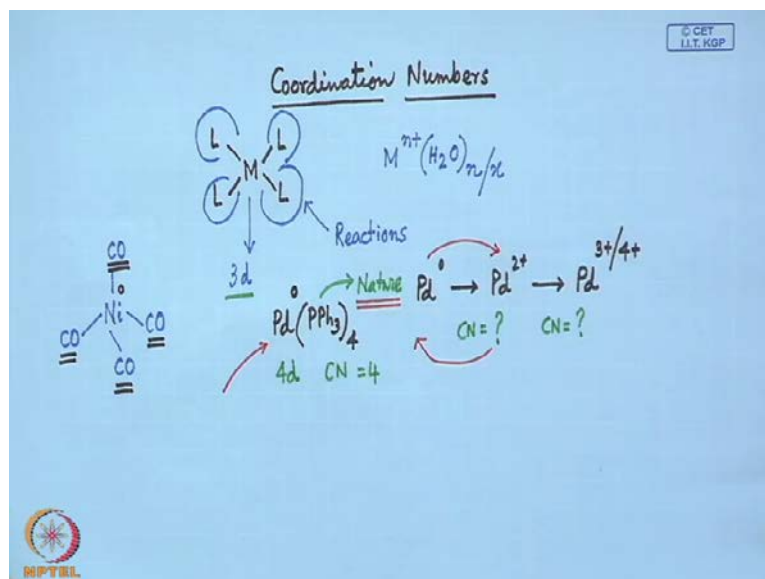


Coordination Chemistry
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Lecture - 8
Coordination Number – II

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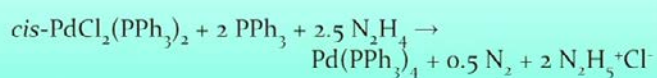
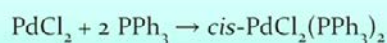


Good evening everybody. So, today we will just see, what are the other coordination numbers, which can help us to know the minimum number of ligands, which can bind to the metal ion, which is completely different from a system, where only the metal ion is present as M^{n+} . So, the presence of so many of these ligands, so they are either the neutral molecule or the charged one, particularly the anionic one, when they are in a typical geometry compared to the free one, where we just simply write when we dissolve it in a typical metal salt, that it can have n or x number of water molecules surrounding the central metal ion. But what are the different ligands, which can bind to the metal center and give some important reactivity pattern related to the metal ions, if it is a 3 D metal ion or related to the corresponding substitution and addition reactions.

So, reactions we can expect from the ligand side and the electronic properties and other stereo chemical properties, which can be obtained entirely from the metal centre.

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Coordination Number-II



is widely used to catalyse C-C coupling reactions in organic synthesis.



1

So, we just see the second part of this coordination number. One typical example is in our hand, which is tetra phenyl phosphonium, which is a 4 in number attached to the palladium centre and that is very much similar to that of our nickel centre, which is the corresponding tetra carbonyl species. So, we get some properties related to this center, interestingly this one, which is a nickel 0 system. Similarly, in case of this palladium system, where in place of these small molecules, carbon monoxides are comparatively small molecules compared to tri-phenyl phosphine.

So, they are again 4 in number and palladium n 0 oxidation state and this will give some important properties related to the palladium 0 oxidation state, because it can go from palladium 0 to palladium 2 plus or sometimes the same centre can go to some other oxidation states like the trivalent as well as the tetravalent oxidation states. So, in terms of the corresponding electron transfer behavior centered on this platinum; that means, the d electron configurations, which is now in the 4 d level. So, how the reactivity of this particular centre can be manipulated and when we concentrate our attention on this particular aspect; that means, the coordination numbers. So, in this particular case, if the coordination number is 4, what we can expect, if there is a redox transformation from a complex, which is palladium 0 having a coordination number of 4 is going from palladium 0 to palladium 2 plus.

Further, if it codes further oxidation to the trivalent palladium state or the tetravalent palladium state, so, what would be their expected coordination number? So, these are the two important questions what we can ask at this particular point and we can get some information or some answers related to this particular ligand; that means the nature. What we have been discussing in our last class, that is the bulky tri-phenyl phosphine ligand always will have some tendency to go away from the centre, if some entering group, so, incoming group is there, which is attacking the palladium centre and some phosphine can go. So, the steric bulk of this particular ligand system, which is the existing one, also has some important role to play to control these redox transformations, if they are cycling between these two oxidation states.

That means, if they are going from 0 to 2 plus and 2 plus to 0, so, we can expect that some of these important reactions, where the palladium metal ion can take part and playing the corresponding catalytic role, then this particular system or this particular complex, the coordination complex at the 0 oxidation state of palladium can function as a very good catalyst in this particular case. So, if we have the tetrakis tri-phenyl phosphine palladium 0 compound, which can be very easily prepared through this particular reaction scheme, where we all know like nickel chloride, palladium chloride is little bit bigger one compared to the nickel in the 4 d series of elements, which is reacting with two molecules of tri-phenyl phosphine giving a product, which is basically a cis product.

That means, the coordination number is increasing from, say 8. Sometimes, this is can be a corresponding species, where polymeric structure of palladium chloride is known and in the solid state, it can have the different structure. But this particular molecular species, which is basically in cis geometry; that means, 2 chloride and 2 phosphine groups are in adjacent positions. That means, they are cis to each other forming 90 degree angles. So, chlorine palladium chlorine bond is 90 degree. Similarly, the phosphorous palladium phosphorous bond is also 90 degree. So, once we get this particular species, our target is that, we will have a species where palladium will be in the 0 oxidation state and it will have 4 coordinated phosphine ligands. So, what thing we can do in the next step is, the thing which we can do in the next step is, the use of hydrogen; use of one particular reducing agent.

So, hydrogen is well suited reducing agent, which can reduce this palladium from plus 2 oxidation state to palladium 0. We also add the extra amount of tri-phenyl phosphine

because already the molecule has only 2 phosphine tri-phenyl phosphine ligand. So, we have to provide two more and the reaction stoichiometry is 1 is to 2 is to 2.5, where this particular hydrogen is broken into two fragments. One is the nitrogen gas is eliminated from there and hydrazinium chloride is forming. So, two molecules of hydrogenium chloride is also forming abstracting this particular Cl.

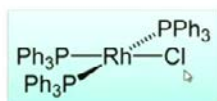
So, once we reduce this hydrazinium ion is playing double role in this particular reaction system, where this hydrogen is the source for its electron to reduce the palladium 2 plus 2 palladium 0 and at the same time, when we reduce it to 0 oxidation state, it will not have any attraction for the chloride, as their ligands. Instead, it has some surrounding available tri-phenyl phosphine group. So, it will attract more number of tri-phenyl phosphine groups towards it and this Cl minus will be taken away by the corresponding same hydrogen molecule, where the hydrogen is now behaving as a corresponding base in this particular system.

So, we have this particular preparation based on this palladium chloride molecule and is a very useful molecule. Just now, what we are talking about, that if we can settle between the two oxidation states of palladium for palladium 0 to palladium 2 plus and if they can go for some interesting reactions, so, this particular species is widely used in very important reaction in organic chemistry is the C C coupling reactions.

So, in different organic synthesis, if we want to elaborate the molecule, if we want to increase the molecular structure by making new carbon carbon bonds, which can be achieved by two reagents. One having one carbon centre and another having another carbon centre. But if we want to make a carbon carbon bond between them, we can use this palladium tri-phenyl phosphine molecule as a very good catalyst.

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Wilkinson's catalyst



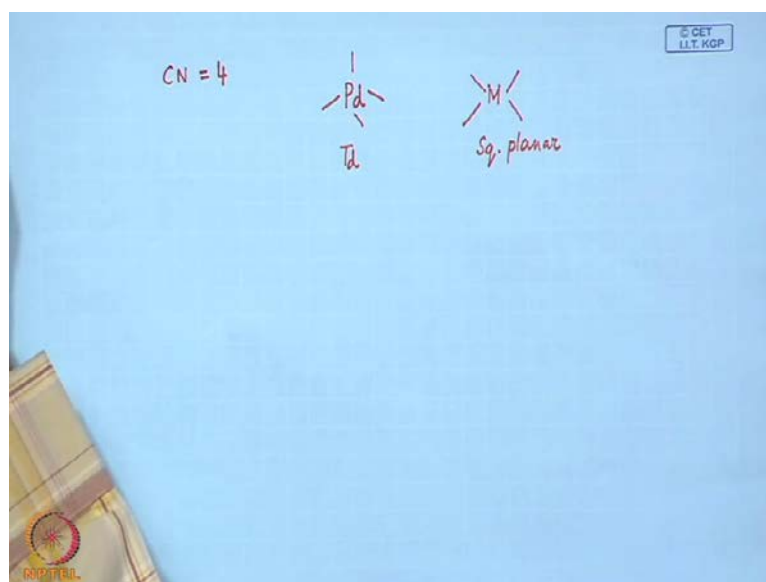
chlorotris(triphenylphosphine)rhodium(I)



2

So, after getting that, we can have some more examples of catalyst, as well as the corresponding coordination compound, where we see that we are just focusing our attention on a coordination number of 4.

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So, if we have a coordination number of 4 and just now, we have seen that, we can have the palladium centre and then we can have any other metal centre, where we can go from a tetrahedral geometry to a square planar one. So, one such example is our Wilkinson catalyst, which is nothing but chlorotris tri-phenyl phosphine rhodium I. Just now, what

we have seen, we have seen one example, where palladium was present as palladium 0. So, that was tetrakis tri-phenyl phosphine palladium 0 and what we have started from only that palladium chloride; that means, Pd Cl 2. So, as some intermediate product we got some Pd Cl 2 P 2. That means, 2 tri-phenyl phosphine and 2 chloride groups are added to the palladium centre, where the palladium oxidation states still remains in plus 2.

But, in this particular case, this is one other situation. Instead of going to the 0 oxidation state, we can go to a plus 1 oxidation state and using the metal ion rhodium and that is why the compound will have 1 chloride anion as the ligand and 3 ion positions are occupied by 3 tri-phenyl phosphine molecules. So, this is another example of a coordination complex, where the coordination number is 4. So, this is the molecule, where will see that, we have 3 tri-phenyl phosphine and 1 Cl. So, the Cl molecule will have 1 trans t Ph 3 molecule and 2 cis Ph 3 molecule. So, this positioning of these groups are important for the different catalytic reactions what we can have and some important reactions based on this is well-known. It is a dark red compound; powder compound. We can make it from the corresponding rhodium chloride and the tri-phenyl phosphine as the ligand.

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$\text{RhCl}(\text{PPh}_3)_3$ is a square planar Rh(I) complex of historical significance used to catalyze the hydrogenation of alkenes.



Structurally analogous to Vaska's complex



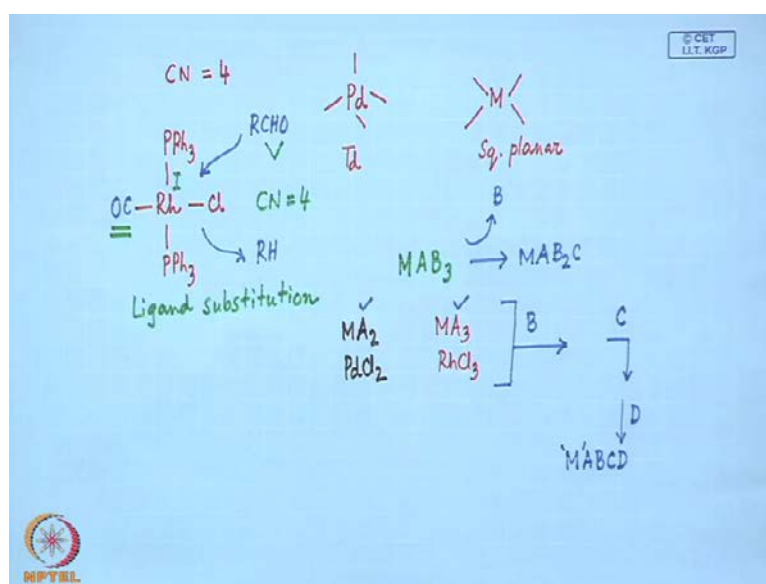
The preparation is also very much straightforward compared to that palladium compound, where we can use the rhodium tri-chloride. In case of palladium, we use the palladium di-chloride, but rhodium is in the cobalt series. So, cobalt rhodium and iridium

as you all know, so, in that particular series, the stable oxidation state of rhodium would be plus 3. So, rhodium tri-chloride like cobalt chloride is available with 3 water molecules of crystallization. When we react it with 4 phosphine molecules, this particular one is utilized for the reduction of the rhodium centre. On the left hand side, this rhodium is present in that trivalent state, which is getting reduced to the monovalent state, which is rhodium 1 compound with the elimination of the PPh_3O and 2 HCl and 2 water molecules. So, tri-phenyl phosphine is going away from the medium as a tri-phenyl phosphine oxide leaving behind the molecule.

So, again we have a molecule with a coordination number of 4 and which is square planer one and it has long been known as a corresponding useful catalyst for alkyne hydrogenation. So, it has also some historical importance, which we all know, that it can catalyze the corresponding hydrogenation reaction for different types of alkynes. This particular molecule is further reactive towards some aldehyde molecules also.

So, when we react this particular reagent; that means, Wilkinson catalyst when reacted with any aldehyde RCHO , we get the corresponding trans Ra Cl CO Ph_3 whole 2 molecule, where the RCHO has been converted to RH and 1 phosphine group has been eliminated from the system. So, in this particular case, whatever we have, we have already the molecule is in the trans geometry.

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So, the phosphine group which is present with a trans position of rhodium; so, we have, this is the phosphine and this is the phosphine. So, what was present over there as the trans position, which was also occupied by another phosphine molecule, but during the reaction with any aldehyde, it can be the corresponding benzaldehyde also. So, it is converting to, so, RCHO is entering in the medium and the corresponding hydrocarbon is removing. That is why it is taking away this particular carbonyl function as the corresponding CO molecule and this particular tri-phenyl phosphine also is living away.

So, is a very physically a corresponding ligand substitution reaction. So, ligand substitution reaction is nicely taking place on this particular system and we are not going for anything because the tri-phenyl phosphine, what is being removed from this particular position was a neutral ligand and is now newly occupied by a carbon monoxide molecule, which is also a neutral one. So, the oxidation state of this particular centre is not getting changed, which is still in monovalent state. That is why it has the corresponding preference for the original coordination number of 4 and it will remain as a corresponding square planer molecule and it is preferring the corresponding square planer geometry.

So, no ligand additive reaction; that means, both the phosphine as well as the carbon monoxide is not occupying the position around the rhodium centre. Only reaction what is taking place over there is the corresponding ligand substitution reaction. So, it is a very nice example for the corresponding transition metal complex of carbonyl group because the carbonyl clusters, all we have seen that case of nickel tetra carbonyl, similarly, very easily we can make the corresponding carbon monoxide compound of rhodium in presence of tri-phenyl phosphine. In terms of the corresponding structure; that means, this is a 4 coordinated compound in trans geometry. When we will consider the corresponding isomers, we will discuss again in detail of the corresponding effect of the donor groups. What they are manipulating and what they are doing due to the presence of these two groups trans to each other as well as cis to each other.

So, another example of compound in the same geometry. We are now giving example for that is the Vaska's complex, which is structurally analog. So, whatever compound we have, this Vaska's complex would be again a 4 coordinated square planer compound. Since, these are the corresponding nature of these ligands, so, 4 coordinated square planer compound and these are two information what we are getting from the

Wilkinson's catalyst. But in this particular case also, we see that we have a corresponding carbonyl ligand. So, 3 types of ligands are present in this molecule. The Cl minus, which was originally present with the metal salt, because we are using rhodium chloride as a starting material.

So, it is a chloride salt. So, Cl minus is still present, which is one of the ligand. Then we have reacted it with tri-phenyl phosphine. So, tri-phenyl phosphine is our second choice. So, tri-phenyl phosphine is coming as a second ligand to it and then we are reacting this particular catalyst, which is the Wilkinson catalyst, where we have two types of ligands with any aldehyde giving rise to a species, where the system is changing from a compound, which is a metal and any type of ligands to another, where we have A B and C type of ligands.

So, what we get is, we get a corresponding M A B 3 type of compound, which is 4 coordinated and square planer, which is getting changed to M and A is still there. A is the corresponding chloride one and B 3 is now B 2; that means, one phosphine is going away. B is going away and the incoming ligand is the corresponding carbon monoxide.

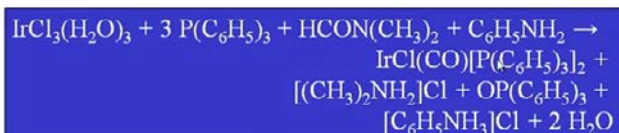
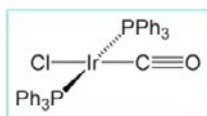
So, these sort of things are very useful and very good examples for the corresponding ligand substitution reactions because whenever we have a M A 2 types of species, say what we have seen in the case of palladium chloride, what we have taken or sometime the metal as the 3 anion is MA 3 type, which is rhodium tri-chloride. So, from there, basically how we can utilize the different ligands?

So, A is already present over there. Here, A is already there. So, how we can use this particular molecule for the reaction with A and then reaction C and if possible, with the reaction with D, such that, for a square planer type of compound or a 4 coordinated compound, we can have a species like MABCD. So, this is the metal centre and we can have 4 different ligands attaching to the system.

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Vaska's complex

trans-chlorocarbonylbis(triphenylphosphine)iridium(I)



4

So, let us now see, what is that Vaska's complex, which is similar to that of the product what we are getting from the corresponding Wilkinson catalyst. So, is a yellowish green powdery compound, which can be very easily prepared and if we just see the 3 types of ligands present to this, which is the Cl, the carbon monoxide and the tri-phenyl phosphine. Only difference is that, now, we have the iridium one. Instead of rhodium, we have now the iridium as the corresponding metal ion and the geometry is again trans. So, if we have A B and C type metal complex with 4 coordination number, that is why whatever product we are getting from the reaction of the Wilkinson catalyst with any aldehyde, which will be very much similar to that of our Vaska's complex, because this is a very important compound. Very interesting compound to study and it has again some historical importance. So, is getting instead of rhodium, what we have just now seen. Then the trans position of Cl is occupied by carbon monoxide and we have 2 tri-phenyl phosphine groups. This has some other property, which is related to the nature of the iridium. What is not observed in case of the presence of rhodium. So, iridium compound which is there, so, it can also react further for some addition reaction with molecular oxygen. So, like hemoglobin and mioglobin, this particular centre also have some affinity to react with molecular oxygen.

So, O₂ can be a very good ligand to the Vaska's complex, which is not possible, and which we are not getting with the corresponding rhodium compound. So, that information is also very much useful to us because for some catalytic reaction, already

we have seen that this is the product what we got from the reaction of any aldehyde to that of our Wilkinson catalyst. So, Wilkinson catalyst was already a catalyst and that particular system giving rise to the corresponding iridium analog and iridium analog, if it can activate with the dioxygen molecule like myoglobin and hemoglobin. So, we get some species, some catalytic species, where iridium is activating the dioxygen molecule.

So, people has studied long for these type of molecules, where we can go for some oxygen transfer reaction or oxygenation reaction based on the iridium because whatever we are getting that dioxygen molecules would definitely be activated through the corresponding coordination to the iridium centre.

So, that gives us and that opens up some important area of research study and understanding, where the iridium centre is utilized as a catalytic centre and which can activate the small neutral molecule, which is very important like dioxygen molecule. So, if dioxygen is getting converted to the super oxide species or the peroxide species through some electron transfer, we can get some of that type of information from this molecule itself, where the molecule is a very simple one and with very simple coordination number of 4. This particular species, like that of the previous compound, where we have been preparing the corresponding Wilkinson catalyst from the rhodium chloride, similarly, we can now take iridium chloride.

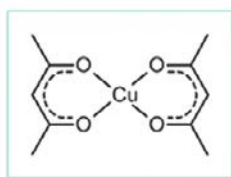
But now, instead of taking any aldehyde to the system, now we directly react this particular thing with tri-phenyl phosphine and di-methyl formamide, which is a very useful solvent, organic solvent, non-aqua solvent and well-known to us, which is di-methyl formamide, which is amide di-methyl amide of the formic acid. So, it is a d m f. This molecule is d m f to us and $C_6H_5NH_2$ is also given, which is the aniline molecule and that aniline molecule like our hydrogen molecule in the previous case is being utilized as a base.

So, we have Ir Cl is already present. 1 Cl already remains there. CO is derived from this particular species; that means, the d m f; that means, from the solvent itself, the CO is coming and the corresponding tri-phenyl phosphine of 2. So, 2 molecules are tri-phenyl phosphine are going to attach to the iridium centre and what will left behind will be the corresponding amine, the free amine, that di-methyl amine, as its corresponding chloride salt. So, di-methyl ammonium chloride will be formed over there and the chloride will be

taken care of from there and aniline what is added over there, so, aniline is also another base. So, aniline is also forming the corresponding anilinium chloride $C_6H_5NH_3Cl$, which is anilinium chloride.

The tri-phenyl phosphine basically is utilized for the corresponding reduction reaction of iridium plus 3 to iridium plus 1 and for that purpose, 1 molecule of tri-phenyl phosphine will be converted into tri-phenyl phosphine oxide with the elimination of 2 molecules of water. So, this is basically a very straight cut reaction and a single step reaction because in the previous case, what we have done is, we have done with the rhodium tri-chloride and we have reacted with tri-phenyl phosphine and we got the Wilkinson catalyst first. Then Wilkinson catalyst was reacted with the aldehyde molecule to get the corresponding analogs compound of Vaska's.

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Copper(I) acetylacetonate is an air sensitive oligomeric species. It is employed to catalyze Michael additions.

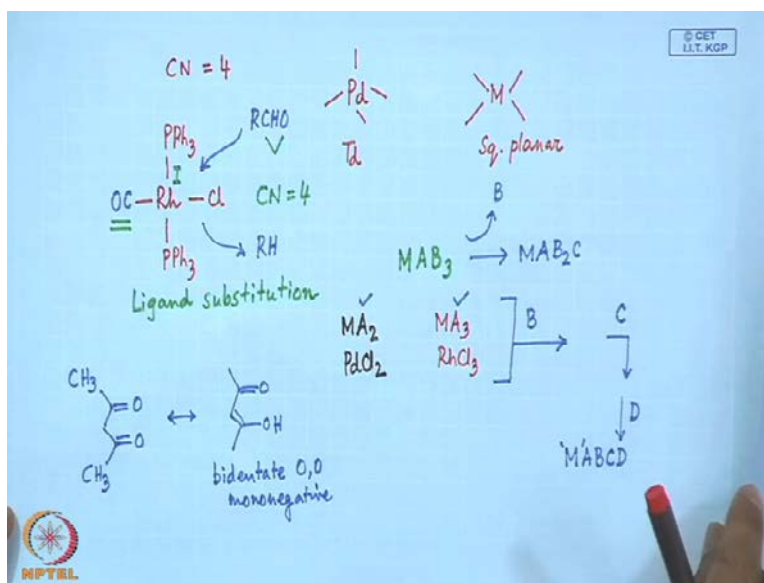
Inorganic Chemistry 3rd ed -Miessler & Tarr



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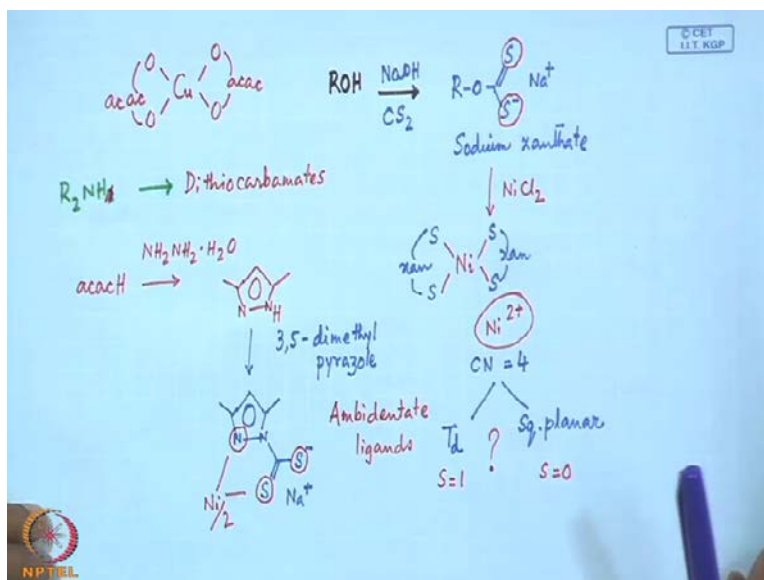
So, further of this particular coordination number, we can take the use of the corresponding bidentate ligand.

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So, when we have been talking about several bidentate ligand, one good example what we have seen is the acetyl acetone, which is $CH_3COCH_2COCH_3$. So, it basically goes for enolization and the keto-enol tautomerism can give us some bi-dentate O donor mono-negative ligand. So, this after deprotonation, this will give rise to some O O minus ligand. So, in a very simple and straight cut way, we can have any metal centre like palladium, like nickel, and like platinum.

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So, is also true for copper. So, when it is copper, we get the $O O 1$, which is abbreviated as ace ace ligand, which is acetyl acetonate anion. So, two of these acetyl acetonate ligand will give rise to the corresponding coordination to the metal centre. So, this gives us some other important opportunity to study these bi-dentate ligands. One good example we have already seen is the ethylene-di-amine. Similarly, if we start from any alcohol, so that can be derivatised basically. So, any alcohols, say ethanol, propanol, butanol, anything if we react it with sodium hydroxide and carbon di-sulphide, we basically end up with some interesting ligand of bi-dentate nature, which is sodium xanthate.

So, sodium xanthate is formed and we have the sulphur donor groups. Sulphur donor groups are bigger atoms and these bigger atoms basically can go and bind to the metal centre. So, if we add simple nickel chloride, it gives rise to the corresponding nickel compound of this type like ace ace. Like this ace ace type of compound.

But in this case, we have both the sulphur groups attached to it. So, it will have the xanthate sulphur. Similarly, if we take instead of alcohol, if we take the corresponding amine $R_2 NH$, what we will be getting by doing the same type of reaction is, we will be getting the corresponding dithiocarbomates.

Similarly, one good ligand we can derive from all these things, whatever we are talking over here, is that, if we have the acetyl acetone, which will abbreviate as a c a c h and reacts it with hydrogen hydrate, we get the corresponding di-methyl pyrasolmet. That means, here we have the NH group. So, this is NH. So, you have the NH function over here and this NH function, if we can further modify like this transformation of O minus to the corresponding xanthate to $R_2 NH_2$ dithiocarbomate, we get the corresponding ligand as the corresponding pyrasol based 3 5 di-methyl pyrasolmet, which is nothing but 3 5 di-methyl pyrasol. So, 3 5 di-methyl pyrasol based ligand we are now having and what we were just talking about this particular coordination because this is a different one, where we will just see, we will just give some example in our coming classes, which are known as ambi-dentate ligands because we can have the donor groups available on this particular system is N S S.

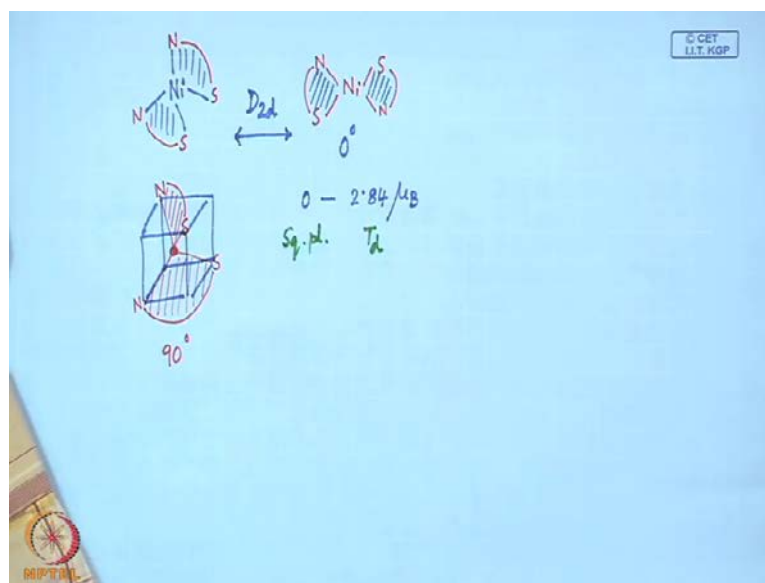
So, here the metal complex what we are getting through the use of xanthate is the corresponding sulphur sulphur coordination. Here, if the same backbone is utilized; this S S bond is utilized here. So, like this, here we can go for the corresponding nickel

coordination. But if this nitrogen is utilized for the coordination, we get a different type of compound, say if we react with nickel, it will get the corresponding bis compound. So, nickel will be attached to it.

Now, two of these will be attaching to the system. So, we will have a coordination number of 4 in our hand. Already what we have seen that, we can have a situation that this particular coordination can give rise to a tetrahedral geometry and a square planer geometry. So, these are well-known fact that one of the species what we have seen in case of nickel chemistry, the coordination chemistry of nickel 2 plus. We will see that in this particular case, tetrahedral, which is a spin triplet state and which is a spin singlet state in case of a square planer geometry. So, the magnetic movement, if you can measure, the magnetic movement can differentiate these two geometries, that means, whether we have a corresponding coordination geometry of tetrahedral structure or a square planer structure.

But, in this particular case, where the ligand is NH type and we will find that something, that means, when we have some corresponding magnetic movement, which is in between the square planer or the tetrahedral. Because in case of the tetrahedral, which is spin triplet situation, we have a magnetic movement of 2.84 bold magneton and case of square planer it is 0. But if we have some intermediate magnetic movement, then we can expect that we have some other geometry, which is in between a square planer and a tetrahedral one.

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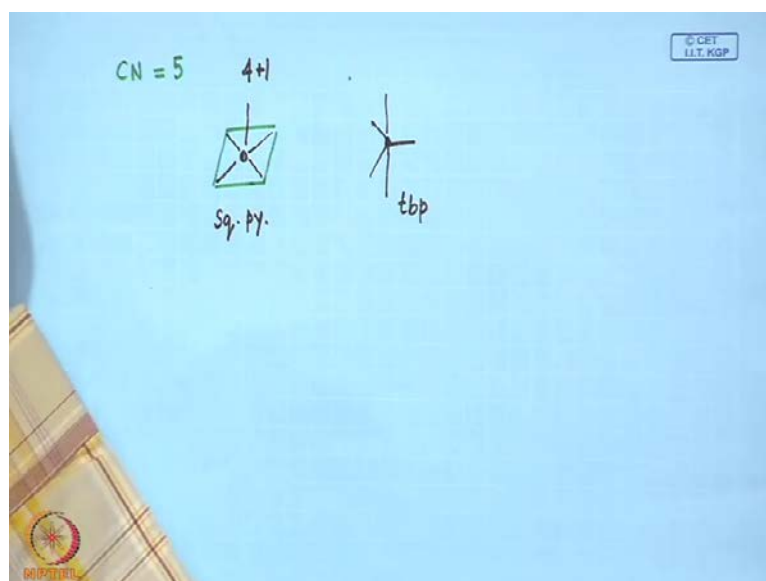
So, what we see that the tetrahedral one is basically, if we just consider this tetrahedral one, so, they can have the same ligand what we are utilizing, the pyrasol diether carbonate. If it is square planar is a trans one, it can be also the cis variety. So, what we see that these two planes, these coordinating planes, when we consider them within a cube, where the nickel is sitting at the central of the cube and these alternate corners are occupied by these groups.

So, if these two coordination planes are 90 degree to each other, then we get the corresponding tetrahedral geometry. If these two planes, basically these two corresponding nickel nitrogen sulphur planes, if they are co-planar, it would be 0 degree and we have a square planar geometry. So, now, in between we have the corresponding other distortion. So, is basically going from 0 degree to perpendicular one. So, one plane will remain in the plane of the paper and this plane will go perpendicular to the plane of the paper giving rise to a 90 degree orientation.

So, for some in between geometries, we have corresponding structures as a D_{2d} geometry and these D_{2d} geometry is basically varying from 0 to 90 degree. So, within the coordination number of 4 situation, we can have a magnetic moment of 0 to 2.84 μ_B . If you can routinely monitor the corresponding magnetic moment, then we can have some indication, whether we have a square planar geometry, the left or a tetrahedral geometry or some intermediate positions.

So, in case of copper, we just can have the corresponding situation for the copper 2 compound. This is basically, if it is a neutral compound, we have a corresponding copper compound, where copper it is present in the bivalent state. But some more compound like the reduced form of copper, which can also be stabilized in the cuprous state. So, copper acetyl acetonate, which is not easy to make that particular compound is because is air sensitive and oligomeric species, because it can have some more number of species within a same molecular fragment. In organic chemistry, it is a very useful reagent for Michael addison reactions. So, what we do for any kind of these organic transformations, for those reaction in a single part, we add the copper 1 salt. Any copper 1 starting with real and the acetyl acetone as ligand. But the most reactive species is the corresponding copper 1 acetyl acetone compound. Some of these information and all these geometries will be available in the inorganic chemistry by Miessler and Tarr.

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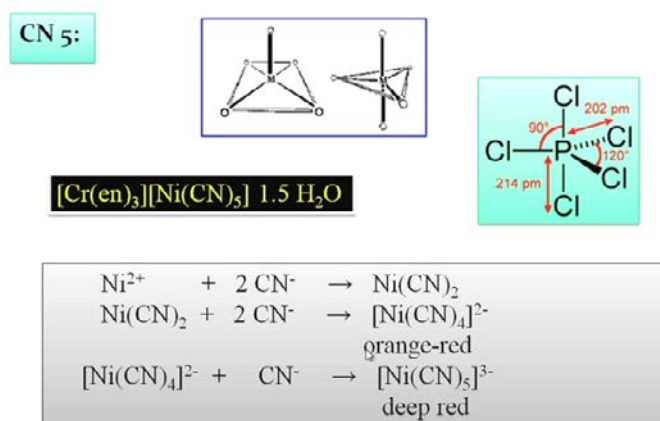


So, next we can move on to a coordination number of 5. So, if we can have the corresponding coordination number from 4 to 5, what we see that we will just talk about the corresponding basic geometry, which is the square planer one. Now, we will take the square planer one. So, we have one bond, second bond, third bond and the fourth bond. So, this coordination number, if we have a 4 bond already to us, so we will add up only 1. So, if we can have a situation, where we can have a 1 pyramidal interaction. So, basically is a square pyramidal geometry, which will have a coordination number of 5.

Similarly, all we know that another important geometry, which is also possible for simple inorganic molecules also.

It is also true for the corresponding coordination compound is the corresponding trigonal bi-pyramidal geometries. So, this is square pyramidal and this is tbp, the trigonal bi-pyramidal and these two can also be inter-convertible to each other because the positioning of some bonds are only different. But we can move from one particular arrangement to the other through some movement of these bonds.

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So, one such example with an inorganic example, typical inorganic molecule not a coordination compound is PCl₅, the phosphorous penta-chloride. This phosphorous penta-chloride will remain only in a trigonal bi-pyramidal geometry and this trigonal bi-pyramidal geometry will have some differences between these. So, we have one type of phosphorous chlorine bond, which is in the plane, where the chlorine phosphorous chlorine bond angles, we have 3 such bond angles which are 120 degree and then another bond which is in the apical side. These 3 are in the base of this particular trigonal plane, which is a trigonal plane.

So, trigon and these two are in the bi-pyramidal sides, so which is one pyramidal side and the low one is the other pyramidal side. So, these two are quite longer at 2.14 Armstrong and this is 2.0 to Armstrong. So, this phosphorous chlorine bonds are longer

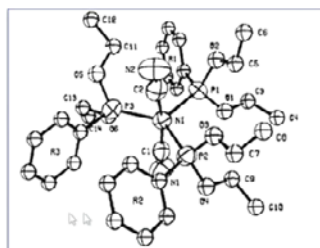
compared to the other three phosphorous chlorine bonds in plane. So, this is a classic example of a coordination number of 5 in a geometry of Trigonal bi-pyramid.

So, we have two possibilities. One can be the square pyramid and other would be that trigonal bi-pyramidal one. So, we can have a typical example, which we all know that this particular species can be made, where the cation is a particular complex species as well as the anion. Here, the cation, which is surrounding the chromium centre by 3 ethylene-di-amine molecules is basically the octahedral one and that we will discuss very soon after coordination number of 5. But what about the anionic part? The anionic part which is a different one, which is Ni C and whole 5 species. So, Ni is bipositive with a charge of 2 plus and cyanide is balancing with 5 charges and this 5 charges will give rise to a overall charge on the anionic part as 3 minus.

So, this particular compound chromium should be in the trivalent state. So, in this particular species, which we can have by gathering more number of cyanides surrounding the nickel has a coordination number of 5. So, not in that cationic part, but in the anionic part, we have a coordination number of 5. So, this is a classic example of a coordination complex, where the cationic part and anionic part as two different metal centers and they also have two different coordination geometries and the coordination numbers. So, this is well-known fact that how we can get this particular species because we can substitute some other compound and this particular cationic compound, the tris ethylene-di-amine chromium 3 cation or anion can be obtained as its corresponding perchlorate salt or tetra phenyl phosphonium salt.

But, that can be substituted very easily, if we can go for the corresponding penta-cyanonickelate salt. So, nickel, we all know is very easily reacting with cyanide. Then we can go for further reaction with cyanide and this is well-known compound to us. This particular compound as the corresponding square planer compound, which is orange red in color and this orange red compound can further react with another CN minus to give us a deep red compound of nickel in a tri-anionic species form, which is deep red in color.

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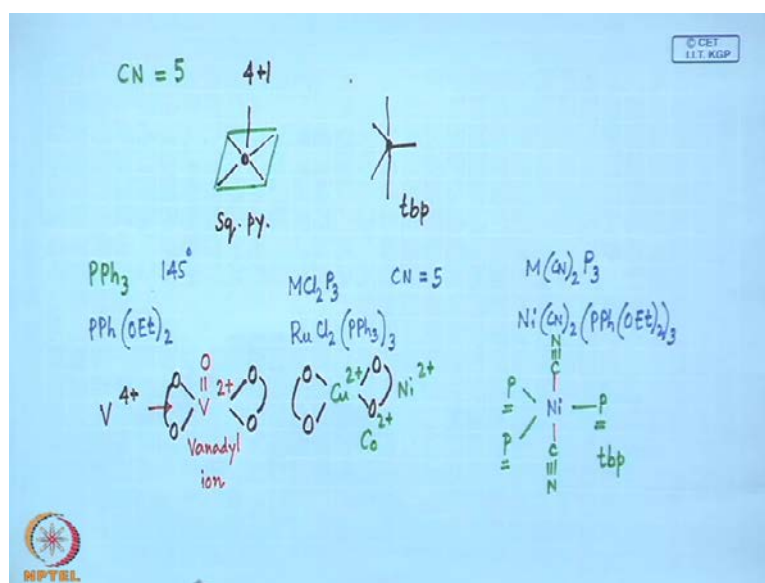


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So, when this anion can go and substitute the corresponding chloride of the salt, we get a compound, where we get a typical example of a corresponding coordination number of 5 in the anionic part of the compound. Similarly, this is one more example of this nickel with 2 cyanide and 2 phosphine type of ligands. So, this is one more square bracket is there. So, we have the tri-phenyl phosphine of this. There are 3 tri-phenyl phosphine and 2 CN minus groups are attaching to it.

So, this is another example of a molecule, where we have a coordination number of 5. So, is not a typical tri-phenyl phosphine type of molecule, but is a substituted tri-phenyl phosphine.

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So, what we see, that so far we have discussed so much about the tri-phenyl phosphine. But as we have seen that it has a very standard cone angle, which is 145 degree and which is not always very easy to give rise to some molecules. So, we can substitute this tri-phenyl phosphine group, say, so, 2 of the tri-phenyl phosphine groups can be substituted by OEt group. So, this is also another tri-phenyl phosphine, which is 2 phosphine groups substituted by o t molecule. So, any molecule of this type, which is $NiCl_2P_3$ will have a coordination number of 5. So, most of these types, so, we can have this or $M(CN)_2P_3$, which is a present example, where m is the nickel, where this m can be a different one, which is well-known $RuCl_2$ tri-phenyl phosphine and this we are getting this $Ni(CN)_2(PPH(OEt)_2)_3$.

So, this basically gives us an important geometry of the nickel centre, where we find that because just now, we have seen that the reaction of nickel 2 plus with CN minus, so, this CN will come first and will bind to the nickel centre like C triple bond N. So, this nickel cyanide is well-known to us. If we add further CN, it will give the corresponding square planer geometry.

But, in case of the phosphine, so, it is simply getting some reaction, where nickel cyanide can be reacted with this special type of phosphine ligand, is that we have these three positions like this and we will have now this $PPH(OEt)_2$ as the ligand. So, we have a corresponding geometry of tbp . So, this is also true for the ruthenium and some other

type of compounds, where will see that the phosphine groups which are present basically occupying some of these positions, where we get these particular; so, the repulsion is there still because they are 190 degree apart.

But, in this particular case, they will be 180 degree apart. But still they will not go for the corresponding species because the nickel can have the possibility of getting the corresponding compound as Ni CN 2 PPh 3 2 because the phosphine, these phosphine groups are the neutral ligand. But when they try to expand their coordination number from 4 to 5, they basically go for the corresponding coordination number of 5.

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So, this is a good example for a coordination number of 5. Similarly, if we can go for another good example is the vanadium species, where we all know that the vanadium compounds unlike our copper compound or nickel compound, where ace ace is the acetyl acetone ligand. Just now we have seen that acetyl acetone is basically binding towards the copper centre giving a coordination number of 4. But if we have some situation, where already the corresponding oxo species of the metal centre, the vanadyl species is present, the vanadyl species, so, b O 2 plus.

So, instead of vanadium 4 plus, so, tetravalent vanadium, since it has some affinity for oxygen atom, which can form very easily the corresponding vanadyl ion. So, this vanadyl ion having a di-positive charge will be very much useful or very much equivalent metal ion species like that of our copper 2 plus or nickel 2 plus or cobalt 2

plus. So, just now what we have seen that the copper 2 ion can bind to 2 acetyl acetone molecule giving rise to a bis compound with a coordination number of 4. So, if the same vanadyl ion can bind in a similar fashion with 4 of the oxygen atoms of 2 acetyl acetone molecule, we get a corresponding VO ac ac 2 molecule. So, we have the VO ac ac molecule, which can be directly obtained from vanadium penta-oxide. This is the acetyl acetone molecule.

So, reaction of this particular species is basically giving us the corresponding compound as the corresponding vanadyl acetyl acetone and we have the oxidized form of the acetyl acetone. One part of the molecule is a very useful one, where this is the vanadium centre and we have the vanadium oxo bond and two such acetyl acetone ligands are attached to these two points. So, is basically a square pyramidal geometry. So, the other geometry what we are getting over here is the corresponding geometry as the square pyramidal one and which is little bit distorted towards this vanadium oxygen bond, because this vanadium oxygen bond is a double bond and this vanadium is little bit above the corresponding O 4 plane.

This is the O 4 plane and which will be little bit lifted towards the vanadium oxygen bond, due to the strong vanadium oxygen double bond, and it will be above the corresponding O 4 plane. This particular molecule has some catalytic activity and all these and sometime, it can also react with pyridine or amine type of donor atoms to expand its coordination number from 5 to 6. So, next day we will discuss how we can move from this coordination number of 5 to a situation, where coordination number will be 6 and other regular geometries where the coordination number is 6 and above.

Thank you very much.