

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.

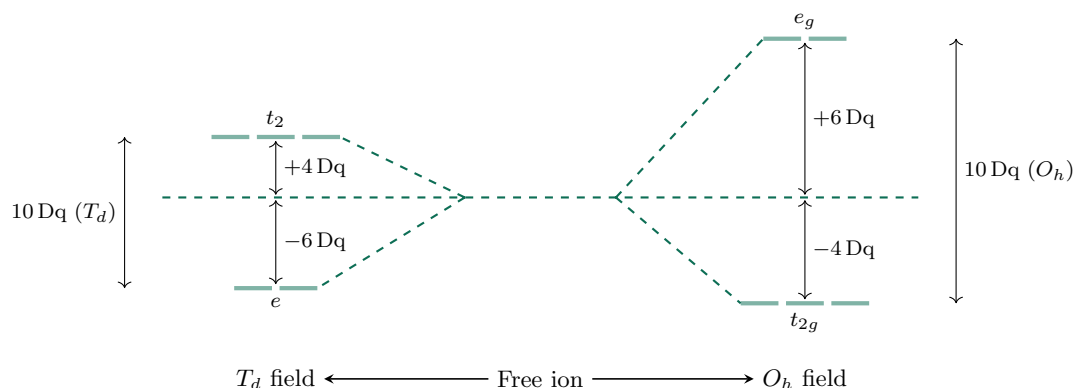


Figure VI.1: T_d vs. O_h splitting.

- 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:

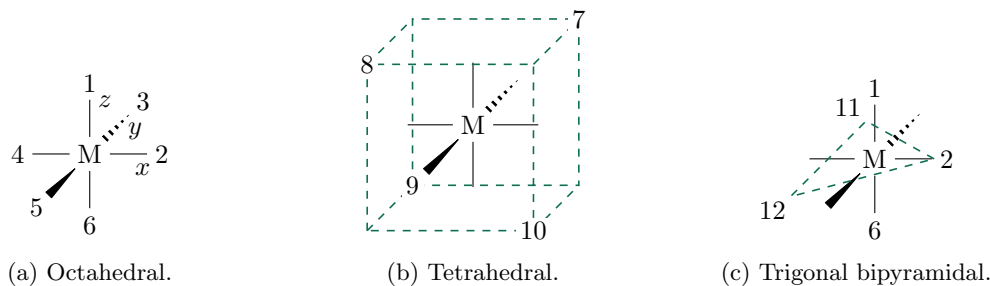


Figure VI.2: Angular overlap model: Labeling of positions.

- 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!