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We have been talking about the properties of transition metal complexes, coordination complexes, in the context of a simple crystal field theory model.

And I just wanted to make reference at the beginning, today, to state diagrams.

And, in the context of octahedral complexes, you saw that an array of six ligands surrounding a central metal ion would lead to a  $t_{2g}$  and what we are calling an  $e_g$  star manifold of orbitals on the metal in which we can populate with the number of  $d$  electrons that we have present. And the graph that I am making here is related to the idea that for a system with only a single electron, so this could be, for example, titanium  $OH_2$  six times three plus.

This is a  $d^1$  system. And it can go from a ground state configuration of  $t_{2g}^1 e_g^0$ .

And then, upon absorption of light, it can be promoted from the ground state, represented here, into the excited state.

And the excited state has the configuration  $t_{2g}^0 e_g^1$ , showing that that electron has been promoted through absorption of a photon.

And this gap here between  $t_{2g}$  and  $e_g$ , of course, is our  $\Delta_o$  value.

And the axis on the bottom, here, is ligand field strength.

This is supposed to tell you that different ligands give rise to different values of  $\Delta_o$  accounting for the fact that this  $d^1$  titanium  $3+$  ion in a field of water molecules has one color, whereas, if you, in fact, look at  $TiCl_6^{3-}$ , you will be able to tell that that also is a titanium  $3+$  or  $d^1$  system. But they do not have the same color. And the one absorption band that you find in the visible part of the spectrum that corresponds to promotion of an electron from  $t_{2g}$  into  $e_g$  is just moving around a little bit in energy because these ligands behave differently with respect to what we call their ligand field strength that they exert, that leads to a particular energy gap between  $t_{2g}$  and  $e_g$ . I will get into this a little bit further in the moment, but the point here is that  $d^1$  or  $d^9$  are special electron counts.

And the reason that they are special is that these have a single absorption peak due to what we call  $d-d$  transitions.

They have a single d-d transition.

And that means there is a ground state and then just one excited state that the system can be promoted to in the presence of impinging photons of the right energy.

And what happens is that if you have more d electrons than just one, or d nine is special because we treat that using a whole formalism, like there is just one electron missing from a complete manifold, a completely full d shell minus one. With  $d^n$  systems, for example, d two is much more complex. And this is beyond the scope of 5.112, but it is something that they are treating in 5.04, for example. If you go on in organic chemistry, you will learn how come different states can arise, multiple states arise when you have more than just a one electron picture.

For example, if you have a vanadium three plus ion, there are three bands observed.

And so the simple picture that you have, just a  $t(2g)$  level and an  $e(g)$  level is correct and maps onto the picture of the electronic states that are available, as long as we are just talking about a one electron picture.

With more electrons in play, depending on just which of the orbitals they go into, they will have inter-electron repulsion terms that come into play and give rise to more excited states. Here, with three bands being observed in the visible, that means there are three possible transitions and three possible excited states that can be accessed. So it is a very complicated picture. And so we are going to be, for the purposes of this, focusing on the one electron picture. But I just wanted you to be aware that it does get a lot more complex as soon as you go to many electron systems. Now, let's talk just briefly about pairing energy.

In the case of 3d system, we typically find that the pairing energy is around 15 to 18,000 reciprocal centimeters, the typical energy unit given for pairing energy.

But then if we go to heavier transition elements, to the 4d or the 5d elements, then typically the pairing energy is about 8,000 to 12 reciprocal centimeters.

And what that says is that it is easier to pair up electrons in 4d or 5d orbitals than it is to put two electrons in the same 3d orbital. And the reason for that is just what the radial extension is of these orbitals.

In effect, these orbitals are larger than the 3d orbitals.

And it means that if you put two electrons into the same 4d or 5d orbital, much of the time they can stay farther apart from each other than if they are in a 3d orbital. And so this has the practical consequence that 4d and 5d systems often are low spin.

And so this high spin/low spin issue that we talked about last time is mostly focused on complexes of the 3d ions.

So then we are talking about titanium, vanadium, chromium, etc. And, if we come over here, we can ask, what is the effect of charge on  $\Delta O$ ?

This is all pointing back to the state diagram that I showed you over there in this kind of sliding scale, where you can change things like just what type of metal ion you have, 3d, 4d, or 5d.

Or you can change the nature of the ligands.

Or you can even change the charge on the metal as a way of changing  $\Delta O$ . And so we can look at, for example, chromium hexaaquo two plus versus chromium hexaaquo three plus.

The first is a d four ion.

And then, the second is a d three ion. You should practice going from a formula into the  $d^n$  count. And then we can look at what  $\Delta O$  does. This is roughly 14,000 wave numbers. And then, when we oxidize from 2+ to 3+, higher charge on the central metal,  $\Delta O$  shoots up to about approximately 17,000.

And this is in reciprocal centimeters.

We see that putting a higher charge on the metal center leads to a larger value of  $\Delta O$ . And that is also true if we look at some other metal systems along these lines.

For example, there are just a number of different metals for which the hexaaquo systems can be generated in both the 2+ and the 3+ state of charge.

And here, we go from about 12,000 and then oxidize, and we get up to about 18,000, so even a larger increase in the value of  $\Delta O$  on going from the 2+ to the 3+ oxidation state of the metal. And then in the notes you will find that I put in another example that behaves similarly based on cobalt. If you go from cobalt two to cobalt three hexaaquo, you go from about 9,000 up to 18,000 reciprocal centimeters. So almost doubling the value of  $\Delta O$  by removing one electron from the system.

What is going on here is that the greater charge -- -- pulls the ligands in closer to the metal.

And if the ligands are in closer to the metal, then what that ends up saying is you will see in a moment because we are going to get to the MO picture for octahedral coordination complexes, is that putting electrons in e g star becomes more difficult.

$\Delta O$  is larger. The ligands come in closer, and that is effectively shrinking that value of  $r$  when we talked about our spherical coordinates as applied to the angular parts of the d-orbital wavefunctions and looking at that. So we

are changing  $r$ .

The ligands are coming in closer to the more positively charged metal ion in that case. And then we can also look at the effect of changing the ligand.

In the system on the left, we were looking at pairs of metal complexes with the same ligand and changing the charge.

And now we are just going to say, what happens if you change the ligand? And this will be a series of vanadium complexes. We have five of them.

We have the vanadium hexaaquo.

This one is  $3+$ . We have the vanadium with six urea molecules. And this is also  $3+$ .

We have vanadium hexafluoride three minus.

And these are all vanadium in the  $+3$  oxidation state.

Then we have vanadium hexachloride three minus, and down here the fifth one will be vanadium with six cyanide ligands and three minus.

So these are all d two systems with vanadium in the  $+3$  oxidation state.

And here, we are going from 18,000 reciprocal centimeters to the hexafluoride. And we drop down to 16,000.

And this is all approximate. And six urea on vanadium, we go up to about 17,000. And then, with the hexachloride, we are down to about a  $\Delta O$  of 12,000 reciprocal centimeters.

And then we put cyanides on, and  $\Delta O$  pops up to about 23,000 wave numbers. So this is the same metal ion but in five different ligand environments.

It has five very different values of  $\Delta O$ .

And from this, we can derive a spectrochemical series -- -- for organizing ligands with respect to the magnitude of  $\Delta O$  that they exert for a given metal ion.

And this one just gives us a series that contains five ligands. But, as you can imagine, many more ligands than just these five simple ligands have been looked at with a variety of different metal ions to make a pretty big overall comprehensive spectrochemical series that sort of allows you to pick out which ligand you want when you are

interested in generating a particular value of  $\Delta O$ .

And here what you see is that the weakest one is chloride.

We have chloride. And then next was fluoride.

And then next was urea followed by water.

And then the strongest in this small series of five was cyanide. And when we try to understand the order that these different ligands appear in, in the spectrochemical series, we are going to find out, as we study the properties of the molecular orbitals of these systems, that cyanide is a pi acid.

And that down here, chloride is a pi donor.

And in the middle, you have systems like water which is more or less sigma only.

So we can understand where specific ligands appear in the spectrochemical series on the basis of their orbital considerations. And that will be the focus of the next part of the lecture.

I would like to talk a little bit about sigma-only ligands.

The process in which we are now about to engage is very similar to that which we used in class for generating the molecular orbital energy level diagram for the BH<sub>3</sub> molecule.

In that case we had a central boron and three hydrogens around it, and we made some hydrogen linear combinations.

And we saw how they would interact with the atomic orbitals of the boron. And now we are going to do the same thing, except we have a lot more orbitals in the system as a whole, so we are approximating some of them.

Here is a typical sigma-only ligand, NH<sub>3</sub>.

And for NH<sub>3</sub>, we have a lone pair on the nitrogen here. And I am drawing it in very simplified fashion, as you will no doubt appreciate. There is our lone pair.

And, when this points directly at the metal, the lone pair can make a sigma bond to the metal.

I think you will appreciate that if we have a metal out here such that this lone pair of electrons is directed right at the metal, then that results in a cylindrically symmetric lone pair about that metal-nitrogen internuclear axis.

And so that would be a sigma-type of interaction.

So this is called a sigma-only ligand.

And other ligands, like cyanide or like chloride, we are going to have to add in pi effects, but this is the simple sigma-only case. And so if you take a molecule such as this cobalt hexamine two plus, -- -- or, actually, let's say three plus for simplicity here. Cobalt three plus.

And we have these NH three ligands at each of the six positions. And, in each case, the orientation of the hydrogens on these nitrogens is such as to promote a sigma directing effect of that lone pair toward the metal. And so that lone pair of electrons on the nitrogen for each of these ammonia ligands directed right at the metal is providing this repulsion that pumps  $e(g)$  up in energy. And you will see that, hopefully, very clearly now. And let me point out that this orbital, here, that I am focusing on is the HOMO of NH three. What we are doing is saying you have a central metal ion and then you have six ammonia ligands pointing at it, each of them pointing their HOMO at the metal, their highest occupied molecular orbital. What does that do?

What kinds of bonds arise as a consequence of that between the metal ion and these six ammonia molecules?

And so we will now see what that is on the basis of some of the linear combinations that we can generate between the six HOMOs of the NH three's in this kind of a geometry.

I will do the first one over here.

I would like to use a different color for that.

I am going to use my blue. All right.

I am going to draw for you some linear combinations of ammonia lone pairs. These are simplistically representing the homo of each NH three directed at the metal. That one has the symmetry of a cobalt s orbital. It has the same sign everywhere. And then, we are going to see that you can draw three of these.

And I will draw them all right here -- -- in pairs. And this one has the symmetry of a cobalt pz atomic orbital. You see it has positive up there. And down here, we are taking this to be x, this to be y, and this to be z for each of our diagrams, so that the phase properties of this combination is that of pz.

This one is like px. This one is like py.

And the only reason we have to take these linear combinations is because we have multiple equivalent ammonia molecules in this problem. And then, we have two more that are of interest to us. One of these will have a couple of big lobes located on z, pointed at the metal and then four small lobes, each with negative phase.

I will shade them to indicate that negative phase.

And that one will have the same phase properties as a cobalt  $d_{z^2}$  orbital. Plus above, plus below.

And then, to match up with the torus in the center of  $d_{z^2}$  in the  $x,y$ -plane, the negative phase shown there. And then, finally, over here we have one where all four contributions to this one are in the  $x,y$ -plane, along the  $x$  and  $y$  axes and with shading as shown there. And that is of the same symmetry as our  $d_{x^2 - y^2}$  orbital. Having written down this set of six linear combinations that we can generate from our six ammonia HOMOs, we are done because the cobalt has atomic orbitals of these symmetries.

We can now use these to make bonds between the ammonia molecules and the cobalt. And we can use them to make corresponding antibonds.

Here is the MO diagram for the sigma-only case.

What we have is an energy level diagram that will represent the interaction of these linear combinations with the metal valence orbitals. And so I am going to draw the metal valence orbitals over here as follows.

We have, on the metal, the 3d, the 4s, and the 4p. And some of you will notice that this ordering of energies is a little different than what you saw when you just built up atomic configurations, because what I have drawn here is the set of five 3d atomic orbitals is down lower in energy than the cobalt 4s and lower in energy, that is, even still, than the cobalt 4p.

This is our cobalt atom here. And the reason this energy ordering for the valence orbitals is different is because we have an ionized cobalt.

And the energies change around when you remove an electron from the system as compared to the neutral atom.

But one thing that will help you remember this ordering of energy levels is that it goes in the order of the principle quantum number, which kind of does make a little sense. In fact, these energies switch around, depending on which of the metals you are talking about. But generally 3d and 4s, or alternatively 4d and 5s, are pretty close in energy to each other, depending on the ion that you are talking about.

And then 4p is usually energetically a bit separated from that. And then the thing that makes us focus our attention so strongly on the d orbitals is that those are the ones closest in energy to the ligand orbitals that can interact with them. And so let me draw over here a bar that represents the six LCs of NH<sub>3</sub> HOMOs.

In essence, this represents these six drawings that I drew over here, linear combinations that have the right symmetry to interact with certain of valence orbitals on the cobalt, here on the left. And what we will find is that--

And we will start with the 3d, since that is what we are going to be principally interested in here.

We come over and find that three of the d orbitals do not match any of these because these NH three HOMOs all lie in nodal surfaces of them. And that will be, of course, our t(2g) set.

Those have the same energy as in the ion itself.

They come straight over and don't get involved in bonding or antibonding interactions. These are nonbonding.

That is t(2g). And then, what we find is that of these six linear combinations, two of them, shown right here, have the correct phase properties to make bonding and antibonding combinations by interacting with d z squared and d x squared minus y squared.

We show that down here.

Here is a bonding combination. This has e(g) symmetry, and it represents the formation of two bonds between the metal and the ligands. And, of course, we also make an antibonding combination of the same symmetry. This should just remind you of the hydrogen H two molecule molecular orbital problem built into this much larger structure.

And this one, this antibonding case is e g star. And let's just quickly look at them.

Here, what we have is a d z squared orbital with its torus interacting in an out-of-phase manner with these ammonia lone pairs. That creates antibonding character here and here, making this a high-energy orbital. And then, we have antibonding character, too, in between each of the ammonias located on the x,y-plane and the torus of the d z squared.

So that is one of our two e g star orbitals. And over here, we have our d x squared minus y squared orbital making antibonding interactions with this other linear combination, as shown here, such that we get antibonding all the way around. That is e g star.

That is the reason why the e(g) set, derived from our set of d orbitals, is marked with an asterisk.

It is antibonding with respect to these bonds.

If you start to populate e(g)\* with electrons, as you will do in certain cases that are high-spin, for example, those electrons that go into e(g)\*, if you reflect back on the way that we calculate bond order, they go in there and weaken these two metal ligand bonds. And these two bonds look just identical to the ones I drew here for e(g)\*, just reversing the phase and making them bonding everywhere.

Let's just look at those.

Here, we have  $d_{z^2}$  making a nice bonding combination.

It is interacting in an in-phase manner with that linear combination, so we have bonding both in the  $x,y$ -plane and strongly along the  $z$ -axis. That is one of these two bonds.

And then over here, we will have  $x^2 - y^2$ , making bonds also -- -- like that. Down here, this is bonding, and this is antibonding.

Now, that is not the entire diagram.

One runs out of space pretty quickly on these horizontally-oriented boards for putting together tall MO diagrams, but there were six LCs over here.

And you will see that there will be another one that makes a bond with the 4s orbital. And so, accordingly, the 4s orbital comes up here. There will be an antibond derived from 4s. There will be also a set of three that are antibonding derived from interaction of 4p with the other ones, here.

And there is a big energy mismatch between 4p and these, so we will draw these as the least stabilized of the set.

But now, what you can see down here is that we have found a way to form six bonds, six pairs of electrons, each coming from the highest occupied molecular orbital of the six ammonia molecules. We have formed six bonds using these valence orbitals of the metal.

And how many more electrons do we have to put into the diagram?

We have six because this, in the case of our cobalt (NH<sub>3</sub>)<sub>6</sub><sup>3+</sup> six three plus -- This is Group 9. Minus three for the 3+ charge.

All the ammonia ligands are neutral, equals six.

So this is a  $d^6$  case.

The orbitals here that we called  $t_{2g}$  and  $e_g$  star can now take up six more electrons.

And I am drawing them in here with the assumption that this is a low-spin case. And that is reasonable based on the 3+ charge of this ion. We have already discussed the effective charge. It draws the ligands in.

It tends to increase the value of  $\Delta O$ , as we have seen.

And so this is how I would populate that diagram, with the 6d electrons going into the nonbonding  $t(2g)$  constituting the highest occupied molecular orbital of this system. And then, stabilize the lone pairs. Down here what is really going on, you can think about these six ammonia molecules acting simultaneously as six Lewis bases to a metal that has enough empty orbitals to accept six lone pair donations to that same metal. So it is a Lewis acid times six. And it is positively charged, which of course tends to draw electron density to it.

And that is our simplified molecular orbital diagram for the sigma-only case. Now, there are a lot of other interesting cases. As you can see here from this spectrochemical series where the ligands in the middle are basically sigma-only urea, water.

But then at either end of the spectrochemical series, you get into systems where you must take pi effects into account.

And we will treat, first, the case of a pi donor.

Remember that if we are talking about a donor, that means we are effectively talking about a Lewis base.

And you have to ask yourself the question in a system that has a ligand that can make pi bonds, are the orbitals on the metal that have pi symmetry filled, or are they empty?

And, similarly, are the pi symmetry orbitals on the ligand in question filled or are they empty?

And, if you can get all that right, you will really understand what happens in terms of attenuating  $t(2g)$  when you add in pi effects. We have seen that the  $e(g)$  orbitals of a metal are the  $d_{z^2}$  and  $d_{x^2-y^2}$  that point along the axes. The  $xz$ ,  $yz$ , and  $xy$  that point between the axes have the potential to make pi bonds with ligands. And so here is an example of a type of ligand that can make pi bonds to a metal.

This ligand is  $NH_2^-$ .

And it can make both sigma and pi bonds to a metal.

It is usually the case that if a ligand is capable of making pi bonds to a metal, it is also capable of making sigma bonds. And so the pi effects are sort of mapped onto the sigma framework.

And so what we found over here and here about the sigma only case, that will also be true for pi systems.

But then we are superposing on that diagram the pi bonds that can form in the system. And the way that  $NH_2^-$  can make both sigma and pi bonds with a metal is, first of all, it has a lone pair that is directed at the metal, like this.

For forming sigma contacts. And, if you have six of these around a metal, the situation would be just the same as what we derived over here for the cobalt hexamine.

But this is a planar system. The sum of the bond angles around the nitrogen in systems like this are 360 degrees meaning that, unlike ammonia itself, which is a trigonal pyramid, this is a planar system.

And so it has a lone pair perpendicular to that plane.

I will draw it that way. It is just a pure p-orbital, perpendicular to the plane of the substituents on that nitrogen. And the way that could make a pi bond with the metal is through simultaneous donation above and below the plane of its substituents on that nitrogen, so that this ligand can interact as a double Lewis base with a metal if the metal has appropriate orbitals available.

And so a situation in which you might find this would be the following.

An example of such a molecule, this would be a neutral one.

And what you see is that the planes of these NH two units are lining up with the coordinate xz, yz, and xy Cartesian planes in the molecule.

Since each of these ligands is negatively charged and the molecule is neutral, the chromium is therefore in the +6 oxidation state to balance the six negative charges on the amido ligands, we call them.

This is amido. And so this one, in fact, is a d zero case.

And d zero is an electron count that is pretty typical for the formation of pi bonds from ligands that can donate into the metal center. If you have d electrons present in a system like this, then you won't have the empty d-orbitals on the metal that are necessary to accept bonds formed by lone pair donation of this sort.

The system will become choked up on itself with too many electrons. Let's see what those perturbations will lead to for our MO diagram.

I am going to focus in on linear combinations of amide lone pair orbitals that, in fact, have the correct symmetry to interact with our t(2g) set, since that is our pi set of orbitals from the d manifold on the metal.

So let's look at this.

This would be d(yz).

And then, let me choose -- We can make a pi bond of this sort using a linear combination that I am mating up

together with the  $d(yz)$  orbital.

And while I have drawn here the bonding counterpart there, of course, will be an antibonding counterpart for that. Let's draw the one that belongs to  $d(xz)$ .

And that will be the one up top, here.

So what we have is  $\pi$  bonding happening here, here, here, and here that corresponds to  $\pi$  lone paired donation into that metal orbital.

And then, finally, we have one that involves the  $d(xy)$ .

And this would be with our hydrogens up and down, here and here. Sorry.

Up and down in front and in back like that, so that we can make two  $\pi$  bonding interactions over here with this. There is  $\pi$  bonding,  $\pi$  bonding, bonding, bonding.

At this point, we have gotten to where we can recognize how there are three linear combinations of the  $\pi$  lone pairs from these amido ligands that will have the correct symmetry to interact with the  $t(2g)$  set from our metal. There are three more where you would just flip one of the two on each, and those would have the correct symmetry to interact with the  $p_x$ ,  $p_y$ , and  $p_z$  orbitals on the metal. I am not going to draw those out since we are focusing on the  $d$  part of our diagram at the moment.

And what we will find then, in the molecular orbital diagram for a system of this sort, is that our  $d$  manifold, this is our  $3d$ ,  $4s$ ,  $4p$ , is such that, you remember previously  $t(2g)$  came straight over.

And now, instead, we are going to see that it goes up in energy because what  $t(2g)$  now is, it still has a lot of  $d(xz)$ ,  $d(yz)$  and  $d(xy)$ .

But now,  $t(2g)$  has acquired a  $\pi$  star character due to the fact that we have these linear combinations over here. These are our  $\pi$  LCs that we drew over there that are of the appropriate symmetry to interact with  $d(xz)$ ,  $d(yz)$  and  $d(xy)$ . And, therefore, these that are filled are stabilized, come down here and form a  $t(2g)$  set that is bonding because those, of course, are filled in,  $NH_2^-$ .

And, if the metal has an empty  $t(2g)$  set, you see that we do get three  $\pi$  bonds.

$t(2g)$  now gives us  $\pi$  antibonds.

This is being mapped on the sigma framework that is the same as what we have right here for the cobalt

hexamine, so that above  $t(2g)$  we will have the  $e(g)^*$ .

And will now recognize that  $e(g)$  is sigma star rather than pi star, so it is more strongly destabilized due to the greater overlap considerations of forming sigma bonds versus the side to side overlap of pi bonds. And the key observation here is that pi donors -- -- decrease the magnitude of  $\Delta O$  by raising the energy of  $t(2g)$ , by making  $t(2g)$   $\pi^*$  in character.

Antibonding. We can see, not only that  $t(2g)$  should be raised up, but that mapping that onto our full sigma framework diagram,  $\Delta O$  is shrinking.

We still have our six sigma bonds between the  $NH_2$  ligands and the metal. They are down here, just not drawn. It is the same as up here.

And now, we have three additional pi bonds.

There are another three additional pi bonds that you can draw because we do have six of these  $NH_2$  minus ligands. And then, the corresponding antibonding orbitals involve 4p. And they are way up here somewhere in energy and very empty.

Since this was a d zero case, what we have is that you have we pairs of electrons on six  $NH_2$  minus's that are down here in this manifold of metal ligand sigma and pi bonding.

And so we have 12 pairs of electrons down here that describe the sigma plus pi bonding between the metal and the ligands. And then you come here to your d manifold, these are empty because this is a d zero case, because I happened to choose chromium in the six plus oxidation here. So it is a d zero case, and we wouldn't have any electrons to put in here.

But, under these circumstances, in order to get color in a system like this, you would have to be promoting an electron from down here from these pi bonds probably into the d manifold, for example. And what we have seen here, namely that pi donors decrease  $\Delta O$  should give you a clue as to what is going on with chloride and fluoride.

Since those have small values of  $\Delta O$ , they lie at a position of weakness in the spectrochemical series.

And in the converse, that ligands like cyanide and especially carbon monoxide are very high in the spectrochemical series because they are pi acid ligands.

And this is something you will be getting more information about in recitation this week. See you all on Wednesday.

