Schedule

- Last week: $\pi$-Acceptor Ligands and Biology
  CO, O$_2$, N$_2$ and NO complexes, introduction to M-M bonds
- Lecture 7: M-M bonds
  $\delta$-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 Course – week 6

Metal-metal bonding
- be able to predict bond order for M$_2$L$_x$ 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

Summary of Last Lecture

Metal-N$_2$ complexes
- N$_2$ is isoelectronic with CO but M-N$_2$ bonding is much weaker
- N$_2$ is non-polar and bond is strong

NO complexes
- Can bond as 1 electron donor (NO$^-$: bent M-NO)
- Can bond as 2 electron donor (NO$^+$ linear M-NO)

Today’s lecture
- Metal-Metal bonding in complexes
Maximum Bond Order – d-Block

- The maximum bond order is 5
- But...complexes also contain ligands which use some of the d-orbitals reducing number of bonds

Complexes Containing d-d Bonds

- In complexes, not all of these molecular orbitals will form as some of the d-orbitals will be involved in bonding to ligands
  - \([\text{Re}_2\text{Cl}_8]^2-\) contains two ~square planar \(\text{ReCl}_4\) units
    - There must be a Re-Re bond as the two units are attached
    - The geometry is eclipsed
    - \([\text{Re}_2\text{Cl}_8]^2- = 2\text{Re}^{3+}(d^4) + 8\text{Cl}^-\)

Quadruple Bonds

- In complexes, not all of these molecular orbitals will form as some of the d-orbitals will be involved in bonding to ligands
  - \([\text{Re}_2\text{Cl}_8]^2-\) contains two ~square planar \(\text{ReCl}_4\) units
    - \(d_{x^2-y^2}^2\) bonds with the four ligands
    - Leaving: \(d_{z^2}, d_{xz}, d_{yz}\) and \(d_{xy}\) to form M-M bonds
Quadruple Bonds

- \([\text{Re}_2\text{Cl}_8]^{2-}\) quadruple bond:
  - \((\sigma)^2(\pi)^4(\delta)^2\): one \(\sigma\)-bond, two \(\pi\)-bonds and one \(\delta\)-bond
  - the \textit{sterically unfavourable} eclipsed geometry is due to the \(\delta\)-bond

- \([\text{Re}_2\text{Cl}_6]^{4-}\) quadruple bond:
  - \((\sigma)^2(\pi)^4(\delta)^2(\delta^*)^2\): one \(\sigma\)-bond, two \(\pi\)-bonds and two \(\delta\)-bonds
  - \(\delta\)-bond: eclipsed geometry
  - number of pairs / number of edges = 6/3 = 2
  - 3 \(\times\) Re-Re double bonds

Larger Clusters – \(M_3\)

- \(\text{ReCl}_3\) exists \(\text{Re}_3\text{Cl}_6\) clusters
  - detailed view of cluster bonding more involved ...
  - \(\text{Re}_3\text{Cl}_6\) \(\equiv\) \(3\text{Re}^{3+}(d^4) + 9\text{Cl}^-\)
  - \(3 \times\) Re-Re connections in triangle
  - number of pairs / number of edges = 6/3 = 2
  - 3 \(\times\) Re-Re double bonds

Slide 9/20

Slide 10/20

Slide 11/20
Larger Clusters – $\text{M}_6$

- $[\text{Mo}_6\text{Cl}_{14}]^{2-}$
  - Mo$_6$ octahedron with 8Cl capping faces and 6 Cl on edges
  - $[\text{Mo}_6\text{Cl}_{14}]^{2-} \equiv 6\text{Mo}^{2+} (d^4) + 14\text{Cl}^-$
  - $6 \times \text{Mo}^{2+} (d^4) \rightarrow 24 \text{e}^-$ or 12 pairs
  - 12 $\times$ Mo-Mo connections in octahedron
  - number of pairs / number of edges = $12/12 = 1$
  - 12 $\times$ Mo-Mo single bonds

- $[\text{Nb}_6\text{Cl}_{12}]^{2+}$
  - Nb$_6$ octahedron with 12Cl on edges
  - $[\text{Nb}_6\text{Cl}_{12}]^{2+} \equiv [\text{Nb}_6]^{14+} + 12\text{Cl}^-$
  - $6 \times \text{Nb} (d^5) \rightarrow 30 \text{e}^-$
  - $[\text{Nb}_6]^{14+} \rightarrow$ number for M-M bonding is $30 - 14 = 16 \text{e}^-$ or 8 pairs
  - 12 $\times$ Nb-Nb connections in octahedron
  - number of pairs / number of edges = $8/12 = 2/3$
  - 12 $\times$ Nb-Nb bonds with bond order = $\frac{2}{3}$

Carbonyl Clusters

- In carbonyl clusters, some of the metal orbitals are used to $\sigma$ and $\pi$-bond to the CO ligands
- The number and order of the M-M bonds is easily determined by requiring that all of the metals obey the 18 e$^-$ rule
- $\text{Mn}_2(\text{CO})_{10}$
  - total number of electrons = $2 \times 7 (\text{Mn}) + 10 \times 2 (\text{CO}) \rightarrow 34 \text{e}^-$
  - $\text{Mn}_2$ so each Mn has $34/2 = 17 \text{e}^-$
  - to complete 18 e$^-$ configuration, a Mn-Mn single bond is formed

- $\text{Fe}_2(\text{CO})_9$
  - total number of electrons = $2 \times 8 (\text{Fe}) + 9 \times 2 (\text{CO}) \rightarrow 34 \text{e}^-$
  - $\text{Fe}_2$ so each Fe has $34/2 = 17 \text{e}^-$
  - to complete 18 e$^-$ configuration, a Fe-Fe single bond is formed
Carbonyl Clusters

• Larger clusters are again possible

- \( \text{Os}_3(\text{CO})_{12} \)
- total number of electrons = \( 3 \times 8 \, (\text{Os}) + 12 \times 2 \, (\text{CO}) \rightarrow \, 48 \, \text{e}^- \)
- Os\(_3\) so each Os has \( 48/3 = 16 \, \text{e}^- \)
- to complete 18 e\(-\) configuration, each Os makes two Os-Os bonds
- Os\(_3\) triangle results

By now you should be able to

• Draw out the MO diagram for \( L_4\text{ML}_4 \) complexes
• Complete this diagram by filling in the appropriate number of electrons
• Explain the appearance of eclipsed geometries due to \( \delta \)-bonding
• In larger clusters, use the total number of pairs of metal electrons and number of metal-metal connections to work out the bond order
• In carbonyl clusters, use the 18 e\(-\) rule to work out how many bonds have to be formed

Next lecture
• Ligand-substitution reactions

Practice

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Marks
- Consider the diamagnetic complex, \([\text{Os}(\text{NH}_3)_3(\text{CO})]^2+\).
  3 i) For the carbonyl complex, give the oxidation state and the \( \delta \)-electron configuration for the Os centre, draw appropriate d-orbital energy diagrams, and illustrate the distributions of the \( \delta \) electrons within them.

  4 ii) With the aid of orbital diagrams, describe the nature of the Os-CO bond in \([\text{Os}(\text{NH}_3)_3(\text{CO})]^2+\).

  3 iii) The Os(III/II) redox potential of \([\text{Os}(\text{NH}_3)_3(\text{CO})]^3+\) is 1.7 V more positive than that of \([\text{Os}(\text{NH}_3)_4]^2+\). Briefly explain these results in terms of the natures of the bonding of the CO and NH\(_3\) ligands to metal ions.

Practice

• What is the Mo-Mo bond order in the complex \([\text{Mo}_2(\text{CH}_3\text{CO}_2)_4]\)?

• What is the Os-Os bond order in the cluster \( \text{Os}_4(\text{CO})_{12} \)?