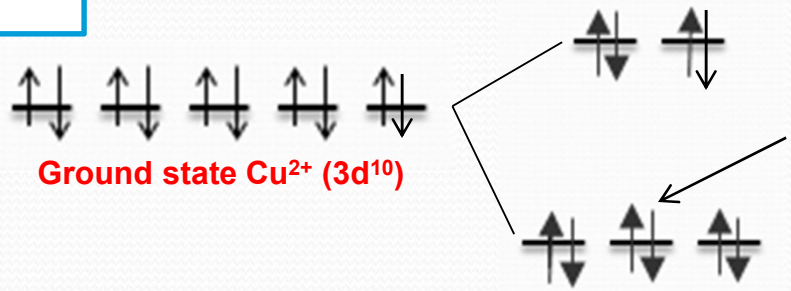
Transition Metals (d block elements) – Coloured Complexes

$[Cu(H_2O)_6]^{1+}Cl$
- Filled 3d orbitals
- No colour

Cu^{1+} ion with H_2O ligands - Colourless



Ground state Cu^{2+} ($3d^{10}$)

Ligands split the 3d orbitals

Fully filled in 3d orbital
No electron transition

NO Colour

Cu^{2+} ion without H_2O ligands – Colourless

No ligands
No splitting of 3d orbitals
No electron transition
No colour

NO Colour

Transition Metals (d block elements) – Coloured Complexes

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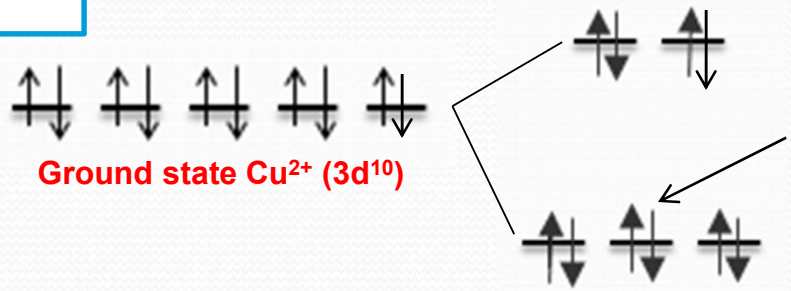


Ground state Cu^{2+} ($3d^{10}$)

Fully filled in 3d orbital
No electron transition

Ligands split the 3d orbitals

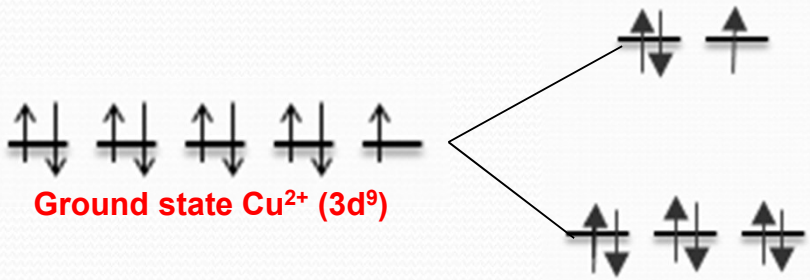
NO Colour

Cu^{2+} ion without H_2O ligands – Colourless

No ligands
No splitting of 3d orbitals
No electron transition
No colour

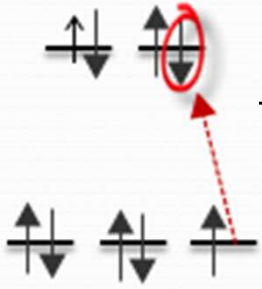
NO Colour

Cu^{2+} ion with H_2O ligands – Blue Colour



Ground state Cu^{2+} ($3d^9$)

Ligands split the 3d orbitals



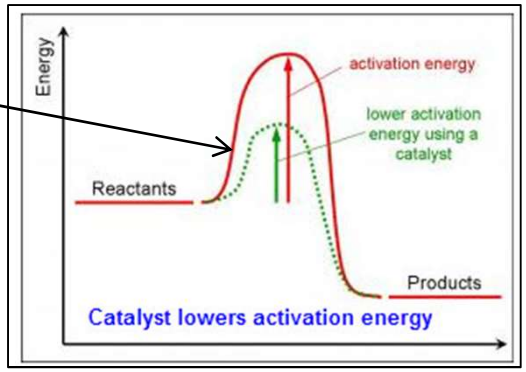
Electron transition from lower to higher level by absorbing ΔE

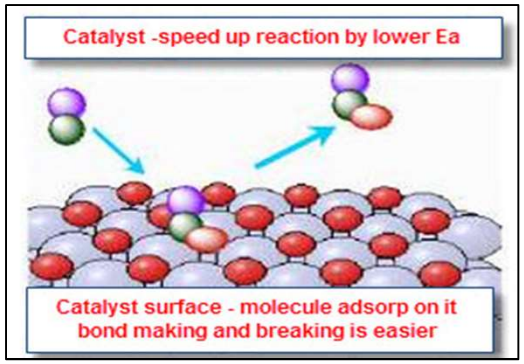
Colour

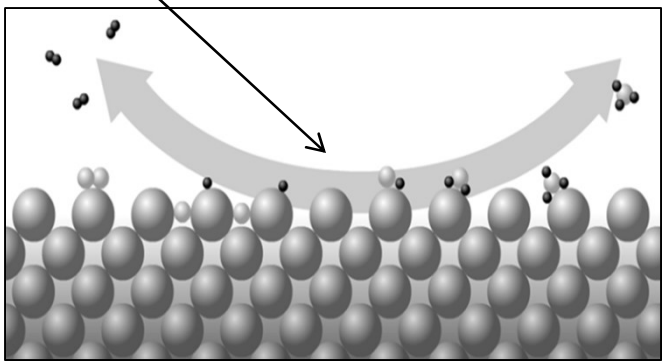
$[Cu(H_2O)_6]^{2+}SO_4$ – splitting 3d orbitals by ligand – Blue colour

Catalytic Properties of Transition metal

- Variable oxidation state - lose and gain electron easily
- Acts as Homogeneous or Heterogenous catalyst – lower activation energy
- Homogeneous catalyst – catalyst and reactants are in the same phase
- Heterogeneous catalyst – catalyst and reactants are in different phase
- Heterogenous catalyst- Metal surface provide active site (lower Ea)
- Surface catalyst bring molecule together (close contact)
  -bond breaking/making easier







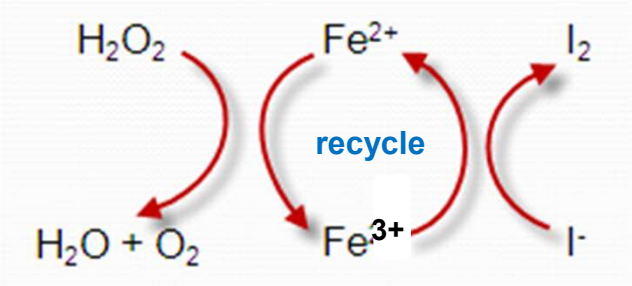
Transition metal work as a catalyst with diff oxidation states

$2\ H_2O_2 + Fe^{2+} \rightarrow 2H_2O + O_2 + Fe^{3+}$

$H_2O_2 + Fe^{2+} \rightarrow H_2O + O_2 + Fe^{3+}$

$Fe^{3+} + I^- \rightarrow Fe^{2+} + I_2$

$Fe^{2+} \leftrightarrow Fe^{3+}$



Reaction is slow if only I- is added $H_2O_2 + I^- \rightarrow I_2 + H_2O + O_2$

Reaction speeds up if Fe^{2+}/Fe^{3+} added

Fe^{2+} changes to Fe^{3+} and is change back to Fe^{2+} again

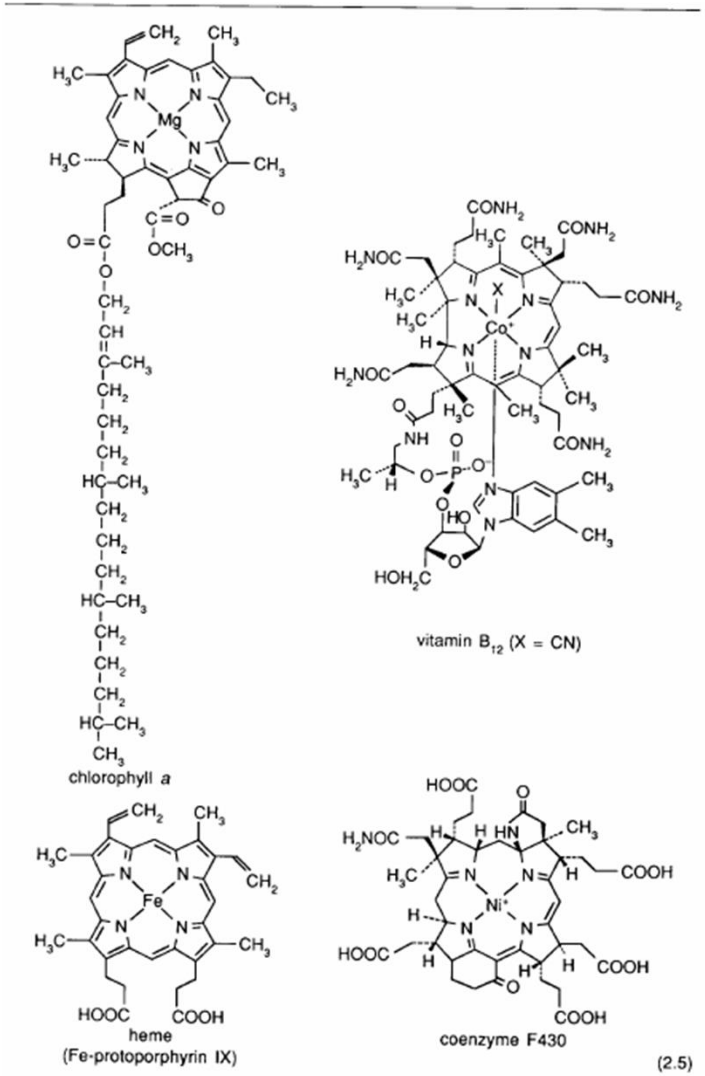
http://comp.chem.umn.edu/itccd/Catalytics.html/ http://gcserevision101.wordpress.com/chemistry-c3/

Some Biological Functions of Metals

Body Function	Metal
Blood pressure and blood coagulation	Na, Ca
Oxygen transport and storage	Fe
Teeth and bone structure	Ca
Urinary stone formation	Ca
Control of pH in blood	Zn
Muscle contraction	Ca, Mg
Maintenance of stomach acidity	K
Respiration	Fe, Cu
Cell division	Ca, Fe, Co

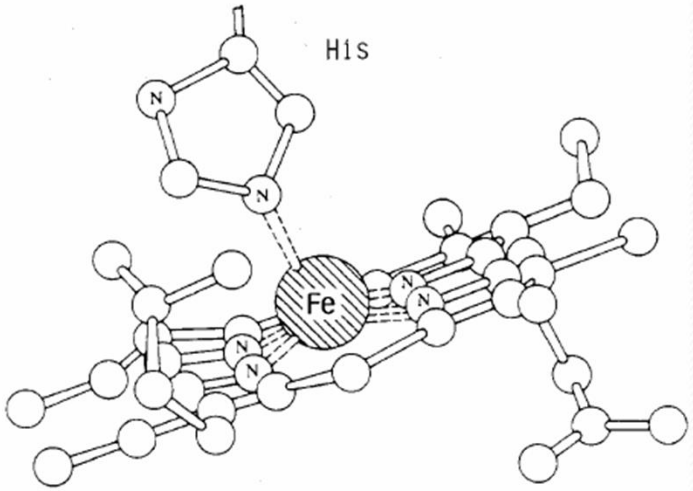
Coordination complexes and transition metals in biological systems

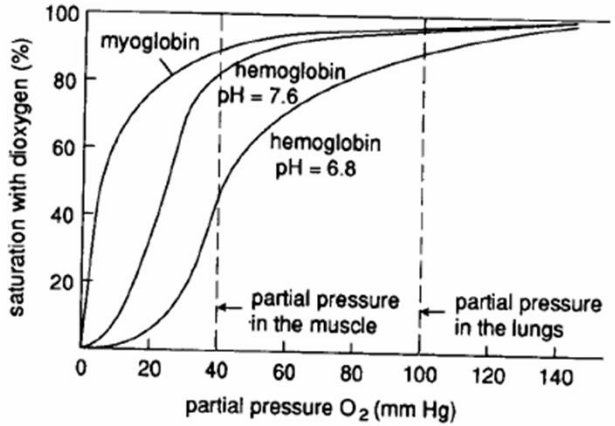
- Metal complexes and transitions metals are of considerable importance in biological systems
  - Responsible for many biological redox processes
  - Useful for oxygen transport
  - Useful in various drugs
  - Can be highly toxic



Oxygen transport

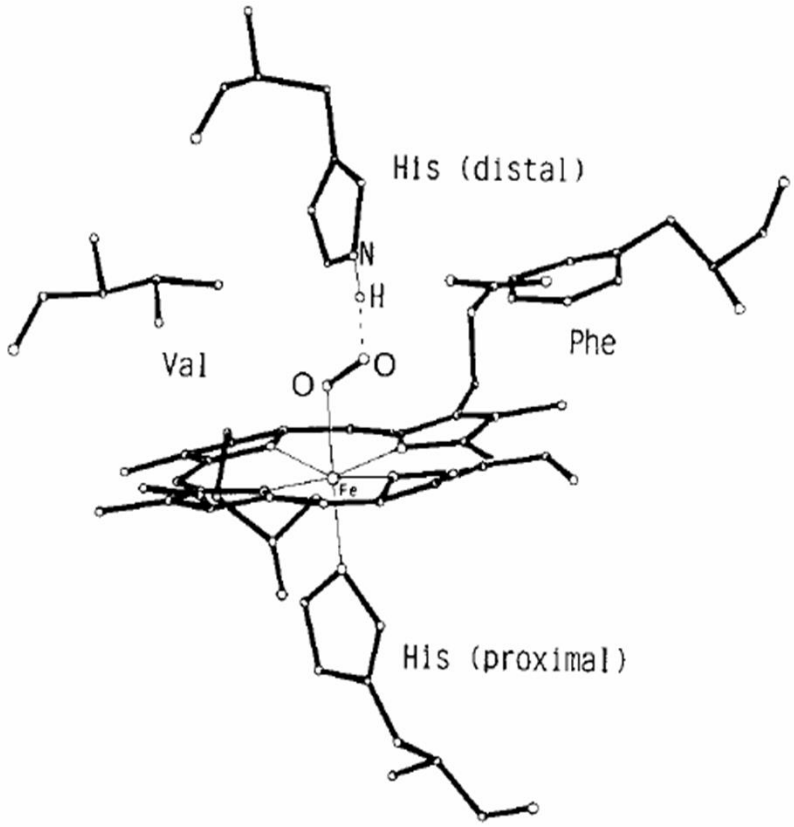
- The iron containing proteins hemoglobin and myoglobin are involved in oxygen transport
  - Hemoglobin moves oxygen through the body
  - Myoglobin stores and moves oxygen within muscle
  - Hemoglobin has a lower oxygen affinity than myoglobin and its oxygen binding is pH dependent. This provides a mechanism for oxygen transfer from hemoglobin to myoglobin in the muscle





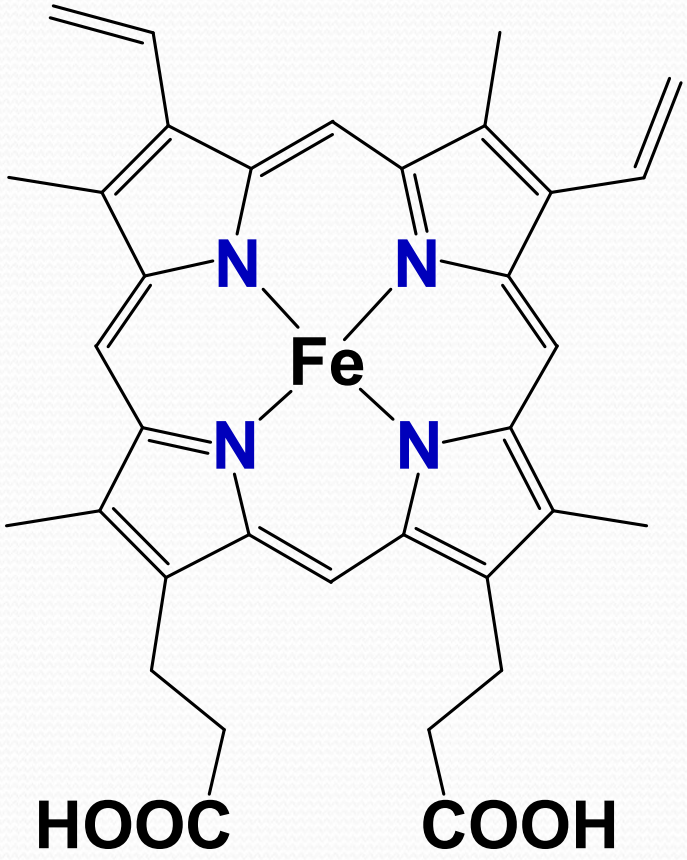
Oxygen binding in myoglobin

- Oxygen binds to the metal center end on, but it sits at an angle to the plane of the porphyrin ring ligand.
  - Oxygen binding in this mode is efficient



Myoglobin (Mb); Hemoglobin (Hb)

- Both contain iron protoporphyrin IX (heme b)
- heme b = active site of myoglobin and hemoglobin



heme b

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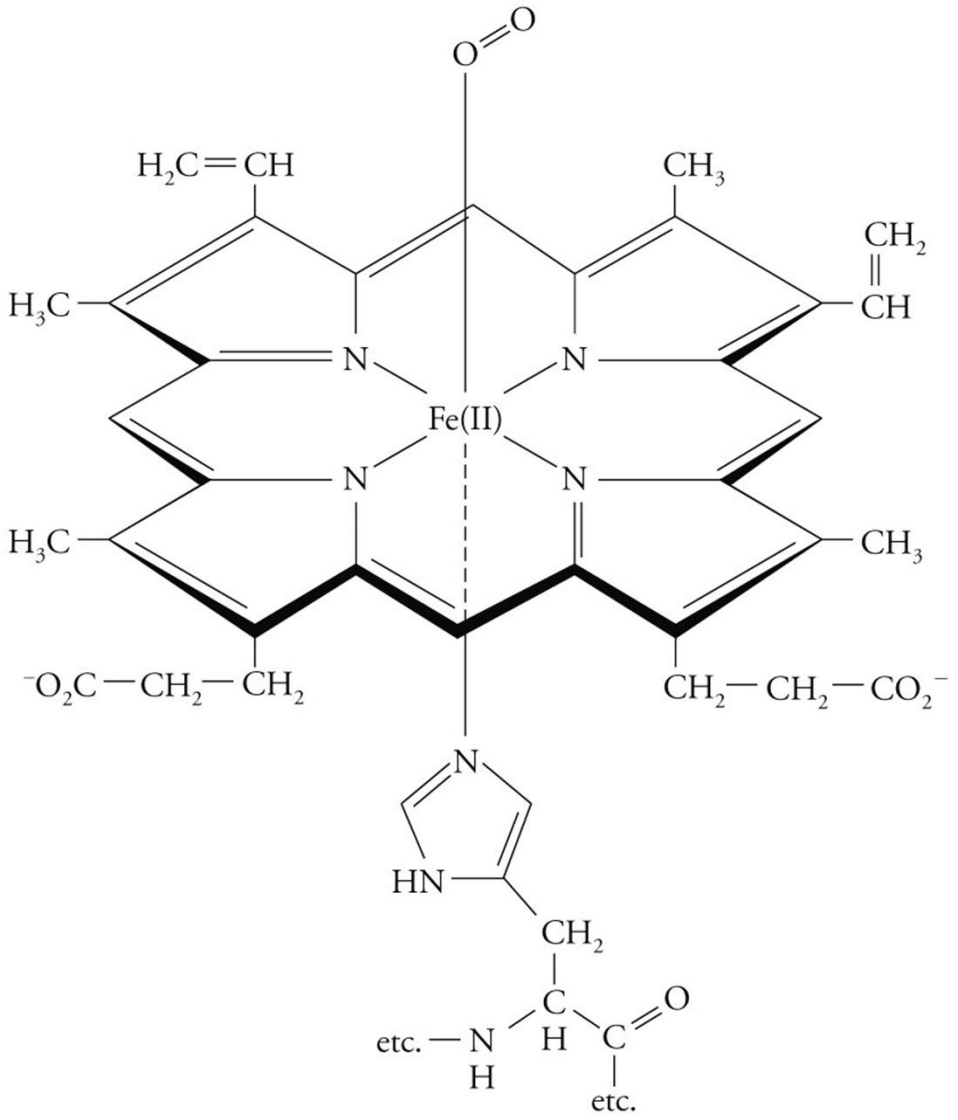
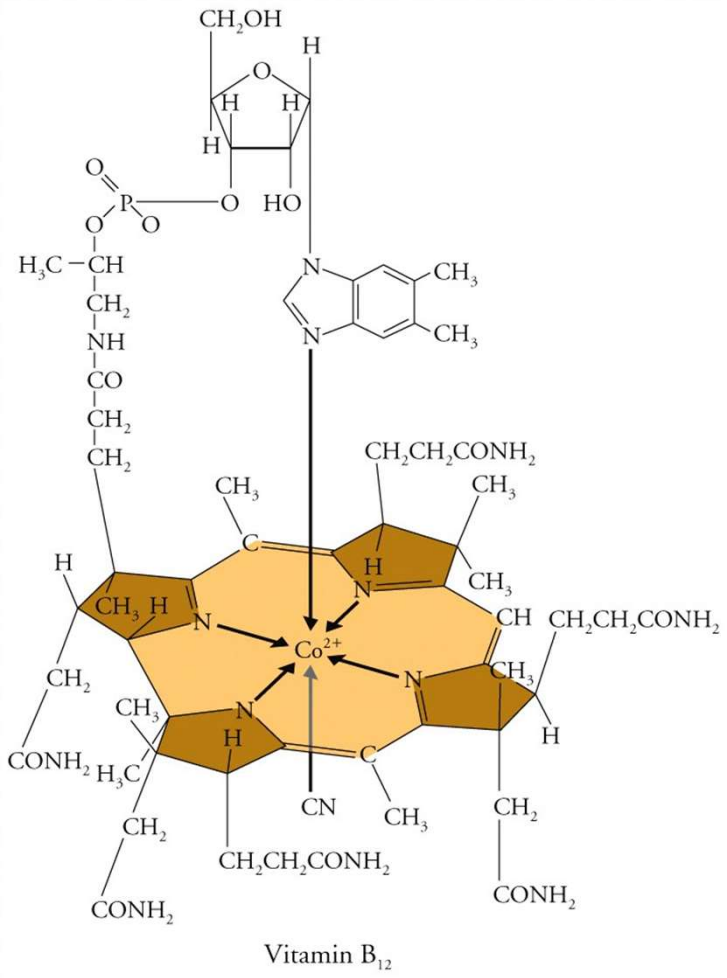
Hemoglobin

- Each heme ring has Fe in center
- ~ octahedral coordination
- Oxy-hemoglobin
  - O_2 bound
  - Color is bright red
- Deoxy-hemoglobin
  - O_2 not bound
  - Color is blue-violet



Vitamin B_{12}

- Co^{2+} in ~ octahedral environment
- Ligands
  - 4 nitrogen atoms in Corrin ring
  - CN^- and adenosine
- Co-factor for many enzymes
- Essential to diet
  - Humans do not make this in their bodies
  - Absence leads to *pernicious anemia*
- Enzymes where vitamin B_{12} is needed
  - *Ribonuclease reductase*
  - *Glutamate mutase*
  - *Diol dehydratase*
  - *Methionine synthetase*

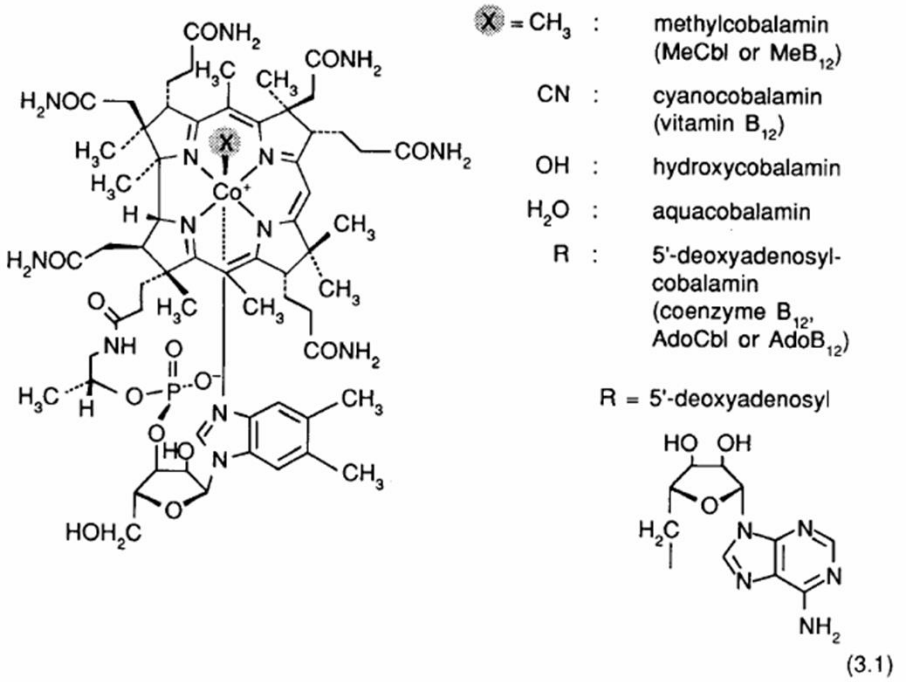


Vitamin B_{12}

79

Vitamin B_{12}

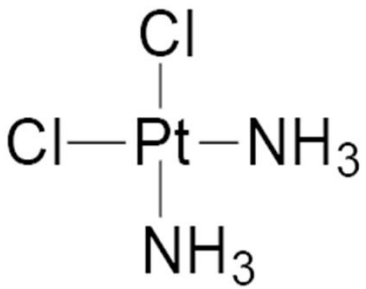
- Vitamin B_{12} is a cobalt containing complex
  - The cyanocomplex is not the biologically active species. X = R or CH_3 are involved in biological redox processes and alkylation reaction
- Cobalt containing species is a coenzyme - it does its biological job with the aid of an apoenzyme



Note that the presence of a cobalt carbon bond makes many of these species examples of organometallics

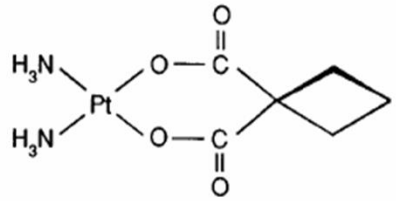
Anticancer drugs

- The platinum complexes cisplatin and carboplatin are widely used anticancer agents. Cisplatin is very useful for testicular cancers. They bind to DNA and prevent replication.

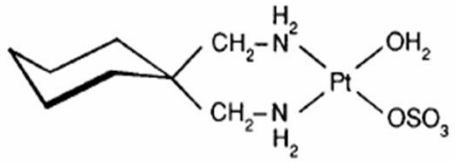


Cisplatin

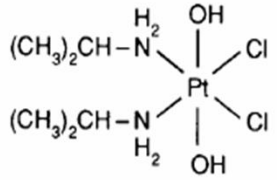
carboplatin: *cis*-diammine(1,1-cyclobutanedicarboxylato)platinum(II)



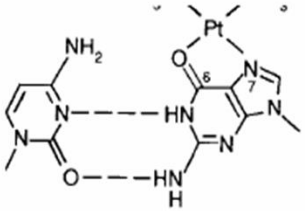
spiroplatin: aqua-1,1-bis(aminomethyl)cyclohexanesulfatoplatinum(II)



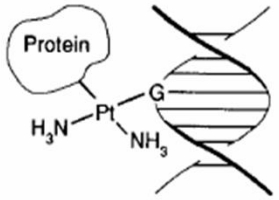
iproplatin, CHIP: *cis*-dichlorobis(isopropylamine)-*trans*-dihydroxoplatinum(IV)



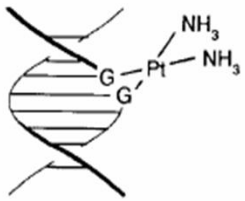
(19.4)



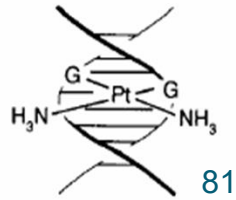
chelate coordination to a guanine base



DNA-protein cross-linking



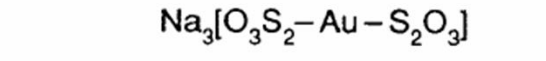
1,2-intrastrand cross-linking



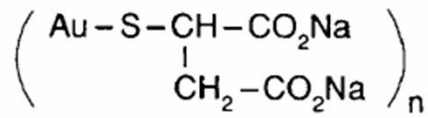
interstrand cross-linking

Anti arthritis drugs

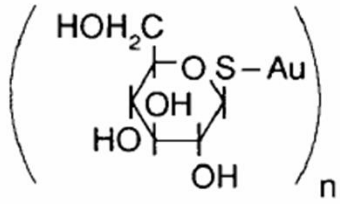
- Some gold compounds have been employed to treat arthritis.



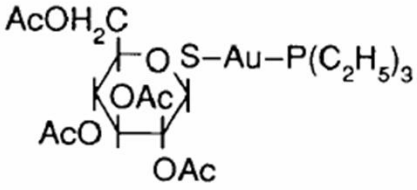
trisodiumgold(I)bis(thiosulfate) ('sanocrysin')



disodiumgold(I)thiomalate ('myochrisin')

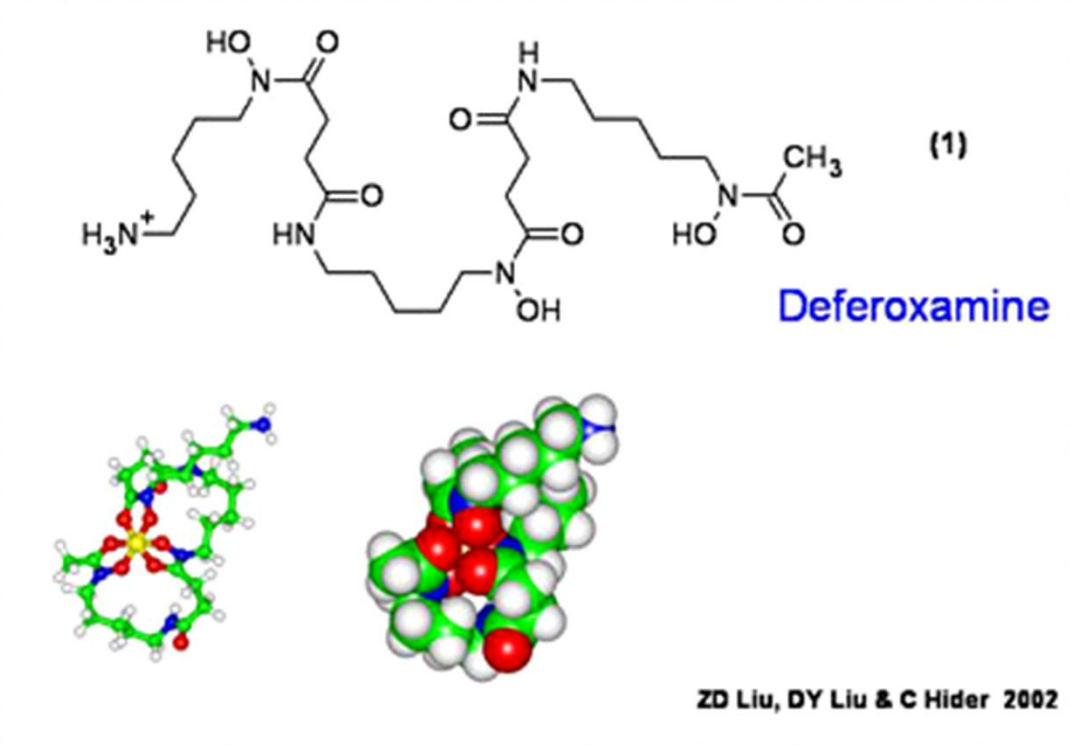


gold(I)thioglucose ('solganol')



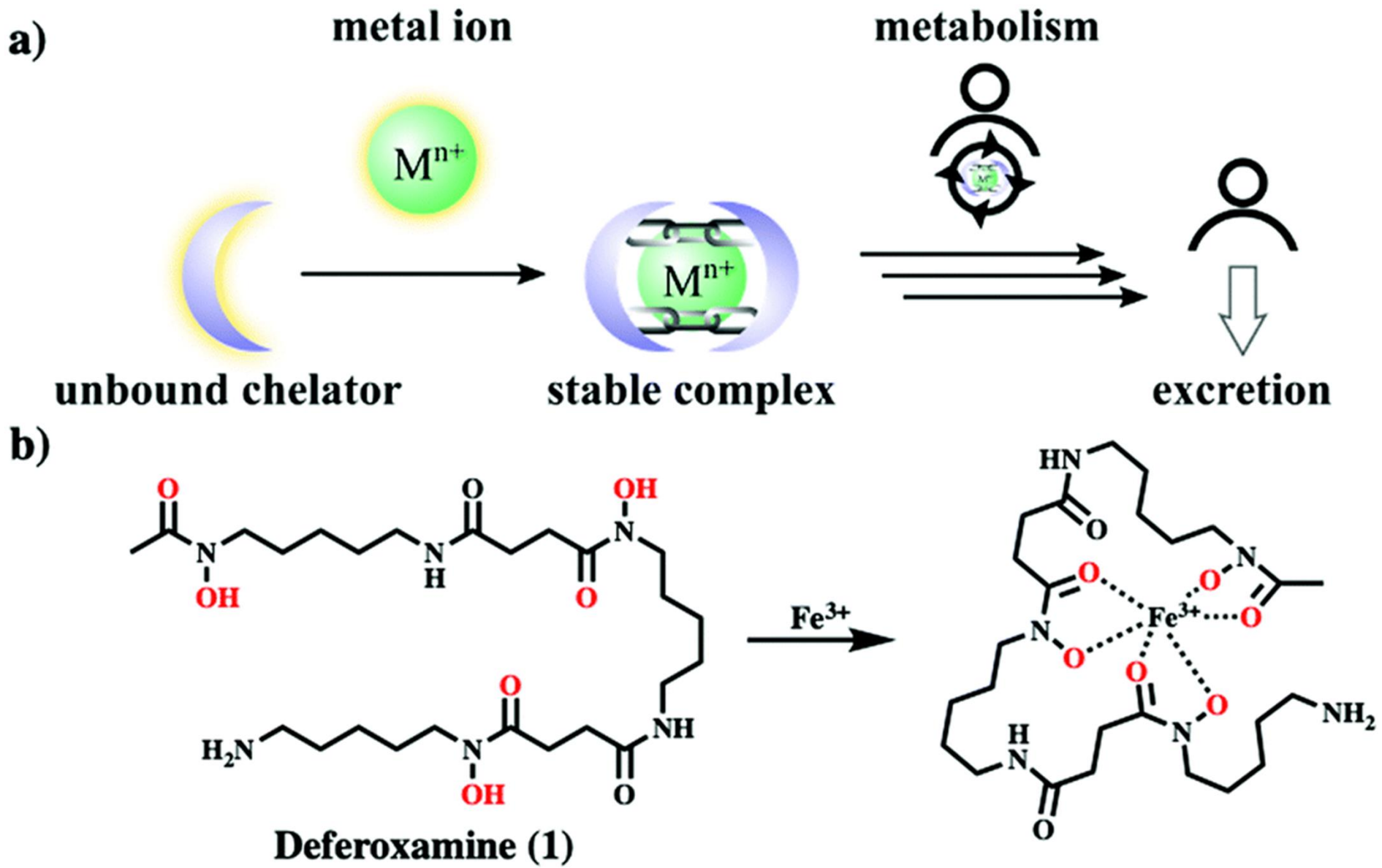
(2,3,4,6-tetrakis-*O*-acetyl-1-thio-β-D-glucopyranosido)gold(I)triethylphosphine ('auranofin', 'ridaura®')

Deferoxamine



- Standard treatment of Iron overload
- Hexadentate (1:1) iron chelator
- 1 molecule of DFO binds 1 atom of iron
- Forms a stable complex
- Excreted via the bile and urine
- Can provide effective chelation therapy

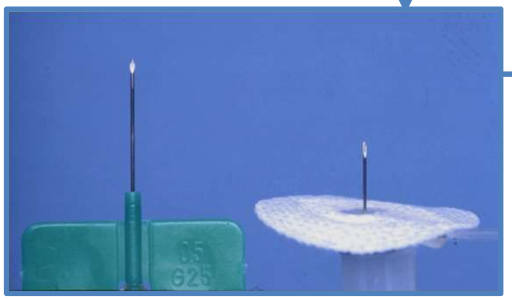
DFO = deferoxamine


a)
metal ion
metabolism
M^{n+}
M^{n+}
unbound chelator
stable complex
excretion
b)
Deferoxamine (1)
Fe^{3+}
Fe^{3+}

Limitations of deferoxamine therapy

Poor oral bioavailability
and a short plasma half-life

Slow subcutaneous infusion
3–7 times weekly



Injection-site reactions
and pain

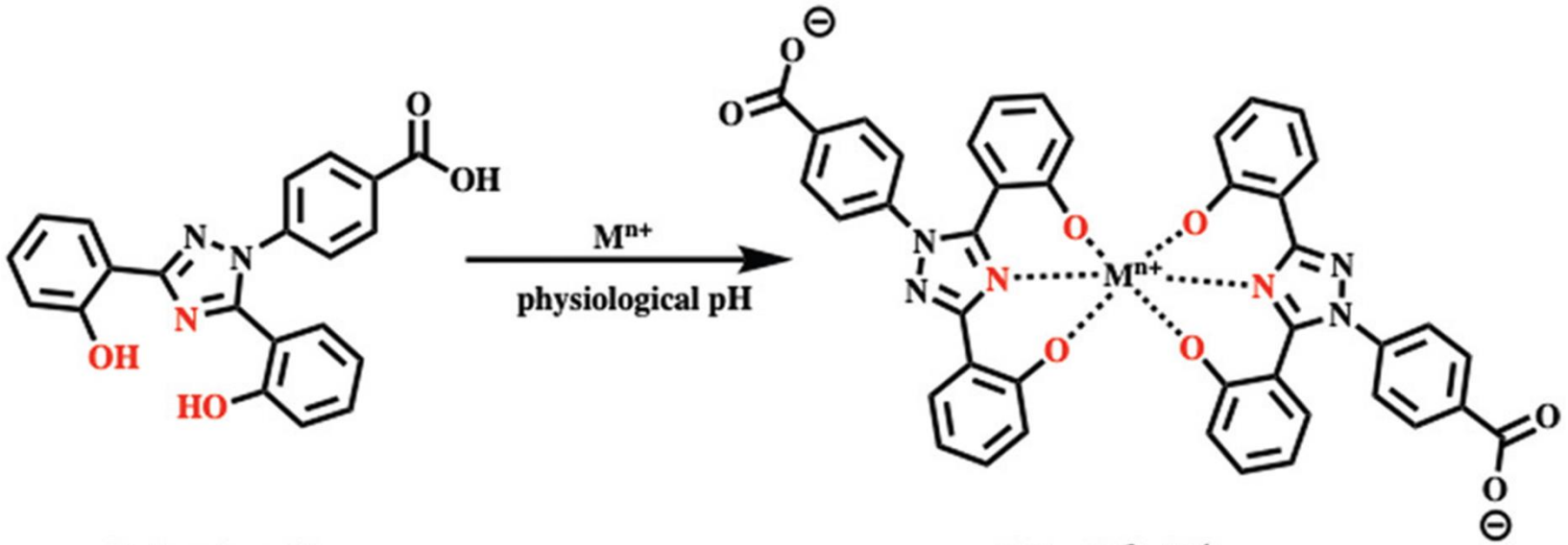
Inconvenient
administration

Poor compliance
reported to lead to
increased mortality

Equipment not widely
available in many
countries

Deferasirox (Exjade)

- Tridentate* iron chelator
  - an oral, dispersible tablet
  - highly specific for iron
  - 70% oral bioavailability, increased with food
- Half-life of 8 to 16 hours supports once-daily dosing
- Chelated iron excreted mainly in faeces (< 10% in urine)



Deferasirox (5)

$M^{n+} = Fe^{3+}, Ti^{4+}$