1.3 Transition Metals

Electronic Configuration of Transition Metals

- d-block transition metals have an incomplete d-subshell in at least one of their *ions*.
- 4s electrons are lost *before* 3d electrons during ionisation to positive ions
- filling of d-orbitals follows the Aufbau Principle

Element	Electronic Configuration	
	Spectroscopic Notation	Orbital Box Notation (d-block only)
Scandium	$[Ar]\ 3d^1\ 4s^2$	↑ □ □ □ □
Titanium	$[Ar]\ 3d^2\ 4s^2$	↑ ↑ □ □ □
Vanadium	$[Ar]\ 3d^3\ 4s^2$	↑ ↑ ↑ □ □
Chromium	$[Ar]\ 3d^5\ 4s^1$	↑ ↑ ↑ ↑ ↑
Manganese	$[Ar]\ 3d^5\ 4s^2$	↑ ↑ ↑ ↑ ↑
Iron	$[Ar]\ 3d^6\ 4s^2$	↑↓ ↑ ↑ ↑ ↑
Cobalt	$[Ar]\ 3d^7\ 4s^2$	↑↓ ↑↓ ↑ ↑ ↑
Nickel	$[Ar]\ 3d^8\ 4s^2$	↑↓ ↑↓ ↑↓ ↑ ↑
Copper	$[Ar]\ 3d^{10}\ 4s^1$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓
Zinc	$[Ar]\ 3d^{10}\ 4s^2$	↑↓ ↑↓ ↑↓ ↑↓ ↑↓

Cr and Cu are exceptions

$$\left.\begin{array}{ll} \circ\ Cr & [Ar]\ 3d^5\ 4s^1 \\ \circ\ Cu & [Ar]\ 3d^{10}\ 4s^1 \end{array}\right\}\ \text{Electron borrowed from 4s to achieve half-filled or completely-filled d-subshell}$$

Oxidation States

- Fe^{2+} ions have an oxidation state of +2
- Fe^{3+} ions have an oxidation state of +3

But what is the oxidation state of Mn in the MnO_4^- ?

Rules for Oxidation States

1. Oxidation number in a free or uncombined element in zero
   e.g. Mg(s) and Cl in Cl_2 gas

2. For single atoms ions, the oxidation number is the same as the charge on the ion
   e.g. Cl^- has oxidation number= –1
   O^{2-} has oxidation number= –2
   Al^{3+} has oxidation number= +3

3. In *most* compounds oxidation number of
   i. hydrogen is +1 [except hydrides where H is –1]
   ii. oxygen is –2 [except peroxides where O is –1]

4. The algebraic sum of all the oxidation numbers in a molecule must be zero

5. The algebraic sum of all the oxidation numbers in a polyatomic ion must be equal to the charge on the ion
   e.g. S in SO_4^{2-} S has oxidation number = +6

- Oxidation numbers can be used to work out if oxidation or reduction has taken place
    - increase in oxidation number - oxidation has occurred
    - decrease in oxidation number - reduction has occurred

e.g. $\underset{\text{oxid}^{n}\text{ no.}=+7}{MnO_4^-} + 8H^+ + 5e^- \xrightarrow[\text{reduction}]{} \underset{\text{oxid}^{n}\text{ no.}=+2}{Mn^{2+}} + 4H_2O$

- compounds containing metals with high oxidation numbers tend to be oxidising agents
    - agents are reduced themselves to lower oxidation number

- compounds containing metals with low oxidation numbers tend to be reducing agents
    - agents are oxidised themselves to increase oxidation number

- Transition metals exhibit various oxidation states of differing stability
    - It is very common to have an oxidation state of +2 as the $4s^2$ electrons are lost before 3d electrons
    - Subsequent loss of 3d electrons by transition metals forms further oxidation states

- Changing from one oxidation state to another is important in transition metal chemistry
    - It is often characterised by a change in colour

Ion	Oxidation State of Transition Metal	Colour
VO_3^-	+5	Yellow
VO^{2+}	+4	Blue
V^{3+}	+3	Green
V^{2+}	+2	Violet

Transition Metal Complexes

- A complex consists of a central metal ion surrounded by ligands

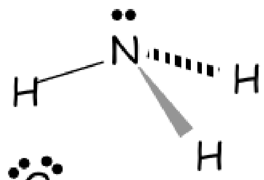
- A ligand is a molecule or ion electron donor which bonds to the metal ion by the donation of one or more electron pairs to unfilled metal ion orbitals

    - Water is a common neutral ligand with 2 lone electron pairs

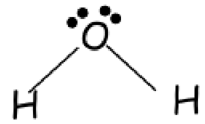
    - Ammonia NH_3 is neutral ligand with one lone pair

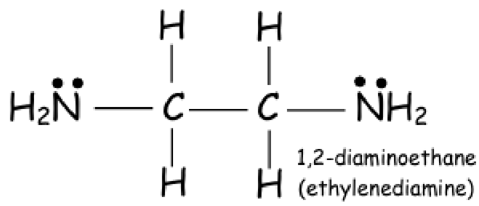
    - There are negative ions which are ligands

        - cyanide ion CN^-
        - halide ions: F^-, Cl^-, Br^-, I^-
        - nitrite ion NO_2^-
        - hydroxide ion OH^-

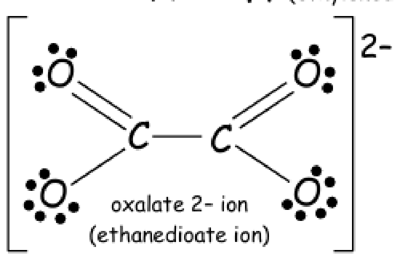


- Ligands which donate 1 pair of electrons are *monodentate*
    - Dentate comes from Latin for tooth
    - H_2O and NH_3 are monodentate





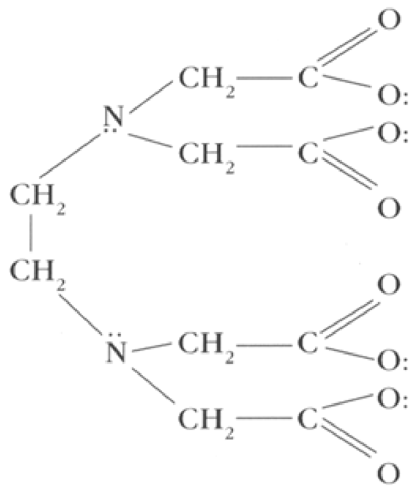
- Ligands which donate 2 pairs of electrons are *bidentate*
    - The 2 pairs of electrons must be on different parts of the molecule, not the same atom
    - Oxalate ions and 1,2-diaminoethane are both *bidentate*



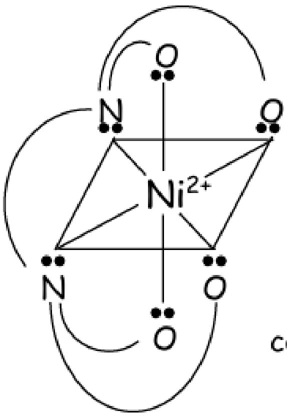
- polydentate means that a ligand has more than one pair of electrons is donated to the central metal ion

- ligands are called chelating agents (chelate: from the Greek for claw)

- **E**thylene**di**amine**te**tra**a**cetic acid (**EDTA**) is a common hexadentate ligand used in volumetric analysis and complexes with metal ions in a ratio of 1:1



E.D.T.A.



Hexadentate EDTA complexing with Ni^{2+} ion

Co-ordination Number

- The number of bonds of the ligand(s) to the central ion is called the co-ordination number
  - EDTA has a co-ordination number of 6
  - $[Cu(H_2O)_6]^{2+}$ has a co-ordination number of 6 as the central Cu^{2+} ion is surrounded by 6 water molecules
  - $[CuCl_4]^{2-}$ has a co-ordination number of 4 as the central Cu^{2+} ion is surrounded by 4 negative chloride ions

Naming Complexes

a) Writing the Formula of Complexes

- standardised set of rules (IUPAC)
- Formula of complex ions are written in square brackets
- Metal symbol comes first
- Negative ligands come next
- Neutral ligands come next
- Overall charge written after square brackets
  e.g. $[CuCl_4]^{2-}$, $[Cu(H_2O)_6]^{2+}$

b) Writing the Name of Complexes

- Ligands should be named first (alphabetically) followed by the name of the central metal ion

- If the ligand is a negative ion
  - *ide* ending becomes –id**o**
    e.g. chloride ions become chlorido
    cyanide ions become cyanido
  - *ate* ending become –at**o**
    e.g. nitrate NO_3^- ions become nitrato
  - *ite* ending becomes –it**o**
    e.g. nitrite NO_2^- ions become nitrito

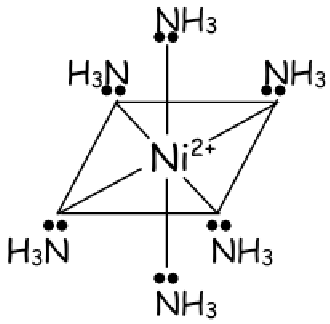
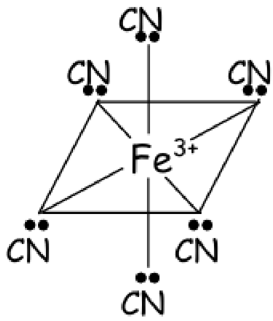
- If ligand is neutral
  - If ligand is water aqua
  - If ligand is ammonia ammine
  - If ligand is CO carbonyl

- Mono, di, tri, tetra, penta, hexa, etc prefixes are used for multiple ligands of the same type

- If complex ion is overall a negative ion (anion), the suffix –ate is added to the metal
  - nickel becomes nickelate (II)
  - iron becomes ferrate (III) [not ironate]
  - copper becomes cuprate (II) [not copperate]

- If complex ion is overall a positive ion (cation), the metal does not have the suffix –ate

- The oxidation state of the metal is written after the metal (roman numerals in brackets)

Complex Diagram	Formula of Complex	Name of Complex
	$[Ni(NH_3)_6]^{2+}$	Hexaamminenickel(II)
	$[Fe(CN)_6]^{3-}$	Hexacyanidoferrate(III)