A very simply little demonstration.

And I would like you to take a look at the two materials that are in the two vials I have here.

One of these that I am taping is a beige-colored solid, and it is iron dichloride, ferrous chloride.

And then over here, I have an organic molecule that is colorless, just white.

And what I am going to do is first make a solution of the ferrous chloride in water.

I am just using a very small amount.

And what you will see is that the FeCl two dissolves up pretty nicely in water, and it gives a solution that has very little color to it. You might be able to see that it looks maybe pale yellow. Can you see that?

Okay. To that solution of ferrous chloride in water, I am now going to add this organic molecule. I will draw the molecule for you before we finish today. And I am just going to add a small amount of this colorless organic molecule -- -- to get a very nice intense red color in the aqueous solution. And the person I am going to be talking about today is the one who really figured out what is going on in a reaction like that.

And this was a great mystery for a long period of time, until Alfred Werner came along.

I would encourage you while you are at home, perhaps, or visiting friends over this coming weekend, to go onto the Internet and go to the Nobel Prize website, where you can read a very nice short bibliography of Alfred Werner, because he won the Nobel Prize in 1913.

And he won this prize based on a theory that he developed stemming from observations he made regarding reactions of metal salts with various substances.

And I am going to point out initially, here, that he studied the reaction of cobalt three chloride.

I just used iron dichloride. This is cobalt trichloride reacting with six equivalents of ammonia.

And he observed that if to aqueous solution of cobalt trichloride was added six equivalence of NH three, ammonia, followed by silver nitrate, that that resulted in no AgCl precipitate. And that is rather astounding.

Sorry. We will get to "no," but this one is "all." How does he do this experiment?

He just puts these things in solution, adds silver nitrate, and either there is or is not a precipitative silver chloride, which is very insoluble. And that precipitate can be collected by filtration, dried, and then weighed.

And then, in comparison with the mass of the added substances, you would know how much of the chloride that was put into the reaction actually came out as insoluble silver chloride precipitate. And he did a series of experiments. And so, if he uses cobalt trichloride and less ammonia, namely five equivalents of ammonia, then he finds that that leads instead to two-thirds of the possible AgCl precipitate. And continuing down.

If he uses now only four equivalence of ammonia, then the addition of silver nitrate provides one-third of the possible of the total precipitated chloride.

And then, finally, if he drops down the number of equivalents of ammonia to three, then we get none, zero of the AgCl precipitating. And a further observation, to add to these four observations, was that in no case, here, did the solution give a reaction with hydrogen chloride. What is the significance of that? Hydrogen chloride, of course, is a strong Bronsted acid.

And, if you have a base in solution, it should react with that Bronsted acid. And what are we adding here?

We are adding ammonia. And ammonia is a base, isn't it? But when you do the experiment like this and then test for any reactivity with hydrogen chloride, there is no reactivity with hydrogen chloride.

So what is going on? And, secondly, normally, this reaction with silver nitrate is used to quantitatively precipitate chloride from solution.

So it is a quantitative analytical test for chloride in solution. And the less ammonia we add, the less silver chloride we are getting as a precipitate.

How are these facts related? Well, Alfred Werner put it all together, and he correctly formulated these complexes.

Let me write this as follows.

In that first instance, when we have added six ammonias, Werner decided that the reason that ammonia is not in solution in a form that is reactive with hydrogen chloride is because the ammonia is coordinated to the metal.

And so he wrote the formula this way.

Cobalt NH three six times. And this species is a trication. And to balance those three positive charges, we find that there must be three chloride ions outside of what we are going to call the inner coordination sphere of the cobalt

complex.

Now, there were lots of different preparations that had been reported in the literature back at this time of materials that seem to be composed of metal ions and mixtures of chloride or ammonia or other types of molecules.

And this kind of a formulation of them was completely unique.

And I really think that in the history of chemistry, you can compare Alfred Werner's leap, his development of the coordination theory as very much analogous to Kekule's description of planar benzene with all equivalent C-C bond distances. This is really a tremendous leap in our thinking about molecules.

And then, in the case where he is adding five equivalents of ammonia, those five equivalents all go onto the cobalt, and so does one chloride ion. So he writes it that way.

And that chloride ion is balancing one of the three positive charges on the cobalt plus three ion.

So this overall, now, has a two plus charge, and there are two chlorides external to balance the charge on that. And then in case three, we have added four NH three per cobalt to solution.

Four of them go on the metal and two chlorides remain and interact with the metal in a way that we will discuss shortly.

And that system now has two of the plus three charges on cobalt three balanced by chlorides that are in the inner coordination sphere. And only a single chloride, now, is needed externally to balance that charge to give overall a neutral system. And then, finally, when only three equivalents of ammonia are added to solution, those three equivalents per cobalt bind to the metal.

And all three of the original chlorides can be included in the primary coordination sphere, balancing the three positive charges on the cobalt three ion and giving overall a neutral coordination complex. This is coordination theory.

And the dominance of organic chemistry at that point in time was very great. Most of the people who were thinking about these unusual substances were thinking that they might have structures analogous to those that organic molecules have. And typical hydrocarbon molecules like n-pentane or n-hexane have sequential joined CH two groups, repeating CH two groups in a line. And so the type of formula that you were seeing people write for these molecules at that point in time was, for example, a cobalt.

And then NH three, NH three, NH three, NH three, somehow all stuck together in a way that does not seem very intuitive to us today because we know so much more now, partly due to the accomplishments of Alfred Werner.

This systematic set of observations, the use of silver chloride's insolubility as a means of precipitating it out so that you could distinguish between external chloride from chloride that is actually in the coordination complex. And let me define coordination complex.

The coordination complex is a metal ion.

Plus its ligands.

So there is another word that you need to learn in this context. Here, I would like to define the term ligand as an atom, or a molecule, or an ion, that can bind directly to a metal like cobalt in its primary coordination sphere.

And that means that they are directly connected to the metal.

And the amazing thing here and what was so different from organic chemistry at this time was the idea that a single metal ion can have a fairly large number of ligands.

In this particular case, Werner analyzed his experiments with the assumption of coordination number being equal to six.

So here, it is six. But coordination number is a variable that depends on the metal itself and depends on the specific choice of the ligands. Some molecules are known in which there are very low coordination numbers.

A coordination number can be as small as two or one in some very special instances for insoluble molecules.

And for very large metal ions, sometimes the coordination number can be as great as about So 12 atoms or ions or molecules directly connected to a central metal atom. And ligands don't have to be as simple as chloride or ammonia. Ligands can have some pretty interesting architectures. And you can even dream up new ligands with which to decorate a metal ion and with which to imbue it with special properties for purposes like catalysis.

We will be talking soon about metaloenzymes.

These are proteins as ligands to metal complexes.

And very many important enzymes are metaloenzymes that have these elements from the 3D part of the periodic table bonded.

Here is what we call the d-block, -- -- or transition elements.

And, in the case of the 3D series, you will know that we have metals like titanium, vanadium, chromium, manganese, iron, cobalt, nickel.

These are called transition elements because oftentimes in ions stemming from these elements, as you go from left to right across the periodic table, you are adding more electrons to an incompletely filled d-shell.

And at the end today, we are going to talk a little bit about the bonding properties of transition elements.

And that will hearken back to what I said with my discussion of carbon monoxide and why it is a poison.

And it is the interaction, actually, with certain d-orbitals on the iron in hemoglobin that makes CO a toxic substance. And so how does this work?

How do ligands coordinate two metals?

Well, one simple way is if you have a ligand like ammonia that is a base, it can also be a nucleophile, and the metal can be the corresponding electrophile.

I can draw that to represent a lone pair of electrons on the nitrogen. Now that we have studied molecular orbital theory, you will know that I can also call this the highest occupied molecular orbital of the NH three molecule. And it is the one responsible for the basicity of the ammonia molecule and the one responsible for its ability to serve as a ligand in coordination complexes, like these. And you might also suspect that we might have some contributions to this highest occupied molecular orbital from hydrogen 1s linear combinations.

I will just draw that in to make it a little bit more accurate. And so, you can think of this as a big fat lone pair that will coordinate to Lewis acids.

And the metal ion is a Lewis acid.

But it is a very interesting Lewis acid because, unlike the BH three molecule that has a single empty orbital, this metal seems to be able to act as a Lewis acid six times and coordinate six bases to it in forming this coordination complex. And if we go ahead and crystallize molecules of this sort and use X-ray diffraction studies to determine the bond angles and bond distances in systems like this, what we would find is that these nitrogens are located at the vertices of a nice, regular octahedron. So, in the case of our first one, we can draw it out this way.

This first one is what would result if, to that aqueous solution of cobalt trichloride, we were to add six equivalents of ammonia. This is Werner's first system.

It is a molecule oriented like this.

That lone pair that comes from the highest occupied molecular orbital of ammonia is directed right at the metal

from each of the six ammonia ligands. And this system does have a three plus charge that is balanced by three chloride ions in solution. This locating of six nitrogens in an array in space that approximates a regular octahedron is what makes the octahedron such a central aspect of the theory of transition element chemistry.

And, if you are going to design molecules that do include these transition metal ions, -- -- whether you are going to do it for their color, like the red color there of the iron complex that we made a few moments ago, or whether you are going to do it to take advantage of the properties associated with unpaired electrons like magnetism, for example, you would begin any such approach with the octahedron as your starting point.

Let's go ahead and consider some of the other examples provided to us by Alfred Werner.

If instead of six, we are adding only five NH three molecules for every cobalt, then what happens -- -- is indeed we do get an octahedron, but one of the chlorides is not ionized. It is bound directly to the metal, and it is serving as a ligand.

And this species, therefore, has a two plus charge. The cobalt ion is still considered here to be in the plus three oxidation state.

And this system is balanced by two chloride ions that are floating around externally in solution and that are not in the primary coordination sphere. These atoms here that are part of ammonia molecules that are bonded directly to the metal are in the inner coordination sphere.

That is, the inner or primary coordination sphere.

What do you think happens if you take a metal salt and dissolve it in water? I did that a moment ago with ferrous chloride. I dissolved it in water.

Water is a very polar solvent. It promotes the formation of ions in solution because of its great polarity.

It is good at solvating ions, water is, as a medium.

If I take FeCl two and add it to water, as I did a moment ago, and it ionizes, what is happening to the iron?

The iron is going to take up water molecules into its inner coordination sphere. When you dissolve FeCl two in solution, which might often be written quite simply as FeCl two aqueous, what you really have in solution is the system in which six water molecules are bonded to that iron.

And, because I used FeCl two, this system had a two plus charged balanced by two of the chloride ions that dissociate from the iron and ionize and go out into solution to be solvated separately from the cation by water.

That initial weakly-colored solution contained iron in this form, hexaaquairon two.

And I will tell you a little bit about what made the color change in a moment.

But first I would like to discuss an issue that arises in the Werner system. And this is the problem of isomerism.

Werner found that you could make different cobalt complexes that would have the same chemical formula, but, for example, one would be red and one would be green, or one would be yellow, for example, even though they have the same chemical formula.

And that was because, as he correctly reasoned, they were forming isomers.

And this comes into play, for example, when you add only four equivalents of ammonia to solution. And here is why.

If I put the first chloride up on top, as I have done here, there are two choices of where to put the second one that are not the same. I can either put a chloride here, such that we have a bond angle of 90 degrees between the two chlorides. And I will draw in our remaining ammonia molecules that are coordinating to the cobalt.

This is an isomer that we would call "cis." Cis denotes a proximal arrangement of the two chlorides with a 90 degree bond angle between them. And then the alternative here would be to put the other chloride 180 degrees away from the first one. And that gives us what we call the trans iosomer.

And note that both of these would have a single plus charge.

Trans means across. So the two chloride ligands are located in a mutually trans disposition here.

Isomerism is very important. I will discuss a couple other types of isomerism that you can get and that Werner contributed to our understanding of very greatly.

And let me do that by completing consideration of this. You might ask yourself in the case where we added only three ammonias to the solution is there a possibility for the formation of isomers?

And the answer again would be yes, we can have two possibilities. And this is for a neutral system that contains three ammonias and three chloride ligands. And let's say I put the first one here, the second one here, the third one here.

That is one of our possible isomers of this neutral coordination complex. And then the other possibility, the only other possibility is with one there, one there, -- -- and then the third one here.

And so you can try to draw different structures.

And you will see that these are the only two possible structures that you can draw for a combination of three ammonia ligands and three chloride ligands surround a central cobalt three plus ion in an octahedral array.

And these have names, too.

This one is the so-called fac isomer.

And that fac is an abbreviation of the word facial, because if you remember that the octahedron is composed of a set of eight equilateral triangles, then the polyhedron that we call the octahedron has both vertices and faces.

And these chlorides, in this particular case, can be seen to define one of the eight faces of the octahedron. And so that is the facial isomer. And then, the other type of isomer for this type of structure is called mer.

And that is an abbreviation of the word meridional, which would be like the meridians of longitude that you see on the globe. They start at the top and run down through the equator and all the way down to the South Pole.

That is your meridional isomer. These isomers, here, are called geometric isomers.

There are different types of isomerism.

Because the complexes that differ only with regard to the spatial arrangement of the ligands, but not with respect to the formula of the system, these would be types of isomers known as geometric. We have the possibility of CIS, TRANS, FAC, MER geometric isomers for molecules that have the same formula. And then, there is a further type of isomerism. And here, again, the contributions of Alfred Werner were exceedingly important, because it was thought that this next type of isomerism was restricted to organic molecules.

And this is stereoisomerism.

Stereoisomerism is a little more subtle than geometric isomerism. And it is a little more subtle because two molecules that are stereoisomers of each other are related in the same way that your left hand and your right hand are related. They are non-superimposable mirror images. If you can find a way to separate molecules that are chiral, then you can have a sample that can do interesting things, like rotate the plane of polarized light. This happens when you have chiral molecules. And if a molecule is chiral, that is to say it is non-superimposable on its mirror image.

And in order to see whether a molecule is or is not superimposable on its mirror image, you really need to get good at visualizing things in three-dimensions and at rotating molecules around in your mind. You can also do it

on the computer. And doing it on the computer will help you prepare for doing it on the exam, where you have to do it in your mind.

But if you like architecture, and you like visualizing things in three-dimensions, you should know that that is a lot of what we do in chemistry. You should think about these molecules, these 3D structures, in ways that allow you to test for a property like stereoisomerism.

And I mentioned that it was thought that stereoisomerism was a property associated with organic molecules.

And organic molecules were compounds of carbon that were thought to be associated very fundamentally with life and living things. And so the fact that Werner in one of his most amazing accomplishments was ultimately able to synthesize a coordination complex that contained no carbon at all but exhibited stereoisomerism just shattered that theory and really helped to bring science onto a much more firm footing. And that parallelism between organic and inorganic chemistry, I think, has stemmed from this aspect of its history. And so let's look at an example of a molecule that is chiral -- -- that could be made from cobalt.

And if you imagine carrying out a reaction like we were talking about up above but not even giving it enough ammonia to displace all the water molecules then you could have an intermediate like this.

And in this type of species what I've got are two water molecules, two ammonia molecules, two chlorides.

And so if this is cobalt three, we would have a single positive charge on that ion. And what I can represent here by a dashed line would be a mirror plane.

That is our mirror. And we are going to reflect this molecule through that mirror plane to see what its mirror image would look like. And then, if you can rotate it around in your mind, we can determine whether it is or is not superimposable on that mirror image.

I am generating the mirror image by reflecting this water to this position. This ammonia back here reflects over to here. The top ammonia reflects still into the top position. This water behind the board reflects behind the board. And over here, this chloride coming out in front of the board reflects over to here. And we have one more chloride, down on the bottom. That molecule is now our mirror image. And let's go ahead and rotate it, like this. Because it is a little hard, I am going to highlight the position of the two ammonia ligands. And to see if this mirror image is superimposable on the structure we started with, I am going to rotate this around so that we can put the two ammonia ligands coincident with the two shown here underlined in green on the left. We are going to do a rotation.

And I need to rotate this. I am going to rotate here, around the cobalt-chlorine bond access.

And I am actually going to go in the negative direction to generate the following structure.

This puts this ammonia up top, and it will put this one down below. We have NH three and NH three here. Let me underline them.

So those are in positions, coincident.

And this rotation also will carry that chloride from the bottom up here, into what I may call an equatorial position. And it puts a water molecule down. And that rotation about this cobalt chlorine bond left the cobalt and chlorine on that bond axis unrotated. And then in the back, we have this OH two molecule.

And what you can see is, if you now bring this over, what we have, in fact, is a situation where we are not currently superimposable with that choice.

I generated the mirror image. I have rotated it by 90 degrees around the cobalt-chlorine bond axis to bring these two ammonias coincident with these two. So you can see that, whereas we have a water molecule on the bottom here, we have a chloride over here. So that is not superimposable.

But we can do one more rotation to check the other possibility, and that rotation will be a rotation by 180 degrees around an axis, here, that bisects the nitrogen-cobalt-nitrogen bond angle of 90 degrees.

We will rotate 180 degrees around that axis, and that will bring our ammonias, again, into a position so as to be coincident.

And rotating around that axis brings a water around front here and puts a chloride in back, rotating around there, and it swaps this chloride with that water molecule.

So we now have chloride down and OH two over here.

And so if we take this, we identify our ammonia positions by green underlining, they're coincident, here. And now where we have a chloride coming out, we have a water coming out, so our mirror image is not superimposable on the structure that we generated it from through the process of reflection through that mirror plane.

And so, what we can say is that this molecule and this one constitute a pair of stereoisomers.

And because this condition was satisfied that the mirror image was not superimposable on the structure we generated it from, the molecule is chiral. And you will see that I have chosen a molecule that contains no carbon, and yet it is chiral and it has stereoisomers. And that was thought impossible prior to the time of Werner.

Let me show you another example of a molecule that is chiral.

And I am going to use this example, also, to illustrate another important feature that ligands can have.

And that is that they can have more than one atom that can bond to the metal at the same time.

I am drawing a cobalt ion three plus complex that has six nitrogens directly bonded to the cobalt.

But now, look what I am going to do.

I am going to put some organic material in here and link these nitrogens by a CH two CH two unit, a CH2-CH2 chain here. So it is CH2-CH2.

These carbons that I am representing as vertices here each have two additional hydrogens that I am not showing.

And that is typical organic shorthand.

And I am going to suggest that this molecule would be generated by adding three of these ligands to the metal center.

And for each nitrogen, if you consider it as being derived from ammonia, one of the hydrogens of the ammonia is replaced with a nitrogen-carbon bond.

And we have used this organic moiety here to tether two nitrogens together. This is a very popular and ancient ligand in coordination chemistry.

And, by drawing in simplistic form the two lone pairs on the two nitrogens, you can see that this set of four atoms is able to organize itself so as to simultaneously point two lone pairs at the same metal center.

That is permitted by this bridge.

This particular ligand is called ethylenediamine.

And it is called en for short, ethylenediamine.

And it is an example of a bidentate ligand.

And that means that it has two teeth with which to bite down on the metal center. It is a double Lewis base.

And when it binds to the metal center, we call that the process of chelation. When a bidentate or a multidentate, which would be maybe a tridentate or a tetradentate ligand, binds to a metal through multiple points, we call that a

ligand chelate.

And we call the process one of chelation that forms these ring structures with the metal as part of the ring produced through multipoint binding of the ligand to the metal center.

And you are going to see that it is possible to have all kinds of different architectures for ligands in proteins or in synthetic systems. And the reason that I carried out over here earlier is one in which I added three equivalents of a bidentate ligand to this solution of iron two plus.

And, when that occurred, this bidentate ligand displaced the water molecules from the inner coordination sphere of the metal.

And the bidentate ligand that I used was this one.

This is a very common chelating ligand, a planar aromatic ligand. And you can see that, like ethylenediamine, its architecture promotes the pointing of a pair of electrons toward the same point in space.

So that this ligand can bind itself to a metal center through two nitrogen lone pairs simultaneously.

And it is the interaction of the d-electrons on the iron center with the unsaturated pi system of this organic ligand that produces the red color in ways that we are going to explore in more detail in one of our next lectures.

But, before we do that, we are going to need to understand something about d-orbitals.

And, as you have learned, when you are forming molecular orbitals in systems that consist of either s or p orbitals, you needed to know something about the nodal properties of those atomic orbitals in order to build proper molecular orbitals. And that will certainly be the case for these more interesting elements that have d orbitals.

Not just s and p valance orbitals, but also a set of d-orbitals. And I call those the 3d elements because their principle quantum number for those elements is three. And what we need to now know is what do these orbitals have, as far as nodal properties, depending on the other quantum numbers?

And I will draw a set of coordinate axes, here, on which to map these orbitals.

It should be pretty straightforward for you to keep straight the nodal properties of the d orbitals of which there is a set of five. We had one s orbital for a given valance shell, and we had a set of three p orbitals, and there is a set of five d orbitals for the d-block elements. And they can have different values for the quantum number m. One is zero.

One is plus one. One is plus two.

And m can be minus one, and m can equal minus two.

And this quantum number determines the angular nodal properties of the d orbital in question.

Here, let's draw a fairly simple one.

Let's say that we have x, y, and z.

Then what we might have is a d orbital that looks like this.

d orbitals often have four lobes.

In fact, you will see that we represent four of the d orbitals this way and not the fifth. And let me use this pink to represent the negative phase. And so this orbital here is (d)xz. And that means that it has nodes. You have two planes that are nodes for a (d)xz orbital. And one of these is the x,y-plane. And then the other one is the y,z-plane. Those are planes when you go from one side through one of those planes to the other side.

The wave function changes sign. And, just like each p orbital has a single nodal plane, each d orbital has two.

And this is (d)xz. And we can also have one that we call d x squared minus y squared.

And that one lies right along the coordinate axes like this, with the four lobes being skewered by the x-axis and the y-axis. And we have negative phase located along y for the d x squared minus y squared.

And you can see that the nodal surfaces here both contain z. The nodes contain the z-axis and bisect the x and y coordinate axes.

There is one plane up here that contains the z-axis and one over there located at 90 degrees to the first one.

Those are the nodal planes for d x squared minus y squared.

In addition to that (d)xz orbital, I have a (d)yz orbital, which is located with its lobes lying between the y and z coordinate axes.

And it will have phasing as indicated here in pink.

That is (d)yz. And it looks exactly like (d)xz. And it is just rotated by 90 degrees around the z-axis relative to (d)xz.

And then, finally, we have one that looks just like d x squared minus y squared.

And this one is (d)xy. And, like d x squared minus y squared, the (d)xy orbital lies in the x,y-plane.

And its lobes point between the axes, as shown here with that phasing. And then, finally -- And we will return to this point next week.

Our m equals zero orbital is our d z squared **d(z^2)**.

And d z squared lies along and is skewered by the z-axis.

It looks like a p orbital, except the sign is the same on top and on bottom. And then it has this beautiful torus here that is in the x,y-plane like that, so that its nodal surfaces are actually conical rather than planes. That is our set of five d orbitals with which we are going to do a lot more to understand the chemistry and coordination complexes.

Have a great break, and please don't forget to read about Alfred Werner.