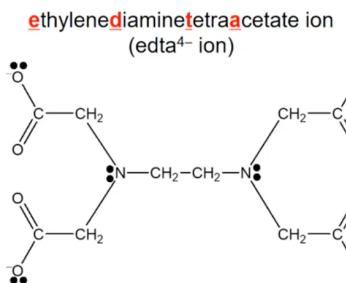


Transition Metals Notes

- (/) A transition element is a d-block element which forms at least one stable ion with a partially filled d subshell.¹
- (/) A complex contains a central metal atom or ion bonded to one or more surrounding ligands.
- (/) A ligand is an ion or molecule which contains at least one atom bearing one lone pair of electrons which can be donated into the energetically accessible vacant orbital of the central metal atom or ion, forming a coordinate (dative) bond.
- The coordination number of the central metal atom or ion is the number of coordinate bonds from the ligands to the central metal atom or ion.
- A monodentate ligand is one which can form only one coordinate bond with a central atom or ion (e.g. :NH₃, H₂O:, :Cl⁻, :CN⁻²)
- A polydentate ligand is one which can form more than one coordinate bond with a central atom or ion.
- A bidentate ligand is one which can form two coordinate bonds with a central atom or ion.
- A hexadentate ligand is one which can form six coordinate bonds with a central atom or ion. (e.g. EDTA⁴⁻ ion)



A very useful ligand that can remove/ render metal ions ineffective.

		Group																		
1	2													13	14	15	16	17	18	
														1 H hydrogen 1.0						
3 Li lithium 6.9	4 Be beryllium 9.0													5 B boron 10.8	6 C carbon 12.0	7 N nitrogen 14.0	8 O oxygen 16.0	9 F fluorine 19.0	10 Ne neon 20.2	
Key																				
atomic number atomic symbol name relative atomic mass														13 Al aluminum 27.0	14 Si silicon 28.1	15 P phosphorus 31.0	16 S sulfur 32.1	17 Cl chlorine 35.5	18 Ar argon 39.9	
3 Li lithium 6.9	4 Be beryllium 9.0	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8			
11 Na sodium 23.0	12 Mg magnesium 24.3	3 K potassium 39.1	20 Ca calcium 40.1	21 Sc scandium 45.0	22 Ti titanium 47.9	23 V vanadium 50.9	24 Cr chromium 52.0	25 Mn manganese 54.9	26 Fe iron 55.8	27 Co cobalt 58.9	28 Ni nickel 58.7	29 Cu copper 63.5	30 Zn zinc 65.4	31 Ga gallium 69.7	32 Ge germanium 72.6	33 As arsenic 74.9	34 Se selenium 79.0	35 Br bromine 79.9	36 Kr krypton 83.8	
19 K potassium 39.1	20 Ca calcium 40.1	39 Y yttrium 88.9	40 Sr strontium 87.6	41 Zr zirconium 91.2	42 Nb niobium 92.9	43 Mo molybdenum 95.9	44 Tc technetium –	45 Ru ruthenium 101.1	46 Rh rhodium 102.9	47 Pd palladium 106.4	48 Ag silver 107.9	49 Cd cadmium 112.4	50 In indium 114.8	51 Sn tin 118.7	52 Te antimony 121.8	53 I iodine 127.6	54 Xe xenon 131.3			
37 Rb rubidium 85.5	38 Sr strontium 87.6	39 Y yttrium 88.9	40 Zr zirconium 91.2	41 Nb niobium 92.9	42 Mo molybdenum 95.9	43 Tc technetium –	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Te antimony 121.8	52 I iodine 127.6	53 Xe xenon 131.3				
55 Cs caesium 132.9	56 Ba barium 137.3	57–71 lanthanoids 138.9	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.8	75 Re rhenum 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.6	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 209.0	84 Po polonium –	85 At astatine –	86 Rn radon –			
87 Fr francium –	88 Ra radium –	89–103 actinoids –	104 Rf rutherfordium –	105 Db dubnium –	106 Sg seaborgium –	107 Bh bohrium –	108 Hs hassium –	109 Mt meitnerium –	110 Ds darmstadtium –	111 Rg roentgenium –	112 Cn copernicium –	114 Fl flerovium –	116 Lv livernormium –	118 Lv livernormium –	119 Ts tennessine –	120 Og oganesson –				
lanthanoids		57 La lanthanum 138.9	58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium –	62 Sm samarium 150.4	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.1	71 Lu lutetium 175.0				
actinoids		89 Ac actinium –	90 Th thorium 232.0	91 Pa protactinium 231.0	92 U uranium 238.0	93 Np neptunium –	94 Pu plutonium –	95 Am americium –	96 Cm curium –	97 Bk berkelium –	98 Cf californium –	99 Es einsteinium –	100 Fm fermium –	101 Md mendelevium –	102 No nobelium –	103 Lr lawrencium –				

¹ Must meet both criteria to be considered a transition element and some transition elements in some oxidation states may not meet both criteria and do not show typical properties of transition metals

² Lone pair on C is used instead of that on N, because lone pair on N is bound more tightly to nucleus of N and is less available for dative bond.

Remarks:

- Form for electronic configuration: $1s^2 2s^2 2p^6 3s^2 3p^6 \mathbf{3d^x 4s^y}$
- Exception: 24Cr, 29Cu where half-filled or fully filled 3d orbitals are preferred for stability

		3d	4s	
Scandium	[Ar]	1	1L	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1 4s^2$
Titanium	[Ar]	1 1	1L	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$
Vanadium	[Ar]	1 1 1	1L	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$
*Chromium	[Ar]	1 1 1 1 1	1	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$
Manganese	[Ar]	1 1 1 1 1	1L	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$
Iron	[Ar]	1L 1 1 1 1	1L	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$
Cobalt	[Ar]	1L 1L 1 1 1	1L	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$
Nickel	[Ar]	1L 1L 1L 1 1	1L	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^8 4s^2$
*Copper	[Ar]	1L 1L 1L 1L 1L	1	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$
Zinc	[Ar]	1L 1L 1L 1L 1L	1L	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2$

- General properties: **hard, high density, high melting and boiling point**
- Loss of electrons from transition elements can result in stable electronic configuration when:
 - all 3d and 4s electrons lost (noble gas configuration)
 - only all 4s electrons lost
 - all 4s and some 3d electrons lost
- Why do transition elements form ions by losing 4s electrons first, followed by 3d electrons?
 Prior to occupation by electrons, 4s orbital energetically more stable (lower energy level) than 3d orbital. After 3d orbitals (nearer the nucleus) are occupied by electrons, these electrons from inner shell (3rd PQS) repel the 4s electrons further away from the nucleus and to a higher energy level.

Physical Properties:

(Small and relatively constant) Atomic Radius	(High) Melting and Boiling Point																																																																																				
<p>To explain small variation:</p> <p>Across the period from Sc to Cu, electrons are being added to the inner 3d subshell → shield the valence 4s electron from the attraction of the nucleus → the influence of each additional proton in the nucleus (i.e. increasing nuclear charge) is reduced considerably → increase in e.n.c. over the series of d-block elements is negligible → atomic radii remain almost constant (∴ similar melting point, boiling point, densities and IE)</p> <p>To explain for smaller atomic radius:</p> <p>Argue that 3d orbital does not shield as well, so e.n.c will still increase relative to s-block elements.</p> <table border="1"> <caption>Estimated data for atomic radius graph</caption> <thead> <tr> <th>Element</th> <th>Atomic Radius (nm)</th> </tr> </thead> <tbody> <tr><td>Ca</td><td>0.20</td></tr> <tr><td>Sc</td><td>0.14</td></tr> <tr><td>Ti</td><td>0.13</td></tr> <tr><td>V</td><td>0.12</td></tr> <tr><td>Cr</td><td>0.12</td></tr> <tr><td>Mn</td><td>0.12</td></tr> <tr><td>Fe</td><td>0.12</td></tr> <tr><td>Co</td><td>0.12</td></tr> <tr><td>Ni</td><td>0.12</td></tr> <tr><td>Cu</td><td>0.12</td></tr> <tr><td>Zn</td><td>0.13</td></tr> </tbody> </table>	Element	Atomic Radius (nm)	Ca	0.20	Sc	0.14	Ti	0.13	V	0.12	Cr	0.12	Mn	0.12	Fe	0.12	Co	0.12	Ni	0.12	Cu	0.12	Zn	0.13	<p>Explanation:</p> <p>4s and 3d electrons are very close in energy → both can be contributed to form the sea of delocalised electrons → metals form cations of higher charge → ionic radii of the transition element cations are smaller than those of typical s-block elements → more energy required to overcome stronger EFOA between transition metal cations and sea of delocalised electrons</p> <table border="1"> <caption>Estimated data for Melting and Boiling Point graph</caption> <thead> <tr> <th>Element</th> <th>Melting Point (°C)</th> <th>Boiling Point (°C)</th> </tr> </thead> <tbody> <tr><td>Ca</td><td>1000</td><td>1500</td></tr> <tr><td>Sc</td><td>1500</td><td>2800</td></tr> <tr><td>Ti</td><td>1800</td><td>3300</td></tr> <tr><td>V</td><td>2000</td><td>3400</td></tr> <tr><td>Cr</td><td>2000</td><td>2600</td></tr> <tr><td>Mn</td><td>1200</td><td>2000</td></tr> <tr><td>Fe</td><td>1500</td><td>2600</td></tr> <tr><td>Co</td><td>1500</td><td>2800</td></tr> <tr><td>Ni</td><td>1500</td><td>2600</td></tr> <tr><td>Cu</td><td>1000</td><td>2500</td></tr> <tr><td>Zn</td><td>500</td><td>1000</td></tr> </tbody> </table>	Element	Melting Point (°C)	Boiling Point (°C)	Ca	1000	1500	Sc	1500	2800	Ti	1800	3300	V	2000	3400	Cr	2000	2600	Mn	1200	2000	Fe	1500	2600	Co	1500	2800	Ni	1500	2600	Cu	1000	2500	Zn	500	1000																								
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³ $\propto \frac{m}{v} \alpha \frac{\text{relative atomic mass}}{\text{atomic radius}}$

Chemical Properties:

Q: State and explain in terms of electronic structure ([chemical properties](#)), three characteristic properties of transition metals or their compounds (no need go into detail due to mark allocation).

- Ability to exhibit variable oxidation states

This is primarily due to [the closeness in energy of the 3d and 4s electrons](#), which means that both the [3d and 4s electrons](#) are available for bond formation (ionic/ covalent).

- Ability to form coloured compounds

The [presence of ligands](#) causes the [3d orbitals](#) to split into two sets of non-degenerate orbitals with different energies. Transition metal compounds are coloured due [to electron transitions between thesee two sets of 3d orbitals](#).

- Ability to form complexes

This is due to the [presence of low lying vacant oerbitals in the metal atom or ion](#), which allows the [ligands to form dative bonds](#) with the central metal atom or ion.

- Ability to act as catalysts

This is primarily due to [the closeness in energy of the 3d and 4s electrons](#) which allows transition metals [to exhibit variable oxidation states \(homogenous catalysis\)](#) or the [presence of low lying vacant or partially filled 3d and 4s orbitals](#) to allow for [adsorption of reactant moelcuels \(heterogenous catalysis\)](#).

Variable oxidation states

- Common os +2/ +3
- Lower os usually found in ionic cmpd
- Higher os usually found in covalent cmpds/ ions that contain covalent bond

Least O.S. → Most O.S. ← Least O.S.									
Sc*	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn*
+1	+1	+1	+1	+1	+1	+1	+1	+1	+1
+2	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	+3
+4	+4	+4	+4	+4	+4	+4	+4	+4	
+5		+5	+5	+5	+5	+5	+5		
+6		+6	+6	+6	+6	+6			
+7									

Max number of oxidation states for each element
= Number of 4s e⁻ + Number of unpaired 3d e⁻

All 3d and 4s e⁻ used for bonding
Paired 3d e⁻ not available for bonding

Transition elements acting as catalysts

Homogenous catalysis	Heterogenous catalysis
<ol style="list-style-type: none"> Ability of transition element to exist in different oxidation states Relative ease with which the oxidation state can be converted from one to another which will facilitate the formation and decomposition of reaction intermediates 	<ol style="list-style-type: none"> Availability of energetically accessible vacant/ partially filled 3d subshells which allow ready exchange of electrons to and from reactant particles, thus facilitating the formation of weak bonds with the reactant particles Availability of 3d and 4s electrons for bond formation with reactant particles

(Reaction Kinetics) Outline catalysis in: (i) the Haber process (ii) the catalytic removal of oxides of nitrogen in the exhaust gases from car engines (iii) the catalytic role of atmospheric oxides of nitrogen in the oxidation of atmospheric sulfur dioxide (iv) catalytic role of Fe²⁺ in the I⁻/S₂O₈²⁻ reaction

Nomenclature of Complexes

- Name cation then anion
- Within cation/ anion complex, name ligands before metal in alphabetical order. Use di-, tri-, tetra-, penta-, hexa- if necessary.
- If cationic complex, use name of metal.
- If anionic complex, modify the name of the metal to end with suffix-ate

Ligand	Prefix
H ₂ O	aqua
NH ₃	ammine
CO	carbonyl
Cl ⁻	chloro
CN ⁻	cyano
SCN ⁻	S-thiocyanato

Ligand	Prefix
OH ⁻	hydroxo
NO ₂ ⁻	nitro
NO ₂ ⁻ (ONO ⁻)	nitrito
NO	nitrosyl
H ₂ NCH ₂ CH ₂ NH ₂	ethane-1,2-diammine

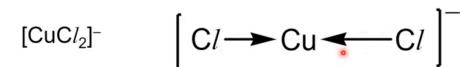
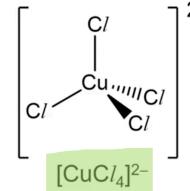
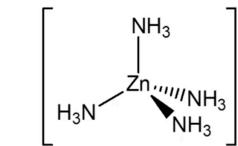
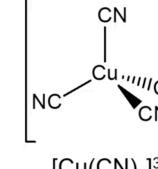
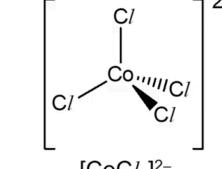
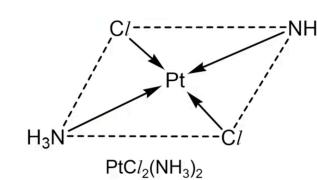
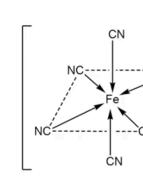
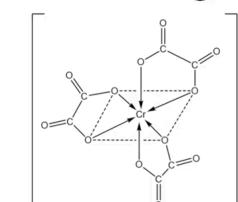
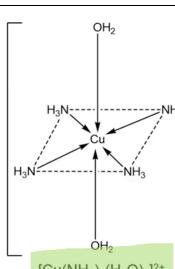
Element	Name in complex	Element	Name in complex
Ti	titanate	Cu	cuprate
V	vanadate	Zn*	zincate
Cr	chromate	Ag	argentate
Mn	manganate	Au	aurate
Fe	ferrate	Al*	aluminate
Co	cobaltate	Sn	stannate
Ni	nickelate / nickelate	Pb*	plumbate

Example:

tetraaminediaquacopper(II) chloride: [Cu(NH₃)₄(H₂O)₂]Cl₂

potassium amminepentacyanoferrate (III): K₂[Fe(CN)₅NH₃]

Stereochemistry of Complexes

Coordination Number	Shape	Example
2	linear	$[\text{Ag}(\text{NH}_3)_2]^+$  $[\text{CuCl}_2]^-$ 
4	tetrahedral	 $[\text{CuCl}_4]^{2-}$
		 $[\text{Zn}(\text{NH}_3)_4]^{2+}$  $[\text{Cu}(\text{CN})_4]^{3-}$  $[\text{CoCl}_4]^{2-}$
	square planar	 $\text{PtCl}_2(\text{NH}_3)_2$
6	octahedral	 $[\text{Fe}(\text{CN})_6]^{4-}$  $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$  $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$

* Need to know complexes of copper (II) ions with water, ammonia and chloride ions as ligands

Reason for transition element complexes being coloured (usually):

In isolated metal ion in gaseous phase, 5 3d orbitals have the same energy (**degenerate**).

In complex ion, presence of ligands cause 3d orbitals to split into two sets of non-degenerate orbitals with different energies.

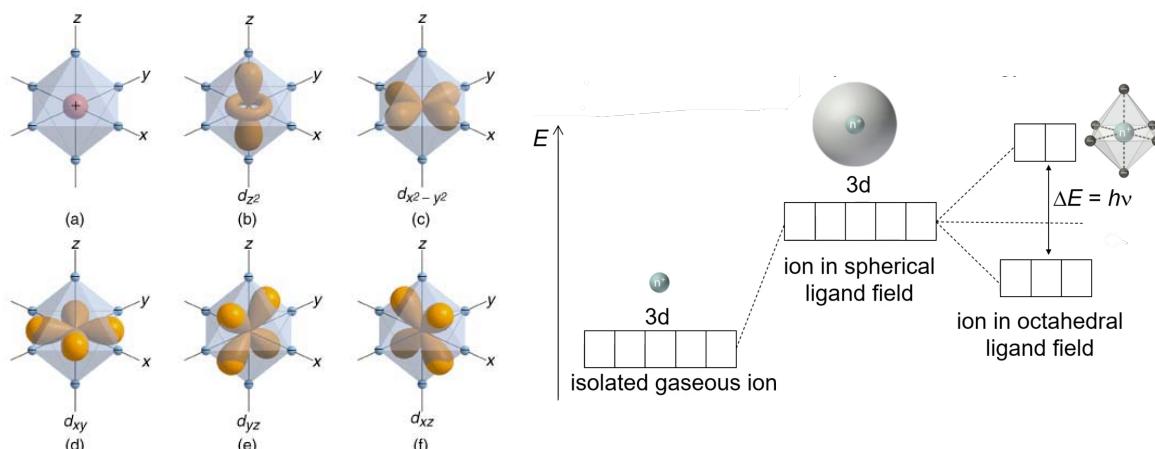
The difference in energies between the two sets of 3d orbitals is relatively small and falls within the energy range of the visible spectrum of the EM spectrum. Thus, radiation in the visible region is absorbed when an electron from a lower energy d orbital is promoted to a partially filled/ empty d orbital of higher energy. This is known as d-d transition.

Conditions:

Metal atom/ ion must possess ① At least one d electron ② An empty or partially filled 3d orbital at the upper level to accommodate the d electron to be promoted

N.B. The colour observed is the complement of the colours absorbed. (See next page)

Splitting of degenerate d orbitals into 2 energy levels in octahedral complex:



In an octahedral complex, ligands are modelled as six point negative charges that surround the positively charged transition metal ion.

The d_{z^2} and $d_{x^2-y^2}$ orbitals have lobes that project towards the negative charges, while the d_{xy} d_{xz} and d_{yz} orbitals have lobes that project between the charges.

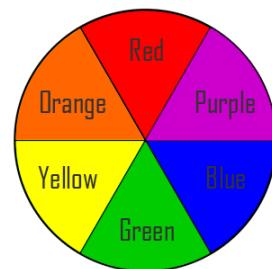
As a result, the orbitals on the ligands repel the d_{z^2} and $d_{x^2-y^2}$ orbitals more than the other d orbitals, causing the splitting of degenerate d orbitals into two different energy levels, where d_{z^2} and $d_{x^2-y^2}$ are at a higher energy level than the other d orbitals.

Reason for transition element complexes being uncoloured (i.e. white):

1. d block metal ions with d^0 configuration e.g. Sc^{3+} and Ti^{4+}
No d electrons → d-d transition is not possible
2. d block metal ions with d^{10} configuration e.g. Zn^{2+} and Cu^{+}
No empty or partially filled d orbital of higher energy level to accommodate d electron to be promoted
3. non d block metal ions e.g. Al^{3+}
No d electrons → energy gap is too large (transition of electrons from 2p to 3s require too much energy outside visible range)

Visible EM Spectrum and Colour Wheel

Wavelength range/ nm	Colour	Complementary colour
400 – 450	violet	yellow
450 – 490	blue	orange
490 – 550	green	red
550 – 580	yellow	violet
580 – 650	orange	blue
650 – 700	red	green



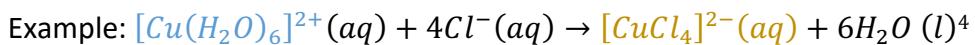
Determinants of colour of transition element complexes

Energy gap which is dependent on

- Identity of metal
- Oxidation state of metal
- Nature of ligand

Ligand Exchange

K_s indicates the inherent tendency of a particular ligand to replace water in the aqua-complex.



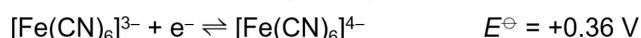
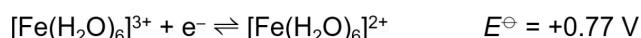
$$K_s = \frac{[\text{CuCl}_4]^{2-}}{[\text{Cu}(\text{H}_2\text{O})_6]^{2+}[\text{Cl}^-]^4}$$

- Affected by relative concentrations of ligands
- **Higher K_s = stronger binding ligand**
- Stability of complexes involving **polydentate ligands** usually **greater** than that of complexes involving **monodentate ligands**
- Ligands which form complexes with **higher K_s value** will **displace** those which form a complex with **lower K_s value**.

⁴ may result in green solution (blue + yellow)

- Ligand exchange will have impact on E values for electrochemistry.

Example:

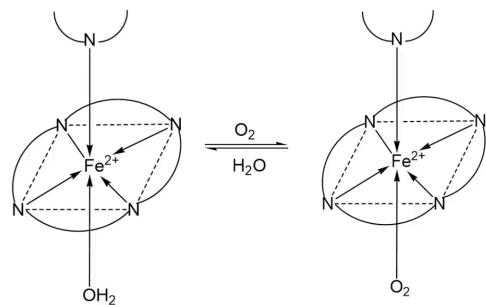


More energy is required to add an electron to the negatively charged $[\text{Fe}(\text{CN})_6]^{3-}$ due to repulsion, it is less easily reduced and is a weaker oxidising agent

Application of Ligand Exchange (CO/O_2 exchange in haemoglobin)

Haemoglobin

- has 4 haem group
- each consist of a Fe^{2+} ion with coordination number 6
- five of the coordination sites are occupied by N
- sixth site can accommodate an oxygen molecule as ligand via coordinate bond
- $\text{Fe}^{2+} - \text{O}_2$ bond is relatively weak
- oxygen molecule can easily be released to cells
- site is then occupied by H_2O ligand



(Reaction Kinetics) Ligands like CO may replace water molecule i.e. oxyhaemoglobin is converted to carboxyhaemoglobin \rightarrow CO **strongly and irreversibly bonded** at site \rightarrow destroys haemoglobin's oxygen carrying capacity

