Advanced Transition Metal Chemistry – Periodic Table
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Lecture – 7
Introduction to Transition Elements

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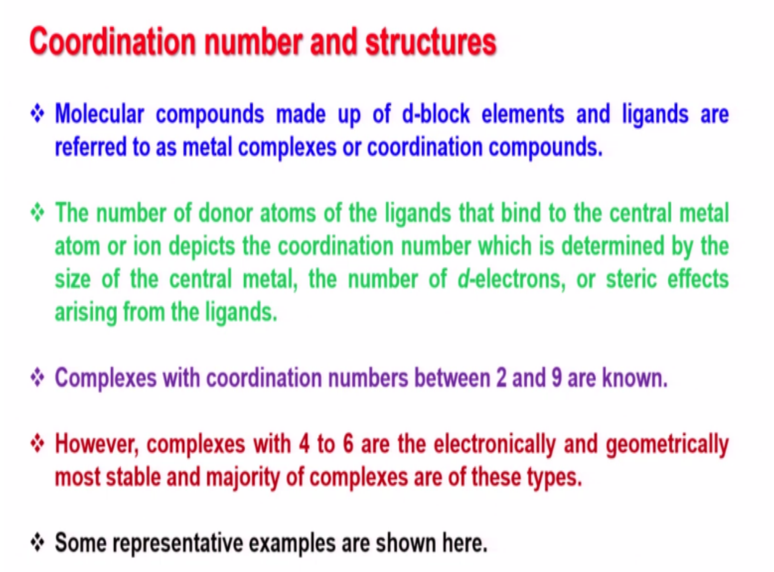

Coordination number and structures

- Molecular compounds made up of d-block elements and ligands are referred to as metal complexes or coordination compounds.
- The number of donor atoms of the ligands that bind to the central metal atom or ion depicts the coordination number which is determined by the size of the central metal, the number of *d*-electrons, or steric effects arising from the ligands.
- Complexes with coordination numbers between 2 and 9 are known.
- However, complexes with 4 to 6 are the electronically and geometrically most stable and majority of complexes are of these types.
- Some representative examples are shown here.

Hello everyone, welcome you all to MSB lecture series on advanced transition metal chemistry. This is the seventh lecture in the series. So, in my previous lecture, I was discussing about reactivity and gave some introduction to coordination number. So, let me continue from where I had stopped. So, let us discuss some information about coordination number and structure, of course later we will be discussing these aspects in a more elaborated manner.

So, molecules or compounds made up of *d*-block elements and ligands are referred to as metal complexes or coordination compounds. That means in order to call a compound as a coordination compound we should have a transition metal that should have bonding to ligands coming from main group elements. They can be group of atoms or a single atom or an ion which should have a pair of electrons that can be readily donated. So, we call it as ligand.

So, the number of donor atoms of the ligands that bind to the central metal atom or ion depicts the coordination number. So, that means the number of ligands, monodentate ligands making bond with a metal ion or metal atom is referred to as coordination number, which is determined by the size of the central metal, the number of *d*-electrons or steric effects arising from the ligands.

That means when you have a certain set of ligands whether they can offer coordination number 3, 4, 5 or 6 that depends on whether metal is capable of having that many ligands surrounding it and also the number of *d*-electrons and also the steric bulk of the ligands. All these factors are very, very important and we have to understand all these things when we talk about coordination compounds.

When we look into various coordination numbers, complexes with coordination numbers between 2 to 9 are quite well known with not only 3*d*, but also with 4*d* and 5*d*. Of course, in case of 3*d* because of smaller size, maximum coordination number we can look for is 6 having mostly octahedral geometry, and in some cases, we may have different geometries that also I will be discussing later. However, complexes with 4 to 6 are the electronically and geometrically most stable.

That means complexes having the coordination number of 4 to 6 are the electronically and geometrically most stable complexes and majority of the complexes would like to have either coordination number 4 or coordination number 6 and also depending upon the type of oxidation and type of ligands and type of metal we are considering. When the coordination number is 4, they can have tetrahedral geometry or square planar geometries. Some representative examples.

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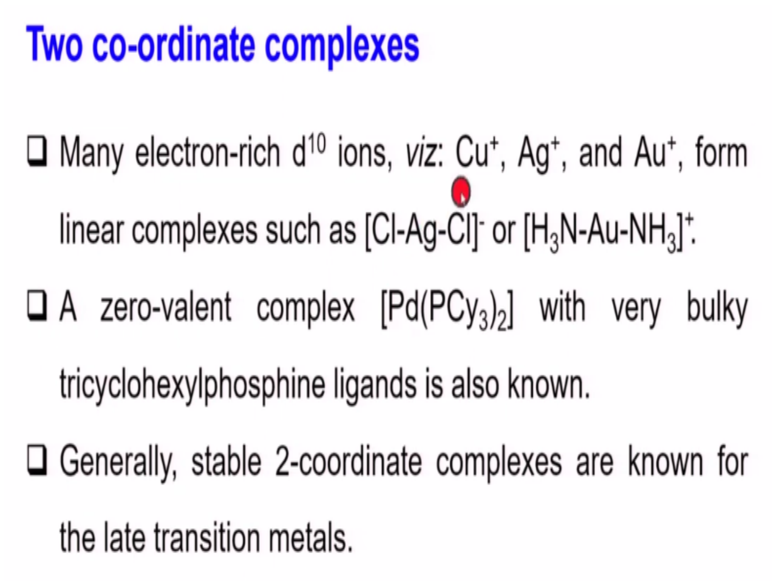

Two co-ordinate complexes

- ❑ Many electron-rich d^{10} ions, *viz:* Cu^+, Ag^+, and Au^+, form linear complexes such as $[Cl\text{-}Ag\text{-}Cl]^-$ or $[H_3N\text{-}Au\text{-}NH_3]^+$.
- ❑ A zero-valent complex $[Pd(PCy_3)_2]$ with very bulky tricyclohexylphosphine ligands is also known.
- ❑ Generally, stable 2-coordinate complexes are known for the late transition metals.

Let us look into two-coordinate complexes. So, many electron-rich ions that means particularly having 10 electrons in the valence shell or d^{10} electronic configuration. Copper 2+, copper is $3d^9\ 4s^2$ and if one electron is promoted, it would help $3d^{10}4s^1$ and if we get rid of that electron to make mono cationic and then will be having d^{10} electronic configuration.

Similarly, in case of Ag^+ and Au^+ all these three have d^{10} electronic configuration and they prefer a geometry with coordination number 2, for example $[AgCl_2]^-$ and a zero valent complex $[Pd(PCy_3)_2]$, having two coordination with palladium. That means the preference is always for four coordination in case of nickel, palladium and platinum with d^8 electronic configuration. However, with bulky ligands we should be able to stabilize palladium with two coordination number.

In this case phosphines come very handy and especially bulky phosphines, in this case tris tricyclohexylphosphine because of its bulkiness it palladium is stabilized with gold two coordination number and having linear geometry. So, another example is triteritiary butylphosphine, there also two, triteritiarybutylphosphine ligands stabilize palladium in linear geometry with coordination number two. So, generally, stable two coordinate complexes are known for the late transition metals.

(Refer Slide Time: 04:53)

Three co-ordinate complexes

Although $[Fe\{N(SiMe_3)_3\}_3]$ is one example, very few 3-coordinate complexes are known.

The three coordinate complexes are less common. One very important example I have shown here. In this case, because of the bulkiness of this amide, hexamethyldisilylamide. what happens? It is stabilizing iron with coordination three. Here one can prepare starting from iron, that is $FeCl_3$ and its treatment with lithium amide of hexamethyl disilyl. So, this is one example where a three coordinated complex can be seen.

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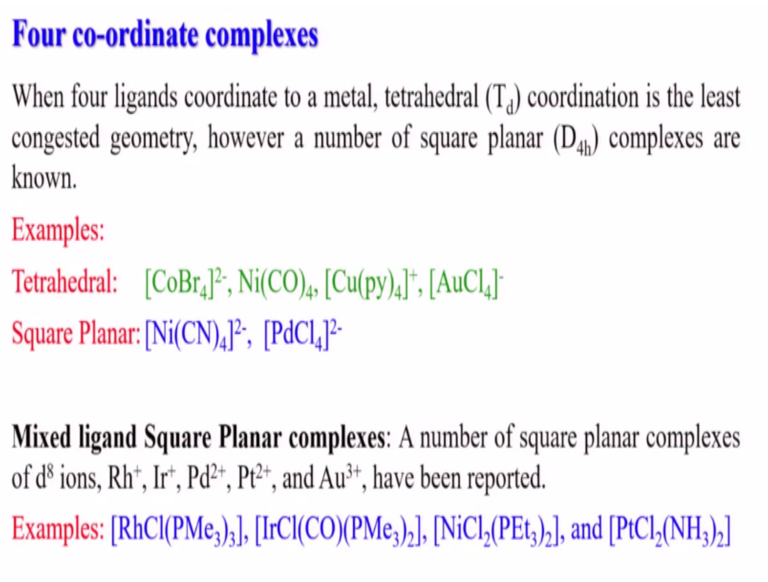

Four co-ordinate complexes

When four ligands coordinate to a metal, tetrahedral (T_d) coordination is the least congested geometry, however a number of square planar (D_{4h}) complexes are known.

Examples:

Tetrahedral: $[CoBr_4]^{2-}$, $Ni(CO)_4$, $[Cu(py)_4]^+$, $[AuCl_4]^-$

Square Planar: $[Ni(CN)_4]^{2-}$, $[PdCl_4]^{2-}$

Mixed ligand Square Planar complexes: A number of square planar complexes of d^8 ions, Rh^+, Ir^+, Pd^{2+}, Pt^{2+}, and Au^{3+}, have been reported.

Examples: $[RhCl(PMe_3)_3]$, $[IrCl(CO)(PMe_3)_2]$, $[NiCl_2(PEt_3)_2]$, and $[PtCl_2(NH_3)_2]$

And as I mentioned four coordinate complexes are very common. So, with four coordination number one can think of tetrahedral coordination or square planar complex formation. And I have given some examples here. For tetrahedral examples are $[CoBr_4]^{2-}$ or $Ni(CO)_4$ or tetrapyridyl copper plus, $[CuPy_4]^+$ or $[AuCl]^{4-}$. In all these cases, the respective metals are in tetrahedral environment and for square planar geometry tetracyanonickelate and tetrachloropalladate are examples.

We have plenty of examples, only representative examples I have shown here. These are all, if you see, are homoleptic complexes, we also come across mixed ligand complexes where you can have tetrahedral as well as square planar geometries. When we talk about mixed ligand square planar complexes, we come across number of square planar complexes from cobalt and nickel group.

When we look into the cobalt group with +1 oxidation state. For example, rhodium(+1) and iridium(+1) and then in case of nickel group, nickel(2+), palladium(2+), platinum(2+) and gold(3+), they have a preference for square planar geometry and we can see a large number of mixed ligand complexes. For example, if you see here this is very similar to Wilkinson catalyst, instead of triphenylphosphine we have trimethylphosphine and also here this is again very similar to Vaska's compound.

We have trans-[chlorocarbonylbis(trimethylphosphine)Iridium] compound and this is an example of mixed ligand complex having halide and phosphine and then this is well known diaminedichloroplatinum compound and of course here we also come across when we have two different type of complexes or two different type of ligands, have a square planar geometry like, MA_2B_2. We also come across geometrical isomerism *cis* and *trans*.

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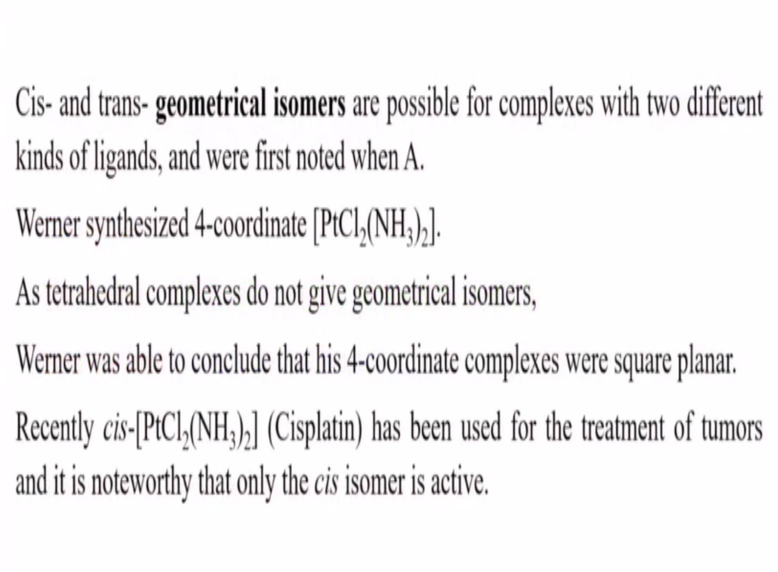

Cis- and trans- **geometrical isomers** are possible for complexes with two different kinds of ligands, and were first noted when A.

Werner synthesized 4-coordinate $[PtCl_2(NH_3)_2]$.

As tetrahedral complexes do not give geometrical isomers,

Werner was able to conclude that his 4-coordinate complexes were square planar.

Recently *cis*-$[PtCl_2(NH_3)_2]$ (Cisplatin) has been used for the treatment of tumors and it is noteworthy that only the *cis* isomer is active.

Cis and trans geometrical isomers are possible for complexes with two different kinds of ligands and were first noted when Werner synthesized both cisplatin and transplatin. And of course, I shall tell you fascinating story of discovery of coordination concepts by Werner, but tetrahedral complexes do not give geometrical isomers. Werner was able to conclude that his 4-coordinate complexes were square planar.

So, he did a series of experiment and also used conductivity measurements and also used stoichiometry and all those things to arrive at 4-coordinated square planar geometries for certain complexes and those very famous complexes are cis and transplatin. And of course, you are all familiar with the application of cisplatin. Cisplatin has been used for the treatment of tumors. And it is again noteworthy that only the cis isomer is active, but not the trans isomer.

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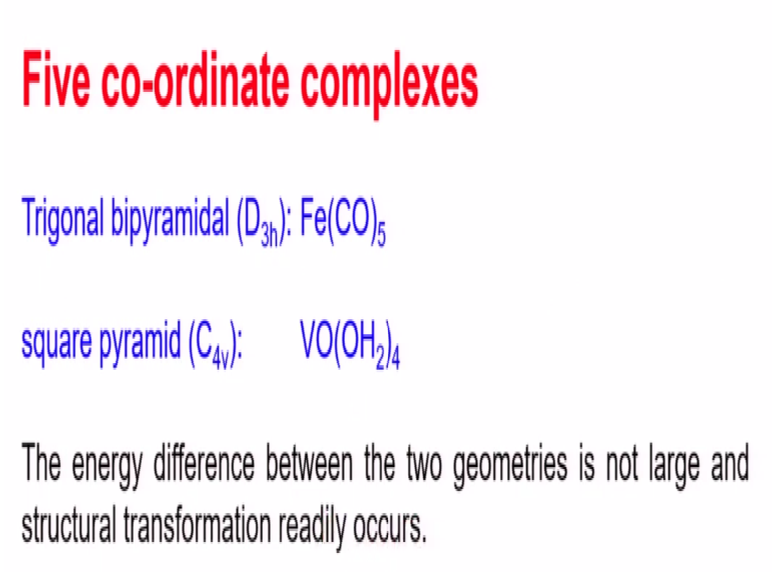

Five co-ordinate complexes

Trigonal bipyramidal (D_{3h}): $Fe(CO)_5$

square pyramid (C_{4v}): $VO(OH_2)_4$

The energy difference between the two geometries is not large and structural transformation readily occurs.

When we look into five coordinate complexes, we have quite a few examples. The preferred geometry for coordination number 5 is triangular bipyramidal geometry with the D_{3h} point group. For example, iron pentacarbonyl. In case of square pyramidal, we have this complex here having C_{4v} point group and $V(O)(H_2O)_4$. The energy difference between the two geometries is not large and structural transformation readily occurs.

And if you consider any complex having coordination number 5 always you can think of two structural isomers, one is square pyramidal, one is trigonal bipyramidal. And if the energy difference between two geometries is not significant, then you can come across some sort of fluxional behaviour and switching from one geometry to another one.

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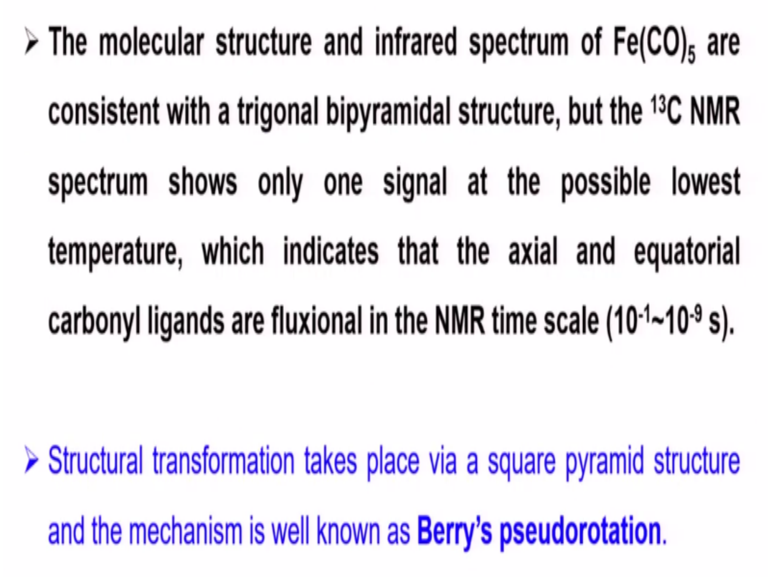

- The molecular structure and infrared spectrum of $Fe(CO)_5$ are consistent with a trigonal bipyramidal structure, but the ^{13}C NMR spectrum shows only one signal at the possible lowest temperature, which indicates that the axial and equatorial carbonyl ligands are fluxional in the NMR time scale (10^{-1}~10^{-9} s).
- Structural transformation takes place via a square pyramid structure and the mechanism is well known as **Berry's pseudorotation.**

So, the molecular structure and infrared spectrum of iron pentacarbonyl are consistent with trigonal bipyramidal structure, so it is not a square pyramidal. But when we look into ^{13}C NMR spectrum, it shows only one signal for carbonyl groups even at the lowest possible temperature. So, that means, if you just look into pentacarbonyl say trigonal bipyramidal complex, in this one we have three in the equatorial plane and two in the axial (carbonyls).

So, if strictly speaking, when we look into ^{13}C NMR, it will show two signals, one for equatorial and one for axial in a ratio of 3:2, but nevertheless even at low temperature ^{13}C NMR shows only one signal. So, that indicates fluxional process in which there is a rapid conversion of equatorial into axial and axial into equatorial. The structural transformation takes place via a square pyramid structure and the mechanism is well known as Berry pseudorotation.

We also use another example such as PF_5 to explain Berry pseudorotation. I have depicted this in the next slide, you can see here how that happens.

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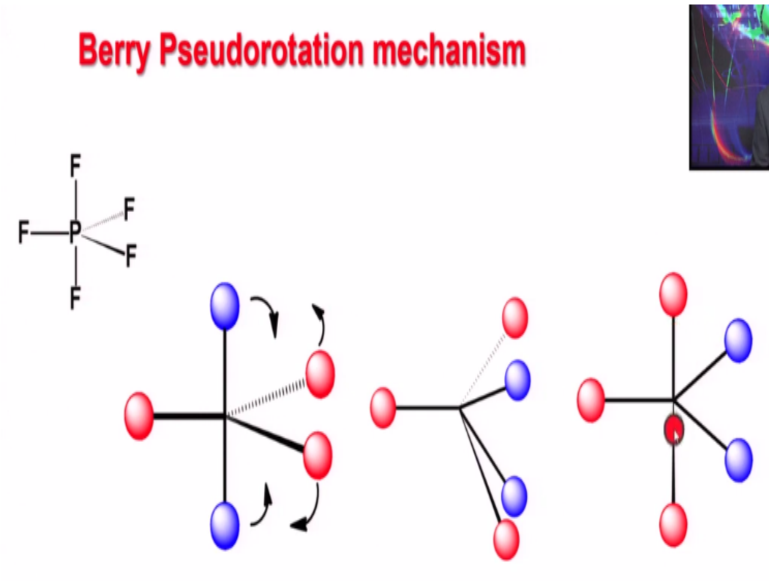

Berry Pseudorotation mechanism

For example, you consider pentafluorophosphine and this is very similar to iron pentacarbonyl. For better understanding I have given different colours for axial and equatorial ones, you see what happens, due to the fluxional process, these two axials will start moving towards the plane, equatorial, and the same time these two in the plane will start moving towards the axial position by increasing this angle.

That means simultaneously this linear angle is decreasing, and this 120 angle is increasing and we reach an intermediate stage where these two are also decreasing from 180 and these are also increasing from 120, so that we have a situation, it looks like a square pyramidal geometry. You can see these four are almost in the plane and this is in axial position. And then once the switching is completed, the equatorial ones have come to the axial position and those in the axial position have come to equatorial position.

I had a very nice model to explain, probably in my next lecture, I can show you the model for this one. It is very easy to understand, you can see clearly these two axial ones are moving towards the plane that means this angle is shrinking from 180 and at the same time these two have a 120 degree apart they will be start moving and we reach this intermediate transition stage where these four ligands, fluorides in this case, are in the plane giving an intermediate square pyramidal geometry.

And once this rotation is completed, you can see axial is turning to equatorial and equatorial is turning into axial, so this is called Berry pseudorotation.

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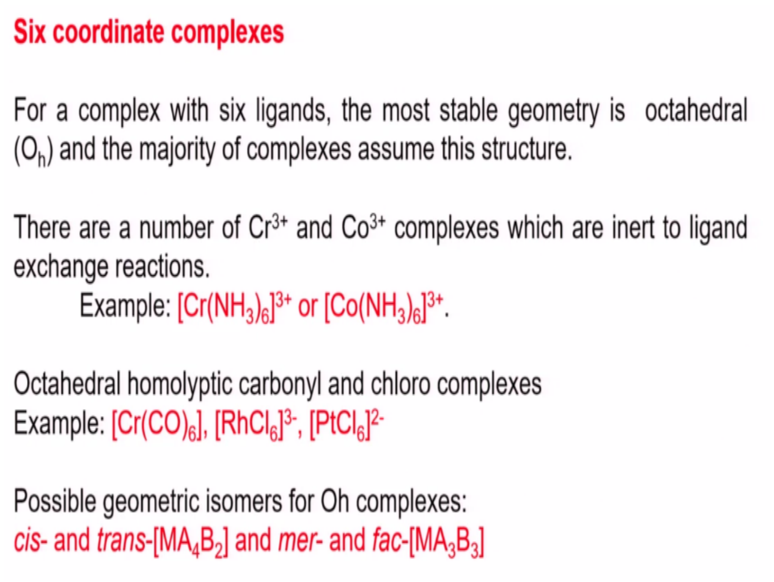

Six coordinate complexes

For a complex with six ligands, the most stable geometry is octahedral (O_h) and the majority of complexes assume this structure.

There are a number of Cr^{3+} and Co^{3+} complexes which are inert to ligand exchange reactions.
Example: $[Cr(NH_3)_6]^{3+}$ or $[Co(NH_3)_6]^{3+}$.

Octahedral homolyptic carbonyl and chloro complexes
Example: $[Cr(CO)_6]$, $[RhCl_6]^{3-}$, $[PtCl_6]^{2-}$

Possible geometric isomers for Oh complexes:
cis- and *trans*-$[MA_4B_2]$ and *mer*- and *fac*-$[MA_3B_3]$

The six coordination complexes are very common among not only 3*d* but also with 4*d* and 5*d* elements. For a complex with the six ligands, the most stable geometry is octahedral and the majority of complexes with coordination number 6 assume this structure, but there are a number of chromium3+ and cobalt3+ complexes which are inert to ligand exchange reactions. For example, if you take hexamminechromium 3+ and hexammine cobalt3+, they are inert complexes.

But usually when we make such homoleptic complexes with metal in lower oxidation states chromium2+ is labile, cobalt2+ is labile, whereas chromium3+ or cobalt3+ complexes are quite inert for ligand exchange reactions. Octahedral homoleptic carbonyl compounds and also chloro compounds are quite well known; for example, chromium hexacarbonyl, molybdenum hexacarbonyl, tungsten hexacarbonyl, iron pentacarbonyl.

So, these are all examples for homoleptic carbonyl. And herein all these carbonyl complexes, metals are in their zero valence state and this is an example for rhodium in +3 state, hexachlororhodate, you can say $[RhCl_6]^{3-}$ and also this is hexachloroplatinate, $[PtCl_6]^{2-}$, so Platinum is in +4 state. And possible isomers for octahedral complexes when we have two different types of ligands in a ratio of 2 : 4 or 1 : 2 or 1 : 1, are these things.

For example, you can have MA_4B_2 in this case you can have geometrical isomers such as cis and trans. When you have MA_3B_3, we can again have two isomers, one called *meridiona*l and other one is *facial*.

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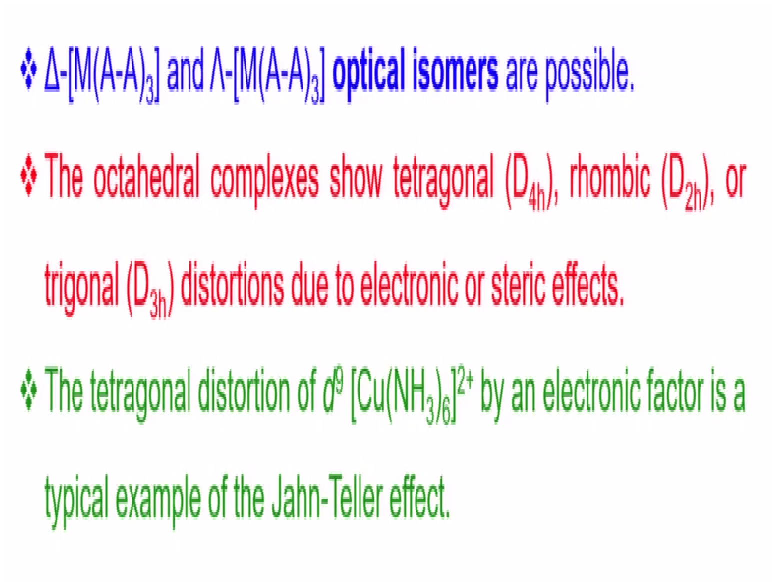

- Δ-$[M(A\text{-}A)_3]$ and Λ-$[M(A\text{-}A)_3]$ **optical isomers** are possible.
- The octahedral complexes show tetragonal (D_{4h}), rhombic (D_{2h}), or trigonal (D_{3h}) distortions due to electronic or steric effects.
- The tetragonal distortion of d^9 $[Cu(NH_3)_6]^{2+}$ by an electronic factor is a typical example of the Jahn-Teller effect.

And when you have coordination number 6 with the three bidentate ligands, optical isomers are possible. The octahedral complexes show tetragonal, rhombic or tribunal distortions due to electronic or stearic effects. That means octahedral complexes with even same type of ligands or homoleptic octahedral complexes need not be regular all the time, they can show some distortion.

And this distortion can cause elongation of two axial or it can be in the plane and thus you can come across different type of distortions and having different type of point group and of course we shall learn in more detail when we move on to crystal field theory at later stage. And tetragonal distortion in case of copper2+ cases because of d^9 electronic configuration is a typical example of Jahn-Teller effect, again I shall elaborate more about Jahn-Teller effect in my future lectures in this series.

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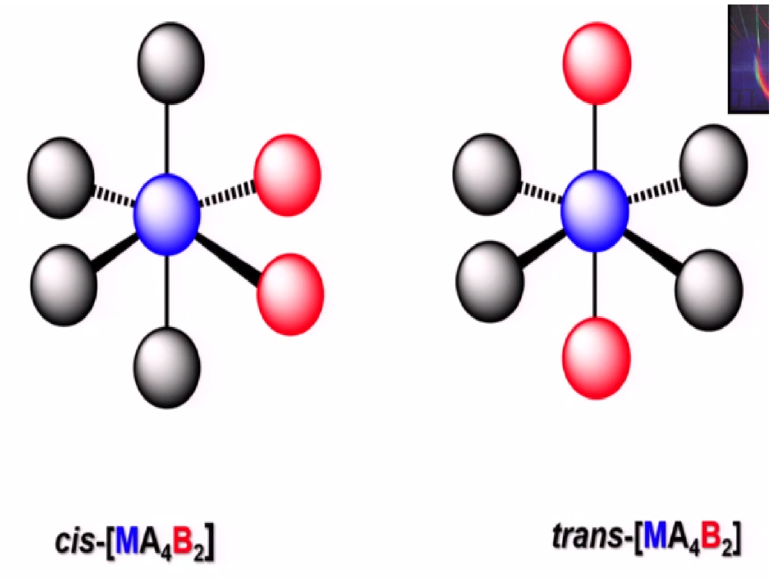

You can see here octahedral complexes having MA$_4$B$_2$ type showing cis and trans geometries.

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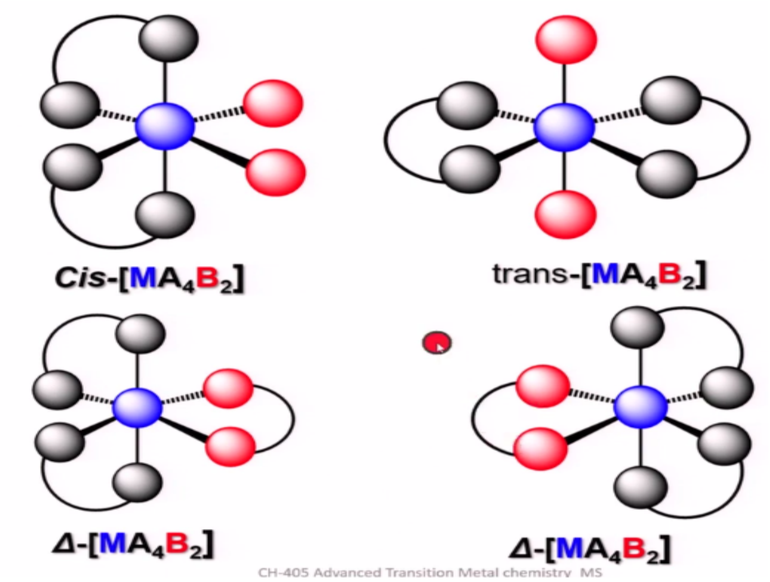

Similarly, when we have two bidentate ligands and to monodentate ligands and if the relationship of two dentate can be sis or they can be trans, when they have cis again this can exhibit optical isomerism whereas this one does not exhibit any optical isomerism because of planarity. And here when it exhibits optical isomer the nonsuperimposable mirror image will be looking like this. So, that means MA$_4$B$_2$, with B being monodentate ligand, can exhibit optical isomerism as well as geometrical isomerism.

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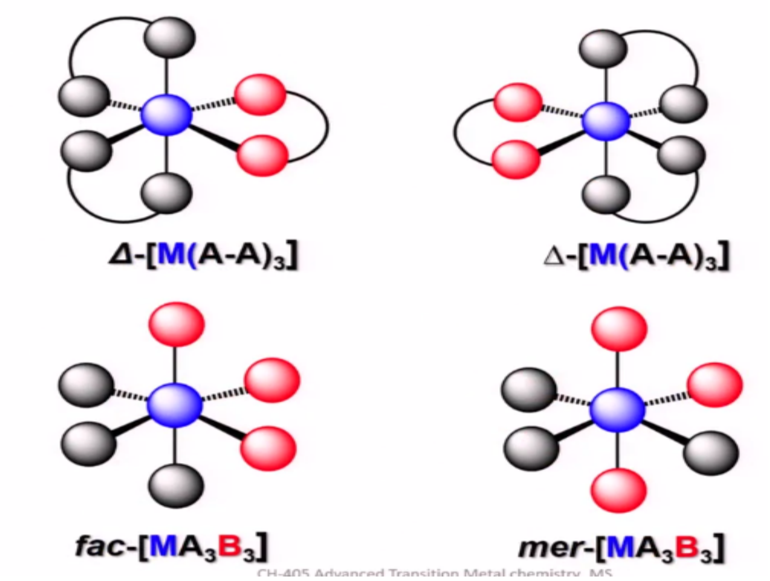

So, when we have three bidentate ligands even if it is homoleptic, just for understanding, I have given different colour here, all are homoleptic, even when they are homoleptic, you can think of having nonsuperimposable mirror image and hence they can also exhibit optical isomerism. And when you have MA_3B_3 composition, octahedral complexes having two sets of three ligands, they also exhibit geometrical isomerism.

These three ligands are in one plane, so this is called *facial*. But in this case, one set of ligands are in different phase as a result they are called *meridiona*l complexes. That means you can come across even in case of octahedral complexes, cis and trans geometries and *facial* and *meridional* geometries and also optical isomerism also.

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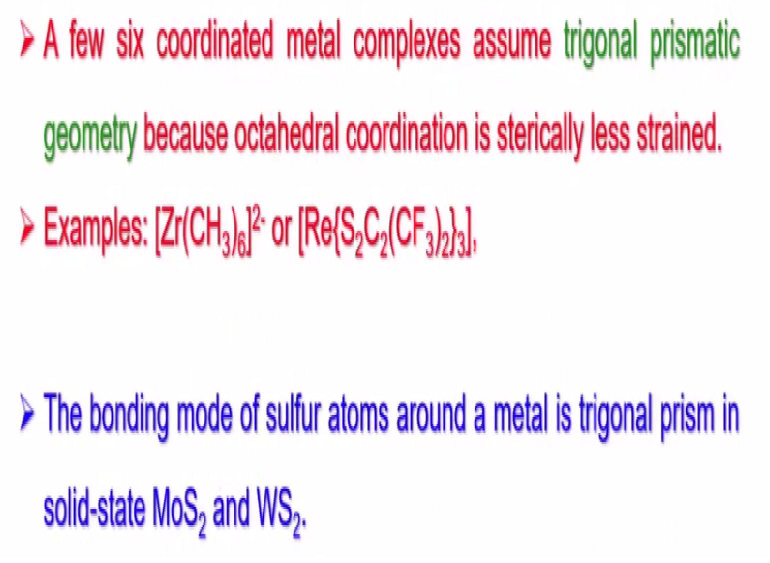

- A few six coordinated metal complexes assume trigonal prismatic geometry because octahedral coordination is sterically less strained.
- Examples: $[Zr(CH_3)_6]^{2-}$ or $[Re\{S_2C_2(CF_3)_2\}_3]$.

- The bonding mode of sulfur atoms around a metal is trigonal prism in solid-state MoS_2 and WS_2.

A few six coordinated metal complexes also can adopt trigonal prismatic geometry; preference for octahedral is there, because octahedral coordination is sterically less strained. For example, if you look into hexamethyl zirconium 2– or if you just look into this rhenium complex, in both the cases here, we have bidentate ligand and here we have monodentate ligands, coordination number 6 and in this case and also, in case of hexamethyltungsten, the geometries are trigonal prismatic.

I shall tell you why these complexes adopt or have a preference for triangular prismatic geometry or octahedral geometry when I go to bonding concepts, I shall explain all these things in more detail. The bonding mode of sulfur atoms around a metal is trigonal prism in solid state. So, for example if we consider the solid state structures of MoS_2 or WS_2, the metal is in trigonal prismatic geometry, that means metal is surrounded by 6 sulfur atoms in a trigonal prismatic way in these cases.

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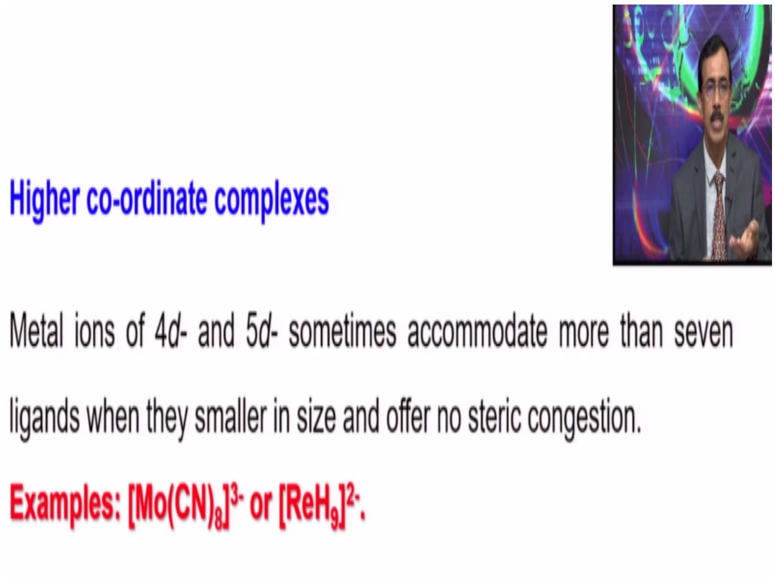

Higher co-ordinate complexes

Metal ions of 4*d*- and 5*d*- sometimes accommodate more than seven ligands when they smaller in size and offer no steric congestion.

Examples: $[Mo(CN)_8]^{3-}$ or $[ReH_9]^{2-}$.

How about higher coordination? If we think of any coordination number higher than 6, virtually it is not possible in case of 3*d* metals, but we can see in case of metals 4d and 5d because of their larger size and there are several examples of 4d and 5d metal complexes exhibiting more than seven-coordination number and hence corresponding geometries.

For example, many W^{II} and Mo^{II} complexes are known with mixed ligands such as carbonyls, halides, and phosphines having coordination number 7 adopting either capped-octahedral geometry or pentagonal bipyramidal geometry. And here I have shown one with coordination number 8, in case of molybdenum, octacyanomolybdate. Here, the geometry adopted by this one is square antiprismatic.

And in this case, $[ReH_9]^{2-}$ there are 9 hydrogen atoms surrounding rhenium, tricapped trigonal prismatic geometry. So, let me stop this lecture here. Let me continue discussing more about chemistry of transition elements in my next lecture.