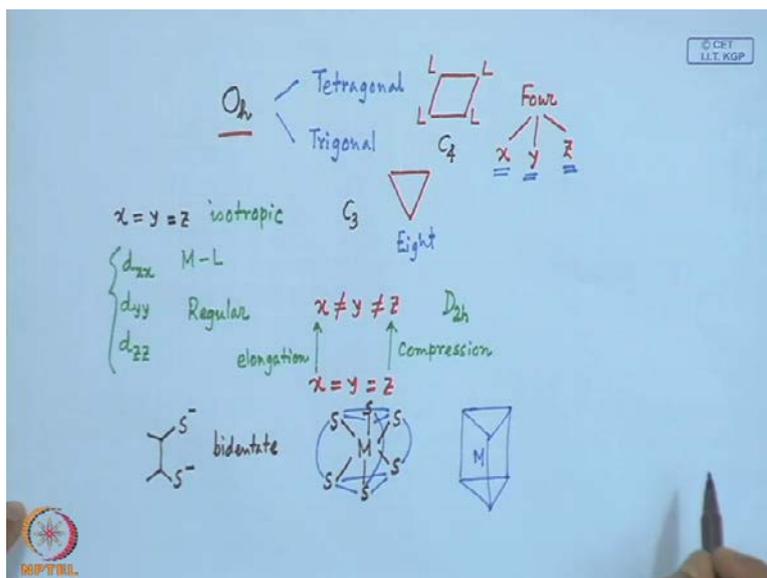**Coordination Chemistry**
Prof. Debashis Ray
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 10
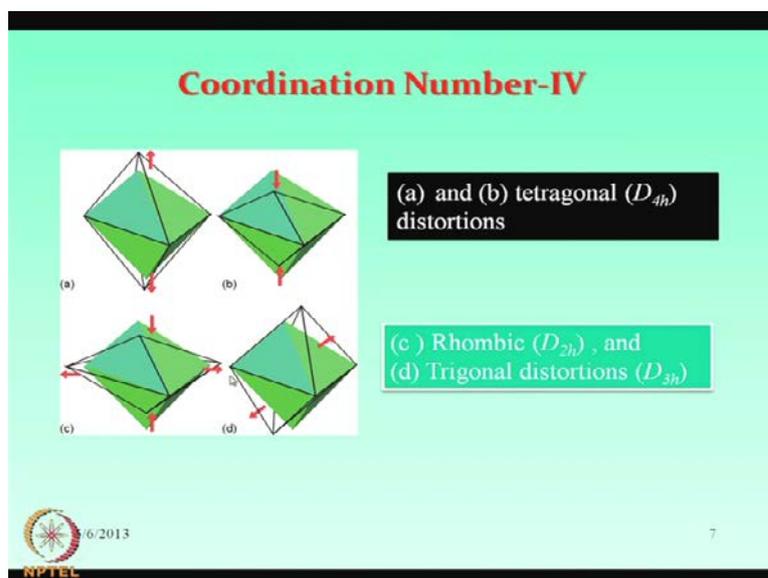**Coordination Number - IV**

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Good evening everybody. So, we will just still continue the higher coordination numbers, and we were with some octahedral geometry, and there we are just talking about the two types of distortions - one is tetragonal distortion, and another is trigonal.

So, in case of tetragonal distortion what we see, that we were focusing on a tension on a tetragon; that means the plane, which is the square plane, which contains 4 ligands, and 2 other ligands in the octahedral situation- one is above this square plane, another is below this square plane. But when we talk in terms of the trigonal distortion, we will be focusing on a tension on the corresponding trigonal planes. Because one particular octahedron can have 4 such corresponding tetragonal planes; they are mostly in 3 directions along the 3 cardigan axis x, y and z. So, we can have both the elongation and compression along the tetragonal axis - along x, along y, and along z. So, we can have elongation as well as compression along x, elongation and compression along y, and elongation and compression along z.

Similarly, in a particular octahedron, we can have 8 such trigonal faces. And along these trigonal faces which we will consider along the axis, which we will consider as the C 3 axis. So, along the C 3 axis, how the corresponding elongation and compression and distortion can take place, that will all be known as the corresponding trigonal distortion of the octahedral geometry. And in this particular case, when we are focusing on a tension on the C 4 axis, perpendicular to the plane of the square planes, we will call in then as tetragonal distortions.

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So, in this part of this lecture, of this coordination number 4, we will see that; this already we have seen, that along this axis; that means, this is the original size, the green and the corresponding colored sphere is that this corresponding. So, when they are elongated, these are the elongated positions. So, this is the original position basically. So, this is the original heptahedron.

When they are compressed, they are compressed along these 2 directions. If we consider these 2 directions are z axis, we call that, you have z axis compression; and your octahedron is typically distorted; and your, the corresponding metal ligand bond lengths along this axis are less compared to the other axis. But in this particular case, in a second situation; so these a and b, both are tetragonal distortions; we also call them, we also level them as D4h distortions.

But, the second situation, that means, the situation c and d, they are call as rhombic distortion and trigonal distortions. The second situations, what we are talking about is that along the trigonal plane; this is the C 3 plane, this is another C 3 plane. So, we have, above this we have 4. So, if we just focus our attention at this particular point altogether, this is the meeting point of 4 trigonal planes above the basic square plane, and this is also another meeting plane where we have the 4 trigonal planes are coming. So, we have these, if this is getting elongated along this C 3 axis, we get trigonal distortions; and, rhombic distortions are such that we have the compression along the z axis, elongation along y axis. So, z axis will remain untouched.

So, in this particular situation where we consider that, when all x, y and z, all these 3 axis are same, we consider them as, corresponding situation is isotropic in nature; that means, all the M L distances, we have 6 distances, so distances along the x axis, distances along the y axis, and distances along the z axis, if they are all same, we get a situation where we consider that all the M L distances all most same. So, we get a regular octahedral geometry.

But, this is not true always. So, we can have, that x is not equal to y, not equal to z; that means, we have, when we have this situation, that means how we get that, we have x is equal to y, is equal to z; when this situation is there, we do not have any other distortion. So, in one axis, we have, say, along z axis we have compression, along x axis we have elongation and y remains same, y is not changing. As a result, what happens, that x is not equal to y and y is not equal to z, we get rhombic distortion, and this distortion is known as D 2 h distortion; the symmetry level is D 2 h, and we consider this distortion as D 2 h distortion. So, this is the situation where we have the D 2 h distortion in figure c.
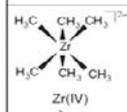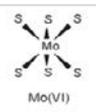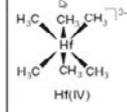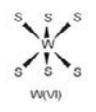
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So, if we have the distortion along the trigonal axis, we get the corresponding complexes which are not octahedral in geometry; we get a corresponding trigonal-prismatic complexes, and this type of complexes are really not found very much in number; they are rare and mostly found in solid molybdenum sulphide and tungsten sulphides. So, when this sulphide groups are packed around molybdenum and tungsten, they are getting a geometry where the coordination number is 6, but the corresponding geometry is not the position in regular spheres, like molybdenum spheres and sulphides spheres in a octahedral geometry, but they are placed in a trigonal-prismatic geometry.

A trigonal prism is also found in other types of complexes, which are diethylene type of ligands we consider, like Jantech and dithiocarbamate; these are diethylene compound, where we have the backbone, C C backbone, and 2 thiol units are present. So, is a bidentate S S ligand. When 3 such bidentate S S ligands are bound to the metal center, we get a trigonal-prism geometry.

So, we get that, we get that situation where we have the sulphur sulphur groups. And this is a different type of bidentate ligand. And this bidentate geometry, when it is bound to the metal center, we get in this form, where we find that this sulphur is there, in this sulphur is there, this is there. So, if we just consider top plane, so top plane is like this. So, this is a trigonal plane, and the bottom plane is also a trigonal plane. So, this is the first bidentate ligand, this is the second bidentate ligand, and this is the third bidentate

ligand. So, overall, the geometry is like this, and we should also be able to draw it nicely, like drawing of the octahedron. This is the trigonal prismatic structure, and we have the metal inside, and which is completely different from the octahedral geometry.

So, we see that, when we have M S 2 C 2 R 2 molecule, which will be in the trigonal prismatic geometry, and the symmetry level for that would be D 3 h; is not a octahedral geometry, is D 3 h molecule. So, this is one trigonal face, and this is the other trigonal face at the bottom; and 4 other are square plane, so 3 of these ligands over here, and 3 other ligands on this other 3 corners.

So, few more examples of these are of this type, where zirconium 4, hafnium 4, of this group, and molybdenum in group 6, molybdenum 6 and tungsten 6, this we are discussing about the MS 2 and WS 2 molecule. So, we have trigonal prismatic environment, where molybdenum is surrounded by 6 sulphur groups; here tungsten is also surrounded by 6 sulphur groups; similarly, here also the methyl groups are there, which are small there, so metal methyl. So, metal carbon bonds are there, so metal methyl groups are there. And 6 such methyl groups surrounding hafnium, and 6 methyl groups surrounding the zirconium also giving rise to trigonal prismatic complexes.

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Trigonal-prismatic complex
[Re(S₂C₂(CF₃)₂)₃]
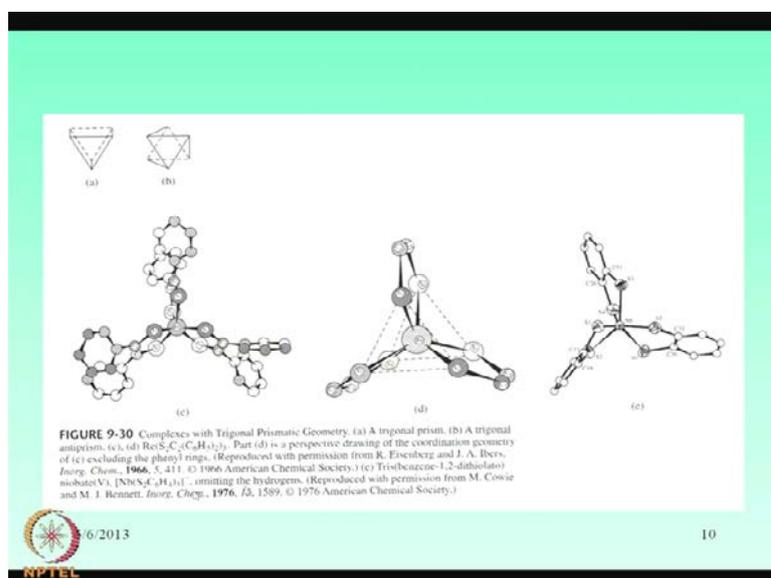
Tris(maleotriflourome thyldithiolato)rhenium (VI)
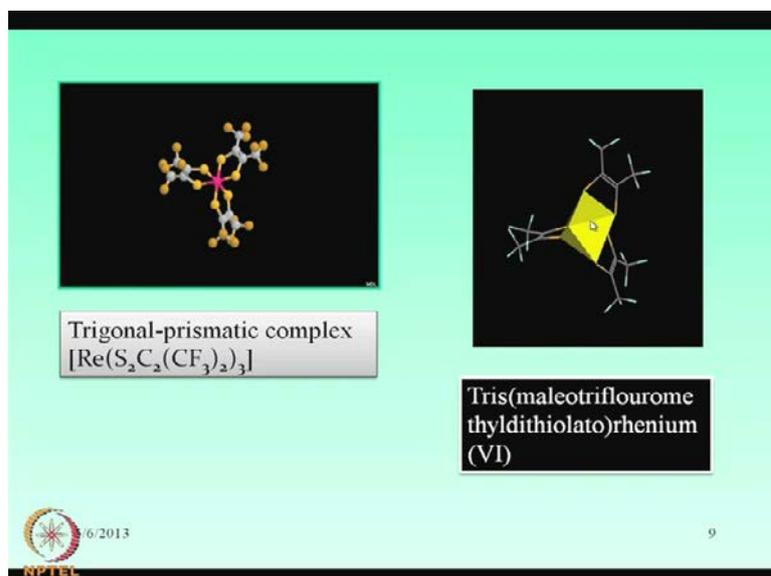
So, other example is that, is the rhenium complex; and, rhenium complex instead of Cr 3 molecule. Now, CF 3 is another possibility for the ligand system on the diethylene backbone, and that diethylene backbone is also giving again these particular

coordination. But when we draw in this particular geometry, occasionally we will think in this fashion that, it is a octahedral geometry, but is not octahedral when we draw like this, is a typically trigonal prismatic geometry.

Similarly, again another maleotriflourmethyldithiolato of rhenium compound is that, is that tris compound of this one; in another geometry, this is a, when we, showing the corresponding trigonal prismatic geometry. So, trigonal prism, this is the corresponding trigonal prism. And when the trigonal prismatic geometry is available, and the binding of these 3 ligands are like this, we get the corresponding compound in this particular geometry.

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FIGURE 9-30 Complexes with Trigonal Prismatic Geometry. (a) A trigonal prism. (b) A trigonal antiprism. (c), (d) Re(S₂C₂(C₆H₅)₂)₃. Part (d) is a perspective drawing of the coordination geometry of (c) excluding the phenyl rings. (Reproduced with permission from R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **1966**, *5*, 411. © 1966 American Chemical Society.) (e) Tris(benzene-1,2-dithiolato) niobate(V), [N(n-S₂C₆H₄)₃]⁻, omitting the hydrogens. (Reproduced with permission from M. Cowie and M. J. Bennett. *Inorg. Chem.*, **1976**, *15*, 1589. © 1976 American Chemical Society.)

So, this is another form, and is taken from some journal paper, this inorganic chemistry 76 paper, where we see that this particular geometry where we get this for the corresponding neodymium compound, and where we have the neobate compound, so d is a rhenium compound. So, this is the trigonal prism, a is the trigonal prism, basically the trigonal prism geometry; and this is, when we just rotate the top plane, when we rotate the top plane or we rotate the bottom plane, clockwise or anti clockwise, we get the corresponding trigonal-anti prism geometry. So, trigonal anti prism geometry is the corresponding octahedral geometry.

So, when we view, when we view that situation through this particular trigonal plane, we basically get 2 geometries together; that means, if we just compare the octahedral as well

as trigonal prismatic geometries together, we should see through the molecules, through this trigonal planes- one is trigonal prismatic, and this is trigonal antiprismatic. So, another name of the octahedral geometry would therefore be trigonal antiprismatic.

So, in the, this particular case, in the molecule like c and d is the corresponding rhenium compound; this is the detail of this; and, it is the corresponding positioning of the 6 sulphur atoms in a corresponding trigonal prism. So, this is one trigonal plane and this is the second trigonal plane, on the back side. And the last example is the corresponding neodymium compound, which again hydrogen atoms are not shown; and, in this particular case also, we have 2 trigonal planes one after another, and they are in eclipse geometry, giving rise to a corresponding trigonal prismatic configuration.

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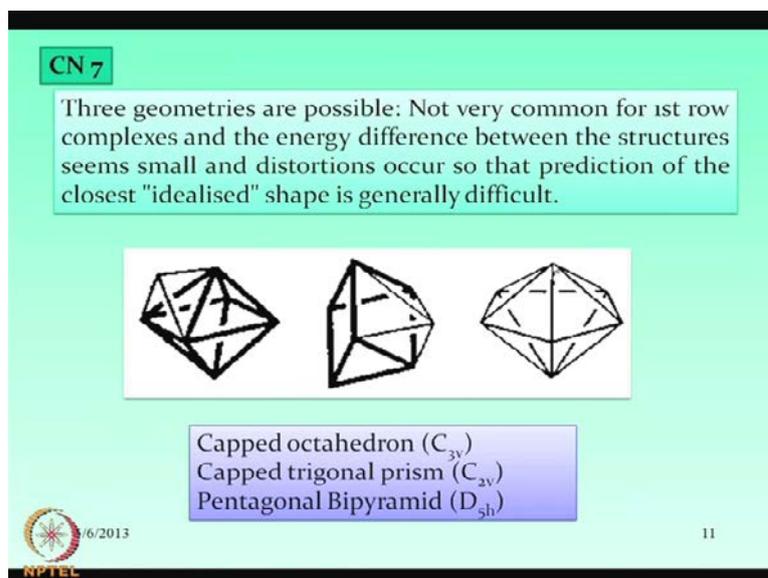
Then, we move on to the coordination number of 7. And from here, basically, we have a corresponding difficulty, because up to a coordination number of 6.
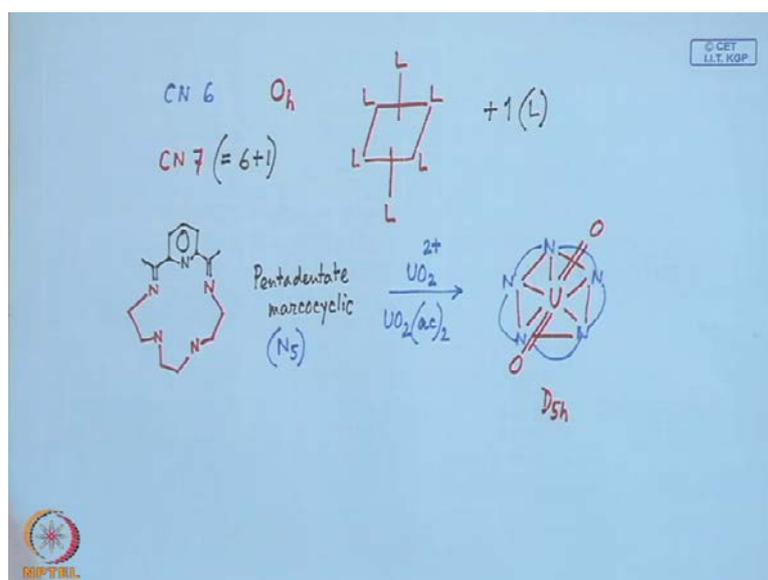
And, from a very regular geometry of octahedron, we can consider that how the 6 groups are surrounding a particular center of metal ion with 6 ligand groups, and we have a corresponding octahedral geometry. But when we move to a coordination number of 7, basically what we can do, we can add one more ligand. So, is basically a spherical arrangement, is a sphere like arrangement. So, this is highly symmetric sphere like arrangement, so to how to put the extra ligand?

The coordination number 6 should be equivalent to 6 plus 1. So, how we put? So, if all the positions are symmetric in nature, so preferentially we should take one such positions, such that we put 1 extra coordination, 1 extra ligand to get a corresponding coordination number of 7.

So, let us see, how we put that particular extra ligand? And when we put that extra ligand, we have 3 geometrical possibilities, which are not common for the first 2 elements, because we need some bigger atom, bigger metal center, such that we can put more than 6 number of ligands surrounding this particular center. So, they are seems small and distortions occur so that prediction of the closest idealised shape is generally difficult. So, these are the situation; these are the 3 situations for a coordination number of 7, where we have added 1 extra position over here, to the octahedral geometry; 1 extra position over here to a trigonal prismatic geometry; and, this is 1 other situation, where

we change the corresponding square plane from a square geometry to a pentagonal geometry.

So, these are, only 3 options we can have- one is known as capped octahedron, and the symmetry level is also changing, it is changing from OH to C 3 v; capped trigonal prism, so we are capping 1 particular face, this is the trigonal face we are capping, this is the square plane we are capping, which is known as capped trigonal prism structure; and, the third one is the pentagonal bipyramid structure, instead of a square plane we have a pentagonal plane, and above we have 1 ligand and below we have 1 more ligand to give a coordination number of 7.

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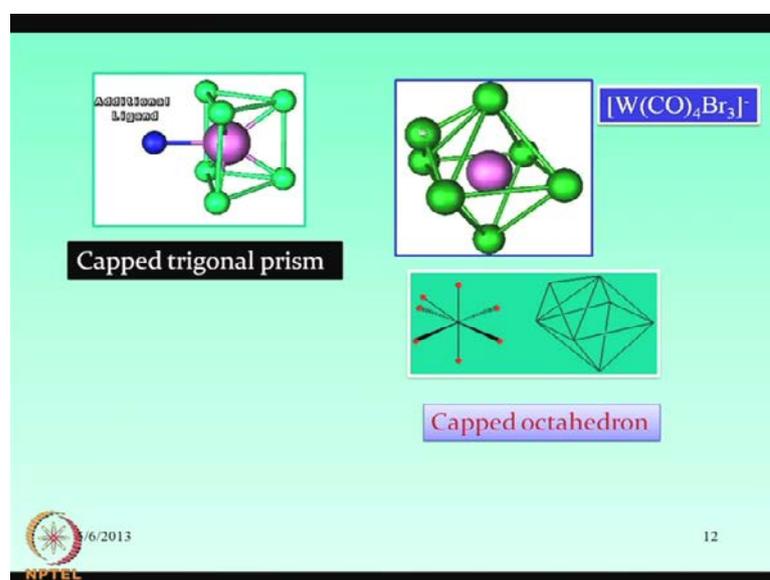
So, the first example, if we can see with that of our capped trigonal prism structure. So, already this green spheres if we can have; so we have 6 such green spheres in our hand. So, the coordination number using 6 such green spheres are 6; and we picked the corresponding additional ligand that blue ligand as the seventh coordination. So, if go from this particular square plane; so we are capping this particular square plane, this particular face of the trigonal prism by this extra donor atom, and we are capping from this side, so it will be known as a capped trigonal prism, capping from the tetragonal face.

Then, we can have capped octahedron, where we have this regular octahedral geometry connecting all 6 positions and the sphere arrangement. And if we can cap one particular

trigonal face by another atom, the another ligand atom, we get a coordination number of 7; and the positioning of all 7 would be like this. So, this 3 and this 3, are for the regular octahedral geometry, and this one is the corresponding extra. So, example for this 7 coordinated molecules are like this.

When we have this capped one, this particular one is the capped one. So, tungsten surrounded by 4 carbon monoxide ligands and 3 bromine ligands, we will give rise to this particular geometry, or one particular face is being capped. So, 3 plus 3 situation is well known to us, is can be visualized nicely also; but it can be either in one particular face, or it can be through some meridional plane. So, 3 of one type, that means, the Br ligand, and 4 of another type, that means, 3 from the other sides, and 1 extra giving rise to this 4 carbon monoxide ligands.

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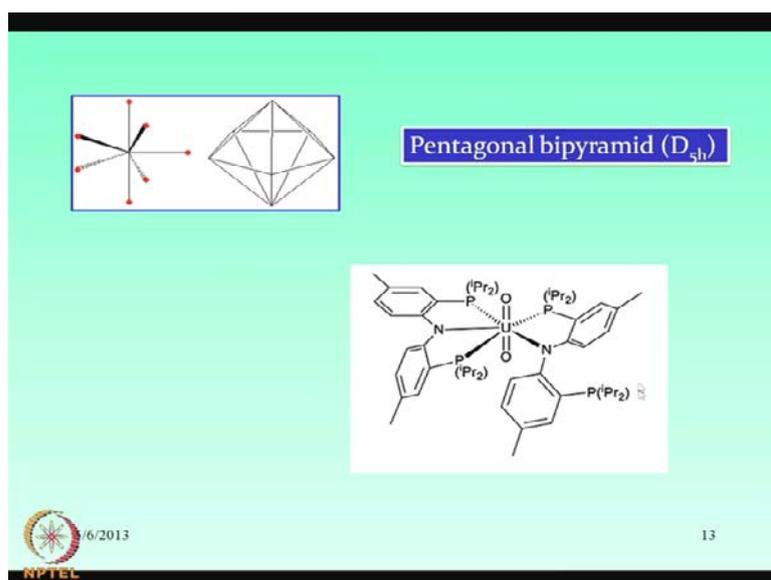
Then, we can have the pentagonal bipyramidal geometry, which has a symmetry level of D 4 h. So, we have the pentagonal plane- one above and another below. So, these are the corresponding donor points in the plane, and one above and another is below the molecule.

So, this is one particular situation where we can have this, where we have one particular plane is occupied by 2 such ligands of these. So, they are of same ligand, which is a tridentate ligand; nitrogen phosphorus bearing N P 2 type ligand; is a tridentate N P 2 type of ligand; in one half, it is just coordinating through 1 phosphorus, nitrogen and

phosphorus, so this ligand is fully coordinated to the uranium center; is a diuranium like molybdyl and vanadyl molecule; and, other ligand is not coordinating through this phosphorus, it is only coordinating through 1 phosphorus and 1 nitrogen; that means, it is bearing as a bidentate ligand system. So, that is why the ligand, the organic ligand parts are providing 3 plus 2, 5 coordination positions.
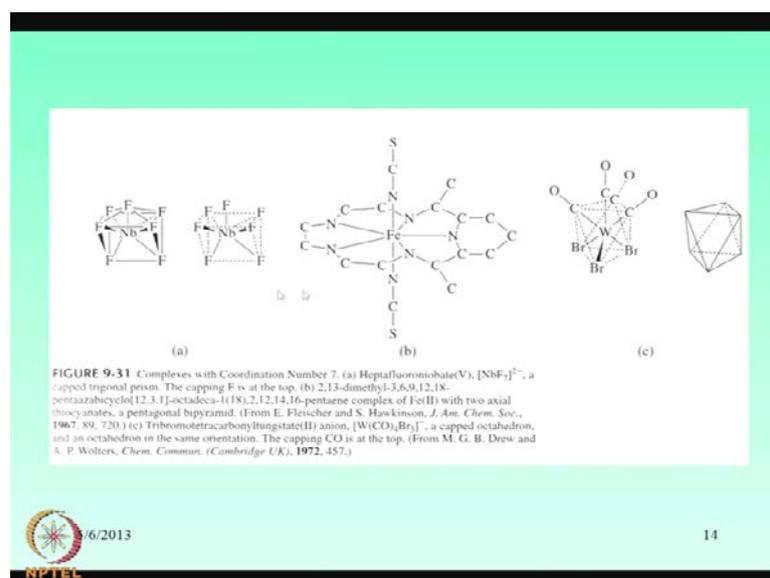
So, the 5 coordination positions from this particular pentagonal plane; one oxo is above the pentagonal plane, and another oxo is below the pentagonal plane. So, this sought of situation can also we can get, if we have a ligand system, which is pentadentate deriving from 2 6 diacetyl pyridine. So, this is 2 6 diacetyl pyridine.

So, when 2 6 diacetyl pyridine is condensed through some 6 base condensation reaction with tri ethylene tetramine, this is tri ethylene tetramine. So, we get a corresponding ligand system which is pentadentate. And since, it is a typical cyclic ligand, which is therefore, can be leveled as pentadentate macrocyclic ligand. So, this pentadentate macrocyclic ligand, when it is reacting with u O 2, u O 2 type of metal center. So, it is u O 2, 2 plus. So, it can be uranyl acetate also, uranyl acetate is a well known static material, we use in the laboratory also.

So, when it is reacting with u O 2. So, we have basically the ligand system is N 5 pentadentate macrocyclic, which can bind to the metal center through 5 nitrogen atoms. So, we now see that how this particular pentadentate macrocyclic ligand looks like. So, it will be this nitrogen, it will be the second nitrogen, this will be the third nitrogen, fourth nitrogen, and the fifth nitrogen.

So, basically what we get from here is a situation where we have a pentagonal arrangement. So, if our uranium is coordinating over here, so we get 5 bonds from one plane, and this double bond is here, and another double bond- above and below the pentagonal plane. So, we get a pentagonal bipyramidal geometry, where symmetry level would be D 5 h. So, we get also a macrocyclic ligand where the restrictions are there for this geometry.

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FIGURE 9-31 Complexes with Coordination Number 7. (a) Heptafluoroniobate(V), [NbF₇]²⁻, a capped trigonal prism. The capping F is at the top. (b) 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]-octadeca-1(18),2,12,14,16-pentaene complex of Fe(II) with two axial thiocyanates, a pentagonal bipyramid. (From E. Fleischer and S. Hawkinson, *J. Am. Chem. Soc.*, 1967, 89, 720.) (c) Tribromotetracarbonyltungstate(II) anion, [W(CO)₄Br₃]⁻, a capped octahedron, and an octahedron in the same orientation. The capping CO is at the top. (From M. G. B. Drew and A. P. Wolters, *Chem. Commun. (Cambridge UK)*, 1972, 457.)

This is also another type of ligand system, where we have restricted our thing is, that we have 5 donor atoms in one particular plane. And if it is iron center, so one will be bound above the plane and another will be bound to the below the plane. If they are thiocyanate, so this is also a thiocyanate complex, using a macrocyclic ligand similar to that what we have just shown. And another is that heptafluoroneobate compound, heptafluroneobate compound is also a capped trigonal prism structure. So, this capped trigonal prism structure, we have tracon moderate 7 fluorine ligands surrounding this niobium. So, this is one particular form.

Then, we have, what we have shown just now, is the corresponding geometry for the capped, corresponding capped trigonal prism structure for tungsten Co 4 Br 3. So, Br 3 in one particular face, one trigonal face we have the Br 3 units; in another trigonal face we have 3, corresponding 3 C O units; and one is above this particular face, that means, it is capping. So, this is the cis particular structure where we have the capping C O is at the top. So, this capping C O, this capping C O will be here. So, below we have 3 Br and we, another case we have 3 C O, still we have 4 C O from this particular face, though we have some steric crowding.

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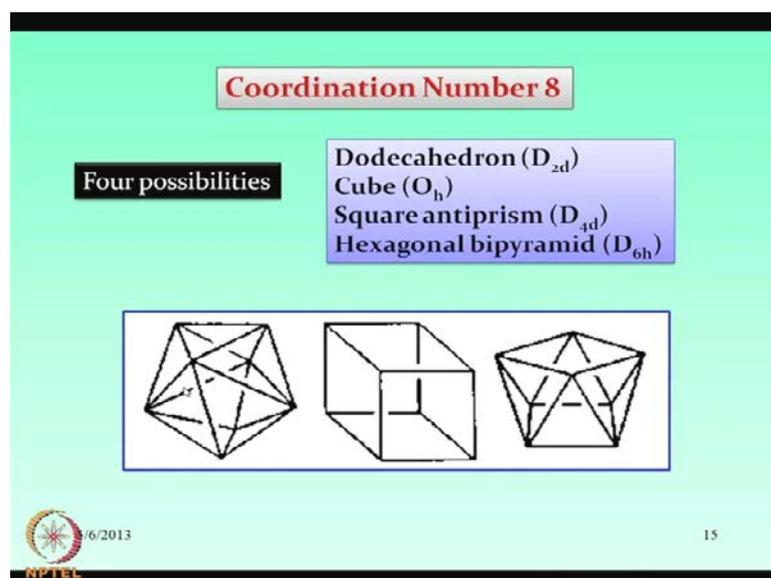
So, now, we move on to a coordination number of 8. Above 7, we are just moving to a coordination number of 8. And again in this particular case, we have 4 possibilities. And the much and much, the corresponding polyhedral levels are complicating, complicated. So, we should little bit slowly remember all these names. And first of these, is the cube arrangement. So, whatever we are just now discussing about the octahedral geometry, which can be derived from a typical cube arrangement.

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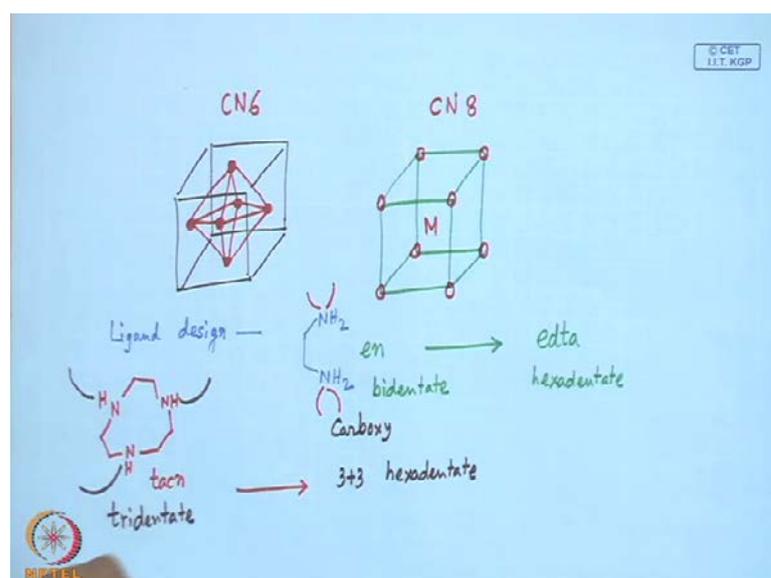
So, if we just see, how we can draw a nice cube, so this is the cube. So, how we can derive a octahedral geometry out of a cube, because we are talking a corresponding coordination number of 6. So, we have one ligand here, another ligand here, another ligand here. So, all the central positions of the 6 faces of the cube, so if we just connect all them, we get a nice octahedral. So, this is the octahedron what we can have within the corresponding cube arrangement.

So, now, if we just consider that we have increased; we can increase the corresponding coordination number from 6 to 8. So, we have, instead of the center positions of all the 6 faces, now we can have the ligands which are occupying these positions; that means, all the corners of the cube which will give rise to an arrangement, which has a coordination number of 8. So, metal will be at the center.

So, one such arrangement will be the cubic arrangement, and cubic field is, symmetry wise which is same, which has a symmetry level of O h also. Then cube is the square prism, like that we are relating the octahedron with the trigonal prismatic structure. But if go for a square antiprism structure, the symmetry level will be changed from O h to D 4 d. Then we have the dodecahedron geometry which has a D 2 d level, and hexagonal bipyramid like that of our pentagonal bipyramid. The pentagonal bipyramid, just now we have seen it. Similarly, if the plane you have is the hexagonal one, then above we have one point and below we have another point, we get a hexagonal bipyramidal geometry of coordination number 8, with a symmetry level of D 4 h.

So, this is, are the situations. This is cube structure, this is square antiprism, this is one square, and this is another square. So, if we just rotate the top plane. So, top plane will be rotated, and if they are connected each other we get a square antiprism structure, where we have 2 of this faces are square face; like this face, we have 6 square faces in a cube structure; here we have 2 of these are square faces; but others are 1, 2, 3, 4, 5, 6, of them are corresponding trigonal faces.

So, 6 plus 2 again 8 faces, but our face number is also changing when we move from cube to a square antiprism. And this is dodecahedral structures. So, we have the corresponding one structure, there we get this particular one. So, we have 4 at the top and 4 at the bottom. And we basically, these 2 corners we distort. If we move these 2 corners

upward and these 2 corners downward, we get this arrangement. So, distortion from a cube, also give rise to a dodecahedral structure.

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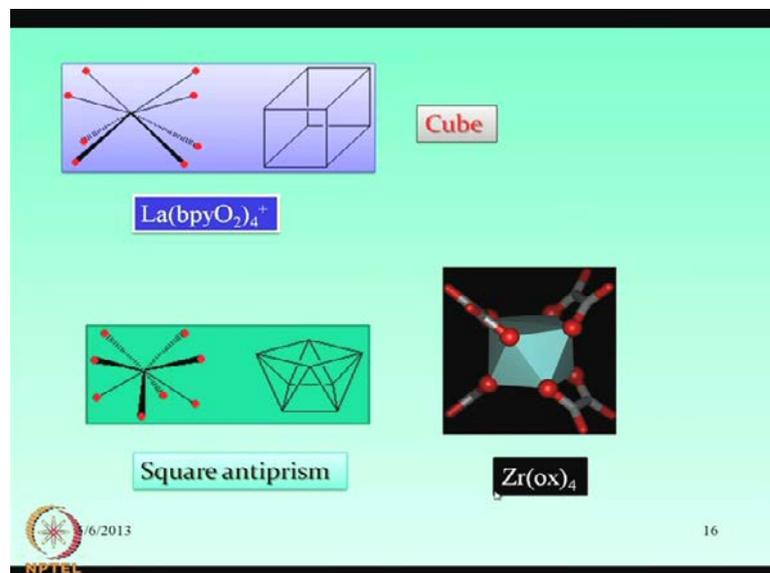
So, some examples of this cube structure, how we see. So, these are the positions. So, these, all 8 corner positions are occupied, we get the corresponding cube geometry. So, this is lanthanum b p y O 2 ligand, which are 4 in number, and we just get this particular compound in this form. So, 4 such ligands, so 4 these ligands will occupy in surrounding lanthanum. So, we have the bidentate ligand; here one, here two, then here three, and then we have the fourth one. So, b p y bipyridine, when they are oxidized by hydrogen peroxide we get b p y O 2 ligand.

Similarly, the square antiprism geometry can be obtained nicely in this form, what we have seen just now in case of Z r o x whole 4, zirconium tetra trisoxalato. So, we have the corresponding geometry of this, which is square antiprism. And 4 such oxalate ligands. So, this is the first oxalate ligand, this is the second one, this is the third one, and this is the fourth one.

So, we have, at the top we have the square plane, at the bottom we have the another square plane. So, this is the top square plane. And here we have the bottom square plane, and, where we see that the top square plane is occupied by one oxalate this side and another oxalate that side; similarly, for the bottom side we have one oxalate this side and

another oxalate this side, will give rise to the corresponding square antiprismatic geometry for Z r o x whole 4 molecule.

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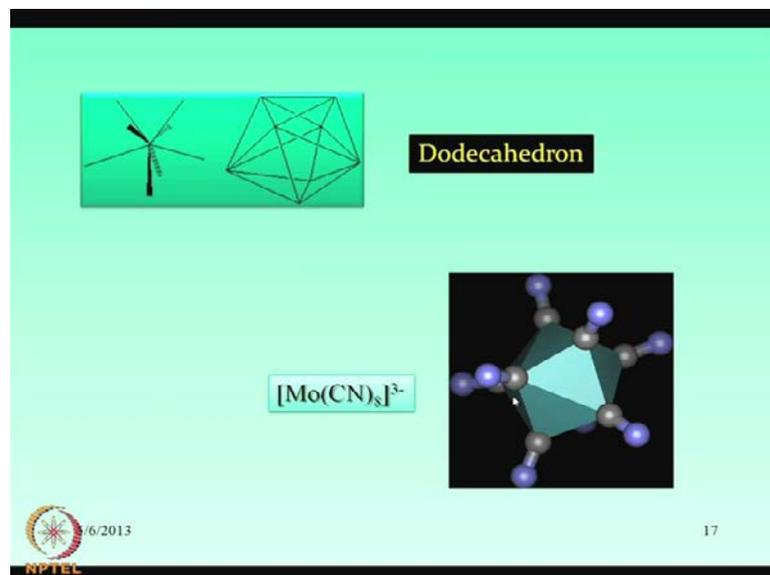
Now, we see the corresponding dodecahedral geometry. So, dodecahedron, we have the coordination number of 8, but the corresponding faces we can have. This is the corresponding pentagon basically. So, this side we have 5, then another side we have 5, 10 plus 12. So, it has 12 faces. So, dodecahedron is, has 12 faces. The face number is basically changing. Number of faces are getting changed. And unlike our square antiprismatic structure, this has no 4 membered rings, they are all 3 membered rings. So, you have the trigonal planes only. No tetragonal plane is there, that is why the number of planes have increased. So, you have the 12 faces present in the dodecahedral geometry.

An example is molybdenum octacyno complex. So, this particular molybdenum center is in plus 5 oxidation state, that is why we have a charge of 3 minus. It can be isolated, as its corresponding ammonium salt, or potassium salt, or sodium salt, giving rise to a formula of k 3 N a 3, or N h 4 whole 3. So, the coordination number of 8, that means, 4 CYNO groups will be surrounding the corresponding structure in all these corner points.

So, this is the corresponding structure. So, when we see the polyhedral structure, it is not always easy to visualize this particular geometry. So, at least this geometry is embedded within this polyhedral arrangement. And this geometry, when we have, we can see these particular one, so we can basically 3 plus 3, 6 positions we are seeing over here. So, this,

5 from this pentagonal part, this is the entire part; the outside, the periphery of this molecule is the pentagon. So, the pentagonal face is visible; then we have this one particular point. So, we have, here also we have the pentagonal face, and this is the other one. So, 5 plus 1, 6 groups we see; 2 are back, on the back side. So, this is the first one, and this is the second one; these are also slightly visible; this is the one, and this is the other one.

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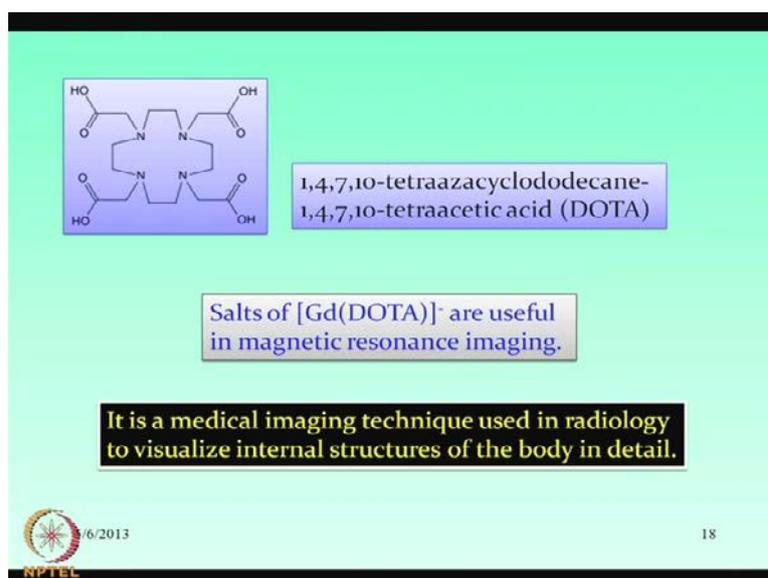
This is one more example of a ligand system; how we move form a typical macrocyclic ligand? And how we derivatize these things? So, this is well known architectural thing on the ligand design. So, how we can change the ligand design? The ligand design gives us some important clues in our hand, that we have seen, that we can talk about ethylene diemine. This ethylene diemine is nothing but a bidentate ligand, with it abbreviation of e n. It can go to ethylene diemine tretraactic acid, or all capital EDTA.

So, when we are derivatizing this particular ligands; so the ligand denticity, this is bidentate. So, bidentate ligand can be changed to hexadentate, how? Is very simple thing; we are studying on this because we simply derivatizing this 2 NH 2 groups by the carboxy acid arms. So, each NH 2 groups has been derivatized by these 2 arms. So, 2 plus, 2 plus 2, giving rise to a hexadentate ligand.

Similarly, if we have a tridentate ligand of NH backbone which is tacn, tri azacyclononane. And this tri azacyclononane which is specially capping tridentate

ligand. In a same way, if we can derivatize by substituting this NH group by 1 arm, another carboxy arm, because these arms are carboxy. Similarly, one arm from here, and we can put another arm from here. So, tridentate ligand can again be 3 plus 3 means, hexadentate.

Similarly, if we can go from a macrocyclic ligand, which is tetradentate which is 1, 4, 7, 10-tetraazacyclododecane. So, this tertraazacyclododecane is the tetradentate ligand bearing nitrogen's in the macrocycle at position number 1, 4, 7 and 10. And if we derivatized all 4 nitrogen groups by acetic acid functionality, that means, carboxy acid functionality, at all the same positions, we get a ligand which is octadentate in nature and known as DOTA, which is abbreviated as DOTA.

So, this is the parent macrocyclic ligand which is tetradentate N 4 ligand, derivatized from this arm, second arm, third arm, and fourth arm, it become the corresponding octahedron, octadentate ligand. And it can trap basically that particular metal center which can give rise to a coordination number of 8, because this ligand is providing a system where the ligand is octadentate. So, is a very useful ligand system which can trap the gadolinium ion, which is the lanthanum. So, the lanthanide complex can be obtained.

So, we have basically 4 negative charge on, after deportonation of these OH of the carboxy groups. And gadolinium in plus 3 oxidation state, can bind to this ligand, this dota ligand, and 1 charge will be there, and is a very useful molecule from the medical point of view. It is a very useful reagent for MRI scanning, which is known as magnetic resonance imaging. So, MRI scan can be done with the use of this particular metal complex of gadolinium. So, this is the lanthanide metal complex; is a medical imaging technique; MRI is therefore, a special type of medical imaging technique, used in radiology to see the internal structure of the body in detail, is the complimentary technique related to nuclear magnetic resonance, NMR technique.

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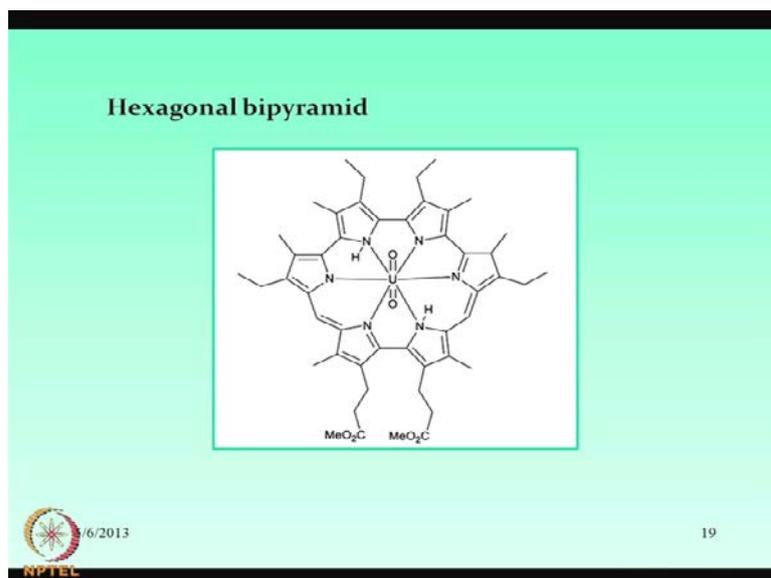
So, we see the last one that is the hexagonal bipyramidal structure, where the plane is hexagonal in structure. And we have from bottom 1, and from top side we have 1 coordination side. So, this is also a bigger macrocyclic structure.

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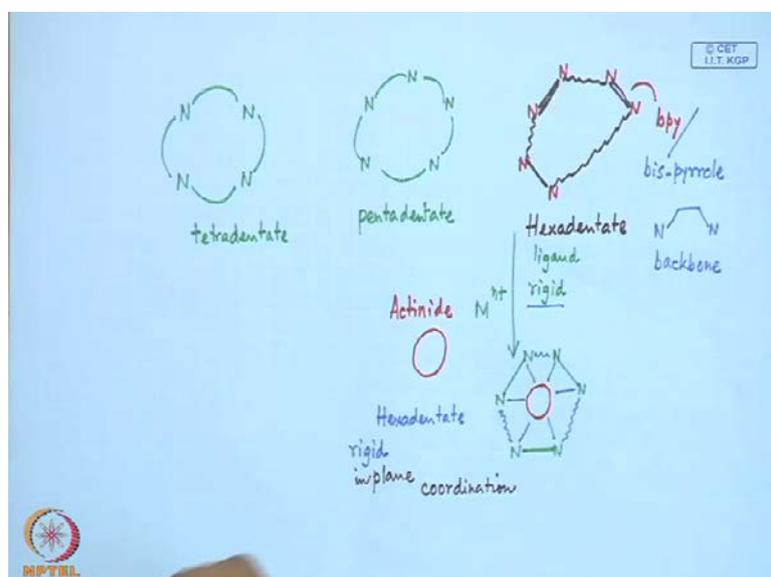
So, most of the time what we see that either we can derivatize the thing; that means, if it is a nitrogen base system, we can go for simple derivatization of these nitrogen positions; or we can just simply, through some Schiff base condensation, or some other type of, tetraplural type of condensation reactions we can move from, this is tetradentate ligand.

We can put one more nitrogen making it pentadentate . So, now, if we want to go further is not so easy to make a corresponding, this sort of linear chain pentadentate to hexadentate one, because if we make such hexadentate ligand and if it goes to bind the metal center, we can have the corresponding folding within this backbone.

But, if we can do something that to make the corresponding hexadentate one, we can put some rigid backbone. So, we can have one rigid backbone here, we can have another rigid backbone over here, we can have another rigid backbone over here, then we can connect it. So, it can be a hexadentate ligand, if we have the fixed positions as nitrogen's. So, it can be b p y type of rigid molecule fixing over there, or it can be bis-pyrrole type of unit, such that we can have two adjacent nitrogen's.

Idea is that we can have 2 adjacent nitrogen's which are fixed with some nitrogen carbon, carbon nitrogen backbone; this is the backbone. So, this would be the corresponding backbone, and that will give rise to the some rigid structure. So, we have the hexadentate ligand which is rigid in structure; that means, when we put any metal center, obviously, that would be a bigger one. It can be from actinide series, which will be bigger in size.

So, we have within this cavity of the hexadentate ligand the metal ion will be sitting nicely over there; and we have one nitrogen backbone here, one nitrogen backbone here, and one nitrogen backbone here. So, we have, so all 6 nitrogen atoms which are connected. So, this basically gives us something which can be called as the coordination, because all, will, all nitrogen is showing coordination to the metal center. So, hexadentate; this structure is rigid also, rigid, and all the coordinations are taking place in a particular plane. So, hexadentate rigid in plane coordination is possible.

So, now, if we can get one above this particular plane, so this is our corresponding rigid coordination, hexadentate rigid coordination through all these 6 nitrogen atoms of the bis-pyrrole unit. And if we have the uranium oxo group above the plane and another below the plane, we get a corresponding hexagonal bipyramidal geometry, which is nicely achieved for a coordination number of 8.

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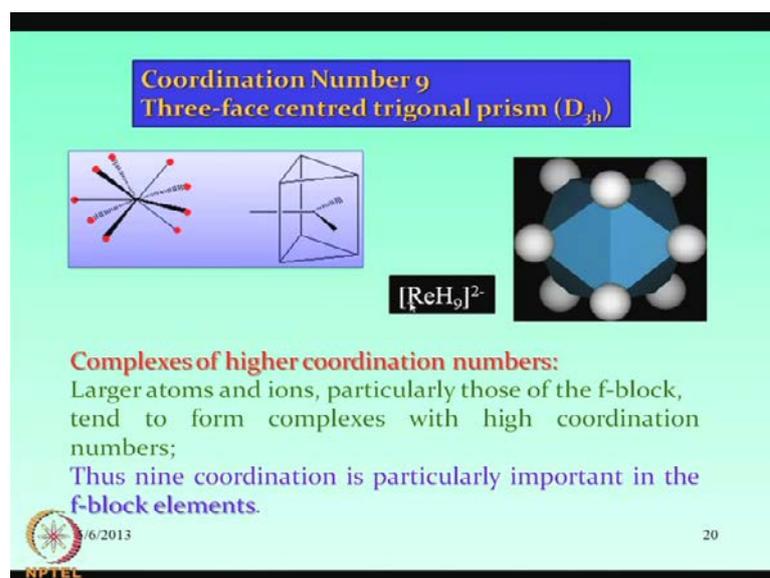
Then, we have the coordination number of 9, which is three faced coordination centered trigonal prism structure of D 3 h. And this is the face, and this is one other face; and if all the face centered trigonal prism is there, all the 3 faces; that means, all the square faces, this is one square plane, and this is another square, and this is another square plane, all the 3 are capped, we get 6 plus 3, 9 coordination, which is possible for uranium hydrido compound, uranium monohydrate compound which is there, and which can be going for the corresponding coordination of this uranium, is in the group of manganese. So, manganese technician in uranium, this uranium center is in plus 7 oxidation state, attaching to 9 hydride groups, giving an overall charge of 2 minus.

So, this is the structure fitting with this particular capped trigonal prism. So, this complexes of higher coordination numbers are basically larger atoms, and ions are participating, and they are mostly form f block, and, they tend to form complexes with high coordination numbers. And this 9 coordination number is particularly important in the f block elements. If it is true with f block elements, that mean, the lanthanides or the actinides, it can be true with the 5 d elements. So, this is the 5 d transitions metal ion uranium in that series, which can also give rise to a coordination number of 9, when the ligand is very small which is hydride. The hydridonoid ligand can give rise to that situation.

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Then, we have a coordination number of 10 which can, we have square antiprism we know now, with a coordination number of 8, which can be bicapped; that means, 2 of the faces can be capped to give rise to a corresponding bicapped square antiprismatic structure of symmetry level D 4 d.

Similarly, if we can go one point further for a coordination number of 11, we can get a corresponding geometry where we have a trigonal prism structure where all faces are capped. The 9 we have seen that 4 square faces are, 3 square faces are capped, so 6 plus 3, 9 coordination number. Then 2 other faces remaining, which can also be capped to give a coordination number of 11.
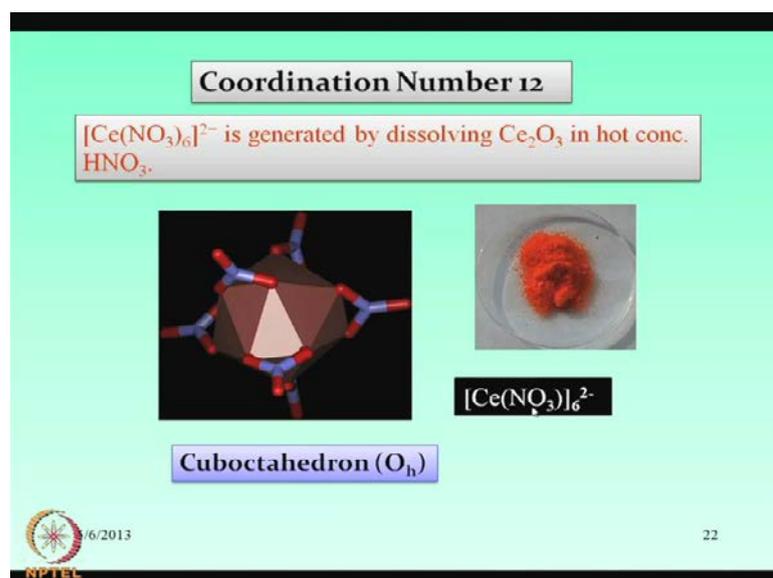
And lastly, we see, because mostly we just go, most of the cases, examples we can have for coordination number of upto 12. So, how we get a coordination number of 12, which is very difficult to visualize sometime, and one well known example is there in our hand, which is the corresponding compound of cerium.
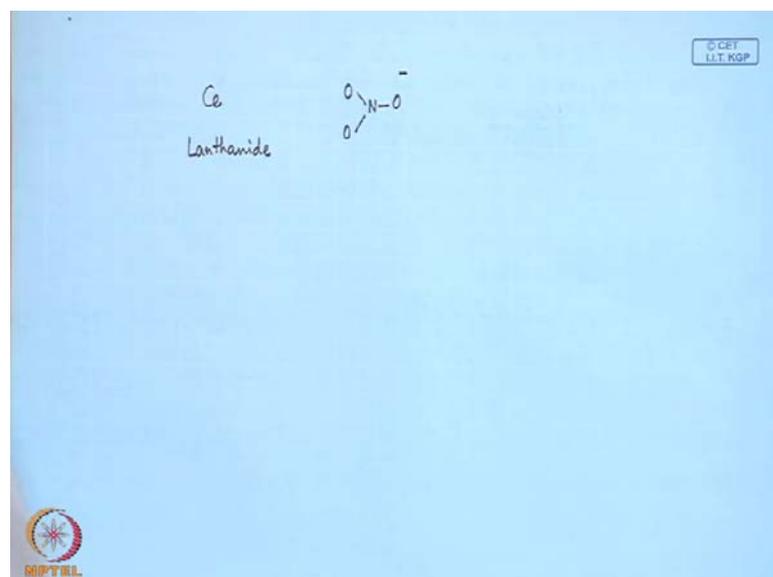
Cerium, which is a lanthanide, and this cerium compound when forming the corresponding compound with nitrate groups. So, how many nitrates we can accommodate around a cerium center; that is our question to think.

So, 6 such nitrate groups can be surrounded to cerium center which is in plus 4 oxidation state, can be very easily generated from the trivalent compound of cerium which is cerium oxide. So, Ce2O3 in hot concentrated nitric acid basically generate the corresponding compound as the anionic form of the corresponding hexa nitrito cerium compound, which can be isolated as its corresponding ammonium salt.

So, ammonium ceric nitrate, or ceric ammonium nitrate, sometime is also known as ceric ammonium nitrate, and organic chemist sometime level it as C a N molecule. C a N ceric ammonium nitrate, is a beautiful red colored compound, red powder compound which is shown here on a petritis; and this red color compound can be obtained by this way; and this ammonium salt is also looks like this; ammonium salt can be isolated like this; and in this particular case we have a corresponding coordination number of this 12. So, where we have a corresponding geometry, and this geometry we have a typical corresponding cube octahedron, which has also an octahedron geometry where it is derived from a corresponding cube structure.

And this is a cube octahedron form is that, if we can have, because the problem is that we have to accommodate. We have to accommodate basically 6 such nitrate groups around the cerium atom. So, basic idea for getting that cube octahedron geometry is very simple, that we all know that accommodating 6 ligands around a metal center is through the octahedral points; that means, if we can draw the 6 octahedral points around this cerium center, we get a octahedral geometry which is facing towards nitrogen of the nitrate, but here the nitrogen is not making the bond, this nitrogen. So, all center, that means, these nitrogen's facing towards the central cerium is in octahedral geometry.

So, they are in octahedral geometry, but they are not forming any cerium nitrogen bond, they are forming cerium oxygen bond. So, these 2 adjacent oxygen atoms of one cerium group is forming new bonds with the cerium center, making 2 into 6 of such nitrate groups, making 12 bonds to the cerium center in a geometry which is known as cube octahedron geometry.

Thank you very much.