

Bonding in Transition Metal Compounds

Oxidation States and Bonding

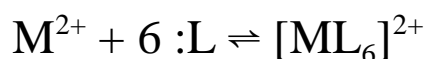
- Transition metals tend to have configurations $(n - 1)d^xns^2$ or $(n - 1)d^xns^1$, Pd having $4d^{10}5s^0$.
 - ☛ All lose ns electrons first, before any d electrons, when forming cations.
- Most have two or more principal oxidation states, with +2 and +3 being most prevalent.
- In a few cases the metal has a negative state [e.g., Mn(-III) in $\text{Mn}(\text{NO})_3\text{CO}$].
- First-row transition elements have the following positive states (most stable listed first).

Sc	3	Fe	3, 2
Ti	4, 3	Co	2, 3
V	5	Ni	2, 3
Cr	3, 6, 2	Cu	2, 1, 3
Mn	2, 7, 6, 4, 3	Zn	2

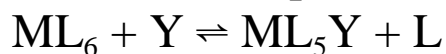
- Transition metals form the usual ionic compounds and a number of complex ions (mostly with O) in which they tend to have high oxidation states (e.g., $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , MnO_4^-).
- Coordination complexes are unique to transition metals.

Transition Metal Complexes

- In complexes the metal ion is surrounded by several anions or neutral molecules (sometimes cations) called *ligands*.
- The coordinate bond results from the Lewis acid character of the metal ion and Lewis base character of the ligands; e.g.,



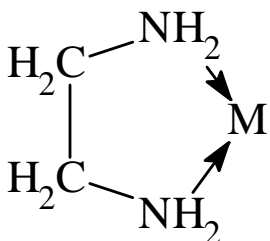
- Relative to typical covalent bonds, the M–L bonds are weak.
 - Displacement of ligands by other ligands is a common feature of transition metal complex chemistry.



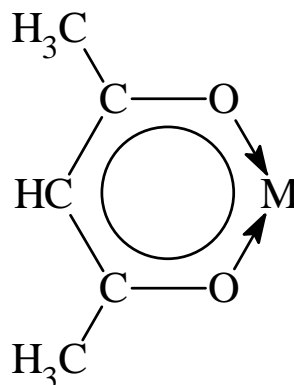
- Transition metal ions in a given oxidation state generally exhibit a characteristic *coordination number* (CN) corresponding to the number of electron pairs donated by the set of ligands.
 - CN2 to CN16 are known, with CN4 and CN6 being most common.
 - CN corresponds to the number of coordination sites of the related molecular geometry; e.g., CN4 – tetrahedral, CN5 – trigonal bipyramidal, CN6 – octahedral.

Ligand Types

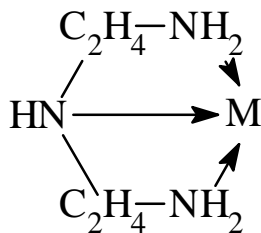
- Ligands may coordinate through one or more sites in the coordination geometry.
- Ligands that occupy only one site are called *unidentate* ("one toothed"); e.g., NH_3 , CN^- , CO , H_2O , Cl^- .
- Ligands that coordinate through more than one atom and occupy more than one coordination site are called *multidentate* and may be *bidentate*, *tridentate*, *tetradridentate*, etc.
 - Multidentate ligands are also called *chelates* (kē'·lāt – Gk., *chela* = crustacean claw).



ethylenediamine (en)



acetylacetonate (acac)



diethylenetriamine (dien)



triethylenetetraamine

Theories of Bonding

- Theories of bonding in transition metal complexes attempt to understand geometries, magnetic properties, color (electronic spectra, uv/vis), and reactivity (displacement reactions, redox).
- Four main theories have been used.
 - (1) Crystal Field Theory (CFT) – Assumes electrostatic (ionic) interactions between ligands and metal ions.
 - Useful for understanding magnetism and electronic spectra.
 - (2) Ligand Field Theory (LFT) – Modified CFT.
 - Makes empirical corrections to account for effects of M–L orbital overlap, improving quantitative agreement with observed spectra.
 - (3) Molecular Orbital (MO) Theory – Approach using M–L general MOs.¹
 - Excellent quantitative agreement, but less useful in routine qualitative discussions.
 - Qualitatively equivalent CFT.
 - (4) Valence Bond (VB) Theory – Assumes covalent M–L bonds formed by ligand electron donation to empty metal hybrid orbitals.
 - Popular from 1930s to 1950s.
 - Useful for rationalizing magnetic properties, but cannot account for electronic spectra.
 - Offers little that cannot be covered better by other theories.

¹Miessler & Tarr treat MO theory as part of LFT.

Magnetic Properties - Fundamental Concepts

- Every substance (except H₂) exhibits *diamagnetism*, owing to the behavior of paired electrons (equal numbers of α and β spins) in an applied magnetic field.
 - In a magnetic field, electron currents are induced that create a magnetic moment in opposition to the applied field (induced diamagnetic moment).
 - The diamagnetic moment causes the material to be repelled slightly relative to the applied field.
 - If there are no unpaired electrons, this is the only effect and the substance is said to be *diamagnetic*.
- If a substance contains unpaired electrons, it has a permanent *paramagnetism* from the net electron spin (S) and the net orbital angular momentum (L).
 - The paramagnetic moment will align with an applied magnetic field.
 - In the applied field, both this permanent magnetic moment and the induced diamagnetic moment exist simultaneously.
 - The permanent paramagnetic moment is always stronger, so the net effect is attraction for the applied field.
 - The substance is said to be *paramagnetic*, despite the presence of the weaker induced diamagnetic moment when in an applied field.
- *Ferromagnetism* results from the coupling of paramagnetic centers in a material to produce a stronger bulk magnetism.
- *Antiferromagnetism* results from coupling to produce a weaker bulk magnetism.
- Paramagnetism, ferromagnetism, and antiferromagnetism are temperature dependant.

Magnetic Moment, μ

- The magnitude of the *magnetic moment*, μ , in actual complexes depends upon the degree of coupling of spin and orbital momenta (*L-S* coupling).
- For free gaseous atoms and *f*-block complexes, complete coupling occurs and the magnetic moment depends upon $J = L \pm S$.

$$\mu_J = g\sqrt{J(J+1)} \text{ B.M.}$$

- Units are *Bohr magnetons* (B.M.), where

$$\text{B.M.} = eh/4\pi mc$$

where e = electron charge, m = mass of electron.

- The constant g is the *gyromagnetic ratio*, the ratio of the electron's magnetic moment to its angular momentum², which for a free gaseous atom is given by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

- In many transition-metal complexes the ligands effectively quench the orbital moment, and a *spin-only moment* results,

$$\mu_s = g\sqrt{S(S+1)} \text{ B.M.}$$

where $g = 2.00023$ for a free electron.

- Assuming $g = 2.00$ and n is the number of unpaired electrons in the metal ion,

$$S = |\Sigma m_s| = n/2$$

and

$$\mu_s = \sqrt{n(n+2)} \text{ B.M.}$$

²The angular momentum of the electron is given by $(h/2\pi)\sqrt{s(s+1)}$.

Spin-Only Moments

- From $\mu_s = \sqrt{n(n+2)}$ B.M., the expected values of μ_s for transition-metal complexes with $n = 1-5$ unpaired electrons are as follows.

n	S	μ_s (B.M.)
1	1/2	1.73
2	1	2.83
3	3/2	3.87
4	2	4.90
5	5/2	5.92

- In cases with half-filled and fully-filled subshells, the ground state term is S ($L = 0$) and very good agreement with μ_s values is expected.
 - Complexes with d^5 configurations and no paired electrons (high-spin) typically show this behavior (e.g., $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$).

Incomplete Orbital Quenching

- In some cases, such as $\text{Fe}^{2+} (d^6)$ and $\text{Co}^{2+} (d^7)$, the orbital contribution is not fully quenched but remains decoupled from the spin.

- If the full orbital momentum contribution occurs, the moment is

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

but because $g = 2.00$

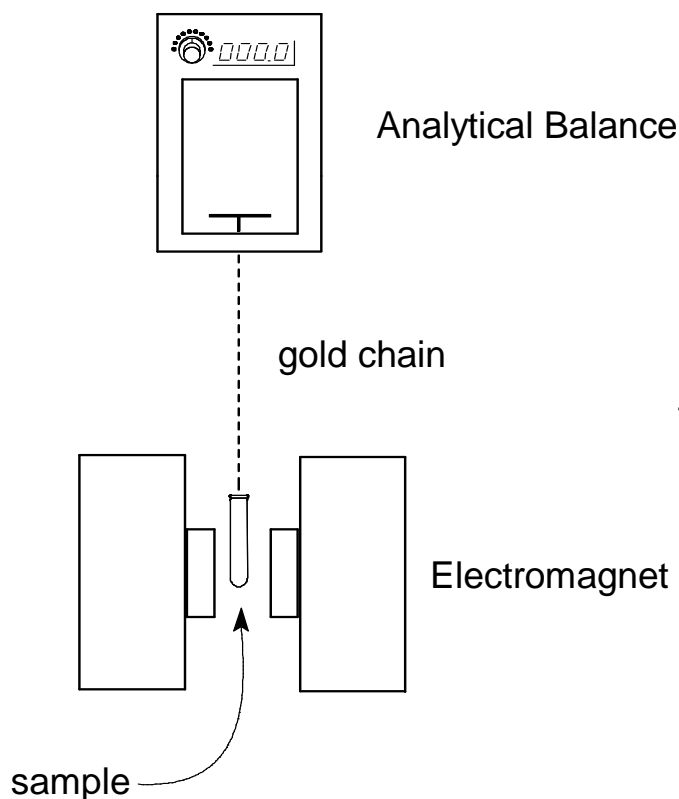
$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

- This behavior, to some degree, is typical of ions with D or F free-ion ground state terms.

☞ If $L > 0$, $\mu_{\text{obs}} > \mu_s$ is to be expected.

Determining Magnetic Moment

- Magnetic moment is not directly measured, but rather the *magnetic susceptibility*, χ , is observed.
- In the Gouy balance method, the behavior of a sample and reference are compared, both in and out of an applied magnetic field.



- A newer version of the apparatus³ has a fixed sample with a moveable magnet attached to a torsion balance.

³D. F. Evans, *J. Phys. E; Sci. Instr.*, **1974**, 7, 247.

Gouy Balance Method

- The *mass susceptibility*, χ_g^s of the sample is obtained relative to the mass susceptibility of a reference, χ_g^r , of known magnetic moment, by

$$\chi_g^s = \left(\frac{\Delta W_s}{\Delta W_r} \right) \left(\frac{W_r}{W_s} \right) \chi_g^r$$

where W is weight out of the field (true mass) and ΔW is apparent change in weight in the field resulting from paramagnetic and diamagnetic moments.

- The experimental *molar susceptibility*, χ_M , is given by

$$\chi_M = \chi_g^s M$$

where M is the molecular weight of the sample.

- χ_M includes diamagnetic contributions from electron pairs in the metal core, ligands, and counter ions.
 - The *corrected molar susceptibility*, χ_A , is

$$\chi_A = \chi_M - \{ \chi_M(\text{core}) + \chi_M(\text{ligand}) + \chi_M(\text{ion}) \}$$

- Values of the diamagnetic correction terms, called *Pascal's constants*, can be obtained from tables of average experimental values.⁴

⁴G. A. Bain, J. F. Berry, *J. Chem. Educ.*, **2008**, 85, 532.

Curie-Weiss Law

- The relationship between χ_A and μ is given by the *Curie-Weiss Law*.

$$\chi_A = \frac{N\beta^2\mu^2}{3k(T + \theta)}$$

where N = Avogadro's number

β = Bohr magneton

k = Boltzmann constant

T = temperature in kelvin (K)

θ = Weiss constant

- θ indicates the degree of coupling of paramagnetic centers in the sample (i.e., ferromagnetism or antiferromagnetism).
- Substituting the constants, the Curie-Weiss Law becomes

$$\mu = 2.828\sqrt{\chi_A(T + \theta)}$$

- In the absence of coupling, ideal Curie Law behavior is observed ($\theta = 0$), and the simpler Curie Law equation applies:

$$\mu = 2.828\sqrt{\chi_A T}$$

- Units of μ are Bohr magnetons (B.M.)