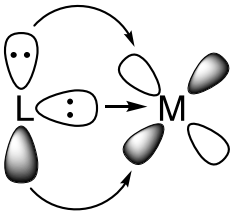
The Spectrochemical Series

Introduction. Inorganic chemists use specific terms to indicate the various properties of ligands. These include things like "strong field", "weak field", "hard", "soft", "monodentate", "chelating", or "pi-donor". These ligand properties influence the stability and electronic structure of the complexes that are formed when they are combined with a metal atom or ion. One useful way to estimate the electronic effects that a ligand has on a metal is to find the ligand's position in the spectrochemical series, shown below. The spectrochemical series places ligands in order of increasing Δ; that is, the magnitude of the energy difference between the d-orbitals that an electron jumps between when light is absorbed.

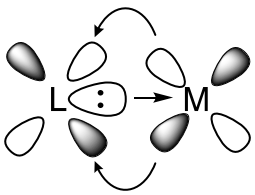
$$I^- < Br^- < Cl^- < F^- < OH^- < H_2O < py < NH_3 < en < phen < NO_2^- < PPh_3 < H^- < CN^- \cong CO$$

Ligands on the left are commonly referred to as weak-field ligands, and ligands on the right side are called strong-field ligands. It's important to remember that this series does not necessarily correspond to the binding strength of a ligand; this is just about Δ. Ligands are broken up into three major categories:

σ-donor ligands: **All ligands are *σ*-donors**. The ligand lone pair that forms a bond with the metal will maximize its overlap with the metal's orbital by pointing directly at it. The more readily a ligand can share its lone pair, the higher its position on the spectrochemical series. This is why hydride is so high in the series; it can't hold on to its lone pair well at all.[1]



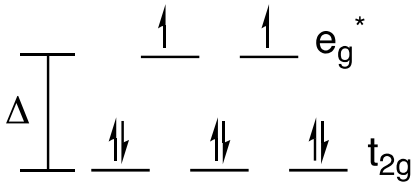
π-donor ligands: Some ligands have extra lone pairs on their binding atom beyond the one that forms the σ-donor interaction. These additional lone pair electrons can also interact with the metal's d-orbital in a side-on fashion, creating an additional bond. Despite this, we don't generally draw bonds to π-donor ligands as double bonds because the interaction is usually very weak. Strangely, π-donor interactions actually **cause Δ to shrink** compared to a σ-donor of equal strength. Halide ions are the most common examples of this type of ligand. Don't confuse the small Δ value of halides for weak metal-ligand binding; halides can form extremely strong bonds with metals.



π-acceptor ligands: Sometimes a ligand can donate electrons with its lone pair to form one bond, but also accept electrons from the metal with one of its empty orbitals. This phenomenon is sometimes called back-donation or back-bonding. The interaction is very strong, and results in **very large Δ values**. If a ligand can kill you, chances are good that it's a π-acceptor. In addition to creating large Δ values, π-acceptors tend to bind very tightly to metals, sometimes irreversibly.

The way we determine a ligand's position on the spectrochemical series is by using UV/vis spectroscopy to measuring the size of Δ (hence, the name). In order to compare ligands in a valid way, we need to measure a series of complexes that contain the same metal, that have the same oxidation state, and that have the same geometry. This way, we can be sure that the spectral differences we observe are due only to the ligand.

In this experiment, each lab group will synthesize one octahedral Ni(II) complex and measure its UV/vis spectrum to determine electronic absorption energies. The energies of these absorptions will be used to place the ligands on the spectrochemical series relative to each other. Some of the ligands used in this lab are not included in the series provided above, so you will need to make an educated guess as to where the ligand should be placed.



It's natural to expect that the UV/vis spectrum should contain just one peak corresponding to the energy jump between the t_{2g} and e_g d-orbitals. Unfortunately, the world isn't simple. As it turns out, Ni(II) actually has three excited states that have very different energies (the explanation goes beyond this course). All of the compounds synthesized in this experiment are octahedral d^8, and will exhibit the same three absorption peaks whose energies are directly proportional to the size of Δ. Since your job here is determine each ligand's position on the spectrochemical series, it's enough to simply compare the energies of one of the transitions across the series of compounds.

Experimental Procedures (You will receive your group's assignment before lab day):

Procedures adapted from "Laboratory Manual - Inorganic Chemistry III" by chemistry faculty at Universiti Malaya – Kuala Lumpur

***tris*(2,2'-bipyridine)nickel(II) sulfate heptahydrate** – Dissolve 6.0 mmol of 2,2'-bipyridine in 10 mL of methanol in a conical flask. In a 50 mL round bottom flask, dissolve 2.0 mmol nickel(II) sulfate hexahydrate in 5 mL of water. With magnetic stirring, use a pipet to transfer the bipyridine solution into the round bottom flask. Stir for about 5 minutes. Concentrate the solution on the rotary evaporator until crystal begin to form. Chill the solution on ice and collect the red precipitate by suction filtration.

UV/vis: Using a volumetric flask, prepare a 0.05 M solution of your product in water.

***tris*(ethylenediamine)nickel(II) chloride dihydrate** – In a conical flask, dissolve 5 mmol of nickel(II) chloride hexahydrate in 50 mL of water. To this solution, add 2.2 mL of ethylenediamine and stir to combine. At this point, some insoluble impurities may have formed that should be removed by gravity filtration. Transfer the solution to a beaker, add a wooden stick to aid boiling, and boil until the total volume of the solution is about 30 mL. Add

two drops of ethylenediamine and cool the solution in an ice bath. Collect the lilac precipitate by suction filtration and wash twice with 95% ethanol.

UV/vis: To prevent ligand dissociation, your solution and blank will contain an excess of ethylenediamine (20% w/w in water). Using a volumetric flask, prepare a 0.05 M solution of your product in 20% ethylenediamine.

hexamminenickel(II) chloride – In a conical flask, dissolve 8.0 mmol nickel(II) chloride hexahydrate in 3 mL water. Move to a fume hood and add 6 mL concentrated ammonia. Heat to about 80 ^{o}C and then cool in an ice bath. Once the solution is cooled, remove from the ice bath, add a magnetic stirbar, add 6 mL of 95% ethanol dropwise with stirring. Collect the precipitate by suction filtration. Wash the solid once each with ethanol and acetone.

UV/vis: To prevent ligand dissociation, your solution and blank will contain an excess of ammonia (5 M in water). Using a volumetric flask, prepare a 0.05 M solution of your product in 5 M ammonia.

***hexakis*(dimethylsulfoxide)nickel(II) chloride** – Into a conical flask, place 2.0 g nickel(II) chloride hexahydrate and add 30 mL anhydrous ethanol (another anhydrous alcohol may be substituted if ethanol isn't available). Swirl to dissolve. Add 30 mL diethyl ether and then 51mmol of dimethylsulfoxide. Seal the flask with a cork, cover with parafilm, and place in the refrigerator. Check for crystals periodically. Do not place into the freezer because you will likely freeze the DMSO instead of precipitating your product. Collect your product by suction filtration and dry in a desiccator.

UV/vis: Using a volumetric flask, prepare a 0.05 M solution of your product in DMSO. Blank with DMSO.

potassium hexathiocyanatonickelate(II) tetrahydrate – In a 100 mL round bottom flask, dissolve 10 mmol nickel(II) sulfate hexahydrate and 60 mmol potassium thiocyanate. Remove all the solvent on the rotary evaporator. Add 20 mL anhydrous ethanol and swirl, sonicate, and/or scrape until you have formed a colored solution and an off-white solid. Remove the solid by filtration and concentrate the solution on the rotary evaporator until crystals begin to form. Cool the flask and collect the solid product by suction filtration.

UV/vis: To prevent ligand dissociation, your solution and blank will contain an excess of KSCN (10 M in water). Using a volumetric flask, prepare a 0.05 M solution of your product in 10 M KSCN.

Questions to Answer:

1. Using common ligand abbreviations, write the formula of each of the compounds synthesized in this lab. The formula should preserve structural information. For example: hexaaquanickel(II) sulfate should be written as $[Ni(H_2O)_6]SO_4$, and not as $NiH_{12}O_{10}S$.

2. Use ChemDraw to draw the structure of your assigned compound. Make sure the structure looks professional and conveys important information like the overall charge of the complex.

3. Plot the UV/vis spectrum of your compound. Since absorption is a mostly useless quantity, you should place the molar absorptivity coefficient on the y-axis. Do not keep the default settings for a scatter plot from Excel because those look horrible!

4. Construct a table that communicates the wavelengths, energy (in eV), and molar absorptivity coefficient (ε) values for every compound synthesized in this experiment. This table must be thoughtfully laid out and neat. Again, the default table settings in Word look terrible, and should not be used. This paper has a well laid out table communicating UV/vis data, though you aren't presenting quite the same things:

http://www.plantphysiol.org/content/plantphysiol/77/2/483.full.pdf

5. Rank the 6 ligands according to their relative positions on the spectrochemical series. Make it very clear which is the strongest field ligand, and which is the weakest field ligand. Water is the ligand in the aqueous solution of nickel(II) sulfate.

6. For anionic ligands, σ-donor strength is directly proportional to the pK_a of the acid made by combining H^+ and the anionic ligand. Using acid/base concepts, explain why this is the case. A good answer will use two example acids from opposite ends of the pK_a scale.

7. Using the Advanced Search at https://pubs.acs.org find a paper published in *Inorganic Chemistry* or *Journal of the American Chemical Society* within the last 5 years that describes the synthesis of a nickel compound. Draw that compound in ChemDraw and provide the ACS-style citation for the article. Be sure to follow the citation format exactly.