

# CHEM 20200 (Inorganic Chemistry II) Notes

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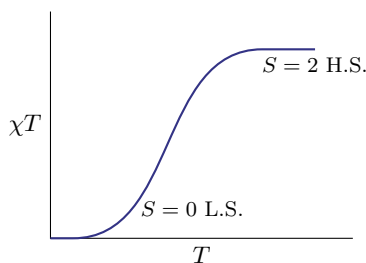
# Unit 1

## Electronic Phenomena

### 1.1 Lecture 1: Introduction/Key Trends

- 3/29:
- Largely asynchronous, but synchronous discussions, office hours, and tests.
    - Refer to the Canvas site for all information; it's the class hub.
  - To understand transition metal trends and properties, start with *atomic* properties and trends.
  - **Electronegativity:** The energy that an atom will gain when it gains an electron.
    - Fluorine really wants to gain an electron; thus, it has high electronegativity.
      - Do you mean electron affinity?
    - Increases across a row; decreases down a column.
      - Transition metals, in general, are an exception to this rule.
      - This is because of the **lanthanide contraction**.
    - Discontinuities in the transition metals (Mn and Ni) correspond to half-filled and filled *d* shells, respectively.
      - Extra stability means less of a desire to gain an electron.
  - **Ionization potential:** The energy required to remove an electron.
    - Varies with the identity of an element *and* its oxidation state.
    - Increases across a row; decreases down a column.
  - Size:
    - Many different definitions (depending on the specific thing you're interested in, one may be more useful than another). For example,
      - Atomic radius: Specific to an element.
      - Ionic radius: Specific to an oxidation state; as in salts and coordination complexes.
      - Covalent radius: Distance that one would expect for a bond; varies with bond order.
    - Decreases across a row; increases down a column (a notable exception to the latter trend follows from the lanthanide contraction).
    - Things that affect size:
      - Oxidation state.
      - Spin state (high spin [larger; this is because the  $e_g$  orbitals are antibonding, and antibonding electrons both push the bounds of the atom and weaken bonds, increasing the covalent radius] vs. low spin [smaller]).

- **Lanthanide contraction:** In the transition metals, there is a small/no increase in size between the second and third rows.
  - This is because the shell added in between contains the  $f$  orbitals, which are small, do not extend past the noble gas core, and do not provide good shielding.
  - $Z$  goes up a lot with little shielding, so the  $5d$  orbitals are contracted; thus,  $4d/5d$  orbitals are similar in size.
- **Oxidation state:** The number of electrons a metal center is below its valence.
  - Typically, the maximum oxidation state is defined by the  $d$ -count for the 0-valent metal.
- Having discussed four trends, how are they related?
  - As oxidation state increases, “electronegativity” and ionization potential will increase, and the radius will decrease.
    - This is because removing an electron  $\Rightarrow$  reduces shielding  $\Rightarrow$  higher positive charge  $\Rightarrow$  all orbitals decrease in energy  $\Rightarrow$  all orbitals decrease in size (hence radius decreases, too).
    - Watch out for discontinuities such as  $\text{Mn}^{2+}$ .
- **Magnetic properties:** Unique to the transition metals and the  $f$  block.
  - Consider  $\text{Fe}^{\text{II}}\text{L}_6^{2+}$  ( $d^6$ ).
  - Possible states: Low spin ( $S = 0$ ), intermediate spin ( $S = 1$ ; rare), and high spin ( $S = 2$ ).
  - We predict which state dominates by the:
    - **Pairing energy.**
    - **Ligand field stabilization energy.**
- **Pairing energy:** The energy cost of putting two electrons in the same orbital. *Also known as PE.*
  - Trends with orbital size/radius.
  - Decreases down a column.
- **Ligand field stabilization energy:** *Also known as LFSE.*
  - Can be thought of in terms of crystal field theory.
    - Extra thoughts on Figure VI.10 of Labalme (2021): Donating negative charge to a free metal ion in a spherically symmetric fashion uniformly raises the energy of the  $d$  orbitals by increasing repulsions and size.
    - Low-spin LFSE:  $6 \cdot -4 \text{ Dq} + 3 \text{ PE} = -24 \text{ Dq} + 3 \text{ PE}$ .
    - Intermediate-spin LFSE:  $5 \cdot -4 \text{ Dq} + 1 \cdot 6 \text{ Dq} + 2 \text{ PE} = -14 \text{ Dq} + 2 \text{ PE}$ .
    - High-spin LFSE:  $4 \cdot -4 \text{ Dq} + 2 \cdot 6 \text{ Dq} + 1 \text{ PE} = -4 \text{ Dq} + 1 \text{ PE}$ .
    - Thus, the energy difference between the low-spin and high-spin configurations is  $20 \text{ Dq} + 2 \text{ PE}$ . It follows that if  $10 \text{ Dq} > 1 \text{ PE}$ , then the complex will be low spin; and if  $10 \text{ Dq} < 1 \text{ PE}$ , then the complex will be high spin.
    - This also explains why the intermediate spin state is rare: if  $\Delta_o$  is large enough to make  $10 \text{ Dq} > 1 \text{ PE}$ , then it will likely take the complex all the way to a low-spin configuration (and vice versa for high spin).
    - Lastly, this means that  $\text{Fe}^{\text{II}}$  is a good **spin-crossover** ion.
- **Spin-crossover (ion):** An ion that can have both high- and low-spin states.
  - The graph of the magnetic moment  $\chi T$  of  $\text{Fe}^{\text{II}}$  vs. temperature  $T$  (see Figure 1.1) moves from  $S = 0$  at the bottom left to  $S = 2$  at the top right.
  - $d^2$  ions are never spin-crossover ions:  $-8 \text{ Dq} + 0 \text{ PE}$  for high spin vs.  $-8 \text{ Dq} + 1 \text{ PE}$  for low spin.

Figure 1.1: Magnetic moment vs. temperature for the  $\text{Fe}^{\text{II}}$  ion.

- Dq and PE values depend on:

- Ligand field strength.

- $\Delta O_h$  increases as  $\sigma$  donation increases.
- $\Delta O_h$  increases as  $\pi$  acceptance increases.
- $\Delta O_h$  decreases as  $\pi$  donation increases.
- To what extent do we need to have the spectrochemical series memorized?

- Metal center.

- Larger, more diffuse metals (i.e., second- and third-row transition metals) have better overlap with the ligands, giving rise to larger  $\Delta O_h$ .
- Note that pairing energy decreases in second- and third-row transition metals (due to the larger orbitals).
- These two factors imply that second- and third-row transition metals are almost always low spin.

- Oxidation state.

- As oxidation state increases,  $\Delta O_h$  increases (due to better energy matching, higher “electronegativity,” the role of electrostatics, and the electron configuration [ $d^5$  is almost always high spin, and  $d^6$  is often low spin]).
- Why do  $d^5$  and  $d^6$  exhibit the above behavior? Shouldn’t the stabilized orbitals be split more?
- See the below spectrochemical series for metals.

- Geometry.

- In a  $\sigma$ -only sense, lower coordination numbers tend to have smaller LFSEs.
- $T_d < C_{4v} \approx D_{3h} < O_h < D_{4h}$ .
- $\Delta_{\text{sq. pl.}} \approx 1.74 \Delta O_h$ .

- Spectrochemical series for metals (not as precise as the one for ligands, but a decent approximation):



- Hard/soft acid-base theory:

- Common Lewis acids:

- Proton:  $\text{H}^+$ .
- Molecules with no octet:  $\text{AlCl}_3$ ,  $\text{BR}_3$  (boranes),  $\text{BeH}_2$ .
- Metal cations:  $\text{Na}^+$ ,  $\text{Ti}^{4+}$ .
- $\pi$  acids:  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{PR}_3$ .

- Common Lewis bases:

- Carbanions:  $\text{CR}_3$ .

- Hydrides:  $\text{KH}$ ,  $\text{NaH}$ ,  $\text{LiAlH}_4$ .
  - Amines, amides, and phosphines:  $\text{NH}_3$ ,  $\text{PR}_4$ ,  $\text{NH}_2^-$ .
  - $\text{OH}_2$ ,  $\text{SR}_2$ ,  $\text{OH}^-$ .
  - Halides:  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ .
  - Carbonyl:  $\text{CO}$  (means  $\text{CO}$  is amphoteric).
  - Olefins:  $\text{C}_2\text{H}_4$ .
- Distinguishes hard vs. soft<sup>[1]</sup>.

## 1.2 Office Hours (Whitmeyer)

- 3/30:
- Electron affinity, not electronegativity, for the periodic trend?
    - At higher levels, people don't really distinguish between the two.
  - To what extent do we need to have the spectrochemical series memorized?
    - You don't need to memorize them, but it's good to know some of them off the top (exams are open note, but there are time constraints).
  - In connection with oxidation state, Prof. Anderson mentioned that  $d^5$  is almost always high spin, and  $d^6$  is often low spin. Why? Shouldn't the stabilized orbitals be split more?
    - 5  $d$  electrons each in their own orbital minimizes the pairing energy.
    - 6  $d$  electrons all occupy the lower orbitals to minimize antibonding contributions.
  - Using the textbook:
    - The lectures are essential in this course, and if you don't understand something in the lecture, ask Sophie or John or read the textbook.
    - If it's in those chapters, it could be asked about, but it probably won't be if John doesn't talk about it.

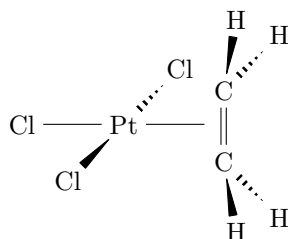
## 1.3 Chapter 1: An Overview of Organometallic Chemistry

*From Spessard and Miessler (2010).*

- 4/1:
- **Cluster compound:** A compound containing two or more metal-metal bonds.
  - **Sandwich compound:** A compound with a metal sandwiched between two ligand rings with cyclic delocalized  $\pi$  systems.
  - $\text{CO}$  is the most common of all ligands in organometallic chemistry.
  - **Carbide cluster:** A metal cluster encapsulating a carbon atom.
  - "Strictly speaking, the only compounds classified as organometallic are those that contain metal-carbon bonds, but in practice, complexes containing several other ligands similar to  $\text{CO}$  in their bonding, such as  $\text{NO}$  and  $\text{N}_2$ , are frequently included" (Spessard & Miessler, 2010, p. 4).
  - In the anionic component of Zeise's salt, the  $\pi$  electrons of ethene bond to a  $\text{PtCl}_3^-$  fragment (see Figure 1.2).
  - Complexes with chiral ligands can "catalyze the selective formation of specific enantiomers of chiral molecules. In some cases, the enantioselectivity of these reactions has even equaled that of enzymatic systems" (Spessard & Miessler, 2010, p. 7).

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<sup>1</sup>Hard vs. soft is the basis for the solubility rules!

Figure 1.2:  $\pi$  bonding in Zeise's salt.

## 1.4 Chapter 2: Fundamentals of Structure and Bonding

From Spessard and Miessler (2010).

- Review of the Schrödinger wave equation atomic orbitals, and molecular orbitals.
  - *Shell* and *subshell* are older terminology.
  - “In a bonding interaction, electrons are concentrated between the nuclei and tend to hold the nuclei together; in an antibonding interaction, electrons avoid the region of space between the nuclei and therefore expose the nuclei to each other’s positive charges, tending to cause the nuclei to repel each other” (Spessard & Miessler, 2010, p. 18).
- Discusses a bit of computational chemistry in the abstract.
  - Some of this stuff relates to what I talked about with Dr. Vázquez-Mayagoitia; I should reread this before I email him.
- There may be some stuff here that CHEM 20100 didn’t cover, but I’ll only come back if necessary.

## 1.5 Lecture 2: Electron Counting, $18e^-$ Rule

- 3/31:
- Organometallic chemistry: Strictly speaking, compounds containing metal-carbon bonds. More broadly, it’s homogeneous transition metal chemistry ([frequently diamagnetic] metals bonded to light atoms).
    - Deeply related to catalysis (both fine and bulk chemical synthesis, and biology).
  - Transition metal trends:
    1. Early transition metals tend to have higher oxidation states.
      - It’s easier to remove electrons from less electronegative elements (electronegativity increases across a period).
    2. Size: 1st row < 2nd row  $\approx$  3rd row.
    3. M–L bond strengths increase down a column.
      - Two reasons: Size (larger, more diffuse orbitals have better overlap) and electronegativity (increases down a column; this trend is unique to the transition metals).
    4. Higher coordination numbers are found for heavier metals.
    5. More high-spin species in the first row.
    6. First row transition metals prefer  $1e^-$  coupled.
      - Why?
    7. More difficult to reduce as you go down a triad (column).
  - Common structures:



– 4 coordinate:

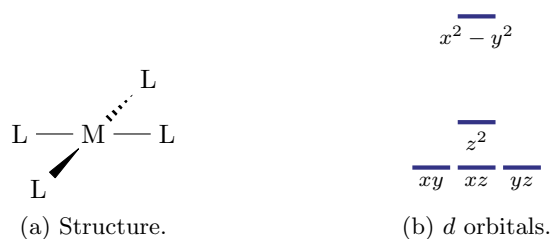


Figure 1.3: Square planar information.

- Square planar (note that the  $z^2$  orbital can swap with the three degenerate orbitals beneath it fairly easily; what's important is that  $x^2 - y^2$  is higher).



Figure 1.4: Tetrahedral information.

- Tetrahedral (much smaller splitting energy than some of the others).

– 5 coordinate:

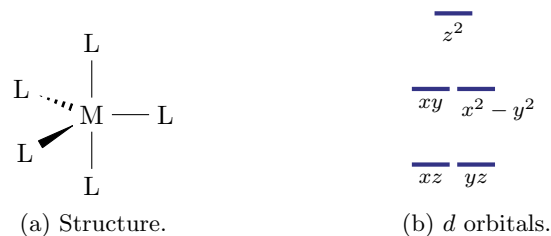


Figure 1.5: Trigonal bipyramidal information.

- Trigonal bipyramidal (the axial ligands push  $d_{z^2}$  high in energy,  $d_{xy, x^2-y^2}$  are degenerate by the threefold  $D_{3h}$  symmetry, and  $d_{xz, yz}$  are nonbonding and thus lowest in energy; note also that this geometry has **fluxional ligands**).

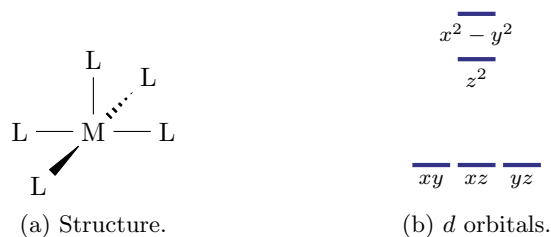


Figure 1.6: Square pyramidal information.

- Square pyramidal (think of it either as square planar with an axial ligand on top, or as octahedral missing one axial ligand on the bottom; thinking of it this way also rationalizes Figure 1.6b as the mean of Figures 1.3b and 1.7b).

- 6 coordinate.

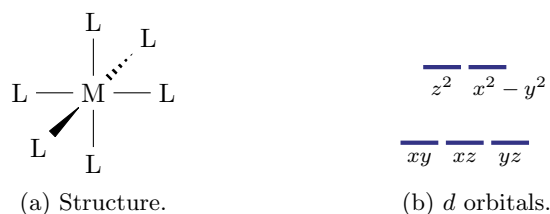


Figure 1.7: Octahedral information.

- Octahedral ( $d_{xy,xz,yz}$  are nonbonding in a  $\sigma$ -only framework, but can take on bonding character when  $\pi$  interactions are considered).

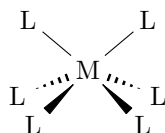


Figure 1.8: Trigonal bipyramidal information (structure).

- Trigonal bipyramidal (each pyramid is eclipsed, rather than staggered as in octahedral; Pfenig and Seppelt (1996) explores this geometry in greater depth).
- **Fluctional ligands:** A set of ligands that readily exchange positions around the molecular center via a **Berry pseudorotation**.
- Ligand types (see Labalme (2021, p. 93)).
- **X-type** (ligand): Typically anionic, covalent donors.
- **L-type** (ligand): Typically neutral. *Also known as dative donor*.
- **Z-type** (ligand): Typically neutral, but can be cationic (no electrons to donate; these are acceptors).
- Note that a carbonyl group can be both an L- and a Z-type ligand (L if it participates in  $\sigma$  donation, and Z if it participates in  $\pi$  acceptance).
  - Similar to how  $\text{Cl}^-$  can be both a  $\sigma$  and  $\pi$  donor.
- On hard/soft matching: remember that harder ligands will prefer harder metals, and vice versa.
- Electron counting:
- Organic chemistry concerns itself with an octet.
- But the octet rule is really a large HOMO-LUMO gap rule; filling stable orbitals and leaving the unstable orbitals empty.
  - In  $\text{CH}_4$  for example, we want to fill the  $\sigma$  and  $\pi$  MOs with all 8 electrons that they can hold, but leave  $\sigma^*$  and  $\pi^*$  unfilled (see Figure III.17 in Labalme (2021)).
  - However, in  $\text{ML}_6$  for example (considering only  $d$  orbital/ligand  $\sigma$  orbital interactions), we have nine  $\sigma$ /nonbonding orbitals that are ok to fill up and two  $\sigma^*$  orbitals that we should try to avoid filling up (see Figure 1.7b as well as Figure VI.2 from Labalme (2021) for a decent approximation).
- The nine orbitals that are ok to fill up in an  $\text{ML}_6$  compound can hold 18 electrons; this gives rise to the **18 electron rule**.

- **18 electron rule:** An octahedral  $ML_6$  transition metal complex with 18 electrons is fairly energetically favorable.
- Low-spin square planar:
  - 4  $\sigma$ /NB ligand orbitals plus 4 nonbonding metal  $d$  orbitals gives 8  $\sigma$ /NB orbitals that can hold 16 electrons in total (see Figure 1.3b).
  - Figure VI.13 of Labalme (2021) says that *two* metal orbitals form bonding/antibonding orbitals with the ligand orbitals, so why does Dr. Anderson assert that only *one* does? Is it because of what he said about  $d_{z^2}$  being practically interchangeable with the  $d_{xy,xz,yz}$  ligands in square planar complexes?
- **16 electron rule:** A square planar  $ML_4$  transition metal complex with 16 electrons is fairly energetically favorable.
- Note that the 18 and 16 electron rules respectively imply that octahedral complexes prefer  $d^6$  configurations and square planar complexes prefer  $d^8$  configurations.
- Note also that since the HOMOs in both 18-electron octahedral and 16-electron square planar complexes are nonbonding, the 18/16 electron rules are more of a suggestion.
  - In general, these numbers are more of a maximum; lower counts can still be stable.
  - However, there are cases of 19 and 20 electron systems.
- 2 schools of thought on electron counting: the **ionic method** and the **covalent method**.
  - Dr. Anderson prefers the covalent method; he's of the opinion that it's a bit more foolproof.
  - Proponents of the ionic method argue that it's nice because it gives you the oxidation state of the metal center throughout the process, but it can run into snags with certain ligands (in step 1 below, it is not always clear what splitting electronegativity dictates).

Ionic Method	Covalent Method
1. Break all M–L bonds according to electronegativity (or accordingly, to form the most stable fragments). Note that M–L bonds split homolytically.	1. Draw a legitimate Lewis structure (no half bonds or circles [as in benzene]). Don't forget lone pairs.
2. The charge on the metal after step 1 is its oxidation state.	2. Assign formal charges (in a dative bond, these belong to the ligand).
3. From 2, assign a $d$ -electron count.	3. The number of electrons that a given ligand donates is equal to its formal charge plus twice the number of dative bonds plus the number of covalent bonds.
4. The electron count equals the $d^n$ count plus the ligand donors (typically 2 electrons per ligand).	4. The electron count is that $d^n$ count for $M^0$ plus the sum of the ligand electron donations minus the charge on the complex.

- Gain familiarity with the  $d$  counts of common transition metals.
- A metal can actually have multiple oxidation states in resonance with each other, whereas the electron count is indisputable, i.e., the only number that you can definitively assign to a complex.
  - This is why it's better to use the covalent method; it goes straight to assigning the electron count, foregoing any possible issues with the oxidation state.
- If you apply each method correctly, they should both give the same answer.
- Examples (ligands):

- A phosphine  $\text{PR}_3$ .
  - The phosphine has a lone pair to donate to the metal center, forming a **dative bond**.
  - Alternatively, the formal charge on phosphorous in a  $\text{M}-\text{PR}_3$  situation is +1 and there is 1 covalent bond.
  - Either way, the phosphine is a 2-electron donor; this is further confirmed by the fact that phosphines are L-type ligands.
- CO.
  - We have multiple possible resonance structures for a  $\text{M}-\text{C}\equiv\text{O}$  bond, but we can robustly treat this with the covalent method.
  - $\text{M}-\text{C}\equiv\text{O}^{\oplus}$  has a +1 formal charge and 1 covalent bond, suggesting that CO is a 2-electron donor.
  - $\text{M}=\text{C}=\text{O}^{\cdot\cdot}$  has no formal charge and 2 covalent bonds, suggesting that CO is a 2-electron donor.
  - $\text{M}\equiv\text{C}-\text{O}^{\ominus}$  has a -1 formal charge and 3 covalent bonds, suggesting that CO is a 2-electron donor.
  - $\text{M}\leftarrow\text{C}\equiv\text{O}^{\oplus}$  has a net 0 formal charge and 1 dative bond, suggesting that CO is a 2-electron donor.
- NO.
  - If NO bonds linearly, it's a 3-electron donor (take  $\text{M}-\text{N}\equiv\text{O}^{\oplus}$  as a possible resonance structure).
  - If NO bonds bent, it's a 1-electron donor (take  $\text{M}-\ddot{\text{N}}=\ddot{\text{O}}$  for example).
- **Dative bond:** A covalent bond between two atoms where one of the atoms provides both of the electrons that form the bond.
- Examples (metal complexes):
  - Ferrocene, a sandwich compound with an iron atom between two cyclopentadienyl (or Cp) groups (covalent method).
    - Each carbon atom forms a single covalent bond to iron. This gives each iron four covalent bonds (two to its neighbors in the ring, one to its hydrogen, and one to iron), so there are no formal charges.
    - Thus, each Cp ligand donates 5 electrons by the covalent method, and iron as a  $d^8$  compound donates 8 electrons.
    - Therefore, this is an 18 electron complex.
  - Ferrocene (ionic method):
    - The cyclopentadienyl anion has a 1- charge, making it a  $6\pi$ -electron aromatic system.
    - There are two of these anions, with a total charge of 2- between them, so iron must be in the  $\text{Fe}^{2+}$  oxidation state to compensate.
    - This makes iron  $d^6$ , which plays well with 18 electron systems.
  - Hexamethyl tungsten  $\text{W}(\text{CH}_3)_6$  (covalent method):
    - Each  $\text{CH}_3$  ligand forms a single covalent bond with W without formal charge; thus, each donates 1 electron.
    - W is  $d^6$ .
    - Thus, the  $d$  count is 12, making it a pretty reactive compound.
  - $\text{W}(\text{CH}_3)_6$  (ionic method):
    - For each ligand, we split to  $\text{W}^+$  and  $\text{CH}_3^-$ .
    - This makes the metal center oxidation state  $\text{W}^{\text{VI}}$ , with a resultant  $d^0$  configuration.

- $\text{W}(\text{CO})_6$  (covalent method).
  - From above, CO is a 2-electron donor. Thus, the 6 CO's donate 12 electrons. This combined with the fact that W is  $d^6$  makes this an 18 electron system, i.e., pretty stable.
- $\text{W}(\text{CO})_6$  (ionic method):
  - We split  $\text{W}-\text{CO}$  into  $\text{W}^0 + \text{CO}$ .
- $\text{Pt}(\text{Cl})_4^{2-}$  (covalent method):
  - Each chloride forms 1 covalent bond (donates 1 electron).
  - Platinum is  $d^{10}$  (because it's chemically bound, the 6s electrons fall to the d orbitals; what would the d count of copper or zinc be? 10 as well?).
  - The charge on the complex is 2–, so the electron count is  $4 \cdot 1 + 10 - (-2) = 16 e^-$ 's.
- $\text{Pt}(\text{Cl})_4^{2-}$  (ionic method):
  - $\text{Pt}-\text{Cl} \longrightarrow \text{Pt}^+ + \text{Cl}^-$ .
  - Thus, we have  $\text{Pt}^{4+}$ . But the charge is 2–, so we actually have  $\text{Pt}^{2+}$ , which is  $d^8$ , which plays well with the 16-electron system.
- An enzymatic cofactor (covalent method):

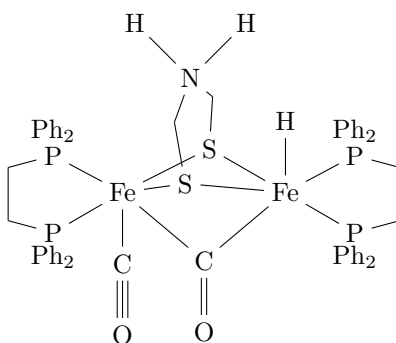
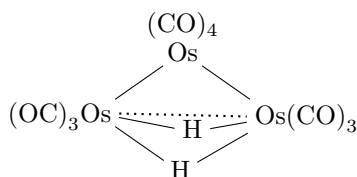


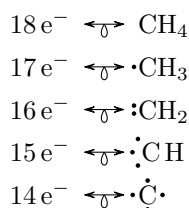
Figure 1.9: An enzymatic cofactor.

- Each phosphine and each carbonyl is a 2-electron donor.
  - The hydride is an X-type ligand with a covalent bond, and thus a 1-electron donor.
  - Now for the big bulky center bridging ligand: The sulfurs each carry a +1 formal charge and form two covalent bonds to the metal centers, so they each contribute three electrons. The nitrogen has an additional +1 formal charge, so the ligand overall is a  $2 \cdot 3 + 1 = 7$ -electron donor.
  - Summing all of this gives us 20 electrons.
  - Now for the metal centers: Each iron is  $d^8$ .
  - Thus, that's 36 electrons in total, but divided over two iron centers.
  - Therefore, the electron count for each iron is 18.
- Metal-metal bonds:
    - Assume that each metal will want to get to an electron count of 18.
    - Thus, the number of M–M bonds you would expect is
 
$$\# \text{ of M-M bonds} = (18 e^- \cdot \# \text{ of metals} - \# \text{ of } e^- \text{'s from L's and M}^0 \text{'s}) / 2$$
    - Essentially, one M–M covalent bond contributes one electron to each M, or two electrons to the complex as a whole.

- As we can see, this number would be 0 for the enzymatic cofactor in Figure 1.9, which is why we'd expect no metal-metal bonding between the two iron centers.
- Bridging hydrides and halides:
  - We can treat this by putting a +1 formal charge on the bridging atom:  $M-\overset{\oplus}{X}-M$ .
  - Alternatively, we can recognize what the nature of the interaction is:  $M-\overset{\cdot\cdot}{\underset{\cdot\cdot}{X}}-M$ .
    - From the above picture, it is clear that there is one covalent and one dative bond at play, making the bridging X-type ligand a 3-electron donor.
- We are now prepared to treat one final example:

Figure 1.10: Electron counting for  $\text{Os}_3(\text{CO})_{10}(\mu_2\text{-H})_2$ .

- Each carbonyl ligand is a 2-electron donor.
- Each bridging hydride is a 3-electron donor.
- Each Os–Os bond contributes 2 electrons.
- Thus, the ligands donate 30 electrons in total.
- Each osmium is  $d^8$ .
- Thus, the metal centers donate 24 electrons in total.
- Therefore, the number of Os–Os bonds is  $\frac{18 \cdot 3 - (30 + 24)}{2} = 0$ , i.e., there are no Os–Os bonds.
- Now this question could just be a relic of my previous understanding of bonding, and the answer may just be “MO theory,” but I’m still gonna ask: Where do the electrons in all of the bonds come from? It seems like if the osmiums are giving electrons to Os–Os and Os–H bonds, and we still count osmium as  $d^8$ , we are counting some electrons twice.
- Isolobal/isoelectronic analogy:
  - We can assume based on the fact that  $\text{Cr}(\text{CO})_6$  has 18 electrons and is stable that the isoelectronic compounds  $\text{V}(\text{CO})_6^-$  and  $\text{Mn}(\text{CO})_6^+$  have identical electron counts and similar properties.
    - Note that all of these compounds are both isoelectronic and isolobal. What does isolobal mean?
  - We can do the same thing between  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}(\text{NO})(\text{CO})_3$ , and  $\text{Fe}(\text{NO})_2(\text{CO})_2$ .
  - Also  $\text{Mn}(\text{CO})_5$ ,  $[\text{CpMn}(\text{CO})_2]^-$ , and  $\text{CpFe}(\text{CO})_2$  (these are isoelectronic, but not isolobal).
- We can also consider isolobal analogies between transition-metal-complex electron counts and organic fragments.
  - For example,



- We can also make analogies between other atoms/metal fragments:  $\cdot\dot{\text{P}} \cdot \leftrightarrow \cdot\dot{\text{C}}\text{H} \cdot \leftrightarrow (\text{CO})_3\text{Co}$ .
- Multiply bonded fragments can also work:  $\text{M}=\text{O} \leftrightarrow \text{M}=\text{N}-\text{R} \leftrightarrow \text{R}_2\text{C}=\text{O}$  for double bonds, and for triple bonds:  $\text{M}\equiv\text{O} \leftrightarrow \text{M}\equiv\text{N}-\text{R} \leftrightarrow [\text{R}-\text{C}\equiv\text{N}-\text{H}]^+$ .
- **Oxidation state:** The number of electrons a metal has given up or acquired.
- **Chemical valence:** The number of electrons from the metal that are engaged in bonding.
- In many cases, the valence and oxidation state are the same, but they can differ.
  - They notably differ when M–M bonds and Z-type ligands are in play.
- Consider the structure formed by two dimerized fic (is this the right spelling? Does it have a charge by itself?) fragments (a fic fragment is  $\text{CpFe}(\text{CO})_2$ ).

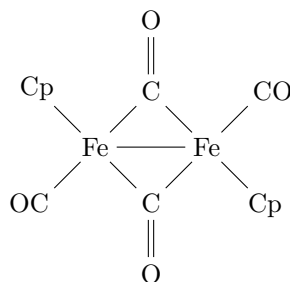


Figure 1.11: Two dimerized fic fragments.

- The oxidation state of each iron is  $\text{Fe}^{\text{I}}$  (since Cp is the only electronegative ligand).
- The valence of each iron is  $\text{Fe}^{\text{II}}$  (since Cp takes 1 electron and the Fe–Fe bond takes another).
- Note that as this is an 18-electron complex, it makes sense that the bound “iron ion” should be  $d^6$  ( $\text{Fe}^{\text{II}}$ ), not  $d^7$  ( $\text{Fe}^{\text{I}}$ ).
- Does the iron have tetrahedral or square planar geometry and why?
- Now consider the compound  $[\text{CpFe}(\text{CO})_2\text{AlMe}_3]^-$ .
  - The oxidation state of the iron is  $\text{Fe}^{\text{II}}$ .
  - The valence of the iron is  $\text{Fe}^{\text{III}}$  (confirm this?).
  - Here, unlike the last example, the oxidation state is a better descriptor (we can think of the iron as donating two electrons to  $\text{AlMe}_3$ ).

## 1.6 Lecture 3: TM Magnetism

4/2:

- Magnetism is unique to the transition metals, and actually predominantly the lanthanides.
- Goes through the “Theoretical background for determining magnetic spins experimentally” derivation from Module 34.
  - $\kappa$  can also be denoted by  $\chi_V$ .
  - More on  $\chi_M$ : Copies Table VI.2 from Labalme (2021). Some differences?
- Diamagnetism:
  - Arises from the circulation of paired electrons.
  - These currents generate a field opposite of  $H$ , which implies that  $\chi_{\text{dia}}$  is negative.

- Contributions from atoms, bonds, and molecules (anything with paired electrons). These can just be summed for a given molecule (see Pascal's constants).

- Paramagnetism:

- Arises from the spin-orbit angular momentum of unpaired electrons.
- Note that  $\chi_{\text{para}} = \chi_{\text{measured}} - \chi_{\text{dia}}$ .
- We can consider a value called the magnetic moment  $\mu$  of the electron. We define

$$\mu = -g\beta\vec{s}$$

where  $g$  is the  $g$ -factor of the free electron (*also known as* the gyromagnetic ratio in Labalme (2021, p. 119)),  $\beta$  is the Bohr magneton, and  $\vec{s}$  is the spin angular momentum.

- The Hamiltonian  $\mathcal{H}$  describing the energy of the interaction of the magnetic field with the magnetic moment of the electron is as follows:

$$\mathcal{H} = -\vec{\mu} \cdot \vec{H} = g\beta\vec{s} \cdot \vec{H}$$

- We can visualize this with a Zeeman splitting diagram.

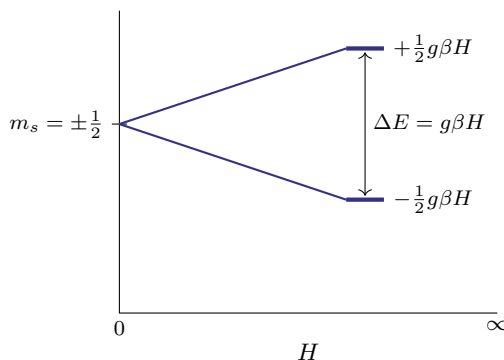


Figure 1.12: A Zeeman splitting diagram for a single electron.

- Consider a single electron.
- Under zero magnetic field ( $H = 0$ ), there will be no preference for spin-up or spin-down ( $M_s = \pm \frac{1}{2}$ ).
- However, as we apply a magnetic field of increasing strength, a preference develops (and the diagram splits). Indeed, under some nonzero magnetic field  $H$ , the system will be higher energy if the electron spin is  $+\frac{1}{2}$  and lower energy if the electron spin is  $-\frac{1}{2}$  (why these specific spins to higher and lower energy? Or is it arbitrary?). This effect is heightened by increasing  $H$ .
- The magnitude of  $\Delta E$  in Figure 1.12.
  - Let  $H = 25 \text{ kG} = 2.5 \text{ T}$ . We know that  $g = 2.0023$ . Thus,  $\Delta E = 2.3 \text{ cm}^{-1}$  (which is very small).
  - What is a Boltzmann population?
  - When we sum the magnetic contributions from all possible spin states, we find that the magnetization constant can be written as

$$M = \frac{N g^2 \beta^2}{4 k_B T} H$$

where  $N$  is Avogadro's number,  $k_B$  is the Boltzmann constant, and  $T$  is temperature.



- But since  $\chi_M = \frac{M}{H}$ , this implies that

$$\chi_M = \frac{Ng^2\beta^2}{4k_B} \cdot \frac{1}{T} = C \cdot \frac{1}{T}$$

where  $C = \frac{Ng^2\beta^2}{4k_B}$  is the Curie constant. How does this relate to Curie's law from last quarter?

- The above relationship is useful because it tells us that we can get a linear relationship through the origin between magnetic susceptibility and  $\frac{1}{T}$ . Additionally, it tells us that as temperature increases, magnetic susceptibility decreases (inversely proportionally).
- Ferromagnetism and antiferromagnetism:
  - Temperature's influences on these types of magnetism vary from their effects on paramagnetism.

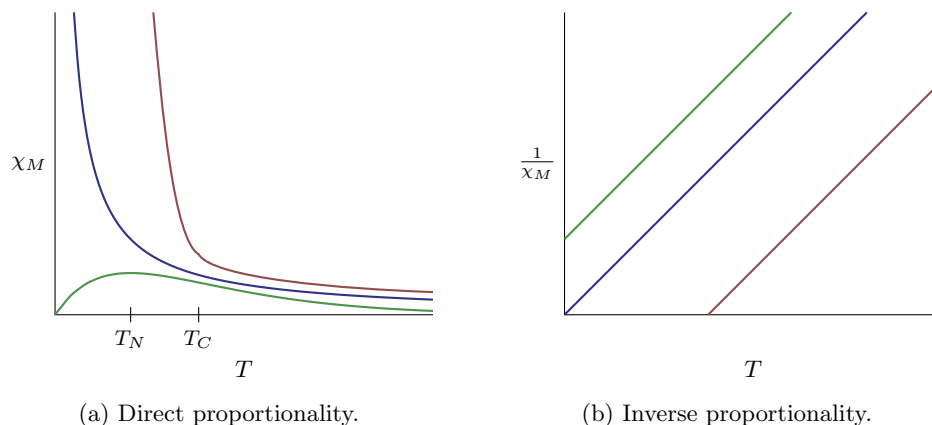


Figure 1.13: Temperature vs. magnetic susceptibility in different magnets.

- The blue lines correspond to paramagnetism, the red lines correspond to ferromagnetism (which, under direct proportionality, have an abrupt inflection point at the Curie temperature  $T_C$ ), and the green lines correspond to antiferromagnetism (which, under direct proportionality, have a maximum at the Neel temperature  $T_N$ ).

- **Curie-Weiss law:** The relationship

$$\chi_M = \frac{C}{T - \theta}$$

where  $\theta$  is the Weiss temperature.  $\theta > 0$  for a ferromagnet and  $\theta < 0$  for an antiferromagnet.

- Measuring and observing magnetism:

- Goes through the  $\mu_S$  derivation on Labalme (2021, p. 119).
- Arrives at the following important equations (defining our observables  $\chi T$  and  $\mu_{\text{eff}}$ ):

$$\mu_{\text{eff}} = g\sqrt{S(S+1)} \qquad \chi T = \frac{g^2}{8}(S(S+1))$$

- Allows us to experimentally determine if a complex is high- or low-spin.
- However, experimental values actually deviate substantially from the spin-only predicted values.

- This is because of **spin-orbit coupling**.

- **Spin-orbit coupling:** A phenomenon where a single electron hops between degenerate orbitals, generating a ring current that either reinforces or opposes the applied magnetic field. *Also known as S.O.C.*

- To account for S.O.C., we need a new Hamiltonian with  $L, S$ .

$$\mathcal{H} = \lambda L \cdot S$$

- In the above equation,  $\lambda$  is the S.O.C. constant.
- Because the equation contains the product of  $L$  and  $S$ ,  $L$  and  $S$  are no longer good quantum numbers. Thus, we need a new quantum number, namely  $J$ .
- Adding  $J$  into our new Hamiltonian gives us

$$\mathcal{H} = \lambda L \cdot S + \beta(L + g_e S) \cdot H$$

where  $g_e$  is the free-electron  $g$  value and  $H$  is the applied magnetic field.

- Let's break the above Hamiltonian down.
  - It tells us that the energy  $E$  that we get from an applied magnetic field is

$$E = \vec{B} \cdot \vec{m} = \mu \vec{m} \cdot \vec{H}$$

where  $\vec{B}$  is the induced magnetic field and  $\vec{m}$  is the magnetization.

- Additionally, we have that  $\chi = \frac{m}{H}$ , so

$$\Delta m = -\frac{dE_i}{dH} = -E_i^1 - 2w_i^2 \cdot H$$

- Thus, the total energy  $E_{\text{total}}$  is given by

$$E_{\text{total}} = E_i^0 + H E_i^1 + H^2 E_i^2$$

where  $H E_i^1$  is the first-order term, and  $H^2 E_i^2$  is the second-order term.

- We can break this down even further.

- We find that

$$m_i = \frac{d}{dH} (E_i^0 + E_i^1 H + E_i^2 H^2 + \dots) = -E_i^1 + 2E_i^2 H$$

- Additionally, we know that  $\chi = \frac{m_i}{H}$ , so

$$\chi_i = \left( -\frac{dE_i}{dH} \right) \frac{1}{H}$$

- The final result above tells us that the magnetic susceptibility depends on the magnetic field. This is rooted in the fact that there are different Boltzmann populations in different ligand field states.
- Now we can account for all of the Boltzmann populations and math that back to the observed  $\chi$ .
- To begin,

$$\chi = \frac{N}{H} = \frac{\sum_i [-E_i^1 - 2E_i^2 H] \exp\left(-\frac{E_i}{k_B T}\right)}{\sum_i \exp\left(\frac{E_i}{k_B T}\right)}$$

where  $N$  is the number of atoms (if it's molar,  $N$  is Avogadro's number).

- Additionally, we know that

$$\begin{aligned} e^{-E_i/k_B T} &= 1 - \frac{E_i}{k_B T} \\ &= e^{-(E_i^0 + E_i^1 H + E_i^2 H^2 + \dots)/k_B T} \\ &= e^{-E_i/k_B T} \left( 1 - \frac{E_i^1 H}{k_B T} \right) \left( 1 - \frac{E_i^2 H^2}{k_B T} \right) (\dots) \end{aligned}$$

- Note that if  $E_i^1 \ll k_B T$ , then  $e^{-x} = 1 - x$  for small  $x$ . This is what allows us to get from the second to the third line above.
- Combining the above two equations, we have

$$\chi = \frac{N}{H} \cdot \frac{(-E_i^1 - 2E_i^2 H) e^{-E_i/k_B T} \left(1 - \frac{E_i^1 H}{k_B T}\right) \left(1 - \frac{E_i^2 H^2}{k_B T}\right)}{\sum_i e^{-E_i^0/k_B T} \left(1 - \frac{E_i^1 H}{k_B T}\right) \left(1 - \frac{E_i^2 H^2}{k_B T}\right)}$$

- If we measure at a constant field, we can simplify the above to

$$\chi = \frac{N\beta^2}{3k_B T} \mu_{\text{eff}}^2$$

- This implies that

$$\mu_{\text{eff}} = \sqrt{\frac{8 + \left(\frac{3\lambda}{k_B T} - 8\right) \left(\exp\left(\frac{-3\lambda}{2k_B T}\right)\right)}{\frac{\lambda}{k_B T} \left[2 + \exp\left(\frac{-3\lambda}{k_B T}\right)\right]}} \cdot \beta^2$$

- **Van Vleck equation:** The above equation<sup>[2]</sup>.
  - It is only valid for  $S = \frac{1}{2}$  (single electron terms).
    - Multi-electron terms are too complicated to do by hand and must be handled by computer modeling.
  - You can explicitly account for S.O.C. with a known  $\lambda$ .
    - For  $\text{Ti}^{3+}$  for example,  $\lambda = 154 \text{ cm}^{-1}$ .
    - For  $\text{Zr}^{3+}$  for example,  $\lambda = 500 \text{ cm}^{-1}$ .
- S.O.C. constants increase for heavier elements. Elements with large relativistic effects have large S.O.C. constants.
- Intuitive insight into the conditions surrounding a large degree of spin-orbit coupling:
  - An applied magnetic field causes the electron to rotate through the  $d$ -orbitals.
    - If an electron hops between  $d_{x^2-y^2}$  and  $d_{xy}$  for instance, this creates rotation (and a ring current).
  - The ring current will create a magnetic field  $B$  around the  $z$  axis that opposes  $H$ .
  - This opposing magnetic field gives a lower magnetic moment than spin-only calculations would predict.
  - Note that rotation of a single electron in a  $d^1$  complex lowers the magnetic moment, but rotation of a single “hole” (positive charge) in a  $d^9$  complex raises the magnetic moment.
    - In  $d^5$  (and technically  $d^{10}$ ), no electrons can move without violating the Pauli exclusion principle, so we would expect the observed moment to be close to the spin-only value. (Quantum mechanical explanation: The electronic symmetry of a totally symmetric state precludes any mixing of the orbital angular momentum with the spin angular momentum.)
- A first approximation of S.O.C.:
  - For a less than half-filled set of orbitals, expect  $\mu_{\text{eff}} / \chi T$  to be lower than the spin-only value, i.e.,  $g < 2$ .
    - Typically  $\mu_{\text{eff}} / \chi T$  is close to the spin-only value.

<sup>2</sup>Having seen this equation is all that is required for this course (it's good to have seen it). The derivation will never come up again.

- For a greater than half-filled set of orbitals, expect  $\mu_{\text{eff}} / \chi T$  to be larger than the spin-only value, i.e.,  $g > 2$ .
  - $\mu_{\text{eff}} / \chi T$  can be much larger.
- For a half-filled set of orbitals, we expect little to no S.O.C. Thus,  $\mu_{\text{eff}} / \chi T$  should be roughly equal to the spin-only value, i.e.,  $g \approx 2$ .
- The magnitude of S.O.C.: The key is orbital degeneracy.
  - For example, if we have a  $d^3 \text{Cr}^{3+}$  complex, we would predict more S.O.C. in the tetrahedral state (Figure 1.4b) than in the octahedral state (Figure 1.7b).
    - This is because in the tetrahedral orbitals, there is only one electron in the upper orbitals; thus, we have a set of degenerate orbitals with a non-degenerate electron configuration, which promotes S.O.C. Note that  $d^3$  octahedral is totally degenerate by contrast.
  - Note that this is totally dependent on the ligand field: Stronger ligand fields increasingly break degeneracy, thus quenching S.O.C.
- S.O.C. trends:
  1. Heavy elements have larger S.O.C.
  2. Lanthanides have larger S.O.C. from larger  $\lambda$ 's.
    - Lanthanides in general also just have very large S.O.C. effects; this effect arises from the degenerate  $f$  set.
      - Since the  $f$  orbitals do not extend beyond the noble gas core to engage in bonding, they do not split; thus, they are totally degenerate; thus, there is large S.O.C.
    - Note that neodymium magnets are strong because they combine a lanthanide that contributes massive S.O.C. effects, lots of electrons, and anisotropy (neodymium) and a transition metal that effectively couples with orbitals that aren't as buried as neodymium's  $f$  orbitals (iron).

## 1.7 Office Hours (Anderson)

- 4/5:
- Electron counting for a metal center bonded to a  $\pi$  bond?
    - As in PSet 1 Questions 1.2 and 1.6.
    - Example:  $\text{Ni}^-\text{ethene}$ .
      - The  $\pi$  electron density can donate to the nickel atom in a dative fashion.
      - We can also think of two covalent bonds to the nickel; one from each carbon.
    - Example:  $\text{Ni}(\text{COD})_2$ .
      - Electron count: 18 (8 from the ligands [2 from each of 4  $\pi$  bonds] and 10 from the  $d^{10}$  nickel atom).
  - Electron counting for a metal center bonded to a  $\sigma$  bond?
    - Also donates two electrons datively, as in PSet 1 Question 1.9.
  - M–M bonds and oxidation states?
    - Reviews the discussion surrounding Figure 1.11.
  - The binding of a Z-type ligand does not affect the electron count of a compound at all.
  - The formal charges on the molecules in the PSet are the charges of the molecules as a whole, not any one part.
  - **Metal-organic frameworks** or MOFs.

## 1.8 Office Hours (Whitmeyer)

- 4/6:
- Transition metal trends: Why do first row transition metals prefer to have  $1e^-$  coupled?
    - Referring to reactivity? B/c higher oxidation states are more stable for early row transition metals.
  - Figure VI.13 of Labalme (2021) says that *two* metal orbitals form bonding/antibonding orbitals with the ligand orbitals, so why does Dr. Anderson assert that only *one* does? Is it because of what he said about  $d_{z^2}$  being practically interchangeable with the  $d_{xy,xz,yz}$  ligands in square planar complexes?
    - Yes it is.
  - Now this question could just be a relic of my previous understanding of bonding, and the answer may just be “MO theory,” but I’m still gonna ask: Where do the electrons in all of the bonds come from? It seems like if the osmiums are giving electrons to Os–Os and Os–H bonds, and we still count osmium as  $d^8$ , we are counting some electrons twice.
    - It’s fine to count them twice. The electron count is a computational tool, not a count of electrons.
    - Does the electron count have physical meaning?
      - Guides you toward what compounds are more reactive. And other chemical properties.
  - What does isolobal mean?
  - The fic fragment: Right spelling/charge?
  - Does the iron in Figure 1.11 have tetrahedral or square planar geometry and why?
  - Copies Table VI.2 from Labalme (2021). Some differences?
  - Why these specific spins to higher and lower energy (Figure 1.12)? Or is it arbitrary?
  - What is a Boltzmann population?
  - Differences in Curie’s Law from last quarter?
  - How do you define  $d$  count? Green (1995) defines it as  $d^n - x$  where  $d^n$  is the ground state configuration and  $x$  is the number of X-functions.
    - The  $d^n$  count should reflect the oxidation state.
  - Charges on compounds affect the oxidation state of the metal.
  - Where do the extra electrons come from in the CO resonance structures (the ones that are bonded to the metal)?
    - All M–C bonds are 2-electron? The IR stretching frequency just changes in some resonance structures so we call this a multiple M–C bond even though it isn’t.
  - How do we handle ligands with preexisting charges (i.e.,  $\text{NO}^+$ ,  $\text{SO}_4^{2-}$ ,  $\eta^3\text{-C}_3\text{H}_5^+$ , etc.)

## 1.9 Discussion Section

- No discussion or office hours on the April 20; instead, there will be a special 2-hour exam review on April 15, 16, 17 (she will send a When2Meet poll). There will be 3 lectures per week, of 2-3 videos on Panopto. Office hours (one for Dr. Anderson and one for Sophie) will be one time per week. Please come to discussion: this is your question venue! Feel free to send along things you want discussed to Sophie in advance. Sophie can answer things much more thoroughly in discussion.
- Difference between L- and X-type ligands:

- Draw out lone pairs. Break bonds (pushing electrons back onto ligands). If the ligand is neutral, it's L-type. If it's negatively charged, it's X-type.
  - So if you have an oxygen as a singly bonded ligand and break the bond, oxygen will be negative. If you do the same thing with nitrogen, it will be neutral. *draw a picture*
- When dealing with *f*-block compounds, be careful about the periodic placement (different periodic tables place lanthanum and actinium in different places).
- Why *f*-block electrons for the electron count?
  - The lanthanides and actinides don't follow the 18 electron rule.
  - This is a very active area of research (at the forefront of bonding actually), but the growing consensus is that...
    - The lanthanides do not engage in covalent bonding; they're purely ionic.
    - The actinides can engage in limited covalent bonding with their *f* block because their larger *f* block extends a little bit further.
- We can do isolobal analogies with bridging ligands, too!
- One should never *assume* that there's a M–M bond, but one should always *wonder* if there's one.
- Potentially you can invoke  $\pi$  donation from a ligand to get a compound to 18 electrons.
- **Hapticity**: The number of carbons in the  $\pi$  system. *Also known as  $\eta$ .*

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