Transition Metals and Coordination Compounds

Introduction

- Transition Metals are defined as elements in the d-block (Groups 3–12) that possess a partially filled d-orbital in their neutral atom or in one of their stable oxidation states.
- Unlike main group elements, whose chemistry is often dominated by simple ion formation to achieve noble gas configurations, transition metals exhibit a rich chemistry involving complex ion formation, variable oxidation states, and catalytic activity.
- Guiding Question: How does the unique energy degeneracy of d-orbitals—and their subsequent splitting by ligands—govern the magnetic properties, vibrant colors, and geometric structures of coordination complexes?

Learning Objectives

By the end of this module, you will be able to:

- Recognize and predict the molecular geometry of coordination complexes (tetrahedral, square planar, octahedral) based on coordination number, steric factors, and electronic configuration (d^n).
- Classify and distinguish between structural isomers (ionization, linkage, hydrate) and stereoisomers (geometric, optical) in coordination chemistry.
- Analyze the electronic structure of complexes using Crystal Field Theory (CFT) to explain why certain complexes are paramagnetic (magnetic) or diamagnetic (non-magnetic) and why they exhibit specific colors.
- Predict the stability and reactivity of complexes by differentiating between thermodynamic stability (formation constants) and kinetic lability (rate of ligand exchange).
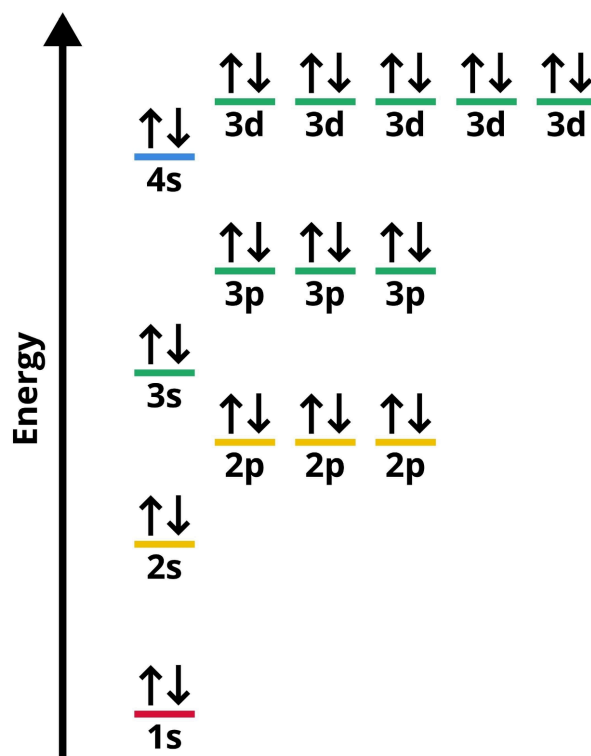
Key Concepts and Definitions

Ligand	Definition
Ligand	An ion or molecule with a lone pair of electrons that bonds to a central metal atom. Ligands act as Lewis bases, while the metal acts as a Lewis acid.
Coordination Sphere	The central metal ion and its attached ligands, enclosed in brackets in a chemical formula (e.g., $[Co(NH_3)_6]^{3+}$). Ions outside the brackets are counter-ions.
Crystal Field Splitting (Δ)	The energy difference created between sets of d-orbitals (e.g., t_2g and eg) when ligands approach the metal ion.
Spectrochemical Series	A ranked list of ligands based on the strength of the field they produce ($I^- < H_2O < NH_3 < CN^-$). Strong field ligands cause large splitting (Δ).
Chelate Effect	The observation that complexes containing polydentate (ring-forming) ligands are significantly more stable than those with monodentate ligands.

Detailed Discussion

Electronic Structure and Variable Oxidation States

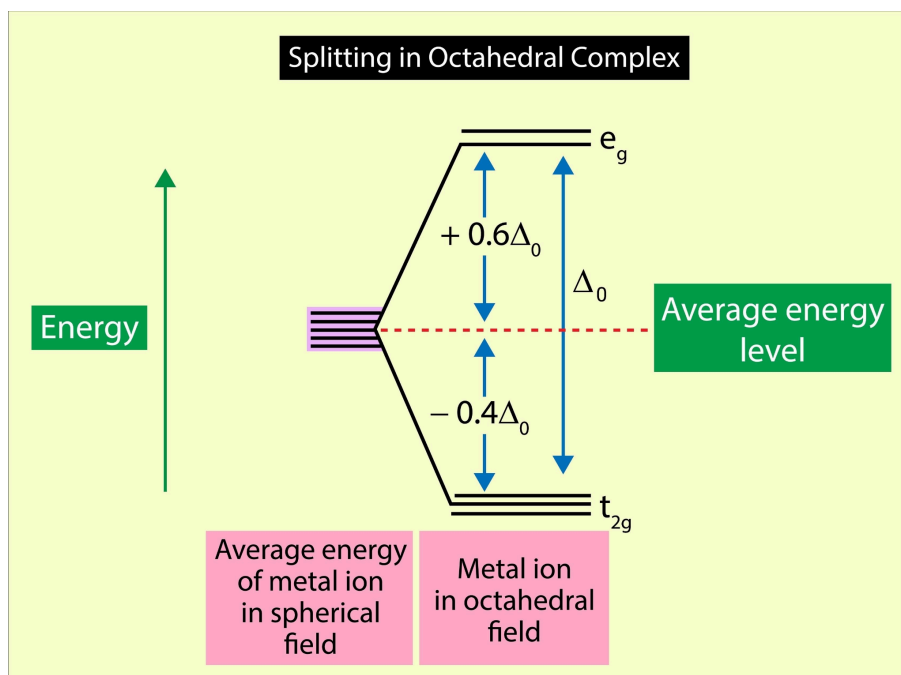### ATOMIC ORBITAL ENERGY LEVELS

Transition metals have a general valence electron configuration of [Noble Gas] $(n-1)d^{1-10}$ ns^{1-2}.

- **The "s" vs. "d" Energy Inversion:** When filling orbitals for neutral atoms (Aufbau principle), the 4s orbital fills before the 3d. However, once the electrons are in place, the 3d orbitals drop lower in energy than the 4s due to shielding effects. Therefore, when transition metals form ions, **electrons are always removed from the s-orbital first**.
    - *Example:* Iron (Fe) has the configuration [Ar] $3d^6 4s^2$. The Fe^{2+} ion is [Ar] $3d^6$ (s-electrons removed), not $3d^4 4s^2$.

- **Variable Oxidation States:** Because the energy gap between the (n-1)d and ns orbitals is very small, the metal can lose varying numbers of d-electrons in addition to s-electrons. This leads to a wide range of oxidation states.
  - Manganese (Mn) has the widest range (+2 to +7) because it has 5 unpaired d-electrons and 2 s-electrons to lose.
  - Stability is often enhanced by half-filled (d^5) or fully-filled (d^{10}) subshells. This is why Mn^{2+} (d^5) is very stable and pale in color, while Mn^{3+} (d^4) is a strong oxidizing agent.
- **Origin of Color (d-d Transitions):** In a free metal ion, all five d-orbitals are equal in energy (degenerate). When ligands bond, they create an electrostatic field that splits these orbitals into different energy levels.
  - If a photon of light hits the complex with energy equal to this gap (Δ), an electron jumps from a lower d-orbital to a higher one.
  - The specific wavelength absorbed corresponds to the energy gap. The color we see is the **complementary color** of the light absorbed (e.g., if red light is absorbed, the compound appears green).
  - *Note:* Ions with d^0 (e.g., Sc^{3+}) or d^{10} (e.g., Zn^{2+}) configurations are colorless because there are no possible d-d transitions.

Geometry, Coordination Numbers, and Crystal Field Theory

The geometry of a coordination complex is a balance between steric factors (ligands trying to stay apart) and electronic factors (d-electrons avoiding ligand electrons).

- **Coordination Number 6 (Octahedral):** This is the most common geometry. The ligands approach along the x, y, and z axes.
    - **CFT Explanation:** The metal d-orbitals lying directly on the axes (dx^2-y^2 and dz^2) experience maximum repulsion from the ligands and are raised in energy (forming the **eg set**). The orbitals lying between the axes (dxy, dyz, dxz) experience less repulsion and remain lower in energy (forming the **t₂g set**).
- **Coordination Number 4 (Tetrahedral vs. Square Planar):**
    - **Tetrahedral:** Favored by small metal ions with large ligands (like Cl^-) to minimize crowding. In CFT, the splitting pattern is reversed compared to octahedral (though the gap Δt is much smaller), and these complexes are almost always **High Spin** (electrons spread out before pairing).
    - **Square Planar:** Favored by **d⁸ metal ions** (like Ni^{2+}, Pd^{2+}, Pt^{2+}) and strong-field ligands. By removing ligands along the z-axis, the repulsion on the dz^2 orbital drops drastically, making it very stable. The 8 electrons fill the low-energy orbitals, leaving the highest-energy orbital (dx^2-y^2) empty. This electronic stabilization outweighs the steric cost of crowding ligands into 90° angles.

Isomerism in Coordination Compounds

Isomerism in coordination chemistry is complex because of the high coordination numbers involved.

- **Stereoisomerism (Spatial Arrangement):**
    - **Geometric (Cis-Trans):** Occurs in square planar (MA_2B_2) and octahedral (MA_4B_2) complexes.
        - *Cis:* Identical ligands are adjacent (90° apart). This creates a polar molecule.
        - *Trans:* Identical ligands are opposite (180° apart). This often cancels dipole moments, creating a non-polar molecule.

- ○ **Geometric (Fac-Mer):** Unique to octahedral complexes with three identical ligands (MA_3B_3).
  - ■ *Facial (fac):* The three ligands occupy the corners of one triangular face of the octahedron (all are 90° to each other).
  - ■ *Meridional (mer):* The three ligands form an arc or "meridian" around the center (two are trans to each other).
- ○ **Optical Isomerism (Enantiomers):** Molecules that are non-superimposable mirror images. This typically occurs in octahedral complexes containing bidentate ligands (like ethylenediamine, "en").
  - ■ *Criteria:* The complex must lack a plane of symmetry. A classic example is $[Co(en)_3]^{3+}$, which looks like a propeller. The "left-handed" and "right-handed" propellers are distinct isomers.
- **Structural Isomerism (Bonding Connectivity):**
  - ○ **Linkage Isomerism:** Occurs when a ligand is **ambidentate**, meaning it can bind through different atoms. For example, the nitrite ion (NO_2^-) can bind through Nitrogen (Nitro isomer) or Oxygen (Nitrito isomer). This is often controlled by the "hardness" or "softness" of the metal acid.
  - ○ **Ionization Isomerism:** Occurs when a counter-ion outside the bracket swaps places with a ligand inside the bracket.
    - ■ Example: $[Co(NH_3)_5Br]SO_4$ (Violet) vs. $[Co(NH_3)_5SO_4]Br$ (Red). In the first case, SO_4^{2-} precipitates with Barium; in the second, Br^- precipitates with Silver.

Reactions and Mechanisms

Just because a complex is stable (energetically favorable) doesn't mean it is unreactive (kinetically inert).

- **Thermodynamics vs. Kinetics:**
  - ○ **Stable/Unstable:** Refers to **Thermodynamics** (Keq). Does the reaction favor products? For example, $[Ni(CN)_4]^{2-}$ is extremely stable (large formation constant), meaning it doesn't fall apart on its own.
  - ○ **Inert/Labile:** Refers to **Kinetics** (Reaction Rate). How fast are ligands exchanged? Interestingly, $[Ni(CN)_4]^{2-}$ is **labile**—if you put it in water with radioactive $C^{14}N^-$, the cyanide ligands swap almost instantly. Conversely,

$[Co(NH_3)_6]^{3+}$ is **inert**; it can sit in water for days without exchanging ligands, even though it might be thermodynamically favorable to do so.

- **Substitution Mechanisms:**
  - **Dissociative (D):** The rate-determining step is the breaking of the Metal-Ligand bond. The coordination number decreases temporarily (e.g., 6 → 5 → 6). This is common for Octahedral complexes.
  - **Associative (A):** The rate-determining step is the forming of a new bond with the incoming ligand. The coordination number increases temporarily (e.g., 4 → 5 → 4). This is characteristic of **Square Planar** complexes because the open space above and below the plane allows an attacking ligand to enter easily.
- **The Trans Effect:** In square planar substitution reactions (especially for Platinum), the ligand *trans* (opposite) to the leaving group influences the rate of substitution. Strong ligands (like CN^-, CO) weaken the bond opposite to them, making that ligand leave faster. This is crucial for synthesizing specific isomers like Cisplatin.

Example Ligand Substitution in Copper(II): Adding concentrated Hydrochloric Acid to aqueous Copper Sulfate results in a color change from blue to yellow/green.

- **Reaction:** $[Cu(H_2O)_6]^{2+}$ (aq) + $4Cl^-$ (aq) $\rightleftharpoons$ $[CuCl_4]^{2-}$ (aq) + $6H_2O$ (l)
- **Detailed Analysis:**
  - The reactant is an **octahedral** complex (blue). The H_2O ligands are neutral and small.
  - The product is a **tetrahedral** complex (yellow). The Cl^- ligands are negatively charged and large.
  - *Why the geometry change?* Four large chloride ions cannot fit around the small copper ion in an octahedral shape due to steric repulsion. Furthermore, the negative charge repulsion between chlorides favors the wider 109.5° angles of a tetrahedron over the 90° angles of a square plane or octahedron.

References

1. Miessler, G. L., & Tarr, D. A. (2010). *Inorganic Chemistry* (5th ed.). Pearson.
2. Atkins, P., & Overton, T. (2010). *Shriver and Atkins' Inorganic Chemistry*. Oxford University Press.
3. Housecroft, C. E., & Sharpe, A. G. (2018). *Inorganic Chemistry* (5th ed.). Pearson.