CHAPTER 10

Coordination Chemistry II: Bonding
10-2 Theories of electronic structure

10-2-1 Terminology

(I) Valence bond theory: This method describes bonding using *hybrid orbitals & electron pairs*, as an extension of the *electron-dot & hybrid orbital methods (Lewis structures)* used for simple molecules.
(II) Crystal field theory: This is an electrostatic approach, used to describe the split in metal d-orbital energies. It provides an approximate description of the electronic energy levels that determine the UV-Vis spectra, but does not describe the bonding.
(III) Ligand field theory: This is a more complete description of bonding *in terms of the electronic energy levels of the frontier orbitals*. It used some of the terminology of crystal field theory *but includes the bonding orbitals*.
(IV) Angular overlap theory: This is a method of estimating the relative magnitudes of the orbital energies in a molecular orbital calculation.

*It explicitly takes into account the bonding energy as well as the relative orientation of the frontier orbitals.*
10-2-2 Historical background

valence bond theory

The valence bond theory, originally proposed by Pauling in the 1930s, used the hybridization ideas. For octahedral complexes, $d^2sp^3$ hybrids of the metal orbitals are required. However, the $d$ orbitals used by the first-row transition metals could be either 3d or 4d.
FIGURE 10-2 Inner and Outer Orbital Complexes. In each case, ligand electrons fill the $d^2sp^3$ bonding orbitals. The remaining orbitals contain the electrons from the metal.
The **valence bond theory** was of great importance in the development of bonding theory for coordination compounds. Although it provides a set of orbitals for bonding, *the use of the high energy 4d orbitals seems unlikely*, & the results *do not lend themselves to a good explanation of the electronic spectra of complexes.*
Crystal field theory: the split in metal d-orbital energies by the electrostatic field.

\( d_{x^2-y^2}, d_{z^2} \): increase in energy
\( d_{xy}, d_{xz}, d_{yz} \): slight increase in energy

\[ \Delta_o (10Dq) \]
When the d orbitals of a metal ion are placed in an octahedral field of ligand electron pairs, any electrons in them are repelled by the field.  

As a result, the $d_{x^2-y^2}$ & $d_{z^2}$ orbitals, which are directed at the surrounding ligands, are raised in energy. The $d_{xy}$, $d_{xz}$, & $d_{yz}$ orbitals, which are directed between the surrounding ions, are relatively unaffected by the field.
This approach provides a simple means of identifying the d-orbital splitting found in coordination complexes & can be extended to include more quantitative calculations.

\textit{It requires extension to the more complete ligand field theory to include \( \pi \) bonding & more accurate calculations of the resulting energy levels.}
The chief drawbacks to the crystal field approach are in its concept of the repulsion of orbitals by the ligands & its lack of any explanation for bonding in coordination complexes.

The purely electrostatic approach does not allow for the lower (bonding) molecular orbitals & thus fails to provide a complete picture of the electronic structure.
10-3 Ligand field theory

The electrostatic crystal field theory & the molecular orbital theory were combined into a more complete theory called ligand field theory, described qualitatively by Griffith & Orgel.
10-3-1 Molecular orbitals for octahedral complexes

\( d_{x^2-y^2}, d_{z^2} \): bonding orbitals
\( d_{xy}, d_{xz}, d_{yz} \): nonbonding orbitals
The six *ligand donor orbitals* collectively form a reducible representation $\Gamma$ in the point group $O_h$.

$$\Gamma = A_{1g} + T_{1u} + E_g$$

### Table 10.4

**Character table for $O_h$**

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<th>i</th>
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$\Gamma = A_{1g} + T_{1u} + E_g$

- $x^2 + y^2 + z^2$
- $(2z^2 - x^2 - y^2, x^2 - y^2)$
- $(x, y, z)$

**Notes:**
- $x, y, z$
- $(2z^2 - x^2 - y^2, r^2 - y^2)$
The six ligand $\sigma_{\text{donor}}$ orbitals (p orbitals or hybrid orbitals with the same symmetry) match the symmetries of the 4s, 4p$_x$, 4p$_y$, 4p$_z$, 3d$_{z^2}$ & 3d$_{x^2-y^2}$ metal orbitals.

The combination of the ligand & metal orbitals form six bonding & six antibonding orbitals with a$_{1g}$, e$_g$ & t$_{1u}$ symmetries. The six bonding orbitals are filled by electrons donated by the ligands.
The metal $T_{2g}$ orbitals ($d_{xy}$, $d_{xz}$ & $d_{yz}$) do not have appropriate symmetry to interact with the ligands & are nonbonding. Any electrons of the metal occupy these orbitals & the higher energy anti-bonding orbitals.
Frontier orbitals

From σ donor ligands (all π interactions are ignored)
Most of the discussion of octahedral ligand fields is concentrated on the $t_{2g}$ & higher orbitals ($e_g$). Electrons in bonding orbitals provide the potential energy that **holds molecules together**, & electrons in the higher levels affected by ligand field effects help determine **the details of the structure, magnetic properties, & electronic spectrum**.
10-3-2 Orbital splitting & electron spin

In octahedral complexes, electrons from the ligands fill all six bonding MOs, & any electrons from the metal ion occupy the nonbonding \((t_{2g})\) & antibonding \((e_g)\) orbitals.

The splitting between these two sets of orbitals \((t_{2g} \text{ & } e_g)\) is called \(\Delta_o\) (10 Dq, o for octahedral).
*Strong-field ligands*: ligands whose orbitals interact strongly with the metal orbitals (large $\Delta_o$).

*Weak-field ligands*: ligands with small interactions (small $\Delta_o$).

* $d^0$-$d^3$, $d^8$-$d^{10}$: only one electron configuration

* $d^{4-7}$: high-spin & low-spin states
# Table 10-5: Spin States and Ligand Field Strength

**Complex with Weak Field Ligands (High Spin)**

<table>
<thead>
<tr>
<th>$\Delta_0$</th>
<th>$d^1$</th>
<th>$d^2$</th>
<th>$d^3$</th>
<th>$d^4$</th>
<th>$d^5$</th>
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<td></td>
<td>↑_↑</td>
<td>↑_↑</td>
<td>↑_↑</td>
<td>↑_↑</td>
<td></td>
</tr>
<tr>
<td></td>
<td>↑<em>↓</em>↑</td>
<td></td>
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<td></td>
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<tr>
<td>$d^6$</td>
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<table>
<thead>
<tr>
<th>$\Delta_0$</th>
<th>$d^7$</th>
<th>$d^8$</th>
<th>$d^9$</th>
<th>$d^{10}$</th>
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<tbody>
<tr>
<td></td>
<td>↑_↑</td>
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<td>↑<em>↓</em>↑</td>
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<td></td>
<td></td>
<td></td>
<td>↑<em>↓</em>↑</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>↑<em>↓</em>↑</td>
</tr>
</tbody>
</table>

(continued...)
Strong ligand field = large $\Delta_o = low spin$
Weak ligand field = small $\Delta_o = high spin$

Electron configurations depend on $\Pi_c$, $\Pi_e$, & $\Delta_o$.
$\Delta_o : \Pi (\Pi_c + \Pi_e)$
Example: determine the exchange energies for high-spin & low-spin d⁶ ions in an octahedral complex.
### TABLE 10-6
Orbital Splitting ($\Delta_o$) and Mean Pairing Energy ($\Pi$) for Aqueous Ions$^a$

<table>
<thead>
<tr>
<th>Ion</th>
<th>$\Delta_o$</th>
<th>$\Pi$</th>
<th>Ion</th>
<th>$\Delta_o$</th>
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<td></td>
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<td>V$^{3+}$</td>
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<td>Cr$^{3+}$</td>
<td>17,400</td>
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<td>Mn$^{3+}$</td>
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<td>Fe$^{3+}$</td>
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<td>30,000</td>
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<td>Co$^{3+}$</td>
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<td>Ni$^{3+}$</td>
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<td>27,000</td>
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<td>Cu$^{2+}$</td>
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<td>Zn$^{2+}$</td>
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</table>


**Note:** $^a$ Values given are in cm$^{-1}$.

$^b$ Estimated value.
From Table 10-6

1. $\Delta_o$ for 3+ ions is larger than $\Delta_o$ for 2+ ions with the same number of electrons.

2. Most of the first-row transition metals require a stronger field ligand to give low-spin complexes.


*** $\Delta_o > \Pi : \text{low-spin}; \Delta_o < \Pi : \text{high-spin}$
Why 2\textsuperscript{nd}, 3\textsuperscript{rd} transition series favor low-spin?

(1) The greater overlap between the larger 4d & 5d orbitals & the ligand orbitals. (\textbf{major})

(2) A decreased pairing energy due to the larger volume available for electrons in the 4d & 5d orbitals compared with 3d orbitals. (\textbf{minor})
10-3-4 $\pi$ bonding

$\text{p}_y (M)$: for $\sigma$ bonding
$\text{p}_{x,z} (M)$: for $\pi$ bonding / $p$ or $\pi^*$ (L)

**FIGURE 10-8** Coordinate System for Octahedral $\pi$ Orbitals.

<table>
<thead>
<tr>
<th>$O_h$</th>
<th>$E$</th>
<th>$8C_3$</th>
<th>$6C_2$</th>
<th>$6C_4$</th>
<th>$3C_2(-C^2)$</th>
<th>$i$</th>
<th>$6S_4$</th>
<th>$8S_6$</th>
<th>$3\sigma_h$</th>
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<td>0</td>
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<td>$-4$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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</tbody>
</table>
\[
\Gamma_\pi = T_{1g} + T_{2g} + T_{1u} + T_{2u}
\]

\( T_{1g} & T_{2u} \) (L) : nonbonding
\( T_{2g} \) (L) : \( d_{xy}, d_{yz}, d_{xz} \) (M); available
\( T_{1u} \) (L) : \( p_x, p_y, p_z \) (M); not available (used for \( \sigma \) bonding.)
\[ \pi^* \]

**FIGURE 10-9** Cyanide Molecular Orbitals.
**FIGURE 10-10** Overlap of $d$, $\pi^*$, and $p$ Orbitals with Metal $d$ Orbitals. Overlap is good with ligand $d$ and $\pi^*$ orbitals, but poorer with ligand $p$ orbitals.
$\pi$-donor ligands

$\Delta_o$ decreases, favoring high-spin state

$\Delta_o$ increases, favoring low-spin state

$\pi$-acceptor ligands

\textbf{FIGURE 10-11} Effects of $\pi$ Bonding on $\Delta_o$ (using a $d^3$ ion as example).
From Figure 10-11(a): A larger $\Delta_0$ value & increased bonding strength ($\pi$ acceptor ligands: CN$^-$, CO...).

Significant energy stabilization can result from this added $\pi$ bonding. This *metal-to-ligand* (M $\rightarrow$ L) $\pi$ bonding is also called *$\pi$ back-bonding*, with electrons from d orbitals of the metal donated back to the ligands.
From Figure 10-11(b): A smaller $\Delta_0$ ($\pi$ donor ligands: $F^-$, $Cl^-$…).

The metal ion d electrons are pushed into the higher $t_{2g}^*$ orbital by the ligand electrons. This is described as **ligand-to-metal** ($L \rightarrow M$) $\pi$ bonding, **with the $\pi$ electrons from the ligands being donated to the metal ion.**
Summary:

Empty higher energy $\pi^*$ or d orbitals on the ligands result in $M \rightarrow L$ $\pi$ bonding & a larger $\Delta_o$ for the complex.

Filled $\pi$ or p orbitals on ligands (frequently with relatively low energy) result in $L \rightarrow M$ $\pi$ bonding & a smaller $\Delta_o$ for the complex.
Metal-to-ligand $\pi$ bonding usually gives increased stability & favors low-spin configuration.

Ligand-to-metal $p$ bonding usually gives decreased stability for the complex, favoring high-spin configuration.
Part of the *stabilizing effects* of π back-bonding is a result of transfer of negative charge away from the metal ion. The positive ion accepts electrons from the ligands to form the σ bonds. The metal is then left with a large negative charge. When the π orbitals can be used to transfer part of this charge back to the ligands, *the overall stability is improved.*
10-4-4 Types of ligands & the spectrochemical series

Ligands are frequently classified by their donor & acceptor capability. Some, like $\sigma$ donors only, with no orbitals of appropriate symmetry for $\pi$ bonding.

The ligand field split, $\Delta$, then depends on the relative energies of the metal ion and ligand orbitals & on the degree of overlap.
(1) en > NH$_3$ : proton basicity

(2) F$^-$ > Cl$^-$ > Br$^-$ > I$^-$

F$^-$, Cl$^-$ : hard base; Br$^-$ : borderline base; I$^-$ : soft base (proton basicity / electrostatic interaction)
Ligands that have occupied p orbitals are potentially \( \pi \) donors. They tend to donate these electrons to the metal along with the \( \sigma \)-bonding electrons \((this \ \pi\text{-donor interaction decreases } \Delta)\).
As a result, most halide complexes have high-spin configurations (OH\textsuperscript{-} below H\textsubscript{2}O in the series because it has more $\pi$-donating tendency).
(3) CO, CN⁻ > phen(anthroline) > NO₂⁻ > NCS⁻

π acceptors (when ligands have vacant π* or d orbitals, there is the possibility of π back bonding, & the ligands are π acceptors)
The covalent bonding character & electrostatic effect are also considered. The trend is also related to: **different metal ions, different charge on the metal ions, ligands with different substituents, & co-ligands present.**
For a given geometry & ligand set,

*Low $\Delta$ metals*: (1) first row metals; (2) low oxidation state

*High $\Delta$ metals*: (1) 2nd & 3rd row metals; (2) high oxidation state
The *spectrochemical series* of metal ions in order of increasing $\Delta$.

$\text{Mn}^{2+} < \text{V}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{Ni}^{2+} < \text{Fe}^{3+} < \text{Co}^{3+} < \text{Mn}^{4+} < \text{Rh}^{3+} < \text{Ru}^{3+} < \text{Pd}^{4+} < \text{Ir}^{3+} < \text{Pt}^{4+}$

$\leftarrow$ low $\Delta$                       high $\Delta$ $\rightarrow$

$\leftarrow$ low valent, 1st row                   high-valent, 3rd row $\rightarrow$

$\blacklozenge$ 3rd row metals tend to form stronger $\text{M}--\text{L}$ bonds & more thermally stable complexes and & more likely to give diamagnetic complexes.
<table>
<thead>
<tr>
<th>Configuration</th>
<th>Examples</th>
<th>Strong field</th>
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<th>Weak field</th>
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<td>$e_g$</td>
<td>Number of</td>
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<td>4</td>
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$a$ Dq is smaller for weak-field ligands.
Table 9.11  Ligand-field splitting for some octahedral complexes
(10 $Dq$ values in italics indicate low-spin complexes)*

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<th>6F$^-$</th>
<th>6H$_2$O</th>
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<th>3 en</th>
<th>6CN$^-$</th>
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</table>

*The values of 10 $Dq$ are in kilokaysers (1 kK = 1000 cm$^{-1}$); 10 kK, or 1000 nm, corresponds to 119.7 kJ/mol (28.6 kcal/mol); 20 kK, or 500 nm, corresponds to 239.4 kJ/mol (57.2 kcal/mol).
10-5 The Jahn-Teller effect

The Jahn-Teller theorem states that there cannot be unequal occupation of orbitals with identical energies. To avoid such unequal occupation, the molecule distorts so that these orbitals are no longer degenerate (Cu$^{2+} = d^9$).
FIGURE 10-26 Jahn-Teller Effect on a $d^9$ Complex. Elongation along the $z$ axis is coupled to a slight decrease in bond length for the other four bonding directions. Similar changes in energy result when the axial ligands have shorter bond distances. The resulting splits are larger for the $e_g$ orbitals than for the $t_{2g}$. The energy differences are exaggerated in this figure.
The resulting distortions are most often an elongation along one axis, but compression along one axis is also possible.
### $d^n$

<table>
<thead>
<tr>
<th>Number of electrons</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-spin Jahn-Teller</td>
<td>w</td>
<td>w</td>
<td>s</td>
<td>w</td>
<td>w</td>
<td>w</td>
<td>w</td>
<td>w</td>
<td>s</td>
<td>s</td>
</tr>
<tr>
<td>Low-spin Jahn-Teller</td>
<td>w</td>
<td>w</td>
<td>w</td>
<td>w</td>
<td>w</td>
<td>w</td>
<td>w</td>
<td>w</td>
<td>s</td>
<td>s</td>
</tr>
</tbody>
</table>

$w =$ weak Jahn-Teller effect expected ($t_{2g}$ orbitals unevenly occupied); $s =$ strong Jahn-Teller effect expected ($e_g$ orbitals unevenly occupied); No entry = no Jahn-Teller effect expected.
Low-spin Cr(II) (d⁴) : for an octahedral geometry, $O_h \rightarrow D_{4h}$. They show two absorption bands, one in the visible and one in the near-infrared region, caused by the following distortion.

$\text{Cr}^{\text{II}}(d^4)$
Cr(II) also forms dimeric complexes with Cr—Cr quadruple bonds and [Cr₂(OAc)₄] is nearly diamagnetic.
Cu$^{2+}$ forms the most common complexes with significant Jahn-Teller effects.

(1)

\[
\begin{align*}
[Cu(H_2O)_6]^{2+} + NH_3 & \leftrightharpoons [Cu(NH_3)(H_2O)_5]^{2+} + H_2O & K_1 = 2 \times 10^4 \\
[Cu(NH_3)(H_2O)_5]^{2+} + NH_3 & \leftrightharpoons [Cu(NH_3)_2(H_2O)_4]^{2+} + H_2O & K_2 = 4 \times 10^3 \\
[Cu(NH_3)_2(H_2O)_4]^{2+} + NH_3 & \leftrightharpoons [Cu(NH_3)_3(H_2O)_3]^{2+} + H_2O & K_3 = 1 \times 10^3 \\
[Cu(NH_3)_3(H_2O)_3]^{2+} + NH_3 & \leftrightharpoons [Cu(NH_3)_4(H_2O)_2]^{2+} + H_2O & K_4 = 2 \times 10^2 \\
[Cu(NH_3)_4(H_2O)_2]^{2+} + NH_3 & \leftrightharpoons [Cu(NH_3)_5(H_2O)]^{2+} + H_2O & K_5 = 3 \times 10^{-1} \\
[Cu(NH_3)_5(H_2O)]^{2+} + NH_3 & \leftrightharpoons [Cu(NH_3)_6]^{2+} + H_2O & K_6 = \text{very small}
\end{align*}
\]
(2) The formation constant for the addition of a third molecule of en to Cu$^{2+}$ is much lower than for Ni$^{2+}$.

$[\text{Cu(en)}_3]^2+$ v.s. $[\text{Ni(en)}_3]^2+$

Cu$^{2+}$: tetrahedral, square-planar, distorted TBP or SP, but not octahedral.
13-3-2 Why 18 electrons?

Main group chemistry: the Octet rule/$s^2p^6$
Organometallic chemistry: 18-electron rule/$s^2p^6d^{10}$

This cannot provide an explanation for why so many complexes violate the 18-electron rule.
\( \text{Cr(CO)}_6 \) (\( d^6 / 18 \text{ e} \))

**Lowering \( t_{2g} \) orbitals**

**Raising \( e_g \) orbitals**

\( \Delta_0 \)
Cr(CO)$_6$:

(1) The *strong σ-donor ability* of CO raises the $e_g$ orbitals in energy (more antibonding).

(2) The *strong π-acceptor ability* of CO lowers the $t_{2g}$ orbitals in energy (more bonding).
Ligands that are both *strong σ donors* & *π acceptors* should therefore be *the most effective at forcing adherence to the 18-electron rule.*
FIGURE 13-9 Exceptions to the 18-Electron Rule.
Exceptions:

1. \([\text{Zn(en)}_3]^{2+}\) (22-electron species): *en is a good \(\sigma\) donor, but not as strong as CO*. As a result, \(e_g\) is not so antibonding to cause significant stabilization of the complex, & thus 22-e species is stable.
2. **TiF$_6^{2-}$ (12-electron species):** F$^-$ is a $\pi$ donor as well as a $\sigma$ donor. The $\pi$-donor ability of F$^-$ (poor $\pi$ donor) destabilizes the $t_{2g}$ orbitals, making them slightly antibonding. The species TiF$_6^{2-}$ has 12 electrons in the bonding $\sigma$ orbitals and no electrons in the antibonding $t_{2g}$ or $e_g$ orbitals.
**18-Electron Rule** is a way to decide whether a given *d*-block transition metal organometallic complex is likely to be stable. The rule works best for **low-valent metals with high-field ligands** such as H⁻ and CO. The rule works least well for **high-valent metals with weak-field ligands**.
**Octet Rule** — For \( s \) and \( p \) valence shells main group compounds follow the 8-electron rule.

**The 32-Electron Rule** — A way to decide whether a given \( f \)-block transition metal organometallic complex is likely to be stable.
The most common exception is square-planar geometry, in which a 16-electron configuration may be the most stable, especially for complexes of d^8 metals.
16-Electron Complexes — An important class of complexes follow a 16-e, rather than an 18-e rule, because of one of the nine orbitals is very high-lying & is usually empty. These complexes normally adopt the square planar geometry.
### Table 2.3 The $d^8$ Metals that can adopt a 16e configuration

<table>
<thead>
<tr>
<th>Group</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(0)$^a$</td>
<td>Co(I)$^b$</td>
<td>Ni(II)</td>
<td>Cu(III)$^c$</td>
<td></td>
</tr>
<tr>
<td>Ru(0)$^a$</td>
<td>Rh(I)$^b$</td>
<td>Pd(II)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Os(0)$^a$</td>
<td>Ir(I)$^b$</td>
<td>Pt(II)</td>
<td>Au(III)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$These metals prefer 18e to 16e.

$^b$The 16e configuration is more often seen, but 18e complexes are common.

$^c$A rare oxidation state.
Splitting of the energy levels in an octahedral field elongated along the $z$ direction (tetragonal).
Energy levels for square-planar nickel(II) complexes such as $[\text{Ni(CN)}_4]^{2-}$. 

Ni$^{2+}$ $d^8$  Octahedral complex  Square planar
Figure 9.14  Ligand-field splitting for tetrahedral complexes. The orientation of the tetrahedron relative to the axes is shown.
$T_d$

$t_2$  

$d^3$

$d^4$

$d_{xy}$

$+ d_{xz}, d_{yz}$

$+ d_{x^2-y^2}$

$+ d_{z^2}$

Elongate along $z$

Compress along $z$
Figure 9.7  Metal–carbon double bonding.
<table>
<thead>
<tr>
<th>Coordination Number</th>
<th>Geometry</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
<td>$\text{Me}_3\text{SiCH}_2\text{H}_2\text{Mn}$</td>
</tr>
<tr>
<td>3</td>
<td>trigonal</td>
<td>$\text{Al(}	ext{mesityl)}_3$</td>
</tr>
<tr>
<td></td>
<td>T-shaped</td>
<td>$\text{Rh(PPh}_3)_3^+$</td>
</tr>
<tr>
<td>4</td>
<td>square planar</td>
<td>$\text{RhCl(CO)(PPh}_3)_2$</td>
</tr>
<tr>
<td></td>
<td>tetrahedral</td>
<td>$\text{Ni(CO)}_4$</td>
</tr>
</tbody>
</table>
5 trigonal bipyramidal

Fe(CO)$_5$

square pyramidal

Co(CNPh)$_3^{2+}$

6 octahedral

Mo(CO)$_6$
<table>
<thead>
<tr>
<th>Table 2.5 (continued)</th>
</tr>
</thead>
</table>

| 7 | capped octahedron | ReH(PR₃)₃(MeCN)₂⁺ |
|   | pentagonal bipyramid | IrH₅(PPh₃)₂ |
| 8 | dodecahedral* | MoH₄(PR₃)₄ |
|   | square antiprism | TaF₅⁻ |
| 9 | tricapped° trigonal prism | ReH₉⁻ |

*The smaller ligands tend to go to the less hindered A sites. Two A and two B sites each lie on a plane containing the metal. One such plane is shown dotted; the other lies at right angles to the first.
°The tricapped trigonal prism is shown as viewed along its threefold axis. The vertices of the triangles are the axial ligand positions. The equatorial M—L bonds are shown explicitly.
The Trans Effect —

- Certain ligands facilitate the departure of a second ligand \textit{trans} to the first, & their replacement by an external ligand. Ligands are more effective at this labilization are said to have higher \textit{trans effect}.
The effect is kinetic in origin (the change of properties of the transition state for the substitution reaction). The effect is most clearly marked in substitution of Pt(II).

\[ L : \text{neutral two-electron donor} \]
Highest trans effect ligands usually forming:

(1) strong σ bonds with metal, such as H\(^{-}\), Me\(^{-}\), SnCl\(_3\)^{-}…

(2) strong π bonds with metal, such as CO, C\(_2\)H\(_4\), (NH\(_2\))\(_2\)CS…
Trans Influence — The (same) ligands (also) weaken the trans M—L bond by a lengthening of the M—L distances (characterized by NMR or IR). This will cause the change in the ground state thermodynamic properties.
An important application of the trans effect is the synthesis of specific isomers of coordination compounds.

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \quad \text{Cl}^{2-} \\
\text{Cl} & \quad \text{Cl} \quad \text{Cl} \\
\text{NH}_3 \quad & \rightarrow \\
\text{Cl} & \quad \text{Cl} \quad \text{Cl} \\
\text{Cl} & \quad \text{NH}_3 \\
\text{NH}_3 \quad & \rightarrow \\
\text{Cl} & \quad \text{NH}_3 \\
\text{NH}_3 \quad & \rightarrow \\
\text{Cl} & \quad \text{NH}_3 \\
\end{align*}
\]

\[
\begin{align*}
\text{H}_3\text{N} & \quad \text{NH}_3 \quad \text{H}_3\text{N}^{2+} \\
\text{H}_3\text{N} & \quad \text{NH}_3 \quad \text{H}_3\text{N} \quad \text{Cl}^{+} \\
\text{H}_3\text{N} & \quad \text{NH}_3 \quad \text{H}_3\text{N} & \quad \text{Cl} \\
\text{H}_3\text{N} \quad & \rightarrow \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\text{H}_3\text{N} & \quad \text{NH}_3 \\
\end{align*}
\]

A trans-effect series for a typical Pt(II) system is given below.

\[\text{OH}^- < \text{NH}_3 < \text{Cl}^- < \text{Br}^- < \text{CN}^- < \text{CO, C}_2\text{H}_4, \text{CH}_3^- < \text{I}^- < \text{PR}_3 < \text{H}^-\]

← low trans effect  high trans effect →
Explanations of the *trans effect*

1. *σ-bonding effects* (ground-state effects)
   The Pt—X bond is influenced by the Pt—T bond, because both use the Pt $p_x$ & $d_{x^2-y^2}$ orbitals. When the Pt—T $σ$ bond is strong, it uses a large part of these orbitals & leave less for the Pt—X bond (weaker & higher in energy at its ground state; lower $E_a$).

![Diagram](image)
2. **π-bonding effects (transition-state effects)**

(i) When the T ligand forms a strong π-acceptor bond with Pt, charge is removed from Pt & the entrance of another ligand to form a 5-coordinate species is more likely.

(ii) The \( d_{x^2-y^2} \) orbital is involved in σ bonding in the square-planar geometry, & both the \( d_{xz} \) & \( d_{yz} \) orbitals can contribute to π bonding in the trigonal-bipyramidal transition state.
Two factors dominate the explanations of the trans effect, weakening of the Pt—X bond and stabilization of the presumed 5-coordinate transition state. The energy relationships are given in Figure 12-13, with the activation energy the difference between the reactant ground state and the first transition state.

**FIGURE 12-13** Activation Energy and the trans Effect. The depth of the energy curve for the intermediate and the relative heights of the two maxima will vary with the specific reaction. (a) Poor trans effect, low ground state, high transition state. (b) σ-Bonding effect, higher ground state (trans influence). (c) π-Bonding effect, lower transition state, (trans effect).

\[\sigma\text{-bonding effect} \quad \pi\text{-bonding effect}\]
**Diamagnetism** — spin-paired state (or zero unpaired electron) is very weakly repelled by the magnetic field.

**Paramagnetism** — with unpaired electron(s) is attracted into the magnetic field. The spins are lining up together under an external magnetic field but are not aligned in the crystal in the absence of the external field.
Ferromagnetism — The spins are aligned in the crystal even without an external magnetic field.

\[ \text{[Re(CO)}_3\text{(PCy}_3\text{)}_2] : \text{[(CO)}_5\text{Re—Re(CO)}_5\text{]} \]

(e ? Magnetism ?) (e ? Magnetism ?)
Figure 2.2  Common spin coupling behaviors.

Antiferromagnetic coupling of spins of $d$ electrons on Ni$^{2+}$ ions through $p$ electrons of oxide ions.
**Magnetic susceptibilities**

<table>
<thead>
<tr>
<th>Behaviour</th>
<th>Typical $\chi$ value</th>
<th>Change of $\chi$ with increasing temperature</th>
<th>Field dependence?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetism</td>
<td>$-1 \times 10^{-6}$</td>
<td>None</td>
<td>No</td>
</tr>
<tr>
<td>Paramagnetism</td>
<td>0 to $10^{-2}$</td>
<td>Decreases</td>
<td>No</td>
</tr>
<tr>
<td>Ferromagnetism</td>
<td>$10^{-2}$ to $10^{6}$</td>
<td>Decreases</td>
<td>Yes</td>
</tr>
<tr>
<td>Antiferromagnetism</td>
<td>0 to $10^{-2}$</td>
<td>Increases</td>
<td>(Yes)</td>
</tr>
</tbody>
</table>
Some d⁰ alkyls. No back donation to σ* orbital of C-H bond to break the C-H bond (resemble CO).
**Agostic interaction** can be detected by X-ray or neutron crystal structure work & by the high-field shift of the agostic H in the $^1$H NMR. The lowering of the $J(C,H)$ and $\nu(CH)$ in the NMR & IR, respectively, on binding is symptomatic of the reduced C-H bond order in the agostic system.
Taube has suggested a reaction half-life (the time of disappearance of half the initial compound) of one minute or less as the criterion for lability. Compounds that react more slowly are called inert or robust. An inert compound is not inert in the usual sense that no reaction can take place; it is simply slower to react. The kinetic terms must also be distinguished from the thermodynamic terms stable & unstable.
**Slow Reactions (Inert)**

- $d^3$, low-spin $d^4$, $d^5$, and $d^6$
- Strong-field $d^8$ (square planar)

**Intermediate**

- **Weak-field** $d^8$

**Fast Reactions (Labile)**

- $d^1$, $d^2$, high-spin $d^4$, $d^5$, and $d^6$
- $d^7$, $d^9$, $d^{10}$
FIGURE 12-2 Energy Profiles for Dissociative and Associative Reactions. (a) Dissociative mechanism. The intermediate has a lower coordination number than the starting material. (b) Associative mechanism. The intermediate has a higher coordination number than the reactant.
(a) Hydration isomerism – \([\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3 \text{ & } [\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2.\text{H}_2\text{O}\)

(b) Coordination isomerism— \([\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]\text{ ] and } [\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]\text{ ]
\[\text{Pt}(\text{NH}_3)_4][\text{PdCl}_4]\text{ ] and } [\text{Pd}(\text{NH}_3)_4][\text{PtCl}_4]\text{ ]

(c) Linkage isomerism— \([\text{Ir}(\text{NCS})(\text{NH}_3)_5]^{2+}\text{ ] and } [\text{Ir}(\text{SCN})(\text{NH}_3)_5]^{2+}\text{ ]
\[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2 \text{ (N bonded) and } [\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2 \text{ (O bonded)}

(d) Ionization isomerism— \([\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2 \text{ and } [\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2\text{ ]

(e) Geometrical isomerism— \text{cis } [\text{CrCl}_2(\text{NH}_3)_4]^+ \text{ and } \text{trans } [\text{CrCl}_2(\text{NH}_3)_4]^+
\text{cis } [\text{PtCl}_2(\text{NH}_3)_2] \text{ and } \text{trans } [\text{PtCl}_2(\text{NH}_3)_2]\text{ ]
1. (a) \([\text{Co}(\text{H}_2\text{O})_6]^{2+}\) (b) \([\text{Co}(\text{NH}_3)_6]^{2+}\) \(\rightarrow\) \([\text{Co}(L)_6]^{3+}\)

2. (a) \([\text{FeF}_6]^{3-}\) (b) \([\text{FeI}_6]^{3-}\) \(\rightarrow\) \([\text{FeL}_6]^{4-}\)

3. M-C≡O

4. 2\(^{nd}\), 3\(^{rd}\) transition series

5. Lanthanide contraction (4f\(^{1-14}\)) / the oct rule?