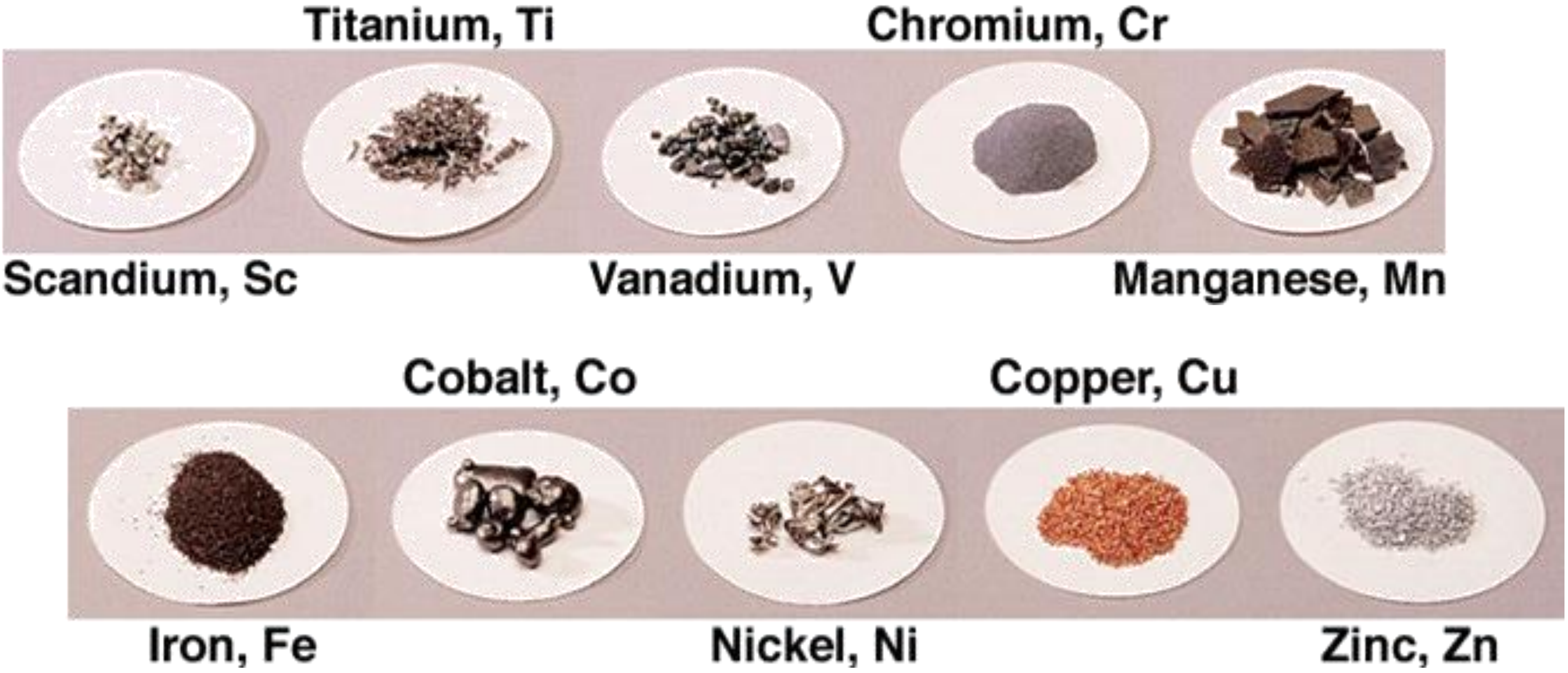
AH Chemistry – Unit 1

Transition Metals

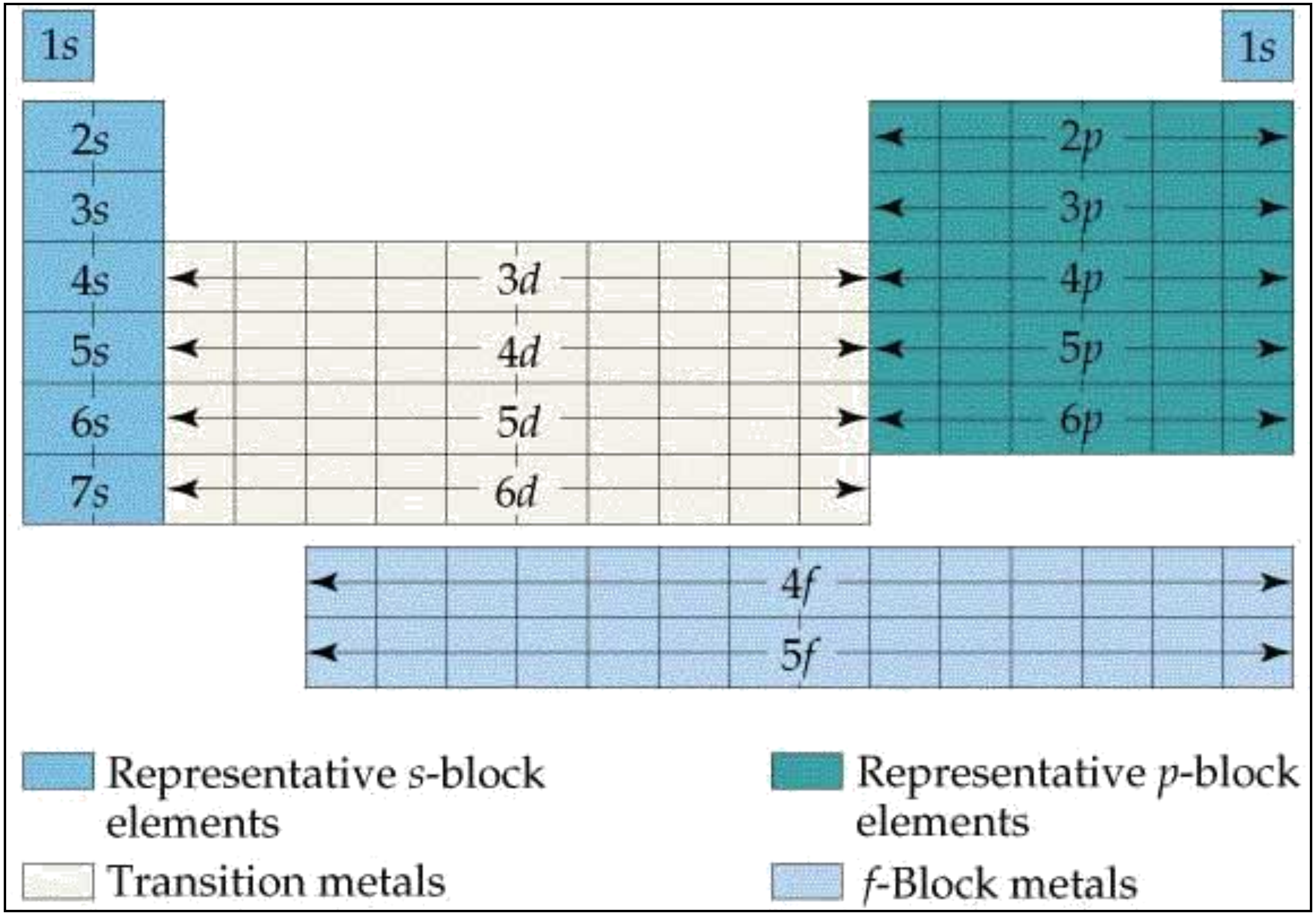
Introduction



Aspects of the ***Transition Metals*** are studied with particular reference to their ***Electronic Configurations***

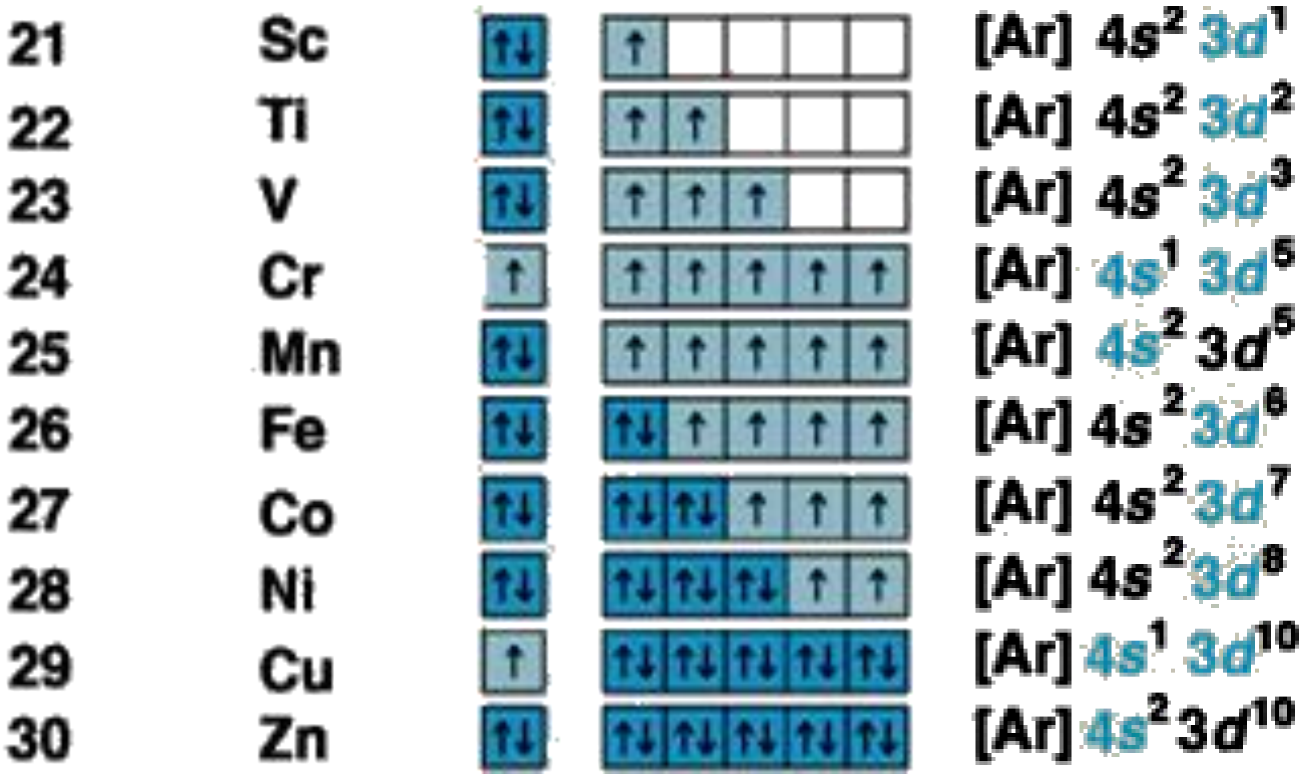
Transition Metals - Definition 1

The easiest, but least useful, definition of a Transition metal is that ***it is found in the d-block of the table***.



Transition Metals - Definition 2

Another definition of a Transition metal is that ***it has an incomplete d subshell***. This excludes **Cu** and **Zn**.



Atomic No.	*Symbol*	*4 s*	*3 d*	*Configuration*
21	Sc	[↑↓]	[↑] [ ] [ ] [ ] [ ]	[Ar] $4s^2 3d^1$
22	Ti	[↑↓]	[↑] [↑] [ ] [ ] [ ]	[Ar] $4s^2 3d^2$
23	V	[↑↓]	[↑] [↑] [↑] [ ] [ ]	[Ar] $4s^2 3d^3$
24	Cr	[↑]	[↑] [↑] [↑] [↑] [↑]	[Ar] $4s^1 3d^5$
25	Mn	[↑↓]	[↑] [↑] [↑] [↑] [↑]	[Ar] $4s^2 3d^5$
26	Fe	[↑↓]	[↑↓] [↑] [↑] [↑] [↑]	[Ar] $4s^2 3d^6$
27	Co	[↑↓]	[↑↓] [↑↓] [↑] [↑] [↑]	[Ar] $4s^2 3d^7$
28	Ni	[↑↓]	[↑↓] [↑↓] [↑↓] [↑] [↑]	[Ar] $4s^2 3d^8$
29	Cu	[↑]	[↑↓] [↑↓] [↑↓] [↑↓] [↑↓]	[Ar] $4s^1 3d^{10}$
30	Zn	[↑↓]	[↑↓] [↑↓] [↑↓] [↑↓] [↑↓]	[Ar] $4s^2 3d^{10}$

NB 4*s* is of lower energy so fills before 3*d*. Cr and Cu are exceptions to ***Aufbau rule***

Filling of d-orbitals - exceptions

Cu and ***Cr*** are exceptions to the ***Aufbau principle***.

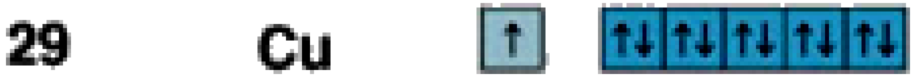
Cr should be:

Cr actually is:

There is a ***special stability*** associated with ***all the d-orbitals being half-filled***.

Cu should be:

Cu actually is:

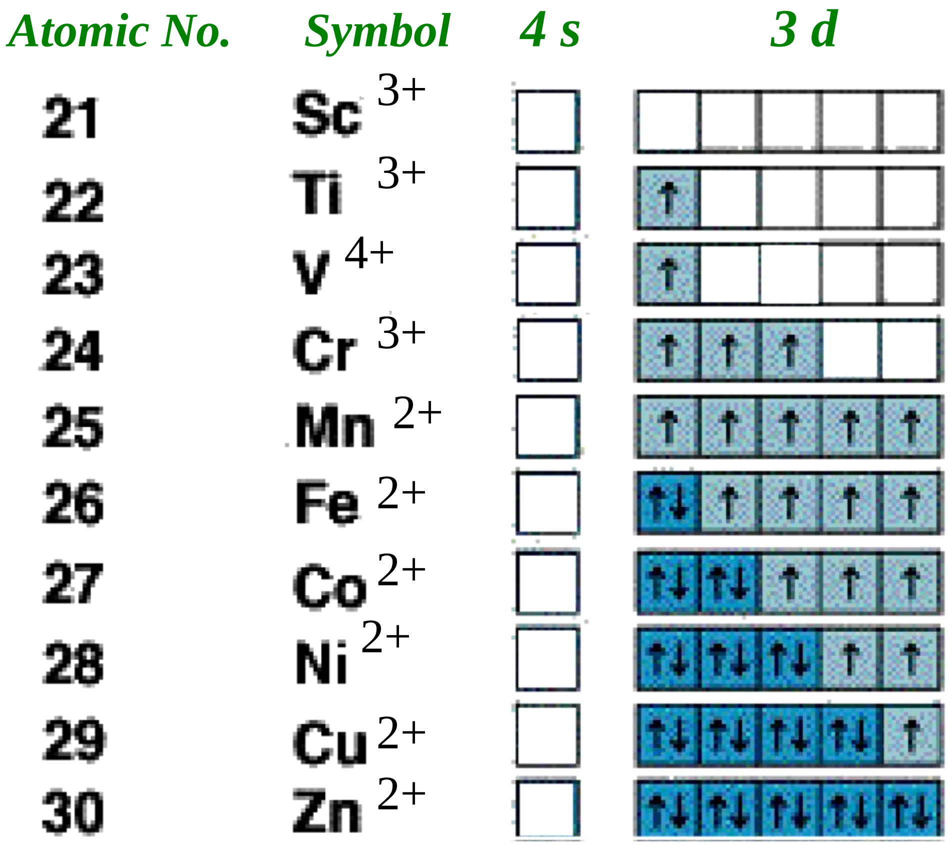


There is a ***special stability*** associated with ***all the d-orbitals being completely filled***

Transition Metals - Definition 3

Another definition of a Transition metal is that ***it has at least one ion with an incomplete d subshell***.

NB 4*s* is now at higher energy so empties before 3*d*.



Atomic No.	Symbol	4 s	3 d				
21	Sc $^{3+}$						
22	Ti $^{3+}$		↑				
23	V $^{4+}$		↑				
24	Cr $^{3+}$		↑	↑	↑		
25	Mn $^{2+}$		↑	↑	↑	↑	↑
26	Fe $^{2+}$		↑↓	↑	↑	↑	↑
27	Co $^{2+}$		↑↓	↑↓	↑	↑	↑
28	Ni $^{2+}$		↑↓	↑↓	↑↓	↑	↑
29	Cu $^{2+}$		↑↓	↑↓	↑↓	↑↓	↑
30	Zn $^{2+}$		↑↓	↑↓	↑↓	↑↓	↑↓

Sc only forms a Sc^{3+} ion so would be excluded by this definition.

Zn only forms a Zn^{2+} ion so would be also be excluded by this definition.

Transition Metals - Best Definition

There are 3 main characteristics of a Transition metal

- they can produce ions with ***different valencies***
  - Sc & Zn produce ***only one possible ion each***
- they produce ***coloured compounds***
  - Sc & Zn have ***no coloured compounds***
- they can act as ***catalysts***
  - Sc & Zn have ***no catalytic applications***

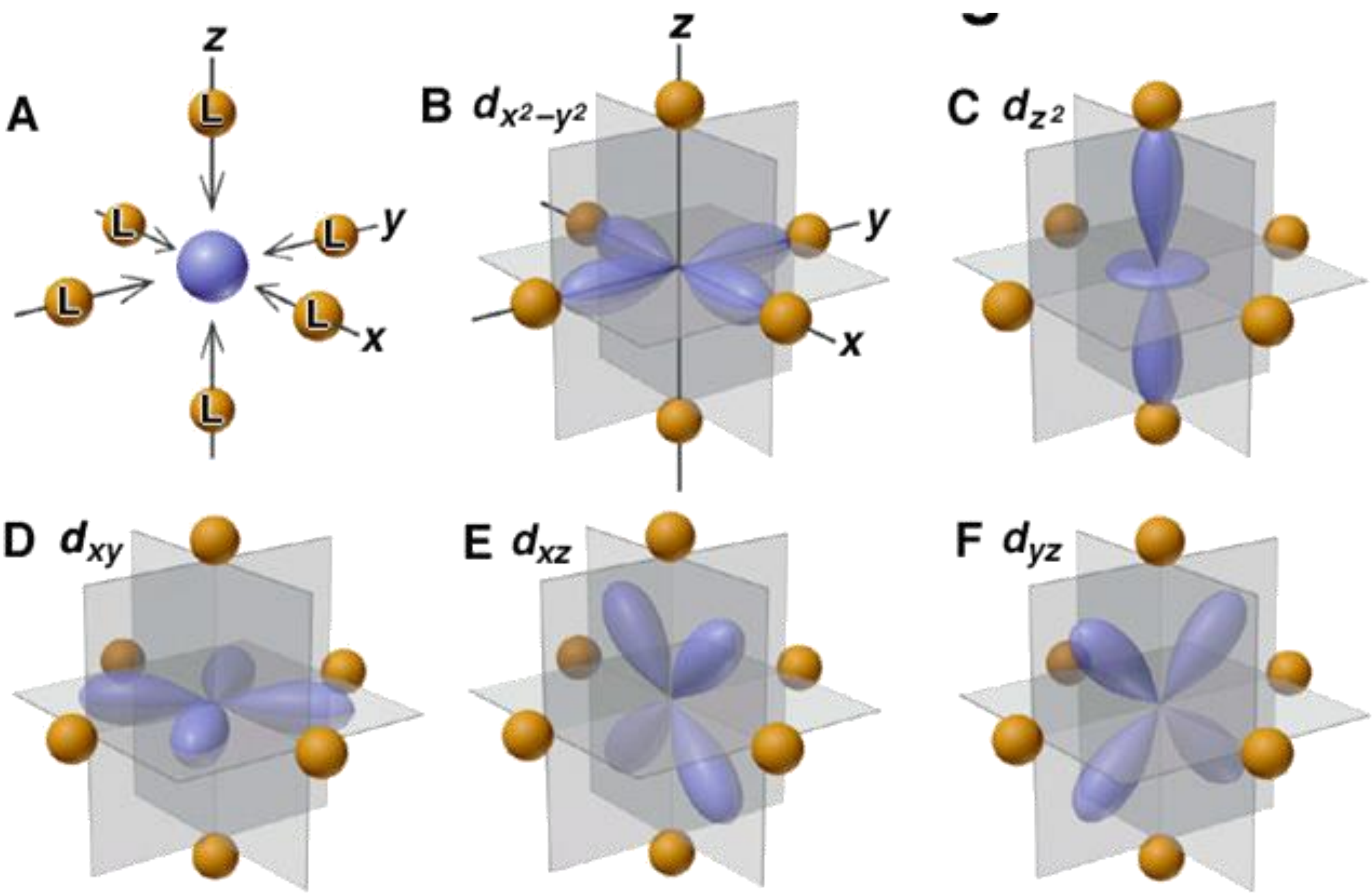
Therefore, the best definition of a Transition metal is that ***it has at least one ion with an incomplete d subshell***.

Coloured Transition Metal Complexes

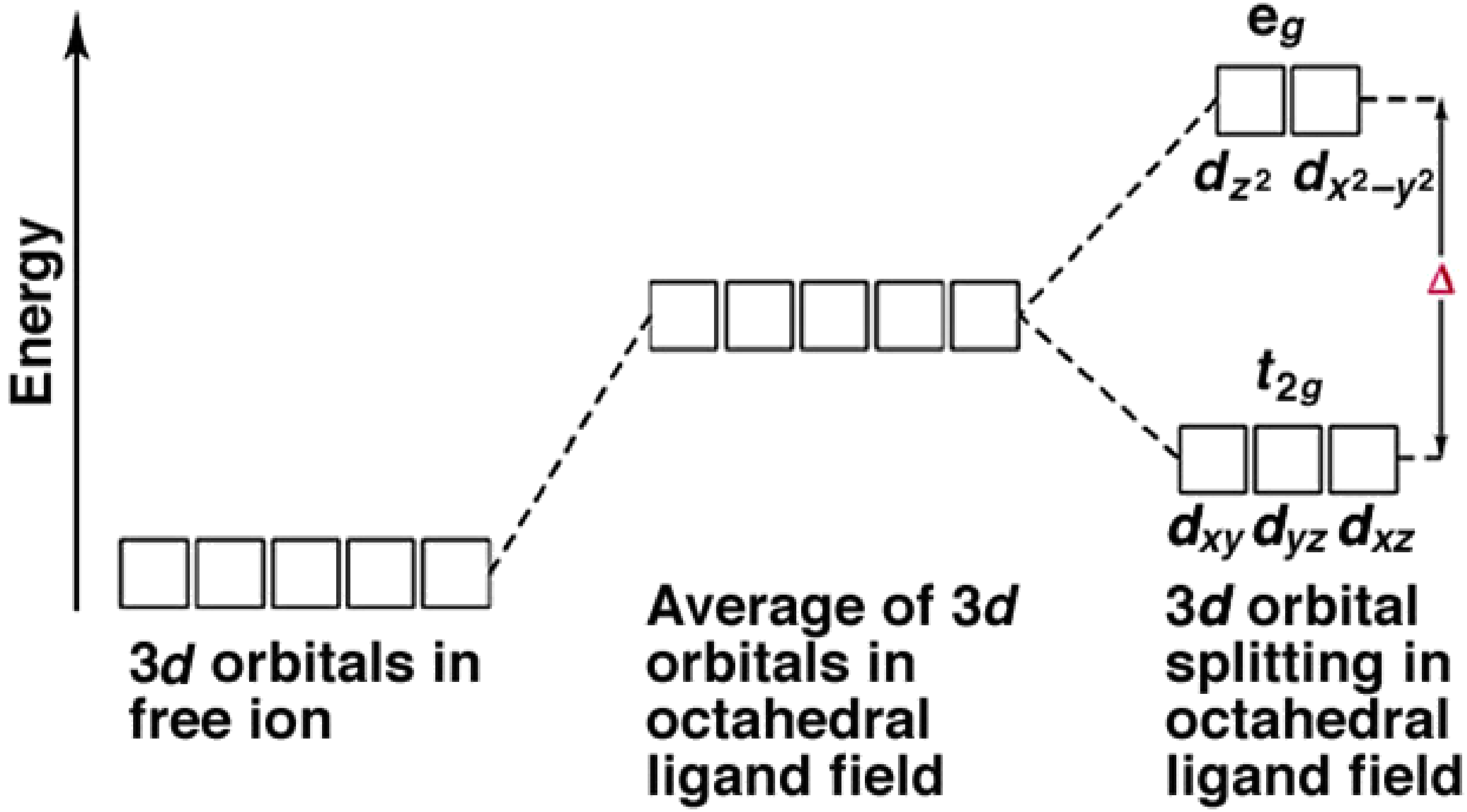
The ***ligands*** surrounding metal ions in these complexes are responsible for the characteristic ***colours*** seen in so many of their compounds.

Interactions between the ***ligands*** and electrons occupying the ***d-orbitals*** create the circumstances that lead to the ***absorption*** of some light from the ***visible*** spectrum.

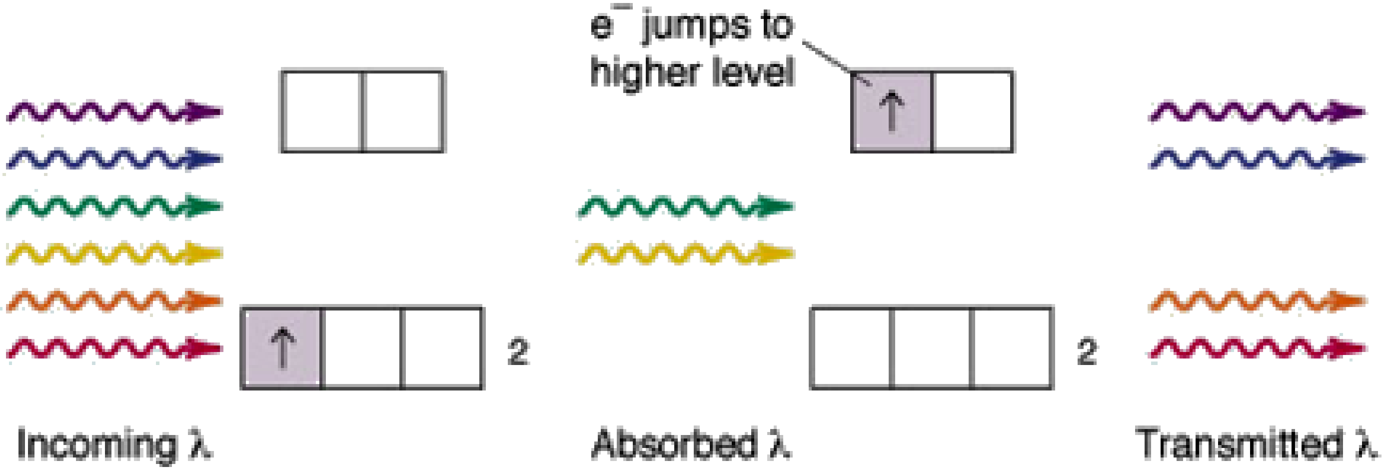
Repulsive Forces - octahedral

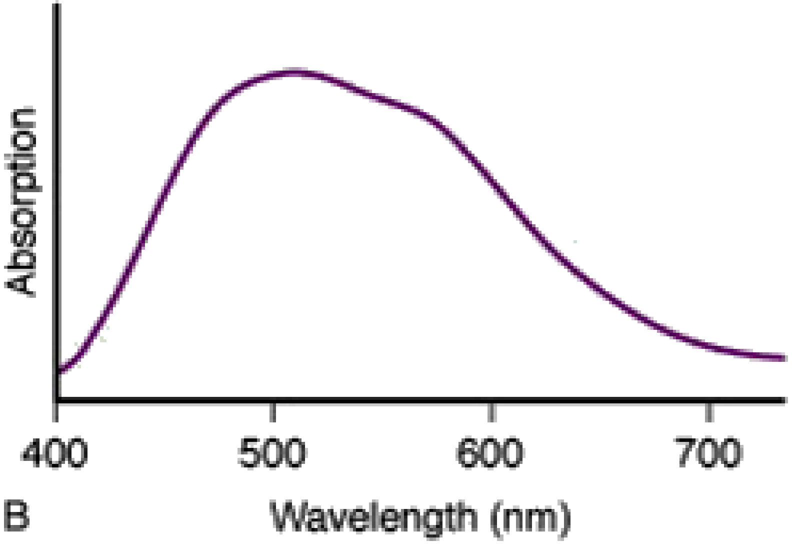


Splitting of d-orbitals



Colour of [$Ti(H_2O)_6$]$^{3+}$



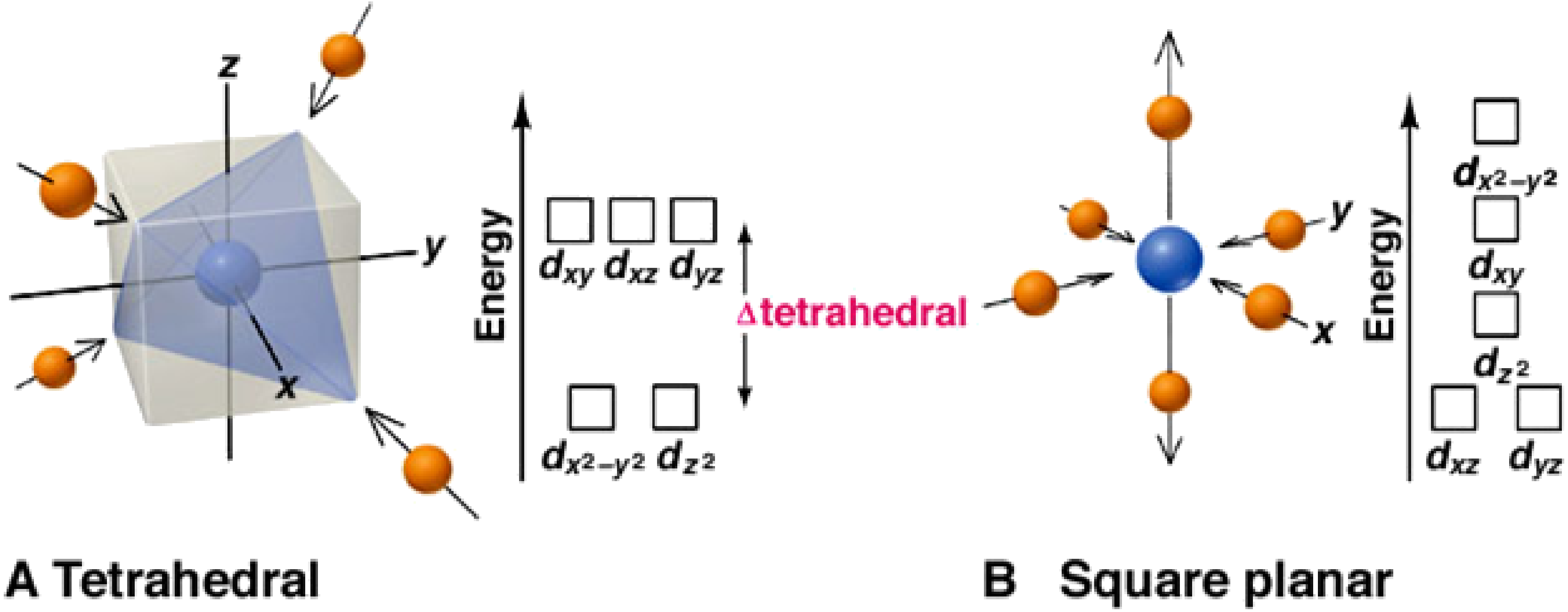


Green-yellow light is ***absorbed*** as an electron is promoted from one set of *d-orbitals* to the other set of *d-orbitals*.

d → d transitions

The blue & red light ***transmitted*** makes the compound a purple colour

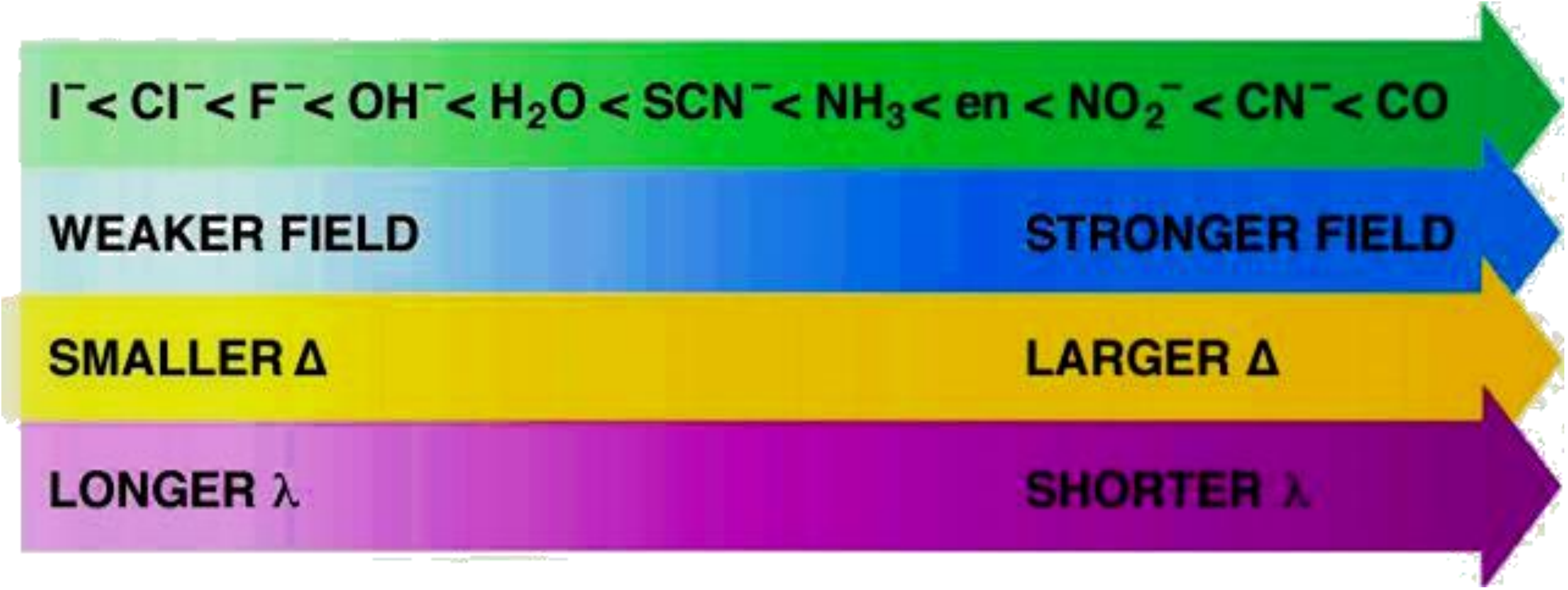
Tetrahedral & Square Planar



Details about splitting of d-orbitals do not need to be learnt.

Just need to know that ***d → d transitions*** are possible

Spectrochemical Series



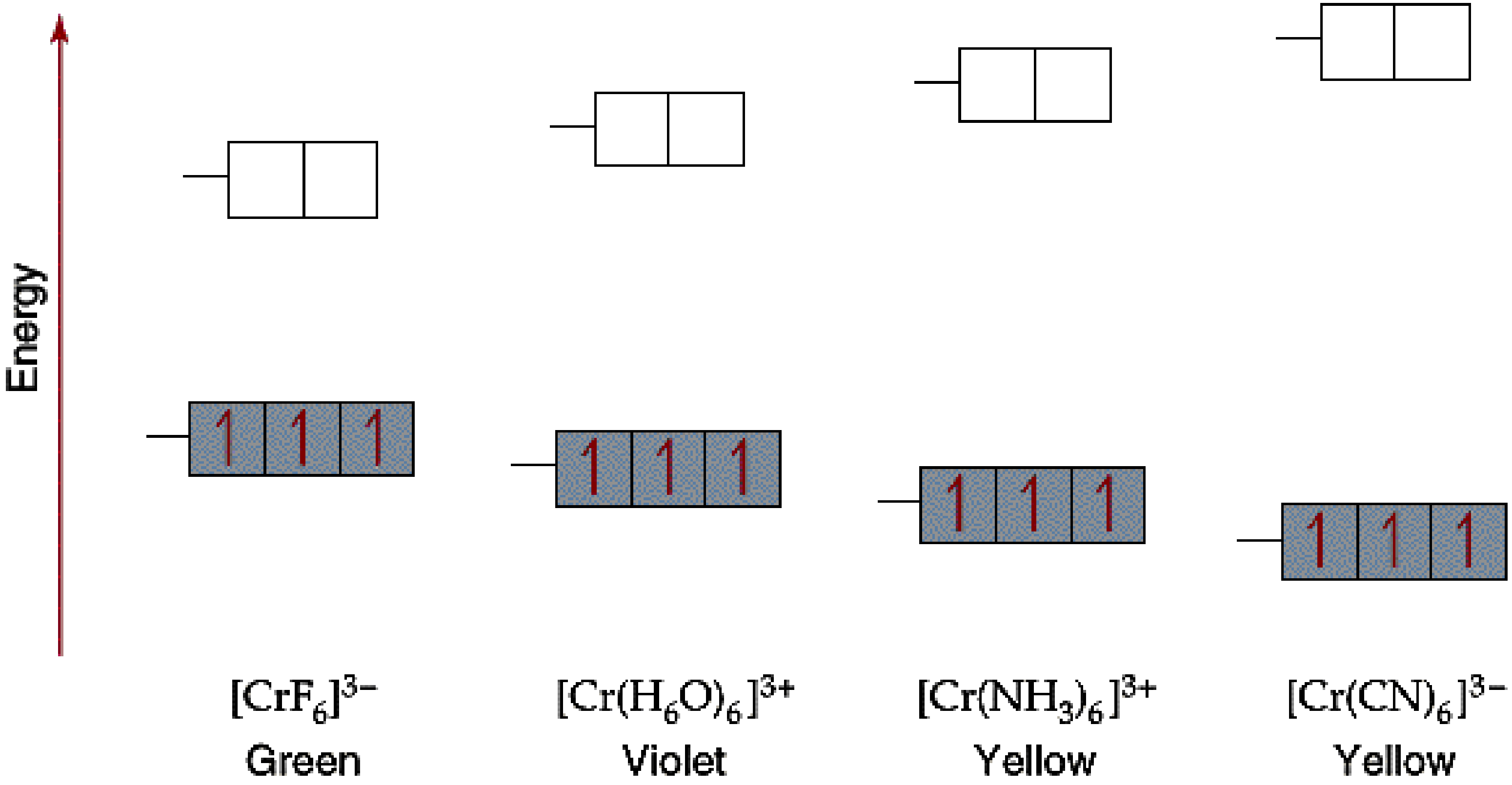
$I^- < Cl^- < F^- < OH^- < H_2O < SCN^- < NH_3 < en < NO_2^- < CN^- < CO$

WEAKER FIELD STRONGER FIELD

SMALLER Δ LARGER Δ

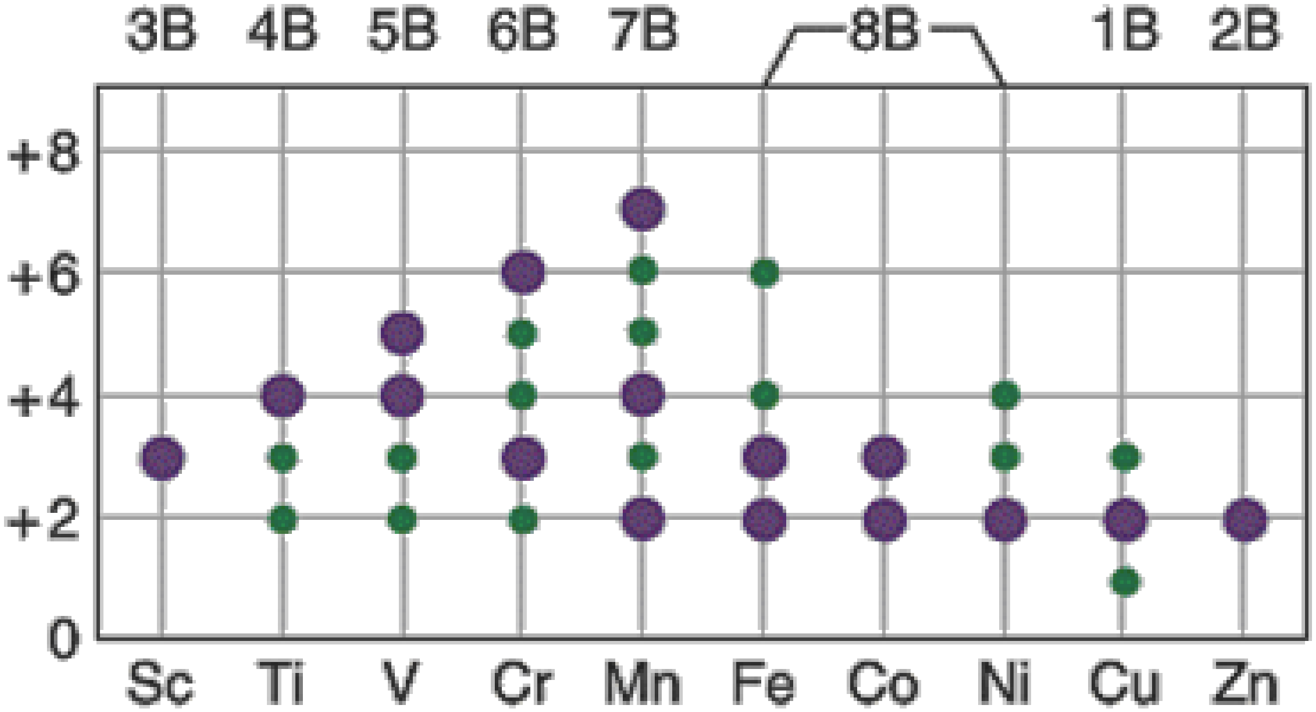
LONGER λ SHORTER λ

Effect of Ligand Field



Oxidation States

Transition metals exhibit ***variable oxidation states*** of ***differing stability***.

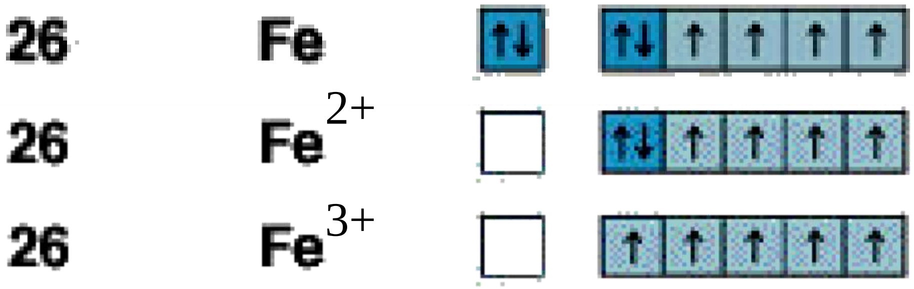


Transition metals exhibit ***variable oxidation states*** because they can not only lose their 4*s* electrons but some or all of their 3*d* electrons.

Oxidation States - stability 1

Sometimes ***electron configurations*** can be used to explain why one ***oxidation state*** is more stable.

For example, during rusting Fe^{2+} ions are formed first, but they then change into Fe^{3+} ions.

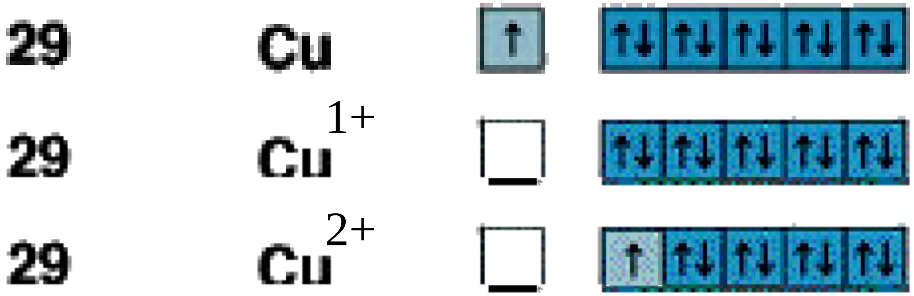


The Fe^{3+} ion forms in preference to Fe^{2+} because of the ***extra stability*** associated with ***all the d-orbitals being half-filled***.

Oxidation States - stability 2

Sometimes ***electron configurations*** ***cannot*** be used to explain why one ***oxidation state*** is more stable.

For example, copper forms two ions Cu^+ and Cu^{2+}. Most copper compounds contain the soluble Cu^{2+} ion.



The Cu^+ ion should form in preference to Cu^{2+} because of the ***extra stability*** associated with ***all the d-orbitals being filled***.

In fact the Cu^{2+} ion usually forms in preference to Cu^+ because there is even more ***extra stability*** due to forming in solution.

Oxidation Numbers

Oxidation numbers are a way of keeping track of electrons. They do not necessarily represent the ‘true’ charge on a particle but they work!

Rule 1	Simple ions such as Na^+, K^+, Cl^- etc continue to count as + 1 or - 1 .
Rule 2	Oxygen is always assumed to be - 2 .
Rule 3	Hydrogen is always assumed to be +1 .
Rule 4	Overall charge on a compound is always 0 .
Rule 5	In polyatomic ions, the sum of all the oxidation numbers is equal to the overall charge on the ion.

Oxidation Numbers - example 1

What is the oxidation number for Mn in KMnO$_4$?

Rule 1	We assume K counts as + 1
Rule 4	Overall the compound is 0, so MnO$_4$ must be -1.
Rule 2	We assume each oxygen is -2, so 4 x O = - 8
Rule 5	Overall charge on ion is -1, so Mn must be +7 .

When permanganate reacts to form Mn^{2+} ions we can ***calculate*** that ***5e*** must be ***gained***;

$$Mn^{7+} \quad + \quad 5e \quad \rightarrow \quad Mn^{2+}$$

Alternatively,

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

Oxidation Numbers - example 2

What is the oxidation number for S in SO_4^{2-} ?

Rule 2. We assume each oxygen is -2, so 4 *x* O = - 8

Rule 5. Overall charge on ion is -2, so S must be +6 .

What is the oxidation number for S in SO_3^{2-} ?

Rule 2. We assume each oxygen is -2, so 3 *x* O = - 6

Rule 5. Overall charge on ion is -2, so S must be +4 .

When sulphite ions react to form sulphate ions we can calculate that 2e must be lost;

$$S^{4+} \rightarrow S^{6+} + 2e$$

Alternatively,

$$SO_3^{2-} + H_2O \rightarrow SO_4^{2-} + 2H^+ + 2e$$

Oxidation Numbers - example 3

What is the oxidation number for Cr in CrO_4^{2-} ?

Rule 2. We assume each oxygen is -2, so 4 *x* O = - 8

Rule 5. Overall charge on ion is -2, so Cr must be +6 .

What is the oxidation number for Cr in $Cr_2O_7^{2-}$?

Rule 2. We assume each oxygen is -2, so 7 *x* O = - 14

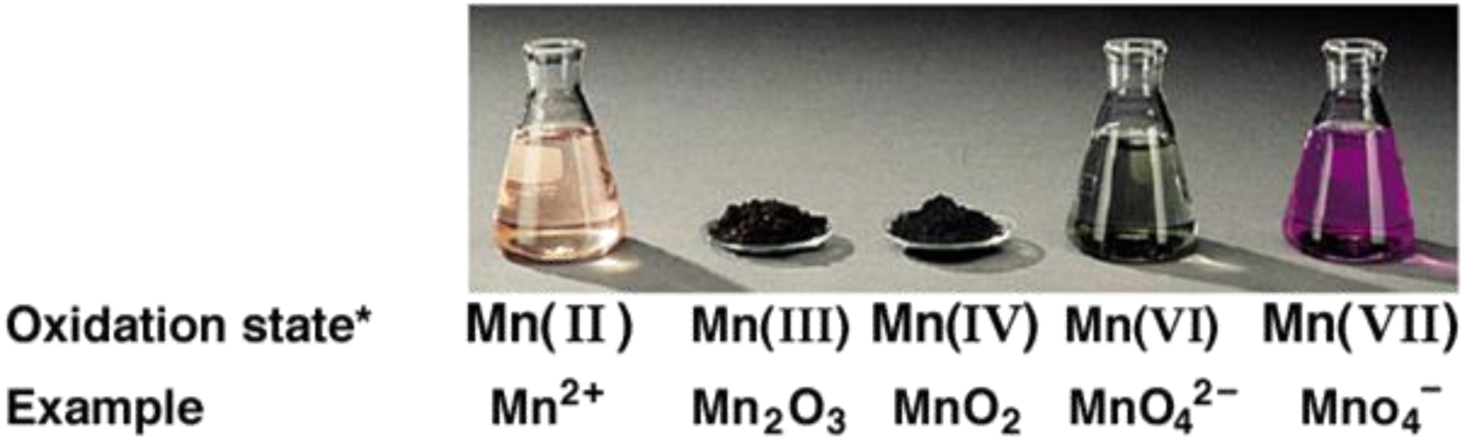
Rule 5. Overall charge on ion is -2, so 2 *x* Cr must be +12
so Cr must be +6

When chromate ions react to form dichromate ions we can calculate that no electrons are gained or lost.

Alternatively,

$$2CrO_4^{2-} + 2H^+ \rightarrow Cr_2O_7^{2-} + H_2O$$

Oxidising & Reducing Agents



Oxidation state*	Mn(II)	Mn(III)	Mn(IV)	Mn(VI)	Mn(VII)
Example	Mn^{2+}	Mn_2O_3	MnO_2	MnO_4^{2-}	Mno_4^-

Compounds containing metals in a high oxidation state tend to be oxidising agents

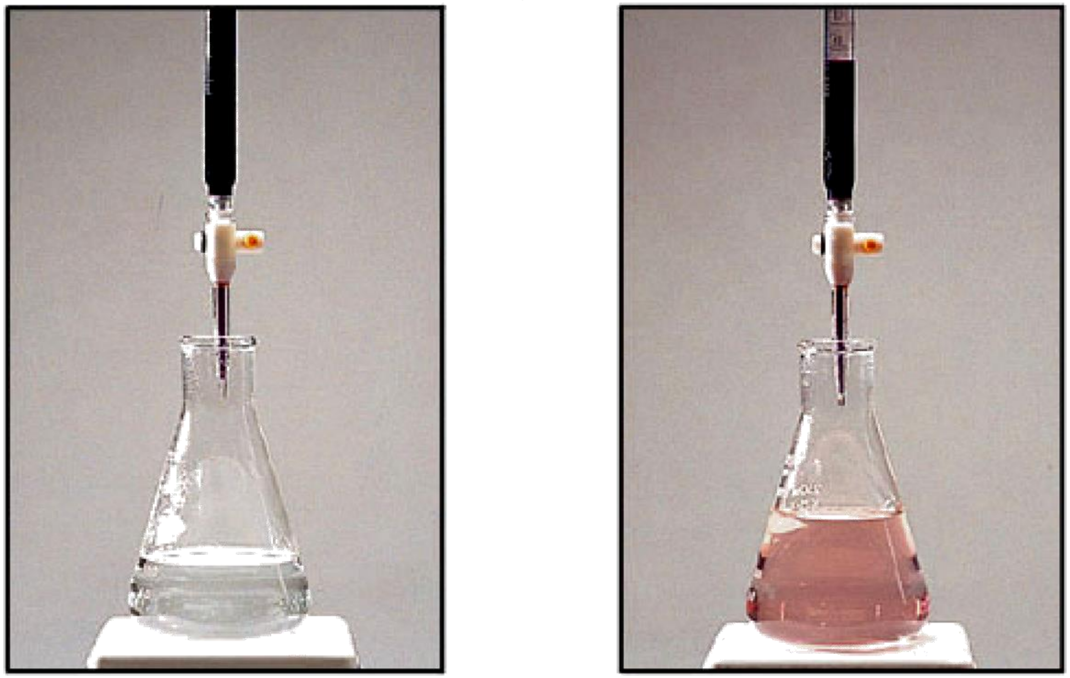
e.g. $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Compounds containing metals in a low oxidation state tend to be reducing agents

e.g. $Fe(OH)_2 + OH^- \rightarrow Fe(OH)_3 + e^-$

Redox Titration

A Redox Titration



Net ionic equation:

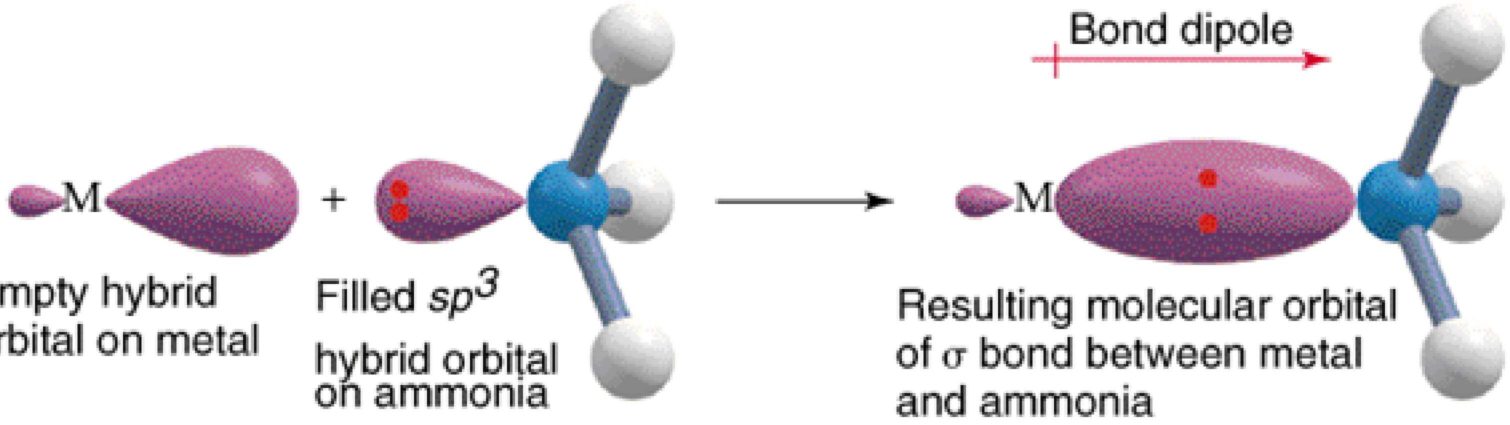
$$2\overset{+7}{\mathrm{Mn}}\mathrm{O_4^-}(aq) + 5\overset{+3}{\mathrm{C}}\mathrm{{}_2O_4^{2-}}(aq) + 16\mathrm{H^+}(aq) \longrightarrow 2\overset{+2}{\mathrm{Mn}}\mathrm{{}^{2+}}(aq) + 10\overset{+4}{\mathrm{C}}\mathrm{O_2}(g) + 8\mathrm{H_2O}(l)$$

Transition Metal Complexes

Metal (atom or ion), ***surrounded by ligands***, with the ligands bound to the metal through ***coordinate covalent*** bonds.

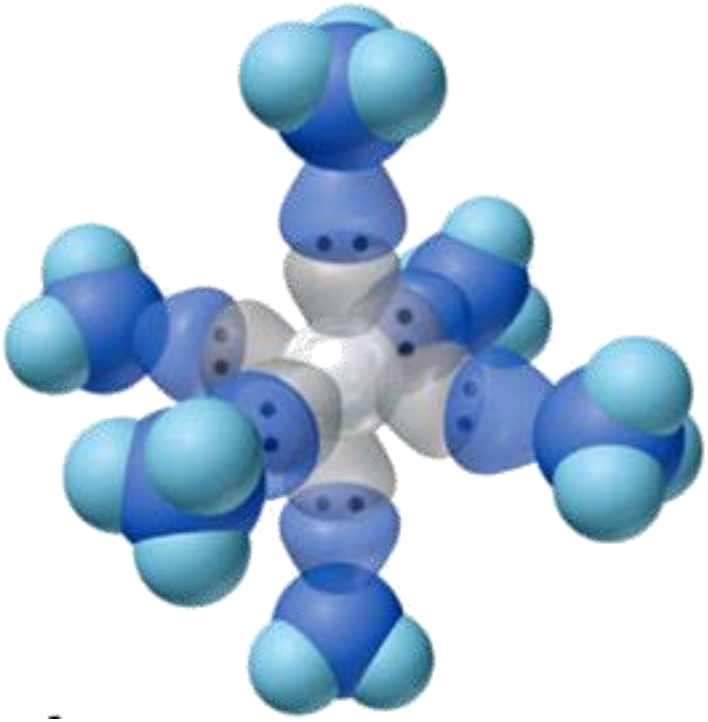
Metal : makes use of empty hybrid orbitals, usually involving at least some *d*-orbitals.

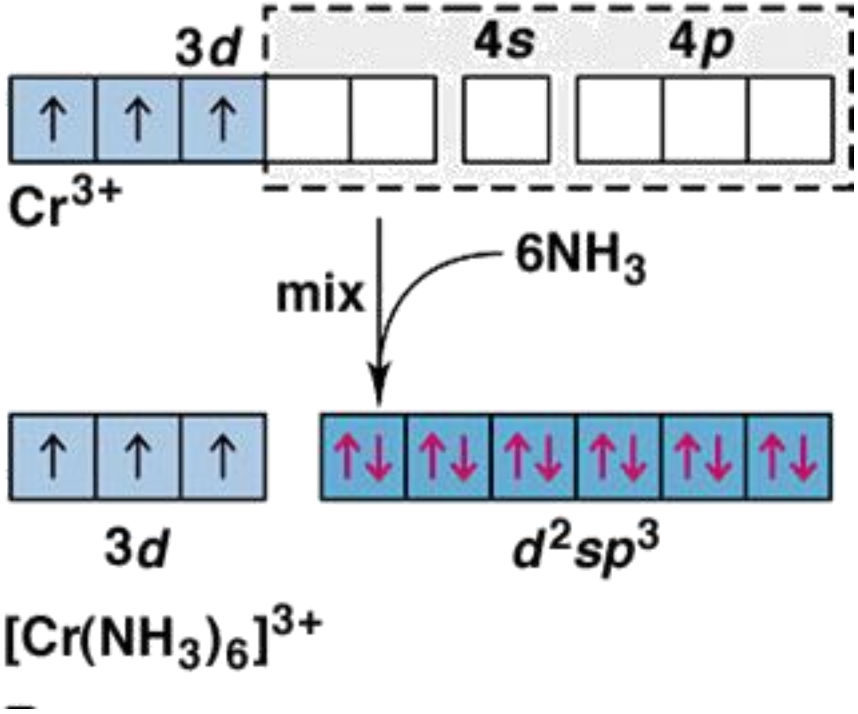
Ligand : atom, molecule or ion that contain at least one ***lone pair***.



Transition Metal Complexes

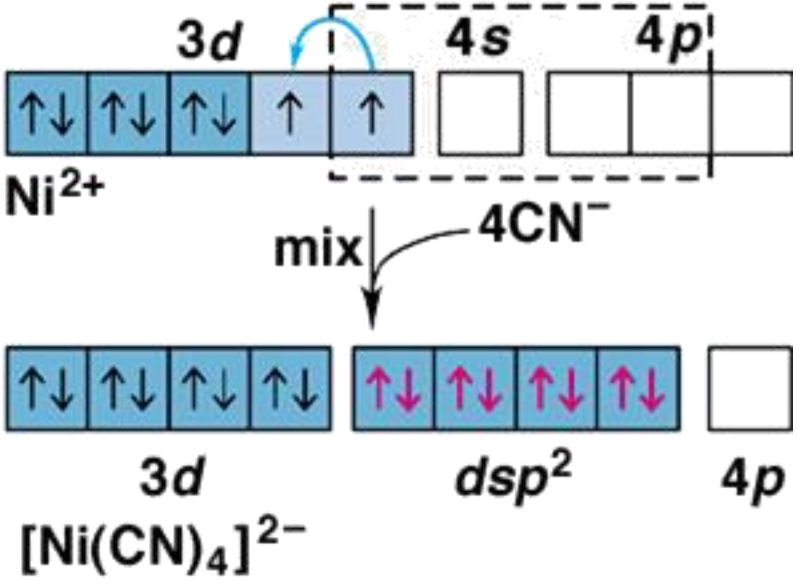
Octahedral Complex





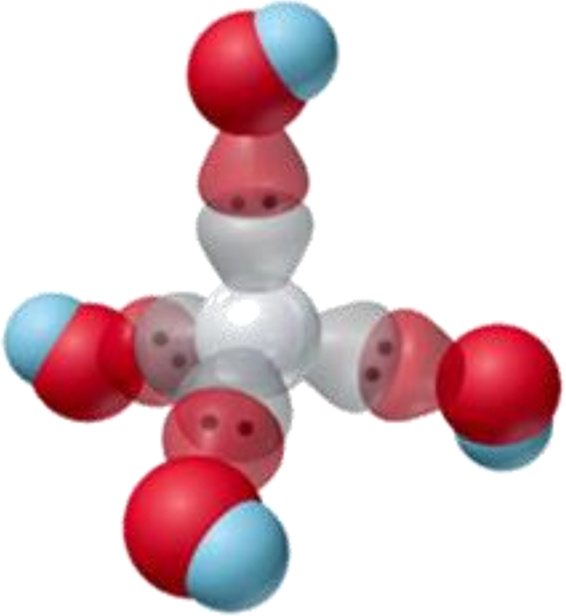
Transition Metal Complexes

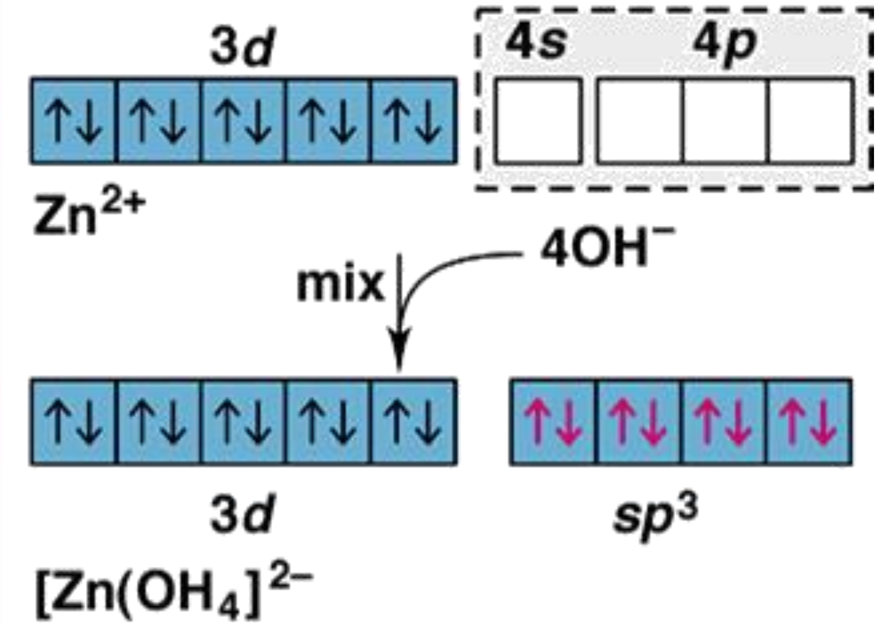
Square Planar Complex



Transition Metal Complexes

Tetrahedral Complex





Ligands - monodentate

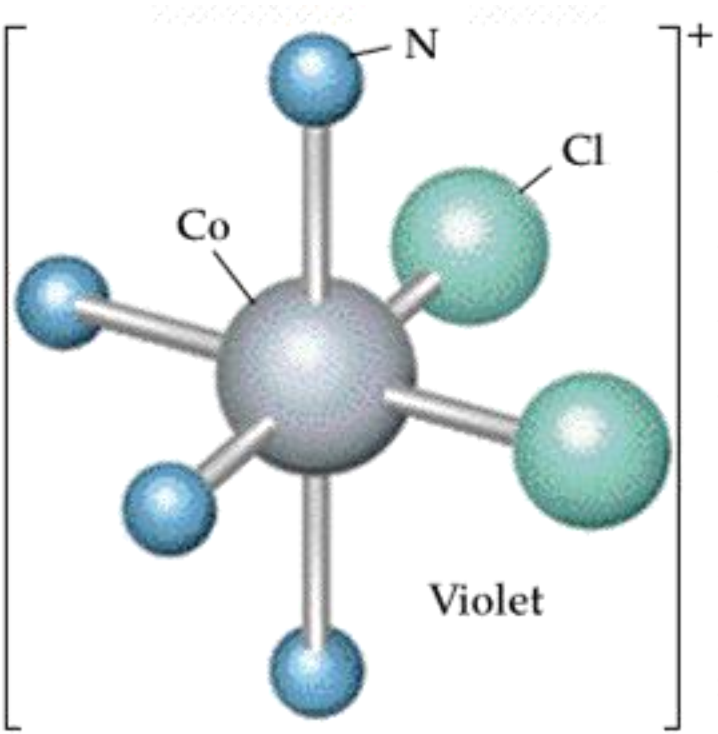
Can only form ***one bond*** with the metal atom/ion

$:NH_3$ **ammonia**

$:\ddot{\underset{..}{Cl}}:^-$ **chloride ion**

$:C\equiv N:]^-$ **cyanide ion**

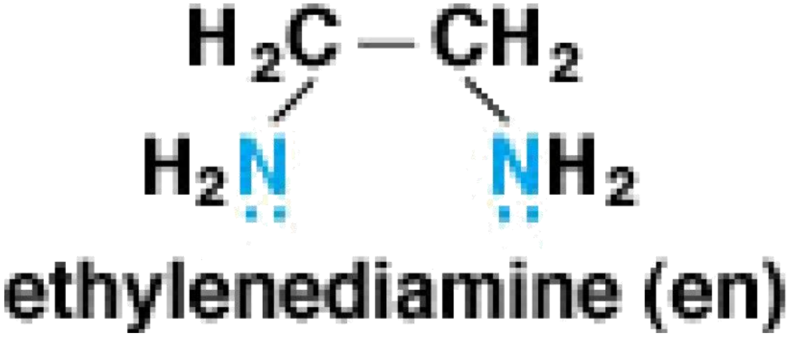
$H_2\ddot{O}:$ **water**



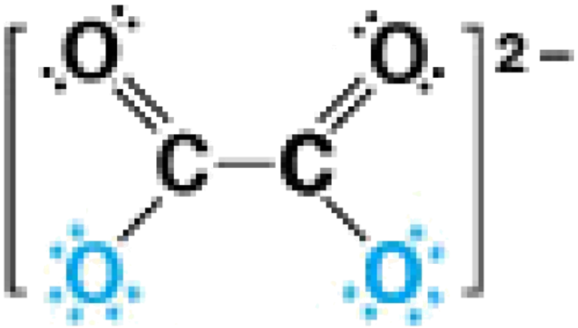
$[Co(NH_3)_4Cl_2]^+$

Ligands - bidentate

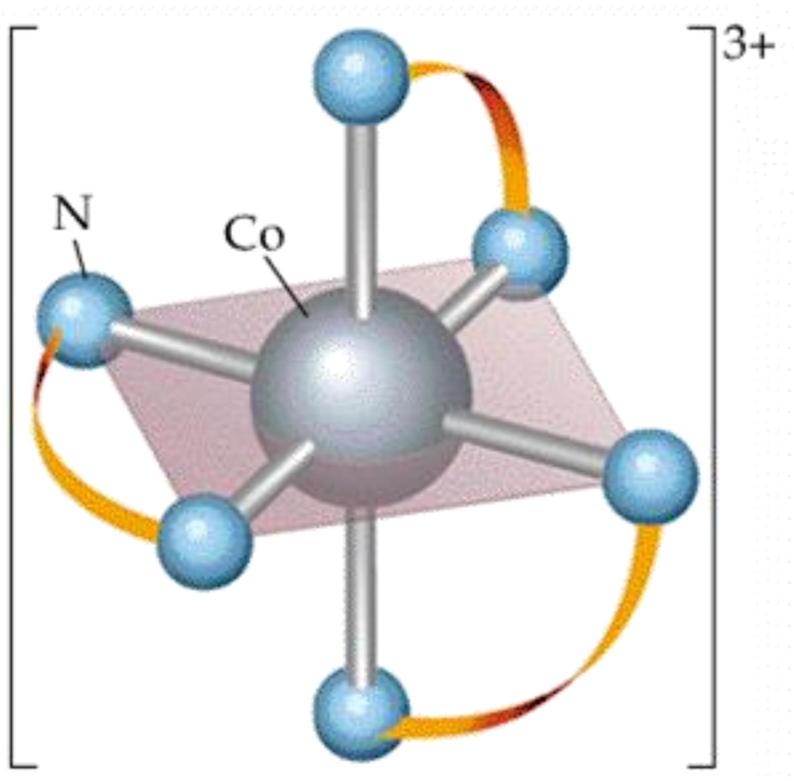
Can form ***two bonds*** with the metal atom/ion



ethylenediamine (en)



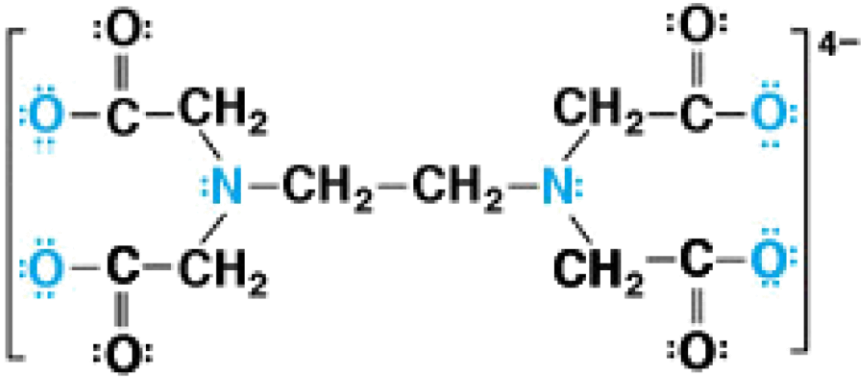
oxalate ion



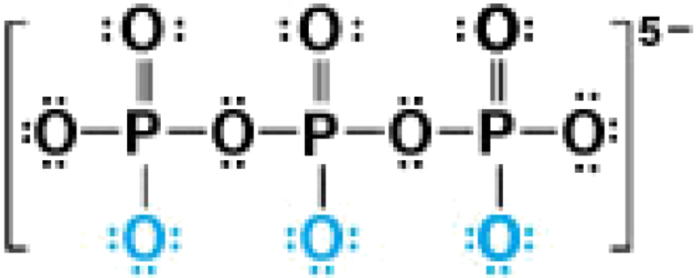
$[Co(en)_3]^{3+}$

Ligands - polydentate

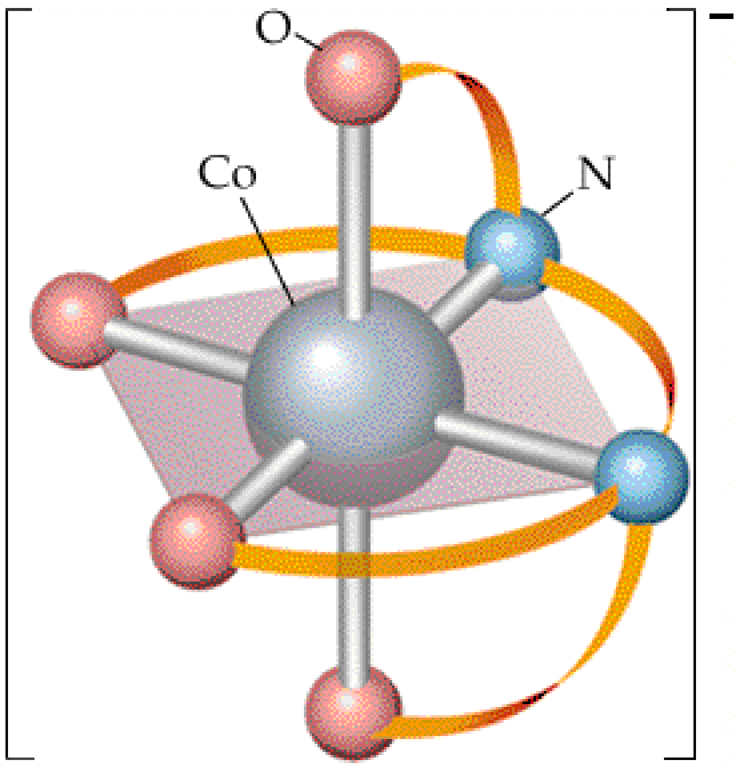
Can form ***many bonds*** with the metal atom/ion



ethylenediaminetetraacetate (EDTA) ion



triphosphate ion



$[Co(EDTA)]^-$

Coordination Number

number of bonds formed between the metal ion and the ligands in the complex ion.

Varies from two to eight

Depends on the size, charge, and electron configuration of the transition metal

Most common coordination number is 6

Next is 4, then 2

Many metals show more than one coordination number

No way to predict which coordination number

Naming Complexes 1

***Cation* (+ve ion) is named before the *anion* (-ve ion)**

Eg hexaquairon(III) sulphate

potassium hexacyanoferrate(III)

Naming Complexes 2

Ligands are named before the metal ion

Eg hexaquairon(III) sulphate
potassium hexacyanoferrate(III)

Naming ligands

Add an -o to the root name of an ***anion*** (fluoro, chloro, hydroxo, cyano, etc.)

Neutral ligand, use the name of the molecule except for the following:

H_2O = aqua
NH_3 = ammine

Naming Complexes 3

Use prefixes to indicate number of simple ligands (mono, di, tri, tetra, penta, hexa)

Eg hexaquairon(III) sulphate

potassium tetrachlorocuprate(II)

Oxidation state of central metal ion is designated by a Roman numeral in parentheses

Eg hexaquairon(III) sulphate

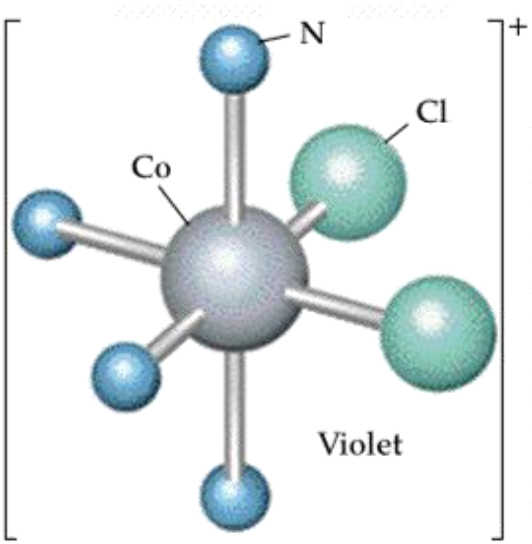
potassium tetrachlorocuprate(II)

Naming Complexes 4

When more than one type of ligand is present, they are named alphabetically, (prefixes do not affect the order).

Eg tetramminedichlorochromium (III) chloride

$[Cr(NH_3)_4Cl_2]Cl$



Naming Complexes 5

If the complex ion has a negative charge, add –ate to the latin name of the metal (eg. ferrate or cuprate)

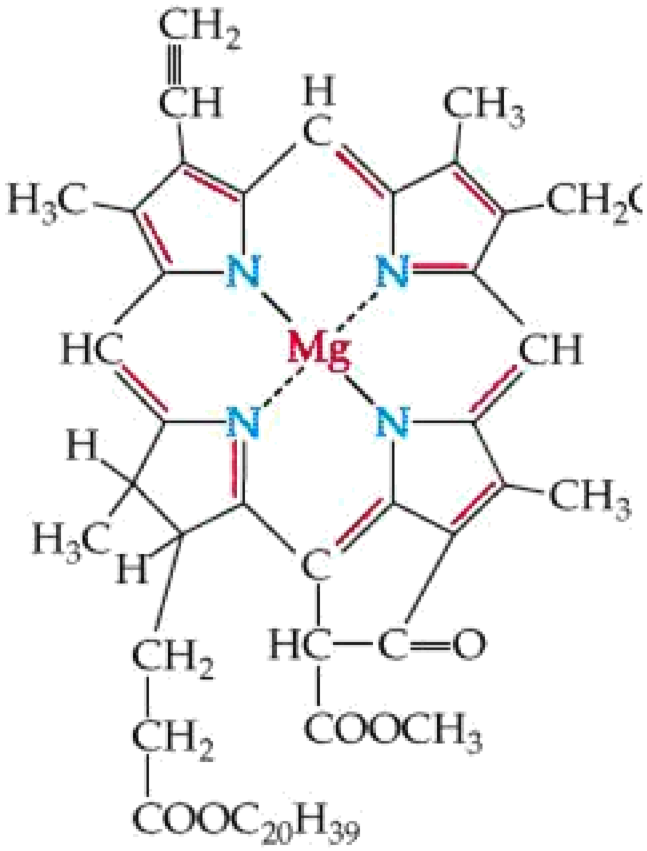
Eg potassium hexacyanoferrate(III)

$(K^+)_3[Fe(CN)_6]^{3-}$

sodium hexafluorocobaltate(III)

$(Na^+)_3[Co(F)_6]^{3-}$

Complexes in Living Things 1

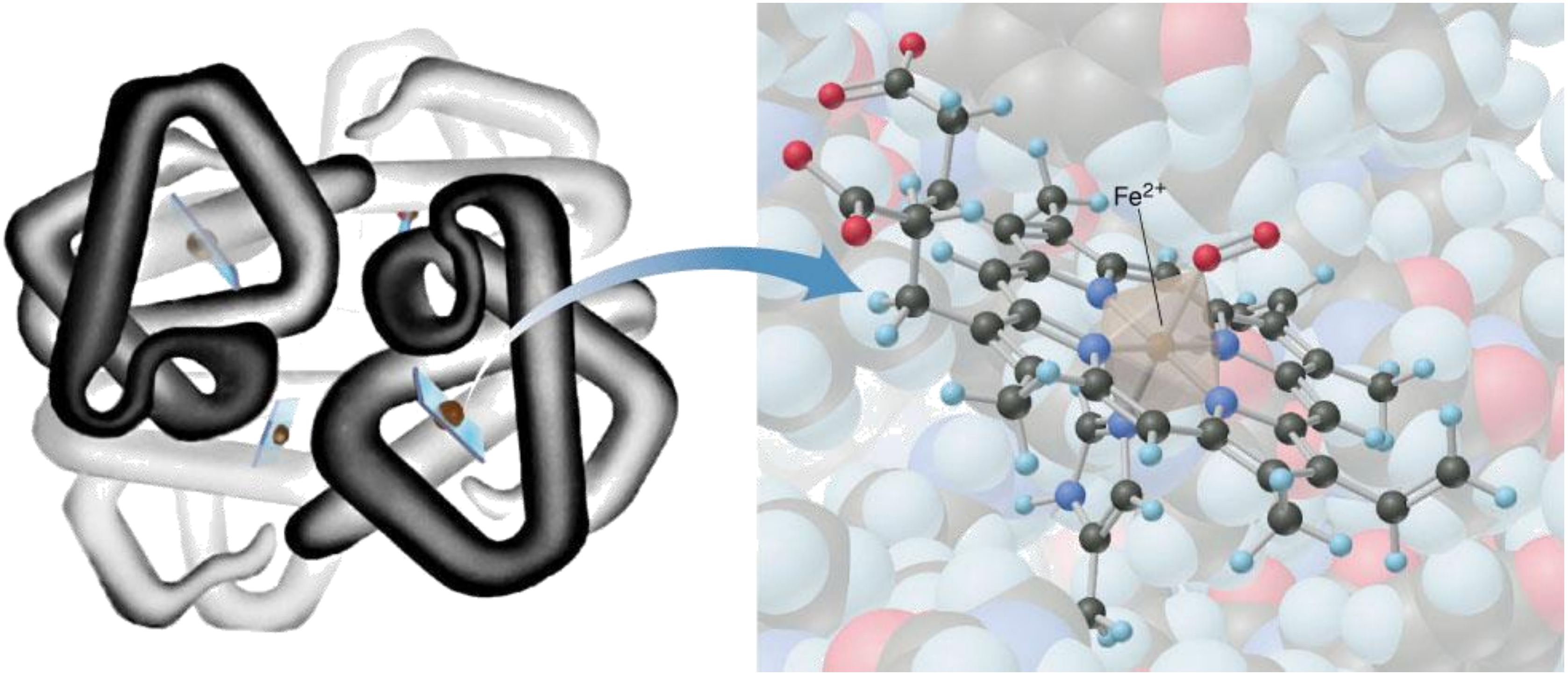


Mg^{2+} is in the center of the chlorophyll molecule.

The alternating double bonds give chlorophyll its green color (it absorbs red light).

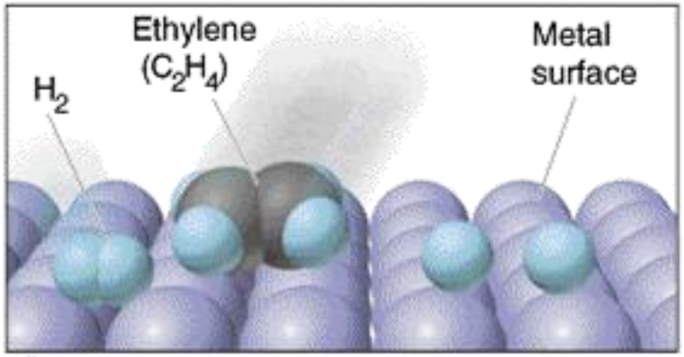
Chlorophyll absorbs red light (655 nm) and blue light (430 nm).

Complexes in Living Things 2

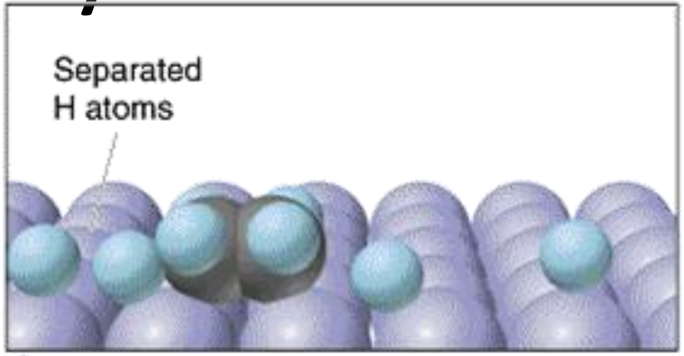


An octahedral complex of Fe^{2+} is in the center of the haemoglobin molecule.

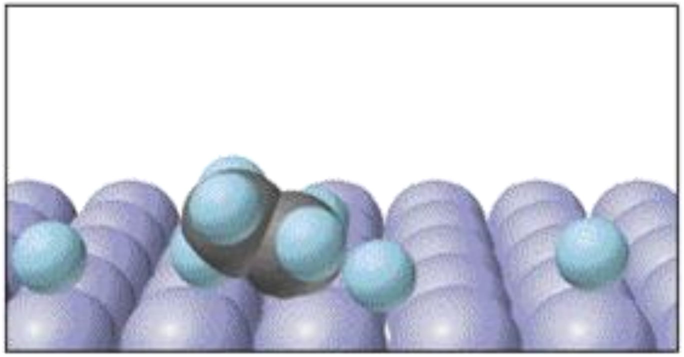
Catalysis 1



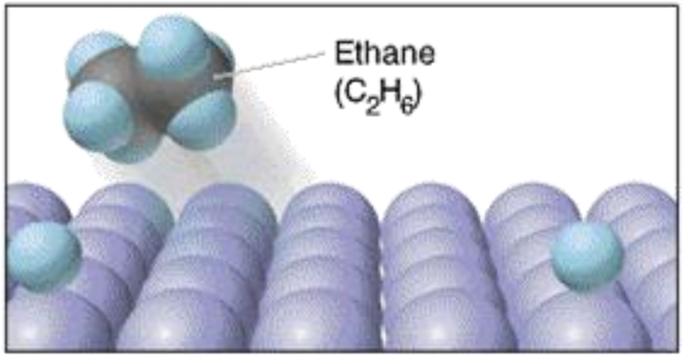
① *H_2 and C_2H_4 approach and adsorb to metal surface.*



② *Rate-limiting step is H—H bond breakage.*



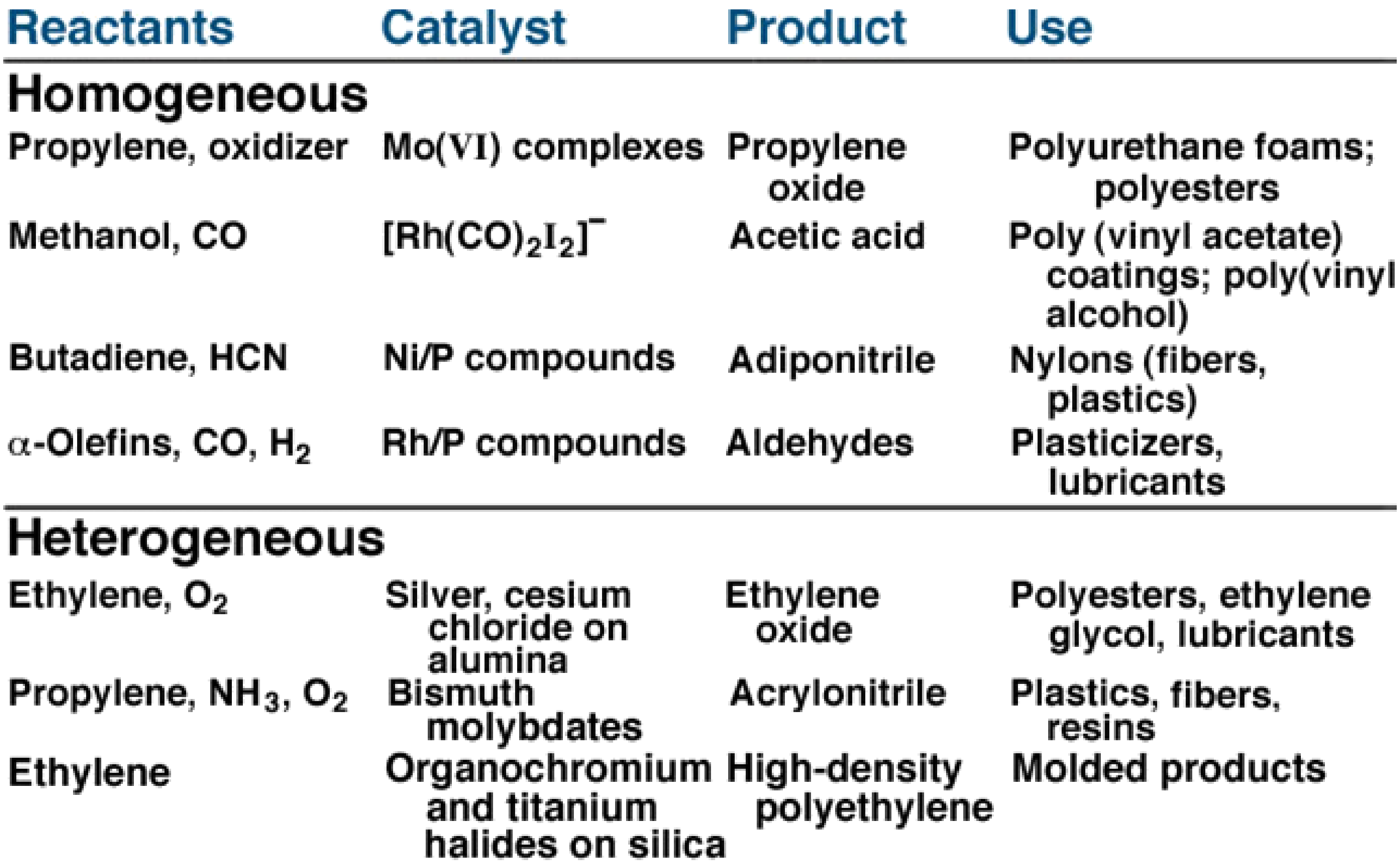
③ *One H atom bonds to adsorbed C_2H_4.*



④ *Another C—H bond forms and C_2H_6 is released.*

The presence of ***unpaired d-electrons*** or ***empty d-orbitals*** allow ***intermediate complexes*** to form, providing ***alternative reaction pathways*** of ***lower activation energy***

Catalysis 2



Reactants	Catalyst	Product	Use
Homogeneous			
Propylene, oxidizer	Mo(VI) complexes	Propylene oxide	Polyurethane foams; polyesters
Methanol, CO	$[Rh(CO)_2I_2]^-$	Acetic acid	Poly (vinyl acetate) coatings; poly(vinyl alcohol)
Butadiene, HCN	Ni/P compounds	Adiponitrile	Nylons (fibers, plastics)
α-Olefins, CO, H_2	Rh/P compounds	Aldehydes	Plasticizers, lubricants
Heterogeneous			
Ethylene, O_2	Silver, cesium chloride on alumina	Ethylene oxide	Polyesters, ethylene glycol, lubricants
Propylene, NH_3, O_2	Bismuth molybdates	Acrylonitrile	Plastics, fibers, resins
Ethylene	Organochromium and titanium halides on silica	High-density polyethylene	Molded products

Catalysis 3