Schedule

- Lecture 4: Re-cap
- Lecture 5: \(\pi\)-Acceptor Ligands and Biology
  CO and O\(_2\) complexes
- Lecture 6: N\(_2\) and NO complexes, M-M bonds
  More on \(\pi\)-acceptor ligands, introduction to metal-metal bonding

Summary of the Last Lecture

**Metal-carbonyl complexes**
- Bonding is due to synergic OC \(\rightarrow\) M s-donation and M \(\rightarrow\)
  CO p-back donation
- Reduction in \(v_{CO}\) stretching frequency is related to the extent of back-bonding
- Number of \(v_{CO}\) in IR and Raman can be used to work out structure

**O\(_2\) complexes**
- Haemoglobin and myoglobin bind weakly to O\(_2\) allowing transport and storage of highly reactive molecule

**Today’s lecture**
- N\(_2\) complexes and Metal-Metal bonding
Molecular Orbitals for N₂ and CO

- CO:
  - bond order = 3 (C≡O triple bond)
  - HOMO is dominated by C 2pₓ ("C lone pair")
  - LUMOs are dominated by C 2px and 2py:

- N₂:
  - bond order = 3 (N≡N triple bond)
  - HOMO delocalized over both N (not a "lone pair")
  - LUMOs are also shared equally:

Metal-N₂ Complexes

- N₂ bonds to transition metals in a similar way to CO (see Lecture 5 Slide 5)
  - σ-donation from N≡N → M
  - π-back donation from M → N≡N: (reduces N≡N bond strength)
  - synergic
  - weaker than for M-CO

free N₂: \( v_{N≡N} = 2331 \text{ cm}^{-1} \)

- M
  - N
  - N
  - M
  - M

1900–2200 cm⁻¹

\(~2100 \text{ cm}^{-1}\)

- \( M \equiv N \equiv N \equiv M \)

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Fixing Nitrogen

- Nature needs to obtain nitrogen from atmospheric N₂
  - nitrogen content of soil is often the growth limiting factor
  - natural fixation about 2.5 times more important

- To use atmospheric N₂, nature uses metal-enzymes:
  - nitrogen fixation (nitrogenase) converts N₂ to NH₄⁺
  - nitrification converts NH₄⁺ to NO₃⁻ which can be taken up by plants

- Nitrogenase faces a number of problems:
  - thermodynamic stability of N≡N bond means reaction is unfavourable
  - N₂ is non-polar and unreactive: efficient enzymes/catalysts are required
  - M-N₂ bonds are weak

Nitrogenase – Fe protein

- Nitrogenase contains Fe and Mo and is made up of two proteins
  - 'Fe protein' contains a pseudo-cubic [4Fe-4S] cluster:
    - Cluster contains 2 × Fe²⁺ and 2 × Fe³⁺
    - Tetrahedral coordinate about Fe from 2 × S²⁻ and 2 × S from cysteine

Nitrogenase – FeMo protein

- Nitrogenase contains Fe and Mo and is made up of two proteins
  - 'FeMo protein' contains two [8M-8S] clusters
    - role: oxidation of Fe²⁺ to Fe³⁺ provides electrons
      (energy for oxidation comes from hydrolysis of 2 ATP molecules per electron)
  - role: transfer of electrons from Fe protein
Nitrogenase – FeMo protein

- Nitrogenase contains Fe and Mo and is made up of two proteins
  - ‘FeMo protein’ contains two [BM-8S] clusters

2. [Mo7Fe-8S]

role: attachment and reduction of N₂

Nitrogenase – FeMo protein

- Site and mode of attachment of N₂ to [Mo7Fe-8S] cluster is not known
  - probably Fe rather than Mo
  - possibly between two central Fe atoms:

role of Mo: asymmetry in cluster probably induces a small polarity in N₂ bond, facilitating electrophilic attack

Nitrogenase – Reduction of N₂

- Multiple stepwise addition of e⁻ and H⁺
  - e⁻ from Fe protein
  - energy from ATP hydrolysis:

  - LM-N=N
  - LM=NH
  - LM=NH₂
  - LM=NH₃

  N₂
  H⁺
  2e⁻ and 2H⁺
  e⁻ and H⁺

  LM
  LM-NH₂
  LM-NH₃
  LM=NH
  LM=NH₂

  NH₃⁺
  NH₂⁺

Slide 10/18

Slide 11/18

Slide 12/18
Molecular Orbitals for N₂ and NO

Bonding in M-NO Complexes

- NO - two ways of bonding:
  - as NO⁺ - isoelectronic with CO
  - 2e⁻ σ-donation from O=N: → M
  - π-back donation from M: → NO

- as NO⁻ - isoelectronic with O₂
  - 1e⁻ σ-donation from O=N: → M

NO Synthase and Nitrophorin

- NO is used as a signalling molecule in mammals
- NO synthase is a haem protein which produces NO upon receipt of a signal
- Nitrophorin is found in some bloodsucking parasites ("kissing bugs")
  - it is a haem protein that binds NO tightly pH = 5 (in saliva of bug)
  - it releases NO at pH = 7.4 (in blood of victim)
  - NO release signals to dilate blood vessels, aiding 'blood donation'
Maximum Bond Orders – s and p-Block

- maximum bond order for s-block is 1
- maximum bond order for p-block is 3

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

Summary

By now you should be able to:
- Explain that why M-N₂ bonding is much weaker than M-CO bonding
- Count electrons in NO complexes containing bent M-NO (1 e⁻ donor) or containing linear M-NO (2 e⁻ donor)

Next lecture
- Metal-Metal bonding in complexes