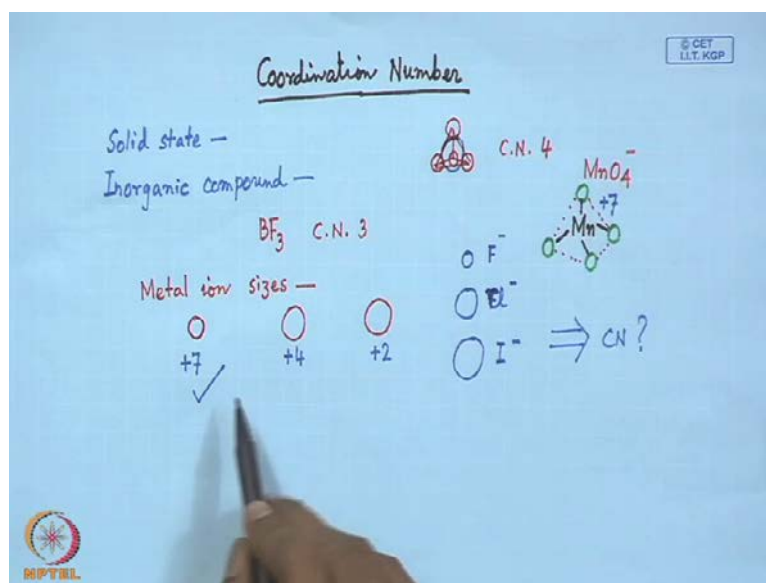


**Coordination Chemistry**  
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**Department of Chemistry**  
**Indian Institute of Technology Kharagpur**

**Lecture - 7**  
**Coordination Number – I**

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Good evening to everybody. So, today we will see how we can define the coordination number of any metal complex; which is the most general term related to some other species, as well in solid state also we can use this particular terminology. As well as in simple inorganic compound, we use this particular number. So, in solid state what we find? That if a particular center is attached to some more like this one, where the center bigger one is attaching to four such species in a typical tetrahedral geometry, then we can consider that this has a coordination number of four. Similarly, the simple species like the corresponding inorganic anionic species such as permanganate anion.

We all know that  $\text{KMnO}_4$  when dissolved in water we get  $\text{MnO}_4^-$ , and in that particular case that manganese center which is in plus seven oxidation state is bound to four oxygen atoms, and again in a typical tetrahedral geometry. So, we get something; where in three-dimensional space and how the entire species will behave, and how the manganese center will activate some other atoms is also clearly visible, if we know if we consider the corresponding coordination number of this permanganate anion. Similarly,

some inorganic compounds like boron trifluoride by knowing the stoichiometry of the compound we can see that boron is attached to three fluorine atoms.

So initially, only that particular information is sufficient to us to say a coordination number of three to boron. But afterwards, if there are different possibilities related to this coordination number we will find that, in one particular geometry is preferred, compared to the other possibilities where  $BF_3$  molecule will remain in that particular geometry. So coordination number, the geometry and sometimes the corresponding stereochemistry of the coordination compound; they are all interrelated.

So, if we just proceed in this manner, for this first class which is devoted to coordination number part one. And how we can define this particular system is that, the total number of points what are attached to the central element. But we are just now discussing. The total number of fluorine atoms attached to the boron center; we can call them as the coordination number.

Similarly, the total number of oxygen atoms attached to the manganese center in permanganate anion is also known as the corresponding coordination number of manganese center in permanganate anion. And it can vary from a small number of two. And sometime it can also be absorbed in different time as they are corresponding coordination number of one, which is very unusual.

If we have a huge and bulky ligands in center and which can only allow one point of attachment, the number of points of attachment is important. If it allows only one point of attachment to the metal center, we can consider; in that particular special case, we can have only a coordination number of one. Similarly, very smoothly we can go from a coordination number of two to six. Six will give us a corresponding octahedral geometry that will find.

And, beyond that it can go to up to sixteen where we can have some heavy metal centers like lanthanides and actinides, which has a size of say some compared to the three dimensional metal ions; relatively bigger tennis ball like structure of size. So, it can attach more number of donor atoms. And more number of points of attachment it can have. And it can have the corresponding coordination number up to sixteen. So, what we are just seen during the... nomenclature of some compounds? We have encountered with the corresponding medicinal coordination complex, which can be used as very good

medicine; which is diamminedichloroplatinum. And this diamminedichloroplatinum immediately tells us the number of ligands giving the corresponding attachments to the platinum center will have two amine ligands and two chloro ligands.


So, we have this two chloro and two amine and this particular molecule ...form; that means, two of the chlorine atoms are in the 90 degree position. They are not 180 degree apart. So, if is diamminedichloroplatinum, and as the definition tells us that the total number of points of attachments; so this platinum center will have a total number of points of attachment equal to four. So, the corresponding coordination number of this platinum center is four. So, apart from its oxidation state what we all know there to knowing the molecule, this is platinum attached to two neutral ligands and two anionic ligands giving a corresponding oxidation state of platinum in plus two.

So, we get the corresponding oxidation state. And next, the number of attachments to the center gives us the corresponding number as the coordination number. And some time we abbreviate it as C N. So, the relative size of the metal ions and ligands are the corresponding determining factors. And the relative size of this ligands and metal ions will solve the purpose of choosing the corresponding coordination number. So, if we have a corresponding small metal ion; that means, the metal ions sizes are important. And if we can have relatively bigger and bigger one, so what we immediately consider it as, it can be the corresponding this manganese which is in plus seven oxidation state. So, the smallest one is in plus seven, then we can have plus four or we can have the plus two.

And then the size of the corresponding ligands; the smaller, the medium size ligand and the bigger ligands say the corresponding typical anions what we can see as the corresponding salts; F minus, then Cl minus and then I minus. So, this particular one will how many of these size parity can take place around a corresponding oxidation state of the metal ion as plus two, plus four or plus six, that will basically dictate us what will be the resultant coordination number of this particular combination.

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**Coordination Number-I**




Cl[NH3]Pt(NH3)Cl

Diamminedichloroplatinum

Total number of points of attachment to the central element is termed the **coordination number** (can vary from 2 to 16).

It is influenced by the relative sizes of the metal ion and the ligands and by the electronic factors, such as charge which is dependent on the **electronic configuration** of the metal ion.

These competing effects are described by the term **ionic potential** which is defined as the charge to radius ratio ( $q/r$ ).

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So, the relative sizes which are dictated by different electronic factors such as the charge; that means, what is the corresponding charge on the metal ion and charge on the ligands, if the ligands are negatively charged. They are not neutral ligands.

So, this particular charge is also dependent on the electronic configuration of the metal ion. We all know the number of electrons factor occupying the different d levels. In case of three dimension elements, whether the electrons are in the  $d \times \text{square minus } y \text{ square}$  or  $d \times y$  or that will provide us different sizes of the metal ions and we get the corresponding high spin and low spin configurations. The sizes of these high spin and low spin configurations of the metal ions are different. That is why we get in our system, in our body, in the blood, the corresponding size of the metal ions; iron in myoglobin and hemoglobin are different. And when we pass from one particular configuration to the other, and in one case it is sitting above the... In another case it is fitting nicely within the pocket of the... And that gives us a very important phenomenon in blood which is known as cooperativity.

So, this size factors are definitely a tremendous role not only in the coordination number for the different metal ions in metal complexes, but also in biological systems which are dealing with some metal ions. So, these competing effects are described by the term ionic potential. If we consider the charge and the radius and the corresponding ratio of these two, we will be talking in terms of the corresponding ionic potential. So, ionic

potential of the metal ion will control the corresponding coordination number for the different metal complexes.

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Radius ratio - the bigger the charge on the central ion, the more attraction there will be for negatively charged ligands, however at the same time, the bigger the charge the smaller the ion becomes which then limits the number of groups able to coordinate.

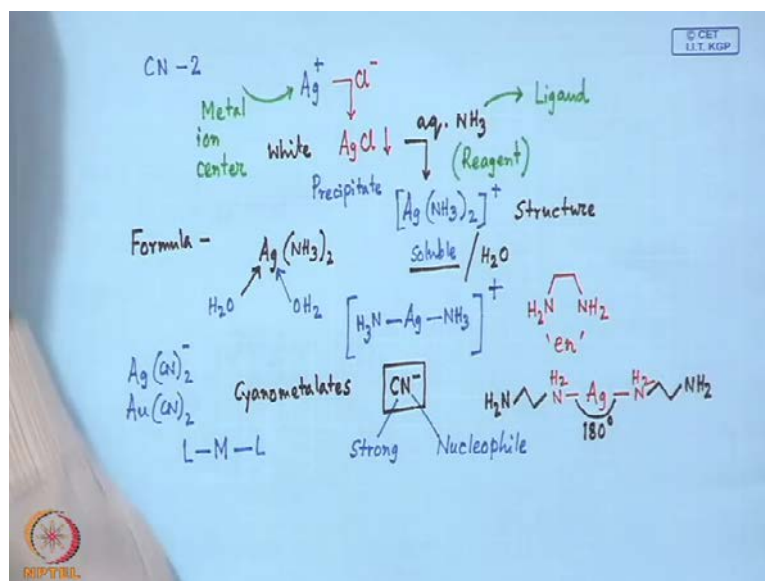
**CN 2:** Best known examples are for Silver(I). A low charge and an ion at the right hand side of the d-block indicates smaller size.



So, we get like that of our solid state geometry, the radius ratio. The bigger the charge on the central ion, the more attraction there will be for negatively charged ligands. So, if we have the negatively charged ligands like fluoride, like chloride and iodide, the more attraction there will be if the charge on the central ion is more. That means if we have a plus seven charge in the metal ion, the corresponding attraction between this charge and this negative charge will be more.

But when we have the charge, the smaller the ion becomes; that means when you have the plus seven in oxidation state for manganese, it will have a smallest size in the series, which then limits the number of groups able to coordinate. So, when the size is small we cannot accommodate or we cannot cover the corresponding metal ion by large number of ligands, though the corresponding attractive force between the positive center to the negative center is more. So, we have several situations like that of our thing where we have a coordination number of two.

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So, how we get very simply the coordination number of two which is the smallest one, where we can have a corresponding coordination number of two. And this is also giving us some practical example for identification of chloride or the silver ion.

So, when we have unknown chloride in the system in any form, we add silver nitrate, the water solution or aqua solution of silver nitrate as the reagent and we get silver chloride as the precipitate in the medium. So, once silver chloride is getting precipitated which is white in color, so we have to identify that this particular precipitation is due to silver chloride. So, what we do? We just simply add aqueous ammonia solution. And when we add aqueous ammonia solution, we should at the same time consider that we are just looking for something where silver ion is the metal ion center. And what we are adding as a reagent? Aqueous ammonia is our reagent and which can be a good ligand.

So, what we get? We can have the corresponding interaction between silver chloride and the amine complex resulting in corresponding silver amine coordination complex, which is soluble. So, we have the precipitate which is solubilizing due to the addition of the ligand as ammonia. So, what will be the structure? That is very important. So, first of all if we just exactly or precisely know the formula that silver has only the ammonia in its environment; because it is soluble and we have plenty of water molecules around. And we should also establish at this particular point that, water molecules are not interacting with the silver centers in the ammonia molecule. And this particular one will show that,

this is the corresponding structure what we can have for silver and two ammonia molecules with the cationic charge on the overall complex. So, basically we get a corresponding two points of attachment to the metal center by two ligands. As a result, we get a corresponding coordination number of two.

So, this is the well-known example for silver (I). And it has a low charge and an ion at the right hand side of the d-block indicates smaller size. So silver; copper one, silver one, gold one as well as zinc, cadmium and mercury also. So, the right hand side d-block elements can provide us only some low coordination number because the charge is less. So, when we talk about the corresponding compound as silver one or the gold one or the mercury one, we can have only corresponding coordination number of two.

And this particular case, when we get that silver chloride is reacting with ammonia giving  $Ag(NH_3)_2^+$ , what we have seen just now that the corresponding reaction is like this. Similarly, if we change the corresponding ligand from ammonia to cyanide and we get another species where the ligand is the anionic one, so what will be the corresponding structure if we have cyanide as the corresponding silver or cyanide on gold? So, cyanometallates; these are all general group of molecules which are known as cyanometallates. And this cyanometallates are providing us some complexes where  $CN^-$  is the ligand. And  $CN^-$  is a very good nucleophile and is the very strong ligand. So, it is a strong one and is a good nucleophile also. Similar to the binding of ammonia, it can also bind from two points. That means if we have M, we can have L this side and L; we can have L on these two sides.

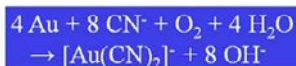
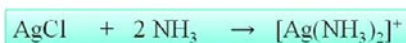
So, whenever we are talking about this coordination from this ammonia or cyanide, we can have some important information at this end time that if we have the corresponding ligand instead of ammonia, some ammonia like ligand and the organic molecule like this ... ligand, ethylenediammine. So, how ethylenediammine can react with silver(I) or gold(I)? So, in this particular case if we have the silver (I) side and if we try to have this  $NH_2$  function from this end and  $NH_2$  function from this end, we see that whether it can spend this entire range. That means, whether it can spend a angle of an angle of 180 degree, which is not permissible for a corresponding byte backbone as ethylene. So, what we will find in that? We find that we have only the monodentate coordination of ethylenediammine from one side and another from the other side giving rise to a different type of species. But only the monodentate ligands is permissible to the silver

center or if it is with the gold one it will also give the corresponding interaction from one point of attachment only.

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Radius ratio - the bigger the charge on the central ion, the more attraction there will be for negatively charged ligands, however at the same time, the bigger the charge the smaller the ion becomes which then limits the number of groups able to coordinate.

**CN 2:** Best known examples are for Silver(I). A low charge and an ion at the right hand side of the d-block indicates smaller size.



Because cyanide is a powerful nucleophile and a strong ligand, cyanometallates are generally prepared by the direct reaction of cyanide salts with simple metal salts.



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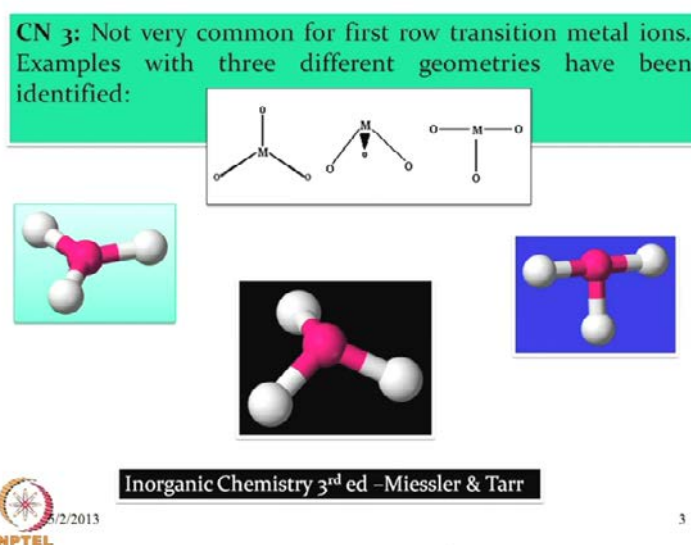
So, this gives us some important reaction also due to the formation of this  $[\text{Au}(\text{CN})_2]^-$  and whole 2 minus, which can also be true for other charged monodentate ligands like chloride, like bromides and this particular one the elemental gold. Since the cyanide is a very strong ligand, the elemental gold in the metallic form can react with cyanide in presence of oxygen and it can oxidize the gold center to the corresponding gold three. And this particular one, where the gold is present in the class three oxidation state and  $[\text{Au}(\text{CN})_2]^-$  and whole 2 minus is forming along with the formation of some eight hydroxide molecules of medium, turns to be basic from the four water molecules present over there along with one molecule of di oxygen.

Since, it is the very strong and powerful ligands of cyanometallates such generally prepared. How we can prepare all these cyanometallates is that, they are generally prepared by direct reaction of cyanide salts with simple metal salts. So, if we use the corresponding potassium cyanide or sodium cyanide, we can use it directly with the simple metal salt or some time we can use with the corresponding metal in the elemental form. So, elemental form is reacting with the cyanide giving these. And for the purification, if  $\text{H}^+$  is present in no other corresponding cationic species is present like potassium or sodium, we give this as the corresponding hydrogen from  $[\text{Au}(\text{CN})_2]^-$  whole



two. And this particular procedure, that means these corresponding complexes in procedure is useful for the purification of the gold where the gold quality is not good. Some impure gold can be treated with these and this can be list out as the salt. And followed by the deduction again, back to the elemental gold can give rise to the pure variety of gold in our hand.

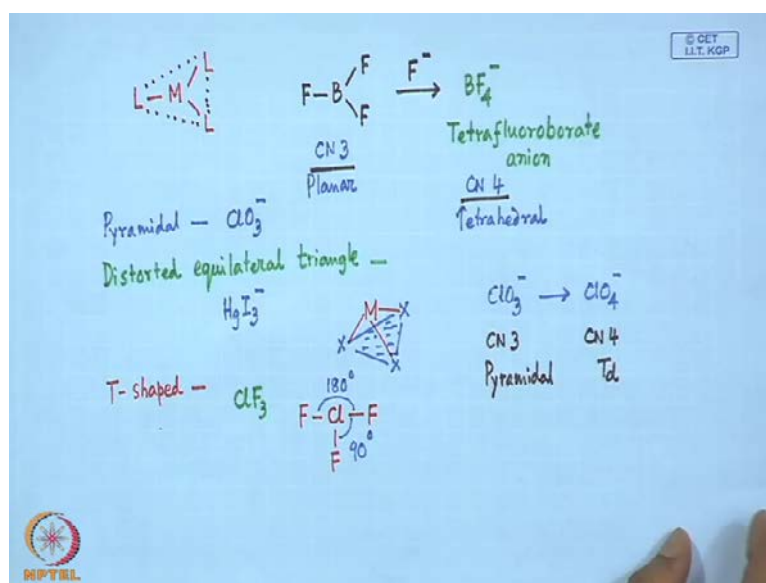
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Now, we just simply move on to a corresponding coordination number of three. So, in this particular case which is not very common for first row transition metal ions, examples with three different geometries have been identified. So, how we can get those three? So, which is simply the triangle one, while the metal center is sitting at the center and three oxygen or three fluorine or three chlorine atoms are attaching at the three corners of a regular triangle. So, if we have a regular triangle and it can bind to these three points with this oxygen at fluorine, we can get a corresponding coordination number of three. It can have a pyramidal structure at the same time. So, this is trigonal planar, this is pyramidal and this is T-shaped. The third variety is basically the corresponding one is T-shaped structure.

So, these three different configurations are pretty common. so the first one, this one, which is basically a planar one, where this particular center it can be occupied by the metal and is attaching to three ligands.

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So, if we have the metal at the center and the three ligands at three positions, three different positions of the equilateral triangle, we get this particular geometry which is known as possible for boron tri fluoride. So, boron is there which is attaching to three fluorine atoms giving rise to boron tri fluoride. And we all know one the corresponding structure because this particular can react with another fluoride anion to giving rise to a different species which is a well-known anionic species or corresponding species, which is present in so many metal complexes as tetrafluoroborate anion. So, this tetrafluoroborate anion have a different geometry and its coordination number is also changing.

So, if we have a coordination number of three on the left, we can have a coordination number of four on the right. So, this is therefore a planar geometry and this is a tetrahedral one. Similarly if we can have this particular, center is occupied by the metal. We can have three ligands at three different positions. Similarly, you can have the corresponding pyramidal geometry. So, this particular central metal ions or the other atom, if it is moved upward we can have the corresponding geometry like this. That means this is sitting above the corresponding triangular plane found by three white spheres. So, we can have the corresponding species like these.

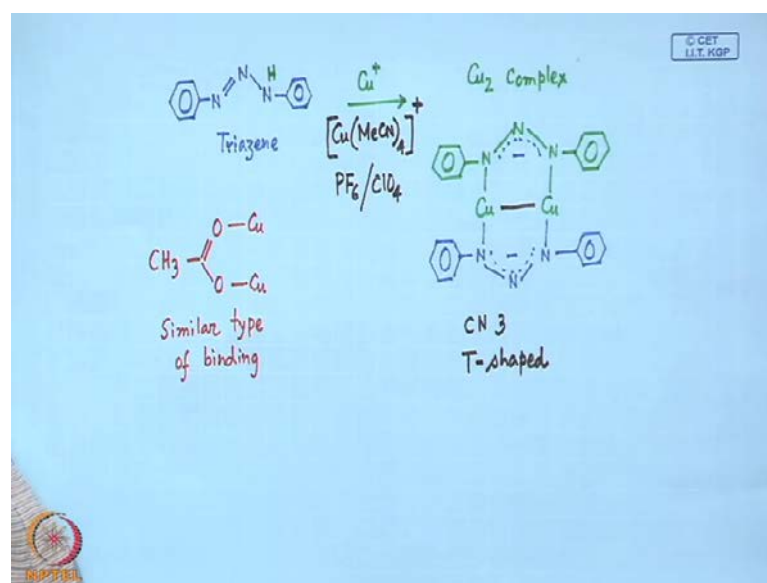
And, if we have this particular geometry which we will call it as pyramidal; so this pyramidal geometry or some distorted equilateral triangle. So, sometime we get a typical

pyramidal geometry or distorted equilateral triangle. And these are also possible to have with silver triiodide minus as  $\text{HgI}_3^-$ . So, which gives us corresponding distorted equilateral triangle geometry or sometimes some particular case, this is moving from the planar structure which we can have with that three ligands. If these three ligands are in plane and if the corresponding metal center is sitting above, we get a corresponding pyramidal geometry. And the third one, the third variety which is very important to know which is basically a T-shaped geometry; where these two atoms which are 180 degree apart, giving rise to an angle of 180 degree from one side to the other. But the third one is in between which is giving 90 degree to each other.

So in this particular case, if we have a planar geometry we will be getting an angle of 120 degree along the metal center. If this is a pyramidal structure, we get around 105 degrees, but when this is T-shaped we get two types of bond angles. So, metal ligand bond are different. So, this particular M L and this M L will have an angle of 90 degree. This L M L angle is also ninety degree, but this L M L angle is 180. So, this T-shaped structure which is not very common.

So, all the different types of the T-shaped molecules like that of this pyramidal one because one more example for this pyramidal structure is  $\text{ClO}_3^-$ , the chlorate anion. So, when we move from the chlorate to or chlorate, we get a corresponding structural change as well as the coordination number change here like this,  $\text{BF}_3$  to  $\text{BF}_4^-$  conf change, here also we get a corresponding coordination number of three to coordination number of four. But in this particular it was a change from pyramidal to a tetrahedral structure. Here, we have a instead of planar structure we have a pyramidal to a tetrahedral geometry. So, the best example for inorganic molecule having a T-shaped structure is  $\text{ClF}_3$ . So, this  $\text{ClF}_3$  gives us some immediate idea that some metal complexes can also have this type of geometry. So, this geometry is not very uncommon with an angle of 180 degree on this side and another at an angle of 90 degree on the other side.

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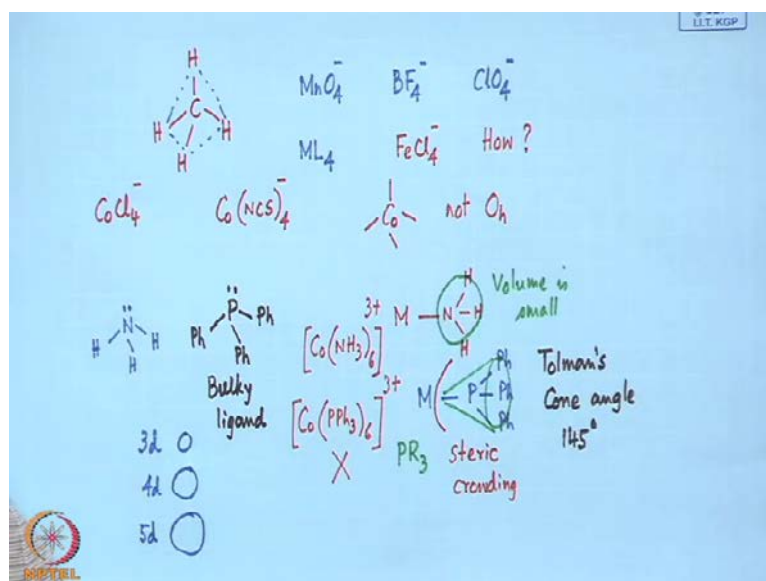
So, how we get this from a typical coordination compound? So, if we have a typical organic ligand like this, which is known as the corresponding triazene. So, the reaction of this triazene ligand; obviously it will have one hydrogen over here, so this reaction of this triazene with copper one salt. How it goes? So, this gives a very useful molecule. It is binuclear compound. So, what we get? We get a copper two compound or copper two complex, where this nitrogen will bind one copper and this will bind to another copper. And through this, the of this hydrogen we have a negative charge on this. So on the other hand, that means the other side of the compound, we can have the same thing with one negative charge.

Since both the two copper centers, we utilize this as a very well known starting material of copper one with coordination of 4 MeCN molecules over it and which can be a salt of  $PF_6^-$  or perchlorate. So, it can be a salt of  $PF_6^-$  and perchlorate. And now if we have some copper-copper bond or copper-copper interaction, we get a corresponding coordination number of copper centers  $CN=3$  and which is also T-shaped.

This is a very unique example where we do not have any other option for any other type of geometry. Only, if we have a copper complex we get this particular geometry. And this type of binding is very common in copper Chemistry. And this triazene type of binding is also possible if we have the simple acetate group. And acetate group also binds like this. So, the binding of these two are of similar type. So, we have similar type

of binding, which we are following with triazene and which we are also following with acetate anion. But since two such triazene molecules are rightly attaching to the copper center, we have a typical center for this copper-copper interaction. And which is basically a T-shape from both sides. So, these give us a very useful example of the center where we can have this particular geometry, which is T-shaped with a coordination number of three. So, all these examples we can have from this useful book of Miessler and Tarr.

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Then, we just move on to a typical coordination number which is very much available to us is corresponding coordination number of four. So, once we have a corresponding coordination number of four, we have in our mind the corresponding compound is the simple one which we are studying from our school days is the methane molecule. So, if it is methane molecule it will have a corresponding coordination number of four.

Similarly if we have the example of  $MnO_4^-$ , just now we have seen, then tetrafluoroborate anion, then perchlorate anion. So, all these are the typical examples of coordination number of four in a typical environment, which is a tetrahedral environment. But how quickly we get a typical example of a coordination number of four, where we have the metal center and we have four ligands. So, is a difficult choice for us when we react a typical metal ion with four such ligands such as, if we want to make the corresponding  $FeCl_4^-$ . So, how we can make this molecule and what

are the number of attachments if they are all only the Cl<sup>-</sup> attachment or some more water attachment and what are the geometry of this four chloride anions around the iron center; that will tell us the corresponding geometry of the product which we are talking as a corresponding ferrate anion.

So tetrachloroferrate anion, what will be its structure? So, this particular geometry which is tetrahedral in nature is therefore a most common one. But the other variety also we can encounter is the corresponding square planar geometry. And they are found almost exclusively with metal ions having a d<sup>8</sup> electronic configuration. So, if we have a d<sup>8</sup> electronic configuration, we think that we can have the corresponding geometry as the square planar one. So, we find that the other alternative for eight is the tetrahedral geometry. And in case of cobalt, we can have a large number of tetrahedral cobalt (II) complexes.

And the well known example we know that the corresponding tetra carbonyl nickel; so the tetra carbonyl nickel which is tetrahedral in structure and also we can have the corresponding cobalt. This FeCl<sub>4</sub><sup>-</sup> also we have seen. Similarly, cobalt CoCl<sub>4</sub> is also tetrahedral in nature. Then cobalttetrathiocyanate into anion is also tetrahedral in structure. So, these are the very good useful examples where we see that the cobalt center is preferring a tetrahedral geometry, not favoring the corresponding octahedral one. So, these are therefore, the very useful examples of coordination number of four. Then another example of the corresponding compound is tetrakis triphenylphosphine palladium. So, like surrounding the nickel center by four carbon monoxide molecule, we get tetracyanide carbonyl nickel center. Similarly, one bulky phosphine ligand we are introducing here.

So, like ammonia we have the lone pair of electrons. And those lone pair of electrons are useful to bind the middle center. So, then we can have so many types of metal complexes like hexamine, tetraamine and the pentaamine complexes. Similarly, if we just use the phosphine center with three bulky phenyl rings, so these are bulky phenyl rings. So, it is a very bulky ligand and this bulky ligand is therefore very much useful, when it is binding to the metal center. And this, we can know this binding; that means the corresponding metal amine complex and the corresponding metal phosphine complex. So the volume of this, that means, the volume of this ammonium molecule by this volume is small.

So, this particular ligand volume will not control the corresponding geometry around the metal center. But when we have these phosphine binding and we see that this particular one, we have a funnel type of structure. And this funnel type of structure can give rise to some cone angle which is known as Tolman's cone angle. And in case of triphenylphosphine it will be around 145 degree. So, these substitutions on the phosphorous atom is very important to change the corresponding cone angle. So this triphenylphosphine, it can have some other triphenylphosphine, substitute triphenylphosphine; that means we can have  $PR_3$  molecules. And depending on the nature of this R we can change the corresponding cone angle.

In some case it is less than this value and in other case it is bigger than this value. So, the changing this particular cone angle will basically have, we are just basically blocking. We are responsible to block this particular side. That means this particular one can give rise to some amount of steric crowding; that means this particular path, this particular size is not available for binding to some other ligand or some other donor atom, which was not possible in case of ammonia.

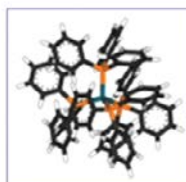
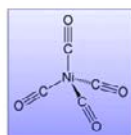
So, ammonia can have cannot have that much choice. And we can have, as a result we can accommodate six ammonia molecules around cobaltic ion; that means trivalent cobalt, which is not possible. That means, we cannot have a cobalt  $PPH_3$  whole six molecule in our hand similar to that particular ammonia; because the steric crowding would be more and will not end up with any situation where six phosphine ligands can go and cover this particular cobalt centers systematically for an octahedral geometry.

So, if we just go down for the other metal center, you can go from cobalt to rhodium to iridium; that means you can move from three dimension to four dimension to five dimension metal center; that means we want to increase the size of the metal centers like this, to this, to this. So, we can have three dimension, we can have four dimension, or we can have five dimension. So, as we move to five dimension also, when you move to five dimension we have the bigger size of the metal center, but it is not possible to accommodate this number of phosphine ligands surrounding these metal ions. So, it is not always very much useful or very much preferable to have or move from one metal center to another to accommodate the bulky ligands.

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**CN 4:** The tetrahedron is the more common while the square planar is found almost exclusively with metal ions having a  $d^8$  electronic configuration.

**Tetrahedral:** There are large numbers of tetrahedral Cobalt(II) complexes known.



Tetrakis(triphenylphosphine)palladium



4

So, one such example is for palladium. So, when we attach this particular phosphine ligands and the corresponding oxidation state also we can have; that means if we have the oxidation state in plus two, plus four or zero. So, these are the three most possible arrangements for palladium. But if we go for palladium zero oxidation state, the size of the palladium would be higher compared to palladium two plus. And we expect that we can accommodate force such triphenyl groups surrounding this palladium.

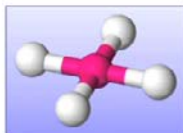
In a geometry which is very much similar to the formation of tetra carbonyl nickel center; that means a typical tetrahedral geometry. And it is the bright yellow compound what we can make with this compound and which is definitely a corresponding geometry is like these; that means a tetrahedral geometry, these are the four phosphorus atoms surrounding this palladium center. So, we can have the one triphenyl unit, the second triphenyl unit and the third triphenyl unit. And on the backside you have the fourth triphenyl unit. So, we will have four into three; that means twelve benzene rings are there surrounding this particular palladium center. That means it is sterically highly crowded arrangement. But still we can get the corresponding stability of this particular palladium triphenyl phosphine compound. And we are not getting that this particular bond is labile. That means the palladium phosphine bond is labile and it is going away. So, like stabilization of this tetra carbonyl nickel salt, we also can stabilize the corresponding palladium center in zero oxidation state as its corresponding tetrakis triphenyl phosphine derivative.



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**Square Planar:** This is fairly rare and is included only because some extremely important molecules exist with this shape.

$\text{NiBr}_2(\text{PPh}_3)_2$  was used by Walter Reppe for the synthesis of acrylate esters from alkynes, carbon monoxide, and alcohols.



$\text{NiCl}_2(\text{PPh}_3)_2$  is a tetrahedral (spin triplet) complex of Ni(II). In contrast  $\text{PdCl}_2(\text{PPh}_3)_2$  is square planar.



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So, what we get? Compared to these also, another geometry in the coordination number four is the square planar one. And this square planar geometry is also very rare and is included only because some extremely important molecules exist with this shape. That means, whenever we have the cyanide as the ligand we get, that means we have  $\text{NiCl}_4^{2-}$  and whole four two minus, and we get four cyanide groups attaching to the nickel center. And that will provide us a corresponding square planar geometry.

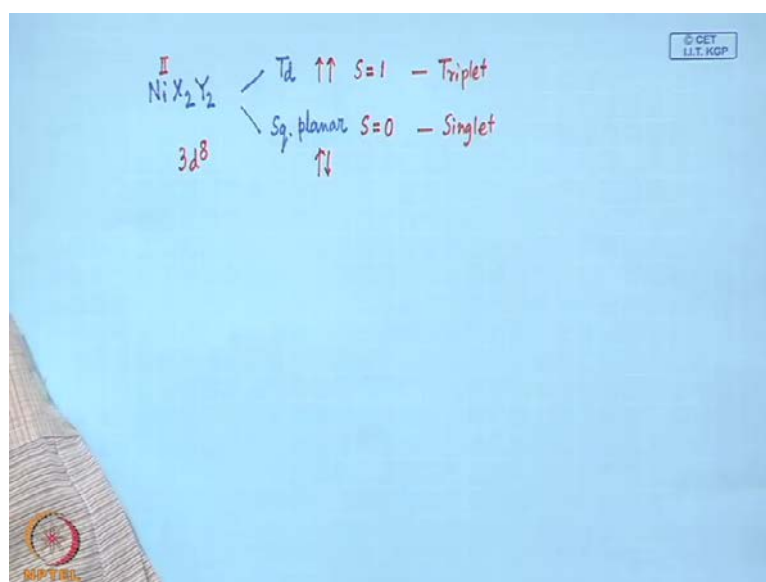
Similarly, we can have the corresponding  $\text{NiCl}_2(\text{PPh}_3)_2$  phosphine, which is used by Walter Reppe for the synthesis of acrylate esters from alkyne, carbon monoxide and alcohol. It is the typical example of the organic transformation, particularly for the acrylate based esters for the formation of polymers afterwards. But if the starting materials are very simple, which are acetylene type of molecules. That means alkynes, carbon monoxide and alcohol, and this particular compound; that means a compound with a coordination number of four.  $\text{NiBr}_2(\text{PPh}_3)_2$  phosphine two which is used as good catalyst.

And, this particular nickel is in class two oxidation state. But what should be the corresponding geometry of this compound, when we attach simple phosphine ligands to the nickel bromide salt? The nickel bromide salt is well known to us and if we attach two more phosphine ligands to it, we get a corresponding complex of nickel where the coordination number is four. So, either we can have a square planar geometry or a tetrahedral geometry like this one because this cannot remain in in the square planar

geometry. So, it will be distorted to a tetrahedral geometry. So, in square planar geometry we have the metal center and four groups attaching at four positions in a square plane. So if it is tetracyanonickelate, let us compare to tetracarbonylnickel, it is square planar and all the nickel carbon bonds attaching to the nickel C N bond groups are in a particular plane.

So, like this NiBr<sub>2</sub> phosphine, this NiCl<sub>2</sub> phosphine two is also tetrahedral in structure. And this spin triplet state, we just discuss afterwards that how we get corresponding spin triplet arrangement, which is related to geometry.

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So, if we have some arrangement of NiX<sub>2</sub>Y<sub>2</sub>. We can have a tetrahedral geometry or we can have a square planar geometry. So, this tetrahedral and square planar geometry we can have when we study in detail the corresponding electronic configurations. We will find, in all these cases the number of unpaired electrons would be different. So, we can have S is equal to some value for here, S is equal to some other value

So, in case of tetrahedral geometry we have two unpaired electrons. But here all the electrons are paired. So, if it is nickel in class two oxidation state which is a 3 d 8 configuration, so all the electrons are paired. So, we have the electronic configuration S is equal to one and here is equal to zero. So, this we will call as a singular spin state and this we will call as a triplet spin state, so in terms of this singlet and triplet definition wherever we get a corresponding compound, which is of 3 d 8 electronic configuration

which is tetrahedral; that means we have two unpaired electron, it is giving rise to the corresponding spin triplet structure of nickel two. But when we get the corresponding palladium two compound having the same number of chloride atom ligands and the phosphine ligand, we get a square planar geometry. That means a corresponding geometry is spin singlet.

So, these are the basically clues if we are able to measure experimentally the state. That means whether the complex is in spin triplet form or in the spin singlet form, we can infer immediately the corresponding coordination number as well as the corresponding geometry for this molecules. That means, whether it is a nickel compound of coordination number four or a palladium compound of coordination number four.

Thank you very much.