October 26, 2004 - Lecture 15: MO Theory of Coordination Compounds

Summary of bonding in coordination compounds:
• valence bond theory: dative bond, electron counting, extreme covalency limit, hybridization 
  ⇒ stoichiometry, overall structure, VSEPR, ground state only
• electrostatic (ionic) model: metal-ligand attraction, ligand-ligand repulsion 
  ⇒ described by Coulomb interactions, complex stability, bond energies
• crystal field theory: splitting of d orbitals, LFSE, Jahn Teller stabilization (d⁹ vs. d¹ in O₆) 
  ⇒ color, qualitative spectroscopy, no overlap/covalency
• ligand field theory: adjusted crystal field with Racah parameters (B,C), Tanabe-Sugano correlation diagrams 
  ⇒ quantitative spectroscopy for σ-bonding, weakness with π bonding, backbonding
• molecular orbital theory: \( \Psi_{M-L} = \frac{2}{\sqrt{1-\alpha^2}} \phi_{Md} \pm \alpha \phi_{SALC} \) (\( \alpha^2 \) is the covalency) 
  \( \alpha = 0 \) Crystal Field Theory; \( 0 < \alpha < 1 \) Ligand Field and MO theories; \( \alpha = 1 \) Valence Bond Theory

Molecular Orbitals of Coordination Compounds in O₆ symmetry (ML₆)

• metal based orbitals:
  nd (t₂g,e₉); (n+1)s (a₁g); (n+1)p (t₁u)
• ligand based orbitals:
  σ: s, pₓ; π: pₓ, pᵧ
where M-L aligned along ligand z'

normal vs. inverted ordering of metal and ligand orbitals
(antibonding more metal, bonding more ligand and vice versa)

reduc.rep. E 8C₃ 6C₂ (L C₃) 6C₄ 3C₂(=C₄)² i 6S₄ 8S₆ 3σₕ 6σₕ (gives shapes)
Γ σ 6 0 0 2 2 0 0 0 4 2 \( a₁g+e₉+t₁u \)
Γ π 12 0 0 0 -4 0 0 0 0 0 \( t₁u+2t₂u \)

a) σ donor (NH₃; LP N 2pₓ+2s - complex [Ni(NH₃)₆]²⁺) b) σ+π donor (Cl⁻, OH⁻, H₂O - complex [Cr(OH₂)₆]³⁺)

note: the relative order of splitting is proportional to the overlap including ligand σ and π orbitals (draw shapes)
c) σ donor and π acceptor (CO, olefin, CN', PR₃) - low lying π* or vacant σ*, d orbitals as for P

Polarized spectroscopy - as experimental probe of MO diagrams:

Multipoles expansion of transition moment operator

\[ M_T = M_{\text{elec.dipole}}(x,y,z) + M_{\text{magnetic dipole}}(R_x,R_y,R_z) + M_{\text{electric quadrupole}}(x^2,y^2,z^2,xy,xz,yz) \]

1. conventional (non-polarized) optical spectroscopy (ABS): envelope of all possible transitions
   a) ligand field transitions (d → d): parity forbidden, weak absorption bands
      \[ \text{d}^9: \text{ground s.}^2E_g(t_{2g}^6e_g^3) \rightarrow \text{excited state}^2T_{2g}(t_{2g}^5e_g^4) \quad g \rightarrow g \quad \text{LaPorte's rule} (\epsilon \sim 10) \]
      \[ \text{d}^5: \text{ground s.}^6A_{1g}(t_{2g}^2e_g^3) \rightarrow \text{excited state}^4T_{1g}(t_{2g}^2e_g^3) \quad g \rightarrow g \quad \text{LaPorte's and spin selection} (\epsilon \sim 0.1) \]
   b) ligand to metal charge transfer (LMCT - short lifetime of the excited state): parity allowed, intense bands
      \[ \text{d}^9: \text{ground s.}^2E_g(t_{1u}^2t_{2g}^6e_g^3) \rightarrow \text{excited state}^2T_{2u}(t_{1u}^1t_{2g}^6e_g^4) \quad - \text{states} t_{1u} \times e_g = t_{1u} + t_{2u} \]
      \[ g \rightarrow u \quad \text{LaPorte's rule} (\epsilon \sim 10^5 \text{ and above}) \]
   c) metal to ligand charge transfer (MLCT): parity allowed, intense bands
      \[ \text{d}^6: \text{ground s.}^1A_{1g}(t_{2g}^2e_g^1t_{1u}^0) \rightarrow \text{lowest excited s.}^2T_{2g}(t_{2g}^5e_g^1t_{1u}^1) \quad g \rightarrow g \quad \text{LaPorte's rule} (\epsilon \sim 10) \]
      \[ \text{next excited s.} (t_{2g}^5e_g^1t_{1u}^1) - \text{states} t_{2g} \times t_{1u} = a_{2u} + e_u + t_{1u} + t_{2u} \]
      \[ g \rightarrow u \quad \text{LaPorte's rule} (\epsilon \sim 10^5 \text{ and above}) \]

2. single crystal spectroscopy with in-plane polarized light
   cubic crystal \quad \Rightarrow \text{isotropic} \quad \Rightarrow \text{unpolarized}
   tri/tetra/hexa-gonal \quad \Rightarrow \text{uniaxial} \quad \Rightarrow \text{light $\parallel$ or $\perp$ to C₃,C₄,C₆, resp.}
   orthorhombic, monoclinic, triclinic \quad \Rightarrow \text{biaxial} \quad \Rightarrow \text{light $\parallel$ or $\perp$ to 3C₂,C₂, no symmetry resp.}
   photon has propagation direction $\vec{v}$ and corresponding electric and magnetic field ($\vec{E}, \vec{H}$) vectors
   if $\vec{E} \parallel \vec{c}$ and $\vec{H} \perp \vec{c}$ \quad magnetic dipole allowed \quad e.g. $T_{1g}$ in O₉
   $\vec{E} \perp \vec{c}$ and $\vec{H} \parallel \vec{c}$ \quad electric dipole allowed \quad e.g. $T_{1u}$ in O₉
   $\vec{E} \perp \vec{c}$ and $\vec{H} \perp \vec{c}$ \quad both electric and magnetic dipole allowed

4. circular dichroism spectroscopy: magnetic and electric dipole allowed transitions
   intensity of CD signal is $10^{-4}$ of the ABS signal - not important in TM complexes

5. magnetic circular dichroism spectroscopy: additional Zeeman effect + CD (selection rule $\Delta M_J = \pm 1$)
   large external field will intensity ligand field transitions - very important in TM complexes