Advanced Transition Metal Chemistry – Classification of Ligands by Donor Atoms

Prof M. S. Balakrishna
Department of Chemistry
Indian Institute of Technology – Bombay

Lecture – 35

Classification of Ligands – Nitrogen, Oxygen

Hello everyone. Once again, I welcome you all to MSB lecture series on transition metal chemistry. In the last few lectures, we have been discussing on the classification of ligands by donor atoms. In my previous lecture, I was talking about nitrogen donor ligands and I did mention before concluding about another important class of ligands come under nitrogen donor atoms are Schiff bases.

And a variety of Schiff bases have been made and explored their coordination chemistry and applications. Let me give the preparation and some important compounds of Schiff bases. As you know, the general method of preparation involves the reaction between ketone and primary amine, it is a typical condensation reaction.

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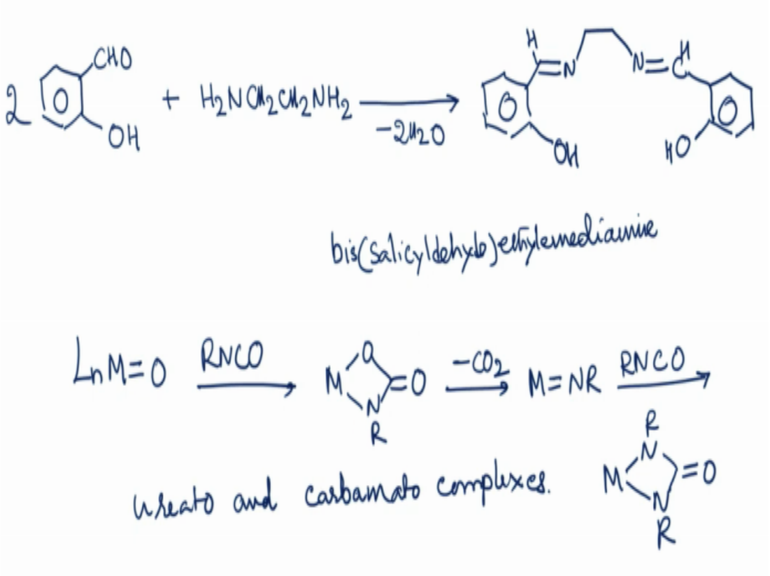

Let me take a specific example here. Just take 2 equivalents of salicylaldehyde and treat this one with ethylenediamine, gives 2 equivalents of water to form bis(salicylaldehyde)ethylene-diamine ligand. So, if you remove this hydrogen, it becomes a dianionic tetradentate ligand. This is bis(diamine). We know the general method of preparation, we can make a variety of bis imine complexes or Schiff bases.

One can also generate those things starting from for example oxides like this. When we treat this one with RNCO it can give a compound like this and this can readily eliminate carbon dioxide to form a compound like this. This on further treatment with another RNCO can give a compound like this. So, these are very important class of ligands called ureato and carbamato complexes.

So, that means we have numerous examples of nitrogen donor ligands that we saw in the last couple of lectures. And there is an important class of macrocycles, I did mention having porphyrin as a base unit.

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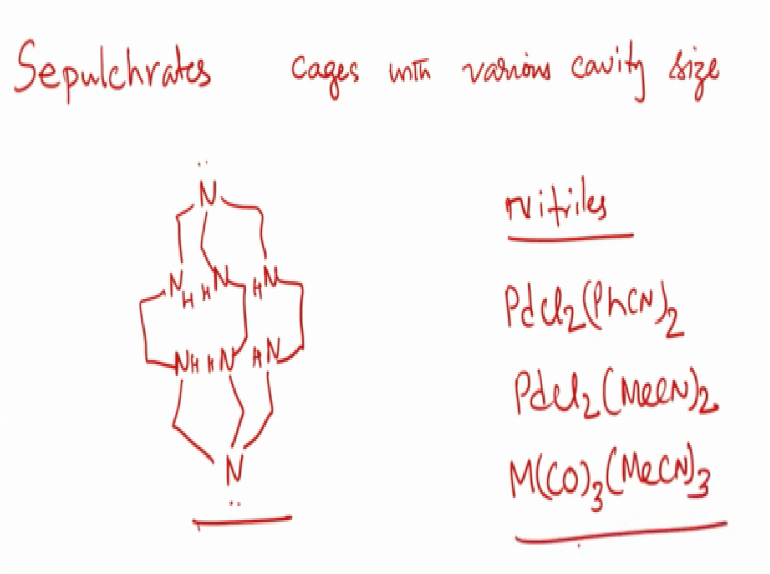

Sepulchrates cages with various cavity size

nitriles

$PdCl_2(PhCN)_2$

$PdCl_2(MeCN)_2$

$M(CO)_3(MeCN)_3$

Apart from that one we also have another interesting cage type compounds, they are called sepulchrates and they are essentially cage ligands with various sized cavities. Let me show one example here. So we have here a typical sepulchrate and you can see all of them have H on the middle nitrogen atoms. So, this is an important class and also we have pyrazolylborate, trispyrazolylborate also we come across. Of course, we can keep on discussing about nitrogen donor ligands in length.

So, at some point of time, we have to stop it and proceed to look for further donor atoms such as oxygen and phosphorus. Because of time constraints, I do not think I should be able to deal with all other nitrogen donors, nevertheless I can show you representative examples. And another class of ligands are nitriles that already I showed you while giving the preparation of important coordination compounds like acetonitrile and benzonitrile complexes.

For example from synthetic point of view, these are all very important nitrile compounds and another important component of group 6 metal carbonyls is this one, this is a very useful component. So, one can prepare this compound.

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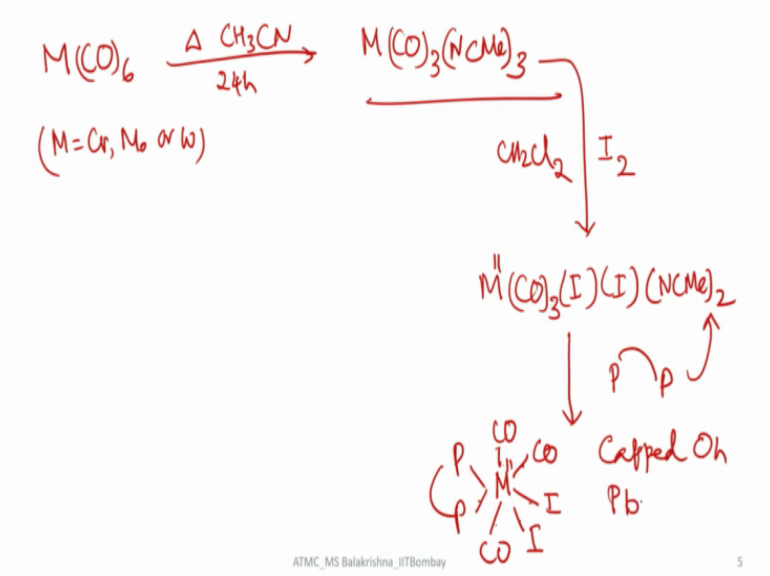

For example, you take metal carbonyl where M can be chromium, molybdenum or tungsten. Reflux for 24 hours in acetonitrile, so it gives a compound of this type. So, this is a very useful ligand. Now, you can ask me why only 3 acetonitriles have been substituted, why not 4 or 5? Yes, you should remember metal is in zero valent state and once this compound is formed it is an 18 electrons species.

Since metal is in zero valence state and more electron density is coming on to the metal, although many complexes do satisfy 18 electron rule and also another effect comes is repulsion, interelectronic repulsion that can always try to destabilize. In that context, CO being pi acceptors they can release little bit of electron density present on metal through back bonding. As a result, these back bonding capable ligands stabilizes metals in their lower valent state.

And here if we consider acetonitrile, acetonitrile is only a sigma donor and it is not a π acceptor. As a result, what happens when metal retains its zero oxidation state, now what would happen is electron density does not change, but on the other hand, number of back bonding ligands are decreasing. So, that means when we have only two sigma donor ligands, then minimum of 3 carbon monoxide are needed to minimize interelectron repulsion.

As a result, no matter how long you reflux metal hexacarbonyls with acetonitrile you cannot get more than three substituted, whether you take acetonitrile or whether you take ammonia or whether you take any other alkyl amines, you can mix it with carbonyl and amine complexes or nitrile complexes, but you have to have a minimum of three carbonyl that is an advantage also. So, one can make this one, for example now if you take this one and reflux with the toluene or something, it can eliminate all acetonitriles to form η^6 arene M(CO)$_3$ compound.

In that context, this is a very useful compound. For example, you take this one here and in dichloromethane. After formation of this compound, you can remove all the solvent under vacuum to get dry stuff. For this one at 0 degree temperature add dichloromethane and iodine, one can generate a compound of this type. Now, it will be oxidative addition, metal will be in +2 state.

So, now let us say if we add any bisphosphine, this bisphosphine is essentially substitute for this acetonitrile to form a compound like this. So, now you can see 1, 2, 3, 4, 5, 6, 7 are there. So, this is a seven coordinated compound and of course here depending upon what kind of phosphines we are using, this can have a capped octahedral geometry or pentagonal bipyramidal.

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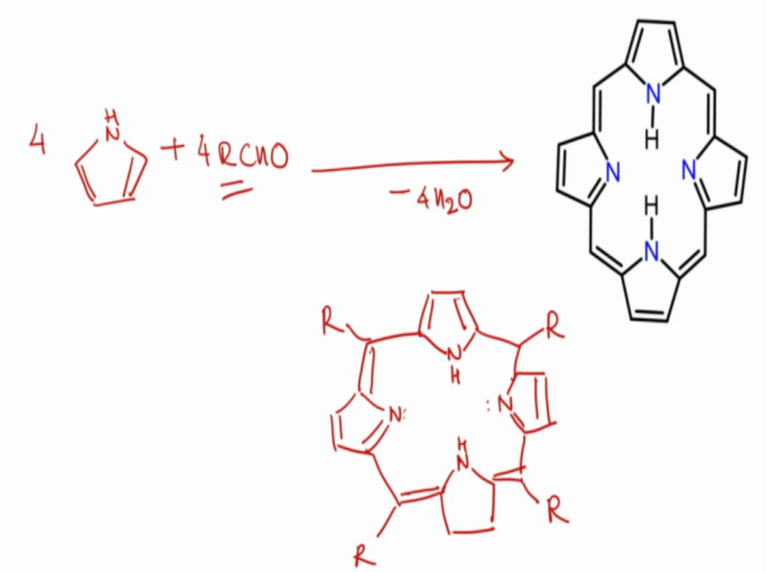

So, now another important class of compounds among macrocyclic ligands are porphyrin. This is the basic unit and it is very easy to prepare this one. One should remember here we have two N with only lone pairs whereas other two have N-H bonds, so opposite side. Now one should remember this compound can be made by simply condensing aldehydes, various aldehydes with 4 equivalents of pyrrole molecules.

For example, if you take 4, treat with 4 aldehydes RCHO, can give through the elimination of 4 equivalents of water molecules. And of course, it is very easy to write the structure. I shall show you how to write the structure, there is no need to remember the structure of this one. First, you just write prophyric units without adding double bonds and one here, one here, for these do not add any hydrogen and then connect them with a methylene bridge.

So, now since N-H is there in this one what you should do is you should start putting double bond here. When you put double bond here conjugation is there. So, one can go here and then one can go here and then only lone pair is there here, now here, next here it comes and then of course double bond is there. Now, double bond should come here, and then this only lone pair is there, there should be something you have here and then this is okay.

So, this is how one can write porphyrin unit and of course here if you take simple acetaldehyde, it will be H, whereas here it can be anything depending upon what you are choosing here. So, this is how the basic porphyrin can be prepared by simply condensing an aldehyde with pyrrole. And of course, we also come across another important cage compound used to trap cations, alkali metal and alkaline earth metal cations that is cryptand.

When I talk about crown ethers, I shall give a preparation of that cryptand as well. With this, let me conclude nitrogen donor ligands. As I said nitrogen donor ligands are very wide in coordination chemistry and starting from as simple as ammonia or dinitrogen to we have macrocyte ligands having as many as 10 to 12 nitrogen atoms in the ring or cages, very nicely they encapsulate.

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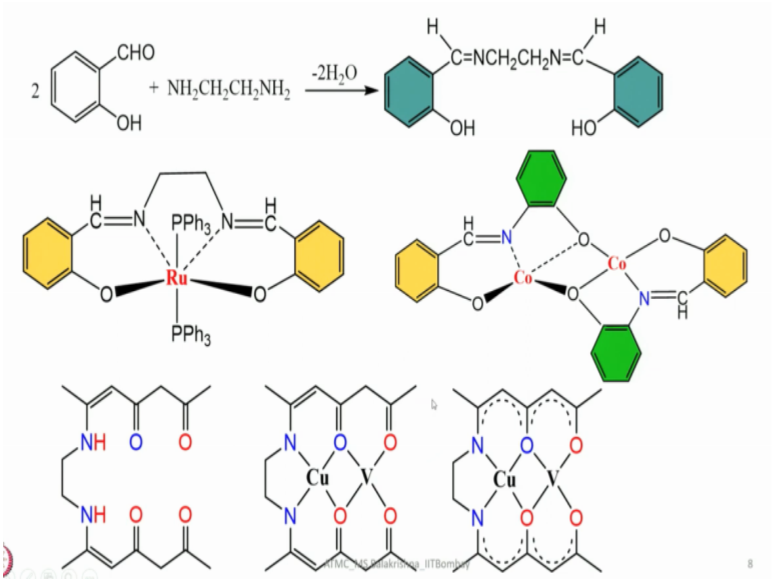

So, this is the typical bis(salicylaldehyde)ethylenediamine complex preparation here. Of course, here you can also take any alkyl one. Instead of OH you can also have PPh_2, then you have Schiff base with p donors or even s donors. And a typical example of a metal complex I have shown here, ruthenium is in +2 state, these two are anionic. And then of course, one can also make very interesting compounds like this here.

You can see two cobalt are bridged by two Schiff bases in this fashion and also they are called compartmental ligands. You can see here we have a N-H, N-H is there and oxygen donors are there and then this can also become anionic once you deprotonate these two nitrogen atoms and homometallic or heterometallic complexes can also be made.

And then once the electrons delocalize, 4 negative charges also can be seen here. This also undergo tautomerism. So very interesting ligand system, of course they come up with lot of applications. So, with this let me stop and start discussion about oxygen donor ligands.

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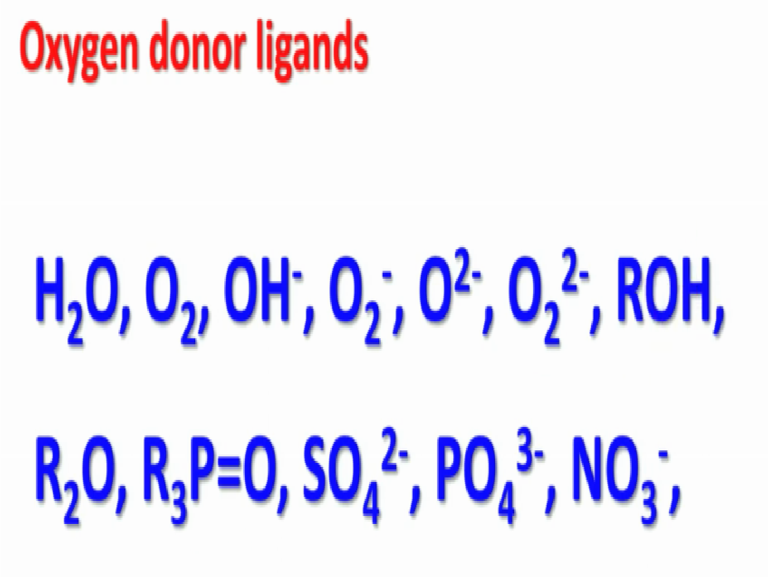

Oxygen donor ligands

$H_2O, O_2, OH^-, O_2^-, O^{2-}, O_2^{2-}$, ROH,

$R_2O, R_3P{=}O, SO_4^{2-}, PO_4^{3-}, NO_3^-$,

When we talk about oxygen donor ligands, the first ligand that comes to our mind is water and then oxygen itself, molecular oxygen itself. Of course, molecular oxygen one can reduce it, to make go to minus then that is called superoxo and then you can also have peroxo and then of course hydroxyl ligands are known like O_2^-, O_2^{2-} is also there, and all alcohols, aryl alcohol, alkyl alcohols, are all one way oxygen donors.

And then you should remember, we have two more electron pairs. Once a covalent bond is established after elimination of H, it can also triply bridge, it can also bridge three metal centres, one through covalent and other two through coordinate bonds. And of course, ethers and phosphine oxides, sulfates, phosphates, nitrates and several other ligands.

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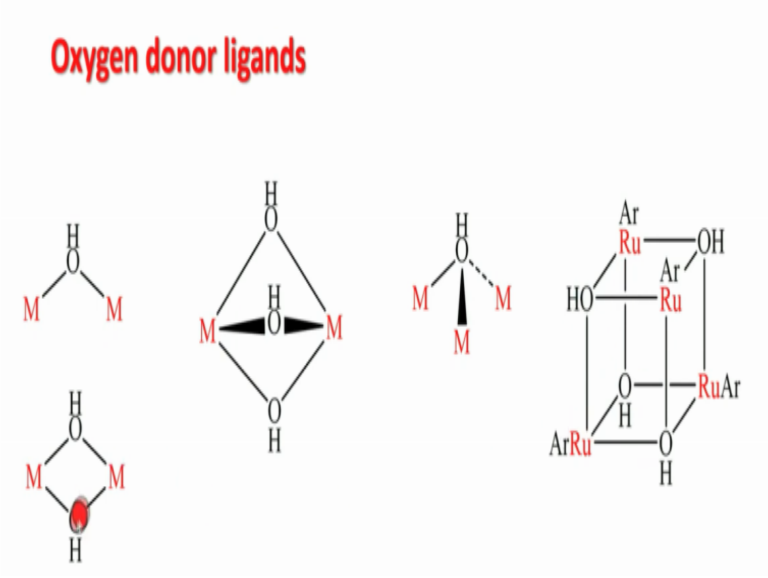

Oxygen donor ligands

So, when we look into the donor abilities and coordination modes in case of hydroxyl, it can bridge in this fashion, two metal centres also. There can be terminal one also simple M-O-H bond, and also two or three hydroxy groups can bridge two metal centres. And then this OH moiety can also bridge three metal centres or one can also have a cubane structure like this, where alternate corners are occupied by metal centres and hydroxyl groups. And one can have something like this also. These are important coordination modes or binding modes of hydroxyl ligands.

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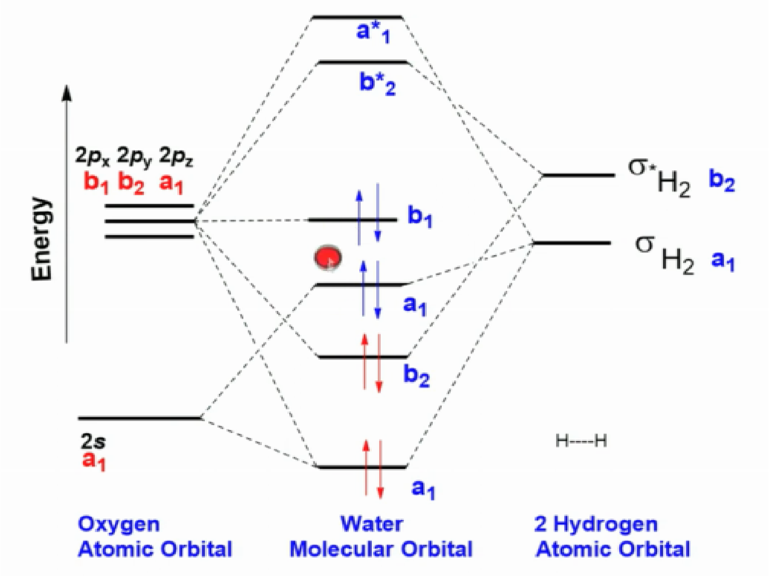

Let us look into the molecular orbital diagram of water here. Of course, we are taking the ligand group orbitals here, 2 electrons are coming from 2 hydrogen atoms and then we are getting 6 electrons here and of course you can see here, this and this one, so this is mainly OH bond and this is the second OH bond and then this is the lone pair on oxygen and this is the lone pair on oxygen, another one.

So, this lone pair itself nonbinding in nature is responsible for making water as a 2 electron donor and we normally do not come across water bridging two metal centres; acting as a bidentate ligand and as a 4 electron donor, because this is little deeply buried, because of this one, what happens, utilization of second lone pair for coordination is not possible. When attempts are made what happens, it loses one of the H and it forms a hydroxyl group and then hydroxyl group can bridge two metal centres.

As long as it remains as water molecule, normally it does not donate two pairs of electrons to perform as a bridging ligand. This for the same reason, the difference in the energy between these two is quite enormous and this is little deeply buried, as a result taking out this one for donation to a metal is not that easy.

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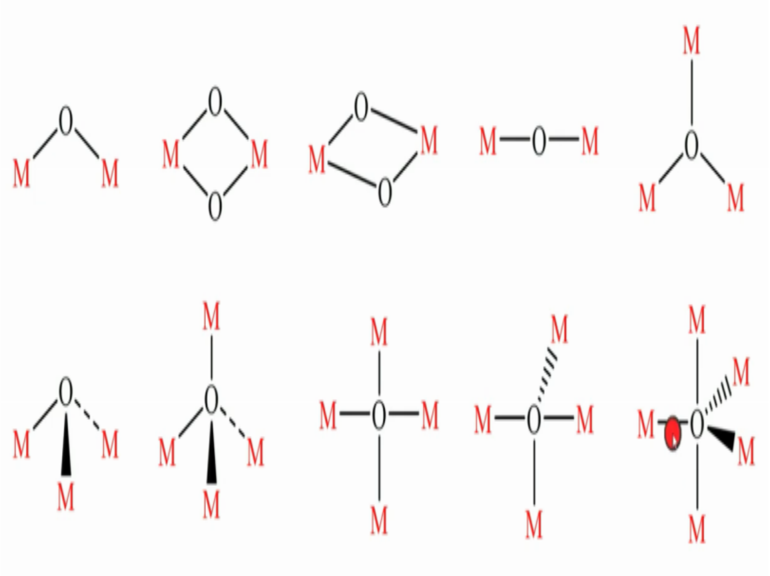

So, these are the binding modes of oxygen. One can see, oxo bridges are quite common and two oxo bridging is also quite common and this is symmetric oxo bridging, this is unsymmetric oxo bridging. So, here what you have is O is there, and then this is a coordinate bond, and then one can also have a linear bond like this, and also μ^3 bridging is also known in this fashion or in this fashion.

Pyramidal fashion, or it can also establish four metals arranged in a tetrahedral fashion or something like this or something like this is also known. In some cases, we also have examples of oxygen bridging as many as 5 metal centres, having these 5 metal centres in trigonal bipyramidal arrangement.

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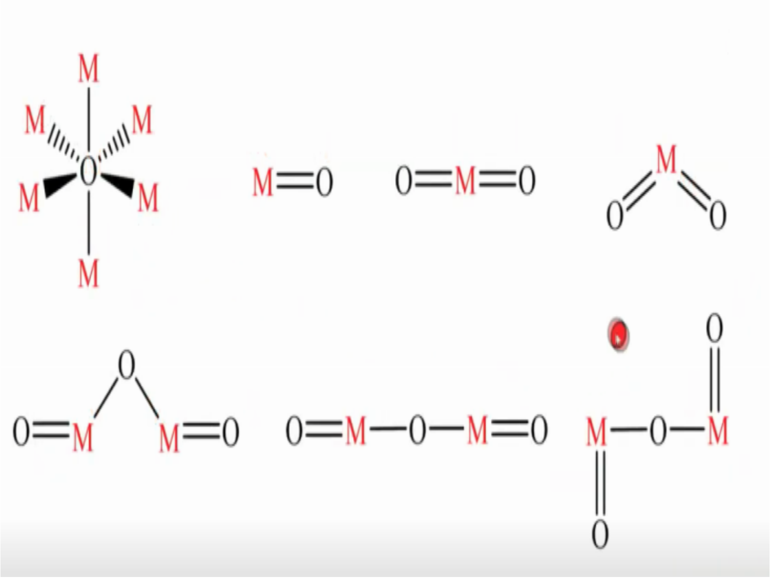

Some more example. Even it is not just 5, it can also bridge 6 metal atoms in an octahedral fashion, you can see here 6 metals arranged in an octahedral fashion directed towards 6 vertices having central oxygen atom. And of course, here another one where you have two oxygens and also you can have something like this or one can have something like this, oxo or it can be like this.

So, these are some of the most commonly seen coordination modes of various oxygen and hydroxyl group with different oxidation states. So, when oxygen is made to react with a metal centre, generally electron density is transferred from metal to oxygen with formal oxidation state of the metal and reduction of O_2.

For example, if we look into metals where we can see only one electron donor properties. In that case we will end up with super oxo complexes where we come across metals capable of donating 2 electrons or they have a stable oxidation state of +2, in that case, we can also come across oxo complexes.

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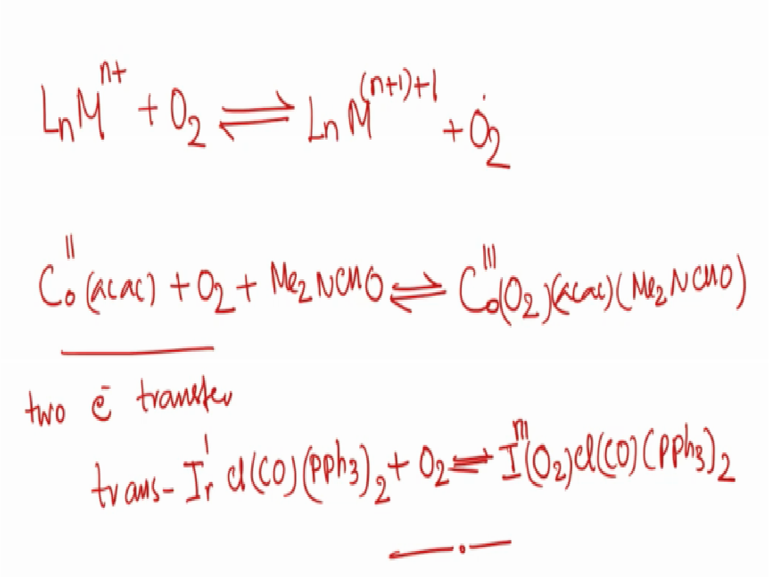

A typical reaction I shall show you. Take this one and put oxygen, so we come across this one here acetylacetonate complex plus if we add O_2, so oxidation state has changed from 2 to 3. So now you know what is the nature of oxygen here, this is about one electron donor. Let us look into two electron donor. Again, I consider a complex that you are very familiar with, Vaska's compound with iridium in +1 state.

This trans-chlorocarbonylbis(triphenylphosphine) complex, on treating this one it forms Iridium(III) complex. So, we have a few more examples of oxygen donor ligands, I do not want to elaborate more about oxygen donor complexes. For example, you consider phosphate, sulphate, carboxylate, acetate or acac, most of the ligands we talk about are all oxygen donor compounds and of course all alkoxides, aryl oxides are also oxygen donor ligands. Even simple ethers, ketones, aldehydes also oxygen donor ligands.

Let me tell you about a couple of more examples of oxygen donor ligands in my next class and I shall move on to discuss another important class of ligands, very important class of ligands that is phosphines which play a major role in organometallic chemistry and also utility of organometallic compounds and coordination compounds in homogeneous catalysis for a variety of organic transformation. Let me stop this lecture and continue in my next lecture about other ligand system.