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**CATHERINE  
DRENNAN:**

And so on today's hand out we're continuing to think about color. We're also going to think about magnetism some more, and we're going to think about more types of geometries. So we've seen that the type of ligand, whether it's a weak field, intermediate field, or strong field ligand makes a difference in terms of the splitting energy. How much the d orbitals are split due in the presence of the ligand, arranged in octahedron geometry. But we'll see that the geometry matters. That if you have different kinds of geometries, then the splitting is going to be different between the d orbitals.

So now we're going to look-- and I'll set this up. We're going to look at a nickel demo, which we'll have in a few minutes. But first, let's think about the colors that we're going to see. So if we have a nickel chloride compound that is greenish, what kind-- it will absorb then what kind of light, if it is a greenish kind of color? What color would it absorb then?

**AUDIENCE:**

Red.

**CATHERINE  
DRENNAN:**

Red. Reddish, which is what kind of wavelength? Long or short?

**AUDIENCE:**

Long.

**CATHERINE  
DRENNAN:**

Long. Right. So we're going to get a long, reddish kind of-- it will absorb a long or red wavelength. And so if we're absorbing a long wavelength, what would be true about the splitting energies? Is it going to be a big or small splitting energy?

So first, if you have long wavelength what's the frequency? Long or short?

**AUDIENCE:**

Short.

**CATHERINE  
DRENNAN:**

Short. And so the energy would be short as well. So it's going to be a small energy associated with it. Just a small splitting. And you remember what we learned about chloride minus? What kind of a ligand is it? It's a weak field ligand, so this makes sense. So a weak field ligand only splits the field a little bit, it's not a very strong ligand, so it can only split it so much.

Now we're going to take this greenish compound and we're going to add some water to it. And that's going to make it a little more blue. Be sort of a blue green. And let's think about what's happening there. And we'll compare it to what we have above. So now, if it looks blue green, what sort of color is going to be what's absorbed?

**AUDIENCE:** Orange red.

**CATHERINE DRENNAN:** Right. So we're going to have a more orange red color here. And so that's going to be longer or shorter than the one above?

**AUDIENCE:** Shorter.

**CATHERINE DRENNAN:** Shorter. Right. So we were here. Now we're moving more into the orange region, so we're going to be absorbing a wavelength that's a bit shorter. So is the energy going to be larger or smaller? Yeah. So it's going to be a larger energy because we have a shorter wavelength so we're going to have a bit of a higher frequency. And so we'll have a higher energy or larger energy.

And do you remember what kind of ligand water is? It's an intermediate field ligand so it's going to be stronger than chloride. So chloride was very weak. Water sort of in the middle. And then we had cyanide as an example of a very strong field ligand. So this makes sense that would be a bit stronger. So we have a larger splitting.

Now they're going to break this sample into two. And batch one you're going to add EDTA. That was our chelating agent that we talked about before, and that's going to make it even a bit more blue. And here we have our model of EDTA bound to our metal. And so if we think about this, then if it's a bit more blue-- so we're going to be absorbing a color that's even more orange. And so that's going to be even shorter than what we had there. So then our splitting energy-- the energy is going to be what? Larger or smaller?

**AUDIENCE:** [INAUDIBLE].

**CATHERINE DRENNAN:** Yeah. So it will be even larger. And I've never told you what kind of ligand EDTA is, but from this, if you're getting a larger splitting, you would predict it's a stronger ligand than water. And in fact it is an even stronger one than water. And again, we're going to be increasing entropy in this room in a few minutes because we're going to be displacing six water molecules with one molecule of EDTA, which will bind to your metal with six points of attachment. So watch

out for that entropy change.

So that was batch one. Now we're going to take some of this nickel hexa-aquo compound and we're going to mix it with another chelating agent. So remember, our nickel water complex is blue green and we're going to add another chelating agent, and now it's going to become red.

And so if it's red, what color is going to be absorbed?

**AUDIENCE:** Green.

**CATHERINE DRENNAN:** Green. And so this wavelength then is going to be what compared to orange? Yeah, so it's even way shorter. We were kind of right up here. Now we've all the way shifted down here so it's way shorter. So the energy is going to be what? Small or big?

**AUDIENCE:** Big.

**CATHERINE DRENNAN:** It's going to be very big. But this isn't an octahedral system anymore, so I didn't have a little O by my energy. And it's actually a square planar system so we're not gonna do sort of a direct comparison here. But this tells us that in square planar you're probably going to get pretty big splitting of our d orbital energies because we can get something that-- the color suggests that there must be a big splitting.

So those are what we're predicting for the colors. Let's see what happens.

**GUEST SPEAKER:** Is it on? Yes it is. OK. So this is the nickel chloride complex that Cathy was talking about. As most of us can see it's very green. Put it under here. You could probably obviously see that it's green. Maybe against this background. Look at that. It's very green. Thank you, Elena.

So we don't need that, do we? No, we don't need that. We're just gonna pour it into the water. So when we pour this into the water we're expecting-- you guys remember? Blue green. So [INAUDIBLE]. And that's fuming. That smells. Terrible. And that's very obviously not that clear.

[LAUGHTER]

Wonderful. Well, it's kind of blue green. Right around the color that you'd expect for water to be.

**CATHERINE DRENNAN:** We should switch gloves from green to blue green as we do the experiment. You can see it a little bit better there maybe. I don't know. Trust us.

**GUEST SPEAKER:** Now we're going to do--

**CATHERINE** The next one's a little more dramatic. Front row. Is it blue green?

**DRENNAN:**

**AUDIENCE:** Yeah.

**GUEST SPEAKER:** So we're going to split this up into two solutions, which is about 180 mls. I should have picked a different colored glove. And we're going to add some EDTA-- thank you. We're going to add some EDTA into this. And that EDTA is where? It's a powder, right? So EDTA is relatively insoluble in water so we're going to add a little bit of base to make sure this works. That's not the base. That's the base.

So let's start with the EDTA. I'm gonna use this to mix, I think. I should mix it with this. I should have gotten something to mix it with. I don't think so. Watch out. Watch out. This is going to be a bit reactive. It worked pretty well, actually. Look at that. Yay. It's blue. Just a second.

[LAUGHTER]

So by comparison it's a little bit more blue. And as we added some hydroxide-- or not hydroxide, acetate-- it allowed the EDTA to dissolve just a little bit more, which is why it reacted. OK, cool.

So now for the last thing we will add-- what are we adding? Oh, right. DMG. And we apologize to Cathy because this smells really, really bad and she has to smell this for the next 20 minutes along with the front row.

**AUDIENCE:** So will the front row.

**GUEST SPEAKER:** Sorry. But after we pour this you're not actually going to see a whole lot of color change. It smell bad. And the reason for that is because this is not quite as good. So the DMG has to come in and actually replace the water, and it's actually kind of hard for DMG to replace water.

So what we're going to do now is we're going to add a bit of ammonia. And the ammonia can replace the water a little better than the DMG can, and the DMG is going to replace the ammonia. And you'll see something kind of cool. It's actually going to very locally change color, and I might actually do this. Maybe over here.

**CATHERINE** What to do it on the document camera?

**DRENNAN:**

**GUEST SPEAKER:** Is going to work on the camera?

**CATHERINE** Mhm.

**DRENNAN:**

**GUEST SPEAKER:** OK. And let's give this a shot. Well, I can't reach that.

**CATHERINE** You have to move your hand.

**DRENNAN:**

**GUEST SPEAKER:** Let me pour it.

**CATHERINE** Yeah, so you can see the local now.

**DRENNAN:**

**GUEST SPEAKER:** So it goes back to being blue green again because the concentration of ammonia that we're adding is not quite enough to counteract the amount of water that's already in here. But if we add enough eventually it will turn totally red. But for it now you can see it's an equilibrium reaction, yay.

**CATHERINE** And it talks about also rates of reactions and rates of exchange, and that's our next unit.

**DRENNAN:**

[LAUGHTER]

**GUEST SPEAKER:** Yay.

[CLASS OOHS]

**GUEST SPEAKER:** Aw. Well, that's a good lead in to the next demo, right?

**CATHERINE** All right. Thank you guys. So you saw that red color develop, and so it's not just about whether something is a strong or weak field ligand. It's also about the geometry. So we're going to talk later about square planar geometry, so keep in mind that we'd expect that there should be some splitting between those d orbitals. But before we get to square planar we're going to do tetrahedral.

So here is our tetrahedral system. Here's my little drawing of tetrahedral, and I have my tetrahedral model here. And so here we're going to have our tetrahedral coordinate frame like this, where we have two ligands in the plane of the screen. One ligand coming out at you and one ligand going back.

And so now we're going to think about how our different sets of d orbitals are going to be affected by tetrahedral geometry. And again, remember crystal field theory is just saying that the ligands are like negative charges pointing toward the d orbitals. So when the ligand and the d orbital are near each other-- big repulsion. When they're farther away-- less repulsion.

So let's look at this case now. And so here we see in this geometry our ligands are now off axis. Here is the z-axis. Here's the y-axis. Here is the x-axis. Our ligands are off axis. So our orbital sets that are also kind of off axis are going to be more affected than our orbital sets that were on axis.

So this is different from what we saw with the octahedral geometry. So now we have more repulsion between those negative point charges that are the ligands and the d orbitals that are off axis. The ones that are 45 degrees away. So our  $d_{yz}$ ,  $d_{zy}$ , and  $d_{xz}$ .

So this is, in fact, the opposite of the octahedral case because in the octahedral case we had-- the ligands were on axis and so the orbitals that were on axes were the most affected. But now with tetrahedral ligand's off axis so the orbitals that are off axis are the most effective. So these switch positions now.

And  $d_{x^2-y^2}$  minus  $d_{z^2}$  squared. They still have the same energy. They're still degenerate with respect to each other, but now these are stabilized compared to these. But they also have the same energy. So all of these three orbital sets are also at the same energy. Also degenerate.

Now, one other really important thing about tetrahedral is not only is it the opposite of octahedral in terms of where those orbitals are, but overall they're sort of less splitting. So even though the orbitals that are kind of off axis are more affected by that tetrahedral geometry than the others, still the ligands aren't really pointing right toward those orbitals at all. They're closer but they're not right at them. So it's very different from the octahedral case where you had the orbitals sort of right on axis and the ligands right on axis. So there's less splitting. It's smaller splitting. So the octahedral, or the tetrahedral crystal field splitting energy,

is this  $\Delta_{t}$ . And that's going to be smaller.

So let's look now at some crystal field splitting diagrams. I'm going to compare the octahedral case with the tetrahedral case. So here is our octahedral case again. We have our octahedral crystal field splitting energy-- our  $\Delta_{O}$ . Now we have our tetrahedral crystal field splitting energy--  $\Delta_{t}$ . And we see again that it's opposite orders. So our  $d_{x^2-y^2}$  and  $d_{z^2}$ , instead of being up here as it is with octahedral, is now down here. And instead of our EG we now just have E. We just lost the G here. And our three sets that were stabilized, compared to the hypothetical spherical crystal field, are now de-stabilized because those orbitals at 45 degrees are closer to our tetrahedral ligands.

So again, we have this switch. And again, our EG goes to just G. The book sometimes has  $E_2$ . I don't know where that came from but you should just ignore it. It's just E. And  $T_2G$  is now is just  $T_2$ .

So again, you can see in this picture really well-- splitting energy is a lot less for tetrahedral. This is much smaller than the octahedral crystal field splitting energy, so much, much smaller because again, none of those ligand point charges are really directly toward those orbitals. So overall, it's less splitting.

And because there's less splitting, when you think about putting electrons in to the system it doesn't take much to go up here. So the pairing energies is going to always be a lot greater than the energy to put it in this higher energy orbital set because it's not very much higher than the first set. So these would all be high spin systems. So we put in our electrons singly to the fullest extent possible before we start to pair them. So you can assume that all tetrahedral complexes are high spins. That's a pretty good assumption.

So just like the tetrahedral case, we have overall-- we're maintaining the energy of the system. So in the tetrahedral case we had three orbitals that were stabilized. So they went down by  $2/5$  and two that went up were de-stabilized, so they went up by  $3/5$  to maintain the overall energy of the system.

In the tetrahedral case we have two orbitals that are stabilized down in energy, so they're down by minus  $3/5$ . And then we have three up, so those are up by  $2/5$ . So same idea, but again, everything is opposite.

So let's take a look at an example of the tetrahedral case, and we'll look at chromium 3 plus.

So what is the d count here? Who can just tell me? Find chromium in our table. Yup. It's going to be three, so group 6 minus 3 is 3. And now, why don't you tell me how we are going to put in those three electrons? All right. 10 more seconds.

OK. Most people got that right. So again, this is not correct for a high spin, which most tetrahedral compounds are. This would be correct. This arrangement of electrons is also correct, but if you look at the orbital names those are incorrect. So on a test you need to be able to write all the correct orbital names and the correct designators as well, as well as putting it in the electrons in the right way. So good to practice.

So we put in now our three electrons over here, and now we can think about our  $d_n$  configuration. So if you're asked to write out the d to the n electron configuration, what that's asking you for is to say how many electrons are in which of the two orbital levels. And so you would say, in the e level here you have two and in the  $t_2$  level you have one. And this is just then a shorthand. That's why they have these little abbreviations. You don't have to write out all the names of your d orbitals.

So how many unpaired electrons do we have then? We have what? Three. And if I'm now telling you that this is a complex with chloride and that the wavelength of the most intensely absorbed light is 740, why don't you predict the color of the complex for me? OK. 10 more seconds.

Yup. So we can look and see this wavelength is going to be in the red so that the predictive color of the complex would be the complimentary, or green. And so green then is one that has-- it's pretty short. This is a pretty long wavelength, which would be consistent with a very tiny splitting energy.

So now let's think about the square planar case. So our square planar system is described-- so we're in the plane here. It's, again, square planar. And now we have our ligands along the y-axis and the x-axis. So we have nothing along the z-axis here. So tell me, based on this and then again our ligands are on axis, which of those d orbitals do you think is going to be the most de-stabilized by this geometry? What do you think? You can just yell it out.

**AUDIENCE:**  $x^2 - y^2$ .

**CATHERINE DRENNAN:**  $x^2 - y^2$ . And what would you think would be next in terms of de-stabilized of those sets?  $xy$ ? Yeah, so that's the case. So most is going to be  $dx^2 - y^2$



squared. Again, those orbitals are on axes. ligands on axis. Next would be the other one that has x and y.

So let's take a look at this now. So we have our dx squared minus y squared. Our orbitals are on axis. Our ligands are on axis. You really have lots of repulsion. So this would be de-stabilized the most compared to all other d orbitals. Really different amount of destabilization. This is a lot of repulsion. All the ligands are right toward those orbitals.

So dz squared, which used to be degenerate with dx squared minus y squared now is not anymore. There's a lot less repulsion for this because there's no ligands along the z-axis anymore.

So let's look at our other orbital set. The next one in terms of being de-stabilized is dxy. Now, these orbitals are off axis so it's not nearly as bad as for dx squared minus y squared. But compared to everything else it's a lot more repulsion than everybody else, but it's less than our dx squared minus y squared. And these guys are then going to be stabilized compared to the others.

So let's now draw our splitting diagrams and think about how this all plays in together. And so again, we'll compare it to our octahedral crystal field. So now, the most de-stabilized way up here, which is this orbital going to be? Which one? x squared minus y squared. Right. That's up in energy the most, so most de-stabilized. It's experiencing the most repulsion.

And then next, but much lower down, dxy. Again, the ligands are along in the xy plane, so that would be second. But those are 45 degrees off axis so it's way down in energy compared to the ones that are on axis. And then down here we kind of have all the rest, and it's usually written with dz squared here and then dyz and dxz over here.

But the order here-- these are all kind of stabilized compared to these two and the exact order is not quite as firm as in octahedral or tetrahedral cases. So again, this is quite different now. Overall, the energy is also maintained, but there's too many orbitals in too many places so you're not expected to know that.

But one thing that I will point out is that remember for the demo square planar-- we said that had to have a pretty big splitting? That's a really big splitting of the energy of the orbital. So square planar complexes can be capable of having big energies-- you need a big energy of your photon to be absorbed by a square planar. Or you could if you're going to bump it all the

way up there. That's really far away.

So now, clicker. Why don't you tell me what you think of a square pyramidal case? And this would be this case here where you have one ligand. You have a square planar geometry, basically, that you've added an extra ligand too. Or you had octahedral you took one away, and that extra ligand is along the z-axis. So what things do you think would be true?

Since we're running out of time let's just take 10 more seconds. So just to put-- that would be true. Now there's a ligand along z, so dz squared is going to be de-stabilized in the square pyramidal case compared to the square planar. Everything that has z's in it would also be de-stabilized, and these would definitely not be degenerate. There's no reason they would have the same energy there.

So we'll get to our bio example on Monday, but first what are the results?

[CHEERING]

Awesome. Congratulations. That was unexpected. Two new groups. All right. Have a good weekend. See you Monday.

So end of lecture 29 last page. We were talking about biological examples. We were talking about transition metals. We're talking about colors of things. And I just wanted to give you an example of why geometry can matter or be interesting from a biological context.

So the video that you heard about nickel showed that nickel allows H.pylori to colonize your stomach because the nickel enzyme creates a buffering system so that it can survive in the low pH of your stomach. And it's very hard to treat H.pylori infections because the antibiotics that you would give to kill the bacteria get destroyed in acidity of the stomach, so it's a very hard problem.

And it's fascinating that they can use this nickel enzyme to kind of allow themselves to live in this environment, so that's pretty cool. This is also really cool and arguably more beneficial to mankind. So nickel dependent enzymes also are responsible for removing a lot of carbon monoxide and carbon dioxide from the environment.

So microbes have these enzymes that allow them to use carbon monoxide and carbon dioxide as their carbon source for metabolism. And so collectively, these microbes are estimated to

remove about 100 million tons of carbon monoxide from the environment every year and produce about 1 trillion kilograms of acetate from greenhouse and other gases, such as CO<sub>2</sub>. So there's a lot of benefit to us from these nickel enzymes.

And so people are interested in doing a couple different things. One thing they're interested in doing is to see what these nickel centers look like so that they can make small molecules to do the same chemistry. People are also interested in taking these microbes as such and getting them to overexpress these enzymes and then convert things like CO<sub>2</sub>, greenhouse gas, into biofuels.

So some people in chemical engineering are doing that right now, and I'm collaborating with them on some of these projects. So this is, again, a very-- everyone is very concerned about climate and so this is a hot area of research.

So of course, if you want to know what something looks like at atomic level, x-ray crystallography is a great thing to do. But if you don't have a crystal structure you can use spectroscopy. In particular, you can think about whether the enzyme and this nickel center is paramagnetic or diamagnetic, and that can help you guess what the geometry of the metal center is. So this is sort of a first experiment you might try to do to understand what's going on in your enzyme.

So say you have a nickel plus 2 or d<sup>8</sup> center and it's found to be diamagnetic. Then we could be asked, can you rule in or out some of the common geometries for nickel based on this single observation? So let's do that.

So we want to add some electrons. So I'm going to go over here, and I have our diagrams on the board. So first, octahedral is a common geometry. Does it matter if this has a big splitting or small splitting for a d<sup>8</sup> center? What do you think? Think about it for a minute. Let's try it and see.

So if we have a small splitting we would go-- we put in our three electrons. And again, this is a d<sup>8</sup> system, so we have eight electrons. We put in our three and now we have to decide if we're going to go up here or if we're going to pair. But let's pretend it's a small splitting, so we'll put an electron up here. Then we're done. Now we have to pair, so we're going to come back down here to pair because we're going to put them in the lowest energy orbitals. So we have five, six, seven, eight, and we're done.

Now, if we said that the splitting was big we would have paired all of these electrons first and then put two electrons singly at the upper level. And that would have given us actually the exact same diagram. So in this particular case, it doesn't matter whether there's a big splitting or a small splitting. You get the same electron configuration. So is this diamagnetic or paramagnetic?

**AUDIENCE:** Paramagnetic.

**CATHERINE DRENNAN:** Paramagnetic. Which means what? It means that you have unpaired electrons. So we have unpaired electrons so it's paramagnetic.

So let's look at the square planar system now. So we have three orbitals that are down in energy, and because our square planar system is in the xy plane and it's on axis and we have-- so our ligands on axis and our ligands on axis point toward the orbitals on axis. So  $d_{x^2-y^2}$  is really high in energy.  $xy$  is a little bit higher, and these guys are down at the bottom.

So we don't really know anything about where we're going to put them in, but let's just put them in singly in these lower ones. So we'll do one, two, three, and then we'll pair them up. Four, five, six. And then we have two more, so that's seven, eight. And we definitely, unless we absolutely have to, don't want to put any electrons in our  $d_{x^2-y^2}$ . That's way up in energy, so we don't want to do that unless we have to.

So is this paramagnetic or diamagnetic?

**AUDIENCE:** Diamagnetic.

**CATHERINE DRENNAN:** Diamagnetic. So we have one option here that is consistent with the spectroscopy.

Now let's look at tetrahedral. Is tetrahedral-- what do you think? Is it going to be high spin or low spin? High spin so we'll have a small splitting, and that is because in the tetrahedral geometry you have-- your ligands are off axis, so we have an opposite of the octahedral system. The orbitals that were higher in energy, more destabilized, are now lower. But the ligands aren't really pointing directly toward any of the d orbitals, so the splitting overall is much smaller.

So this splitting is always going to be pretty small, and so that leads to a high spin system,

which is you have the maximum number of unpaired electrons. So you can always assume it's high spin or splitting is small, so we're going to put your electrons in singly to the fullest extent possible before you pair. So we'll put one, two, three, four, five, six, seven, eight.

So is this diamagnetic or paramagnetic?

**AUDIENCE:** Paramagnetic.

**CATHERINE DRENNAN:** Paramagnetic. So of these three choices, the only one that would be consistent with the spectroscopy is the square planar system, and that turned out to be correct. It was a square planar system. And so here is a picture of that square planar system. So here we have the nickel in the middle and we have four ligands all in one plane. So we have this really nice square planar geometry that people predicted would exist before there was a crystal structure.

And so this is one of the catalysts for allowing microbes to live on carbon dioxide as their carbon source, which is really an incredible thing that an organism can do. Little microbes, bacteria-- super cool. They can do all sorts of chemistry that we struggle to be able to do.