Classes 7.1-2-3 
Intro. to Coordination Complexes

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CHEM 462 
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Coordination Compounds

- Even in cases where we think of solvated cations, evidence for solvent-cation interactions shows that more than electrostatics is involved.
- Example: ionic vs. hydrated radii (Å) of alkali metals:

<table>
<thead>
<tr>
<th>Ion</th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion</td>
<td>0.90</td>
<td>1.16</td>
<td>1.52</td>
<td>1.66</td>
<td>1.81</td>
</tr>
<tr>
<td>Hyd</td>
<td>3.40</td>
<td>2.76</td>
<td>2.32</td>
<td>2.28</td>
<td>2.28</td>
</tr>
</tbody>
</table>

Real Coordination Complexes

- For higher oxidation state, less electropositive, transition and main-group metals, the ionic picture is not adequate.
- Metal ions can be viewed as Lewis Acids, ligands as Lewis bases.
**Types of Ligands**
- Monodentate: X\(^-\), H\(_2\)O, ROH, ROR, THF, \(-\)OH, \(-\)OR, DMSO, NH\(_3\), NR\(_3\), py, PR\(_3\), \(-\)CH\(_3\), \(-\)CN, CO
- Multidentate: en, dmpe, glyme, acac, bpy, phen, dien, terpy, porphyrin, ...
- Some which can be mono- or di-: carboxylates, nitrate, sulfate, dithiocarbamates

**Stability Constants**
Stability constants are defined in aqueous solutions as (six-coordinate case):

\[
[M(OH_2)_6]^{n+} + L \rightleftharpoons [M(OH_2)_5L]^{n+} + H_2O \quad K_1
\]
\[
[M(OH_2)_5L]^{n+} + L \rightleftharpoons [M(OH_2)_4L_2]^{n+} + H_2O \quad K_2
\]
\[
\ldots
\]

\[
K_1 = \frac{[M(OH_2)_5Ln^+]}{[M(OH_2)_6n^+][L]} \quad \text{etc...}
\]

\[
B_6 = \frac{[ML_6^{n^+}]}{[M(OH_2)_6^{n^+}][L]^6} = K_1 \times \ldots \times K_6
\]

\( \Delta G^\circ, \Delta H^\circ, \text{ and } \Delta S^\circ \) can be defined for each process and related to each equilibrium constant.

**Chelate Effect**
- ammine ligands replace aquo ligands on Ni(II) in an enthalpy driven reaction (\(B_6 = 10^{8.6}\)):
  \[
  [\text{Ni(H}_2\text{O)}_6]^{2+} + 6 \text{NH}_3 \rightarrow [\text{Ni(NH}_3)_6]^{2+} + 6 \text{H}_2\text{O}
  \]
- The free energy of a similar reaction with en has an even more negative (\(B_6 = 10^{18.7}\)):
  \[
  [\text{Ni(H}_2\text{O)}_6]^{2+} + 3 \text{en} \rightarrow [\text{Ni(en)}_3]^{2+} + 6 \text{H}_2\text{O}
  \]
- Direct comparison (\(K = 10^{9.7}\)):
  \[
  [\text{Ni(NH}_3)_6]^{2+} + 3 \text{en} \rightarrow [\text{Ni(en)}_3]^{2+} + 6 \text{NH}_3
  \]
  For this \(\Delta H^\circ = -12 \text{ kJ/mol}\)}
Bonding and Electronic Structure

- Molecular orbital picture for Lewis acid-base interaction
- d-orbitals - acceptor orbitals on transition metals
- MO picture for octahedral complexes
- Low-spin vs. high-spin complexes; ligand-field splitting vs. pairing energy

Metal-Ligand bonding

- Concepts of “hardness” and “softness” already discussed (qualitatively).
  (Pearson’s 1963 JACS paper introducing these concepts is posted in the web site “handouts” section.)
- Intro to Ligand fields - an MO scheme for a “typical” octahedral transition metal complex (symmetry adapted “LGOs”) are shown in Figure 4.24).

The Spectrochemical Series

CO, CN⁻ > NO₃⁻ > en, NH₂CH₃ > NH₃ > [NCS]⁻ > H₂O ≈ [oxalate]²⁻ > OH⁻ > F⁻ > Cl⁻ > [NCS]⁺ > Br⁻ > I⁻

Factors affecting d-orbital splittings:
- Lewis basicity
- Electronegativity of donor atom
- π-donating or π-accepting character of the ligand
- Metal atom charge & row (1ˢᵗ < 2ⁿᵈ < 3ʳᵈ)
Properties of complexes

- Structural and Thermodynamic effects of d-orbital splittings.
- Examples: Hydration energies and radii of 2+ ions in 1st row T.M.s

Data to Explain (for +2 ions)

- Hydration Energies (kJ/mol)
- High-Spin ion radii (Å)

Properties of complexes

- Magnetic properties: High-spin and low-spin complexes
- Optical properties:
  - measuring $\Delta_{\text{oct}}$
  - effect of spin on transition probabilities
Spin-Only Magnetism

- $\chi$ is the magnetic susceptibility, and obeys the Curie Law for simple paramagnetic compounds.
- $\mu_B$ is the Bohr Magneton.
- $\mu_B = 5.7884 \times 10^{-5} \text{ eV T}^{-1}$
- $\mu_B N_{av} = 5.585 \text{ J T}^{-1} \text{ mol}^{-1}$
- $(T = \text{Tesla})$

\[ \chi = \frac{C_{molar}}{T} \]
\[ C_{molar} = \frac{N_{av}}{3k_B} \mu_{eff}^2 \]
\[ \mu_{eff} = g_S \sqrt{S(S+1)} \mu_B \]
\[ g_S = 2.0023 \ldots \equiv 2 \]
\[ \mu_B = \frac{e\hbar}{2m_e c} \]

Carbonyl Compounds and the “18 e– rule”

- Carbonyls and other strong field ligands tend to form transition-metal compounds that conform to a so-called 18 e– rule.
- When e– count is low: M-M bonds!
- Other important organic ligands can be included among those that form complexes that tend to conform to the 18 e– rule:
  - H–, CH3– (and other R– - all 2 e– donors), [C5H5]– (Cp– - a 6 e– donor), other organics