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Schedule

• Lecture 7: M-M bonds
  δ-bonds and bonding in metal clusters

• Lecture 8: Rates of reaction
  Ligand-exchange reactions, labile and inert metal ions

• Lecture 9: Redox reactions
  Inner and outer-sphere reactions
Summary of Last Lecture

Ligand substitution reactions

• Dissociative and associative mechanisms possible
• Rates vary widely for transition metal complexes
  ➢ $M^{3+}$ slower than $M^{2+}$
  ➢ $d^n$ with large LFSE are slow ($d^3$, $d^8$ and low spin $d^{5-7}$)

Today’s lecture

• e⁻ transfer reactions
Redox Reactions

• Redox reactions are very important in inorganic and bioinorganic chemistry. The shuttling of electrons between transition metal cations is at the centre of a wide variety of vital biological processes.

• Redox reactions involving transition metal complexes generally occur very rapidly:
  - thermodynamics (using $E^0$ values) is very useful in predicting the outcome of reactions.

• $e^-$ transfer reactions appear to occur via two reaction mechanisms:
  - outer sphere
  - inner sphere
Outer Sphere e\textsuperscript{-} Transfer

- The self-exchange reaction below is believed to occur via an outer sphere mechanism

\[
*\text{Fe(H}_2\text{O)}_6^{2+} + \text{Fe(H}_2\text{O)}_6^{3+} \rightarrow *\text{Fe(H}_2\text{O)}_6^{3+} + \text{Fe(H}_2\text{O)}_6^{2+}
\]

- The two complexes (the **reductant** and the **oxidant**):
  - diffuse together in solution to form **outer sphere** complex,
  - an electron is transferred from reductant to oxidant
  - the complexes diffuse apart
  - the ligands remain attached throughout the reaction

- Most redox reactions in biology occur via this mechanism
  - **Marcus theory** explains the rate of these reactions (1992 Nobel prize for Chemistry)
Outer Sphere $e^-$ Transfer

- The self-exchange reaction below is believed to occur via an outer sphere mechanism

$^{*}\text{Fe(H}_2\text{O)}_6^{2+} + \text{Fe(H}_2\text{O)}_6^{3+} \rightarrow ^{*}\text{Fe(H}_2\text{O)}_6^{3+} + \text{Fe(H}_2\text{O)}_6^{2+} \quad \Delta G = 0$

- $e^-$ transfer occurs very rapidly - nuclei are too heavy to respond the Franck-Condon principle

- The products are formed with the geometries of the reactants

- After formation, they can relax to their true bond lengths
Outer Sphere e\(^{-}\) Transfer

- The products are formed with the geometries of the reactants:
  - ionic radii: Fe\(^{2+}\) (75 pm) > Fe\(^{3+}\) (69 pm)
  - if reactants are in their ground states, the products will be formed in excited states:

\[
\begin{align*}
*[(\text{H}_2\text{O})_5\text{Fe}―\text{OH}_2]^{2+} & \quad \text{e}^- \\
[(\text{H}_2\text{O})_5\text{Fe}-\text{OH}_2]^{3+} & \quad \longrightarrow \\
*[(\text{H}_2\text{O})_5\text{Fe}―\text{OH}_2]^{3+} & \quad \text{bonds too long}
\end{align*}
\]

\[
\begin{align*}
[(\text{H}_2\text{O})_5\text{Fe}-\text{OH}_2]^{3+} & \quad \text{transfer} \\
*[(\text{H}_2\text{O})_5\text{Fe}―\text{OH}_2]^{2+} & \quad \text{bonds too short}
\end{align*}
\]

- These excited states will then relax, releasing energy
- BUT \(\Delta G = 0\) so energy seems to have been created from nothing

\[
*[((\text{H}_2\text{O})_5\text{Fe}-\text{OH}_2]^{3+} \\
\text{relax} \\
[(\text{H}_2\text{O})_5\text{Fe}―\text{OH}_2]^{2+}
\]

\text{REACTION CANNOT BE OCCURRING FROM GROUND STATES}
Outer Sphere e⁻ Transfer

- There is an activation step in which bonds in Fe(H₂O)₅²⁺ are shortened and those in Fe(H₂O)₆³⁺ are lengthened so they are exactly the same.

![Diagram](image)

- Activation energy provided in (1) = relaxation energy in (3) so $\Delta G = 0$.
Outer Sphere e⁻ Transfer

• The activation step involves making the bond lengths in oxidant and reductant the same:
  
  ➢ if oxidant and reductant have very different bond lengths →
    activation energy is large → reaction is slow

  ➢ if oxidant and reductant have similar bond lengths →
    activation energy is small → reaction is fast

Need to compare bond lengths in oxidant and reductant to understand rate:

• Metals get smaller across period due to increasing Z
• Occupation of $e_g^*$ orbitals lengthens bonds
• $M^{3+}$ are smaller than $M^{2+}$ due to charge
Ionic Radii - Recap

Radii of $M^{2+}$ ions (pm)

- Occupation of $e_g^*$ orbitals lengthens bonds
- Metals get smaller across period due to increasing $Z$
Ionic Radii - Recap

- Occupation of $e_g^*$ orbitals lengthens bonds
- Metals get smaller across period due to increasing $Z$
- $M^{3+}$ are smaller than $M^{2+}$ due to charge
Outer Sphere e$^-\$ Transfer

- The activation step involves making the bond lengths in oxidant and reductant the same:
  - if oxidant and reductant have very different bond lengths $\rightarrow$ activation energy is large $\rightarrow$ reaction is slow
  - if oxidant and reductant have similar bond lengths $\rightarrow$ activation energy is small $\rightarrow$ reaction is fast

<table>
<thead>
<tr>
<th>metal ion pair</th>
<th>difference in M-O bond lengths</th>
<th>rate constant (M$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{2+}$(aq) ($d^6$), Fe$^{3+}$(aq) ($d^5$)</td>
<td>13 pm</td>
<td>4</td>
</tr>
<tr>
<td>Cr$^{2+}$(aq) ($d^4$), Cr$^{3+}$(aq) ($d^3$)</td>
<td>18 pm</td>
<td>$2 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
Inner Sphere e⁻ Transfer

- A different and *faster* mechanism operates if
  - either the oxidant or the reductant possesses a ligand capable of bonding to two metals at once ("bridging") AND
  - the other reactant is labile (able to exchange ligands)

\[
\text{[Cr(H}_2\text{O)}_6\text{]}^{2+} + \text{[Co(H}_2\text{O)}_5\text{(Cl)}]\text{]}^{2+} \rightarrow \text{[H}_2\text{O)}_5\text{Cr-Cl-Co(H}_2\text{O)}_5\text{]}^{4+} + \text{H}_2\text{O} \\
\text{inner-sphere complex}
\]

\[
\text{[H}_2\text{O)}_5\text{Cr-Cl-Co(H}_2\text{O)}_5\text{]}^{4+} \underset{\text{e}^- \text{ transfer}}{\rightarrow} \text{[H}_2\text{O)}_5\text{Cr-Cl-Co(H}_2\text{O)}_5\text{]}^{4+} \\
\text{Cr(II)-Cl-Co(III)} \quad \text{Cr(III)-Cl-Co(II)} \\
\text{inner-sphere complex} \quad \text{inner-sphere complex}
\]

\[
\text{[H}_2\text{O)}_5\text{Cr-Cl-Co(H}_2\text{O)}_5\text{]}^{4+} + \text{H}_2\text{O} \rightarrow \text{[H}_2\text{O)}_5\text{Cr-Cl]}^{2+} + \text{[Co(H}_2\text{O)}_6\text{]}^{2+}
\]
Inner Sphere e\textsuperscript{-} Transfer

• The inner sphere reaction is possible as
  - Cl\textsuperscript{-} has >1 lone pair so can bond to Cr and Co in the inner-sphere complex
  - Cr\textsuperscript{2+} is labile (d\textsuperscript{4} – Jahn-Teller distorted)

• Note that
  - once e\textsuperscript{-} transfer has occurred, it is the Co\textsuperscript{2+} which is labile and Cr\textsuperscript{3+} is inert
  - therefore bridging ligand leaves with Cr\textsuperscript{3+}

\[
[(\text{H}_2\text{O})_5\text{Cr-Cl-Co(}\text{H}_2\text{O})_5]^4+ + \text{H}_2\text{O} \rightarrow [(\text{H}_2\text{O})_5\text{Cr-Cl}]^{2+} + [\text{Co(}\text{H}_2\text{O})_6]^{2+}
\]

Cr(III)-Cl-Co(II)
inner-sphere complex
Toxicity of $\text{CrO}_4^-$

- $\text{CrO}_4^-$ is a powerful oxidizing agent:

$$\text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3\text{e}^- \rightarrow \text{Cr(OH)}_3 + 5\text{OH}^- \quad E^0 = +0.6 \text{ V}$$

- It acts as a skin irritant due to oxidation of organic molecules
  - however, as reduction is a $3\text{e}^-$ process, it is metastable as few organic oxidations involve 3 electrons

- It therefore passes through the skin
  - it has a very similar structure to $\text{SO}_4^{2-}$ and is therefore “allowed” to pass through cell and nuclear membranes

- In the cell nucleus
  - it slowly reduces to $\text{Cr(III)}$ (by oxidizing DNA or proteins)
  - $\text{Cr}^{3+}$ binds to DNA and proteins causing mutations and cancers
  - $\text{Cr}^{3+}$ ($d^3$) is inert so it is very difficult to remove
Summary

By now you should be able to....

• Explain that the key steps in the outer sphere mechanism
• Explain why the activation step involves the bond lengths in oxidant and reductant becoming the same
• Explain why and predict why the difference in oxidant and reductant bond lengths affects the rate
• Explain the key steps in the inner sphere mechanism
• Predict whether an e transfer mechanism can occur via the inner sphere mechanism by looking for the presence of a bridging ligand on one reactant and the lability of the other reactant
Practice

1. Explain the differences in the rate constants for the following self-exchange, electron transfer reactions:

\[
\begin{align*}
[\text{Fe(H}_2\text{O)}_6]^{2+} + [\text{Fe(H}_2\text{O)}_6]^{3+} & \rightarrow [\text{Fe(H}_2\text{O)}_6]^{3+} + [\text{Fe(H}_2\text{O)}_6]^{2+} & \text{k} = 4 \text{ M}^{-1} \text{s}^{-1} \\
[\text{Fe(bpy)}_6]^{2+} + [\text{Fe(bpy)}_6]^{3+} & \rightarrow [\text{Fe(bpy)}_6]^{3+} + [\text{Fe(bpy)}_6]^{2+} & \text{k} > 10^6 \text{ M}^{-1} \text{s}^{-1} \\
[\text{Co(NH}_3)_6]^{2+} + [\text{Co(NH}_3)_6]^{3+} & \rightarrow [\text{Co(NH}_3)_6]^{3+} + [\text{Co(NH}_3)_6]^{2+} & \text{k} = 10^{-6} \text{ M}^{-1} \text{s}^{-1} \\
\end{align*}
\]

(Hint: bpy = bipyridyl, a strong-field ligand, [Co(NH₃)₆]³⁺ is diamagnetic).

2. The rate of reduction of [Co(NH₃)₅(H₂O)]³⁺ by Cr²⁺(aq) is seven orders of magnitude slower than reduction of its conjugate base, [Co(NH₃)₅(OH)]³⁺ by Cr²⁺(aq). The rates of the reduction of the same cobalt complexes by [Ru(NH₃)₆]²⁺ differ by only a factor of 10.

Explain these observations.

(Hint: OH⁻ is able to bridge)
Summary of Course – week 4

Ligand-field (‘d-d’) spectroscopy
• be able to predict/explain number of bands for d\(^1\)-d\(^9\) (high-spin)
• be able to calculate \(\Delta_{\text{oct}}\) for d\(^1\), d\(^3\), d\(^4\), d\(^6\), d\(^7\), d\(^8\) and d\(^9\)
• be able to explain differences in band intensity (spin forbidden, orbitally forbidden, Laporte forbidden)
• be able to explain the appearance of charge transfer transitions
• be able to explain and predict the occurrence of the Jahn-Teller effect and its consequences (structural, spectroscopic, reaction rates)

Resources
• Slides for lectures 1-4
• Shriver and Atkins “Inorganic Chemistry” Chapter 9 (4\(^{th}\) Edition)
• Housecroft and Sharpe “Inorganic Chemistry” Chapter 20.6-7 (2\(^{nd}\) Edition)
Complexes of π-acceptor ligands

- be able to explain synergic (σ-donation, π-back donation) model for bonding in M-CO and M-N₂ complexes
- be able to explain reduction in CO stretching frequency in complex
- be able to explain changes in CO stretching frequency with metal charge and with ligands
- electron counting in CO, N₂ and NO complexes: 18 e⁻ rule

Resources

- Slides for lectures 5-6
- Housecroft and Sharpe “Inorganic Chemistry” Chapter 23.2 (2nd Edition)
Summary of Course – week 6

**Metal-metal bonding**
- be able to predict bond order for $M_2L_x$ dimers using d-electron count and $\sigma$, $\pi$ and $\delta$ molecular orbital diagram
- be able to predict bond order in larger metal-halide clusters using d-electron count shared over edges of cluster
- be able to predict bond order in metal carbonyl clusters using 18 e$^-$ rule

**Reaction mechanisms**
- be able to describe ligand exchange mechanisms
- be able to explain role of metal charge and LFSE in rate of ligand exchange
- be able to describe electron transfer reaction mechanisms
- be able to predict relative rate of outer sphere reaction for different metals

**Resources**
- Slides for lectures 7-9
- Housecroft and Sharpe “Inorganic Chemistry” Chapter 23.6, 25