Module 2, Lecture 9
Electron Transfer Reactions
Part 3

Learning Objectives:

- Appreciate the problems with ‘chemical’ oxidants in biological systems
- Recognise some features of biological oxidants
- Understand the term ligand and the nature of the coordinate covalent bond
- Appreciate the types of ligands used in biological systems
- Understand how coordination of a ligand leads to a change in the reduction potential of the transition metal ion
- Appreciate the basic processes of electron transfer in biological systems

Textbook: Chapter 20

1

Oxidants in chemistry

What are the oxidants that we use in chemistry?

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$

But, these are **toxic**, require **low pH** solutions and are **unselective**

→ No good for biological systems

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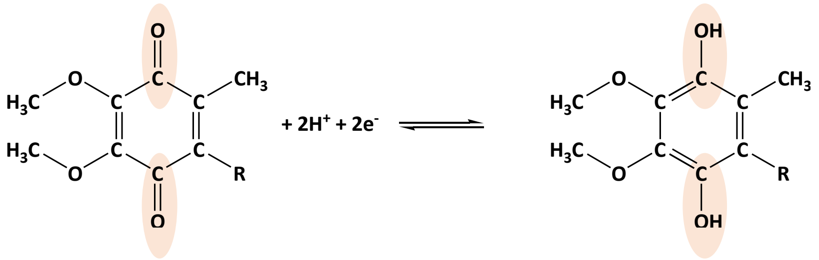
Oxidants in biology

So what does biology use?

Coenzyme Q: $E^{o\prime}$ = 0.060 V



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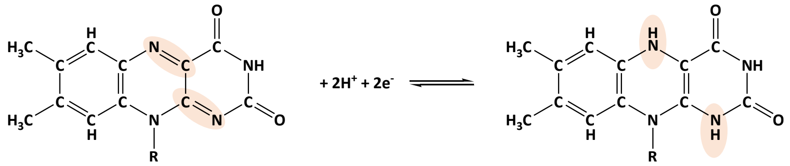
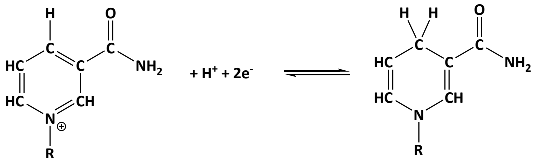
Oxidants in biology

Flavine adenine dinucleotide FAD: $E^{o\prime}$ = -0.219 V



Nicotinamide adenine dinucleotide NADH: $E^{o\prime}$ = -0.320 V



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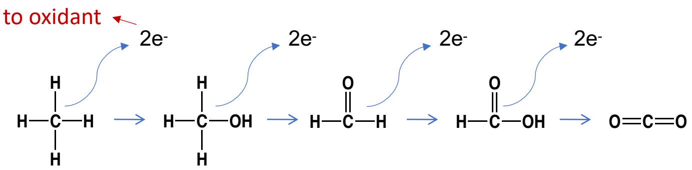
What is being oxidised in biology?

The conversion of food to CO_2 requires molecules to take electrons off the food and give them, ultimately, to O_2 (to make water)

'Food' molecules are oxidized in a series of steps and the change in energy used to perform work;



**biological oxidants must themselves be able to be reduced and then re-oxidised when they pass on electrons i.e. Equilibria*

Electrons are passed from one oxidant to the next, until they eventually are given to O_2.

$$O_2(g) + 4H^+ + 4e^- \rightarrow 2H_2O$$

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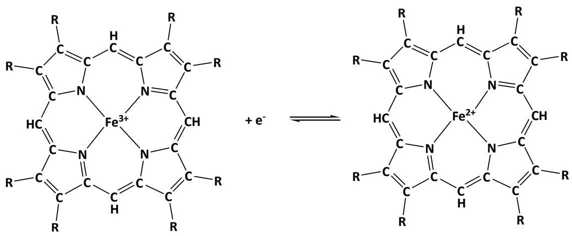
Transition metal oxidants in biology

Other important biological oxidants are based on transition metal ions

e.g. **Cytochromes** are iron-containing molecules in which the iron atom can undergo the reaction

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$$



Basic heme unit
R can be all sorts of things

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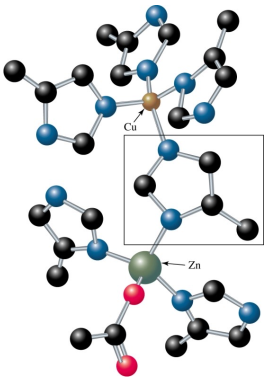
Transition metals in enzymes

Transition metal ions are also found in many enzymes which catalyse redox reactions.



e.g. Cu/Zn superoxide dismutase catalyses the reaction

$$2O_2^- + 2H^+ \rightarrow O_2 + H_2O_2$$

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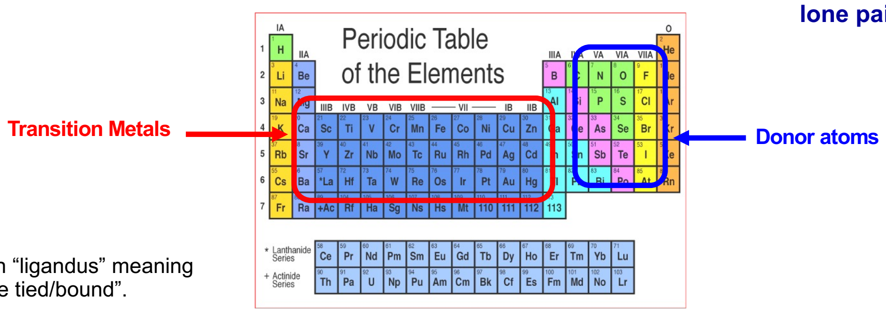
Transition metal complexes

These are compounds in which a **transition metal cation** has bonded to it a number of **ligands**.

The **ligand*** is a molecule or ion in which one or more **donor atoms** that have a **lone pair of electrons**.



*From Latin “ligandus” meaning “that can be tied/bound”.

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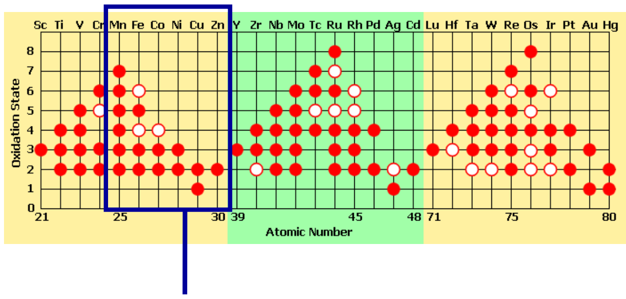
Transition metal complexes

Different transition metal atoms can lose anywhere from 1 to 8 electrons to form cations. The charge on the cation has significant impact on its chemical properties.



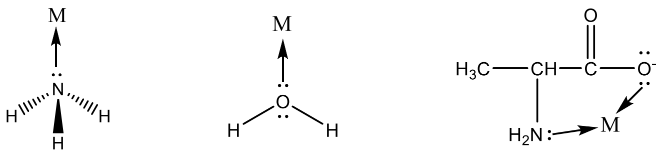
Common biologically important transition metal ions

Ligands

Ligands are **Lewis bases**, as they donate a pair of electrons to the transition metal ion. Ligands can be neutral or negatively charged.

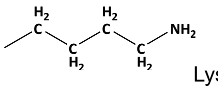
The **transition metal ion** is a **Lewis acid**, as it accepts a pair of electrons. The transition metal ion is always a cation.

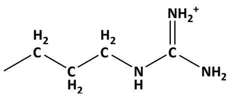
The most common donor atoms found in ligands are **nitrogen** and **oxygen**, each donor atom forms one bond, some molecules can have more than one donor atom.

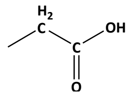


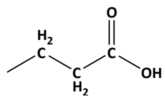
Biological ligands

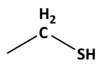
In **metalloproteins**, the donor atoms that bond to the transition metals are found in the side chains (R groups) of the amino acids.

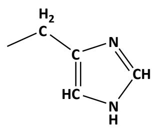
R =  Lysine (Lys)

R =  Arginine (Arg)

R =  Aspartic Acid (Asp)

R =  Glutamic Acid (Glu)

R =  Cysteine (Cys)

R =  Histidine (His)

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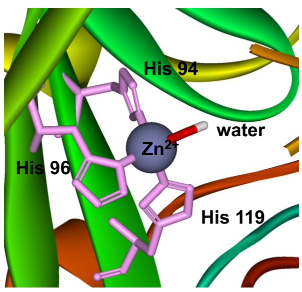
Metalloproteins

Amino acids in protein chains can result in a huge ligand for the metal ion and the folding of the chain brings amino acid side chains close to the ion.

e.g. carbonic anhydrase – a zinc containing enzyme



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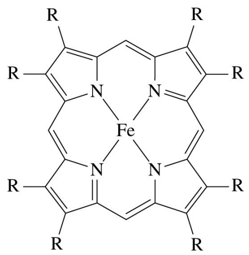
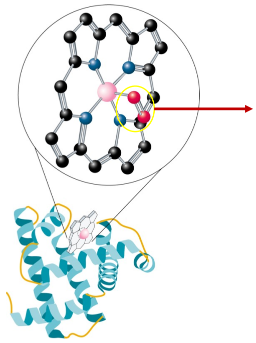
Heme-based ligands

These are ligands in which 4 nitrogen donor atoms are arranged in a cyclic ligand, called a heme. In most cases, these ligands form complexes with Fe^{2+} or Fe^{3+}. Often one or two simple ligands also bond to the Fe as part of the complex.



Basic heme unit
R can be all sorts of things

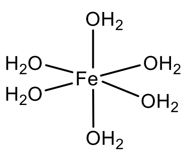


Heme unit in **myoglobin**, with an O_2 molecule attached to the iron

Influence of ligand on transition metal ion

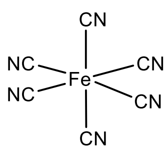
When ligands bond to a transition metal ion, they will change the reduction potential of the metal ion.

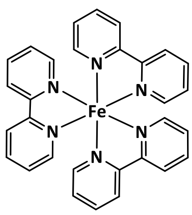
e.g.



$E^o([Fe(H_2O)_6]^{3+}/[Fe(H_2O)_6]^{2+}) = 0.77$ V

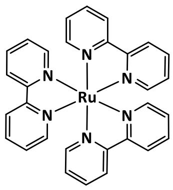
$E^o([Fe(CN)_6]^{3+}/[Fe(CN)_6]^{2+}) = 0.28$ V



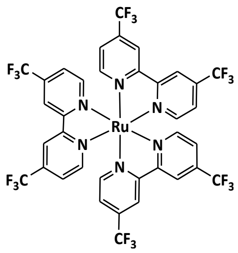


$E^o([Fe(bpy)_3]^{3+}/[Fe(bpy)_3]^{2+}) = 1.18$ V

The reasons for this variation in the reduction potential can be very complicated but we can simplify by considering the affect that the ligand has on the attraction of the metal ion for electrons.

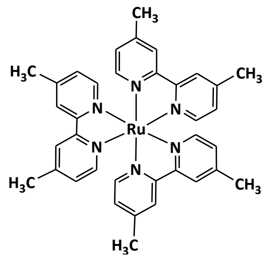


$E^o([Ru(L)_3]^{3+}/[Ru(L)_3]^{2+})$ = 1.27 V



$E^o([Ru(L)_3]^{3+}/[Ru(L)_3]^{2+})$ = 1.75 V

Electronegative F atoms **pulls electron density** away from the metal ion, **increasing attraction to an e^-.**



$E^o([Ru(L)_3]^{3+}/[Ru(L)_3]^{2+})$ = 1.10 V

CH_3 **pushes electron density** onto the metal ion, **decreasing its attraction to an e-.**

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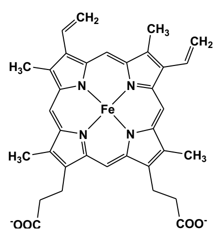
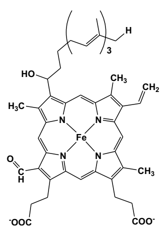
Apparently small changes to the structure of the ligand can change the reduction potential of the metal ion – this is sometimes called **tuning.**

This is the way that biology often does it – especially when it comes to cytochromes.



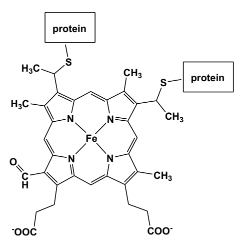
cytochrome *b*

$E^{o\prime}([Fe^{3+}(\text{cyt } b)]/[Fe^{2+}(\text{cyt } b)])$ = **0.050 V**



cytochrome *a*

$E^{o\prime}([Fe^{3+}(\text{cyt } a)]/[Fe^{2+}(\text{cyt } a)])$ = **0.254 V**



cytochrome *c*

$E^{o\prime}([Fe^{3+}(\text{cyt } c)]/[Fe^{2+}(\text{cyt } c)])$ = **0.290 V**

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cytochrome *b*

$E^{o\prime}([Fe^{3+}(\text{cyt } b)]/[Fe^{2+}(\text{cyt } b)])$ = **0.050 V**

cytochrome *a*

$E^{o\prime}([Fe^{3+}(\text{cyt } a)]/[Fe^{2+}(\text{cyt } a)])$ = **0.254 V**

cytochrome *c*

$E^{o\prime}([Fe^{3+}(\text{cyt } c)]/[Fe^{2+}(\text{cyt } c)])$ = **0.290 V**

These values show that the following electron transfer processes are possible

$1e^-$

$$[Fe^{3+}(\text{cyt } a)] + [Fe^{2+}(\text{cyt } b)] \rightarrow [Fe^{2+}(\text{cyt } a)] + [Fe^{3+}(\text{cyt } b)]$$

(1 electron is transferred from cyt *b* to cyt *a)*

$1e^-$

$$[Fe^{3+}(\text{cyt } c)] + [Fe^{2+}(\text{cyt } a)] \rightarrow [Fe^{2+}(\text{cyt } c)] + [Fe^{3+}(\text{cyt } a)]$$

(1 electron is transferred from cyt *a* to cyt *c)*

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cytochrome *b*

$E^{o\prime}([Fe^{3+}(\text{cyt } b)]/[Fe^{2+}(\text{cyt } b)])$ = **0.050 V**

e^-

cytochrome *a*

$E^{o\prime}([Fe^{3+}(\text{cyt } a)]/[Fe^{2+}(\text{cyt } a)])$ = **0.254 V**

e^-

cytochrome *c*

$E^{o\prime}([Fe^{3+}(\text{cyt } c)]/[Fe^{2+}(\text{cyt } c)])$ = **0.290 V**

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

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✱ Homework ✱

Chemistry – the central science 15th Ed

Brown *et al.*

No questions but there is an interesting reading “The battle for iron in living systems” about a type of metal complex called a siderophore and it’s role in the body on p1119 of the text book.

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