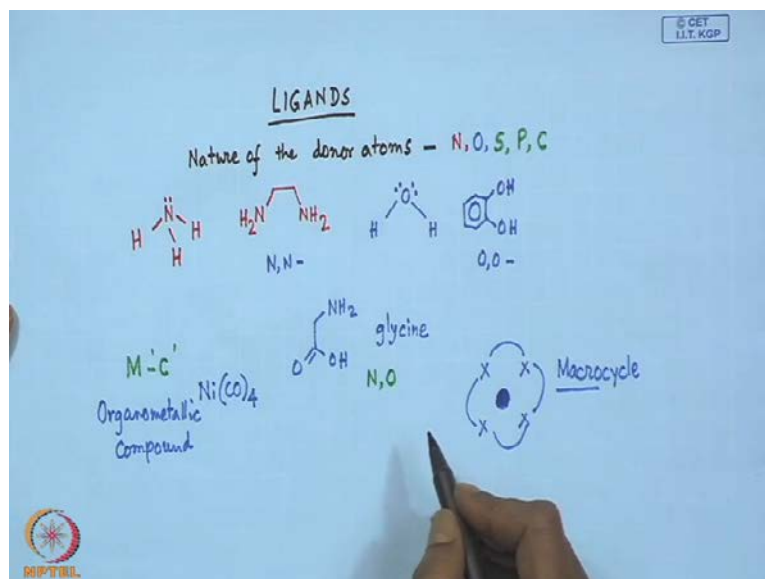


**Coordination Chemistry**  
**Prof. Debashis Ray**  
**Department of Chemistry**  
**Indian Institute of Technology, Kharagpur**

**Lecture - 4**  
**Classification of Ligands-II**

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Good evening everybody. Today, we will just continue the classification of the ligands in the first part we have seen that how we can classify the different ligands in terms of their denticity that means the number of donor atoms.

Now we will see that these ligands can be further classified in terms of the nature of the donor atoms which is very important. So, we can have this nitrogen based donor atoms that means what we have seen in the most simple one which comes to our mind is the simple ammonia molecule and which is also a monodentate ligand.

Then we can have the bidentate ligand based on the same nitrogen which is ethylene diamine. So, one is that that nitrogen based ligands then we can have the oxygen based one. So, oxygen based ligand the simplest possible as monodentate we have seen is the water one then we can have different types of other bidentate ligands like that of catechol and others. So, these are the simple possible bidentate ligands where we can have the nitrogen nitrogen donor atoms or oxygen oxygen donor atoms and at the same time we can also have the combination of these 2. So, the combination of these 2 we can get for

the simple amino acid say glycine. This glycine when binds to a particular metal centre is not a symmetric one and also it is a mixed donor type nitrogen and oxygen donor type.

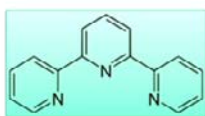
Then we can have the sulphur donor then we can have the phosphorus donor and also the carbon donor. That means when we have the carbon donor ligand present we consider that we can have the corresponding metal carbon bond. So, carbon donor ligand can give us a system where we can have the metal carbon bond and this metal carbon bond from that of our simple compound tetracarbonylnickel0 is a very important class of compound which are also known as the organometallic compound.

So, all these ligands when they are present in a typical backbone and also we see that in some cases if x is the typical donor point and we can encircle the all the 4 donor atoms like this and we can put the metal centre at the centre and we get a bigger cyclic ligand and this particular cyclic ligand. We can consider it as a macrocycle is a bigger cycle so this isthemacro one. So, macrocyclic one so it has also important role to play and is biology also it is very well known.

So, we can have this again that means it can have nitrogen it can have oxygen it can have sulphur or it can have the phosphorus donor atom and which binds to the metal centre. So, depending upon the nature of the donor atoms and the corresponding skeleton the structure of the ligand system we can have the different types of metal complex.

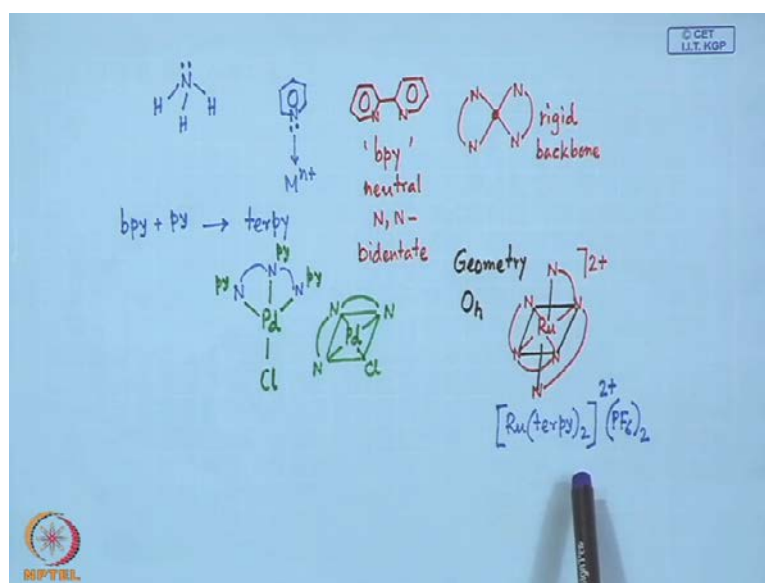
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## Classification of Ligands - II



So, in this class of the classification of the ligands second part we will see the first example which is nothing but, 3 pyridine rings attached together from the ortho position of one pyridine ring to the other ortho position and again another ortho position of the nitrogen to the third ring. So, this we can see we can consider this sort of ligand what we have earlier seen which is has similarity with the Ammonia so ammonia lone pair was utilised for the bonding to the metal centre.

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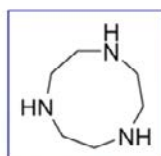
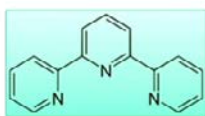
Then we see that the pyridine lone pair also can be donated to the metal centre and if 2 of the pyridine donor atoms are present side by side we get the bipyridine ligand which is abbreviated as b p y so b p y is also a neutral one neutral n n donor bidentate ligand and when it binds to any metal centre we can have like ethylene diamine if it is a bis compound we get a bis compound of this type. But, it is compared to the ethylene diamine compound it has more a rigid backbone. So, the property the catalytic activity and all other things would be different compared to the corresponding ethylene diamine molecule similarly, if we can go for the third one that means b p y backbone plus another p y we get the corresponding ligand which is known as terpyridine. So, this is our terpyridal ligand. Where we see we can have 3 nitrogen donor atoms and which are close to each other. So, if we put metal centre over here so we get one particular side with the attachment of 3 nitrogen donor atoms. So if this terpyridine we can consider as n n n so it is n n n 3type of tridentate ligand and all these.

Nitrogen donor atoms are pyridine based so if we have the metal ion like palladium 2 plus. So, palladium 2 plus will bind with this 3 nitrogen atoms and if we start to make this compound from palladium chloride. So, 1 p d c l bond would be there and roughly speaking the corresponding geometry of the compound would be square planar with 3 palladium nitrogen and one palladium c l bond so we basically enclose the 3 donor points from one side for a square planar compound. And if it is a typical octahedral compound so if the geometry is different is octahedral in nature then we can have the 6 positions for coordination and this 3 coordinations now can be occupied since it is a very rigid one so only 1 type of binding is possible and 1 most important compound is the ruthenium 2 which can be very easily make with 6 ruthenium nitrogen bonds and we can write down this compound when this nitrogens are (( )) as ruthenium (( )) bis (( )) compound and if the ruthenium centre is in the plus 2.

Oxidation state it is the plus 2 and the corresponding salts can be p f 6 can be perchlorate or anything else. So, the sort of ligand is also very important because the photo physical and other properties for this ruthenium (( )) compounds are very rich they can go for electron transfer behaviour it can be oxidised from bivalent to the trivalent state and sometimes in the excited states their electron transfer properties are different.

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## Classification of Ligands - II



$[\kappa^3\text{-TACN}]\text{CuCl}_2$  is a catalyst for hydrolytic cleavage of phosphodiester bonds in DNA.

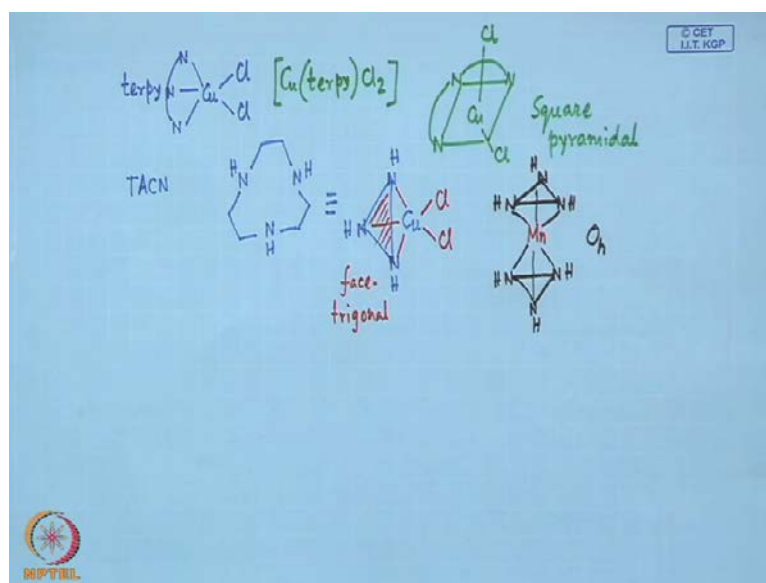
So, this is 1 type of such ligands the tridentate 1 based on only pyridine donor atoms and related to this. Just now we have seen that if we can have a bigger cyclic ligand we call it

as a macro cyclic ligand. But, if the cycle is not so big it is little bit small and if we can have only 3 nitrogen donor atoms and those are of secondary donor atoms that means functions are NH. So, these nitrogen lone pairs from this nitrogen to this nitrogen to this nitrogen are all available to bind to the metal centre. So, binding of this tridentate N 3 type of ligand would be completely different from this binding because this is.

Basically when binding to the palladium or platinum centre it is going from one particular side and only 3 of those sides are bound by these 3 nitrogen but, compared to this the molecule which is known as triazascyclononane so triazascyclononane or abbreviated as t a c n. This tack end ligand will bind in a different mode to the metal centre but, it can also satisfy the 3 donor points so binding to any metal centre can provide us 3 metal nitrogen bonds the first bond with this nitrogen the second bond with this nitrogen and the third bond with this nitrogen so if we can make.

The (( )) 3 tack end compound of copper chloride which is well known as a catalyst for hydrolytic cleavage of phosphodiester bonds of d Na. It has some biochemical reactivity for the esters activity so esters activity can only be shown for this sort of ligand where the binding of this compared to any other tridentate ligand is completely different what we see in this particular case is that when we have (( )) or terpyridil type of ligand.

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We can simply say that terpyridines there and which is providing us 3 nitrogen donor atoms and they are forming 3 bonds in one particular plane. And if the charge is satisfied

by 2 chlorides binding it would be the corresponding copper terpyridine 1 2 molecules which are copper terpyridine 1 2. So, the structure of this particular molecule is completely different because what we have seen that in case of palladium or any other.

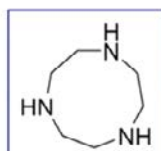
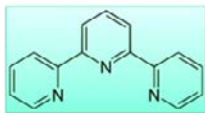
Square planar molecule the nitrogens are binding through these points and if we have copper so this is the C 1 and this is another C 1 so it is square pyramidal in geometry. So, why we need why we are classifying all these ligands in different categories? Because if we go for the tack end ligand we have 3 NH groups which are more or less in one particular plane and which are connected by ethylene backbone.

So, this particular type of ligand cannot go for binding for this square pyramidal geometry instead it can go for one particular face. So, if we have a triangular face of one side of the copper so if (( )) this is copper so this is one NH. This is second NH and this is third NH of the tack end. So, tack end is going to bind the copper centre and we have 3 copper nitrogen bonds and we have 2 such chlorine bonds to copper also, the geometry of this molecule is completely different to that of this one and is a very useful molecule for showing the corresponding phosphor esters activity. So, this particular one means this particular face it is basically a face it is occupying which is trigonal. So, one particular face is the trigonal face of the copper centre and 2 other positions are free. So, all the reactivity pattern for the d n a hydrolysis or any other thing can be achieved from the other side similarly, if a compound like manganese or anything which basically supports the octahedral geometry when it supports the octahedral geometry we can have one tack end from below and another.

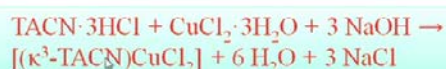
Tack end from above so these are all the nitrogen's n h n h n h n h and n h so these are forming 6 such bonds so is one face one trigonal face is occupied and another trigonal face is also occupied for the coordination of 2 tack end molecules to the manganese centre giving rise to same octahedral geometry but, here now both the sides that means both the trigonal faces are occupied. So, it is basically capped from the top as well as capped from below and in this. Particular geometry its reactivity pattern should be less.

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## Classification of Ligands - II



$[\kappa^3\text{-TACN}]\text{CuCl}_2$  is a catalyst for hydrolytic cleavage of phosphodiester bonds in DNA.



1

So it is showing the esters activity when it is bound to copper centre and we can prepare also its very easily because this cyclisation thing is also we can have this one particular is the ethylene diamine part then another ethylene diamine. So, it is diethylenetriamine part so diethylenetriamine part if it is connected by another ethylene backbone we get the tack end and during the preparation of this we get the corresponding isolation of the tack end.

Compound as its corresponding hydrochloride salt so, is dot 3 HCl is written. So, it is a tack end hydrochloride salt. We can have then simple metal salt like copper chloride is used to react with this and in solution which is alkaline with respect to sodium hydroxide. Sodium hydroxide is given the cuppa 3 tack end copper chloride compound where cuppa 3 gives us the 3 points of attachment like new nomenclature to the tack end to the copper centre then water and NaCl is coming out so we nicelyand. Very simple way we get the corresponding dichloro tack end compound.

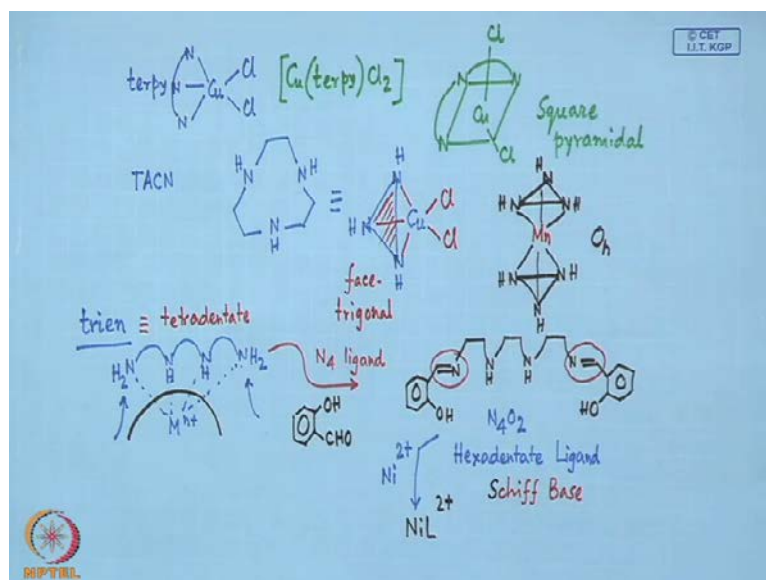
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2

So if we just proceed further where we can have another long linear chain of ligand is that compound.

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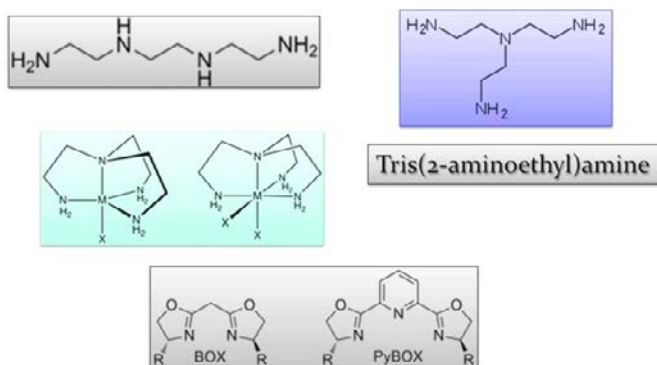
Diethylenetriamine which is known as triene so like that where you have that NH 3 type of ligand. Now, we can have diethylenetriamine, triethylenetetramine sorry the triethylenetetramine molecule using this backbone of diethylenetriamine which one more extension of the ethylene backbone. So, straight away we can see that since we have 4 nitrogen donor atom and all 4 if they are utilised to bind to the metal centre we get a tetra



dentate ligand so very simple way we get the corresponding trion is tetra dentate and this one is n 4 ligand and this n 4 ligand can be further derivatised. Because we have the NH 2.

At the 2 ends of the backbone and these NH 2 ends are very well known for the formation of (( )) bases with say 2 hydroxybenzaldehyde or salysaldihyde. So, not from the ligand itself but, for the trion so trion when reacts with 2 molecules of salysaldihyde. We get the corresponding hexa dented ligand which is very useful ligand. So, in a simple reaction of ion with salysaldihyde we get n 4 o 2 type hexa dentate ligand and this hexa dented ligand can bind very nicely with any 3 d metal ion 4 or d metal ion or 5 d metal ion also say with n i 2 plus giving n i 2 plus as the corresponding perchlorate or acitate salt. As simple n i l2 plus complex where all the 6 positions in octahedral fashion. In this fashion, where the manganese will be substituted by this particular nickel centre. So, octahedral nickel compound can be obtained from a simple condensation product of trion and salysaldihyde and this particular one this ligand has a corresponding amine backbone so at the 2 ends this particular end and this particular end we have the amine backbone.

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Tris(2-aminoethyl)amine

The coordination complexes of bis(oxazoline) ligands are used extensively in asymmetric catalysis.

So this particular ligands are also known as the corresponding sib bases or the sib base ligand so this particular amine that means triethylenetetramine is very useful. One when it is in the pure form or it is condensing with some other aldehydes like salysaldihyde or pyridine 2 aldehyde also when it can be condensed with pyridine 2 aldehyde it can give

us the similar type of sib base ligand. But, the donor atoms all will be nitrogen so it would be a n 6 ligand binding to any octahedral metal ion this is another form of this particular n 4 ligand which is known as tris 2 amino ethyle amine so this is the central nitrogen which is connected by 3 amino ethylebackbone so this you can consider as a derivative of ammonia.

Molecule where ammonia nitrogen is bound to 3 nitrogen atoms but, instead of 3 nitrogen atoms now we can have 2 amino ethyle groups attached to the nitrogen and these nitrogens all can give rise to the corresponding coordination to the metal centre. So, this is a linear tetradentate ligand n 4 type this is not a linear one but, this is a capping one. So, one particular end can be capped with use of this particular train ligand. So, this is abbreviated as train and we can have further (( )) based condensation we can go for the (( )) based condensation at the free NH 3 ends of this once that condensation is taken place with salysaldihyde we can have a hepta dentate ligand because we are further functionalising this nitrogen to No this 2 N o and this nitrogen also to N o. So, 3 such N o donor atoms gives us 6 donor points and this central nitrogen so that would be basically a hepta dentate ligand in our had if we go for the corresponding (( )) based condensation with 3 molecules of Salysaldihyde. So, if we just simply use this particular train ligand the tris 2 amino ethyle amine ligand and when it is binding to any metal centre. So, this is the central nitrogen this nitrogen is bound over here so this is one other amino ethyle backbone. This is the second amino ethyle backbone and other one is the third one so if this particular centre if this metal centre is copper centre and copper chloride is reacting within this fashion such that we can have one copper chlorine bond only and all other 4 positions are occupied by the nitrogen donor atoms of the amine. So, we basically get coordination number of 5 around the metal centre which is copper and charge is neutralised if this is only 1 copper chlorine bond.

So, it is has a different geometry compared to the corresponding tack end copper c l compound and the geometry is also quite different. Since we are occupying this particular nitrogen which is the tertiary nitrogen and this tertiary nitrogen can show some long metal nitrogen bond. So, the overall geometry of this particular system is trigonalbipyramidal so this trigonal plane the baseltrigonal plane is found from 3 NH 2 groups they are a similar the bonding property of these 3 NH 2 groups are of same type.

And these 3 NH<sub>2</sub> groups are directly attaching to the metal centre say copper 2 plus and they remain in a single plane. So, this is our trigonal plane and the part is the trigonal this trigonalbipyramidal part is that one nitrogen from the central nitrogen of the amine this nitrogen and another one can be Cl can be Br or can be F also when we are reacting with copper chloride.

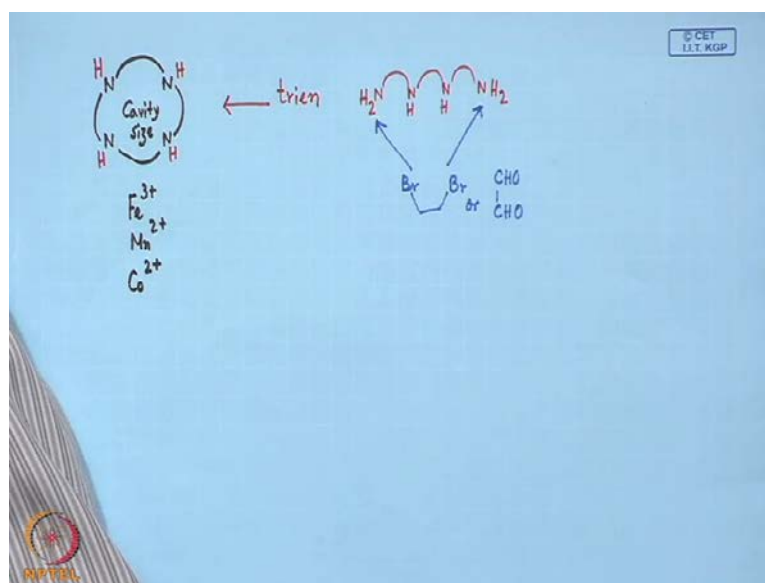
Copper bromide or copper fluoride so we get a t b p geometry. So, very nicely we can have using this sort of ligand so ligand can create a typical geometrical environment around the metal centre which is trigonalbipyramidal and when little bit reorganisation is taking place and if the centre is not copper. But, if it is nickel or if it is iron or cobalt which has a preference for octahedral geometry this particular metal centre can give rise to 6 coordination positions 4 from the ligand and 2 from the halides this can be chloride this can be bromide. So, what happens that this particular geometry as some distortion? Because this particular accommodation of  $\pi$  is required so when this NH<sub>2</sub> MnH<sub>2</sub> bond in this molecule was around 120 degree this bond is around 120 degree which is reduced to around 90 degree for a octahedral geometry. So, squeezing of this NH<sub>2</sub>, MnH<sub>2</sub> bond is required for the movement of the trigonalbipyramidal geometry to an octahedral geometry and which is also possible if we move from one metal centre to other which has a typical preference for octahedral coordination. Then we can have another type of ligand which is very useful in organic synthesis which is box type known as box also which is abbreviated as box which is bisoxazolin type of ligand. So, bisoxazolinis abbreviated so bisoxazolin type of ligand is abbreviated as box because is the oxazolin ring so if we have the methylene spacer here this is the CH<sub>2</sub> group.

So, if we have the CH<sub>2</sub> spacer over here and 2 oxazolin rings oxa and eza in the same ring. So, 2 oxazolin rings are attached on the 2 sides of the methylene ring so which is a tetrahedral carbon, so we can specify the corresponding nitrogen nitrogen geometry. Since this is also a typical bidentate type of ligand but, the geometry pattern is completely different compared to ethylene diamine or bipyridine. So, this gives rise to some n n donor type of bidentate ligand because the free rotation around this Carbon carbon bond or this carbon carbon bond can bring rise to thus oxygen also. But, the preference for this nitrogen coordination which is also dependent on this substitutions are on this 5 membered ring is also required and which is fixing this particular geometry and this ligand has a preference for nitrogen nitrogen coordination to the metal centre. So,

from this methylene backbone the CH<sub>2</sub> backbone. If we just move to a pyridine backbone and pyridine ring can be utilised for fictionalisation from its 2 and 6 positions.

With the use of 2 oxazolin rings so we get a p box ligand p box ligand is a typical tridentate ligand but, this particular ligand is a different one compared to the tripyridine ligand because the geometry is different its coordination is different and the corresponding metal nitrogen bond distance and the corresponding strain on the ligand is also completely different So, several coordination complexes can be made with this particular type of ligand for seeing whether they are catalytically active or not some useful compounds on manganese or copper or bisoxazolin. Ligands are extremely useful in the different types of asymmetric synthesis so in organic chemistry the asymmetric synthesis has been benefitted a lot with the use of this sort of ligands where the typical geometry has been adopted compared to the bipyridial or terpyridial type of ligands.

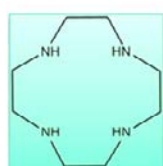
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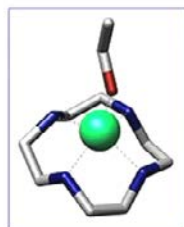
So, these are therefore, one other group of ligands then we can go for a typical macrocyclic ligand where we can have 4 donor atoms and if they are nitrogen bearing as we have defined earlier that these nitrogens can be connected very easily and when we connect we get a complete cyclic geometry and this can be derived. If these are all NH like getting tack end from diethylenetriamine. So, this can be obtained if we consider the train backbone the train was NH

2 NH. NH and NH 2 so only thing that this particular backbone has to be connected. So, if these 2 ends we can connect say by dibromo ethane or say glyoxal using these 2 molecules. So, we can get a cyclic product and this cyclic product is related to the tack end molecule but, is of bigger size so this cavity size is important this cavity size will say what type of ligand can go and enter whether it is f e 3 plus or m n 2 plus or cobalt 2 plus or 3 plus.

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Cyclen or 1,4,7,10-tetraazacyclododecane



Crystal structure of Zn(II)cyclen and an ethanol.

Inorg. Chem., 1997, 4579-4584



3

So, this we get so if we have this only ethylene backbone for this so all the 4 nitrogen atoms are connected by 4 ethylene bridges then we get one particular type of ligand which is known as cyclane. Which is nothing but, one 4, 7, 10 tetra ezacyclododeccan which is like that of tack end triezacyclononane is cyclododeccan. Which is having eight plus 4 twelve atoms in the backbone in tack end we have nine backbone.

That is why the nomenclature ends with the nonane end this is dodeccan end. So, when we find that how this particular geometry can bind because these are all saturated CH<sub>2</sub> groups saturated CH<sub>2</sub> groups those are all tetrahedral carbon. So, when the tetrahedral carbon is try to bind some metal centre this entire ring basically cannot be a planar one. But, it is basically a puckered one where we see that 4 nitrogen atoms these n h groups because n h groups this is nitrogen this is second this is third and the forth one.

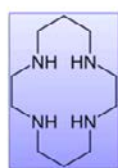
So, all 4 nitrogen donor atoms are basically going towards the upward direction that means this is nitrogen is basically a pyramidal one because the third bond which is

attached to this nitrogen is the NH bond. So, this is pyramidal this is pyramidal so 4 pyramidal nitrogens are pointing towards the upward direction and when these 2 adjacent nitrogens are in the upward direction.

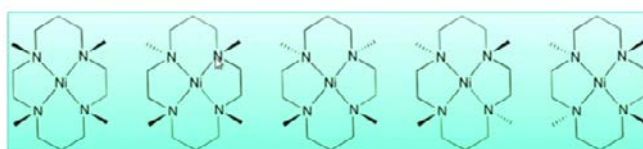
So, we have the downward direction of the backbone and which is trying to coordinate to the metal centre so when we have a corresponding compound of zinc to cyclane. So, zinc atom is basically sitting on this particular ring in this particular cyclic ring zinc atom is sitting over there and ethanol molecule is coordinating fulfilling the fifth coordination site for the zinc atom. So, this ligand is providing 4 donor atoms 4 nitrogen atoms are provided by this ligand and the fifth one is by the corresponding ethanol.

So, this Particular geometry is much more flexible and we have a puckered geometry for this ligand system so this can be found from the reference of an organic chemistry by an American chemical society.

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Cyclam (1,4,8,11-tetraazacyclotetradecane)



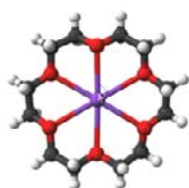
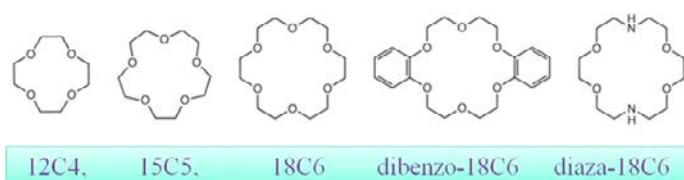
Isomers of a square planar metal cyclam complex.

Then if we just increase the backbone from ethane to propane that means CH<sub>2</sub> whole 2 to CH<sub>2</sub> whole 3. That means we have a little bit relaxed macro cycle which is a different one and we call it as a cyclam. So, cyclam ligand is related to the previous one but, it has a different cavity size for the coordination to the metal centre and we have all isomeric forms. We can have since all the NH groups can be substituted by n methyl or n ethyl. So, depending upon the positioning of 4 methyl or 4 ethyl groups we can have different types of isomers. Because we have seen in the previous example that when the nitrogen

is in pyramidal side we have the hydrogen in the backbone there and hydrogen is now substituted by methyl and ethyl groups so either this methyl group can be up or can be down so in 4 of them are up we have this geometry when 3 of them are up.

So, in this sequence we can have all this possible isomeric forms when simply the nickel is bound to cyclam so we have the corresponding square planar complex and metal cyclam complexes are all isomeric in nature depending upon the corresponding orientation of the n methyl or n ethyl groups.

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18-crown-6 coordinating a K<sup>+</sup>



Similarly, if we just simply go from nitrogen to oxygen which is not so strongly coordinating to the metal centre but, we can have very poorly donating. Ligand system but, which is cyclic in nature like the binding of the ether so if we have the ether say diethyl ether and if we just compare this diethyl ether with that of our water molecule. So, we all know this water molecule so this lone pair of electrons on ether and water molecules are available for coordination but, this binding is not so strong which is weak coordinating to the metal centre. So, when one ethyl is available we get a corresponding coordination to one particular metal centre. But, if we can have more than one such ethyl group such as this one this can also go and bind to the a typical metal ion. So, if we now complete the cycle by 3 or 4 donor atoms 4 ethyl like of this thing we get a cyclic system where this cyclic systems are known as the corresponding crown ethers. So, these are another group of ligands in this particular class they are crown ether ligands because they

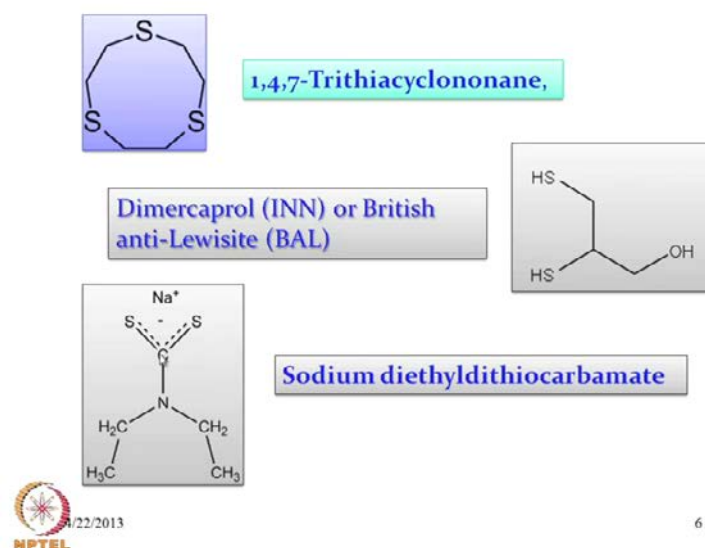
are very useful and they can bind to metal ions like sodium potassium and other very weakly like that of the coordination of the water molecule.

So, when we have 4 oxygen atoms and the backbone is completing with 12 that means 8 carbon and 4 oxygens. Which is 12 C 4 similarly, if we change to 5, 5 oxygen it is C5 18 C 6 and if we have 2 benzo backbone we get dibenzo 18 c 6 crown ether and if one oxygen is replaced by n h we get dieza 18 c 6 which is analog of this 18 c 6 molecule but, 2 oxygen donor atoms of the ether are replaced by 2 eza functions of NH. So, this has been a very useful molecule for binding to the potassium ion the alkali metal or alkaline earth metal which how we just basically transport particular in the biologically system from cell membrane from one side to the other. So, we need some selective ligands for potassium binding which we are not discussing in detail for cordsons chemistry that means the chemistry related to the metal ions but, the binding of this alkali or alkaline earth metals are very important so when potassium ion is coordinating with 18 crown 6.

We have this particular one which is 18 crown 6 so copper potassium is sitting over here and 6 oxygen atoms are binding to this particular potassium because this cavity size is matching very much with that of our potassium ion and this particular geometry. Because this particular geometry is also fulfilling the corresponding puckered movement from one side this is up this is down this is down this is up to make a corresponding 3 dimensional structure that means the coordinating geometry around this potassium is octahedral in nature. So, like that of our other transition metal ions which are based on a typical octahedral geometry potassium is trapped within the crown ether by such 6 oxygen donor atoms related to that of the coordination of water molecules.



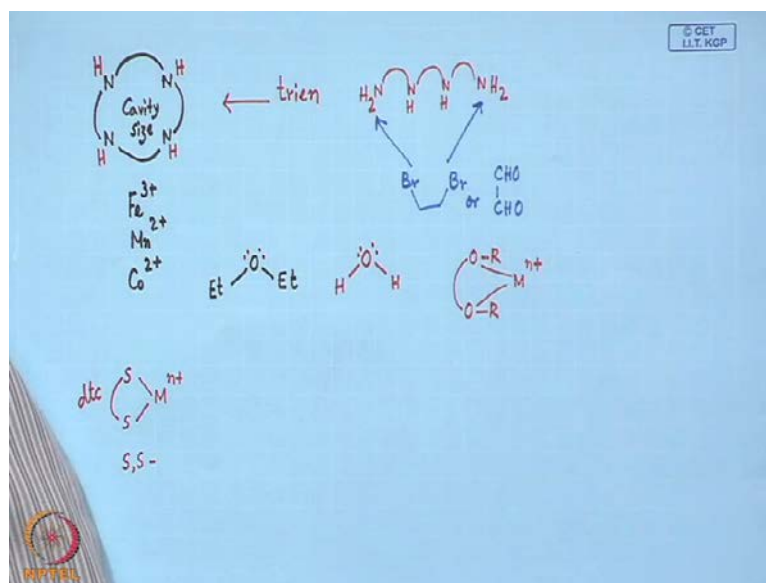
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So, this oxygen can also be substituted by sulphur which gives rise to 1,4, 7 trithayacyclononane. Like that of our tack end molecules where all the sulphur groups were occupied by n h functions then this is also a related ligand compared to this one which is a cyclic one. But, this is an acyclic one bearing 2 sulphur and one oxygen donor which is well known for binding the heavy metal ions and during world war 2 and all. This case time this has been developed is a dimarcraprol or British anti lewisite molecule we call it because it binds heavier metal ions like cadmium zinc mercury and all this which are very much poisonous even it goes if it goes to our body also it has some detrimental effect on our body. So, we want to eliminate by using this sort of ligand or this type of ligand to coordinate to the metal centre and coming out from the body. Similarly, this sulphur binding to the heavy metal ion can also be established through a other simple ligand which is known as diethiocarbamate.

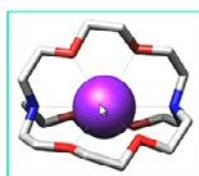
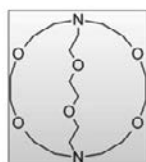
So, a sodium diethyl diethiocarbamate is another type of ligand where we take diethyl amine this is basically diethyl amine and when diethyl amine is reacted with carbon disulphide in sodium hydroxide medium. We get the corresponding sodium diethyl carbamate ligand and like this ligand like this ligand this also binds to these 2 sulphur atoms. So these 2 sulphur atoms when binds to the metal centre it is basically providing the corresponding bidentate sulphur sulphur ligand to the metal centre.

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So, s and s if it is there which is coming from diethyl carbamate and its binds to the metal centre through sulphur so s s bidentate ligand so s s bidentate ligand is our diethyl diethiocarbamate and this diethyl diethiocarbamate.

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K cation  
inside

**Cryptands:** synthetic bi- and polycyclic multidentate ligands for a variety of cations.

We can see can further be categorised to binding to the different metal centres then another class of bicyclic ligand. We can have this is one other type of bicyclic ligand related to the nitrogen coordination and oxygen coordination like that of our crown ether. So, if we have 6 oxygen donor atoms from one side so this is the cyclic backbone and

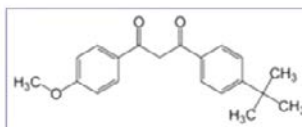
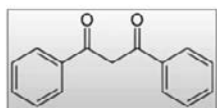
this another kind that means which is connected this nitrogen which were originally NH function. So, we have one cycle and this is another cyclic so this is basically a bicyclic ligand and this type of molecules are known as cryptands and these cryptands are synthetically prepared.

It can be bicyclic or it can be also polycyclic so it is useful for binding a variety of cations and it is also bidentate and polydentate in nature so is one half of this bidentate part can go to bind a metal centre here so if all the 6 donor atoms are utilised for binding. Say one metal centre say potassium like crown ether. So, this potassium when it is centrally located it binds to 6 oxygen atoms only and these nitrogens are not utilised for any coordination to the metal centre because already we are having this particular nitrogen which is pyramidal in nature so if the pyramid is like this the lone pair is available on the other side of this nitrogen.

Similarly, the lone pair is also available from this point to the other side of the ring. So, these 2 nitrogens will not be utilised for coordination to the metal centre instead we are providing in a different way 6 donor atoms like 6 oxygen atoms to the metal centre. In a bicyclic structure so these are all cryptand molecules and they basically encapsulate they trap the metal ion very nicely within this particular cavity. So, apart from this macrocyclic ligand this is a bicyclic one which has a sphere like arrangement and which can trap the metal ion very nicely within this particular cavity and this particular cavity also gives us this particular coordination. So, this nitrogen and this nitrogen when it is puckered this nitrogen is pointing towards this particular end and when this nitrogen is pointing towards this particular atom it is forcing to show some other interaction.

So you have seen that in this structure this particular coordination for this metal centre is from 6 oxygens as well as 2 nitrogens. So, it is 8 coordinated so bigger metal ion like lanthanides and all can be very nicely placed within the cryptand pocket. So, bigger as well as we can put potassium also, starting point when we synthesise the potassium salt of this can be made which can be exchanged with the other lanthanide ions for the coordination with this particular cryptand sphere.

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**Other application:**

Avobenzone (Butyl Methoxydibenzoylmethane) is an oil soluble ingredient used in sunscreen products to absorb the full spectrum of UVA rays.



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So, like that of our acetyl acetone so if we have the substitution for the acetyl group by the 2 phenyl rings in this particular case of these molecules we will see that acetyl acetone can be moved from one particular point to the other where we have more rigid structure more rigid backbone which is known as benzoin acetone. So, this benzoin acetone having this backbone and it can bind to the metal centre in a bidentate fashion.

So, these two donor points through analysis so this will be done through analysis by taking 1 hydrogen from 1 CH group to make it a mono negative bidentate ligand like acetyl acetone similarly, people are also trying to make a newer type of ligand by substitution. Since the phenyl ring has been introduced like benzene ring we can go for substitutions in the para position of this phenyl ring so substitutions in the para position of these phenyl rings can give us some useful information. Because this molecule is not only useful for binding to the metal centre through these 2 oxygen atoms but, it can be useful for some other activity like making this molecule and is known as the corresponding avobenzone. Avobenzone is nothing but, butyl methoxydibenzoylmethane so it has a butyl function and another is the methoxy substitution.

So, 2 substitutions at 2 ends of the phenyl ring particularly the para position by butyl function as the methoxy function of dibenzoylmethane can be useful because it is soluble in non aqueous medium is soluble in oil and any other cream material is very useful ingredient for use as a sunscreen lotion because it absorbs the full spectrum of UVA

radiation so the range of u v ray radiation can be absorbed by this particular molecule and sunburn due to u v exposer can be stopped. And this molecule is therefore, is a ligand but, it has found that it can have some other application as well.

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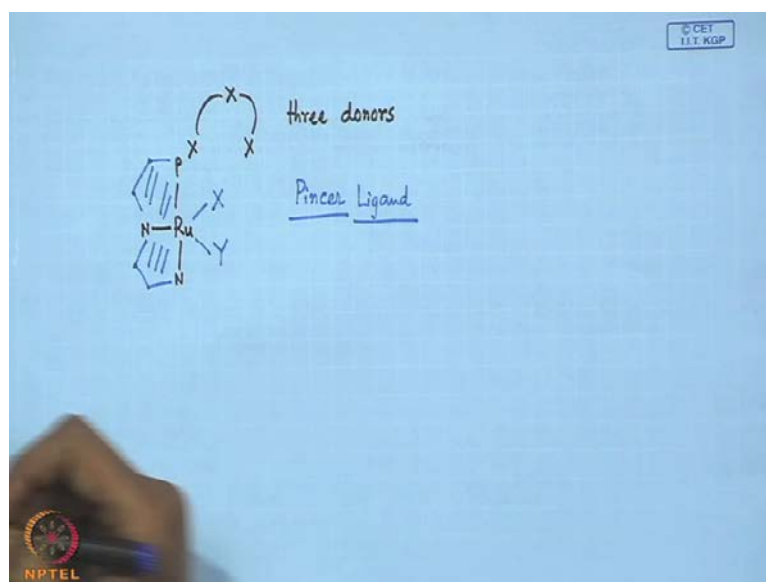
A **pincer ligand** is also a chelating agent which binds tightly to three adjacent coplanar sites, usually in a mer-configuration.



So, another type of ligand is also well known is also another class for the chelating one which is the pincer ligand which binds tightly to 3 adjacent coplanar sites. So, if we have 3 adjacent coplanar sites like that of our (( )) type of ligand. So, if we have one donor point and another donor point and the third donor point. So, 3 such donors if they are available and if this 3 are adjacent coplanar sites that means one plane and the other plane are basically giving rise to a basically a planar tridentate arrangement not that it can move to some other plane and usually it binds in a meridional configuration. That means in plane configuration is available for binding to the metal centre so this particular ligand is one sort of this example of the pincer ligand. This is another pincer type of ligand so like that of our terpyridil ligand what we have seen earlier the terpyridil ligand have one pyridine here second pyridine here and third pyridine here instead of that. Now we can have in 2 ortho positions of the pyridine ring the one as the phosphin donor and another as the nitrogen donor so n n diethyl donor from the right hand side and phosphin donor with butyl groups tertiary butyl function which is a bulky group so if we put bulky groups around this phosphorus and 2 other bulky groups around this nitrogen we will see that we are forcing this particular plane which is a 5 membered chilate ring around ruthenium and this is also another 5 membered chilate ring on the other side. But, this is

bearing phosphorus and and this is bearing nitrogen and if they are pretty close to each other and if the planar arrangement is such that it is very tightly bound. So, what we find that we find a typical geometry for this ruthenium centre where we are providing a tridentate coordination around this ruthenium centre.

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So, basically what we get we get this nitrogen this is another nitrogen and this is the phosphorous. But, the size of this the chelate ring size is very important which is basically this sort of thing we can have when we have this 2 carbon spacer. If we can have so 2 carbon spacer more relaxed so what we get we basically this particular form that means we have Phosphorous also and the 2 carbon spacer and this nitrogen. So this is basically a 5 membered ring and if we can go for other type of ring like this pincer one. In case of pincer ligand we can have these as the corresponding planar part and this planar part basically giving the corresponding meridional configuration and we have two positions available which can be occupied by x and y. It is not that one tridentate half and we can have another tridentate half around this ruthenium such that we get the octahedral geometry. Instead of that we can have a 5 coordinated geometry if we have the ruthenium.

Similarly if we go for iridium when pyridine is substituted by the benzene ring we have the metal carbon bond so it is basically a typical example of organo of metallic compound and 2 hydride bonds are also there. And which is giving rise to a trigonal

pyramidal geometry. So these are very good catalyst in turn so pincer ligands are very useful for their catalytic activity. Because we can use some of these positions for useful catalytic activities that we are not bringing any other ligand but, we will go for only the substrate binding and the reagent binding from these two positions. Here also the substrate binding and reagent binding by removal of this carbon monoxide and hydrogen.

Thank you.