Intramolecular Valence and Spin Interactions

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Naturally Occurring Mixed-Valence Systems

(Cys)$_2$Fe$^{II}$(µ - S)$_2$Fe$^{III}$(Cys)$_2$ ([2Fe-2S]$^+$ centers in proteins)

Fe$_3^{II/III}$O$_4$
Magnetite

Mn$^{II/III/IV}$ clusters in Photosystem II

Cu$^I$/Cu$^{II}$ in cytochrome c-oxidase

First Naturally Occurring Mixed Valence Compound

Prussian blue
By Diesbach of Berlin
In 1704

First designed mixed valence compounds

Creutz-Taube ion:

\[
\text{Fe}\left[\text{Fe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6\right]_3
\]

Creutz and Taube:


Molecular electronics devices: wires, switches, quantum cellular automata and molecular computing or Optical devices

Initial Impetus

Understanding of Biological e\textsuperscript{-} - Transfer processes

Solomon et. al., Chem. Rev., 2000, 100, 235

Recent Focus

Lieberman et. al., J. Am. Chem. Soc., 2003, 125, 1056
Launay et. al., J. Am. Chem. Soc., 2003, 125, 5880
Modes of $M^{n+}$ - $BL^-$ $M^{(n+1)+}$ interaction

- **Electron transfer mechanism**

- **Hole transfer mechanism**

Energy

$\Phi_{\pi^* L}$

$\Phi_{d\pi(M_1)} \rightarrow \Phi_{d\pi(M_2)}$

$\Delta E (d\pi / \pi^*)$

$\Phi_{\pi L}$

$\Phi_{d\pi(M_1)} \rightarrow \Phi_{d\pi(M_2)}$

$\Delta E (d\pi / \pi)$

$\Delta E (d\pi / \pi^*)$
Manifestation of M – BL – M coupling

Charge dependent electrochemical coupling:

\[ [2,2] + [3,3] \rightleftharpoons 2[2,3] \]

\[ \Delta G^0 = -RT\ln K_C = -nF(\Delta E) \]

\[ \log K_C = \Delta E / 0.059 \quad (n = 1) \]

\[ \Delta G_C = \Delta G_S + \Delta G_e + \Delta G_i + \Delta G_r + \Delta G_{ex} + \Delta G_{ip} \]

Three different possibilities:

- **class I**: \( K_C \), 4  
  no coupling between the redox sites

- **class II**: \( K_C \), \( 10^2 \) to \( 10^5 \)  
  thermal activation dependent valence localization

- **class III**: \( K_C \), \( 10^6 \) onwards  
  no thermal barrier-valence delocalization

Orbital controlled electronic coupling (IVCT)

class II (Localized) : Solvent dependent broad IVCT band in the NIR region-
Obeys Hush formula: \( \Delta \nu_{1/2}^{\text{IVCT(Calc.)}} \cong \Delta \nu_{1/2}^{\text{IVCT(Exp.)}} \)

\[
\Delta \nu_{1/2}^{\text{(Calc.)}} = [2.31 \times 10^3 (E_{\text{abs}})]^{1/2}
\]

class III (Delocalized) : Solvent independent narrow IVCT band in the NIR region-
Does not obey Hush formula: \( \Delta \nu_{1/2}^{\text{(Exp.)}} << \Delta \nu_{1/2}^{\text{(Calc.)}} \)


II-III hybrid (Borderline) : e\(^{-}\)-transfer rates are in the order of solvent relaxation time
\(~10^{12} \text{ s}^{-1} \text{ but } <10^{15} \text{ s}^{-1}\)
Structure / Theory:

UV-Vis-NIR Spectroelectrochemistry:

IR Spectroelectrochemistry: Monitoring of $\nu_{CO}$ band

Redox:

EPR Silent

EPR active

B/G

$2^+ \rightarrow \text{III, II}$

$\text{II, III} \rightarrow \text{II, II}$

$\nu / \text{cm}^{-1}$

1720 1680 1640
Redox Non-innocent Bridging Ligand

If frontier orbitals of 'BL' are in competition with those of 'M'

Mixed Valant or Radical Bridged Isovalent or Radical Bridged Mixed Valant

State in Accessible $e^{-}$ - Transfer Series

and

If Mixed valent state in true sense

then

Valence Localized or Delocalized State
Inorg. Chem., 2010, 49, 6565
$K_c \cdot 10^7$

Ligand Reductions
$\Delta \nu_{1/2} \text{Cal/Exp: 3830/1150 cm}^{-1}$

Ru$^{III}$Ru$^{II}$

Ru$^{III}$Ru$^{III}$

Ru1: 0.605; Ru2: 0.579
Ru: 1.7113
L: 0.1049
acac: 0.1838

$E_{S=0} - E_{S=1} : 1.3437 \text{ eV} (10837.4 \text{ cm}^{-1})$

\[
\Delta v_{1/2} / \text{cm}^{-1} = 20 \quad 30 \quad 22
\]

\[\text{Ru}^{III}\text{Ru}^{II}\]

Ru1: 0.4601; Ru2: 0.6853
Inorg. Chem., 2006, 45, 7955

Inorg. Chem., 2007, 46, 3736

Rac : $J = -21.07 \text{ cm}^{-1}$

Meso : $J = -37.14 \text{ cm}^{-1}$
and

Ru$_{III}$Ru$_{III}$ $\xrightleftharpoons{\text{ox1}}$ Ru$_{III}$Ru$_{IV}$  
Ru$_{III}$Ru$_{IV}$ $\xrightleftharpoons{\text{ox2}}$ Ru$_{IV}$Ru$_{IV}$

Ru$_{III}$Ru$_{III}$ $\xrightarrow{\text{red1}}$ Ru$_{III}$Ru$_{II}$  
Ru$_{III}$Ru$_{II}$ $\xrightarrow{\text{red2}}$ Ru$_{II}$Ru$_{II}$
rac and meso

\[
\text{Ru}^{\text{III}}(\mu-\text{L}^-)\text{Ru}^{\text{III}} \quad \text{or} \quad \text{Ru}^{\text{III}}(\mu-\text{L}^0)\text{Ru}^{\text{III}}
\]

\[
\text{Ru}^{\text{III}}(\mu-\text{L}^2^-)\text{Ru}^{\text{III}} \quad \text{or} \quad \text{Ru}^{\text{IV}}(\mu-\text{L}^-)\text{Ru}^{\text{IV}}
\]

\[
\text{Ru}^{\text{III}}(\mu-\text{L}^2^-)\text{Ru}^{\text{III}} \quad \text{or} \quad \text{Ru}^{\text{II}}(\mu-\text{L}^-)\text{Ru}^{\text{II}}
\]

2$^-$ \rightarrow 2$^-$

\[
10^{-3} \varepsilon / \text{M} \cdot \text{cm}^{-1}
\]

\[
\lambda / \text{nm}
\]

\[
3320 \quad 3360 \quad 3400
\]

\[
\text{B / G}
\]

\[
2000 \quad 2500 \quad 3000 \quad 3500 \quad 4000
\]

\[
\text{B / G}
\]

\[
500 \quad 1000 \quad 1500 \quad 2000
\]

\[
0 \quad 5 \quad 10 \quad 15 \quad 20
\]

\[
10^{-3} \varepsilon / \text{M} \cdot \text{cm}^{-1}
\]

\[
\lambda / \text{nm}
\]
J. Am. Chem. Soc., 2009, 131, 8895

<table>
<thead>
<tr>
<th>E (V)</th>
<th>$K_c$</th>
<th>assigned oxidation state distribution</th>
<th>alternative(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>[ClQ°RuIII(μ-tppz)RuIIIQ°Cl]+</td>
<td>[ClQ°RuIV(μ-tppz)RuIVQ°Cl]+</td>
</tr>
<tr>
<td>1.29</td>
<td></td>
<td>$-e^- + e^-$</td>
<td>[\text{ClQ}°\text{RuIII(μ-tppz)RuIIIQ°Cl}^+] \text{ or } \text{ClQ}°\text{RuIV(μ-tppz)RuIVQ°Cl}^+]</td>
</tr>
<tr>
<td>10^6.1</td>
<td>0.93</td>
<td>$-e^- + e^-$</td>
<td>[\text{ClQ}°\text{Ru^II(μ-tppz)RuIIIQ°Cl}^+ \text{ or } \text{ClQ}°\text{RuIII(μ-tppz)RuIIIQ°Cl}^+] \text{ or } \text{ClQ}°\text{RuIV(μ-tppz)RuIVQ°Cl}^+]</td>
</tr>
<tr>
<td>-0.38</td>
<td></td>
<td>$-e^- + e^-$</td>
<td>[\text{ClQ}°\text{Ru^II(μ-tppz)RuIIIQ°Cl}^+ \text{ or } \text{ClQ}°\text{RuIV(μ-tppz)RuIVQ°Cl}^+] \text{ or } \text{ClQ}°\text{RuIV(μ-tppz)RuIVQ°Cl}^+]</td>
</tr>
<tr>
<td>10^{-2.9}</td>
<td>-0.55</td>
<td>$-e^- + e^-$</td>
<td>[\text{ClQ}°\text{Ru^II(μ-tppz)RuIIIQ°Cl}^+ \text{ or } \text{ClQ}°\text{RuIV(μ-tppz)RuIVQ°Cl}^+] \text{ or } \text{ClQ}°\text{RuIV(μ-tppz)RuIVQ°Cl}^+]</td>
</tr>
<tr>
<td>-1.15</td>
<td></td>
<td>$-e^- + e^-$</td>
<td>[\text{ClQ}°\text{Ru^II(μ-tppz)RuIIIQ°Cl}^+ \text{ or } \text{ClQ}°\text{RuIV(μ-tppz)RuIVQ°Cl}^+] \text{ or } \text{ClQ}°\text{RuIV(μ-tppz)RuIVQ°Cl}^+]</td>
</tr>
<tr>
<td>10^{1.9}</td>
<td>-1.44</td>
<td>$-e^- + e^-$</td>
<td>[\text{ClQ}°\text{Ru^II(μ-tppz)RuIIIQ°Cl}^+ \text{ or } \text{ClQ}°\text{RuIV(μ-tppz)RuIVQ°Cl}^+] \text{ or } \text{ClQ}°\text{RuIV(μ-tppz)RuIVQ°Cl}^+]</td>
</tr>
<tr>
<td>-1.86</td>
<td></td>
<td>$-e^- + e^-$</td>
<td>[\text{ClQ}°\text{Ru^II(μ-tppz)RuIIIQ°Cl}^+ \text{ or } \text{ClQ}°\text{RuIV(μ-tppz)RuIVQ°Cl}^+] \text{ or } \text{ClQ}°\text{RuIV(μ-tppz)RuIVQ°Cl}^+]</td>
</tr>
</tbody>
</table>

Ru: 1.116; tppz:-0.280; Cl:0.186; Q:-0.067
Ru---Ru = 8.49 Å


At the metal site

\[ \text{Ru}^{III}\text{Ru}^{III} \rightleftharpoons \text{Ru}^{III}\text{Ru}^{IV} \quad \text{and} \quad \text{Ru}^{III}\text{Ru}^{IV} \rightleftharpoons \text{Ru}^{IV}\text{Ru}^{IV} \]

\[ \text{Ru}^{III}\text{Ru}^{III} \rightleftharpoons \text{Ru}^{III}\text{Ru}^{II} \quad \text{and} \quad \text{Ru}^{III}\text{Ru}^{II} \rightleftharpoons \text{Ru}^{II}\text{Ru}^{II} \]

At the bridging ligand site

\[ L_1^{2-} / L_2^{2-} \]

\[ L_3^{2-} / L_4^{2-} \]

\[ L_5^{2-} / L_6^{2-} \]
(L⁰)Ru IV₂
-e⁻∥+e⁻

(L⁻)Ru IV₂ ↔ (L⁰)Ru III Ru IV
-e⁻∥+e⁻

(L²⁻)Ru IV₂ ↔ (L⁻)Ru III Ru IV ↔ (L⁰)Ru III₂
-e⁻∥+e⁻

(L³⁻)Ru IV₂ ↔ (L²⁻)Ru III Ru IV ↔ (L⁻)Ru III₂ ↔ (L⁰)Ru III Ru II
-e⁻∥+e⁻

(L⁴⁻)Ru IV₂ ↔ (L³⁻)Ru III Ru IV ↔ (L²⁻)Ru III₂ ↔ (L⁻)Ru III Ru II ↔ (L⁰)Ru II₂
-e⁻∥+e⁻

(L⁴⁻)Ru III Ru IV ↔ (L³⁻)Ru III₂ ↔ (L²⁻)Ru III Ru II ↔ (L⁻)Ru II₂
-e⁻∥+e⁻

(L⁴⁻)Ru III₂ ↔ (L³⁻)Ru III Ru II ↔ (L²⁻)Ru II₂
-e⁻∥+e⁻

(L⁴⁻)Ru III Ru II ↔ (L³⁻)Ru II₂
-e⁻∥+e⁻
\[
\begin{align*}
[Ru^{IV}(\mu-\text{BL}^{2-})Ru^{IV}]^{2+} & \quad -e^- + e^- \\
[Ru^{III}(\mu-\text{BL}^{2-})Ru^{IV}]^+ & \quad -e^- + e^- \\
[Ru^{III}(\mu-\text{BL}^{2-})Ru^{III}] & \quad -e^- + e^- \\
[Ru^{III}(\mu-\text{BL}^{3-})Ru^{III}]^- & \quad -e^- + e^- \\
[Ru^{III}(\mu-\text{BL}^{4-})Ru^{III}]^{2-} & \quad -e^- + e^- \\
[Ru^{III}(\mu-\text{BL}^{4-})Ru^{II}]^{3-} & \\
\end{align*}
\]
\[ \text{rac} \]

\[ \text{meso} \]


$\text{Ru}^{\text{II}}(\text{acac})_2$  

$\text{S} = 0$

$\text{Ru}^{\text{III}}(\text{acac})_2$  

$\text{S} = 0$

$\text{Ru}^{\text{III}}(\text{acac})_2$  

$\text{S} = 0$

$\text{RN} = \text{NR}$  

$\text{RN} = \text{NR}$

$+e^- \xrightarrow{\text{+e}^-} (\text{RN} = \text{NR})^-$

$\approx 1.35 \text{ Å}$

$\text{RN} = \text{NR}$  

$\text{RN} = \text{NR}$

$+e^- \xrightarrow{\text{+e}^-} (\text{RN} - \text{NR})^{2-}$

$1.40 - 1.45 \text{ Å}$

$\text{rac}$

$N=N$:  

$1.344 \text{ Å (DFT)}$

$1.365 \text{ Å (X-ray)}$

$\text{meso}$

$N=N$:  

$1.349 \text{ Å (DFT)}$

$1.374 \text{ Å (X-ray)}$
N=N : 1.26 Å
N=N : 1.33 Å
N=N : 1.30 Å
N=N : 1.374 Å

S = 0

M^{II}(\mu-L) M^{II} \xrightarrow{MLCT} [M^{III}(\mu-L^{2-}) M^{II}]
N = N (Å) : 1.299(3)

(RN=NR)$^0$ $\overset{+e^-}{\leftrightarrow}$$\overset{-e^-}{\rightarrow}$ (RN=NR)$^-$

1.23-1.30 Å

(RN=NR)$^-$ $\overset{+e^-}{\rightarrow}$$\overset{-e^-}{\rightarrow}$ (RN–NR)$^{2-}$

$\approx$ 1.35 Å

1.40-1.45 Å

To be Submitted
Strongly divergent “Electronic” and “Coulombic” coupling

The occurrence of “borderline” mixed-valence systems and the case for abandoning the Classical Robin and Day concept

Non-innocent bridges leading to isovalent / mixed valent radical intermediates instead of simple mixed valent situation

The practice of structure/oxidation state correlation involving non-innocent ligands can indeed be a formal exercise, providing valuable insights into the electronic structure without warranting a too literal significance of the valence denomination
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