Metal-ligand and metal-metal bonding of the transition metal elements

Synopsis

Lecture 1:

Lecture 2:

Lecture 3:
Ligand classes. σ-donor complexes. Octahedral ML₆ molecular orbital energy diagram.

Lecture 3:
π–acceptor ligands and synergic bonding. Binding of CO, CN⁻, N₂, O₂ and NO.

Lecture 4:
Alkenes, M(H₂) vs M(H)₂, Mn(O₂) complexes, PR₃.

Lecture 5:
π–donor ligands, metal-ligand multiple bonds, O²⁻, R₂N⁻, RN²⁻, N³⁻.

Lecture 6:
ML₆ molecular orbital energy diagrams incorporating π–acceptor and π–donor ligands. Electron counting revisited and link to spectrochemical series.

Lecture 7:

Lecture 8:
Ligand effects on substitution rates (trans-effect, trans-influence). Metal and geometry effects on substitution rates.

Lecture 9:
Outer sphere electron transfer.

Lecture 10:
Inner Sphere electron transfer. Bridging ligands.
Learning Objectives: by the end of the course you should be able to

i) Use common nomenclature in transition metal chemistry.
ii) Count valence electrons and determine metal oxidation state in transition metal complexes.
iii) Understand the physical basis of the 18-electron rule.
iv) Appreciate the synergic nature of bonding in metal carbonyl complexes.
v) Understand the relationship between CO, the ‘classic’ π-acceptor and related ligands such as NO, CN, N₂, and alkenes.
vi) Describe the nature of the interaction between η²-bound diatomic molecules (H₂, O₂) and their relationship to π-acceptor ligands.
vii) Describe the difference between π-acceptor and π-donor ligands, and why exceptions to the 18-electron rule occur mainly for the later.
viii) Qualitatively describe metal-ligand multiple bonding
ix) To be familiar with common reaction types, in particular ligand substitution reactions (square planar and octahedral complexes)
x) To appreciate the distinctions between associative, dissociative and interchange pathways
xi) To understand the trans-effect, the trans-influence and origin of the spectrochemical series.
xii) To understand the principles of outer-sphere and inner-sphere electron transfer
xiii) To be able to comment on factors that indicate if electron transfer occurs by an outer- or inner-sphere mechanism

Bibliography:

Shriver and Atkins “Inorganic Chemistry” Ch 8, 9, 19, 21.
Cotton, Wilkinson, Murillo and Bochmann “Advanced Inorganic Chemistry” Ch 11, 16
Owen and Brooker “A Guide to Modern Inorganic Chemistry”
Mayer and Nugent “Metal-Ligand Multiple Bonds”

Further reading


Associated Courses

AKDK Transition metal chemistry 1st year
JML Structure and bonding 1st year
CED Atomic structure 1st year
JML Main group chemistry 1st year
DWB Group theory 2nd year
SBD Organometallic chemistry 2nd year
DWB Physical methods for structure determination 2nd year
AP Dynamic Electrochemistry 2nd year
TJD Processes at solid surfaces 3rd year
RNP Photochemistry and UV spectra 3rd year
PHW Bioinorganic chemistry 3rd year
RED Inorganic materials chemistry 3rd year
PHW f-block chemistry 3rd year
PAOB Asymmetric synthesis 3rd year
IJSF Metal mediated synthesis 3rd year
Catalysis option
Bioinspired Chemistry option
Chemistry and Disease option
Reaction Intermediates and Pathways option
Why is metal ligand bonding important?

**Catalysts** – e.g. polymers, pharmaceuticals, bulk chemicals, environmental

- [{\(\eta^5\cdot C_5H_5\)}_{2}TiCl_2]
  - Alkene polymerisation precatalyst

- [Rh(H)(PPh_3)_3]
  - Hydrogenation precatalyst

Catalytic converter for automobile

**Biochemistry** – e.g. oxygen transport, photosynthesis, enzymes, medicines, poisons

- Haemoglobin and myoglobin

Photosynthesis
‘Organic’ chemistry methodology – e.g. M(CO)₃ arenes, Pd catalysed C-X (X = C, N, S, O) bond formation, metathesis.

Inorganic Materials - e.g. magnets, batteries, dielectrics, lasers

Dielectrics

capacitors, microphones and thermal cameras

Smartphone technologies
This course is primarily concerned with the transition metals (‘d-block’ metals).

**Recap**

![Relative Atomic Radii](image)

Important trends:

1. Radius (Covalent/ionic): Increases from right to left and down a group.

2. Electropositivity: Electropositive character increases from right to left and down a group.

The trends observed in 1 and 2 are a result of the effective nuclear charge ($Z_{\text{eff}}$) that is a consequence of shielding and penetration. $s > p > d > f$

The relatively very poor shielding of an electron in an $f$-orbital results in a steady decrease in the radii of the lanthanides (approximately 25%). This is known as the lanthanide contraction. With respect to the transition metals the result is that the radii of the 2nd and 3rd row transition metals are very similar. E.g. Co(III) (0.55), Rh(III) (0.67), Ir(III) (0.68). This has repercussions in metal-ligand bonding and hence chemical properties. In general when descending a group the 1st row transition metal is distinct in terms of its bonding and properties from the 2nd and 3rd row metals.

3. Variety in oxidation state: Earlier metals (group 4 to 7) exhibit the greatest variety in oxidation state. Higher oxidation states more commonly observed for 2nd and 3rd row metals.

   e.g. Fe(III), Ru(VIII), Os (VIII).

4. Stronger bonds down a group (contrast to $p$-block)

**Ionic vs covalent bonding**

The 3$d$ orbitals in the first row metals are not as diffuse as the 2nd and 3rd row 4$d$ and 5$d$ orbitals. This leads to a larger ionic component in the bonding of first row metal complexes. However in many cases the bonding in 3$d$ metals can be described using covalent theories such as molecular orbital theory.

Compare this to the 4$f$ orbitals of the lanthanides that are essentially core orbitals and cannot participate significantly in covalent bonding. The bonding in lanthanide complexes can be considered almost totally ionic and they are often considered to be more similar to the alkaline earth metals than the transition metals.
Nomenclature and electron counting

\( \eta \) – **hapticity** – the number of contiguous atoms of a ligand attached to a metal.

\[ \eta^1 \text{-} O_2 \quad \eta^2 \text{-} O_2 \quad \eta^6 \text{-} C_6H_6 \]

\( \kappa \) – **denticity** – the number of non-contiguous atoms coordinating from a ligand (often a chelating ligand)

\( \kappa^1 \text{-} \text{ethylene diamine} \quad \kappa^2 \text{-} \text{ethylene diammine} \)

\( \mu \) – The number of metal atoms bridged by a ligand

\[ \mu_2 \text{-} \text{CO} \quad \mu_3 \text{-} \text{CO} \]

\( \eta^2, \mu_2 \text{-} O_2 \quad \mu_2 \text{-} O_2 \)

\( \eta^1 \) taken as default
Electron Counting

i) Metal oxidation state

<table>
<thead>
<tr>
<th>Oxidation state</th>
<th>Examples of formal charges on some ligands</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>NO (linear)</td>
</tr>
<tr>
<td>0</td>
<td>CO, NR₃, PR₃, N₂, O₂, H₂, C₂H₄, H₂O, RCN, C₆H₆</td>
</tr>
<tr>
<td>-1</td>
<td>H, CH₃, F, Cl, Br, I, C₅H₅, CN, NO₂, NR₂, NO (bent)</td>
</tr>
<tr>
<td>-2</td>
<td>O, S, CO₃, NR, porphyrin</td>
</tr>
<tr>
<td>-3</td>
<td>N, P</td>
</tr>
</tbody>
</table>

Ignoring NO the charge (n-) can be determined by adding H⁺ until a neutral molecule is obtained

\[
L^{n-} + n \text{H}^+ \rightarrow \text{H}_n\text{L}
\]

\[
\text{e.g. } \text{Cl}^{n-} + n \text{H}^+ \rightarrow \text{HCl} \quad n=1
\]

\[
\text{CH}_3^{n-} + n \text{H}^+ \rightarrow \text{HCH}_3 (\text{CH}_4) \quad n=1
\]

\[
\text{NR}^{n-} + n \text{H}^+ \rightarrow \text{H}_2\text{NR} \quad n=2
\]

\[
\text{CO} + n \text{H}^+ \rightarrow \text{CO} \quad n=0
\]

\[
\text{PPh}_3^{n-} + n \text{H}^+ \rightarrow \text{PPh}_3 \quad n=0
\]

\[
\text{RC(O)} + n \text{H}^+ \rightarrow \text{RC(O)}\text{H} \quad n=1
\]

Electroneutrality principle

The electronic structure of substances is such to cause each atom to have essentially zero resultant charge. No atom will have an actual charge greater than ±1. *i.e. the formal charge is not the actual charge distribution.*
e.g. Photoelectron spectroscopy (PES) is a technique that allows the experimental determination of orbital energies.

PES shows that all three iridium complexes have similar d-orbital energies indicating that the formal oxidation state is not the actual charge on the metal.

ii) metal d-electron count

\[
d\text{-electron count} = \text{group number} - \text{oxidation state}
\]

iii) Total valence electron count (TVEC) at the metal

\[
\text{Total Valence Electron Count (TVEC)} = \text{d-electron count} + \text{electrons donated by the ligands} + \text{number of metal-metal bonds}
\]

There are two methods that are commonly used and it is very important to avoid confusion.

Neutral (or radical) formalism

\[
\text{M-L} \rightarrow \text{M}^+ + \text{L}^- \quad \text{neutral (or radical) formalism}
\]

Ionic formalism

\[
\text{M-L} \rightarrow \text{M}^{2+} + \text{L}^- \quad \text{ionic formalism}
\]

To avoid confusion we will use the ionic formalism to determine the total number of valence electrons (electron count). However for some ligands O₂, NO and organometallics (carbenes, carbynes) the neutral formalism is more appropriate.

Number of electrons donated by each ligand (using ionic formalism)

2e CO, RCN, NR₃ (amines), PR₃ (phosphines), N₂, O₂, C₂R₄ (alkenes), H₂O, H⁺, CH₃⁻ (or any alkyl or aryl group, R), F⁻, Cl⁻, Br⁻, I⁻, CN⁻, NR₂⁻ (bent), (η⁵-C₅H₅)⁻

4e R₂PCH₂CH₂PR₂ (bis-phosphines), η⁴-dienes, NR₂⁻ (linear), (CH₃CO₂)⁻, NR²⁻ (bent), O²⁻ (double bond), S²⁻

6e (η⁵-C₅H₅)⁻, η⁶-C₆H₆, NR²⁻ (linear), O²⁻ (triple bond), N³⁻, P³⁻
Metal-metals bonds

Single bond counts 1 per metal
Double bond counts 2
Triple bond counts 3
Quadruple bond counts 4
Metal – metal bonding is more common for 2nd and 3rd row metals than for 1st row.

e.g.

\[
\begin{align*}
\text{Cr(CO)}_6 & : 6 + (6 \times 2) = 18 & \text{[Co(NH}_3)_6]^{3+} & : 6 + (6 \times 2) = 18 \\
[\text{CoCl}_6]^{3-} & : 6 + (6 \times 2) = 18 & \text{PtBr}_2(\text{PPh}_3)_2 & : 8 + (2 \times 2) + (2 \times 2) = 16 \\
\text{Mn}_2(\text{CO})_{10} & \text{per Mn: } 7 + (5 \times 2) + 1 = 18
\end{align*}
\]

<table>
<thead>
<tr>
<th>Coordination number</th>
<th>metal oxidation state</th>
<th>d-electron count</th>
<th>total valence electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr(CO)_6</td>
<td>6</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>[Co(NH}_3)_6]^{3+}</td>
<td>6</td>
<td>III</td>
<td>6</td>
</tr>
<tr>
<td>[CoCl}_6]^{3-}</td>
<td>6</td>
<td>III</td>
<td>6</td>
</tr>
<tr>
<td>PtBr}_2(\text{PPh}_3)_2</td>
<td>4</td>
<td>II</td>
<td>8</td>
</tr>
<tr>
<td>Rh(CO)(H)(\text{PPh}_3)_3</td>
<td>5</td>
<td>I</td>
<td>8</td>
</tr>
<tr>
<td>TiCl}_4</td>
<td>4</td>
<td>IV</td>
<td>0</td>
</tr>
<tr>
<td>Cr(\eta}_5-C}_8H}_6}_2</td>
<td>6</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>Fe(\eta}_5-C}_5H}_5}_2</td>
<td>6</td>
<td>II</td>
<td>6</td>
</tr>
<tr>
<td>[ReOCl}_5]^-</td>
<td>6</td>
<td>VI</td>
<td>1</td>
</tr>
</tbody>
</table>
Why complexes form

\[ \Delta G = \Delta H - T\Delta S = -RT \ln K_f \]  
\( (K_f = \text{formation constant}) \)

**Enthalpic effects**

1. **The number and strength of metal-ligand bonds.**
The greater the number of ligands, and the stronger the bonds, the greater the thermodynamic stability of the resulting complex. i.e. in general the more ligands the better. Larger metals can accommodate more ligands. In general coordination numbers are greater for the earlier transition metals (groups 4 – 7) compared to the later ones. Coordination numbers for lanthanide complexes are generally higher than for transition metals. d^8 square planar complexes are stable because 4 strong bonds are collectively stronger than 6 bonds that would be collectively weaker for this electron configuration.

2. **Steric factors.**
The number of ligands is limited by ligand – ligand repulsion. The size of metals and common ligands leads to transition metals generally accommodating a maximum of six ligands hence the vast number of 6 coordinate transition metal complexes. For similar reasons there are many 9 coordinate lanthanide complexes.

3. **The charge on the complex.**
Large positive and negative charges cannot easily be supported. Continually removing electrons from a complex will result in increasingly large ionisation energies, and increasing the number of electrons will lead to large electron-electron repulsive forces.

\( \text{(for } M^{2+} \sim -200 \text{ kJ mol}^{-1}, \text{ for } M^{3+} \sim -350 \text{ kJ mol}^{-1} \text{)} \)

4. **The electronic configuration.**
Crystal field stabilisation energy, Jahn-Teller distortion.

**Entropic effects**

1. **Number and size of any chelate rings**
5 and 6 membered rings most stable (enthalpy due to least ring strain) and less likely to dissociate.

2. **Solvation**
Requirement for an ordered solvent cage lowers entropy. Solvent stabilises charge.
Molecular orbital description of metal-ligand bonding in a complex

Recap of molecular orbital theory

a) Orbitals must be of appropriate symmetry
b) Orbitals must overlap
c) Orbitals should be of similar energy
b) and c) determine the energy of the interaction. The interaction energy is stronger for orbitals that have good overlap and are close in energy.

When the MOs are made up of 2 component orbitals of different energies

\[ \text{Rule of thumb} \]

*The bonding orbital looks more like the lower energy component*

*The antibonding orbital looks more like the higher energy component*

Electronic configuration: Transition metal valence orbitals and the 18 electron rule

Valence shell of transition metals nd + (n+1)s + (n+1)p orbitals (where n = 3-5).
5 + 1 + 3 = 9 orbitals. Two electrons per orbital = 18 electrons.
(Just a restatement of the Lewis octet rule with an extra 10 d-electrons)

Recap of Methane

Valence orbitals of carbon: 2s, 2px, 2py, 2pz. Three bonding orbitals and three antibonding orbitals.
For a transition metal complex with \( n \)-ligands

These diagrams not intended to represent degeneracy

For many complexes an electronic configuration of 18 valence electrons is the most thermodynamically stable, especially for diamagnetic organometallic complexes, however as noted earlier the electronic configuration is only one factor that contributes to the overall thermodynamic stability of a complex. Can be highly predictive eg Ni(CO)\(_4\), Co(CO)\(_3\)NO, Fe(CO)\(_2\)(NO)\(_2\), Mn(CO)(NO)\(_3\), Cr(NO)\(_4\) isoelectronic 18e complexes but
There are many important exceptions to the 18 electron rule including:

- 1\(^{\text{st}}\) row coordination complexes where the bonding is predominantly ionic.
  (see bioinorganic chemistry)
- square planar \( d^8 \) complexes (16 e\(^{-}\)).
- early metal complexes with \( \pi \)-donor ligands.
- paramagnetic complexes with an odd number of electrons.
Ligand classification

Metal-ligand bonding can be divided into three basic classes

1. $\sigma$-donor
   e.g. H, CH$_3$ (or any alkyl or aryl group, R), H$_2$O, NH$_3$, NR$_2$ (bent)

2. $\sigma$-donor, $\pi$-acceptor (sometimes referred to as ‘$\pi$-acceptors’ or ‘$\pi$-acids’)
   e.g. CO, CN, NO, H$_2$, C$_2$H$_4$, N$_2$, O$_2$, PR$_3$, BR$_2$

3. $\sigma$-donor, $\pi$-donor (sometimes referred to as ‘$\pi$-donors’)
   e.g. F, Cl, Br, I, O, OR, S, SR, N, NR$_2$(linear), NR (bent and linear), P, $\eta^3$-C$_3$H$_5$, $\eta^5$-C$_5$H$_5$, $\eta^6$-C$_6$H$_6$

In terms of bond strength the $\sigma$-bond is much more important than $\pi$-bonding (donor or acceptor)

1. $\sigma$-donor

In these compounds the bond between the ligand and metal is a $\sigma$- bond. A good example of a $\sigma$-donor is hydride (H$^-$). Some examples of transition metal hydrides are given below. Metal hydrides play a very important role in many catalytic reactions including hydrogenation and hydroformylation.

![Diagrams of metal hydrides]

Characterisation of metal hydrides
IR: $\nu$(M-H)$\sim$1750 cm$^{-1}$  NMR: Hydride resonance at high field ($\delta < 0$ppm)
Neutron diffraction needed to locate hydrogen nuclei.
Molecular orbital diagram of a ML₆ complex (where L is a σ–donor ligand)

atomic orbitals

(n+1)

\begin{align*}
\text{P}_x & \quad \text{P}_y & \quad \text{P}_z \\
\text{s} & \quad \text{a}_{1g} & \quad \text{d}_{x^2-y^2} \\
\text{n} & \quad \text{t}_{2g} & \quad \text{e}_g & \quad \text{d}_{xy} & \quad \text{d}_{xz} & \quad \text{d}_{yz}
\end{align*}

bonding molecular orbital

\begin{align*}
\sigma & \quad \text{le}_g & \quad \text{t}_{2g} & \quad \text{e}_g & \quad \text{t}_{1u} & \quad \text{a}_{1g}
\end{align*}

antibonding molecular orbital

\begin{align*}
\sigma^* & \quad 2t_{1u} & \quad \text{e.g. [Co(NH₃)₆]^{3+}} \\
\sigma^* & \quad 2a_{1g} & \quad \text{a 2e}_g \text{ orbital}
\end{align*}

metal in O_h field

ligands in O_h arrangement

Note that there are no linear combinations of ligand orbitals that have t₂g symmetry. Therefore the t₂g orbitals are non-bonding, completely metal based and pure d-orbitals. The 2e₉ orbitals are σ* and have ligand character but are approximately 80% metal based. When we talk about splitting of metal ‘d-orbitals’ in crystal field theory we are ignoring the ligand character that is present in some of the ‘d-orbitals’, however it is still a good first approximation and the relative energies between d-orbitals are correct. We will see that when we include π-acceptors and π-donors that the t₂g orbitals are no longer pure metal orbitals but also contain some ligand character.
Notes on molecular orbital diagrams

1. The total number of molecular orbitals should be the sum of the number of precursor orbitals.

2. Only orbitals of the same symmetry can interact and the resulting molecular orbitals will have the same symmetry as the precursor orbitals.

3. Where do the $a_{1g}$, $e_g$, $t_{1u}$ linear combinations of atomic orbitals come from?
   Using group theory it is possible to determine the symmetry of the orbitals involved.
   i) determine the point group of the molecule (in this case $O_h$).
   ii) treat the ligand orbitals (in this case $\sigma$) as a single entity and apply each symmetry element of the point group noting how many of the individual orbitals move under each operation. This is the reducible representation.
   iii) determine which characters sum to the reducible representation thus obtaining the irreducible representation. (in this case for the octahedral array of $\sigma$-H orbitals it will be $a_{1g} + e_g + t_{1u}$).
   iv) repeat for the 3 x $p$ and 5 x $d$ orbitals (the 1 x $s$ can be read off directly as having $a_{1g}$ symmetry) or alternatively look at the right hand portion of the group table and read off the orbital symmetries.
   v) apply projection operators to determine the linear combinations of orbitals.

4. The origin of symmetry labels $nxyz$
   Apart from being characters in group tables the labels can be used to describe the symmetry of orbitals.
   $n =$ orbitals of the same symmetry are numbered successively in order of increasing energy
   $x =$ a if singly degenerate and symmetrical to $C_{2n}$ rotation about the principle rotation axis
   $x =$ b if singly degenerate and unsymmetrical to $C_{2n}$ rotation about the principle rotation axis
   $x =$ e if doubly degenerate
   $x =$ t if triply degenerate
   $y =$ 1 if symmetrical to reflection through a reference mirror plane
   $y =$ 2 if unsymmetrical to reflection through a reference mirror plane
   $z =$ 'nothing' if there is no inversion centre
   $z =$ g if symmetrical to inversion
   $z =$ u if unsymmetrical to inversion

5. What group theory cannot tell us.
   i) What the orbitals look like
   ii) The energy of the orbitals and the magnitude of the precursor orbital interactions.
Comparison of Molecular Orbital and Crystal Field Theory

(From yr1 Transition Metal Chemistry) Crystal Field Theory compares the repulsive interactions between metal and ligand electrons to determine the ordering of metal d-orbitals. Crystal field theory is an electrostatic approach using pure metal d-orbitals.

The ordering of the ‘d-orbitals’ is the same as the MO scheme but for CFT there is no knowledge of bonding or antibonding character and the absolute energies and $\Delta_o$ will differ. Can use CFT as a quick approximation to the metal ‘d-orbital’ ordering.
σ-donor, π-acceptor (‘π-acceptors’ or ‘π-acids’)

These include: CO, CN, NO(linear), H₂, C₂H₄, N₂, O₂, PR₃, CR₂

We can view the metal-ligand bonding as a σ-donor interaction (same as for H) with an additional π-interaction that arises from overlap between occupied metal-based orbitals and empty ligand orbitals that can accept electron density.

Metal complexes of CO are a good example.

e.g. Some of the binary metal carbynls

<table>
<thead>
<tr>
<th>Group</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(CO)₆</td>
<td>Cr(CO)₆</td>
<td>Mn₂(CO)₁₀</td>
<td>Fe(CO)₅</td>
<td>Co₂(CO)₈</td>
<td>Ni(CO)₄</td>
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<td>Ru(CO)₅</td>
<td>Ru₂(CO)₉</td>
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<tr>
<td>W(CO)₆</td>
<td>Re₂(CO)₁₀</td>
<td>Os(CO)₅</td>
<td>Os₂(CO)₉</td>
<td>Ir₂(CO)₈</td>
<td></td>
</tr>
</tbody>
</table>

Some structures

Note: Beware the formulation of complexes containing 3centre-2electron bonds such as those with bridging carbonyls. Many structures in text books and papers incorrectly include metal-metal bonds e.g. Fe₂(CO)₉ when none are present (see Chem. Commun., 2012, 48, 11481).
The MO diagram of CO shows the molecular orbitals involved in bonding and antibonding. The frontier MOs often determine the mode of bonding.

Electron density maps of the $\sigma$ and $\pi$ orbitals are shown. The HOMO $5\sigma$ orbital is slightly bonding (or non-bonding) and has significant C 2s character. This is why CO bonds to a metal as a $\sigma$-donor through the C atom and not the O atom (better overlap).

In can be seen that the $2 \times 2\pi$ LUMO orbitals (antibonding) are empty. It is these orbitals that can interact with metal d-orbitals accepting electron density.
The $\sigma$-donor interaction increases the electron density on the metal and decreases the electron density on the CO ligand.

The $\pi$-acceptor interaction decreases the electron density on the metal and increases the electron density on the CO ligand. Both effects ‘reinforce’ each other. Sometimes referred to as **synergic bonding**.

$\pi$-acceptor ligands such as CO can relieve negative charge build-up at a metal centre. e.g. stabilise complexes with metals in a low formal oxidation state.

**Experimental evidence for bonding model**

IR and Raman spectroscopy and single crystal X-ray diffraction.

Characterisation of metal carbonyls

Typical covalent props: solubility, sublimation

As $\nu$(C-O) decreases C-O bonding decreases and M-C $\pi$-bonding increases

$\text{Cr-C} = 195.5$ pm
$\text{C-O} = 114.0$ pm
$\nu$(C-O) = 1984 cm$^{-1}$

$\text{C-O} = 112.8$ pm
$\nu$(C-O) = 2143 cm$^{-1}$
## Trends in $\nu$(CO)

### a) isoelectronic series

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(CO) cm$^{-1}$</th>
<th>$\nu$(CO) cm$^{-1}$</th>
<th>$\nu$(CO) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(CO)$_6$</td>
<td>2094</td>
<td></td>
<td>Ni(CO)(PF$_3$)$_3$</td>
</tr>
<tr>
<td>Cr(CO)$_6$</td>
<td>1984</td>
<td>Mo(CO)$_5$</td>
<td>2073</td>
</tr>
<tr>
<td>V(CO)$_5$</td>
<td>1845</td>
<td>Mo(CO)$_4$</td>
<td>Ni(CO)(PCl$_3$)$_3$</td>
</tr>
<tr>
<td>Ti(CO)$_5^{2-}$</td>
<td>1750</td>
<td>Mo(CO)$_3$</td>
<td>Ni(CO)(PMe$_3$)$_3$</td>
</tr>
</tbody>
</table>

### b) as CO ligands are lost

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(CO) cm$^{-1}$</th>
<th>$\nu$(CO) cm$^{-1}$</th>
<th>$\nu$(CO) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(CO)$_6$</td>
<td>2094</td>
<td>1987</td>
<td>Ni(CO)(PF$_3$)$_3$</td>
</tr>
<tr>
<td>Cr(CO)$_6$</td>
<td>1984</td>
<td>1966</td>
<td>Ni(CO)(PCl$_3$)$_3$</td>
</tr>
<tr>
<td>V(CO)$_5$</td>
<td>1845</td>
<td>1944,1887</td>
<td>Ni(CO)(PMe$_3$)$_3$</td>
</tr>
<tr>
<td>Ti(CO)$_5^{2-}$</td>
<td>1750</td>
<td>1862</td>
<td>Ni(CO)(PMe$_3$)$_3$</td>
</tr>
</tbody>
</table>

### c) as other ligands change

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(CO) cm$^{-1}$</th>
<th>$\nu$(CO) cm$^{-1}$</th>
<th>$\nu$(CO) cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(CO)$_6$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(CO)$_6$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V(CO)$_5$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti(CO)$_5^{2-}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### a) all d$^6$ but lower oxidation state implies greater electron density, therefore Ti(-II) exhibits the most back-donation, weakest CO bonds and lowest $\nu$(CO).

### b) All Mo(0) d$^6$. Fewer CO ligands share the metal electron density therefore Mo(CO)$_3$ exhibits weakest CO bonds and lowest $\nu$(CO).

### c) Electronegativity of F>Cl>Me. Back-donation of PF$_3$ > PCl$_3$ > PMe$_3$ which competes with CO back-donation for the metal electron density.

### d) coordination mode

- **Free**
  - $\nu$(CO) cm$^{-1}$: 2143

- **Terminal**
  - $\nu$(CO) cm$^{-1}$: 1850-2120

- **$\mu_2$-CO**
  - $\nu$(CO) cm$^{-1}$: 1750-1850

- **$\mu_3$-CO**
  - $\nu$(CO) cm$^{-1}$: 1620-1730

More metals = more electrons for back-donation and lower $\nu$(CO)

Always think in terms of CO ligands competing for whatever electrons are available on the metal!

### Non-classical carbonyls

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\nu$(CO)/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd(CO)$_4^{2+}$</td>
<td>2248</td>
</tr>
<tr>
<td>Pt(CO)$_4^{2+}$</td>
<td>2244</td>
</tr>
<tr>
<td>Ag(CO)$_2^{+}$</td>
<td>2200</td>
</tr>
<tr>
<td>Au(CO)$_2^{+}$</td>
<td>2217</td>
</tr>
<tr>
<td>Hg(CO)$_2^{2+}$</td>
<td>2278</td>
</tr>
</tbody>
</table>

In these complexes electron density is not transferred from the metal to the ligand $\pi$-accepting orbitals. The major interaction is $\sigma$-donation from the CO 5$\sigma$ orbital to the metal giving weak M-CO bonding. The CO stretching frequency is $>$ free CO mainly due to electrostatic perturbation. (see JACS 1996, 118, 12159)
Similar $\pi$–acceptor ligands

Other ligands that are expected to exhibit very similar bonding to CO are the isoelectronic ligands CN$^-$ and NO$^+$. (We will see later that NO can also coordinate in an alternative terminal mode). $N_2$ is also isoelectronic with CO.

![MO diagram of $N_2$]

Compare HOMO 5$\sigma$ ($\sigma^*$) of CO and HOMO 3$\sigma_g$ ($\sigma$) of $N_2$. Coordination of $N_2$ decreases N-N bond strength. $N_2$ can act as a $\pi$-acceptor using LUMO 1$\pi_g$ same as for CO.

Very few metal complexes of $N_2$ compared to CO and chemistry of $N_2$ is much less developed. The volume of the 3$\sigma$ $N_2$ orbital used to bond to a metal is much less than that on the 5$\sigma$ orbital on the carbon atom of CO. The same argument also applies to the $\pi$-acceptor interactions. Therefore the orbital overlap is less for the $\sigma$-donating and $\pi$-accepting interactions giving weaker bonding.

Other $\pi$–accepting ligands

Important examples include $O_2$, $H_2$, $PR_3$ and alkenes.
Complexes of dioxygen

\[ \text{Cr}(\eta^2-O_2)_4 \]

\[ \text{Ti}(\eta^2-O_2)\text{(porphyrin)} \]

\[ \text{haem} \]

\[ \text{haemocyanin} \]

\[ \eta^1 \text{ vs } \eta^2 \text{ bonding in } O_2 \text{ complexes} \]

MO diagram of \( O_2 \)

HOMO and LUMO both in \( \pi^* \)
Characterisation – what is the oxidation state of \( \text{O}_2 \)?

In any given complex, all we know for sure is that the \( \text{O}_2 \) molecule is bonded to the metal. Neutral dioxygen, superoxide (\( \text{O}_2^- \)) and peroxide (\( \text{O}_2^{2-} \)) are all well known forms of the ‘\( \text{O}_2 \)’ unit, so any given complex could be \{M-O\_2\}, \{M\textsuperscript{+}-O\_2\} or \{M\textsuperscript{2+}-O\_2\textsuperscript{2-}\}

Comparison of MO diagrams of dioxygen, superoxide, and peroxide
Vibrational frequencies and O-O bond lengths

<table>
<thead>
<tr>
<th></th>
<th>r(O-O) / pm</th>
<th>v(O-O) / cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂⁺(AsF₆⁻)</td>
<td>122</td>
<td>1858</td>
</tr>
<tr>
<td>O₂</td>
<td>121</td>
<td>1555</td>
</tr>
<tr>
<td>O₂⁺(K⁺)</td>
<td>133</td>
<td>1146</td>
</tr>
<tr>
<td>O₂⁺(Na⁺)₂</td>
<td>149</td>
<td>842</td>
</tr>
<tr>
<td>η¹-O₂</td>
<td>115-130</td>
<td>1130-1195</td>
</tr>
<tr>
<td>η²-O₂</td>
<td>130-152</td>
<td>800-930</td>
</tr>
</tbody>
</table>

As the electron density in the π* orbitals increases the O-O distance increases and the vibrational frequency decreases.

What happens if the σ* (3σ_u) orbital becomes occupied?

The Ta complex is reducing and has two electrons in a high-energy orbital HOMO. The Ta complexes have orbitals of the correct symmetry and can donate 4 electrons to a molecule of O₂ occupying 1π_g and 3σ_u of O₂ causing cleavage of the O₂ bond.

Why is η¹-O₂ bent when CO is linear?

Simply because O₂ has to accommodate an extra pair of electrons in the 1π_9 (π*) orbital. These occupy 1π_gx (to form the σ-bond through one lobe of the 1π_gx orbital) leaving 1π_gy to form a π-acceptor interaction.
NO (a ligand that can change binding mode)

NO typically adopts one of two terminal coordination modes (bent and linear)

Cell signalling bound to Fe porphyrin (nobel prize), angina medication and viagra

![Chemical structures](image)

<table>
<thead>
<tr>
<th>Characterisation</th>
<th>M-N-O angle/°</th>
<th>ν(N-O)/cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(CN)₅(NO)²⁻</td>
<td>178</td>
<td>1935</td>
</tr>
<tr>
<td>Mn(CN)₅(NO)³⁻</td>
<td>174</td>
<td>1700</td>
</tr>
<tr>
<td>Co(NH₃)₅(NO)²⁺</td>
<td>119</td>
<td>1610</td>
</tr>
<tr>
<td>CoCl(en)₂(NO)⁺</td>
<td>124</td>
<td>1611</td>
</tr>
</tbody>
</table>

How many electrons does NO donate?

**Linear:**

i) 1 electron goes *from NO to the metal*, giving NO⁺ + M⁻.

ii) NO⁺ is then isolectronic with CO, and donates 2 electrons *from NO to metal*

2+1 = 3, so NO is a 3-electron donor.

**Bent:**

i) 1 electron goes *from metal to NO*, giving NO⁻ + M⁺.

ii) NO⁻ is then isolectronic with O₂⁻, and donates 2 electrons *from NO to metal*

-1 + 2 = 1, so NO is a 1-electron donor

**Strategy for determining bent or linear, electron count and oxidation state:**

1) Remove NO (neutral) from complex and calculate electron count and oxidation state of remaining fragment.

2) Add 1 or 3 electrons per NO to increase electron count to 18 (or as close as possible without exceeding 18). You now have the total electron count at the metal and the M-NO geometry.

3) Determine the metal oxidation state of the complex including the NO ligand(s) and consider linear NO to be NO⁺ and bent NO to be NO⁻.

e.g.

<table>
<thead>
<tr>
<th></th>
<th>total valence electrons</th>
<th>metal oxidation state</th>
<th>d-electron count</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(CO)₄(NO)</td>
<td>18</td>
<td>-I</td>
<td>8</td>
</tr>
<tr>
<td>Co(NH₃)₅(NO)²⁺</td>
<td>18</td>
<td>III</td>
<td>6</td>
</tr>
<tr>
<td>RuCl(NO)₂(PPh₃)₂</td>
<td>17</td>
<td>I</td>
<td>7</td>
</tr>
</tbody>
</table>
Dihydrogen (a reactive ligand)

Complexes of dihydrogen (H-H = 74.1 pm in H₂)

Note: the σ and σ* orbitals of H₂ perform the same roles as the σ and π* orbitals in CO.

The antibonding σ* H₂ orbital is of π-symmetry about an axis perpendicular to the H-H bond and can interact with a metal orbital of π-symmetry.
If sufficient electron density is transferred from the metal to the $\sigma^*$ orbital of $\text{H}_2$ the H-H $\sigma$-bond will break and give two M-H (metal-hydride) $\sigma$-bonds (oxidative addition).

\[ \text{Ph}_3\text{P}-\text{Rh}-\text{PPh}_3 + \text{H}_2 \xrightarrow{\text{oxidative addition}} \text{Ph}_3\text{P}-\text{Rh}^\text{III}-\text{H} \]

**Characterisation – Dihydrogen M(H$_2$) or dihydride M(H)$_2$ complex ?**

<table>
<thead>
<tr>
<th>Technique</th>
<th>$\eta^2$ H-H</th>
<th>dihydride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutron diffraction</td>
<td>H-H$\sim$82 pm</td>
<td>H-H$\sim$160 pm</td>
</tr>
<tr>
<td>NMR</td>
<td>Low field, $J_{\text{HD}}$$\sim$30 Hz</td>
<td>High field, $J_{\text{HD}}$$\sim$5 Hz</td>
</tr>
<tr>
<td>IR</td>
<td>$\nu$(H-H) $\sim$ 3000 cm$^{-1}$</td>
<td>$\nu$(M-H) $\sim$2150-1750 cm$^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$\nu$(M-H) v. low</td>
<td></td>
</tr>
</tbody>
</table>

**Alkenes (a fluxional ligand)**

$\pi$-acceptor ligands. Alkene complexes form basis of many catalytic reactions e.g. polymerisation, hydrogenation and metathesis.

**Complexes of alkenes**
Dynamics in alkene complexes

373K
333K
313K
263K
233K
What determines energy barrier to rotation?
1. $\sigma$-bonding (dominant) interaction is not affected by rotation (no change in overlap)
2. $\pi$-bonding (minor) is broken, but other potential bonding orbitals at 90° to start point help lower activation energy.

**PR$_3$ complexes**
PR$_3$ can also act as $\pi$-acceptor ligands. In this case the orbitals are usually phosphorus $\sigma^*$ orbitals. Complexes of PR$_3$ ligands are very important catalysts for many reactions.
PR$_3$ ligands can stabilise low oxidation states by $\pi$-acceptor interactions and high oxidation states by strong $\sigma$-donation.

$\Pi$-Acceptor Ligand Effects in Action (Catalysis)

Enantioselective synthesis of S-DOPA

The Rh-L bonding of Rh-CO, Rh-H$_2$ (Rh-(H)$_2$), Rh-alkene, and Rh-PR$_3$ all play an integral role in this, and many other, catalytic reactions.
**σ-donor, π-donor (‘π-donors’)**

Ligands that fall into this category include: F, Cl, Br, I, O, OR, S, SR, N, NR₂(linear), NR (bent and linear), P.

We can view the metal-ligand bonding as a σ-donor interaction (same as for H) with an additional π- interaction that arises from overlap between metal-based orbitals and full orbitals on the ligand that can donate electron density.

![Direction of charge transfer](image)

Note: there is no synergic bonding occurring here.

**Metal - ligand multiple bonds**

e.g.

![Examples of metal-ligand multiple bonds](image)

Metal-ligand multiple bonds contain a σ-bond and one or two π-bonds. Complexes of O and N donor ligands usually have metals in high formal oxidation states with a low d-electron count. For π-donation to occur there must be an empty metal d-orbital to accept the electrons.
A very important ligand that exhibits multiple bonding is the oxide ligand (O$^{2-}$)

\[
\begin{array}{c}
\cdot \varepsilon \cdot \\
\cdot \varepsilon \cdot \\
\cdot \varepsilon \cdot \\
\end{array} \\
M \\
\begin{array}{c}
\cdot \varepsilon \\
\cdot \varepsilon \\
\cdot \varepsilon \\
\end{array} \\
M \\
\begin{array}{c}
\cdot \varepsilon \\
\cdot \varepsilon \\
\cdot \varepsilon \\
\end{array} \\
M \\
\begin{array}{c}
\cdot \varepsilon \\
\cdot \varepsilon \\
\cdot \varepsilon \\
\end{array} \\
M
\]

4 electron donor (O$^{2-}$) 6 electron donor 6 electron donor

Electrophilic O

Look at M-O bond lengths to determine bonding

Metal oxides are used as source of oxygen for the oxidation of organic compounds

Stoichiometric dihydroxylation of alkenes

Catalytic epoxidation of alkenes.

Protonation leads to hydroxides and aqua complexes (oxo chemistry is very pH sensitive)

*cf* rust formation
Other common multiple bonds are the amido (NR$_2$), imido (NR$_2^-$) and nitrido (N$^3-$) ligands.

Can we use N$_2$ as a source of nitrogen in organic chemistry?

Electron counting of $\pi$-donor complexes can be difficult. As a rule of thumb invoke as many multiple bonds as possible to get as close to (but not over) 18.

<table>
<thead>
<tr>
<th>Complex</th>
<th>total valence electrons</th>
<th>metal oxidation state</th>
<th>d-electron count</th>
</tr>
</thead>
<tbody>
<tr>
<td>($^t$BuO)$_3$WN</td>
<td>12 (18)</td>
<td>VI</td>
<td>0</td>
</tr>
<tr>
<td>($^\eta$-C$_5$H$_5$)$_2$V(NPh)</td>
<td>17</td>
<td>IV</td>
<td>1</td>
</tr>
<tr>
<td>ReMe$_4$(O)</td>
<td>13(15)</td>
<td>VI</td>
<td>1</td>
</tr>
</tbody>
</table>
What effect do $\pi$-acceptors and $\pi$-donors have on the chemistry of metal complexes?

MO diagram of $O_h$ complex with $\pi$-donor ligands

$[CoCl_6]^{3-}$ is considered 18 electron, even though 42 electrons in MO diagram.

Note the effect on the $t_{2g}$ d-orbitals in comparison to the $\sigma$-only case. These $t_{2g}$ orbitals have risen in energy, closer to the $e_g$ level, resulting in a reduction of $\Delta_{\text{oct}}$ (10 Dq).
MO diagram of $O_h$ complex with $\pi$-acceptor ligands

Note the effect on the $t_{2g}$ d-orbitals in comparison to the $\sigma$-only case. The $t_{2g}$ has been lowered in energy with respect to the $e_g$ level resulting in an increase in $\Delta_{oct} (10 \text{ Dq})$. 
Summary

\[ \Delta_{\text{oct}} \]

\( \pi \)-acceptor ligands usually obey the 18-electron rule, those with \( \pi \)-donors do not necessarily do so.

For \( \pi \)-donor ligands the metal \( t_{2g} \) orbitals are now slightly antibonding (\( \pi^* \)) therefore it is less energetically favourable to fill them.

E.g. \( \text{CrCl}_6^{3-} \) with 15 total valence electrons is stable.

\[ \Delta_{\text{oct}} \]

\( \pi \)-acceptor \( > \) \( \sigma \)-only \( > \) \( \pi \)-donor

\( \pi \)-donors and the 18-electron rule

The spectrochemical series is a list of ligands in order of increasing ligand field strength.

Electrostatic model (Crystal Field Theory) cannot account for the order.

\[ \begin{align*}
\text{CO} & > \text{CN}^- > \text{PPh}_3 > \text{NH}_3 > \text{H}_2\text{O} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{S}^2^- > \text{Br}^- > \text{I}^- \\
\pi \text{-acceptor} & > \sigma \text{-only} > \pi \text{-donor}
\end{align*} \]

\( \Delta_{\text{oct}} \) increases with increasing \( \pi \)-acidity of the ligands

E.g. Field strength determines spin state of metal complexes

\[ [\text{CrCl}_6]^{4-} \quad [\text{Cr(CN)}_6]^{4-} \]

High spin \quad Low spin

The kinetics of ligand substitution is also affected. High spin complexes have electron density in antibonding \( M-L \) \( \sigma^* \) orbitals. Therefore the \( M-L \) bonding is weaker in comparison to low spin complexes. We will see the importance of this behaviour in REDOX electron transfer later.
Trans-effect and Trans-influence

The trans-effect and trans-influence help to rationalise the stability and substitution chemistry of transition metal complexes, particularly square planar Pd and Pt complexes. (see below in inorganic reaction mechanisms of square planar complexes)

The trans effect is a kinetic phenomenon and describes the influence of a non-labile group on the rate of substitution of a ligand trans to it.

\[
\begin{align*}
\text{CO, CN}^- & > \text{PPh}_3 > \text{NO}_2^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{NH}_3, \text{OH}^-, \text{H}_2\text{O} \\
\pi \text{-acceptor} & \quad \pi \text{-donor} \quad \sigma \text{-only}
\end{align*}
\]

e.g.

\[
\begin{align*}
\text{PtCl}_4^{2-} + \text{NH}_3 & \rightarrow \text{Cl}^-\text{Pt}^-\text{NH}_3^{-} \quad \text{Cl}^-\text{Pt}^-\text{NH}_3^{-} + \text{NO}_2^- \rightarrow \text{Cl}^-\text{Pt}^-\text{NO}_2^- \quad \text{Cl}^-\text{Pt}^-\text{NO}_2^- + \text{NH}_3 \rightarrow (1) \\
\text{PtCl}_4^{2-} + \text{NO}_2^- & \rightarrow \text{Cl}^-\text{Pt}^-\text{NO}_2^- \quad \text{Cl}^-\text{Pt}^-\text{NO}_2^- + \text{NH}_3 \rightarrow (2)
\end{align*}
\]

cis-platin \quad trans-platin

testicular cancer treatment

The order of ligand addition is important!
Inorganic Reaction Mechanisms

i) **Ligand substitution**
Most common reaction of coordination compounds
Substitution of one ligand in the coordination sphere for another

\[
\text{H}_3\text{N}\text{PtNH}_3\text{Cl}^{2+} + \text{Cl}^- \rightarrow \text{H}_3\text{N}\text{PtNH}_3\text{Cl}^{+} + \text{NH}_3
\]

ii) Dissociation
Decreases the metal coordination number

\[
\text{Ph}_3\text{P}\text{PdPh} \rightarrow \text{Ph}_3\text{P}\text{PdPOP}_3 + \text{Ph-Ph}
\]

iii) Addition
Increases the metal coordination number

\[
\text{Cu(O)}\text{Cu(O)} + \text{Py} \rightarrow \text{Cu(O)}\text{Cu(O)}\text{Py}
\]

iv) **Redox reactions**
Oxidation, reduction, electron transfer

\[
\text{Ru}^{2+} \text{NH}_3 + \text{H}_2\text{O} \text{Cr}^{3+} \text{OH}_2 \rightarrow \text{Ru}^{3+} \text{NH}_3 + \text{H}_2\text{O} \text{Cr}^{2+} \text{OH}_2
\]

Ru(III) is reduced with Cr(II)

v) Reactions of coordinated ligands
Reactions of a ligand that take place without breaking the M-L bond

\[
\text{Cr}^{3+} \text{OH}_2 + \text{OH}^- \rightarrow \text{Cr}^{2+} \text{OH}_2 + \text{H}_2\text{O}
\]

+ Lots of organometallic and organic chemistry using metal complexes
Ligand Substitutions Reactions

Organic Chemistry: $S_N1$, $S_N2$ etc

For inorganic

**Stoichiometric Mechanism**
Considers reactants, products and intermediates
Each step has a rate or equilibrium constant associated with it
Each species exists in a potential minimum along the reaction coordinate

**Intimate Mechanism**
Usually considers the transition state of the rate-determining step

**Recap:**
Thermodynamically unstable complexes that survive for at least a minute are called inert
Complexes that equilibrate more quickly are called labile

<table>
<thead>
<tr>
<th>Labile</th>
<th>Inert</th>
</tr>
</thead>
<tbody>
<tr>
<td>complexes of $d^{10}$ ions</td>
<td>$d^3$ and low-spin $d^6$ configurations</td>
</tr>
<tr>
<td>complexes of 3d M(II) ions (M(III) less labile)</td>
<td>4d and 5d complexes due to high CFSE and better metal-ligand overlap</td>
</tr>
<tr>
<td>Chelating ligands</td>
<td>Chelating ligands</td>
</tr>
</tbody>
</table>

**Timescale:**

<table>
<thead>
<tr>
<th>Process:</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^8$ s ligand exchange (inert complex)</td>
</tr>
<tr>
<td>1 ms ligand exchange (labile complex)</td>
</tr>
<tr>
<td>1 $\mu$s intervalence charge transfer</td>
</tr>
<tr>
<td>1 ns ligand exchange</td>
</tr>
<tr>
<td>10 ps ligand association</td>
</tr>
<tr>
<td>1 ps rotation time in liquid</td>
</tr>
<tr>
<td>1 fs molecular vibration</td>
</tr>
</tbody>
</table>
Activation Parameters:
Reaction rate examined as a function of temperature:
Eyring equation yields the enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) of activation.

The Eyring equation is obtained by applying activated complex theory to a reaction.

$$\ln\left(\frac{k_{rate}}{T}\right) = \ln\left(\frac{k_{Boltz}}{h}\right) - \frac{\Delta H^\ddagger}{RT} + \frac{\Delta S^\ddagger}{R}$$

A plot of reaction rate in the form of $\ln(k_{rate}/T)$ vs $1/T$ gives both $\Delta H^\ddagger$ and $\Delta S^\ddagger$

Measure the rate as a function of pressures. van't Hoff equation

$$\left(\frac{\partial \ln k_1}{\partial P}\right)_T = \frac{\Delta V^\ddagger}{RT}$$

$\Delta V^\ddagger$ is the volume of activation, volume differences between initial state and the transition state
$\Delta H^\ddagger$ activation enthalpy, bond strength differences between the initial and transition state
$\Delta S^\ddagger$ activation entropy, ordering effects between the initial and transition state

We will consider square-planar and octahedral metal complex ligand substitutions

Square Planar Ligand substitutions

d$^8$ metal ions are the most common

<table>
<thead>
<tr>
<th>Co$^+$</th>
<th>Ni$^{2+}$</th>
<th>Cu$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh$^+$</td>
<td>Pd$^{2+}$</td>
<td>Ag$^{3+}$</td>
</tr>
<tr>
<td>Ir$^+$</td>
<td>Pt$^{2+}$</td>
<td>Au$^{3+}$</td>
</tr>
</tbody>
</table>

Square-planar Pt(II) complexes have been studied most extensively: suitable timescale

In an associative mechanism BOTH bond-breaking and bond-making can be important:

Mechanism and kinetics? What are the features that control which ligand is substituted and metal stereochemistry?
Study temperature and pressure dependence of the reaction rate

Activation parameters $\Delta S^\ddagger$ and $\Delta V^\ddagger$ are negative

A negative $\Delta S^\ddagger$ indicates transition state is more ordered than initial state. A negative $\Delta V^\ddagger$ indicate transition state has smaller volume than initial state. Both indicate an associative mechanism (A):

The experimentally observed rate law for a square-planar substitution:

$$ML_3X + Y \rightarrow ML_3Y + X$$

can be written as:

$$\text{rate} = k_1[ML_3X] + k_2[ML_3X][Y]$$

Where $X =$ leaving group
$Y =$ incoming group, nucleophile

Two pathways: associative mechanism

General Observations

In most cases, stereochemical retention of configuration is observed during substitution. In some cases a 5-coordinated intermediate can be isolated. Bulky groups decrease the rate of substitution.

Formation of a 5-coordinate trigonal bipyramidal intermediate:
If the trigonal bipyramidal intermediate is sufficiently long-lived, isomerisation can be observed (via pseudorotation)

5-coordinate complexes are fluxional: *Berry pseudorotation*

Isomerisation *via* pseudorotation: Square based pyramid and trigonal prism geometries have very similar energy

Factors affecting the rate of substitution

i) The entering group: The rate of substitution is proportional to the nucleophilicity of entering group: i.e. for Pt(II), the rate increases in the order:

\[
H_2O < NH_3 = py < Br^- < I^- < CN^- < PR_3
\]

hard soft

Element specific: the ordering is consistent with Pt(II) being a soft metal centre.

No correlation with other properties of the nucleophiles, such as basicity, redox potentials or pKa

The most important factor is polarisability or "softness":

I^- > Br^- > Cl-

PR_3 > AsR_3 > SbR_3 >> NR_3 (π-back bonding ability increases in the same order)

Exceptions: NO_2^- and SeCN-, "biphilic", exhibit different reactivity depending on the charge on the complex.

ii) The leaving group:

The same principle applies: (but gives reverse order)

hard ligands, such as H_2O and Cl- leave quickly

soft ligands with considerable π-back bonding, such as NO_2^- and CN^- leave slowly
For the reaction:

\[
\text{HN-Pt-X} + \text{py} \rightarrow \text{HN-Pt-} + \text{X}^-
\]

In water at 25 °C the sequence of lability of X⁻ is:

\[\text{H}_2\text{O} > \text{Cl}^- > \text{Br}^- > \text{I}^- > \text{SCN}^- > \text{NO}_2^- > \text{CN}^-\]

With a spread of over \(10^6\) in rate across series.

(The series mirrors the strength of the M-L bond strength)

iii) The nature of other ligands in the complex

The *trans*-effect:

- effect of a coordinated ligand on the rate of substitution of ligands opposite to it.

or

the ability of a ligand to direct the replacement of the ligand trans to it.

Essentially arises from the competition between ligands for the same orbital.

The trans-effect for Pt(II):

\[\text{CN}^- \sim \text{CO} > \text{NO}_2^- > \text{I}^- \sim \text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{py} > \text{NH}_3 > \text{H}_2\text{O}\]

Examples:

Reaction 1: \(\text{[Pt(NH}_3\text{)}_4]^{2+} + 2\text{Cl}^- \rightarrow \text{[PtCl}_2(\text{NH}_3\text{)}_2]\)

Reaction 2: \(\text{[Pt(Cl}_4\text{)}_2]^{2-} + 2\text{NH}_3 \rightarrow \text{[PtCl}_2(\text{NH}_3\text{)}_2]\)

Reaction 1:

\[\text{H}_3\text{N-Pt-NH}_3\text{NH}_3^{2+} + \text{Cl}^- \rightarrow \text{H}_3\text{N-Pt-NH}_3 + \text{Cl}^- \rightarrow \text{H}_3\text{N-Pt} + \text{Cl}^- \rightarrow \text{H}_3\text{N-Pt-Cl} + \text{Cl}^- \rightarrow \text{H}_3\text{N-Pt-Cl}^{+}\]

\text{transplatin}

Reaction 2:

\[\text{Cl-Pt-Cl}^{2-} + \text{NH}_3 \rightarrow \text{Cl-Pt-NH}_3 \rightarrow \text{Cl-Pt-Cl} \rightarrow \text{Cl-Pt-Cl} + \text{NH}_3 \rightarrow \text{Cl-Pt-NH}_3 \rightarrow \text{Cl-Pt-Cl} + \text{NH}_3 \rightarrow \text{Cl-Pt-NH}_3\]

\text{cisplatin}
Conclusion:

Cl\(^-\) has a greater trans-directing effect than NH\(_3\).

*The formed geometric isomer depends on the order in which the reagents are added*

The free energy of activation \((\Delta G^\ddagger)\) of ligand substitution is the difference between the reactant ground state and the first transition state. \((\Delta G^\ddagger)\) can be decreased by:

1) destabilisation of the ground state

*weakening of the bond in trans-position, \(\sigma\)-bonding effect*

2) stabilisation of the transition state

*lower energy of 5-coordinate transition state, \(\pi\)-bonding effect*

1) destabilisation of the ground state:

This is a thermodynamic effect. Some ligands weaken the M-L bond *trans* to them in the ground state and facilitate the substitution. (This is often also called trans-influence)

- e.g. strong \(\sigma\)-donors, such as H\(^+\), I\(^-\), Me\(^-\), PR\(_3\), *destabilise the M-L bond trans to themselves* (they repel electrons in the trans-ligand weakening the M-L bond)

2) stabilisation of the transition state:

In the trigonal plane of the 5-coordinate transition state or intermediate, \(\pi\)-back bonding can occur between a metal d-orbital and suitable orbitals of ligand T (the ligand *trans* to the leaving group) and Y (the entering nucleophile)

This is a kinetic effect.

Strong \(\pi\)-acceptors, such as NO\(^+\), C\(_2\)H\(_4\), CO and CN\(^-\) stabilise the transition state by accepting electron density that the incoming nucleophile donates to the metal through \(\pi\)-interaction (relieves charge build-up at the metal) a strong \(\pi\)-acceptor thus facilitates substitution at the site *trans* to it
Overall:
Ability of selected ligands to direct trans-substitution:

\[ \text{CN}^- \sim \text{CO} \sim \text{NO}^+ \sim \text{C}_2\text{H}_4 > \text{PR}_3, \text{H}^+ > \text{CH}_3^+ > \text{Ph}^+, \text{NO}_2^- > \text{I}^-, \text{SCN}^- > \text{Br}^- > \text{Cl}^- > \text{py} > \text{NH}_3 > \text{H}_2\text{O} \]

\( \pi \)-acceptors \( \pi \)-donors \( \alpha \)-donors

iv) The metal centre

The order of reactivity of the group 10 dications is:

\[ \text{Ni(II)} > \text{Pd(II)} >> \text{Pt(II)} \]

\[ \text{Ni(II)}: \quad k_2 = 33 \text{ M}^{-1} \text{ s}^{-1} \]
\[ \text{Pd(II)}: \quad k_2 = 0.58 \text{ M}^{-1} \text{ s}^{-1} \]
\[ \text{Pt(II)}: \quad k_2 = 6.7 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1} \]

reflects tendency to form 5-coordinate complexes/transition states

Square planar substitution reactions are generally slow due to loss of crystal field stabilisation energy (CFSE) during the formation of trigonal bipyramidal complex from square planar one.

The loss of CFSE increases down the group

Hence the square planar substitutions of 4d and 5d elements are slower

Or

M-L bonding stronger \( 5d > 4d > 3d \) (due to better M-L overlap). Within a series breaking stronger bonds requires more activation energy.
Octahedral ligand substitutions

Possible Mechanisms for:

\[ \text{ML}_5X + Y \rightarrow \text{ML}_5Y + X \]

i) **Associative (A)** via 7-coordinate intermediate (rare)

The rate determining step: formation of the 7-coordinate intermediate \( \text{ML}_5XY \)

(mechanism: \( A_a \) since associatively activated)

The second faster step is dissociation of \( X \) (intermediate cannot be detected)

The rate of reaction depends on the concentration of \( \text{ML}_5X \) and \( Y \)

\[ \text{Rate} = k_2[\text{ML}_5X][Y] \]

The activation parameters \( \Delta S^\ddagger \) and \( \Delta V^\ddagger \) are negative

ii) **Dissociative (D)** via a 5-coordinate intermediate (organic \( S_N1 \))

The rate of the substitution depends on \( [\text{ML}_5X] \) and is independent of \( [Y] \)

(mechanism: \( D_i \) since dissociatively activated)

Overall rate = \( k_1[\text{ML}_5X] \)

The activation parameters \( \Delta S^\ddagger \) and \( \Delta V^\ddagger \) are positive
iii) Interchange (I)

*Most common mechanism in octahedral complexes*

As Y begins to bond X begins to leave. i.e. the bond making to Y and bond breaking to X occur simultaneously (*organic S_N2*)

![Diagram of interchange mechanism]

The designations I_d and I_a are used to differentiate associatively from dissociatively activated processes.

Complication:
There is masking of concentration dependence in aqueous solution.
An associative mechanism is *usually first order in both reactant and incoming ligand.*

*For example:* \( ML_5X + H_2O \rightarrow ML_5(H_2O) \)

However: the concentration of \( H_2O \) in aqueous solution is so large it is very nearly constant.

So it is combined with \( k_1 \) and the resulting rate law is *pseudo* first order
Concentration dependence of the incoming ligand has been masked

In water and other coordinating solvents, such as dmso, the rate laws for the associative and dissociative mechanisms are identical:

\[
\text{Rate} = k_1 [ML_5X]
\]

So we cannot use the rate law to decide between the two mechanisms

**Additional evidence for a dissociative rate-determining step in octahedral substitution reactions:**

i) Entering group effect

\[
[\text{Ni(H}_2\text{O)}_6]^{2+} + L = [\text{Ni(H}_2\text{O)}_5L]^{2+} + \text{H}_2\text{O}
\]

vary L and compare the rate constants

range from \( k = 3 \times 10^3 \text{s}^{-1} \) for \( L = \text{NH}_3 \) to \( k = 30 \times 10^3 \text{s}^{-1} \) for \( L = \text{CH}_3\text{COO}^- \)

only a factor of 10 difference (*entering group has hardly any effect*)
Evidence for a dissociative rate-determining step

\[
\text{[CoX(NH}_3\text{)}_5\text{]}^{2+} + \text{H}_2\text{O} \xrightarrow{k} \text{[Co(NH}_3\text{)}_5(\text{OH}_2\text{})]^3+ + \text{X}^-
\]

formation constant

\[
\text{[Co(NH}_3\text{)}_5(\text{OH}_2\text{})]^3+ + \text{X}^- \xrightarrow{K^-} \text{[CoX(NH}_3\text{)}_5\text{]}^{2+} + \text{H}_2\text{O}
\]

evidence for a dissociative rate-determining step

\[
\ln k \propto \text{activation Gibbs energy}
\]

\[
\ln K \propto \text{reaction Gibbs energy}
\]


Plot of \( \log K \) (reflects bond strength) vs. \( \log k \) (measure of the rate of aquation):

\[
\begin{align*}
\text{X}^- & \quad k, \text{s}^{-1} & \quad K, \text{M}^{-1} (\log K) \\
\text{F}^- & 8.6 \times 10^{-8} & 20 (1.3) \\
\text{H}_2\text{PO}_4^- & 2.6 \times 10^{-7} & 7.4 (0.8) \\
\text{Cl}^- & 1.7 \times 10^{-6} & 1.25 (0.1) \\
\text{Br}^- & 6.3 \times 10^{-6} & 0.37 (-0.4) \\
\text{I}^- & 8.3 \times 10^{-6} & 0.16 (-0.8) \\
\text{NO}_3^- & 2.7 \times 10^{-5} & 0.077 (-1.1)
\end{align*}
\]

\text{In } k \propto \text{activation Gibbs energy} \\
\text{In } K \propto \text{reaction Gibbs energy}

Linear Free Energy Relationship: consistent with a rate determining step in which bonds of varying strength are broken. Or put another way the thermodynamic bond strength determines the kinetic rate of reaction.

evidence for a dissociative rate-determining step
iii) Steric effects

In the dissociative mechanism, the coordination number is decreased in the transition state (TS)

*if L is large, then the steric crowding is decreased in the TS so the rate increases*

*conversely, in an associative mechanism large L decrease the rate*

Effect of the size of the spectator ligands on the aquation of \([\text{Co}(\text{N-N})_2\text{Cl}_2]^+\) (N-N is a bidentate ligand):

<table>
<thead>
<tr>
<th>N—N</th>
<th>rate constant / s(^{-1}), 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)</td>
<td>(3.2 \times 10^{-5})</td>
</tr>
<tr>
<td>(\text{NH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2)</td>
<td>(6.2 \times 10^{-5})</td>
</tr>
<tr>
<td>(\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{NH}_2)</td>
<td>(1.5 \times 10^{-4})</td>
</tr>
<tr>
<td>(\text{NH}_2\text{CH}_2\text{C}(\text{CH}_3)_2\text{NH}_2)</td>
<td>(2.2 \times 10^{-4})</td>
</tr>
<tr>
<td>(\text{NH}_2\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{NH}_2)</td>
<td>immediate reaction</td>
</tr>
</tbody>
</table>


*Increase in rate: dissociative rate-determining step*

*Increase in ligand size exerts chemical pressure on dissociating ligand*

*iv) Electron count* (for 18-electron reactants)

*dissociative mechanisms involving 16-electron intermediates are common*

*associative substitutions involving 20-electron intermediates are less common (unless accommodated by changes in e.g. hapticity)*
Electron Transfer Reactions

One definition of chemistry could be ‘The study and manipulation of valence electrons’. The transfer of electrons between molecular compounds is therefore an extremely important phenomenon.

We will be considering electron transfer between inorganic complexes. There are two mechanisms by which inorganic complexes transfer electrons. The **outer sphere mechanism** and the **inner sphere mechanism**. The outer sphere mechanism is important because of the analogy that can be drawn between electron transfer in metal complexes and electron transfer in metalloenzymes. The inner sphere mechanism is important because atom transfer (bond breaking/formation) can be concomitant with electron transfer. Both are important for photosynthesis.

**Outer sphere** electron transfer occurs between complexes that do not undergo substitution. No new bonds are broken or formed.

**Inner sphere** electron transfer occurs between complexes via a bridging ligand. At least one of the complexes needs to be labile to allow the bridge to form. Bonds are broken and formed.

### Recap

**Substitution: Inert vs labile octahedral complexes**

*From first year transition metals course*

Electron configuration important (LS = low spin)

<table>
<thead>
<tr>
<th>Inert</th>
<th>Labile</th>
</tr>
</thead>
<tbody>
<tr>
<td>d^3, d^4 LS, d^5 LS, d^6</td>
<td>d^0, d^1, d^2, d^4 HS, d^5 HS, d^7 HS</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Low spin complexes</th>
<th>High spin complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong field ligands CO, CN^−, PR_3</td>
<td>Weak field ligands H_2O, NH_3, Cl^−</td>
</tr>
<tr>
<td>All 2\textsuperscript{nd} and 3\textsuperscript{rd} row complexes</td>
<td>All 1\textsuperscript{st} row H_2O complexes</td>
</tr>
<tr>
<td>Most Co(III)</td>
<td>Most Co(II)</td>
</tr>
</tbody>
</table>
Outer sphere electron transfer

\[ \text{oxidant (O)} \quad \text{is reduced} \quad M^{(a+1)+L_x} + \quad \text{reductant (R)} \quad \text{is oxidised} \quad M^{b+L_y} \quad \leftrightarrow \quad M^{a+L_x} + \quad M^{(b+1)+L_y} \]

### Mechanism

1. Formation of precursor complex

\[ M^{(a+1)+L_x} + M^{b+L_y} \quad \underset{K_{\text{eq}}}{\overset{k_{\text{ET}}}{\rightleftharpoons}} \quad \left\{ M^{(a+1)+L_x} M^{b+L_y} \right\} \]

Precursor complex

2. Activation/reorganisation of precursor complex. Electron transfer. Relaxation to successor complex

\[ \left\{ M^{(a+1)+L_x} M^{b+L_y} \right\} \quad \overset{k_{\text{ET}}}{\rightarrow} \quad \left\{ M^{a+L_x} M^{(b+1)+L_y} \right\} \]

Successor complex

3. Dissociation of successor complex

\[ \left\{ M^{a+L_x} M^{(b+1)+L_y} \right\} \quad \overset{k_{\text{diss}}}{\rightarrow} \quad M^{a+L_x} + \quad M^{(b+1)+L_y} \]

Formation of precursor complex and dissociation of successor complex are fast. Electron transfer slow

\[ \Delta G^\ddagger \]

remember from thermodynamics, driving force \( \Delta G^\circ = -nF\Delta E^0 \)
So why is there such a large range of rates?

Factors that affect the rate of outer sphere electron transfer

\[ \Delta G^\dagger = \Delta G^\ddagger_{i} + \Delta G^\ddagger_{o} + \Delta G^\ddagger_{j} \]

- \( \Delta G^\ddagger_{i} \): Energy required for reorganisation of bond lengthening/compressional to make interacting orbitals the same energy.
- \( \Delta G^\ddagger_{o} \): Energy is required to reorganise the solvent.
- \( \Delta G^\ddagger_{j} \): Metal-ligand bond lengths will change when the oxidation state of the metal changes. The Frank-Condon principle states that because nuclei are much more massive than electrons, an electronic transition occurs much faster than the nuclei can respond. Complexes must adjust their M-L bond lengths before electron transfer.

Self exchange reactions (M and M* are isotopes). \( \Delta G^0 = 0 \)

\[ [\text{Ru}^*(\text{NH}_3)_6]^{2+} + [\text{Ru}(\text{NH}_3)_6]^{3+} \xrightarrow{k = 6.7 \times 10^3 \text{ M}^{-1}\text{s}^{-1}} [\text{Ru}^*(\text{NH}_3)_6]^{3+} + [\text{Ru}(\text{NH}_3)_6]^{2+} \]

\( [\text{Ru}(\text{NH}_3)_6]^{3+/2+} E^0 = +0.051 \text{ V} \)

\[ [\text{Co}^*(\text{NH}_3)_6]^{2+} + [\text{Co}(\text{NH}_3)_6]^{3+} \xrightarrow{k = 10^{-9} \text{ M}^{-1}\text{s}^{-1}} [\text{Co}^*(\text{NH}_3)_6]^{3+} + [\text{Co}(\text{NH}_3)_6]^{2+} \]

\( [\text{Co}(\text{NH}_3)_6]^{3+/2+} E^0 = +0.058 \text{ V} \)

\[ [\text{V(H}_2\text{O})_6]^{2+} + [\text{Ru}(\text{NH}_3)_6]^{3+} \xrightarrow{k = 1.3 \times 10^3 \text{ M}^{-1}\text{s}^{-1}} [\text{V(H}_2\text{O})_6]^{3+} + [\text{Ru}(\text{NH}_3)_6]^{2+} \]

Cross reaction

\( [\text{V(H}_2\text{O})_6]^{3+/2+} E^0 = -0.255 \text{ V} \)

Solvents allow two positively charged complexes to approach one another. Solvents that interact strongly with complexes (e.g. via hydrogen bonding) will reduce the rate of electron transfer.
Orbital energies must be of equal for electron transfer to occur (but not sole requirement)

Electron transfer requires orbital overlap and orbitals of the same symmetry

Fe(III)-O = 2.05 Å
Fe(II)-O = 2.21 Å

Identical bond lengths in T.S.

Δo

Fe-O compression Fe-O elongation

Orbital symmetry

In Oₙ field e₉ is σ*: e₉ → e₉ transition = large change in bond length. ‘Slow’ electron transfer

+ poor overlap (ligand steric)
In $O_h$ field $t_{2g}$ is $\pi/\pi^*$: $t_{2g} \rightarrow t_{2g}$ transition = small change in bond length. ‘Fast’ electron transfer

better overlap (depends on ligands)

Overlap

2nd and 3rd row metals generally faster than 1st row due to better overlap of 4d and 5d orbitals. (Also due to stronger ligand fields bond length distortions will be smaller).

Ligands that have extended $\pi$-systems e.g. Phen, bipy etc can assist electron transfer.

Electronic Configuration

Activation energy is required if a complex has to change electron configuration to allow electron transfer.

e.g.

Think of electronic reorganisation being concomitant with bond elongation and compression.
Potential energy diagrams

Why not transfer electron then relax bonds?

At I, the requirement of equal orbital energies is met allowing the possibility of electron transfer. A photon could provide the required energy.

How does electron move from reactant to product?

At I, electronic-vibrational coupling ($\Delta Ec$) determines the probability $\kappa_{el}$ (transmission coefficient) that an electron will transfer. $\kappa_{el}$ increases with increasing $\Delta Ec$.  

1. Where did energy come from to ‘activate’ the electron?
2. $R \xrightarrow{ET} P^* \xrightarrow{relax} P + \text{heat}$ (violation of conservation of energy)
What is the relationship between $\Delta r$, $\Delta G^0$ and $\Delta G^\dagger$?

$\Delta G^\dagger \propto 1/(\Delta G^0)^2$ (however see inverted Marcus region)

$\Delta G^\dagger \propto (\Delta r)^2$ (i.e. small changes in bond lengths = large changes in $\Delta G^\dagger$)

<table>
<thead>
<tr>
<th>Self Exchange Reaction</th>
<th>Configuration</th>
<th>$k$ (M$^{-1}$ s$^{-1}$)</th>
<th>$\Delta r$ Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cr(H$_2$O)$_6$]$^{2+}$ / [Cr(H$_2$O)$_6$]$^{3+}$</td>
<td>$t_{2g}^3e_g^1$ / $t_{2g}^3e_g^0$</td>
<td>10$^{-5}$</td>
<td>0.3</td>
</tr>
<tr>
<td>[V(H$_2$O)$_6$]$^{2+}$ / [V(H$_2$O)$_6$]$^{3+}$</td>
<td>$t_{2g}^3e_g^0$ / $t_{2g}^2e_g^0$</td>
<td>10$^{-2}$</td>
<td>0.2</td>
</tr>
<tr>
<td>[Fe(H$_2$O)$_6$]$^{2+}$ / [Fe(H$_2$O)$_6$]$^{3+}$</td>
<td>$t_{2g}^4e_g^2$ / $t_{2g}^3e_g^2$</td>
<td>4</td>
<td>0.15</td>
</tr>
<tr>
<td>[Ru(H$_2$O)$_6$]$^{2+}$ / [Ru(H$_2$O)$_6$]$^{3+}$</td>
<td>$t_{2g}^6e_g^0$ / $t_{2g}^5e_g^0$</td>
<td>4 x 10$^3$</td>
<td>0.05</td>
</tr>
<tr>
<td>[Fe(phen)$_3$]$^{2+}$ / [Fe(phen)$_3$]$^{3+}$</td>
<td>$t_{2g}^6e_g^0$ / $t_{2g}^5e_g^0$</td>
<td>10$^3$</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Reactions are fast if the reactants have similar bond distances.
Quantitative interpretation of outer sphere electron transfer reaction rates

$$\Delta G^\ddagger = \frac{w}{2} + \frac{\lambda}{4} \left(1 + \frac{\Delta G^o}{\lambda}\right)^2$$

$w =$ work term (energy required to bring two reactants together), $\lambda =$ total reorganisation energy (includes solvent reorganisation and bond length changes of reactants)

For many reactions involving complexes of opposite charge or if the reactants are effectively fixed in space such as in a protein $w \approx 0$. Therefore

$$\Delta G^\ddagger = \frac{\lambda}{4} \left(1 + \frac{\Delta G^o}{\lambda}\right)^2$$

and for a self exchange reaction $\Delta G^o = 0$.

Note that a thermodynamic parameter ($\Delta G^o_{AB}$) is being used in a kinetic expression

Recap

Eyring equation relates rate constants and free energy of activation

$$k = \frac{k_B T}{h} e^{-\Delta G^\ddagger RT}$$

$k =$ rate constant, $k_B =$ Boltzmann constant, $\Delta G^\ddagger =$ free energy of activation (kinetic), $\Delta G^o =$ free energy of reaction (thermodynamic).
**rem** \( \Delta G^o \) is negative for a spontaneous reaction

\[
\Delta G^o = \lambda \quad \Delta G > 0 \\
\Delta G < \lambda \quad \Delta G > 0 \\
\Delta G > \lambda \quad \Delta G > 0
\]

In the inverted region the rate \( k \) decreases as the thermodynamic driving force increases!

This is most easily visualised using a potential energy diagram

1. Normal Region \( \Delta G^\dagger > 0 \)
2. \( \Delta G^\dagger = 0 \)
3. Marcus Inverted Region \( \Delta G > 0 \)

\( \Delta G^o \) 3 > 2 > 1

The Marcus inverted region is probably important in photosynthesis where wasteful back electron transfer reactions (which are highly exothermic) are prevented.

Chlorophyll absorbs the light.
The recombination of the photoelectron with the oxidised chlorophyll is retarded (to \(~30\) ns).
This allows electron transfer away from the reaction centre
Inner sphere electron transfer

Inner sphere electron transfer is mediated by a bridging ligand.

i) Reductant and oxidant share a ligand in the precursor and successor complex.

ii) On activation the electron is transferred between the metals.

iii) The ligand may transfer between complexes.

\[
\begin{align*}
M^{III}L_5X & \quad + \quad M^{II}Y_5 \\
O & \quad R \\
\xrightarrow{k_a \quad \frac{1}{k_a}} \quad \{L_5M^{III}X \quad - \quad M^{II}Y_5\} & \quad + \quad Y \\
k_{ET} \quad \{L_5M^{III}X \quad - \quad M^{II}Y_5\} & \quad \xrightarrow{k_d} \quad L_5M^{II}Y & \quad + \quad XM^{III}Y_5 \\
Y & \quad \{L_5M^{III}X \quad - \quad M^{II}Y_5\} \\
or \quad Y & \quad \{L_5M^{III}X \quad - \quad M^{II}Y_5\} \\
\end{align*}
\]

In \(O_h\) complexes dissociation of a ligand is required to form bridge

\[
[\text{Co}^{3+}(\text{NH}_3)_5]^+ + [\text{Cr}(\text{H}_2\text{O})_6]^{2+} \xrightarrow{k = 10^{-3} \text{ M}^{-1}\text{s}^{-1}} [\text{Co}(\text{H}_2\text{O})_5]^2+ + [\text{Cr}(\text{H}_2\text{O})_6]^{3+} + 6 \text{NH}_3
\]

outer sphere mechanism

add Cl\(^-\):

\[
[\text{Co}^{3+}(\text{NH}_3)_5\text{Cl}]^{2+} + [\text{Cr}(\text{H}_2\text{O})_6]^{2+} \xrightarrow{k = 6 \times 10^{5}} [\text{Co}(\text{H}_2\text{O})_5]^{2+} + [\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}^{2+} + 5 \text{NH}_3
\]

inner sphere mechanism (Cl\(^-\) transfer)

Conclusive proof of inner sphere mechanism

If we use [Co(NH\(_3\)_5Cl]\(^{2+}\) at start and add Cl\(^-\), Cl\(^-\) is not in final product.
However ligand transfer is not a requirement of inner sphere mechanism

\[
\begin{align*}
[\text{IrCl}_6]^{2-} & \quad \text{+} \quad [\text{Cr(H}_2\text{O})_6]^{2+} \\
\text{t}_{2g}^5 & \quad \text{t}_{2g}^3e_g^1 \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{H}_2\text{O} & \quad \text{H}_2\text{O} & \quad \text{OH}_2 \\
\text{Ir} & \quad \text{Ir} & \quad \text{Cr} & \quad \text{Cr} \\
\text{OH}_2 & \quad \text{H}_2\text{O} & \quad \text{H}_2\text{O} & \quad \text{H}_2\text{O} \\
\text{Cl} & \quad \text{Cl} & \quad \text{Cl} & \quad \text{Cl} \\
\end{align*}
\]

Transfer is determined by relevant bond strengths \(\text{Ir-Cl + Ir-OH}_2\) vs \(\text{Cr-Cl + Cr-OH}_2\)

**Factors that affect the rate of inner sphere electron transfer reactions**

\[
\begin{align*}
\text{ET} & \quad \text{bridging complex formation} \\
\text{L Diss} & \quad \text{bridging complex scission} \\
\text{L Assoc} & \\
\end{align*}
\]

reaction coordinate

Self Exchange

i) Formation of the bridging complex can be the rate limiting step \((k_a)\). This will be dependent on how inert or labile the complexes are. \((k_{ET} vs k_a)\). It is also possible that dissociation \((k_d)\) is the rate limiting step.

Formation of bridging complex is rate determining scission

\[
\begin{align*}
\text{ET} & \quad \text{bridging complex formation} \\
\text{L Diss} & \quad \text{bridging complex cission} \\
\text{L Assoc} & \\
\end{align*}
\]

reaction coordinate
ii) Electronic configurations. $\sigma^*$ (‘e$_g$’) orbitals interact strongly with bridging ligand. Orbital symmetries of metal $\sigma^*$ and bridging ligands facilitate electron transfer. Massive acceleration in rates from outer to inner sphere can be achieved.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>HOMO</th>
<th>LUMO</th>
<th>Acceleration IS/OS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cr}^{2+} + \text{Co}^{3+}$</td>
<td>$\sigma^*$</td>
<td>$\sigma^*$</td>
<td>$\sim 10^{10}$</td>
</tr>
<tr>
<td>$\text{Cr}^{2+} + \text{Ru}^{3+}$</td>
<td>$\sigma^*$</td>
<td>$\pi^*(\pi)$</td>
<td>$\sim 10^2$</td>
</tr>
<tr>
<td>$\text{V}^{2+} + \text{Co}^{3+}$</td>
<td>$\pi^*$</td>
<td>$\sigma^*$</td>
<td>$\sim 10^4$</td>
</tr>
<tr>
<td>$\text{V}^{2+} + \text{Ru}^{3+}$</td>
<td>$\pi$</td>
<td>$\pi$</td>
<td>All OS</td>
</tr>
</tbody>
</table>

$\sigma^*$

$\pi/\pi^*$

Cr$^{2+}$  Co$^{3+}$  Large reorganisation for Co$^{3+}$ OS. IS much faster

Cr$^{2+}$  Ru$^{3+}$  Reorganisation of Ru$^{3+}$ less than Co$^{3+}$  Co$^{3+}$ Reorganisation IS faster

V$^{2+}$  Co$^{3+}$  V$^{2+}$  Ru$^{3+}$  Easily go OS.  No reorganisation

iii) Bridging ligand. Inner sphere electron transfer is very sensitive to bridging ligand.

1) The bridge connects the two metals.

$\text{(NH}_3)_5\text{CoO}_2\text{Cr}^{2+}_{(aq)} + \text{Cr}^{2+}_{(aq)} \rightarrow \text{(NH}_3)_5\text{CoO}_2\text{R}^+ + \text{Cr}^{3+}_{(aq)}$

\[ R = \text{H, Me, Ph, } ^{t}\text{Bu} \]

\[ k \text{ M}^{-1}\text{s}^{-1} = 7.2, 0.35, 0.15, 9.6 \times 10^{-3} \]

Increasing bulk of R slows binding of Cr$^{2+}$ to bridge
2) Transfer can be a two step process from metal to ligand then ligand to metal. This circumvents the simultaneous reorganisation energy of both complexes that is required for outer sphere.

![Diagram showing electron transfer processes and reactions](image)

How do we distinguish if electron transfer is outer or inner sphere?

- Is there a vacant coordination site?
- Is there a substitutionally labile reactant?
- Has ligand transfer occurred?
- Are there large differences in rate on addition or substitution of potentially bridging ligand?

A good test is to compare electron transfer rates of N\textsubscript{3}\textsuperscript{-} and NCS\textsuperscript{-} complexes.

\[ \text{E}_{\text{\textit{f}}} (\Delta G^\text{\textit{o}}\textsuperscript{'}s) \text{ of N}_3\textsuperscript{-} \text{ and NCS}\textsuperscript{-} \text{ complexes are similar.} \]

If \( k_{N3^-}/k_{NCS^-} \approx 1 \) (OS). If \( k_{N3^-}/k_{NCS^-} \gg 1 \) (IS). This is because N\textsubscript{3}\textsuperscript{-} is symmetric.

<table>
<thead>
<tr>
<th>O</th>
<th>R</th>
<th>( k_{N3^-}/k_{NCS^-} )</th>
<th>rxn type</th>
</tr>
</thead>
<tbody>
<tr>
<td>[((NH\textsubscript{3})\textsubscript{5}CoX\textsuperscript{2+})</td>
<td>Cr\textsuperscript{2+}</td>
<td>10\textsuperscript{4}</td>
<td>IS</td>
</tr>
<tr>
<td>[((NH\textsubscript{3})\textsubscript{5}CoX\textsuperscript{2+})</td>
<td>V\textsuperscript{2+}</td>
<td>27</td>
<td>intermediate</td>
</tr>
<tr>
<td>[((NH\textsubscript{3})\textsubscript{5}CoX\textsuperscript{2+})</td>
<td>Fe\textsuperscript{2+}</td>
<td>&gt; 3 \times 10\textsuperscript{3}</td>
<td>IS</td>
</tr>
<tr>
<td>[((NH\textsubscript{3})\textsubscript{5}CoX\textsuperscript{2+})</td>
<td>Cr(bipy)\textsubscript{3}\textsuperscript{2+}</td>
<td>4</td>
<td>OS</td>
</tr>
<tr>
<td>[((H\textsubscript{2}O)\textsubscript{5}CoX\textsuperscript{2+})</td>
<td>Cr\textsuperscript{2+}</td>
<td>4 \times 10\textsuperscript{4}</td>
<td>IS</td>
</tr>
</tbody>
</table>

M-N=N=N-M
'faster' electron transfer
A.O. energies are more uniform
M.O. 'smoother'

M-N=C=S-M
'slower' electron transfer
greater difference between A.O. energies
M.O. 'rougher'