Alfred Werner: Father of Coordination Chemistry.

Structure of Co(NH₃)₆Cl₃ is NOT Co(NH₃-NH₃-NH₃-Cl)₃ but rather is an octahedron with 6 NH₃ directly attached to Co(III) and 3 Cl⁻ are dissociable counterions, consistent with electrical conductivity of solutions— a 1:3 electrolyte.

If this analysis is correct then the 1:1 electrolyte [Co(NH₃)₄Cl₂]Cl should exist in two isomeric forms. It does; one is green and one is purple.

Transition metals have 2 valencies: their coordination number and their charge balance requirement. The octahedron is a common geometry in coordination chemistry.
These are real and stable entities. They have thermodynamic stability.

Table 7.4 Formation constants of Ni(II) ammines, $\left[\text{Ni}({\text{NH}_3})_n({\text{OH}_2})_{6-n}\right]^{2+}$

<table>
<thead>
<tr>
<th>$n$</th>
<th>$K_f$</th>
<th>$\log K_f$</th>
<th>$K_n/K_{n-1}$</th>
<th>Experimental</th>
<th>Statistical*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>525</td>
<td>2.72</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>148</td>
<td>2.17</td>
<td>0.28</td>
<td></td>
<td>0.42</td>
</tr>
<tr>
<td>3</td>
<td>45.7</td>
<td>1.66</td>
<td>0.31</td>
<td></td>
<td>0.53</td>
</tr>
<tr>
<td>4</td>
<td>13.2</td>
<td>1.12</td>
<td>0.29</td>
<td></td>
<td>0.56</td>
</tr>
<tr>
<td>5</td>
<td>4.7</td>
<td>0.63</td>
<td>0.35</td>
<td></td>
<td>0.53</td>
</tr>
<tr>
<td>6</td>
<td>1.1</td>
<td>0.04</td>
<td>0.23</td>
<td></td>
<td>0.42</td>
</tr>
</tbody>
</table>

* Based on ratios of numbers of ligands available for replacement, with the reaction enthalpy assumed constant.
Foundation Molecules of Transition Metal Organometallic Chemistry

- Homoleptic Metal Carboxyls
- Ferrocene and Metalloccenes
- Zeise’s “salt”
Metal Carbonyls: German Chemistry, 1930’s

From X-ray crystallography. A portion of a “packing diagram” or the “extended structure” of W(CO)$_6$
A TEP (Thermal Ellipsoid Plot) of a single molecule of tungsten hexacarbonyl, W(CO)₆

Thermal ellipsoids indicate extent of thermal motion. The tighter, rounder the atom, the better the structure. This one looks great.

An octahedron has 48 symmetry operations: E, 8 C₃, 6 C₄, 6 C₂, I, 6 S₄, 8 S₆, 3σₜ, 6 σₜ
\[ W(CO)_6 + PMe_3 \xrightarrow{\triangle} W(CO)_5PMe_3 + CO \]

Ball and Stick structure of \( W(CO)_5(PMe_3) \)

**NOTE:**

- PMe\(_3\) is placed along the unique (z) axis. What is the order of that axis?
- Symmetry operations/elements are lost as compared to \( W(CO)_6 \). What are they?
- What is the point group assignment?
- How about multiply substituted complexes:
  - \( W(CO)_4(PMe_3)_2 \) => Are there isomers? Point groups?
  - \( W(CO)_3(PMe_3)_3 \) => Isomers? Point Group assignments?
What the metal carbonyls have taught us about TM Organometallic Chemistry:

- The Eighteen Electron Rule
- Metal-Metal Bonds
- Clusters
- $\pi$ – backbonding
- Stabilization of Low Oxidation States
- $\nu$(CO) IR and Symmetry
- Ligand Substitution Rxn Mechanisms
- Charge Distribution
- Nucleophilic Attack/Reactivity at CO Ligand
- Conversion of CO to Fischer Carbene
- Applications to Catalysis (as $M(CO)_x$ homoleptic complexes)

- Water Gas Shift Reaction
  \[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \]

- Hydroformylation
  \[ \text{H}_2\text{C}=\text{CH}_2 + \text{CO} + \text{H}_2 \Rightarrow \text{CH}_3\text{CH}_2\text{CHO} \]
Ferrocene: \((\eta^5-C_5H_5)_2\text{Fe}\)

mpt: 172° C; bpt: 250° C  !!  No decomposition.

https://www.youtube.com/watch?v=H6_E6C_e_fg
Ferrocene: \((\eta^5-C_5H_5)_2Fe\)
Ferrocene: \((\eta^5-C_5H_5)_2Fe\) Orbital overlap
Electronic structure and properties

18 Valence e⁻, Closed shell
Diamagnetic
Thermally and air stable
Reversible Fe²⁺/Fe³⁺ potential

http://www.ilpi.com/organomet/cp.html
Reactivity of ferrocene

Electrophilic Aromatic Substitution

1. Friedel-Crafts reactions

   a. Alkylation
   
   R
   Fe
   Alkyl halide
   H₃PO₄
   Fe
   C₄H₉Li
   Li
   Fe
   or
   Fe
   Li
   or

   b. Acetylation

   acetic anhydride
   or acetyl chloride
   H₃PO₄
   Fe
   R
   Fe

2. Lithiation

   Poly(ferrocene) via RAFT and ATRP

   Good Nucleophile

   Fe
   PPh₂
   PP₃n₂
Applications of ferrocene

Solution Electrochemistry Standard

\[
\begin{align*}
\text{Fe} & \overset{+e^-}{\rightleftharpoons} \text{Fe}^+ \overset{-e^-}{\rightleftharpoons} \text{Fe}
\end{align*}
\]
The first olefin complex: Zeise’s salt. (1820’s ! )
Properties of Werner-type Transition Metal Complexes

1. Highly colored (absorb light in visible, transmit light which eye detects)

2. May exhibit multiple oxidation states

3. May exhibit paramagnetism as dependent on metal oxidation state and on ligand field.

4. Reactivity includes:
   
   A) Ligand exchange processes:
      i) Associative ($S_N2$; expanded coordination no.)
      ii) Dissociative ($S_N1$; slow step is ligand loss)

   B) Redox Processes
      i) inner sphere atom transfer;
      ii) outer sphere electron processes
      iii) Oxidative Addition and Reductive Elimination
The magical porphyrin ligand: Hemoglobin, myoglobin and Other proteins have “Heme iron”

When oxygenated, hemoglobin is red and diamagnetic. When deoxygenated, blue and paramagnetic!

What’s going on here????

Hemoglobin (blood)

Myoglobin (muscles)
The magical porphyrin ligand

Protonated porphyrin ligand

Heme Fe$^{II}$

Met-hemoglobin Fe$^{III}$

What’s going on here? Inner or outer sphere redox process?
Overview of Transition Metal Complexes

1. The coordinate covalent or dative bond applies in L:→M

2. Lewis bases are called LIGANDS—all serve as σ-donors; some are π-donors as well, and some are π-acceptors

3. Specific coordination number and geometries depend on metal and number of d-electrons

4. HSAB theory useful
   a) Hard bases stabilize high oxidation states
   b) Soft bases stabilize low oxidation states
### Oxidation States in Transition Metals

<table>
<thead>
<tr>
<th>element</th>
<th>ox. state range* (molecular compounds)</th>
<th>common (stable) ox. states**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>0 → 4+</td>
<td>3+, 4+</td>
</tr>
<tr>
<td>V</td>
<td>1- → 5+</td>
<td>3+, 4+, 5+</td>
</tr>
<tr>
<td>Cr</td>
<td>2- → 6+</td>
<td>2+, 3+, 6+</td>
</tr>
<tr>
<td>Mn</td>
<td>1- → 7+</td>
<td>2+, 3+, 4+, 7+</td>
</tr>
<tr>
<td>Fe</td>
<td>2- → 6+</td>
<td>0, 2+, 3+</td>
</tr>
<tr>
<td>Co</td>
<td>1- → 3+</td>
<td>2+, 3+</td>
</tr>
<tr>
<td>Ni</td>
<td>0 → 4+</td>
<td>1+, 2+, 3+</td>
</tr>
<tr>
<td>Cu</td>
<td>1+ → 3+</td>
<td>1+, 2+</td>
</tr>
<tr>
<td>Zn</td>
<td>2+</td>
<td>2+</td>
</tr>
</tbody>
</table>

*Relative oxidation state stabilities are highly ligand-dependent; very rare oxidation states are omitted. **Most frequently encountered oxidation states in boldface.
Oxidation states and electronic configuration give a clue as to which ligands will form the more stable complexes and also to the coordination number (the number of ligands around the metal) of the metal within the complex.

4. Electron Configurations of Atoms and Common Oxidation States of the First Transition Series

<table>
<thead>
<tr>
<th>Free Atom</th>
<th>Oxidation States</th>
<th>Atom in Molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sc(4s² 3d¹)</td>
<td>Sc³⁺(d⁰)</td>
<td>-</td>
</tr>
<tr>
<td>Ti(4s² 3d²)</td>
<td>Ti⁴⁺(d⁰) Ti³⁺(d¹) Ti²⁺ (d²) Ti⁰ (d⁴)</td>
<td>-</td>
</tr>
<tr>
<td>V(4s² 3d³)</td>
<td>V⁵⁺ (d⁰) V⁴⁺(d¹) V³⁺(d²) V²⁺ (d³) V⁰ (d⁵)</td>
<td>-</td>
</tr>
<tr>
<td>Cr(4s¹ 3d⁵)</td>
<td>Cr⁶⁺ (d⁰) Cr³⁺(d³) Cr²⁺(d⁴) - Cr⁰ (d⁶)</td>
<td>-</td>
</tr>
<tr>
<td>Mn(4s² 3d⁵)</td>
<td>Mn⁷⁺ (d⁰) Mn³⁺(d⁴) Mn²⁺(d⁵) - Mn⁰ (d⁷)</td>
<td>-</td>
</tr>
<tr>
<td>Fe(4s² 3d⁶)</td>
<td>Fe⁴⁺ (d⁴) Fe³⁺(d⁵) Fe²⁺(d⁶) - Fe⁰ (d⁸)</td>
<td>-</td>
</tr>
<tr>
<td>Co(4s² 3d⁷)</td>
<td>Co³⁺(d⁶) Co²⁺(d⁷) Co¹⁺ (d⁸) Co⁰ (d⁹)</td>
<td>-</td>
</tr>
<tr>
<td>Ni(4s²3d⁸)</td>
<td>Ni³⁺(d⁷) Ni²⁺(d⁸) Ni¹⁺ (d⁹) Ni⁰ (d¹⁰)</td>
<td>-</td>
</tr>
<tr>
<td>Cu(4s¹ 3d¹⁰)</td>
<td>Cu³⁺ (d⁸) Cu²⁺(d⁹) Cu¹⁺(d¹⁰) -</td>
<td>-</td>
</tr>
<tr>
<td>Zn(4s² 3d¹⁰)</td>
<td>Zn²⁺(d¹⁰) - -</td>
<td>-</td>
</tr>
</tbody>
</table>
5. Oxidation State

Here, \( z \) = charge on the complex unit.

\[
ox. \text{ state} = z - \sum_{N} L \text{ charge}
\]

examples:

- **Octahedral**
  \[
  [\text{Co(CN)}_{6}]^{3-} \rightarrow \text{Co}^{III} + 6\text{CN}^{-}
  \]
  \[
  [\text{MoOCl}_{4}]^{1-} \rightarrow \text{Mo}^V + \text{O}^{2-} + 4\text{Cl}^{-}
  \]
  \[
  [\text{Rh(en)}_{2}(\text{NO}_{2})\text{Cl}]^{1+} \rightarrow \text{Rh}^{III} + 2\text{en} + \text{NO}_{2}^{-} + \text{Cl}^{-}
  \]

- **Square pyramidal**
  \[
  \text{Fe(PF}_{3})_{5} \rightarrow \text{Fe}^0 + 5\text{PF}_{3}
  \]
  \[
  [\text{V(CO)}_{6}]^{1-} \rightarrow \text{V}^{I} + 6\text{CO}
  \]

- **Trigonal bipyramidal**
  \[
  [\text{Fe}_2\text{S}_{2}(\text{SR})_{4}]^{3-} \rightarrow \text{Fe}^{II} + \text{Fe}^{III} + 2\text{S}^{2-} + 4\text{RS}^{-}
  \]
  \[
  \text{W(CH}_{3})_{6} \rightarrow \text{W}^{VI} + 6\text{CH}_{3}^{-}
  \]

An oxidation state is a formalism which affords that \( d^n \) configuration consistent with molecular properties.
What geometries are prominent?

Octahedral

Trigonal Bipyramidal

Square planar

Tetrahedral

Trigonal planar

Linear
Classification of Ligands, I: type of donor orbitals involved: \( \sigma; \sigma + \pi; \sigma + \pi^*; \pi + \pi^* \)

3. Ligands

- **\( \sigma \):** NH\(_3\), NR\(_3\), H\(_2\)N–NH\(_2\) (en), -CH\(_3\), -C\(_2\)H\(_5\), ...
  - \( \sigma \)-bonding only

- **\( \sigma + \pi \):** F\(^-\), Cl\(^-\), Br\(^-\), I\(^-\), NCO\(^-\), NCS\(^-\), N\(_3\)^-, ...
  - \( \pi \)-donors
  - OH\(^-\), OR\(^-\), H\(_2\)O, O\(^2-\)
  - R\(_2\)S, R\(_2\)Se, R\(_2\)Te
  - SH\(^-\), SR\(^-\), S\(^2-\), Se\(^2-\), Te\(^2-\)
  - R\(_2\)N\(^-\), RN\(_2\)^-, N\(^3-\), R\(_2\)P\(^-\), RP\(_2\)^-, P\(^3-\)

![Chemical structures](attachment:image.png)

- Acac: bidentate chelate
- Salen: tetradeutate chelate
- EDTA: hexadentate chelate
Ligands, Classification I, continued

- $\sigma + \pi^*/\sigma^* \text{ (vacant)}$
  - back-acceptors
  - $\pi$-acceptors
  - $\pi$-acids

\[
\begin{align*}
\text{CO, CN}^-, \text{NO, N}_2, \text{RNC, } & \text{R}_3\text{P, (RO)}_3\text{P, R}_3\text{As} \\
\text{bpy} & \quad \text{bidentate chelate} \\
\text{phen} & \\
\text{cyclopentadienyl} & \quad \text{tropylium}
\end{align*}
\]

- $\pi + \pi^* \text{ (vacant)}$
  - $\pi$-donors and $\pi$-acceptors

These ligands form organometallic molecules.
Classification of Ligands: II
The L, X, Z approach

Malcolm Green: The CBC Method for Covalent Bond Classification used extensively in organometallic chemistry.

**L** ligands are derived from charge-neutral precursors: NH₃, amines, N-heterocycles such as pyridine, PR₃, CO, alkenes etc.

**X** ligands are derived from anionic precursors: halides, hydroxide, alkoxide alkyls—species that are one-electron neutral ligands, but two electron donors as anionic ligands. EDTA⁴⁻ is classified as an \( L_2X_4 \) ligand, features four anions and two neutral donor sites. \( C_5H_5 \) is classified an \( L_2X \) ligand.

**Z** ligands are RARE. They accept two electrons from the metal center. They donate none. The “ligand” is a Lewis Acid that accepts electrons rather than the Lewis Bases of the X and L ligands that donate electrons.
Oxidative addition of $\text{H}_2$ to chloro carbonyl bis triphenylphosphine Iridium(I) yields Chloro-dihydrido-carbonyl bis-triphenylphosphine Iridium(III). Note the neutral precursor, $\text{H}_2$, becomes two $X^-$ ligands once added to Ir.

Electron count:

<table>
<thead>
<tr>
<th></th>
<th>16 e</th>
<th>18e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ir(I) $d^8$</td>
<td>8 e</td>
<td></td>
</tr>
<tr>
<td>L ligands:</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>$X^-$ ligand:</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ir(III) $d^6$</td>
<td>6 e</td>
<td></td>
</tr>
<tr>
<td>3 L ligands:</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>3 $X^-$ ligands:</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>
Classification of Ligands: III
A description of properties

- Strong Field/Weak Field Ligands
- Chelating Ligands and Denticity
  - Polydentate: bi-, tri-, tetra, penta-
  - Hexadentate, etc.
- Bridging Ligands
  - 4-electron bridge: 3 center, 4 electrons
  - 2-electron bridge: 3-center, 2 electrons
- Ambidentate Ligands
- Bulky Ligands
- Chiral Ligands
- Hemi-labile Ligands
- Non-innocent Ligands
- Spectator Ligands
Chelating Ligands/Polydentate Ligands--examples

- ethylenediamine (en)
- dimethylphosphinoethane (dmpe)
- acetylacetonate (acac)
- oxalate (ox)
- ethylenediamine tetraacetate (edta)
- BINAP
- salen
- porphine (from porphyrin family)
- 4,4’-bipyridine
**Chelating Ligands/Polydentate Ligands**

**Ethylenediamine:**
An $L_2$ bidentate ligand

**Ethylenediaminetetraacetate:**
An $L_2X_4$, hexadentate ligand, an exceptional chelating agent with many uses. In medicine, for lead and mercury poisoning; also for thalassaemia (iron overload).
1,2-Bis(diphenylphosphino)ethane: \( \text{Ph}_2\text{PCH}_2\text{H}_2\text{PPh}_2 \)

\[
P(\text{C}_6\text{H}_5)_3 + 2 \text{Na}^0 \rightarrow \text{Na}^+\text{P(}\text{C}_6\text{H}_5)\text{)_2}^- + \text{Na}^+\text{C}_6\text{H}_5^- \\
\]

\[
2 \text{NaP(}\text{C}_6\text{H}_5)\text{)_2} + \text{ClCH}_2\text{CH}_2\text{Cl} \rightarrow (\text{C}_6\text{H}_5)_2\text{PCH}_2\text{CH}_2\text{P(}\text{C}_6\text{H}_5)_2 + 2 \text{NaCl} \\
\]

NOTE: Images for these In Google/internet search are TERRIBLE.
So, how do we mix and match these ligands and metals with their various oxidation states to get stable molecules?

1. Hard/Soft Acid Base Approach to stability

2. Knowledge of preferred coordination numbers and geometries

The Chemical Bond:

a) The sharing of an electron pair between two atoms.

b) A mixture of electrostatic and covalent interaction.
- high oxidation states stabilized by anionic \( \pi \)-donor ligands of electronegative atoms

- low oxidation states stabilized by neutral \( \pi \)-acceptor ligands

examples:

<table>
<thead>
<tr>
<th></th>
<th>&quot;high&quot;</th>
<th>&quot;low&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>([\text{TiF}_6]^2-), (\text{TiO}_2)</td>
<td>(\text{Ti(Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\text{Cl}_2)</td>
</tr>
<tr>
<td>V</td>
<td>([\text{VF}_6]^2-), (\text{VOCl}_4)^{1-}, (\text{VO}_2\text{Cl}_2)^{1-}</td>
<td>([\text{V(CO)}_6]^{0,1-})</td>
</tr>
<tr>
<td>Cr</td>
<td>([\text{CrO}_4]^2-), (\text{CrOCl}_4)^{1-}, (\text{CrF}_6)^{2-}</td>
<td>([\text{Cr(CNR)}_6]^{1+}), (\text{Cr(CO)}_6), ([\text{Cr(CO)}_5]^{2-})</td>
</tr>
<tr>
<td>Mn</td>
<td>([\text{MnO}_4]^{1,2-}), (\text{MnCl}_6)^{2-}</td>
<td>(\text{Mn(CO)}_5\text{Cl}, \text{Mn}_2(\text{CO})_10, [\text{Mn(CO)}_5]^{1-})</td>
</tr>
<tr>
<td>Fe</td>
<td>([\text{FeO}_4]^2-), (\text{FeCl}_4)^{1-}</td>
<td>(\text{Fe(CO)}_5, \text{Fe(PF}_3)_5, ([\text{Fe(CO)}_4]^{2-})</td>
</tr>
<tr>
<td>Co</td>
<td>([\text{CoF}_6]^{3-}), (\text{Cr(en)}_3)^{3+}</td>
<td>([\text{Co(CO)}_4]^{1-}), (\text{Co(CO)}_3\text{NO}, \text{Co}_2(\text{CO})_8, \text{Co(PR}_3)_3\text{Br})</td>
</tr>
<tr>
<td>Ni</td>
<td>([\text{NiF}_6]^2-), (\text{Ni(diarls)}_2\text{Cl}_2)^{1+}</td>
<td>(\text{Ni(CO)}_4, \text{Ni(PF}_3)_4, \text{Ni(PR}_3)_3\text{Br}, [\text{Ni}_2(\text{CN})_6]^{4-})</td>
</tr>
<tr>
<td>Cu</td>
<td>([\text{CuF}_6]^{3-})</td>
<td>([\text{Cu(CN)}_2]^{1-}), ([\text{CuCl}_2]^{1-})</td>
</tr>
</tbody>
</table>

At parity of ligand and coordination number, higher oxidation states become increasingly stable down a vertical group.
But, is the oxidation state the actual charge on the metal?? Let’s Ask Linus Pauling... 

6. Electroneutrality Principle:

In any molecule, bonding electrons are distributed in such a way that individual atoms are as close to electroneutrality as possible.

\[ \text{L}^{2-} + \text{M}^{2+} \rightarrow \text{L}^{\delta-}\text{M}^{\delta+} \]

Metal-ligand bond formation tends to reduce +ve charge on M (and -ve charge on \( \text{L}^{2-} \)), with the result that the actual charge on M is much below that corresponding to its oxidation state. The oxidation state conveys the \( d^n \) configuration of the coordinated metal.
<table>
<thead>
<tr>
<th>Free anion</th>
<th>Coordinated anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amide (\text{NH}_2^-)</td>
<td>amido (or azanido)</td>
</tr>
<tr>
<td>Azide (\text{N}_3^-)</td>
<td>nitrido (azido will also be met)</td>
</tr>
<tr>
<td>Bromide (\text{Br}^-)</td>
<td>bromo</td>
</tr>
<tr>
<td>Carbonate (\text{CO}_3^{2-})</td>
<td>carbonato</td>
</tr>
<tr>
<td>Cyanate (\text{CNO}^-)</td>
<td>cyanato</td>
</tr>
<tr>
<td>Fluoride (\text{F}^-)</td>
<td>fluoro ((\text{not fluo}))</td>
</tr>
<tr>
<td>Hydroxide (\text{OH}^-)</td>
<td>hydroxo (or hydroxido or hydroxy)</td>
</tr>
<tr>
<td>Nitrite (\text{NO}_2^-)</td>
<td>nitro or nitrito-N (see text)</td>
</tr>
<tr>
<td>Oxide (\text{O}^{2-})</td>
<td>oxo (or oxido)</td>
</tr>
<tr>
<td>Thiocyanate (\text{SCN}^-)</td>
<td>thiocyanato-N (\text{N-bonded}), thiocyanato-S (\text{S-bonded})</td>
</tr>
</tbody>
</table>
# Table 7.1

Typical ligands and their names

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Abbreviation</th>
<th>Donor atoms</th>
<th>Number of donors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylacetonato</td>
<td>( \text{acac}^- )</td>
<td>O</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Ammine</td>
<td>( \text{NH}_3 )</td>
<td>N</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Aqua</td>
<td>( \text{H}_2\text{O} )</td>
<td>O</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>2,2-Bipyridine</td>
<td>( \text{bpy} )</td>
<td>N</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>Bromido</td>
<td>( \text{Br}^- )</td>
<td>Br</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Carbonato</td>
<td>( \text{CO}_3^{2-} )</td>
<td>O</td>
<td>1 or 2</td>
<td></td>
</tr>
<tr>
<td>Carbonyl</td>
<td>( \text{CO} )</td>
<td>C</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Chlorido</td>
<td>( \text{Cl}^- )</td>
<td>Cl</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>1,4,7,10,13,16-Hexaoxa-cyclooctadecane</td>
<td>18-crown-6</td>
<td>O</td>
<td>6</td>
<td></td>
</tr>
</tbody>
</table>
### Table 7.1a (Continued)

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Abbreviation</th>
<th>Donor atoms</th>
<th>Number of donors</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,7,13,16,21-Pentaoxa-1,10-diaza-bicyclo[8.8.5]tricosane</td>
<td><img src="image" alt="Structure" /></td>
<td>2.2.1 crypt</td>
<td>N, O</td>
<td>2N, 5O</td>
</tr>
<tr>
<td>Cyanide</td>
<td>CN⁻</td>
<td>C</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Diethylenetriamine</td>
<td>NH₂(CH₂CH₂NH₂)₂</td>
<td>dien</td>
<td>N</td>
<td>3</td>
</tr>
<tr>
<td>Bis(diphenylphosphino)ethane</td>
<td>P₈H₁₄</td>
<td>dppe</td>
<td>P</td>
<td>2</td>
</tr>
<tr>
<td>Bis(diphenylphosphino)methane</td>
<td>P₈H₁₄</td>
<td>dppm</td>
<td>P</td>
<td>2</td>
</tr>
<tr>
<td>Cyclopentadienyl</td>
<td>C₅H₅</td>
<td>C₅</td>
<td>C</td>
<td>5</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>NH₂CH₂CH₂NH₂</td>
<td>en</td>
<td>N</td>
<td>2</td>
</tr>
<tr>
<td>Ethylenediaminetetraaceticato</td>
<td>O₂C⁻N-CO₂⁻</td>
<td>edta⁻⁶</td>
<td>N, O</td>
<td>2N, 4O</td>
</tr>
<tr>
<td>Fluoride</td>
<td>F⁻</td>
<td>F</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Glycinato</td>
<td>NH₂CH₂CO₂⁻</td>
<td>gly</td>
<td>N, O</td>
<td>1N, 1O</td>
</tr>
<tr>
<td>Hydrido</td>
<td>H⁻</td>
<td>H</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Hydroxo</td>
<td>OH⁻</td>
<td>O</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Iodido</td>
<td>I⁻</td>
<td>I</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Nitrito</td>
<td>NO₂⁻</td>
<td>O</td>
<td>1 or 2</td>
<td></td>
</tr>
<tr>
<td>Nitrito − κO</td>
<td>NO₂⁻</td>
<td>O</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Nitrito − κN</td>
<td>NO₂⁻</td>
<td>N</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Oxido</td>
<td>O⁻⁻²</td>
<td>O</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Oxalato</td>
<td><img src="image" alt="Structure" /></td>
<td>ox</td>
<td>O</td>
<td>2</td>
</tr>
<tr>
<td>Pyridine</td>
<td><img src="image" alt="Structure" /></td>
<td>py</td>
<td>N</td>
<td>1</td>
</tr>
<tr>
<td>Sulfido</td>
<td>S⁻⁻¹</td>
<td>S</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Tetrazacyclododecane</td>
<td><img src="image" alt="Structure" /></td>
<td>cyclam</td>
<td>N</td>
<td>4</td>
</tr>
<tr>
<td>Thiocyanoato − κV</td>
<td>NCS⁻⁻¹</td>
<td>N</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Thiocyanoato − κS</td>
<td>SCN⁻⁻¹</td>
<td>S</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Thiolato</td>
<td>RS⁻⁻¹</td>
<td>S</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Triaminoctethyamine</td>
<td>NH₂(CH₂)₁₀NH₂</td>
<td>tren</td>
<td>N</td>
<td>4</td>
</tr>
<tr>
<td>Trialkylphosphine</td>
<td>R₃P</td>
<td>PO₃⁻⁻¹</td>
<td>P</td>
<td>1</td>
</tr>
<tr>
<td>Trimethylphosphine</td>
<td>(CH₃)₃P</td>
<td>PMe₃⁻⁻¹</td>
<td>P</td>
<td>1</td>
</tr>
<tr>
<td>Triphenylphosphine</td>
<td>(C₆H₅)₃P</td>
<td>PPh₃⁻⁻¹</td>
<td>P</td>
<td>1</td>
</tr>
</tbody>
</table>
### Table 7.2
Prefixes used for naming complexes

<table>
<thead>
<tr>
<th>Prefix</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>mono-</td>
<td>1</td>
</tr>
<tr>
<td>di-, bis-</td>
<td>2</td>
</tr>
<tr>
<td>tri-, tris-</td>
<td>3</td>
</tr>
<tr>
<td>tetra-, tetrakis-</td>
<td>4</td>
</tr>
<tr>
<td>penta-</td>
<td>5</td>
</tr>
<tr>
<td>hexa-</td>
<td>6</td>
</tr>
<tr>
<td>hepta-</td>
<td>7</td>
</tr>
<tr>
<td>octa-</td>
<td>8</td>
</tr>
<tr>
<td>nona-</td>
<td>9</td>
</tr>
<tr>
<td>deca-</td>
<td>10</td>
</tr>
<tr>
<td>undeca-</td>
<td>11</td>
</tr>
<tr>
<td>dodeca-</td>
<td>12</td>
</tr>
</tbody>
</table>
Naming transition metal complexes:
1) Cations first, anions second.
2) Within the coordination complex:
   anion ligands first, neutral ligands second, metals last
   give oxidation state of metal in parentheses
   if anionic complex, add “ate” to metal name
   if cationic complex, the metal, followed by ox. state, then the ligands
   and then counter anions. No need to give number of counter anions

Table 3.2 Examples of the nomenclature of simple coordination compounds. Some
of these examples contain, and adequately define, points not explicitly covered in the
text

<table>
<thead>
<tr>
<th>Compound</th>
<th>Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂[ReF₈]</td>
<td>potassium octafluororhenate (note: only ‘potassium’)</td>
</tr>
<tr>
<td>[Cu(NH₃)₄]SO₄</td>
<td>tetraamminecobalt(II) sulfate (note: ‘aa’ and ‘mm’)</td>
</tr>
<tr>
<td>[CuCl₂(py)₂]</td>
<td>dichlorobispyridinecopper(II) (note: bipyridine is the present name for the</td>
</tr>
<tr>
<td></td>
<td>2,2'-bipyridine ligand—see Table 2.3. More strictly, and as in the text,</td>
</tr>
<tr>
<td></td>
<td>di(pyridine) should be used to give dichlorodi(pyridine)copper(II). How-</td>
</tr>
<tr>
<td></td>
<td>ever, in the spoken language an ambiguity can arise)</td>
</tr>
<tr>
<td>[Hg(C₂H₆)₂]</td>
<td>diethymercury(II)</td>
</tr>
<tr>
<td>[Ni(PP₃)₄]</td>
<td>tetra(triphenylphosphate)nickel(0)</td>
</tr>
<tr>
<td>[Ru(NH₃)₅(N₂)]²⁺</td>
<td>pentaamminedinitrogen ruthenium(II) (note: similarly, O₂ is dioxygen, but</td>
</tr>
<tr>
<td></td>
<td>beware confusion with O₂⁻, superoxo and O₂²⁻, peroxy)</td>
</tr>
<tr>
<td>K₂[FeCl₄]</td>
<td>potassium tetrachloroferrate(II)</td>
</tr>
<tr>
<td>(NH₄)₂[SnCl₆]</td>
<td>ammonium hexachlorostannate(IV)</td>
</tr>
</tbody>
</table>
**Isomerism**

All isomers of a molecule:
- Atom connectivity: same or different

- **Stereoisomers**
  - Molecules with the same empirical formula and atom-to-atom bonding sequence (connectivity) but differing atomic spatial arrangements

- **Constitutional isomers**
  - Ionization, solvate, coordination, linkage

- **Enantiomers**
  - Non-superimposable mirror images
  - Lack $S_n$ axis (no $i$ or $\sigma$)
  - Chiral

- **Diastereomers**
  - Stereoisomers that are not enantiomers
  - Achiral

Examples:
- $[\text{Cr(OH}_2)_5\text{NCS}]^{2+}$
- $[\text{Cr(OH}_2)_5\text{SCN}]^{2+}$
- Linkage isomers
Isomers

Constitutional (structural) isomers

Stereoisomers (spatial isomers)

Diastereomers

Enantiomers

cis/trans isomers

Conformers

Rotamers
Structural isomers: diastereomers

66 [Mn(acac)₃] enantiomers

67 cis-[CoCl₂(en)₂]⁺ enantiomers

2 diastereomers
\[ \text{[Co(NH}_3\text{)}_4\text{Cl}_2]\text{]}^+ \]

\[ \begin{align*}
\text{cis } & \quad \text{Cl} \\
& \quad \text{H}_3\text{N} \quad \text{Co} \quad \text{N} \\
& \quad \text{H}_3\text{N} \quad \text{NH}_3 \\
\text{2 diastereomers} & \quad \text{cis } \text{C}_2\text{v} \\
\text{trans } & \quad \text{Cl} \\
& \quad \text{H}_3\text{N} \quad \text{Co} \quad \text{NH}_3 \\
& \quad \text{H}_3\text{N} \quad \text{NH}_3
\end{align*} \]

\[ \text{[Co(tetren)Cl]}^{2+} \]

\[ \begin{align*}
\text{Cl} & \quad \text{Co} \quad \text{N} \\
& \quad \text{N} \quad \text{N} \\
\text{H}_2\text{N} & \quad \text{H} \quad \text{N} \\
& \quad \text{N} \quad \text{H} \quad \text{H} \\
& \quad \text{N} \quad \text{H} \quad \text{NH}_2
\end{align*} \]

each isomer is chiral
Isomers because of the Ligand:

Linkage isomers or Ambi-dentate ligands

Isomers because of the Ligand:

Chirality within the ligand
So, How do we measure stability?

Formation Constant:

$$\Delta G^0 = -RT \ln K_{eq}$$

$$\Delta G^0 = \Delta H^0 - T \Delta S$$
Irving-Williams Stability Order

For the reactions $M + nL \rightleftharpoons ML_n$, the following order of stability constants holds under the indicated conditions (very few exceptions).

$$K_M: \quad Mn < Fe < Co < Ni < Cu > Zn$$

conditions: $M$ has same charge and is high-spin
does not include Cu(II) binding of axial ligands

$$[M(OH_2)_6]^{2+} + H_2N\text{--NH}_2 \rightleftharpoons [M(en)(OH_2)_4]^{2+} + 2H_2O \quad K = 10^{+xx}$$

<table>
<thead>
<tr>
<th>quantity</th>
<th>$Mn^{2+}$</th>
<th>$Fe^{2+}$</th>
<th>$Co^{2+}$</th>
<th>$Ni^{2+}$</th>
<th>$Cu^{2+}$</th>
<th>$Zn^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log K_1$ (M$^{-1}$)</td>
<td>2.79</td>
<td>4.33</td>
<td>5.94</td>
<td>7.70</td>
<td>10.7</td>
<td>5.78</td>
</tr>
<tr>
<td>$-\Delta G_{298}$ (kcal/mol)</td>
<td>3.80</td>
<td>5.90</td>
<td>8.10</td>
<td>10.5</td>
<td>14.6</td>
<td>7.89</td>
</tr>
<tr>
<td>$-\Delta H$ (kcal/mol)$^*$</td>
<td>2.80</td>
<td>5.09</td>
<td>6.88</td>
<td>8.89</td>
<td>13.0</td>
<td>6.69</td>
</tr>
<tr>
<td>$T\Delta S_{298}$ (kcal/mol)</td>
<td>1.0</td>
<td>0.81</td>
<td>1.2</td>
<td>1.6</td>
<td>1.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

$^*$determined calorimetrically
Reaction is favored enthalpically and entropically, but with $|\Delta H| >> T\Delta S$

Similar results for $K_2$ reaction.
- number of chelate rings

Stability increases because enthalpy becomes increasingly negative (increased number of M–N bonds) and entropy increases (more water molecules released).
1,4,7-triazacyclononane (tacn)  
3 rings/ligand

tacn forms relatively stable complexes with $M^{2+,3+}$

$$[M(OH_2)_6]^{2+} + tacn \rightleftharpoons [M(tacn)(OH_2)_3]^{2+} + 3H_2O$$

$\log K_1$

Ni(II) 16.24  
Cu(II) 17.5  
Zn(II) 11.6

favorable $\Delta H$, $\Delta S$;  
difficult to break M–N bonds because of semi-rigid ligand structure
The Chelate Effect

- **Chelate effect**

  compare stability constants (298 K):

  \[
  \begin{align*}
  &\left[\text{Ni(OH}_2\text{)}_6\right]^{2+} + 2\text{NH}_3 \iff \left[\text{Ni(NH}_3\text{)}_2(\text{OH}_2\text{)}_4\right]^{2+} + 2\text{H}_2\text{O} \quad \log \beta, K = 5.04 \\
  &\left[\text{Ni(OH}_2\text{)}_6\right]^{2+} + \text{en} \iff \left[\text{Ni(en)(OH}_2\text{)}_4\right]^{2+} + 2\text{H}_2\text{O} \quad \log \beta, K = 7.45 \\
  &\left[\text{Ni(NH}_3\text{)}_2(\text{OH}_2\text{)}_4\right]^{2+} + 2\text{NH}_3 \iff \left[\text{Ni(NH}_3\text{)}_4(\text{OH}_2\text{)}_2\right]^{2+} + 2\text{H}_2\text{O} \quad \log \beta, K = 0.78 \\
  &\left[\text{Ni(NH}_3\text{)}_2(\text{OH}_2\text{)}_4\right]^{2+} + \text{en} \iff \left[\text{Ni(en)}_2(\text{OH}_2\text{)}_4\right]^{2+} + 2\text{NH}_3 \quad \log \beta, K = 2.41 \\
  &\left[\text{Ni(NH}_3\text{)}_6\right]^{2+} + 3\text{ en} \iff \left[\text{Ni(en)}_3\right]^{2+} + 6\text{NH}_3 \quad \log \beta, K = 9.67
  \end{align*}
  \]

  \[\Delta H = -2.89 \text{ kcal/mol} \quad \text{small favorable contribution}\]

  \[\Delta H_{SE} = -2.75 \text{ kcal/mol}\]

  \[T \Delta S = 13.2 \text{ kcal/mol}\]

  entropy increase (4\(\rightarrow\)7 particles) dominates reaction

  (even though \(\text{NH}_3\) more strongly solvated than en)
The Chelate Effect

\[
[Cu(NH_3)_2(OH_2)_4]^{2+} + \text{en} \rightleftharpoons [Cu(NH_3)_2(\text{en})(OH_2)_2]^{2+} + 2\text{H}_2\text{O}
\]

\[\Delta G = -3.70 \text{ kcal/mol} \quad \Delta H = -1.91 \text{ kcal/mol} \quad T\Delta S = 1.79 \text{ kcal/mol}\]

\[\text{favorable \hspace{1cm} } 2\rightarrow 3 \text{ particles}\]

\[M + 2L \rightarrow ML_2\]

\[\text{repulsion} \]

\[M + L \rightleftharpoons L \rightarrow M(L \rightleftharpoons L)\]

\[\text{repulsion "built in"}\]

Once the first M–L bond is formed, there is a high probability the second bond will form because of the proximity of the other L atom. Corresponding probability is much lower with two unidentate ligands.
Now, How about those colors and the magnetism?

Where are the electrons? Show me the electrons!!

**Color:** Electronic transitions due to energy levels whose gaps are in the visible range of the electromagnetic spectrum.

**Magnetism:** partially filled orbitals, unpaired electrons.
- high spin: maximum no. of d electrons unpaired
- low spin: electrons paired up in d orbitals. WHY??

**Bonding models:** Valence bond (coordinate covalent bond needs empty orbitals on metal)
- Molecular Orbital Theory (all orbitals defined)
- Crystal Field Theory (originally from ionic crystals; influence of ligand lone pair repulsion on d-orbitals)
Penetrates Earth's Atmosphere?

<table>
<thead>
<tr>
<th>Radiation Type</th>
<th>Wavelength (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radio</td>
<td>$10^1$</td>
</tr>
<tr>
<td>Microwave</td>
<td>$10^{-2}$</td>
</tr>
<tr>
<td>Infrared</td>
<td>$10^{-5}$</td>
</tr>
<tr>
<td>Visible</td>
<td>$0.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Ultraviolet</td>
<td>$10^{-6}$</td>
</tr>
<tr>
<td>X-ray</td>
<td>$10^{-7}$</td>
</tr>
<tr>
<td>Gamma ray</td>
<td>$10^{-12}$</td>
</tr>
</tbody>
</table>

Approximate Scale of Wavelength:
- Buildings
- Humans
- Butterflies
- Needle Point
- Protozoans
- Molecules
- Atoms
- Atomic Nuclei

Frequency (Hz):
- $10^4$
- $10^8$
- $10^{12}$
- $10^{15}$
- $10^{16}$
- $10^{18}$
- $10^{20}$

Temperature of objects at which this radiation is the most intense wavelength omitted:
- 1 K (~-272 °C)
- 100 K (~-173 °C)
- 10,000 K (9,727 °C)
- 10,000,000 K (~10,000,000 °C)

Transmittance:
\[
\text{Transmittance} = \frac{P}{P_0} = \frac{\text{intensity of transmitted light}}{\text{intensity of incident light}}
\]
To explain magnetism and colors, need electronic configuration of the Transition Metal Complex

prime example

\[
\begin{align*}
&2t_{1u} (\sigma^*) \\
&2a_{1g} (\sigma^*) \\
&z^2, x^2-y^2 \\
&2e_g (\sigma^*) \\
&\text{antibonding, mainly } M \text{ in character} \\
&(n+1)p \\
&t_{1u} \\
&(n+1)s \\
&a_{1g} \\
&\text{octahedral } d\text{-orbital splitting parameter} \\
&\text{nonbonding, pure } M \\
&\text{frontier orbitals} \\
&\Delta_0 \\
&1t_{2g} \\
&\text{bonding, mainly } L_6 \text{ in character} \\
&1t_{1u} (\sigma) \\
&1e_g (\sigma) \\
&1a_{1g} (\sigma) \\
&M \\
&ML_6 \\
&L_6 \\
&\Phi_1 - \Phi_6 \\
&a_{1g} + e_g + t_{1u} \\
&\text{prime example} \\
&\text{NH}_3
\end{align*}
\]
Case 1. Lπ orbitals filled and more stable than dπ orbitals (L is a π-donor)

Δ_0 decreased relative to σ-bonding only

frontier orbitals mainly M d in character

prime example
Case 2. Lπ orbitals vacant and less stable than dπ orbitals (L is a π-acceptor)

\[ \Delta_0 \text{ increased relative to } \sigma\text{-bonding only} \]
Important Cases of d-Orbital Splittings in Octahedral Complexes

Case 1. Lπ orbitals filled and more stable than dπ orbitals. L are π-donors.

- mainly M orbitals
- mainly L orbitals

weak field high-spin complexes

σ-bonding only

Case 2. Lπ orbitals vacant and less stable than dπ orbitals. L are π-acceptors.

- 2t_{2g}(π^*)
- Δ_0''
- 1t_{2g}(π)
- Lπ

L_{π-donor} = F, Cl, Br, I, H_2O, OH, RS^-, S^2-, NCS^-, NCO^-

(virtually any ligand which, after forming M-L σ-bonds, has lone pairs)

L_{π-acceptor} = CO, NO, CN^-, N_2, bipy, phen, RNC, C_5H_5^-

(virtually any ligand with vacant π^* MO's)

L_π = NR_3, PR_3

Δ_0' < Δ_0 < Δ_0''
CFT-Assumptions

- The interactions between the metal ion and the ligands are purely electrostatic (ionic).
- The ligands are regarded as point charges.
- If the ligand is negatively charged: ion-ion interaction. If the ligand is neutral: ion-dipole interaction.
- The electrons on the metal are under repulsive from those on the ligands.
- The electrons on metal occupy those d-orbitals farthest away from the direction of approach of ligands.
Symmetric Field

- The 5d orbitals in an isolated gaseous metal are degenerate.
- If a spherically symmetric field of negative charges is placed around the metal, these orbitals remain degenerate, but all of them are raised in energy as a result of the repulsion between the negative charges on the ligands and in the d orbitals.
Octahedral Field

• If rather than a spherical field, discrete point charges (ligands) are allowed to interact with the metal, the degeneracy of the d orbitals is removed (or, better said, lifted). The splitting of d orbital energies and its consequences are at the heart of crystal field theory.

• Not all d orbitals will interact to the same extent with the six point charges located on the +x, -x, +y, -y, +z and -z axes respectively.

• The orbitals which lie along these axes (i.e. $x^2-y^2$, $z^2$) will be destabilized more than the orbitals which lie in-between the axes (i.e. $xy$, $xz$, $yz$).
For the Oh point group, the $x^2-y^2$, $z^2$ orbitals belong to the $E_g$ irreducible representation and $xy$, $xz$, $yz$ belong to the $T_{2g}$ representation.

The extent to which these two sets of orbitals are split is denoted by $\Delta_0$ or alternatively $10Dq$. As the baricenter must be conserved on going from a spherical field to an octahedral field, the $t_{2g}$ set must be stabilized as much as the $e_g$ set is destabilized.
Illustration of CFSE

$[\text{Ti(H}_2\text{O})_6]^{3+}$: a d⁰ complex and the e⁻ occupies the lowest energy orbital, i.e. one of the three degenerate t₂g orbitals. The purple colour is a result of the absorption of light which results in the promotion of this t₂g electron into the e₉ level. $t_{2g}^1e_9^0 \rightarrow t_{2g}^0e_9^1$

The UV-Vis absorption spectrum reveals that this transition occurs with a maximum at 20300 cm⁻¹ which corresponds to $\Delta_0$ 243 kJ/mol.

$(1000 \text{ cm}^{-1} = 11.96 \text{ kJ/mol or} 2.86 \text{ kcal/mol or} 0.124 \text{ eV})$

Typical $\Delta_0$ values are of the same order of magnitude as the energy of a chemical bond.
• What happens for more than 1 electron in d orbitals?
• The electron-electron interactions must be taken into account.

• For d^{1-3} systems: Hund's rule predicts that the electrons will not pair and occupy the t_{2g} set.

• For d^{4-7} systems (there are two possibilities): Either put the electrons in the t_{2g} set and therefore pair the electrons (low spin case or strong field situation). Or put the electrons in the e_{g} set, which lies higher in energy, but the electrons do not pair (high spin case or weak field situation).

• Therefore, there are two important parameters to consider: The Pairing energy (P), and the e_{g} - t_{2g} Splitting (referred to as \Delta_0, 10Dq or CFSE)

• For both the high spin (h.s.) and low spin (l.s.) situations, it is possible to compute the CFSE.
For an octahedral complex, CFSE

\[ \Delta_o = -0.4 \times n(t_{2g}) + 0.6 \times n(e_g) \Delta_o \]

Where, \( n(t_{2g}) \) and \( n(e_g) \) are the no. of electrons occupying the respective levels.

If CFSE is very large, pairing occurs (i.e. CFSE > P)
If CFSE is rather small, no pairing occurs (i.e. P > CFSE)

\( d^5 \) system

Case I results in LS complex  Case II results in HS complex
\[ \Delta_0 \text{ is dependent on:} \]

- Nature of the ligands
- The charge on the metal ion
- Whether the metal is a 3d, 4d, or 5d element

Ligands which cause a small splitting are *Weak field ligands* (CFSE in the range 7000 - 30000 cm\(^{-1}\)) and those cause a large splitting are *Strong field ligands* (CFSE typically > 30000 cm\(^{-1}\))

**Spectrochemical Series**

\[ I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^- , F^- < \text{urea}, OH^- < \text{ox}, O^{2-} <\ ]H_2O < NCS^- < \text{py}, \text{NH}_3 < \text{en} < \text{bpy}, \text{phen} < \text{NO}_2^- < \text{CH}_3^- , C_6H_5^- < \text{CN}^- < \text{CO}. \]
<table>
<thead>
<tr>
<th>Complex</th>
<th>Energy</th>
<th>Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{CrCl}_6]^{3-}$</td>
<td>13640 cm$^{-1}$</td>
<td>163 kJ/mol</td>
</tr>
<tr>
<td>$[\text{Cr(H}_2\text{O})_6]^{3+}$</td>
<td>17830</td>
<td>213</td>
</tr>
<tr>
<td>$[\text{Cr(NH}_3)_6]^{3+}$</td>
<td>21680</td>
<td>314</td>
</tr>
<tr>
<td>$[\text{Cr(CN)}_6]^{3-}$</td>
<td>26280</td>
<td>314</td>
</tr>
<tr>
<td>$[\text{Co(NH}_3)_6]^{3+}$</td>
<td>24800 cm$^{-1}$</td>
<td>163 kJ/mol</td>
</tr>
<tr>
<td>$[\text{Rh(NH}_3)_6]^{3+}$</td>
<td>34000</td>
<td>213</td>
</tr>
<tr>
<td>$[\text{Ir(NH}_3)_6]^{3+}$</td>
<td>41000</td>
<td>314</td>
</tr>
</tbody>
</table>
Tetrahedral Field - Considerations

Imagine a tetrahedral molecule inside a cube with metal ions in the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.

The two ‘e’ orbitals point to the center of the face of the cube while the three ‘t₂’ orbitals point to the center of the edges of the cube.

Therefore, the angle between the e-orbitals, metal and ligand is one-half of the tetrahedral angle, i.e. $109^\circ 28' / 2 = 54^\circ 44'$. But the angle between the t₂-orbitals, metal and ligand is one-third of the tetrahedral angle, i.e. $109^\circ 28' / 3 = 35^\circ 16'$.

Thus the t₂ orbitals are nearer to the direction of approach of the ligands than the e orbitals.

Hence, t₂ orbitals have higher energy compared to e-orbitals.
Tetrahedral Field

Δₜ < Δ₀
\[ \Delta_t = \frac{4}{9} \Delta_o \]

There are only 4 ligands in the tetrahedral complex, and hence the ligand field is roughly 2/3 of the octahedral field.

The direction of ligand approach in tetrahedral complex does not coincide with the d-orbitals. This reduces the field by a factor of 2/3. Therefore \( \Delta_t \) is roughly \( \frac{2}{3} \times \frac{2}{3} = \frac{4}{9} \) of \( \Delta_o \).

As a result, all tetrahedral complexes are high-spin since the CFSE is normally smaller than the paring energy.

Hence low spin configurations are rarely observed. Usually, if a very strong field ligand is present, the square planar geometry will be favored.
Special case of $d^8$ Octahedral

Examples:
Ni$^{2+}$, Pd$^{2+}$, Pt$^{2+}$, Cu$^{3+}$, Ag$^{3+}$, Au$^{3+}$

Square-planar complex is formed; attempts to form octahedral complexes become impossible
Special case II
Jahn-Teller Distortion

If both the \( e_g \) orbitals are symmetrically filled - all ligands are repelled equally. **Result:** regular octahedron

If **asymmetrically** filled - some ligands are repelled more than the other. **Result:** Distorted octahedron

Consider \( e_g \) configuration: \((d_{z^2})^1 \; d_{x^2-y^2})^2\)

Ligands along \( x, -x, y, -y \) will be repelled more and bonds elongated. i.e. the octahedron will be compressed along the \( z \) axis.

Consider \( e_g \) configuration: \((d_{z^2})^2 \; d_{x^2-y^2})^1\)

Ligands along \( z, -z \) will be repelled more and bonds elongated. i.e. the octahedron will be elongated along the \( z \) axis.
The Jahn-Teller Theorem was published in 1937 and states:

"any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy"

The $e_g$ point along bond axes. The effect of JT distortions is best documented for Cu(II) complexes (with 3e in $e_g$) where the result is that most complexes are found to have elongation along the z-axis.
Some examples of Jahn-Teller distorted complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bond Distances</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuBr$_2$</td>
<td>4 Br at 240pm 2 Br at 318pm</td>
</tr>
<tr>
<td>CuCl$_2$.2H$_2$O</td>
<td>2 O at 193pm 2 Cl at 228pm 2 Cl at 295pm</td>
</tr>
<tr>
<td>CsCuCl$_3$</td>
<td>4 Cl at 230pm 2 Cl at 265pm</td>
</tr>
<tr>
<td>CuF$_2$</td>
<td>4 F at 193pm 2 F at 227pm</td>
</tr>
<tr>
<td>CuSO$_4$.4NH$_3$.H$_2$O</td>
<td>4 N at 205pm 1 O at 259pm 1 O at 337pm</td>
</tr>
<tr>
<td>K$_2$CuF$_4$</td>
<td>4 F at 191pm 2 F at 237pm</td>
</tr>
<tr>
<td>CrF$_2$</td>
<td>4 F at 200pm 2 F at 243pm</td>
</tr>
<tr>
<td>KCrF$_3$</td>
<td>4 F at 214pm 2 F at 200pm</td>
</tr>
<tr>
<td>MnF$_3$</td>
<td>2 F at 209pm 2 F at 191pm 2 F at 179pm</td>
</tr>
</tbody>
</table>
**Figure 2** Crystal field splittings of d orbitals