Topic V

Coordination Chemistry: Structures and Isomers of Metal Complexes

V.1 Module 28: Introduction to Coordination Compounds

2/12:
- Modern inorganic chemistry is heavily concerned with the transition metals, i.e., the d-block elements.
    - Most industrial catalysts utilize transition metal compounds.
- Transition metals vs. main-group elements:

Transition-Metal Compounds	Main-Group Elements
Multiple oxidation states (e.g., the 11 oxidation states of Mn from -3 to $+7$)	Single oxidation state
Brightly colored (thus a gap between HOMO and LUMO of a few electron volts)	Usually colorless
Usually have partially occupied valence d-orbitals that are often relatively close in energy	The valence s- or p-orbitals are either fully occupied or empty and are far apart energetically
Often paramagnetic	Usually diamagnetic
Often interact with small molecules such as CO, C_2H_4, and H_2	Generally do not interact strongly with CO, C_2H_4, or H_2

- The orbital energy gap matches the bond energies of small molecules pretty well.
    - This is exactly what is needed for activating those chemical bonds, i.e., making catalytic cycles!
- History:
    - Prussian blue ink is the first synthetic blue dye, and one of the first coordination compounds created (used in famous paintings such as *Starry Night*).
    - The structure of coordination complexes was not understood until 1907, however.
    - Blomstrand and Jorgenson tried to determine the structure of $Co(NH_3)_4Cl_3$, but their guess didn't explain isomers.
    - Alfred Werner (late 1800s) was the father of coordination chemistry.
        - He noticed that excess $AgNO_3$ could only liberate and precipitate as AgCl one chlorine from both the green and violet isomers of $CoCl_3 \cdot (NH_3)_4$.
        - However, it could precipitate two chlorines from $CoCl_3 \cdot (NH_3)_5$ and three from $CoCl_3 \cdot (NH_3)_6$.
        - This observation plus a number of controls led him to **Werner's Conclusions**.

- **Werner's Conclusions**:

  1. In this series of compounds, cobalt has a constant **coordination number** of 6.
  2. As the NH_3 molecules are removed, they are replaced by Cl^-, which acts as if it is covalently bonded to cobalt.
  3. Chloride and ammonia are now called ligands.
  4. Ligands are a Lewis base/electron pair donors that can bind to a metal ion.
  5. A metal complex is a metal ion combined with ligands.
  6. Coordination complexes are neutral and counter ions are not bonded to the central metal ion but balance the charge.
     - For example, in $[\overset{+3}{Co}(\overset{0}{NH_3})_6]\overset{-3}{Cl_3}$, the three chloride ions are the counter ions.

- **Coordination number**: The number of groups that can bond directly to the metal.

- Werner also hypothesized an octahedral geometry for all cobalt complexes.

  - If it were hexagonal planar or trigonal antiprismatic, there would be three isomers of the coordination sphere for the compound with two chlorines (think ortho, meta, para isomers for the hexagonal planar example).
  - However, if it is octahedral, the compound with two chlorines will have two isomers (the chlorines can either be 180° to each other or 90° to each other).
  - Octahedral also reduces steric crowding.

- **Coodination compound**: A compound with a metal center, a coordination sphere, and counter ions. *Also known as* **coordination complex**.

- Werner also resolved hexol into optically active isomers. This was the first optically active chiral *inorganic* compound.

V.2 Module 29: Types and Classes of Ligands

- **Monodentate ligand**: A ligand that binds to a metal ion through a single donor site. *Etymology* one-toothed.

  - For example, NH_3 is a monodentate ligand.

- **Bridging ligand**: A ligand that binds to two or more metal ions simultaneously.

  - For example, O^{2-} is a bridging ligand.

- **Ambidentate ligand**: A ligand with two kinds of binding sites that can bind through one or the other but not both simultaneously.

  - For example, thiocyanide can bond through S or N but not both simultaneously.

- **Multidentate chelating ligand**: A ligand bound to a metal through several donor sites. *Etymology* multitooth crab claw (crabs grab their food with two claws in the same way a metal can be attracted to two lone pairs from different groups on the same ligand). *Also known as* **polydentate chelating ligand**.
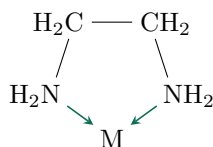

Figure V.1: An example of a bidentate chelating ligand.

- For example, ethylenediamine ($H_2NCH_2CH_2NH_2$; see Figure V.1) can bond to the same metal with both of its nitrogens' lone pairs at the same time.

- Thus, ethylenediamine is is bidentate, and it forms a 5-membered chelate ring.

- The chelate effect: For a given metal ion, the thermodynamic stability of a chelated complex involving bidentate or polydentate ligands is greater than that of a complex containing a corresponding number of comparable monodentate ligands.

  - Note that 5-membered rings are more stable than 6, and 4-membered rings (or smaller) are not stable due to angle strain.

  - For example, ethylenediaminetetraacetate (EDTA) is a hexadentate ligand has two nitrogens and four oxygens that wrap entirely around a metal atom and bond very strongly.

  - β-diketones and acetylacetone are also polydentate ligands.

  - Multidentate bonding is incredibly strong.

  - As one last example, hemoglobin and chlorophyll have extra stability because the iron/magnesium ion is attached to four nitrogens.

- Explanations of the chelate effect:

  - Effective concentration: If one bond breaks, the bridge between the two bonding sites in the ligands still holds the other site in close proximity to the metal, making it more likely that the bond will reform than if the metal and ligand were floating entirely independently.

  - Entropy considerations:

    ■ Imagine you have a coordination complex. If you substitute two monodentate ligands for two other monodentate ligands, you do not change the number of particles.

    ■ However, if you substitute one polydentate chelating ligand for two monodentate ligands, you increase the number of particles by 1, increasing disorder in the universe and favoring the forward reaction.

  - Looking at the temperature-dependence of equilibrium, we can calculate ΔG°. We can then use this to calculate ΔH and ΔS, and we find that the contributions are very similar. Thus, both explanations of the chelate effect contribute about equally.

- Covalent bond classification (CBC) method:

- **X-type** (ligand): A ligand that donates one electron to the metal and accepts one electron from the metal when using the neutral ligand method of electron counting, or donates two electrons to the metal when using the donor pair method of electron counting.

  - Examples: hydrogen, the halogens, hydroxide, cyanide, carbocation, and nitric oxide.

- **L-type** (ligand): A neutral ligand that donates two electrons to the metal center regardless of the electron counting method being used.

  - Examples: carbon monoxide, PR_3, ammonia, water, carbenes (=CRR'), and alkenes.

- **Z-type** (ligand): A ligand that accepts two electrons from the metal center as opposed to the donation occurring with the other two types of ligands.

  - Examples: Lewis acids, such as BR_3.

- LXZ notation:

  - Take the traditional formula and replace the central metal atom with M, each X-type ligand with X, each L-type ligand with L, and each Z-type ligand with Z. Then, if necessary, combine ligands of the same type using subscript arabic numerals, as per usual. Conserve the braces and charge.

  - For example, $[Ir(CO)(PPh_3)_2(Cl)(NO)]^{2+}$ becomes $[ML_3X_2]^{2+}$.

V.3   Module 30: Nomenclature and Isomers of Metal Complexes

2/15:

- Midterm 1:

    - Average: 67.0.
    - Standard deviation: 14.8.
    - Max: 93.
    - 80+ scores: 10.

- Midterm 2 will cover modules 13-31 (with concepts from modules 1-12).

- Suggested reading: Miessler et al. (2014) Section 9.2.

- Naming metal complexes:

    1. For complex ions, write the cation first and anion last.
        - For example, $K_2[PtCl_4]$ is potassium tetrachloroplatinate.
        - Note that you do not use the prefix mono, di, tri, etc. here to indicate the number of cations.
    2. Name the ligands first in alphabetical order, the metals last.
    3. Prefixes to indicate numbers (di, tri, tetra, ...) for all monoatomic ligands, polyatomic ligands with short names and neutral ligands with special names.
    4. Prefixes bis-, tris-, tetrakis-, pentakis-, hexakis- for ligands whose names contain a prefix of the first type, neutral ligands without special names, and ionic ligands with particularly long names.
    5. If the anion is complex, add the suffix -ate to the name of the metal. If the symbol comes from Latin/Greek, then we go back to the Latin/Greek for the name of the anion.
    6. Put the oxidation state in Roman numerals in parentheses after the name of the central metal ion of the ligand.

- Examples:

    - $[CoCl_4]^{2-}$ is the tetrachlorocobaltate (II) ion.
    - $[Fe(CN)_6]^{4-}$ is the hexacyanoferrate (II) ion.
        - ■ Notice the use of "ferr" for iron (this is going back to the Latin/Greek name of the central metal ion as in Step 5).
    - $[Cr(H_2O)_4Cl_2]^+$ is the tetraaquodicchlorochromium (III) ion.
        - ■ No use of -ate because this is a cation (not an anion).
    - $[Cr(NH_2CH_2CH_2NH_2)_3]^{3+}$ is the tris(ethylenediammine)chromium (III) ion.
        - ■ Note that ammine with two m's is correct — an **amine** is a functional group from ammonia, while an **ammine** is a group of coordination compounds where ammonia is a ligand.

- Neutral ligands have the same name as the molecule with 4 exceptions:

    - NH_3 is ammine.
    - H_2O is aquo.
        - ■ Aquo or aqua?
    - CO is carbonyl.
    - NO is nitrosyl.

- Anionic ligands require replacing -ide in the ionic name (if present) with -o. For example:

    - Cl^- becomes chloro.
    - OH^- becomes hydroxo.

– $SO_4{}^{2-}$ is still sulfate.

• Bridging ligands:

$$\left[\begin{array}{c} O \!-\! O \\ (H_3N)_4Co^{III} \qquad\qquad Co^{III}(NH_3)_4 \\ \underset{H_2}{N} \end{array} \right]^{2-}$$
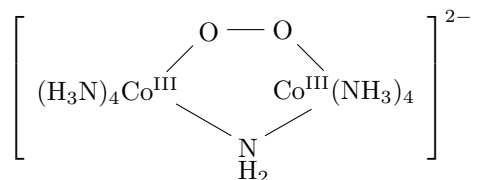
Figure V.2: A coordination compound with bridging ligands.

– Use μ to indicate a bridge.

– If there are more than one of a given bridging ligand, the prefix indicating the number of ligands is placed after the μ.

– If there are more than one different bridging ligands, they are given in alphabetical order.

– For example, the compound in Figure V.2 is the tetraaminecobaltate(III)-μ-amido-μ-peroxo-tetraaminecobaltate(III) ion.

Common Name	IUPAC Name	Formula
nitrido	nitrido	N^{3-}
azido	azido	$N_3{}^-$
oxo	oxido	O^{2-}
thiocyano	thiocyanato-S	SCN^-
isothiocyano	thiocyanato-N	NCS^-
thiocarbonyl	thiocarbonyl	CS
nitro	nitrito-N	$NO_2{}^-$
nitrito	nitrito-O	ONO^-
phosphine	phosphane	PR_3
pyridine	pyridine (abbrev. py)	C_5H_5N
amido	azanido	$NH_2{}^-$
imido	azanediido	NH^{2-}

Table V.1: Irregular and unfamiliar monodentate ligands.

• Table V.1 lists some more common but irregular or unfamiliar ligands.

– Note that when listed in Table V.1, ambidentate ligands bind through the atom listed most to the left in the formula.

– Note also that the slides list a number of common bidentate and polydentate ligands.

• Suggested reading: Miessler et al. (2014) Section 9.3.

• Coordination complex isomers are divided into:

– Structural isomers (different bonds).

  ■ Coordination isomerism.
  ■ Linkage isomerism.

– Stereoisomers (same bonds, different spatial arrangements).

■ Geometric isomerism (*cis-trans*).

■ Optical isomerism.

• **Ionization isomers**: Ligands inside the coordination sphere exchange places with ligands outside the coordination sphere.

  – So named because these give different ions when dissolved in water.

  – Werner's four isomers of $CrCl_3 \cdot 6\,H_2O$ are ionization isomers.

• **Linkage isomers**: Variations in at which site an ambidentate ligand bonds.

• **Geometric isomers**: Found in square planar and octahedral complexes — *cis*- vs. *trans*-isomers.

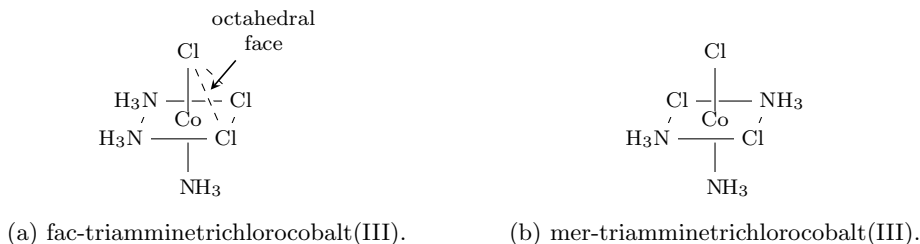(a) fac-triamminetrichlorocobalt(III).   (b) mer-triamminetrichlorocobalt(III).

Figure V.3: Facial and meridional geometric isomers.

  – Be aware of **facial** (fac) vs. **meridional** (mer) geometric isomers.

  – In Figure V.3a, all three Cl–Co–Cl bond angles are 90°.

  – In Figure V.3b, two Cl–Co–Cl bond angles are 90°, and the other is 180°.

• Note that there are several different ways to represent an octahedrally coordinated metal ion.

Figure V.4: Methods of sketching octahedral complexes.

  – Which way you choose depends on what you are trying to show.

• **Optical isomers**: Two compounds with non-superimposable mirror images (two chiral molecules).

  – C_1, C_n, D_n, T, O, and I point groups are chiral.

  – Usually associated with tetrahedral/octahedral geometries.

• Octahedral complexes have special chirality.

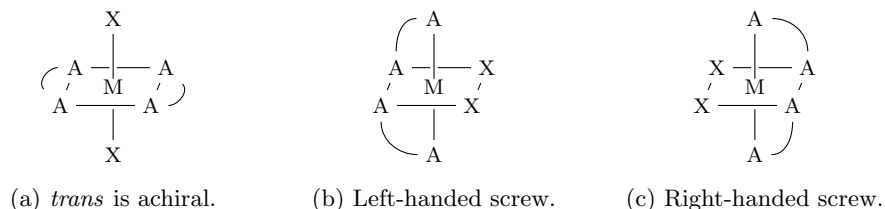 – Octahedral complexes with two bidentate ligands:

(a) *trans* is achiral.   (b) Left-handed screw.   (c) Right-handed screw.

Figure V.5: Chirality of octahedral complexes with two bidentate ligands.

■ As we can see in Figure V.5, *trans*-$M(A-A)_2X_2$ is not chiral, but *cis*-$M(A-A)_2X_2$ is chiral with two specially named forms.

– Octahedral complexes with three bidentate ligands:

■ *Also known as* **propellor chirality**.

■ Left-handed helices are Λ form, while right-handed helices are Δ form.

V.4 Module 31: Crystal Field Theory

- The first attempt to understand and rationalize the electronic structure of transition metal complexes.

  – Originally introduced to analyze crystals' electronic structure.

  – Since the coordination of a central atom in a crystalline closely mimics that of it in a coordination complex, the concepts of crystal field theory can easily be transferred to chemistry.

- Suggested reading: Miessler et al. (2014) Section 10.2.

- Refresher on d-orbitals.

  – There are four d-orbitals with four lobes and one strange d_{z^2} orbital.

  – Higher energy level ones have lobes corresponding to the change in sign of the radial component..

  – The d_{z^2} orbital is a linear combination of two four-lobed orbitals; it is created to reconcile mathematical theory with physical reality (the Pauli exclusion principle).

- Crystal field theory describes an electrostatic (ionic) approach to bonding — it is so named because it was first applied to crystalline substances.

  – Interactions between filled d-orbitals and ligands with excessive electrons are repulsive.

- Assumptions:

  1. Metal ion at the center.
  2. Ligands are treated as point charges.
  3. Bonding occurs through M^+ and L^- electrostatic attraction.
  4. Bonding is purely ionic.
  5. M and L electrons repel each other.
  6. d-orbital degeneracy is broken as ligands approach.

- Consider d-orbitals bonding to six ligands.

  – Keep Coulomb's Law ($E \propto \frac{q_1 q_2}{r}$) in mind: d-orbitals that overlap more with the ligands (smaller r) will be more destabilized (higher E).

  – d_{z^2} overlaps with the two axial ligands, and $d_{x^2-y^2}$ overlaps with the four equatorial ligands.

  – None of d_{xy}, d_{xz}, and d_{yz} overlap significantly with any ligands.

  – Therefore, the five degenerate d-orbitals split into the t_{2g} **set** and the e_g **set**.

  – When the orbitals split, they maintain an energetic "center of mass," i.e., their combined energy as molecular orbitals must still be equal to their combined energy as degenerate, atomic orbitals. Thus, the stabilization energy of the three orbitals in the t_{2g} set is $-\frac{2}{5}\Delta$ while the destabilization energy of the two orbbitals in the e_g set is $\frac{3}{5}\Delta$, where Δ is the **crystal field splitting parameter**.

- t_{2g} **set**: The three orbitals that lie between the ligand donor atoms.

- e_g **set**: The two orbitals that lie along the Cartesian coordinates, and so are adjacent to the donor atoms of the ligands, raising the set in energy.

- **Crystal field splitting parameter**: Different ligands produce different extents of splitting between the e_g and the t_{2g} levels. This energy difference is the crystal field splitting parameter. *Units* cm^{-1}. *Also known as* $\boldsymbol{\Delta}$, $\boldsymbol{10Dq}$.

- Experimental verification of orbital splitting.

  - Consider a coordination complex with just one d-electron, i.e., electron configuration d^1.

    - An example is $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$.

  - In such a complex, the electron will occupy the lowest energy orbital available, i.e., one of the three degenerate t_{2g} orbitals.

  - Shining light on the complex can promote the t_{2g} electron into the e_g energy level.

  - The UV-Vis absorption spectrum reveals that this transition occurs with a maximum at $20\,300\,\text{cm}^{-1}$, or $\Delta = 243\,\text{kJ/mol} \neq 0$.

- Note that $1000\,\text{cm}^{-1} = 11.96\,\text{kJ/mol} = 2.86\,\text{kcal/mol} = 0.124\,\text{eV}$.

- **Crystal field stabilization energy**: The overall change in energy when the d-subshell splits, which is given by $(0.4n(t_{2g}) - 0.6n(e_g))\Delta$ where $n(t_{2g})$ and $n(e_g)$ are the numbers of electrons in the t_{2g} and e_g levels respectively. *Also known as* **CFSE**.

  - When splitting of the d-subshell occurs, the occupation of the lower energy t_{2g} level by electrons causes a stabilization of the complex, whereas occupation of the e_g level causes a rise in energy. The t_{2g} level drops by 0.4Δ, whereas the e_g level is raised by 0.6Δ.

- High and low-spin complexes:

  - Whether a complex is **high-spin** or **low-spin** depends on Δ.

  - If $\Delta > P$ where P is the **spin-pairing energy**, then the complex is low-spin, and vice versa if $\Delta < P$.

- **High-spin** (complex): A complex with d^4 to d^8 electron configuration, where the electrons spread out and occupy the whole d-subshell.

  - High-spin complexes are often paramagnetic.

  - Electrons fill the whole d-subshell according to Hund's rule.

- **Low-spin** (complex): A complex with d^4 to d^8 electron configurations, where the t_{2g} energy level is filled first.

  - Low-spin complexes are often diamagnetic.

- **Spin-pairing energy**: The energy required to take pairs of electrons with the same spin orientation, and pair them up with the opposite spin. *Also known as* $\boldsymbol{P}$.

- Calculating CFSE of d^0 to d^{10} high-spin M (II) ions.
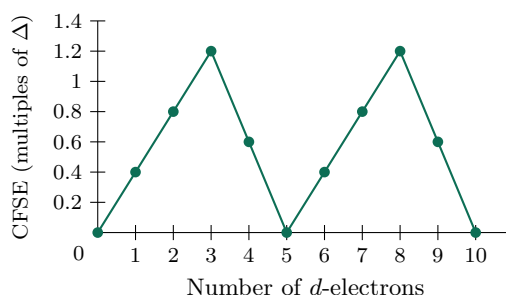
Figure V.6: CFSE as a function of the number of d-electrons.

– Most first row and many second and third row transition elements will be prone to forming high-spin complexes.

– The variation shown in Figure V.6 reveals that complexes of metal ions with high CFSE (such as Ni (II)) will undergo greater stabilization, and vice versa for metal ions with low CFSE (such as Ca (II)).

– The predicted variation matches relatively well with formation constant values ($\log K_1$) obtained experimentally for these compounds.

- We can also look at orbital splitting in coordination compounds of other geometries.

  – In T_d compounds, for example, the splitting is flipped with the $d_{xy,xz,yz}$ orbitals destabilized and the $d_{x^2-y^2,z^2}$ orbitals stabilized.

  – We can also look analyze linear and square planar geometries.

- Merits of crystal field theory:

  – Can be used to predict the most favorable geometry for the complex.

  – Can account for why some complexes are tetrahedral and others are square planar.

  – Useful in interpreting magnetic properties.

  – The colors of many transition metal complexes can be rationalized.

- Limitations of crystal field theory:

  – Becomes less accurate as delocalization (covalent character) increases.

  – Point charge does not accurately represent complexes.

  – Does not account for π bonding interactions.

  – Does not account for the relative strengths of the ligands.

## V.5   Module 32: Ligand Field Theory for the O_h σ-Only Case

2/17:
- Suggested reading: Miessler et al. (2014) Section 10.3.

- Ligand field theory:

  – Application of molecular orbital theory to transition metal complexes.

  – Ligands are not point charges.

  – Takes into account π bonding.

    ■ I.e., accounts for the fact that ligands can be σ-donors, π-donors, π-acceptors, or sometimes multiple simultaneously.

  – Can be used to explain spectrochemical series.

  – Better than valence-bond model or crystal field theory at explaining experimental data.

- Octahedral σ-only MO diagram workflow:

  1. Assign a point group.

  2. Choose basis function.

  3. Apply operations.

  4. Generate a reducible representation.

  5. Reduce to irreducible representations.

  6. Combine orbitals by their symmetry.

  7. Fill MOs with e^-.

8. Generate SALCs of peripheral atoms.

9. Draw peripheral atom SALC with central atom orbital to generate bonding/antibonding MOs.

- MH_6 example.

  - Point group: O_h.

  - Basis funtions: $1s$-orbitals on the ligands (you can also choose the σ-bond vectors if you wish [if it's easier for you]), and s, p, d-orbitals on the metal center.

  - Apply operations & generate a reducible representation.

$$\Gamma_H = (6, 0, 0, 2, 2, 0, 0, 0, 4, 2) = A_{1g} + T_{1u} + E_g$$
$$\Gamma_{M_s} = A_{1g}$$
$$\Gamma_{M_p} = T_{1u}$$
$$\Gamma_{M_{d_{x^2-y^2,z^2}}} = E_g$$
$$\Gamma_{M_{d_{xy,xz,yz}}} = T_{2g}$$

 - Combine orbitals by their symmetry.
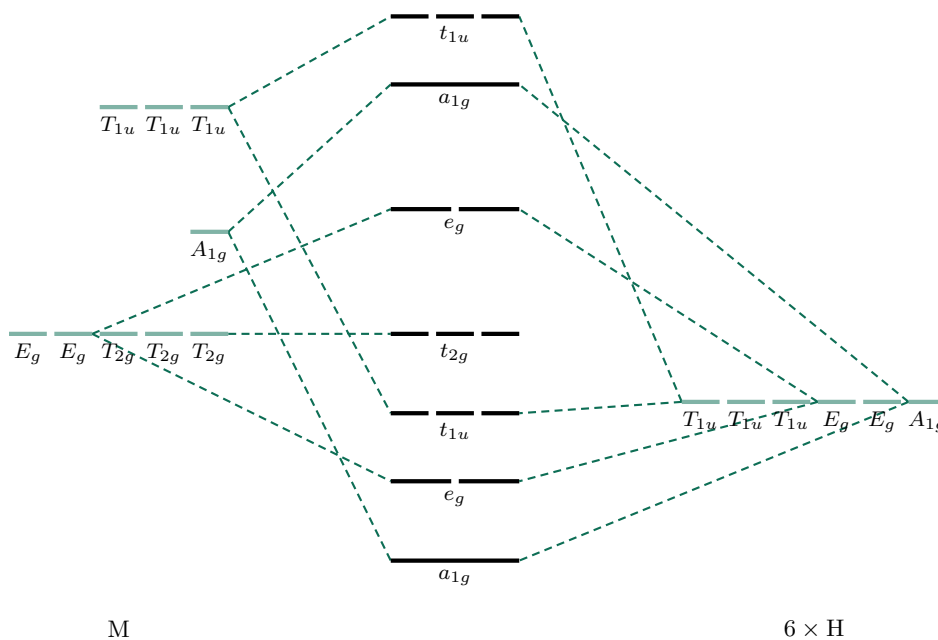
Figure V.7: MH_6 orbital diagram.

- In a transition metal compound/coordination complex, the t_{2g} MOs would be the HOMOs and the antibonding e_g MOs would be the LUMOs.

- Since the t_{2g} orbitals are nonbonding, they are reflective of the energy of the metal d-orbitals. Thus, the energy difference between them and the e_g orbitals is equal to the amount by which the e_g orbitals' energy changes during bonding, i.e., the splitting parameter. This energy change is also indicative of the antibonding character of the e_g orbitals, and consequently the strength of the bonding (bigger Δ implies higher energy e_g orbitals implies stronger bonding).

- In LFT, we call this quantity the **ligand field splitting parameter**, as opposed to the crystal field splitting parameter.

- Pauses to consider **weak field ligands** and **strong field ligands**.

– Generate SALCs of peripheral atoms.

$$\Psi(a_{1g}) = c_1(4s) + c_2(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$$
$$\Psi_z(t_{1u}) = c_3(4p_z) + c_4(\sigma_1 - \sigma_6)$$
$$\Psi_x(t_{1u}) = c_3(4p_x) + c_4(\sigma_4 - \sigma_2)$$
$$\Psi_y(t_{1u}) = c_3(4p_y) + c_4(\sigma_3 - \sigma_5)$$
$$\Psi_{z^2}(e_g) = c_5(3d_{z^2}) + c_6(\sigma_1 + \sigma_6) + c_7(-\sigma_2 - \sigma_3 - \sigma_4 - \sigma_5)$$
$$\Psi_{x^2-y^2}(e_g) = c_8(3d_{x^2-y^2}) + c_9(\sigma_2 - \sigma_3 + \sigma_4 - \sigma_5)$$

■ Recall that the coefficients reflect the degree of overlap.

■ Note that for the $\Psi(t_{1u})$ wavefunctions, the in-plane σ-orbitals have zero overlap with the perpendicular $4p$ orbital, hence their coefficient of 0.

– Draw peripheral atom SALC with central atom orbital to generate bonding/antibonding MOs.

(a) $\Psi(a_{1g})$.

(b) $\Psi_z(t_{1u})$.   (c) $\Psi_x(t_{1u})$.   (d) $\Psi_y(t_{1u})$.

(e) $\Psi_{z^2}(e_g)$.   (f) $\Psi_{x^2-y^2}(e_g)$.
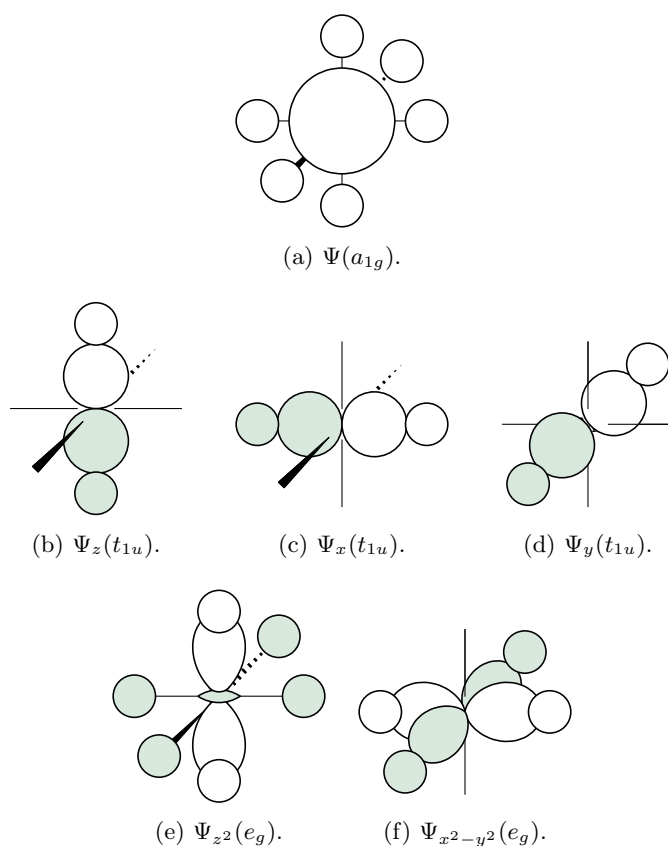
Figure V.8: MH_6 bonding and antibonding MOs.

- **Weak field ligand**: A ligand with high electronegativity, and thus low energy frontier orbitals.

  – Weak σ donor.

  – Weak Lewis base.

  – Weaker bonding interaction.

  – Smaller Δ_o.

- **Strong field ligand**: A ligand with comparable energy frontier orbitals to the d-orbitals of the metal cation.

- Strong σ donor.
- Strong Lewis base.
- Stronger bonding interaction.
- Larger Δ_o.

- Size matters more than Lewis basicity:

  - Stronger Lewis base $\Rightarrow$ larger Δ_o.
  - Smaller ligand $\Rightarrow$ larger Δ_o.
  - However, size overall is more important.
    - ■ This is related to hardness and softness — with a hard Lewis acid metal center, harder ligands will bond with greater strengths.

- For the halides' Δ_o: $I^- < Br^- < Cl^- < F^-$.

- If we use p-orbitals pointing toward the center as bases for our peripheral atoms instead of s-orbitals, we get the exact same result.

- Factors that influence $\Delta_{\text{oct}} = \Delta_o = 10Dq$.

  - Metal oxidation state: Increasing the charge increases Δ.
  - Principal quantum number: Increasing n (going down a period on the periodic table) increases Δ, too.
  - Nature of the ligand:

L	Ligand Type	z	Δ_o (cm^{-1})
Cl^-	σ, π-donor	$3-$	13 700
H_2O	σ-donor	$3+$	17 400
NH_3	σ-donor	$3+$	21 500
CN^-	σ-donor/π-acceptor	$3-$	26 600

Table V.2: How the nature of the ligand influences Δ.

V.6   Module 33: Ligand Field Theory for the O_h $\sigma + \pi$ Case

- Consider cyano-ligands (isoelectronic to CO and NO$^+$).

  - HOMO is perfect for σ bonding via donation.
 - LUMO is perfect for π acceptance from metal d-orbitals.
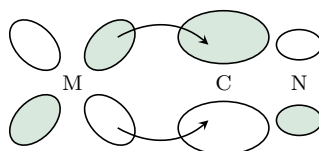
Figure V.9: LUMO π-acceptance.

- ■ d_{xz} and π^* orbitals combine with stabilization energy e_π.
  - This is how we determine what kinds of donors the ligands in Table V.2 are. For H_2O, for example, it is not a π-acceptor because its LUMO is a σ^* orbital, not a π^* one (see Figure III.11).

- Octahedral $\sigma + \pi$ bonding:
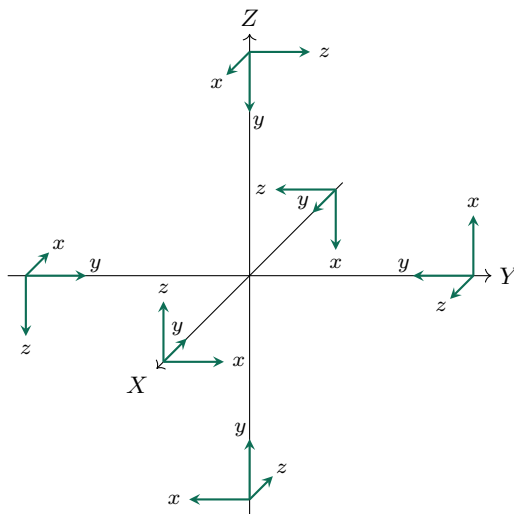
Figure V.10: Octahedral π-ligand coordinate systems.

  – Generate a reducible representation: $\Gamma_{L\pi_{x,z}} = (12, 0, 0, -4, 0, 0, 0, 0, 0) = T_{1g} + T_{2g} + T_{1u} + T_{2u}$.
  – Combine orbitals by their symmetry.
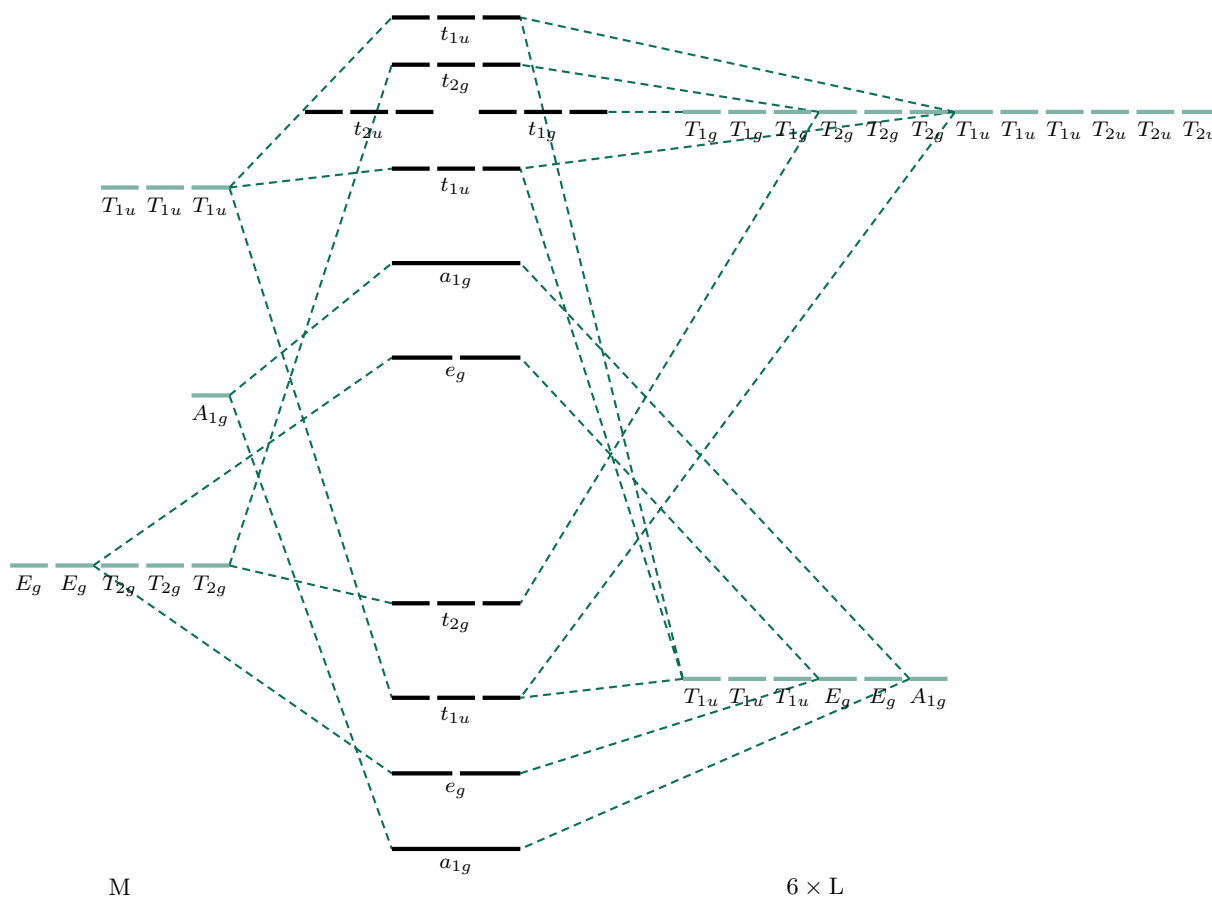
Figure V.11: ML$_6$ orbital diagram.

V.7 TA Review Session 2

2/19:
- σ bonds are stronger than π bonds.

- Steric number is also one-half the sum of the number of electrons around the central atom plus the number of bonding electrons each ligand contributes.

  - For example, in SF_4, $SN = \frac{6+4}{2} = 5$.
  - A_1 orbitals mix more than B_1, mix more than B_2.

- Determining symmetry of SALCs:

  - Multiply unmoved atoms by each row in the character table; nonzero rows indicate symmetry under that SALC.
  - In the SF_4 example, let $F_{a,d}$ be the axial hydrogens and let $F_{b,c}$ be the equatorial ones. Then the projections of F_a are F_a, F_d, F_a, F_d. Multiplying by A_1 gives us $2F_a + 2F_d$...

- When numbering MOs, you're good to start with 1 at the bottom of the diagram (not taking into account the lower energy states).

- We're good to use arcs for bidentate ligand instead of drawing out the full structure.

- We can denote enantiomers with the dashed line (like a mirror plane) between them.

- For neutral coordination centers, put a 0 in parentheses after the compound (in place of a Roman numeral oxidation number).

  - Rubitium tetrafluoroaurate(III).
  - Learn Greek/Latin names!

- $BH_2{}^+$ is linear since it is isoelectronic to BeH_2, i.e., the central atom only has two bonding electrons.

  - Reduce $D_{\infty h}$ to D_{2h}.
  - Empty orbitals can still mix occupied orbitals; empty p orbitals are still present in the orbital diagram.
  - $BH_2{}^-$ would have a different structure (bent).
    - C_{2v}.
  - Know how to create a Walsh diagram!
    - An extra p orbital mixes, lowering energy, in the bent form.

- Compressing a 1D crystal:

  - a decreases, overlap increases, β (interaction integral) increases, band width ($|4\beta|$) increases.
  - Effective mass: $\frac{1}{m^*} = \frac{1}{\hbar^2}(\partial^2 E / \partial k^2)_{k=0}$.

- Review reference materials; skim chapter 9; read over notes.