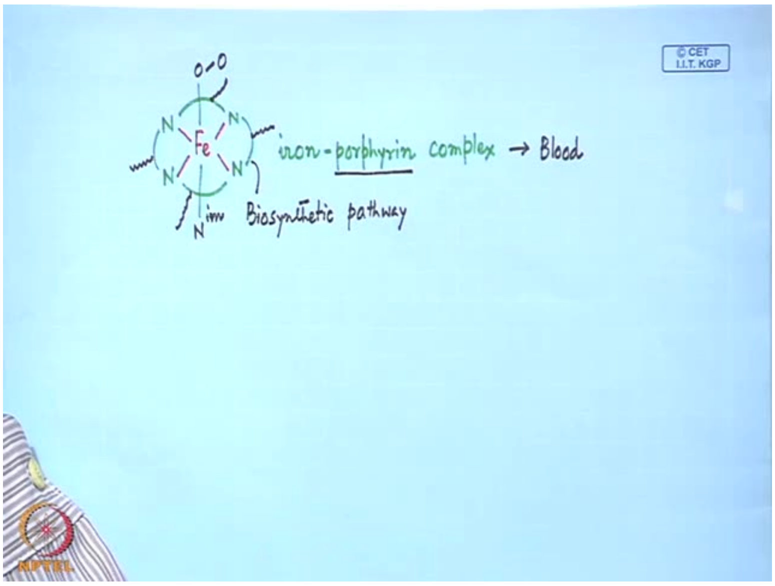

Such that in the area of this bioinorganic chemistry we all know that iron is present in our blood and this iron is bound to a porphyrin ligand which is a different type of ligand will come for the classification of that ligand also. So, when this is there so this the abbreviated form of the porphyrin so we have iron porphyrin complex and it has two other points of attachments also. And this particular one this ligand is synthesized in our body so it has some biosynthetic pathway of the synthesis. So, we get this porphyrin molecule which is attaching to the iron centre.

So, the role of this ligand is very important, role of this porphyrin ligand is important and is also very much specific because the different types of porphyrin molecules are there having different peripheral substitutions from here, from here and from here. And for this iron porphyrin complex which is present in blood as heme is typically synthesized in our body and it has only that particular role of oxygenation. So, it can oxygenate from this particular point and this particular side is bound to nitrogen of the (( )) ring so this particular synthesis of this porphyrin only is important for the formation of blood and it is corresponding reactions with dioxygen molecule.

So, the second is the corresponding molecules which are involved in medicinal chemistry so some good medicines we can have, some drug molecules are important in our hand which basically taking the corresponding important role of the metal centre to different ligand system. One such example is well known to us the basically the cancer drug which is cisplatin which is nothing but a platinum best metal complex. Similarly, in homogeneous catalysis so all different types of an important catalytic reactions we can have and these catalytic reactions are most of the cases are controlled by the metal centre.

So, when catalysis is on the metal centre is bound to several ligand system and those ligands also play some important role for a particular type of reaction which is giving us the corresponding reaction which is catalyzed and lastly the environmental chemistry. So, if metal dependent environmental chemistry is available so metal ions are also play some important role in controlling the environment. Suppose, it can react with the gaseous molecules, it can react with some molecules, some deadly molecules present in water molecules, the methyl radical also forming the methyl mercury compounds and some other type of important compounds.

So, wherever the metalloids present particularly from the industry, the industrially effluents, large amount of cadmium, large amount of zinc and large amount of mercury is people are dumping on the river or the ocean water and some groups like these methyl groups or all other important groups are their which can immediately go and bind to the metal centre and they are ultimately contaminating the aquatic life. Because the aquatic life the fishes and all other species do consume all these deadly and poisonous material and through that food chain the, through that food cycle it also comes to the human being also and human being also by consuming those material the fishes they are also poisoned by these metal ions which are originally forming the metal complex.

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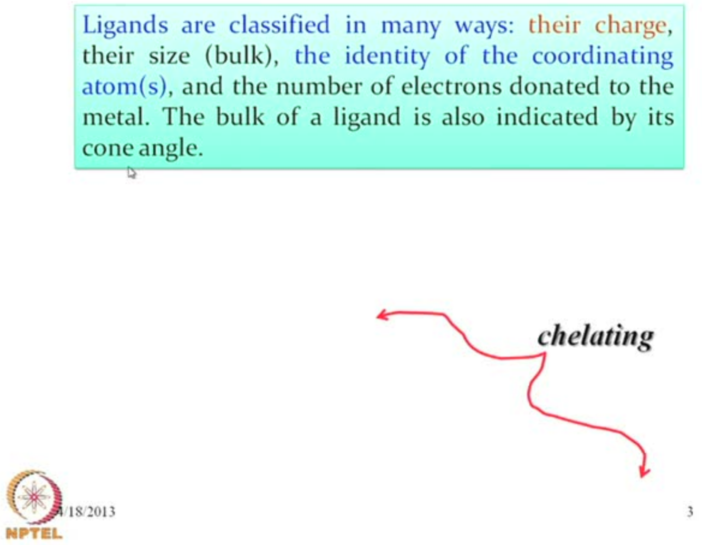

Ligands are classified in many ways: their charge, their size (bulk), the identity of the coordinating atom(s), and the number of electrons donated to the metal. The bulk of a ligand is also indicated by its cone angle.

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So, broadly speaking if we just considered these ligands, so, how they can classify broadly in terms of their not denticity, but also their charge. So, if there is no charge as we have seen just now that if we have only water molecule or only ammonia molecule there is no charge. So, those are considered as the neutral ligand, their size how big they are depending upon the donor atoms such that the donor atom can vary from nitrogen to oxygen to sulphur to phosphorous.

So, depending upon the donor atoms and also if it is chelating one that means it has 2 binding points and the size of the ring is also important. Then the identity of the coordinating atoms, what type of coordinating atom we can have, the number of electrons donated to the metal through this ligands that means how many bonds they are forming with the metal centre whether we are forming a single bond or a double bond or a triple bond to the metal centre. And sometime the steric bulk, this bulk is not related to the size of the atom from oxygen to nitrogen to sulphur, but this bulk is related to the corresponding steric bulk on the ligand and is indicated by its cone angle.

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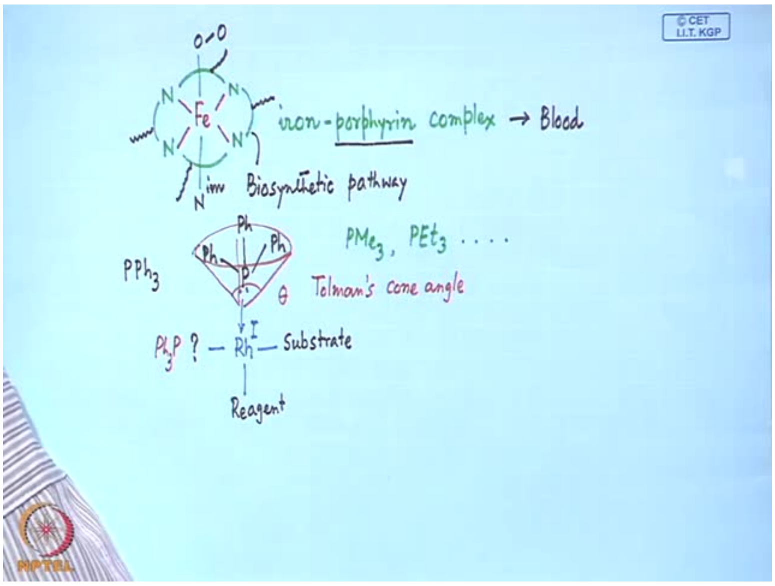

In some catalytic reactions we see one such good ligand is triphenyl phosphine. So, phosphorous is there and we can have like ammonia three phenyl rings attached to this phosphorous. And the phosphorous lone pair which is their, which is being donated to the metal centre say most catalytically important metal ion is the rhodium. So, if the rhodium phosphine bond is formed and in a square planer environment. So, is a four coordinated square planer one and sometime this is in plus 1 oxidation state. So, this particular one that means the reactivity of these sides particularly the transposition of this phosphine side and two other positions, so, we can have the substrate and other position also reagent.

And we can talk in terms of and it has some other groups attached to this rhodium side and these substrate and reagent can react as, but the reactivity pattern will be typically controlled by the corresponding phosphine group because this can also be occupied by another phosphine ligand also. So, this particular cone this 3 dimensional cone is forming and this angle is known as the theta which is Tolman's cone angle.

So, if we vary from one system to the other so only within the phosphine so we can have large amount of substitutions by getting P M e 3 by getting P E t 3 and all. So, we can have different this cone angle, phosphine cone angle. So, this particular one will have some reactivity when we substitute these by tri-methyl phosphine and when tri-methyl phosphine is substituted by tri-ethyl phosphine, we have different cone angle and the reactivity pattern on the rhodium centre will also be different.

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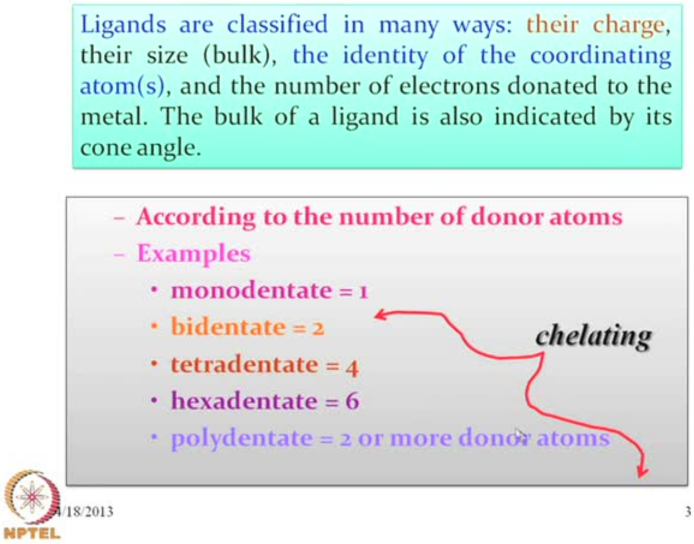

Ligands are classified in many ways: their charge, their size (bulk), the identity of the coordinating atom(s), and the number of electrons donated to the metal. The bulk of a ligand is also indicated by its cone angle.

- According to the number of donor atoms
- Examples
  - monodentate = 1
  - bidentate = 2
  - tetradentate = 4
  - hexadentate = 6
  - polydentate = 2 or more donor atoms

chelating

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So, in terms of the chelation what we see that if we have the number of donor atoms from one point to the other. So, just now what we have seen so the monodentate ligand will be not considered as the corresponding chelating ligand, it is out of this particular list. So, like water, like ammonia, like hydroxide ion, like sulfide ion and all they belong to this particular class, but from bidentate to polydentate system we have more than 1 point of attachment. So, if we have 2 points of attachment we get as a bidentate ligand like ethylene diamine.

We can also a tridentate ligand because most useful tridentate ligands are known. Then we can have the tetradentate ligand as 4 points of attachment, hexadentate ligand as 6 points of attachment and these ligands can also be termed in terms of polydentate when we have 2 or more donor atoms within the one ligand system. So, they basically go for coordination to one particular metal centre from two different points if this is one particular donor atom and this is another donor atom and in between if we have no other donor atom present then we consider this as a bidentate chelating ligand.

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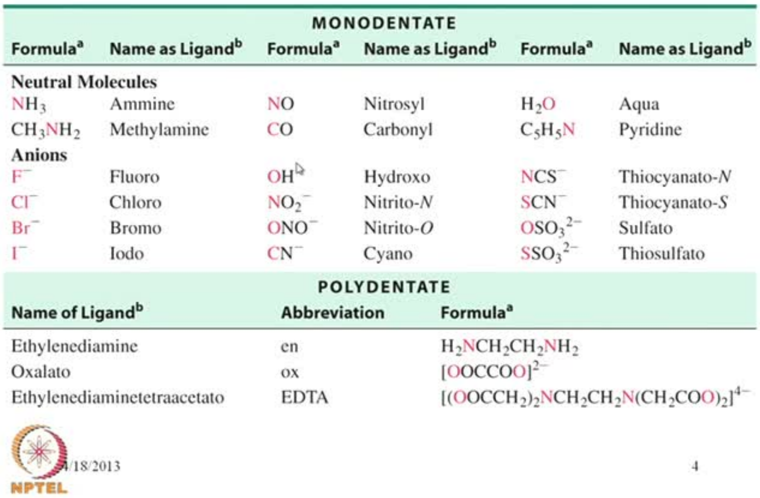

MONODENTATE					
Formula[a]	**Name as Ligand[b]**	**Formula[a]**	**Name as Ligand[b]**	**Formula[a]**	**Name as Ligand[b]**
Neutral Molecules					
NH_3	Ammine	NO	Nitrosyl	H_2O	Aqua
CH_3NH_2	Methylamine	CO	Carbonyl	C_5H_5N	Pyridine
Anions					
F^-	Fluoro	OH^-	Hydroxo	NCS^-	Thiocyanato-*N*
Cl^-	Chloro	NO_2^-	Nitrito-*N*	SCN^-	Thiocyanato-*S*
Br^-	Bromo	ONO^-	Nitrito-*O*	OSO_3^{2-}	Sulfato
I^-	Iodo	CN^-	Cyano	SSO_3^{2-}	Thiosulfato

POLYDENTATE		
Name of Ligand[b]	**Abbreviation**	**Formula[a]**
Ethylenediamine	en	$H_2NCH_2CH_2NH_2$
Oxalato	ox	$[OOCCOO]^{2-}$
Ethylenediaminetetraacetato	EDTA	$[(OOCCH_2)_2NCH_2CH_2N(CH_2COO)_2]^{4-}$

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So, here we have a big list of all these starting from the monodentate one to the polydentate groups. So, if we simply consider one after another which is a very important thing to know because already we have seen the ammine one and these are all monodentate one. So, this ammine giving us the corresponding coordination through this rate bio atom that means the nitrogen, then methyl ammine we can have, where we can have the coordination through nitrogen, then fluoro, chloro, bromo and iodo groups are there. So, we can have all these groups, but the sizes are different from fluoride to iodide, but they only function as monodentate ligand.

Similarly, this nitric oxide gas or the carbon monoxide gas these are the two gases also. So, nitric oxide and carbon monoxide can also function as a good monodentate ligand and from water molecule if we have deprotonation we get the hydroxo group and hydroxido coordination we can have. Then N O 2 minus so sodium nitrite if we supply to the system, sodium nitrite if we supply, this can bind to the metal ion through nitrogen or through oxygen. So, the corresponding complexes will considered as nitrito and a nitrito is two words nitrite oxygen and nitrito nitrogen, then we can have the cyano function, the cyano coordination.

These are the two other neutral groups we can have the pyridine and if we have more than one pyridine groups we get bipyridine antapyridine. Similarly, the pseudo halide like thiocyanate, thiocyanate can bind through nitrogen and through sulphur. So, this is thiocyanate and through nitrogen we call as isothiocyanato or we consider like this type of binding if we just specifically mention that which particular atom is utilised for binding we consider this as thiocyanato nitrogen, the other will be thiocyanateo sulphur.

Then sulfato is also is binding through this oxygen of the sulfato group and when one of these oxygen is substituted by sulphur we know that the corresponding anion is known as thiosulphate and thiosulfato is also a very good monodentate ligand, but the charges are all different. So, starting from neutral monodentate ligand to monodentate ligand. So, to this monodentate by negative ligand we can have where we have 2 negative charges.

So, when the question of polydentate ligand comes to our mind we see that when it is bidentate one we have 2 nitrogen donor atoms from the ethylene back bone and 2 of them are ammine function. So, it is ethylene diamine. So, ethylene diamine can bind through this nitrogen to the metal centre and this nitrogen to the other metal centre. Similarly, oxalato anion is also binding through 2 oxygen's of the oxalate group and this oxalate group is nothing but….

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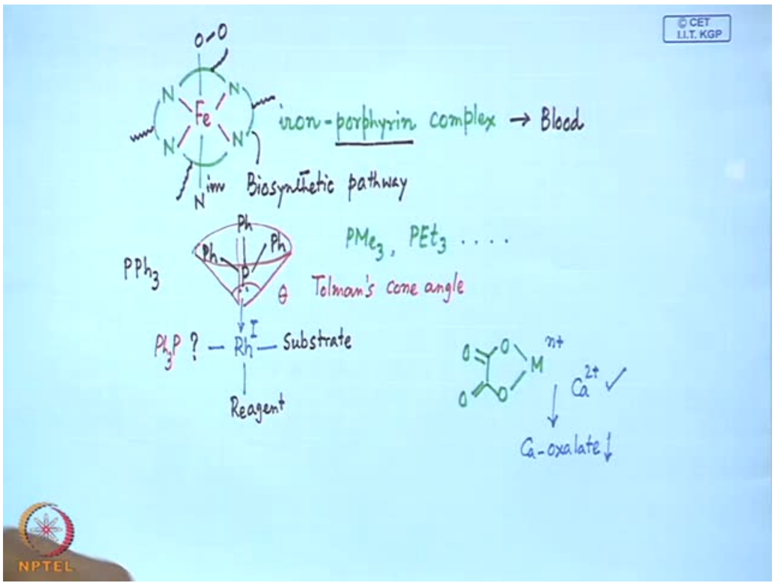

So, 2 negative charges. So, this particular group has 2 negative charges and this is then going and bind to the corresponding metal oxalato complex. The way we determine very easily the calcium, the calcium 2 plus is a very useful species for binding that as the corresponding calcium oxalate which is a very useful dynamitic reagent because if we have in a solution unknown amount of calcium, we add the corresponding sodium salt of oxalate anion or the oxalic acid and at particular pH calcium oxalate is precipitated and we filter it out.

This is the basically the corresponding precipitation and if we can take the corresponding weight we can find out the concentration of this calcium 2 plus. Similarly, one more useful polydentate ligand it is useful for medicine purpose, for the drug purpose also which is ethylenediaminetetraacetato anion. So, if we have this ethylene diamine tetra acetic acid is abbreviated form EDTA. This EDTA is a very useful molecule, it has 2 nitrogen donor points and 4 oxygen donor points and 4 negative charges also. So, it is basically a N 2 O 4 type of hexadentate ligand. So, these hexadentate ligand can also bind to the calcium as well as magnesium also giving a useful M L type of compound where the metal is there and the ligand is there in one is to one stoichiometry.

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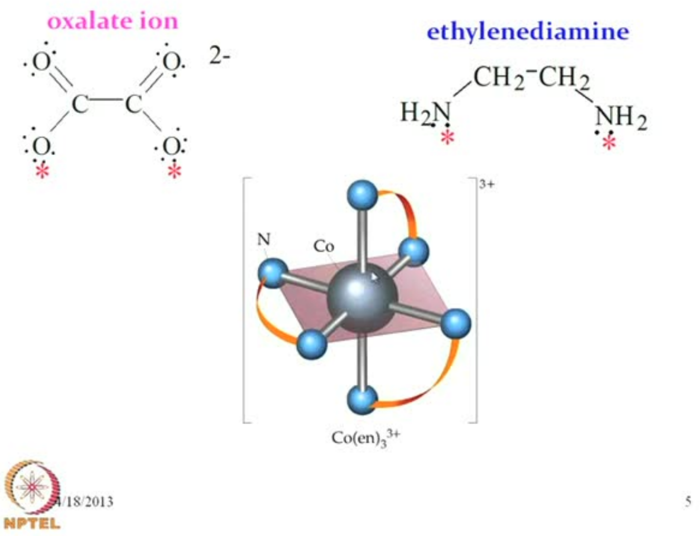

oxalate ion

ethylenediamine

$Co(en)_3^{3+}$

So, this is the corresponding oxalate anion just now we have seen and the ethylene diamine so these two positions. So, this is basically a charged ligand and the back bone is of same type, but it is much more rigid because this carbons are all planer, we do not have any other distortion from that, but this is cannot be planer because this carbon and this two carbons are tetrahedral in nature. So, the ring, the chelate ring what is forming through binding through these two nitrogen and binding through these two oxygen’s on the metal centre they are of different nature and different type.

Oxalate anion can give a very rigid and very useful planer structure, but in case of ethylene diamine it is little bit puckered. And when three such ethylene diamine molecules are attaching to the cobalt centre in a 3 dimensional form, so, this is the only limit of this when we will discuss about the coordination number, the possible coordination number we will discuss once again, how many donor atoms we can assemble around the cobalt centre.

So, when we have three such ethylene diamine groups attached. So, this is one ligand, this is the second ligand and this is the third ligand and we have a typical octahedral geometry where these 2 nitrogen’s like hexamine cobalt 3 chloride, these 2 nitrogen’s are closed to us that means closed to the viewer and these 2 are away from the viewer. So, these 2 are in a typical 3 dimensional (( )) in view and we have different symmetry axis because this is a square plane and if you view along this axis it has a fourfold symmetry.

So, viewing through these symmetry points or the symmetry axis we will find that how the different types of cobalt complexes we can have, but this is a most regular binding pattern of any first transition series or the second transition series of elements like manganese, iron, cobalt, nickel, copper etcetera where if we have a corresponding hexa coordinated complex it basically gives us a geometry which is known as an octahedral geometry. So, this is the octahedral geometry so is basically the polyhedron is the octahedral.

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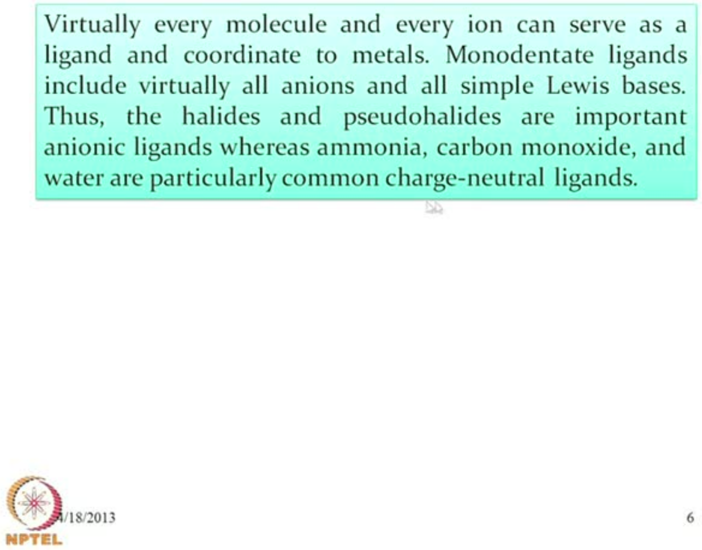

Virtually every molecule and every ion can serve as a ligand and coordinate to metals. Monodentate ligands include virtually all anions and all simple Lewis bases. Thus, the halides and pseudohalides are important anionic ligands whereas ammonia, carbon monoxide, and water are particularly common charge-neutral ligands.

So, next we see that when we consider all these molecules so what we see that most of the molecules what we are talking about, what we are discussing about the either the molecule or the ion if they are surrounding the metal centre they can function as a very good ligand. So, monodentate ligand also include virtually all anions and all simple Lewis bases. So, if very simple Lewis bases are there containing 1 good donor atom, 1 good hetero donor atom they can function as a monodentate ligand. Also the halides and the pseudo halides are very useful anionic ligand whereas ammonia, carbon monoxide and water are particularly well known common neutral monodentate ligands.

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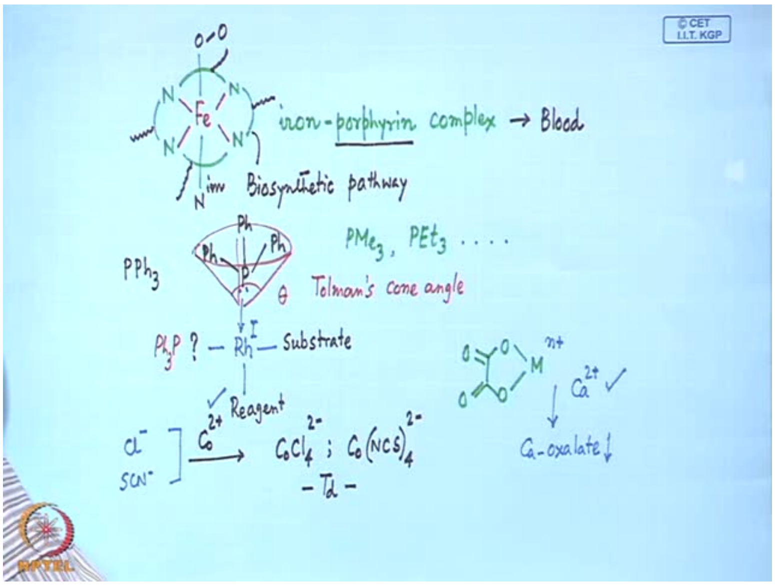

So, when we have the halides and pseudo halides we see that C l minus or S C N minus, if we try to find that whether these halides and pseudo halides, how they are binding to cobalt 2 plus. So, these two will form only the tetrahedral species not octahedral. So, geometry of these species are tetrahedral. So, the typical nature of these ligand that means that chloride and the thiocyanate ligands will tell us that whenever we have the cobalt available in plus 2 oxidation state, this is important, this plus 2 oxidation state not in plus 3. So, they basically give rise to the corresponding tetra 4 this such ligands that means the chloride and the thiocyanate ligands surrounding this particular cobalt centre. So, will end up with only the tetrahedral geometry.

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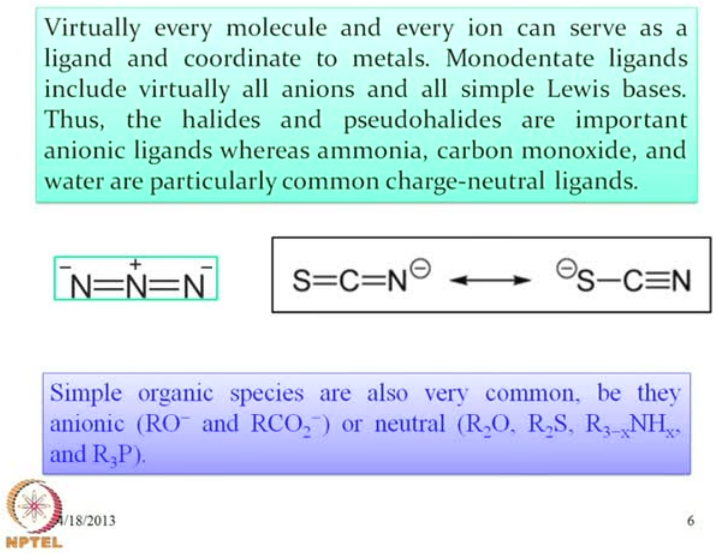

Virtually every molecule and every ion can serve as a ligand and coordinate to metals. Monodentate ligands include virtually all anions and all simple Lewis bases. Thus, the halides and pseudohalides are important anionic ligands whereas ammonia, carbon monoxide, and water are particularly common charge-neutral ligands.

$^{-}N{=}\overset{+}{N}{=}N^{-}$

$S{=}C{=}N^{\ominus} \longleftrightarrow {}^{\ominus}S{-}C{\equiv}N$

Simple organic species are also very common, be they anionic (RO^- and RCO_2^-) or neutral (R_2O, R_2S, $R_{3-x}NH_x$, and R_3P).

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So, another type of group what we can see is related to the thiocyanate is the azide ion. So, azide one is nothing but is N 3 minus ligand and this N 3 minus ligand can, used to have 3 nitrogen atoms and initially immediately what we can think because it has 1 negative charge like hydroxide, like thiocyanate, like chloride, like bromide. So, these also can form immediately to the metal centre 1 metal nitrogen bond. So, initially we will see that this can function as a monodentate ligand to the metal ion.

Similarly, thiocyanate also and this particular case also the if we can have the 2 tautometic geometries like these, we can have the negative charge on nitrogen and negative charge on sulphur and what we have seen just now that this can bind to the metal centre through nitrogen, thiocyanato nitrogen coordination or through thiocyanato sulphur coordination. So, since it has three different donor atoms unlike your azide it has sulphur, it has carbon, it has nitrogen.

Since, carbon is sand which between sulphur and nitrogen so carbon cannot go for any type of coordinating interaction to the metal centre, but sulphur can and the other end that means the nitrogen also can bind to the metal centre. So, these are also very useful ligand what we will see by binding through the sulphur as well as through nitrogen. Other organic species they can also function as very good ligand like when we have alcohol that means R O H function.

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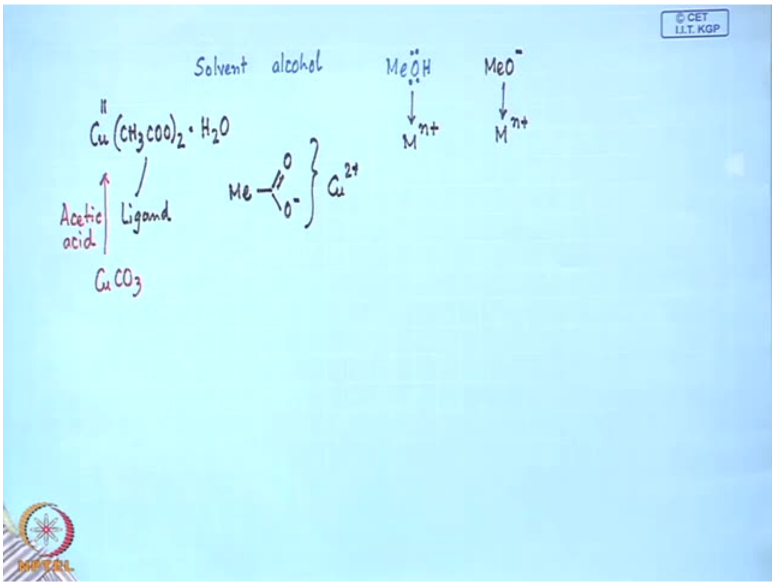

So, any alcohol if we can have particularly when we use as solvent so like water these also has lone pair of electrons. So, when these lone pair of electrons are donated to the metal centre it can function as a very good ligand and like water also it can also go for deprotonation. So, methoxide ion is formed and we can have the corresponding complex of methoxo ion. Similarly, different metals also present as that corresponding metal salts of acetic acid. So, copper acetate containing 2 acetate anion and 1 water of crystallization in bivalent oxidation state. So, this is also our ligand. So, it is also coming in our ligand list and we will discuss in our other classes that how these this is C H 3 C O O O minus how it is binding to the metal centre?

And that also will solve the puzzle related to many other metal acetates because it is very easy to make from the other compounds like the corresponding copper carbonate is a simply add acetic acid and after concentration and crystallization we get the crystals of copper acetate. So, this binding will be very important, but again this can function as a very good ligand to the copper centre, then the other molecules related to water that means R H 2 S that means R 2 O, R 2 S and R N H these are the corresponding ammines groups and the substituted ammines, the primary ammine, the secondary ammine and the tertiary ammine and the different phosphine molecules through phosphorous.

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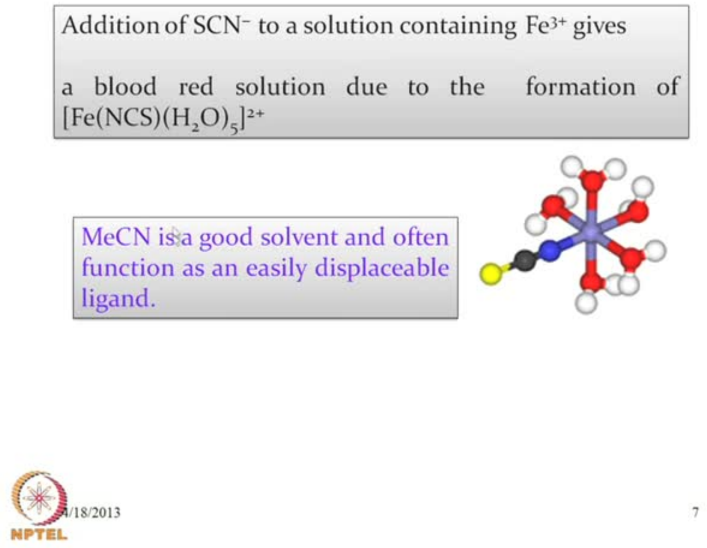

Addition of SCN^- to a solution containing Fe^{3+} gives a blood red solution due to the formation of $[Fe(NCS)(H_2O)_5]^{2+}$

MeCN is a good solvent and often function as an easily displaceable ligand.

So, we see that how this thiocyanate which is a very simple reagent for reacting to any metal centre can also a very good analytical reagent to us. When we add thiocyanate this is colorless also and this is also light yellow in color. So, when we add thiocyanate to the ferric ion because the ferric ion present in water we already know that it is basically the corresponding hexa aqua ferric ion. So, hexa aqua ferric ion will be there and when we add only one is to one stoichiometric amount of thiocyanate to the ferric ion solution, a blood red solution is developed due to the formation of his particular species where one of the bound water molecule around iron has been substituted by thiocyanate anion.

So, what we get? We get a species where 5 of them, 5 of the ligands are already present like that water molecules. Only one is substituted by the corresponding thiocyanate coordination as isothiocyanate coordination or thaicyanito nitrogen coordination through iron nitrogen bond and due to this particular reaction, this particular species giving rise a very good red coloration. So, only one such bond that means the iron nitrogen bond will modify the corresponding electronic transition of the species.

So, if we go on changing the corresponding concentration of these thiocyanates what we can see we can substitute all other present water molecules one after another from this particular iron centre and we can substitute all the water molecules present in this particular complex species by thiocyanate anion. So, if this is the octahedral geometry around this iron. So, when initially we have all these as water molecules and all water molecules are still there except the one where we have 1 water molecule is substituted by this thiocyanate group. So, we have this thiocyanate color change and we get a corresponding color change from light yellow to red blood solution.

So, this will be a very good reaction to know the characteristic reaction to identify the presence of iron in any unknown solution as well as the presence of thiocyanate in any unknown solution as a reagent or as an anion. So, if we want to test the iron solution will add thiocyanate anion or if we want to test the thiocyanate in the medium we should add a solution of ferric chloride. Similarly, the like thiocyanate which is a 3 atom species having a charge is going to bind to the iron centre the solvent like water, this is C H 3 C N that means it is acetonitrile solvent.

It is a very good solvent because it is a organic solvent unlike your water as a solvent or methanol as the solvent and within this particular medium we can dissolve so many metal salts and so many ligands because some ligands are there which are insolvable in water, which are in solvable in alcohol also. So, this M e C N can function as a very useful solvent and when they are binding to the metal centre it can function as a very good ligand.

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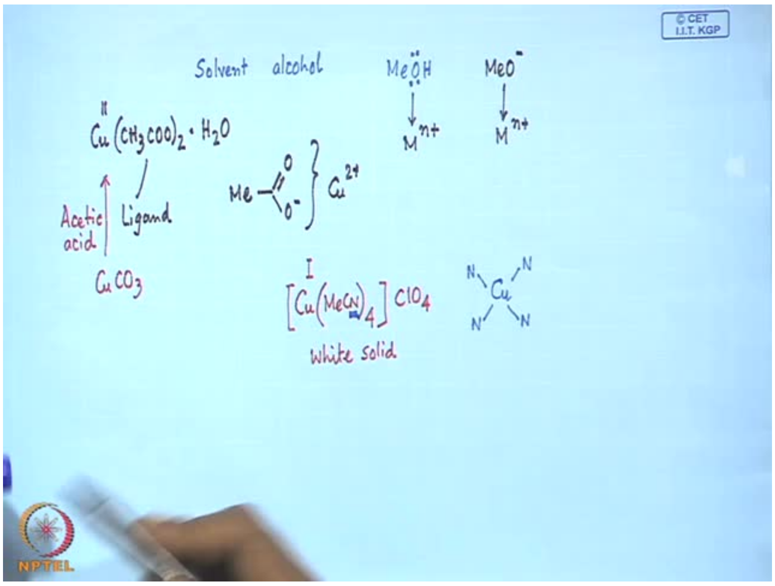

So, one such species what we can make in the solid state by replacing all other donor atoms around iron by M e C N and 4 such M e C N will be there for a Cu plus centre. Copper is present in plus 1 oxidation state. So, it is a white compound in the solid state and if we want to prepare it as perchlorate, it is a corresponding perchlorate salt and this is a very useful reaction to say different types of reactivity pattern related to Cu plus copper because it can activate dioxygen, it can also activate some other molecules, organic molecules where this copper is present, this copper is bound to the 4 nitrogen atoms of the acetonitrile.

So, acetonitrile nitrogen this nitrogen is also a donor atom. It also can function as a donor atom to the metal centre. So, like water, like alcohol it can function as a very good ligand to the metal centre and also one more important function to this acetonitrile is that we can displace it by some other incoming ligand. So, when we will study the ligand displacement reaction or ligand substitution reaction acetonitrile should be a very good ligand surrounding the metal centre. So, acetonitrile will be displaced as some other new ligand system can come and bind to the metal ion.

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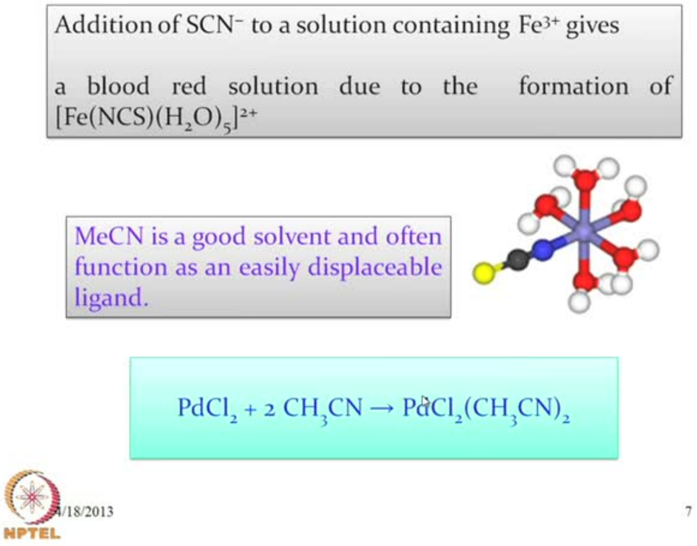

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MeCN is a good solvent and often function as an easily displaceable ligand.

$PdCl_2 + 2\ CH_3CN \rightarrow PdCl_2(CH_3CN)_2$

And in case of palladium it is very easy to make this when we have the palladium chloride is not a very simple monomeric species, but it can be breezed by chloride. So, it is a polymeric compound, but when we dissolve it in acetonitrile in some hot condition we get the corresponding species of palladium chloride with 2 bound acetonitrile. So, it is also a 4 coordinated palladium complex where 2 palladium chlorine bonds are present and 2 palladium nitrogen bonds are there which are due to the coordination of the acetonitrile molecules to the palladium centre.

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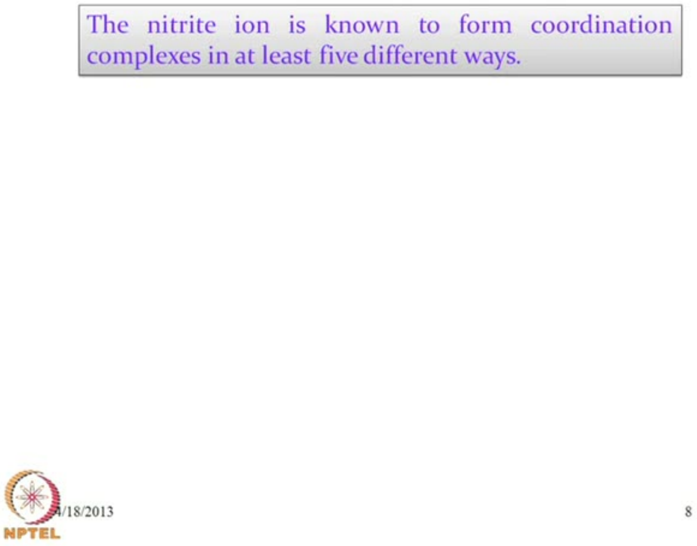

The nitrite ion is known to form coordination complexes in at least five different ways.

So, we will see next the nitrate ion. How the nitrate ion can function as a ligand?

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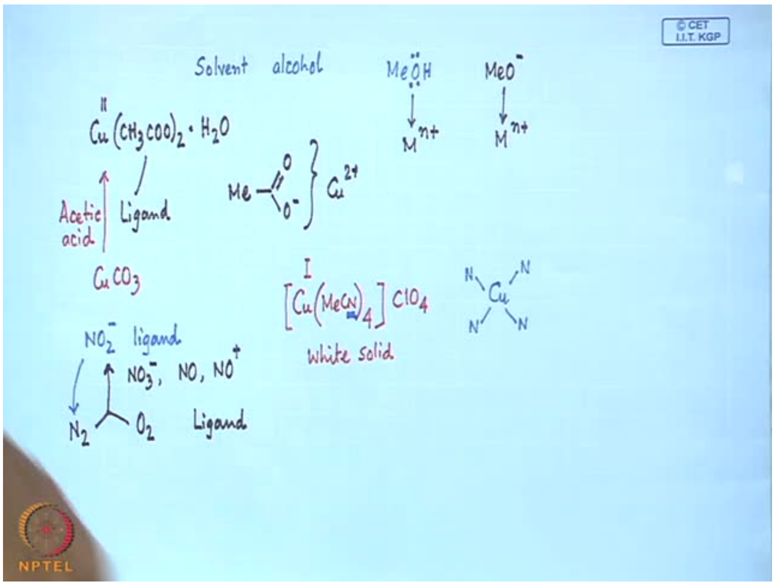

So, N O 2 minus can be also a very good ligand to us. And while talking about the nitrate binding we can also think of related to something which is nitrogen bearing compound like the gaseous dinitrogen as well as the gaseous dioxygen. These two molecules can function as a very good ligand and the reaction products of these two that means N O 2 minus N O 3 minus N O or N O plus all these can function as a very good ligand and starting from the effect of nitrogenous where we can fix these ammonia molecule to, ammonia molecules we get from the dinitrogen molecule to its oxidation to different nitrogen base species, nitrogen oxide base species will see that these are basically going and bind to the metal centre as good ligand.

So, during that conversion, conversion of ammonia molecules to nitride, nitrate, N O, N O plus if there is an intervention of the metal centre. So, in metal centre will bind to all these species and basically go for their activation for their immediate conversion. So, if we just consider the binding of the simple nitrite in the form of the nitrogen binding and oxygen binding, we know there are two types of that binding one through nitrogen and another through the oxygen, but at least five different possibilities we can have.

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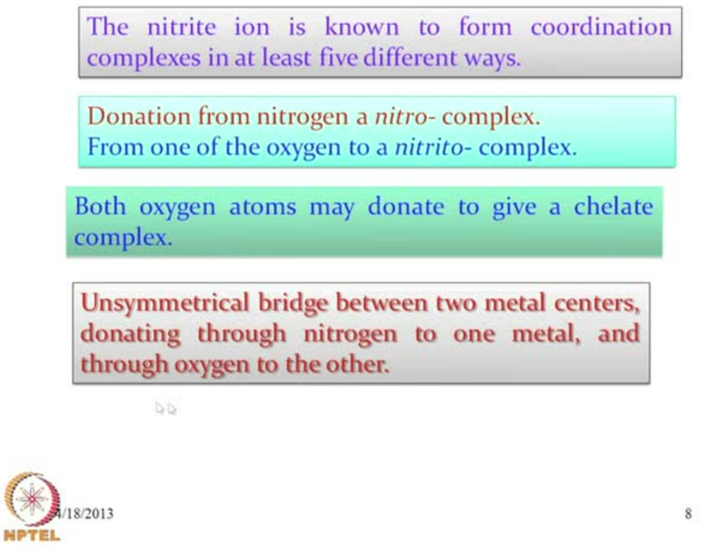

The nitrite ion is known to form coordination complexes in at least five different ways.

Donation from nitrogen a *nitro*- complex.
From one of the oxygen to a *nitrito*- complex.

Both oxygen atoms may donate to give a chelate complex.

Unsymmetrical bridge between two metal centers, donating through nitrogen to one metal, and through oxygen to the other.

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So, donation from nitrogen gives the nitro complex and donation from the oxygen gives the nitrito complex. So, two different complexes we can have and like thiocyanate where we have seen that thiocyanate can bind through sulphur and through nitrogen, here also it can bind through nitrogen and oxygen. So, the corresponding compound even in the solid state the color of the compounds will be different and this show that they can function as some ambidentate nature of the ligand. So, ambidentate binding that means two different donor atoms are present and two of them are utilized, one in one case and another in the other case for binding to the metal centre.

When both the oxygen atoms can donate to the metal centre it can find its position as a chelate complex though it is not so easy and more examples are not there, but in some cases basically these can function as a chelating ligand by binding through both the oxygen atoms because for nitrate it is well known but for nitrite it is not so easy to get, but it can show the corresponding binding in chelating form. Then we can have unsymmetrical bridge between two metal centre donating through the nitrogen to one metal and through oxygen to the other.

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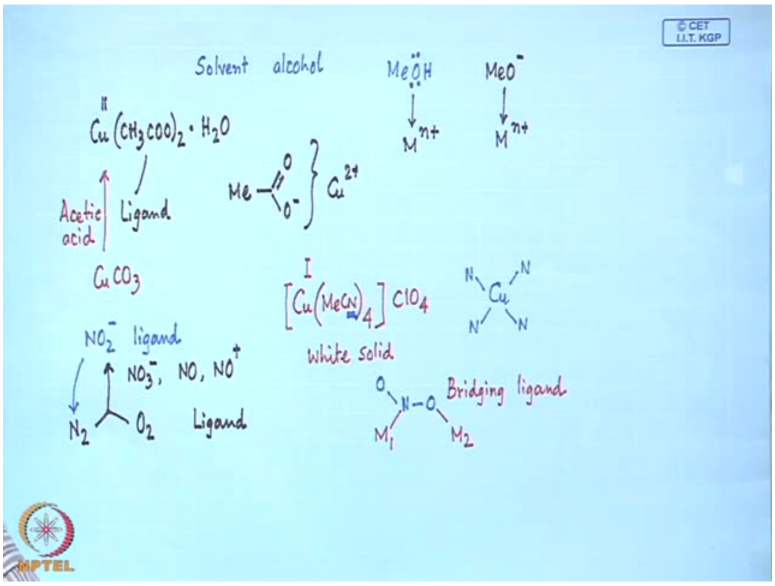

That means if we have this nitrogen and oxygen and this is another oxygen. So, it can bridge between two metal centers. So, it can function as a bridging ligand also to metal 1 and to metal 2. So, this is functioning as a bridging ligand. So, the bridge is possible.

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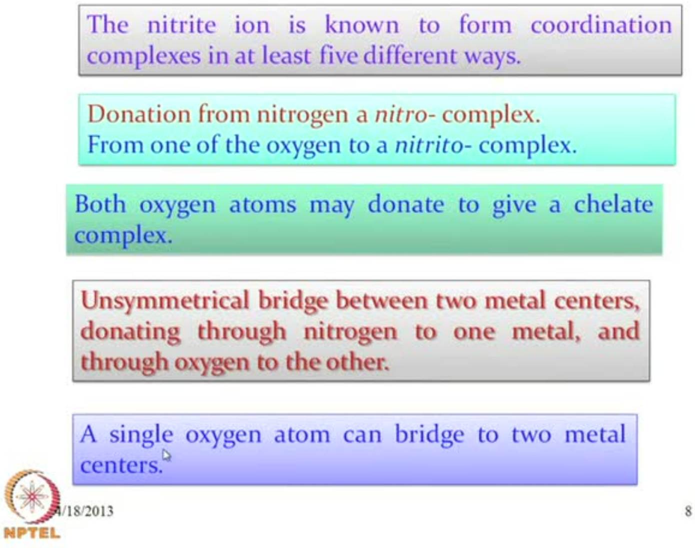

The nitrite ion is known to form coordination complexes in at least five different ways.

Donation from nitrogen a *nitro-* complex.
From one of the oxygen to a *nitrito-* complex.

Both oxygen atoms may donate to give a chelate complex.

Unsymmetrical bridge between two metal centers, donating through nitrogen to one metal, and through oxygen to the other.

A single oxygen atom can bridge to two metal centers.

And sometime a single oxygen atom also can bridge two metal centers.

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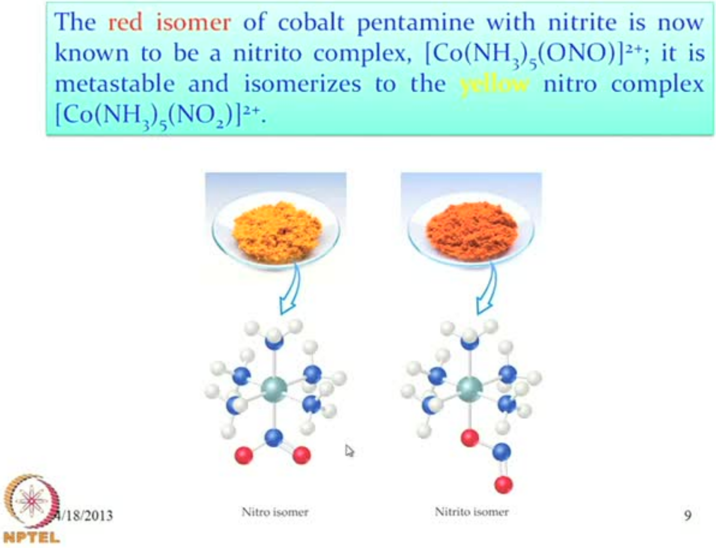

The red isomer of cobalt pentamine with nitrite is now known to be a nitrito complex, $[Co(NH_3)_5(ONO)]^{2+}$; it is metastable and isomerizes to the yellow nitro complex $[Co(NH_3)_5(NO_2)]^{2+}$.

So, we can have for the substitution of the corresponding ammonia molecule from the cobalt centre, we get the corresponding molecule as the corresponding nitrito complex and the other one is also the nitrato complex. So, this nitrito complex when it is bound through oxygen, so, when it is bound through oxygen it is metal stable and it can isomerise to the yellow version of the nitro complex or nitrito complex where this particular species that means this nitrogen is bound to the cobalt centre through this nitrogen. So, these two compounds, the color of these two compound, one is the corresponding isomeric form as the red isomer and another is the corresponding yellow isomer.

So, this red isomer and yellow isomer are present due to the corresponding presence of the corresponding cobalt oxygen bond on the nitrate and on the cobalt nitrogen bond on the nitrite. So, this is a similar situation where we see that the water molecules from the iron centre is substituted by the thiocyanate and it gives some beautiful coloration due to that substitution. So, we can have the corresponding two isomers, one is binding through the corresponding nitrogen another is binding through the corresponding oxygen.

So, this particular one that means the red compound and this is the yellow compound, the red isomer where we have the oxygen of this nitrate group oxygen of this nitrate group is bound and this oxygen of this nitrate group is bound to the cobalt centre and here nitrogen of the nitrate group is bound to the cobalt centre. So, the color is drastically changing from one to other. So, these are the two isomeric form and due to the assimilation of nitrate groups as the different nitrogen oxides these as one of the pathways which is known to us that the metal centre can bind in one form to the other and one is stable to the other. So, that means if we try to activate one particular form to the other it can go from the nitrogen coordination to the oxygen coordination or vice versa.

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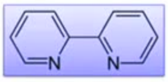

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So, there are some few examples related to the classification of this ligand system.

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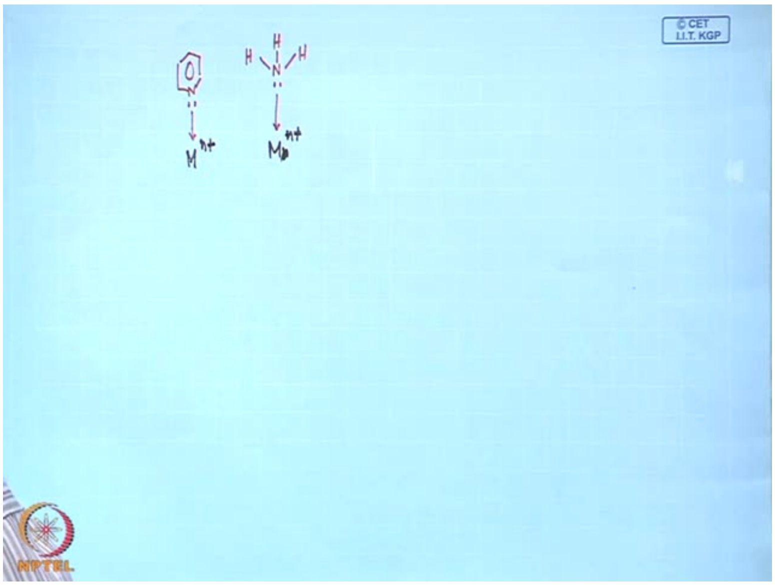

We have seen that the pyridine system that means the pyridine like ammonia it has donor atoms over there. So, pyridine can bind to the metal centre through the donation of its lone pair of electron, this is M n plus this is M n plus. So, the binding of this metal to this this is in the monodentate fashion. So, both pyridine and both ammonia can bind to the metal centre in monodentate fashion for the formation of the corresponding complex.

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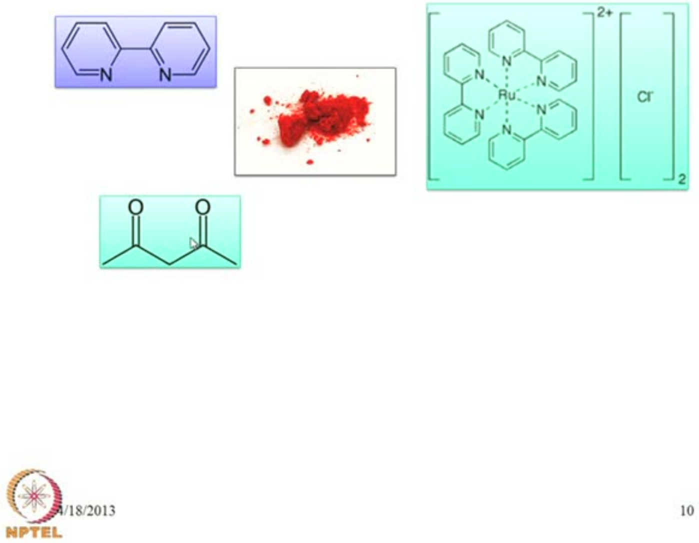

But if we go for the bipyridine ligand using two pyridine units which are in the cis position so this is a very good bidentate ligand like ethylene diamine. And like ethylene diamine it has some rigid back bone, the pyridine type of back bone and when it is binding to the cobalt sorry ruthenium, when it is binding to the ruthenium it can go for the corresponding tris complex that means the 3 bipyridine units are attached to ruthenium, ruthenium in plus twos and 2 chloride ions are outside the coordination sphere. It has very interesting properties, it has also very useful electron transfer behavior also and it has some other catalytic behavior and some practical applications.

So, the ligand modification is important to get some important properties out of the ruthenium which is not available if we just simply use ruthenium chloride. So, some of the reaction, some of the organic transformations we find that metal salt is added along with some ligand, sometime the bi-pyridine is added that means the reactive species, the active species what is forming over there is the corresponding tris bipyridine ruthenium compound and which is beautifully red in color, red powdered solid can be identified very easily by use of this particular ligand. Similarly, one such example of the bidentate O O donor ligand, this is N N donor bidentate ligand, but it is little bit more flexible, O O donor bidentate ligand which is acetyl acetone.

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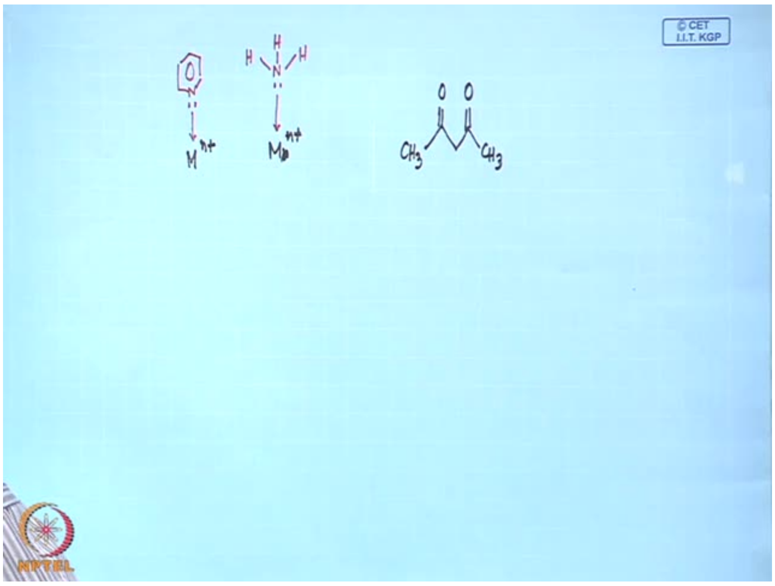

So, acetyl acetone is nothing but is pentane to 4 dion, so, is a dichitom system where 2 oxygen atoms are available for binding to the metal centre. When it binds to the metals centre it forms the corresponding compound like this, like bipyridine it can bind to 2 such positions and it is binding through oxygen, carbon atoms are not utilized for any kind of interaction.

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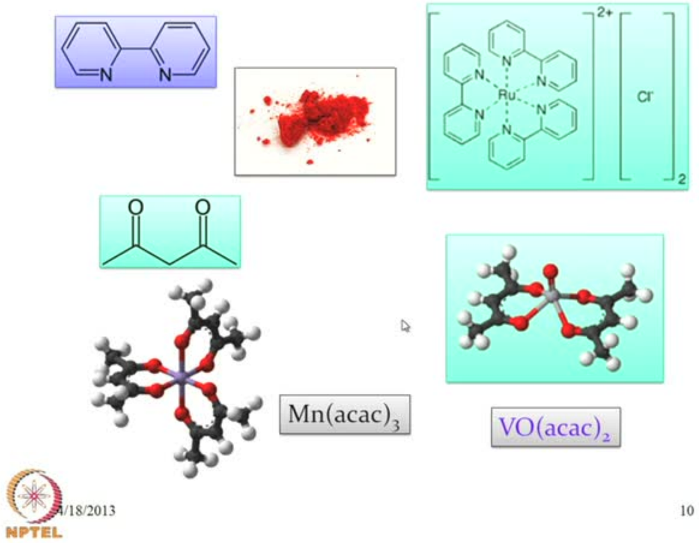

Mn(acac)$_3$

VO(acac)$_2$

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So, these two oxygens when they are bind to this particular metal centre in octahedral form in the manganese acetyl acetone compound. So, usually it is stabilizing the trivalent manganese because after deprotonation it gives us through the keto inert tautomerism 1 negative charge. So, ligand is bidentate mono negative ligand and it is stabilizing manganese in plus 3 oxidation state. Similarly, it can stabilize vanadium center with the vanadium oxo center that means the vanadium center by binding in a different geometry, these geometry is different from that which is a square pyramidal geometry which is V O a c a c whole 2.

So, this is the acetyl acetone ligand which is present with manganese as the tris manganese compound in the octahedral geometry and in vanadium system it is in the V O a c a c system in a square pyramidal geometry. So, we will see more of these type of examples in some of this classification of these ligands and what are the more more and more complex ligand systems we can have, ultimately we reach to the biological system where biological ligands are much more complex to bind to the metal centre.

Thank you.