

Topic VI

Bonding and Physical Properties of Metal Complexes

VI.1 Module 34: Magnetic Properties of Transition Metal Complexes

- 2/22:
- Electrons occupy the lowest energy triply degenerate orbitals in d^1 , d^2 , and d^3 configurations.
 - However, in the d^4 configuration:
 - Low spin: The fourth electron will pair up in the lower t_{2g} energy level.
 - High spin: The fourth electron will occupy a higher energy e_g orbital.
 - The pairing energy Π is made up of two parts (refer to Figure 0.9 and the associated discussion):
 1. Coulombic repulsion energy caused by having two electrons in the same orbital. Destabilization energy contribution of Π_c for each doubly occupied orbital. Has a positive sign because it increases the energy of the system.
 2. Exchange stabilization energy for each pair of electrons having the same spin and same energy. Stabilizing contribution of Π_e for each pair having same spin and same energy. Has a negative sign because it reduces the energy of the system.
 - Deciding whether the fourth electron will go into the higher energy e_g orbital at an energy cost of Δ , or be paired at an energy cost of Π .
 - Strong field ligand has big Δ so $\Pi < \Delta$; this implies a low spin configuration.
 - Weak field ligand has small Δ so $\Pi > \Delta$; this implies a high spin configuration.
 - We can experimentally discriminate between high- and low-spin compounds by measuring magnetic properties.
 - The Gouy balance can determine the magnetic susceptibility of materials.
 - A more modern way to measure magnetic properties uses a Superconducting Quantum Interference Device, or SQUID.
 - This device is just about the most sensitive machine humanity can build (can detect the magnetic field of the heart/brain).
 - Main types of magnetic behavior:
 - Diamagnetism (from electron charge).
 - Paramagnetism (spin and orbital motion of electrons on individual atoms).

- Ferromagnetism and antiferromagnetism (cooperative interaction between magnetic moments of individual atoms).
- Paramagnetism is much stronger than diamagnetism and overpowers it.
 - Ferromagnetism overpowers both.
- Theoretical background for determining magnetic spins experimentally:
 - When we place a sample in a magnetic field of magnitude H , the sample will interact with the magnetic field and magnetize. This magnetization causes the magnetic flux B in the material to differ from the magnetic flux through the space the sample occupies (were the sample not there) by an amount determined by the magnetization parameter M , which is specific to each material. These three quantities are related via the equation

$$B = H + 4\pi M$$

- If we divide the flux by the magnetic field, we obtain the magnetic susceptibility per unit volume κ of the material:

$$\frac{B}{H} = 1 + 4\pi \cdot \frac{M}{H} = 1 + 4\pi\kappa$$

- This quantity can be normalized by the molecular weight and density of the substance to give the magnetic susceptibility per mole

$$\chi_M = \kappa \cdot \frac{\text{molecular weight}}{\text{density}}$$

- Dividing χ_M by Avogadro's number gives the magnetic susceptibility per molecule χ_M^{corr} .
- **Curie's law** relates χ_M^{corr} to the magnetic moment μ by the formula

$$\chi_M^{\text{corr}} = \frac{N\mu^2 k}{3T}$$

where N is Avogadro's number, $k = 1.381 \times 10^{-23}$ J/K is the Boltzmann constant, and T is the absolute temperature of the substance.

- Note that μ is measured in units of Bohr magnetons where $1 \text{ BM} = \frac{eh}{4\pi m_e c}$. As per usual, we have $e = 1.602 \times 10^{-19}$ C is the charge of an electron, $h = 6.626 \times 10^{-34}$ Js is Planck's constant, $m_e = 9.11 \times 10^{-31}$ kg is the mass of an electron, and $c = 2.998 \times 10^8$ m/s is the speed of light.
- We can rearrange Curie's law to express the magnetic moment in terms of χ_M^{corr} as follows.

$$\mu = \sqrt{3k/N} \cdot \sqrt{\chi_M^{\text{corr}} T}$$

- Magnetic moment μ and the spin-only formula: Materials that are diamagnetic are repelled by a magnetic field, whereas paramagnetic substances are attracted into a magnetic field, i.e., show magnetic susceptibility. The unpaired electrons in paramagnetic complexes of 3d-block metal ions create a magnetic field. The magnetic moment μ is then given by the spin-only formula

$$\mu_{\text{spin-only}} = \sqrt{n(n+2)}$$

where n is the number of unpaired electrons.

- In heavier transition metals, we need to account for not just the S quantum number but also L (which accounts for some ground state relativistic effects) by using the formula

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

VI.2 Module 35: Reflections on the Ligand Field Effects in O_h and T_d Complexes

- 2/24:
- Note that 2nd and 3rd row metals almost always low-spin, and 4th row transition metals often high-spin.
 - T_d vs. O_h splitting.

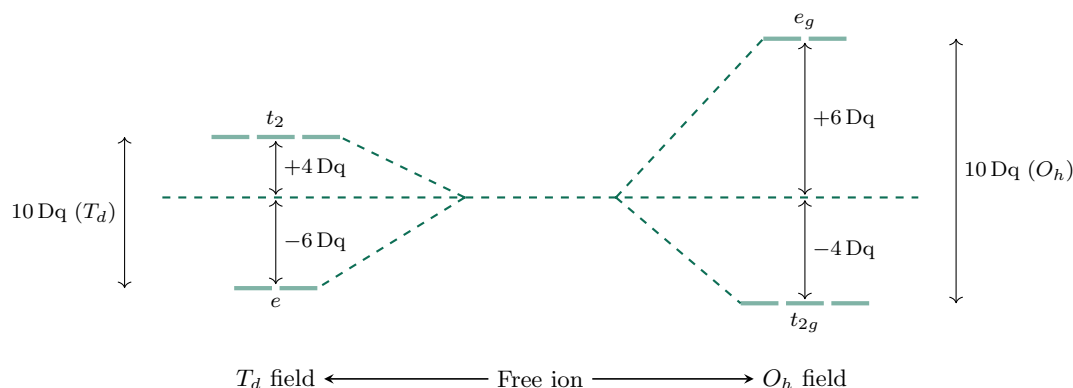


Figure VI.1: T_d vs. O_h splitting.

- For T_d , 2 e -type orbitals are lower in energy and 3 t_2 orbitals are higher.
 - Note that we do not mark with gerade because T_d molecules lack an inversion center.
- For O_h , it's reversed.
- Note that the splitting energy of tetrahedral complexes is less than that of octahedral complexes. This is because there are fewer ligands acting on the d -orbitals of the metal center (4 vs. 6), and the angular overlap of the d -orbitals and the ligand group orbitals is less favorable when tetrahedral (there is a directional factor of $\frac{2}{3}$). Indeed, the tetrahedral splitting energy is generally $\frac{4}{6} \cdot \frac{2}{3} = \frac{4}{9}$ that of a relative octahedral splitting energy.
- Conclusion: T_d complexes are always weak-field and thus high spin.
- Rationalization of coordination geometries (factors that influence the geometry adopted):
 - Electronic factor (the number of bonds): Electrostatic and covalent model favor O_h (6 vs. 4).
 - Steric factor: Ligand-ligand repulsions favor T_d .
 - High charge on cation increases Δ — favors O_h coordination and O_h low spin. Indeed, O_h (l.s.) $>$ O_h (h.s.) $>$ T_d .
 - $CFSE(O_h) \geq CFSE(T_d)$, always.
- In d^5 complexes (e.g., with Mn^{2+} and Fe^{3+}), there is no stabilization energy. Thus, L-L repulsions dominate and T_d complexes are formed.
 - Note however that the higher charge on Fe^{3+} favors low spin O_h complexes in more cases than Mn^{2+} .
- In d^6 complexes (e.g., with Fe^{2+} and Co^{3+}), the stabilization is much higher for O_h low spin than high spin than T_d . Thus, we form low spin complexes.
 - Note that there are exceptions — extremely weak field ligands such as F^- can still form high spin complexes as with CoF_6^{3-} .

VI.3 Module 36: Angular Overlap Model

- In many catalytic cycles, the coordination environment (molecular geometry) changes frequently throughout the cycle.
- To account for changes in the coordination environment, we use the **angular overlap model**.
 - We can also use this model to help account for complexes with different ligands in the coordination sphere.
- Recall that σ -bonding is stabilizing, but π -bonding is stabilizing only in the case of π -acceptance by a ligand, not π -donation.
- Angular overlap parameters:

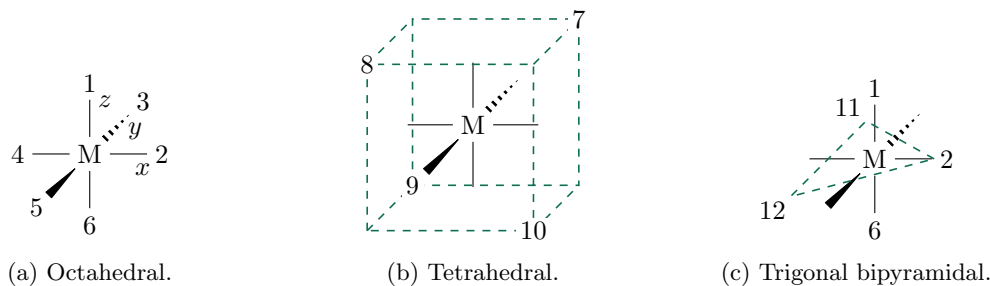


Figure VI.2: Angular overlap model: Labeling of positions.

- With multiple ligands and multiple orbitals, we add the angular overlap interaction coefficients.
- These are tabulated for each orbital of each ligand at each position in the coordination sphere with each metal-center d -orbital.
- Suggested reading (on coefficients' derivation): *TBD*.
- Trigonal planar coordination example:
 - From Figure VI.2c, the ligand positions are 2, 11, and 12.
 - Thus, we add the coefficients in these rows to get $e_\sigma = (\frac{3}{4}, \frac{9}{8}, \frac{9}{8}, 0, 0)$ and $e_\pi = (0, \frac{3}{2}, \frac{3}{2}, \frac{3}{2}, \frac{3}{2})$, where the respective d -orbitals are $z^2, x^2 - y^2, xy, xz, yz$.
 - With these energies, we can now sum $e_\sigma + e_\pi$ to determine that the energies of the orbitals are $(\frac{3}{4}, \frac{21}{8}, \frac{21}{8}, \frac{3}{2}, \frac{3}{2})$.
 - This gives us three sets of degenerate orbitals: Lowest energy ($d_{xz, yz}$), medium energy (d_{z^2}), and high energy (d_{xy, x^2-y^2}).
 - How did we get these energy rankings?
 - Assigning Mulliken symbols with the D_{3h} character table, we have from lowest to highest energy: $e'' < a'_1 < e'$.
- Note that e_σ is always positive (because ligands are σ -donors), but e_π can be negative (because ligands can be π -acceptors).
- Changing the metal and/or ligand affects the magnitudes of e_σ and e_π , thereby changing the value of Δ .
- $e_\sigma > e_\pi$ always.
- Values decrease with increasing size and decreasing electronegativity.
- Both positive and negative values for e_π .

VI.4 Module 37: Jahn-Teller Effect

- The **Jahn-Teller theorem** helps explain why the d^9 configuration is far more stable (far higher peak) than predicted by Figure V.6.
- **Jahn-Teller theorem:** For nonlinear molecules/ions that have a degenerate ground-state, the molecule/ion will distort to remove the degeneracy. *Also known as J-T theorem.*
 - When orbitals in the same level are occupied by different numbers of electrons, this will lead to distortion of the molecule.
 - If the two orbitals of the e_g level have different numbers of electrons, this will lead to J-T distortion so as to stabilize the doubly occupied e_g orbital and destabilize the singly occupied e_g orbital.
 - Cu(II) with its d^9 configuration is degenerate and has J-T distortion.
- Consider the two degenerate e_g orbitals ($d_{x^2-y^2}, d_{z^2}$). *picture*
 - Elongating the z -axis in an O_h complex stabilizes the d_{z^2} orbital and destabilizes the $d_{x^2-y^2}$ orbital.
 - Vice versa for compressing the z -axis.
- Thus, we can see significant elongation of the z -axis bonds in $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.
- History: Before the rigorous formulation and verification of the J-T theorem by Jahn and Teller, Landau proposed the **Landau statement** from his observations.
- **Landau statement:** A molecule in an orbitally degenerate electronic state is unstable with respect to spontaneous distortion of the nuclear configuration that removes the degeneracy.
- Strength of the J-T effect in various configurations:

Number of electrons	1	2	3	4	5	6	7	8	9	10
High-spin Jahn-Teller	w	w		s		w	w		s	
Low-spin Jahn-Teller	w	w		w	w		s		s	

Table VI.1: Jahn-Teller effects in various configurations.

- Unequal occupation of t_{2g} orbitals leads to the J-T effect in principle, but only weakly in practice because t_{2g} orbitals are nonbonding in σ -bonded complexes, i.e., localized on the metal center, i.e., not strongly perturbed by ligand bonding.
- Unequal occupation of e_g orbitals leads to a strong J-T effect since they are antibonding.
- Structural effects of J-T distortion:
 - In $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$, we will have axial aqua groups and equatorial en groups for two reasons.
 - The aqua groups are weaker field ligands that interact less efficiently with the metal center, so it is easier for them to be farther from it.
 - Having the en groups in plane means they don't have to be structurally distorted.
 - In $[\text{Cu}(\text{en})_3]^{2+}$, we observe strong structural distortion from perfect octahedral forced by the J-T distortion; this angle strain is not energetically favorable.
- Jahn-Teller distortion of the excited state:
 - In high spin d^6 complexes such as $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, there will only be weak J-T distortion of the ground state. Thus, we expect to see only one peak in the absorption spectrum, corresponding to the promotion of a t_{2g} electron to the e_g orbitals and its fall back down.

- However, we observe two bands.
- This is because promotion of an electron from the t_{2g} orbitals to the e_g orbitals leads to a much stronger J-T distortion (unequally occupied e_g orbitals).
- The resultant d -orbital splitting causes the two absorption peaks.
- Square planar complexes:
 - Jahn-Teller distortion leads to tetragonal distortion of the octahedron, with the extreme of tetragonal distortion being the complete loss of axial ligands, and formation of a square-planar complex. Tetragonal distortion is the stretching of the axial M–L bonds, and shortening of the in-plane bonds. Cu(II) is usually tetragonally distorted, while low-spin Ni(II) is usually square planar.
 - Since the axial bonds get weaker as they lengthen, eventually we can have enough thermal energy to break them entirely, resulting in a square planar complex.
 - This occurs in the case of Ni(II) bonded to strong field ligands, such as cyano ligands. Essentially, what happens is the splitting of the e_g orbitals exceeds the spin-pairing energy, causing the $d_{x^2-y^2}$ electron to pair with the d_{z^2} electron.
 - The filled d_{z^2} orbital now occupies two coordination sites, and the four donor atoms occupy the plane.
 - The structure is comparable to that of $[\text{IF}_4]^-$, where two lone pairs occupy the axial sites.
 - This is a particularly important special example because such compounds are very reactive, owing to their frontier d_{z^2} orbitals, and can be involved in nucleophilic attacks.
 - All high-spin d^8 metal ions are octahedral (or tetrahedral). Low-spin d^8 metal ions are usually square planar.
 - Both Wilkinson’s catalyst and Crabtree’s catalyst are square planar!

VI.5 Module 38: Applying MO Theory Beyond “Simple” ML_6 Complexes

- 2/26:
- Reviews Figure V.11 and the difference between π -acceptor and π -donor ligands.
 - Mixing different ligands within the same coordination sphere:
 - The MO diagram for O_h complexes proves to be a convenient starting point for deducing the electronic structure of many lower symmetry metal complexes.
 - To analyze lower symmetry compounds, we use the descent in symmetry technique.
 - $[\text{Co}(\text{CN})_5\text{Br}]^{3-}$ example:
 - Five strong-field cyano ligands and one weak-field bromo ligand.
 - Choose to orient the Br^- ligand along the positive z -axis.
 - To build the MO, we could use DFT (first principles), but it’s an unintuitive black box.
 - Alternatively, we can start with hexacyanocobaltate(III), remove one cyano ligand and see how the MOs are perturbed, and add one bromo ligand and see how the MOs are perturbed. This process correlates the electronic structure of this C_{4v} complex with its O_h parent complex.
 - To begin, consider perturbations to σ and π interactions upon substituting π -accepting CN^- with π -donating Br^- .
 - First, let’s simply remove the CN^- ligand.
 - The $d_{x^2-y^2}$ orbital is not greatly perturbed by substitution along the z -axis.
 - The d_{z^2} orbital was $\text{M}-\text{L}\sigma^*$; thus, removal of 1 σ ligand from the z -axis will stabilize it.
 - The $d_{xz,yz}$ orbitals are destabilized owing to the removal of 1 $\text{M}-\text{L}\pi$ bonding interaction.

- The d_{xy} orbital is in-plane and notal with respect to σ - and π -bonding along the z -axis; thus, it is not greatly perturbed by such substitution.
- The d_{z^2} orbital is more greatly stabilized than the $d_{xz,yz}$ orbitals are destabilized because the former is involved in stronger σ -interactions, as opposed to weaker π -interactions.
- Now let's add the Br^- ligand. Addition of Br^- to the C_{4v} fragment will give rise to new interactions.
 - σ : $\text{Br}(p_z)$ will interact with the d_{z^2} , s , and p_z orbitals of cobalt. All of these will be $\text{M-L}\sigma^*$ with respect to M orbitals, and $\text{M-L}\sigma$ with respect to the ligand.
 - π : $\text{Br}(p_x, p_y)$ will interact with $d_{xz,yz}$ in $\text{M-L}\pi^*$ interactions.
 - The formation of a bonding pair causes $\text{Br}(p_z)$ orbital stabilization, at the cost of the destabilization of the d_{z^2} orbital.
 - The metal p_z and d_{z^2} orbitals will be destabilized, but will remain below $\text{Co-CN}\sigma^*$ orbitals because the Co-Br interaction is not as great as the Co-CN interaction.

VI.6 Module 39: Metal-Metal Bonding

- First historical puzzle:
 - Copper (II) acetate has crystalizes with four O-CR-O bridges joining two square pyramidal copper atoms that are also bonded to one aqua group, each.
 - Copper is d^9 , so $\mu = 1.73$ in theory. However, we observe $\mu = 1.4$.
 - We resolve this conflict by noting that the copper atoms are not square pyramidal — they bond to each other, giving both an octahedral geometry.
 - This is important because it gives us a new pair of bonding and antibonding orbitals. We thus have low-spin and high-spin states, and the existence of a nonzero but not super high magnetic moment hints at a high-spin state with some preference for low-lyingness.
- Metal-metal bonding is common for metals in low oxidation state, and generally increases in strength along the series $3d \ll 4d < 5d$.
- Single metal-metal bonded complexes:
 - We will consider the paramagnetic single M-M complex $\text{M}_2(\text{CO})_{10}$.
 - Possible metals are Fe^{2+} , manganese, and uranium.
 - Strategy for group fragment approach: Correlate to $\text{M}(\text{CO})_6$ (O_h), remove a ligand to give $\text{M}(\text{CO})_5$, and dimerize.
 - Note that $\text{Mn}(\text{CO})_5$ is the inorganic analog to CH_3 , i.e., the $\text{Mn}(\text{CO})_5$ fragment is said to be isolobal with CH_3 .
 - The HOMO of $\text{Mn}(\text{CO})_5$ is a singly occupied d_{z^2} orbital.
 - The energetic stabilization of the electrons in d_{z^2} into a σ -bond by dimerization is the driving force for metal-metal bond formation.
 - Note that a diamagnetic complex is formed from the dimerization of two metallic radicals.
 - Also note that the d_{z^2} orbital is cylindrically symmetric, i.e., indicates no preference for the staggered vs. eclipsed conformation. Thus, the molecule will adopt the more torsionally favorable staggered D_{4d} configuration.
- Cluster formation:
 - As mentioned above, odd electron occupancy of the e_g orbitals (O_h) prompts ligand loss in order to destabilize d_{z^2} . Further stabilization occurs by metal-metal single bond formation. We can take limiting argument to explain cluster formation across the periodic table:

- In each case, the clusters assume an octahedral coordination as a result of burying 7 d -electrons in what are formally t_{2g} orbitals. The system loses a number of COs equivalent to the number of electrons in $M-L\sigma^*$; this permits maximum $M-M$ bond formation and thus maximum stabilization.
- Clusters can trimerize or form higher polymers.
- Clusters can act as super atoms, combinations of atoms that you can add and remove electrons from with similar effects to changing the oxidation state in one atom.
- Multiple metal-metal bonded complexes:
 - Inorganic chemists synthesized a compound with a quadruple bond in 1964.
 - The MO strategy will be to correlate $Re_2Cl_8^{2-}$ with $ReCl_6^{3-}$ (O_h), remove two axial Cl^- ligands to give a square planar $ReCl_4^-$ fragment, and then dimerize.
 - Here, we see stabilization of the $d_{xz,yz}$ (the Cl^- ligand had been giving antibonding character) orbitals and massive stabilization of the d_{z^2} orbital (same reason).
 - The d_{z^2} orbital reacts the most to form an a_{1g} σ -bond.
 - The $d_{xz,yz}$ orbitals react the second most to form two e_u π -bonds.
 - The d_{xy} orbitals react the third most to form one b_{2g} δ -bond.
 - The eclipsed D_{4h} structure is a result of the δ bond.
 - Adding up our 8 bonding and 0 antibonding electrons and dividing by two gives us our first quadruple bond.
- Metal-metal bonding vs. configuration: Increases single to quadruple bond as $d^1 \rightarrow d^4$; decreases triple to no bond as $d^5 \rightarrow d^8$.
- f orbitals are deep within the core of the atom and not generally available for bonding, so we will not see higher bonding *because* of f orbitals in lanthanides and actinides.
- The d^8 case:
 - No bonding predicted, but...
 - We actually see one-dimensional crystals, as in band theory.
 - The orbitals responsible are the d_{z^2} orbitals, which mix with the higher energy p_z orbitals to stabilize the d_{z^2} σ -bonding MO (and destabilize the p_z bonding MO, but this orbital is unfilled).
- The $d_{x^2-y^2}$ orbitals cannot participate in ML_4 coupling since they are used for ligand bonding.
 - Thus, the only orbitals available for coupling are $d_{z^2,xz,yz,xy}$.
- Inorganic chemists (including Phil Power, who is probably the greatest currently living main-group inorganic chemist) synthesized a compound with a quintuple bond in 2005.
 - They had to change the coordination environment around the metal center to free up the $d_{x^2-y^2}$ orbital. They did so with sterically bulky ligands that hindered more bonding.
 - The quintuple bonding was verified by observing a very short bond length (not super short on the scheme of things, but shorter than ever reported before, indicating the presence of a weak fifth bond).
 - C_{2h} symmetry.
 - Suggested reading: The full paper.