CHEM334 Lectures 8-9: MT Chapter 10
Crystal and Ligand-field Theories, Ligand Field stabilization, Jahn-Teller distortion

1. Valence bond theory
   - electron counting, hybridization (n)d (n+1)s (n+1)p
   - gives good starting point for stoichiometry + structure + expected reactivity (coordinative saturation, relative ligand bonding energies)
   - VSEPR can be applied on electron density of valence electrons (primarily ligand based)
   - limited description of low/high spin complexes, nothing on excited states, exceptions (18 vs. 16 e⁻ rule)

2. Electrostatic (ionic) models:
   - Coulomb attraction and repulsion between metal-ligand, ligand-ligand (charge, dipole)
   - coordination compounds at the ionic limit give qualitative bond energy and complex stability

3. Crystal Field Theory (Bethe - 1929):
   - splitting of d orbitals in the field of negatively charged ions as ligands
   - at the ionic limit in perfect octahedral complex (no overlap between metal d and ligand p orbitals):
     starting with $\Psi' = \Psi''$,
     where $\Psi_{metal}(x,y,z)$ is the metal d orbital wave function and $\Psi = \Psi' + \Psi''$
     $\Psi_{Crystal} = \sum Z_i \phi_i / r_{i-M}$, where i runs ligand 1 to ligand 6 in O₆, Z_i number of ligand electrons
     1/r_M potential is expressed in spherical harmonics centered at the metal, hence $\phi_{metal} = \sum Y_{ij}$
     solution of the secular equation in block-diagonalized form (irred.reps) gives
     $E_{2g} = 6 \cdot Z \phi^2 / r_{M-L} + 4Dq$ and $E_{4g} = 6 \cdot Z \phi^2 / r_{M-L} + 6Dq$, where $Dq = (35Z/6r_{M-L})R_{metal}$

   gaseous atoms ($0 \text{ eV}$) $\Rightarrow$ spherical perturbation ($6 \cdot Z \phi^2 / r_{M-L} \approx 10 \text{ eV}$) $\Rightarrow$ splitting of d orbitals ($Dq \approx 1 \text{ eV}$)
   - center of gravity rule: sum of the products of energy and orbital occupations must give zero for d⁰, thus no difference to a spherical field $\Rightarrow 4\cdot E(2g) + 6\cdot E(4g) = 0 \Rightarrow$ same for d⁴, d⁶ (S=5/2)
   - in d⁴ (S=3/2): LFSE = 3 \cdot (-4Dq) extra stabilization due to preferential occupation of lower d orbital

   example: (Cr(OH₂)₂)⁺⁺ M-ligand bond 560 kJ/mol; (Fe(OH₂)₂)⁺⁺⁺ bond energy 485 kJ/mol – extend this to d⁹-d¹⁰

   note that LFSE for d⁹ is always -12Dq, but Dq changes by ligand/metal $\Rightarrow$ spectrochemical series

   fixed metal: $I^- < Br^- < S^- < *SCN^- < Cl^- < NO_3^- < F^- < H_2O < CO_3^{2-} < NH_3 < py < Ph_3P < Ph_3N < CN^- < CO$
   σ- and π-donor (atoms) $< \sigma$-donor (lone pairs) $< \pi$-donor and π-acceptor (organometallics) - from MO theory

   fixed ligand: Mn²⁺ < Ni²⁺ < Co²⁺ < Fe³⁺ < Fe²⁺ < Cu²⁺ < Mn³⁺ < Mo⁶⁺ < Rh³⁺ < Ru³⁺ < Pd⁴⁺ < Ir⁴⁺ < Pt⁴⁺
   more positive charge ($Z_{metal} \rightarrow r_{M-L}$ distance) $< \text{ increasing size of the d-orbital (R_{metal} dependence on n) }$ - from CF theory

   - in d⁴: two possibilities - t₂g² e_g² (S=2) LFSE = -6Dq; t₂g² e_g² (S=1,0) LFSE = -16Dq
   determining factors: opposite spin - pairing repulsion energy (PRE) – forcing to be on the same orbital parallel spin - exchange stabilization (EXS) – different orbitals less repulsion

   - in d⁴ vs. d⁶: LFSE = 0 vs. -4Dq for high spin; -20Dq vs. -24Dq for low spin
   why not all low spin? $\Rightarrow$ d⁶ large exchange stabilization and no spin pairing repulsion

   in general if Dq is small $\Rightarrow$ large EXS to PRE ratio $\Rightarrow$ weak field limit $\Rightarrow$ high spin complex (Cr, Sr²⁺)

   if Dq is large $\Rightarrow$ small EXS to PRE ratio $\Rightarrow$ strong field limit $\Rightarrow$ low spin complexes (CO, CN⁻)

   PRE, EXS: increases as the charge/Z_{metal} increases (2⁺ to 3⁺) & decreases as the size increases (3d → 4d)
• Distortion from perfect $O_h$ symmetry:

a) axial elongation to tetragonal $D_{4h}$, such as in (Cu(NH$_3$)$_4$)$^3^+ _\text{+}$:
- in $O_h$, $e_g^4$ $t_{2g}^0$, LFSE = -$4Dq$ ⇒ see correlation table below ⇒ in $D_{4h}$ $b_{2g}^1$ $a_{1g}^1$ $b_{2g}^2$ $e_g^4$, LFSE = -$4Dq$ - $\beta$

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- Jahn-Teller effect: additional LFSE due to distortion to lower symmetry to eliminate orbital degeneracy
- similar stabilization for low spin $d^5$, high spin $d^4$ complexes ($d_{2}$ orbital separates from $d_{2}$)

b) completely remove the axial ligands in $O_h$ (⇒ $D_{4h}$, as in $d^8$ [Ni(CN)$_4$]$^{3+}$, [PdCl$_4$]$^{2-}$; but not in [NiCl$_4$]$^{5+}$)
- with strong field ligands & large $10Dq$: low spin square planar complex, $b_{2g}^0$ $b_{2g}^2$ $a_{1g}^2$ $e_g^2$
- with weak field ligands & large $10Dq$: low spin square planar complex, $b_{2g}^0$ $b_{2g}^2$ $a_{1g}^2$ $e_g^2$
- with weak field ligands & small $10Dq$: small ligand-ligand repulsion (H$_2$O), $b_{2g}^0$ $a_{1g}^2$ $b_{2g}^2$ $e_g^4$
- large ligand-ligand repulsion (Cl$^-$) ⇒ ML$_4$ tetrahedral

c) tetrahedral (⇒ $T_d$, such as in [NiCl$_4$]$^{5+}$):
- from group theory (t$^3$(xz,yz,z$^2$); e(x$^2$-y$^2$,xy) ⇒ only the splitting is given not the order
- same CF theory approach as for $O_h$ ⇒ solution of the secular equation gives
  \[ E_e = 4Ze^2 / r_{M-L} - 6Dq \] and \[ E_{e} = 4Ze^2 / r_{M-L} + 4Dq, \] where \[ Dq = (35Ze^2/9r_{M-L}^3)R_{ad} \]
- opposite order in $T_d$ compared to $O_h$, since $t_1$ more toward ligands; e in between the ligands
- $Dq_{ad} = 4/9 Dq_{ad}$ - generally high spin complexes due to smaller $Dq$ (greater PRE/EXS energies)
- in $d^4$, $d^3$, $d^2$: flattened tetrahedral ($D_{2d}$), tetragonal ($D_{4h}$) or trigonal ($C_3$) Jahn-Teller distortions

d) $d$-manifold splitting for other point groups:
  - hints: a) start from $O_h$ or $T_d$ and distort the structure
  - b) put negative charges along bonds and estimate M.L. repulsions

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<td>0.57</td>
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Check this out:
ML$_6$ = 2-ML + ML$_4$ = 2-ML + 2-ML
ML$_3$ = 3/2 ML$_2$
ML$_6$(TBP) = ML$_6$ + 2ML
ML$_2$(D$_n$) = ML$_2$ - 2-ML
ML$_2$(D$_d$) = ML$_2$ - 3-ML$_2$