Application Magnetochemistry

1. First Principles: What Does Magnetic Moment Tell Us?

The magnetic moment (μ) of a transition metal ion is a direct probe of its **electronic configuration**, specifically the number of **unpaired electrons** in its d-orbitals.

Magnetic Moment and Unpaired Electrons

The most critical concept is the **Magnetic Moment (μ_{eff})**, which is a measure of the strength of a magnetic species. It is directly related to the number of unpaired electrons (n) by the **spin-only formula**:

$$\mu_{eff} = \sqrt{n(n+2)} \text{ Bohr Magnetons (B.M.)}$$

By measuring the magnetic moment experimentally (using a **Gouy Balance** or the **Evans Method**), you can determine the number of unpaired electrons and unlock a wealth of information.

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2. Applications of Magnetic Moment Data

Application 1: Determination of Oxidation State

The oxidation state of a metal ion directly changes the number of d-electrons, which in turn changes the number of unpaired electrons and the magnetic moment.

Example: Cobalt (Co)

- **Co^{2+}** (d^7): Can be high-spin or low-spin.
  - In octahedral complexes, it's usually **high-spin** (e.g., $[CoF_6]^{4-}$).
  - Calculated μ_eff = √[3(3+2)] = √15 ≈ **3.87 B.M.** (Experimental: ~4.4 - 5.2 B.M., the difference is due to orbital contribution).
  - This confirms a d^7 configuration with 3 unpaired electrons.
- **Co^{3+}** (d^6):
  - In low-spin complexes (e.g., $[Co(CN)_6]^{3-}$), all electrons are paired (n=0).
  - μ_eff ≈ **0 B.M.** (Diamagnetic).
  - In high-spin complexes (e.g., $[CoF_6]^{3-}$), it has 4 unpaired electrons (n=4).
  - μ_eff = √[4(4+2)] = √24 ≈ **4.90 B.M.**

If you have an unknown cobalt complex, measuring its magnetic moment can immediately tell you if it's Co(II) or Co(III), and if it's high-spin or low-spin.

Application 2: Distinguishing Between High-Spin and Low-Spin Complexes

This is one of the most important applications, especially for d^4, d^5, d^6, and d^7 ions in octahedral geometry. The magnetic moment is a clear, experimental distinction.

Example: Iron (Fe)

- **Fe^{3+}** (d^5):

  High-spin complex (e.g., $[FeF_6]^{3-}$): Weak field ligand. All 5 electrons are unpaired (n=5).

    - $\mu\_eff = \sqrt{[5(5+2)]} = \sqrt{35} \approx$ **5.92 B.M.** (Experimental is very close).
  - **Low-spin complex** (e.g., $[Fe(CN)_6]^{3-}$): Strong field ligand. Only 1 unpaired electron (n=1).
    - $\mu\_eff = \sqrt{[1(1+2)]} = \sqrt{3} \approx$ **1.73 B.M.**

A measurement showing μ_eff ~ 6 B.M. vs. ~ 2 B.M. is a definitive test for the ligand field strength and the spin state of the complex.

Application 3: Identification of Geometries (Stereochemistry)

The crystal field splitting (Δ) is different for different geometries (e.g., Octahedral vs. Tetrahedral). This affects whether a complex is high-spin or low-spin.

Example: Nickel (Ni^{2+}) - d^8

- **Octahedral Geometry** (e.g., $[Ni(H_2O)_6]^{2+}$): Almost always high-spin for Ni(II). Two unpaired electrons (n=2).
  - $\mu\_eff = \sqrt{[2(2+2)]} = \sqrt{8} \approx$ **2.83 B.M.**
- **Square Planar Geometry** (e.g., $[Ni(CN)_4]^{2-}$): Strong field ligand forces all electrons to pair up (n=0).
  - μ_eff ≈ **0 B.M.** (Diamagnetic).
- **Tetrahedral Geometry** (e.g., $[NiCl_4]^{2-}$): The splitting is small, so it's always high-spin with two unpaired electrons (n=2).
  - μ_eff ≈ **2.83 B.M.** (Note: It can be tricky to distinguish from octahedral based on magnetism alone, but it helps when combined with other data).

Thus, for a Ni(II) complex, a magnetic moment of ~0 B.M. is a clear signature of a square planar structure.

Application 4: Evidence for Metal-Metal Bonding and Cluster Compounds

In some compounds, metal atoms can pair their electrons to form metal-metal bonds, reducing the number of unpaired electrons.

Example: Chromium Acetate Hydrate [$Cr_2(O_2CCH_3)_4(H_2O)_2$]

- A single Cr^{2+} (d^4) ion would be expected to have a high magnetic moment (n=4, μ_eff ~4.9 B.M.).
- However, the measured μ_eff for this dimer is very low.
- **Interpretation:** This indicates that the two Cr atoms are bonded together (a quadruple bond), pairing up their electrons and resulting in a diamagnetic or very weakly paramagnetic compound.

Application 5: Diagnosing Quenching of Orbital Contribution

The spin-only formula is an approximation. For certain ions, there is a significant orbital contribution to the magnetic moment.

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- **Ions with orbital quenching:** High-spin d^5 (Mn^{2+}, Fe^{3+}) and A or E ground terms (e.g., Ti^{3+}). Their experimental μ_eff is very close to the spin-only value.
- **Ions with significant orbital contribution:** Co^{2+} (d^7) and Ni^{2+} (d^8). Their experimental μ_eff is often higher than the spin-only value.
    - For Co^{2+}, spin-only for n=3 is 3.87 B.M., but experimental values are often 4.7 - 5.2 B.M.

Analyzing this deviation helps chemists understand the detailed electronic ground state of the metal ion.

Summary Table for Quick Reference

Ion	d-electrons	Common Oxidation State	High-Spin (μ_eff in B.M.)	Low-Spin (μ_eff in B.M.)	Application
Ti^{3+}	d^1	+3	~1.73 (n=1)	-	Oxidation State
V^{3+}	d^2	+3	~2.83 (n=2)	-	Oxidation State
Cr^{3+}	d^3	+3	~3.87 (n=3)	-	Geometry, OS
Mn^{2+}	d^5	+2	~5.92 (n=5)	~1.73 (n=1)	**Spin State**
Fe^{2+}	d^6	+2	~4.90 (n=4)	~0 (n=0)	**Spin State**
Fe^{3+}	d^5	+3	~5.92 (n=5)	~2.83 (n=1)*	**Spin State**
Co^{2+}	d^7	+2	~4.7-5.2 (n=3)	~1.73 (n=1)	**OS & Spin State**
Ni^{2+}	d^8	+2	~2.83 (n=2)	~0 (n=0)	**Geometry**
Cu^{2+}	d^9	+2	~1.73 (n=1)	-	Oxidation State

Note: Low-spin d^5 has one unpaired electron.

For you, magnetic moment data is a powerful, low-cost, and relatively simple **diagnostic tool**. In the laboratory or while characterizing a new compound, it helps you answer fundamental questions:

1. **What is the metal's oxidation state?**
2. **Are the ligands creating a strong or weak field?** (High-spin vs. Low-spin)
3. **What is the probable geometry around the metal centre?** (Tetrahedral, Square Planar, Octahedral)
4. **Is there something unusual, like metal-metal bonding?**

By integrating magnetic susceptibility measurements with other techniques like UV-Vis spectroscopy and IR spectroscopy, you can build a comprehensive picture of the structure and bonding in transition metal complexes, which is at the very heart of inorganic chemistry.