

Unit 3 - Periodicity

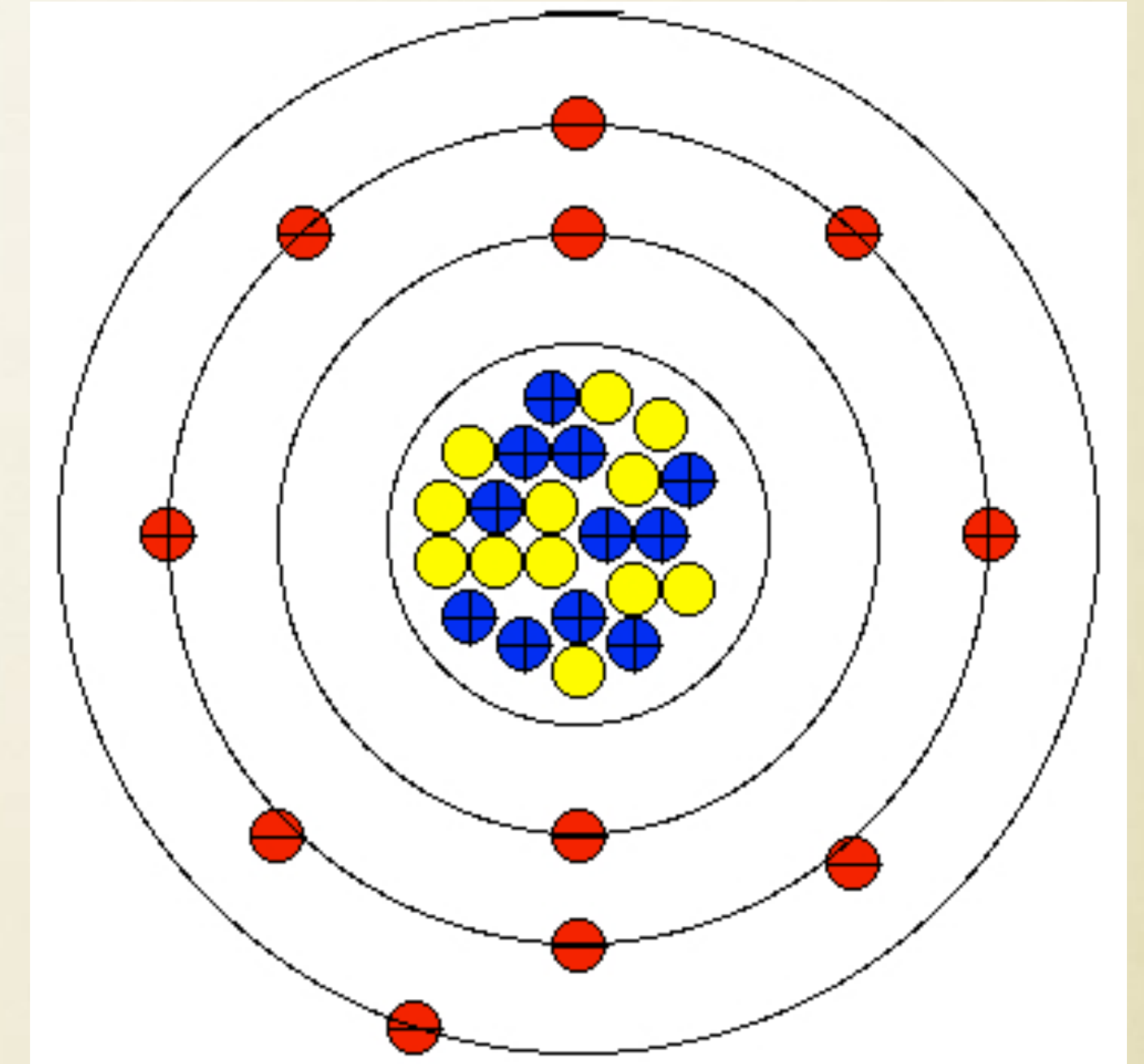
The Periodic Table
Physical and Chemical Properties
Periodic Trends (period 3)
First Row d-Block Elements

Do You know these terms/phrases?

- Distinguish between the terms group and period
- apply the relationship between electron arrangement & their position on PT
- transition elements
- Z (atomic number)
- valence electrons
- describe the arrangement of elements in the PT

Physical Properties

- Periodicity - what is this?
- Nuclear Charge - # of protons
- shielding of electrons - outer electrons do not receive full attraction from the protons in the nucleus because of the inner electrons
- effective nuclear charge - what is 'experienced' by the outer electrons



Shielding...cont'd

- left to right on the periodic table...
 - adding a proton each time with no more shielding electrons...
- top to bottom on periodic table...
 - adding more protons (from the trip across the row) while adding an extra shell of electrons

What affect is this going to have on the atomic radius??

Atomic Radius

Element	Electron Arrangement	No. of occupied shells	Radius 10^{-12} m
Li	2, 1	2	152
Na	2,8,1	3	186
K	2,8,8,1	4	231
Rb	2,8,18,8,1	5	244
Cs	2,8,18,18,8,1	6	262

Atomic Radius

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic Radius	186	160	143	117	110	104	99	-

Ar - too difficult to measure as they do not bond with other elements...

Atomic Radii (pm)

1A	2A	3A	4A	5A	6A	7A
Li 152	Be 112	B 85	C 77	N 75	O 73	F 72
Na 186	Mg 160	Al 143	Si 118	P 110	S 103	Cl 100
K 227	Ca 197	Ga 135	Ge 122	As 120	Se 119	Br 114
Rb 248	Sr 215	In 167	Sn 140	Sb 140	Te 142	I 133
Cs 265	Ba 222	Tl 170	Pb 146	Bi 150	Po 168	At (140)

Ionic Radius

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic Radius	186	160	143	117	110	104	99	-
Ionic Radius	98 Na ⁺	65 Mg ²⁺	45 Al ³⁺	42 Si ⁴⁺ 271 Si ⁴⁻	212 P ³⁻	190 S ²⁻	181 Cl ⁻	-

5 trends in Ionic Radius....

Positive Ions are smaller than their parent atoms

Negative Ions are larger than their parent atoms

Ionic radii decrease (+ ions) as you move from group 1-4

Ionic radii increase (- ions) as you move from group 4-7

Ionic radii increase as you move down a group

Ionization energies

-measure of the attraction between the nucleus and the outer electrons
- Talked about at length in Atomic Structure
 - explained the subshells! (figure 3.4, pg 105)
- Two general trends
 - I.E. increases across a period →
 - I.E. decrease as you go down a group ↓

Electronegativity

- ...the measure of the ability of its atoms to attract electrons in a covalent bond (related to ionization energy)
- trends:
 - increases as you go left to right
 - decreases as you go down a group
- IE - can be measured directly - property of gaseous atoms
- Electronegativity - derived experimentally (bond energy data)

Electron Affinity

- The energy change when one mole of electrons is added to one mole of gaseous atoms to make one mole of gaseous ions.
- $X_{(g)} + e^- \longrightarrow X^{-}_{(g)}$
- Table 8 of your data booklet
- 2nd electron affinity: $O^{-}_{(g)} + e^- \longrightarrow O^{2-}_{(g)}$

Chemical Properties

Noble Gases, Alkali Metals, Halogens and the
Period 3 Oxides

Noble Gases

- What do you know about them?
 - colourless gases
 - monatomic
 - unreactive
 - stable octet

Group 1: Alkali Metals

- Highly reactive - stored in oil
- form single charged ions: M^+
 - to form which type of electron configuration
- low ionization energies
- can conduct electricity (mobility of outer electron)

Alkali metals - Reaction w/ H₂O

- What happens in the reaction??

Group 7 (17) - The Halogens

- Exist as diatomic molecules - X_2 (generally coloured)
- gradual change from gas (F_2 and Cl_2) to liquid (Br_2) to solid (I_2)
- very reactive - decreases down the group
- form ionic compounds with metals and covalent compounds with non-metals

Why do the halogens show this trend
in reactivity?

- electronegativity - attraction for electrons
- atomic radius

Reaction with Group 1 Metals

- React to form Ionic Halides
 - $2\text{Na}_{(s)} + \text{Cl}_{2(g)} \rightarrow 2\text{NaCl}_{(s)}$
 - causes ions of opposite charges
- Most vigorous ionic halide reaction???

Displacement Reactions

- for example - chlorine gas is bubbled through a solution of potassium bromide and it turns from colourless to orange...what happened? what will the reaction look like?
 - $2\text{KBr}_{(\text{aq})} + \text{Cl}_{2(\text{g})} \rightarrow 2\text{KCl}_{(\text{aq})} + \text{Br}_{2(\text{aq})}$
- Why does this occur?

Reactions with Silver

- Halogens form insoluble salts with Ag
- This is useful in identifying halides in solutions

Bonding of the Period 3 oxides

- Depends on electronegativity difference between the atoms
- the greater the electronegativity difference, the greater the ionic character of the bond

Formula	$\text{Na}_2\text{O}_{(s)}$	$\text{MgO}_{(s)}$	$\text{Al}_2\text{O}_{3(s)}$	$\text{SiO}_{2(s)}$	$\text{P}_4\text{O}_{10(s)}$ $\text{P}_4\text{O}_{6(s)}$	$\text{SO}_{3(l)}$ $\text{SO}_{2(g)}$	$\text{Cl}_2\text{O}_{7(l)}$ $\text{Cl}_2\text{O}_{(g)}$
Oxidation #	+1	+2	+3	+4	+5 +3	+6 +4	+7 +1
Conductivity in molten state	high	high	high	very low	none	none	none
Structure	giant ionic			giant covalent	molecular covalent		

Acid-Base Character of Period 3 Oxides

Formula	$\text{Na}_2\text{O}_{(s)}$	$\text{MgO}_{(s)}$	$\text{Al}_2\text{O}_{3(s)}$	$\text{SiO}_{2(s)}$	$\text{P}_4\text{O}_{10(s)}$ $\text{P}_4\text{O}_{6(s)}$	$\text{SO}_{3(l)}$ $\text{SO}_{2(g)}$	$\text{Cl}_2\text{O}_{7(l)}$ $\text{Cl}_2\text{O}_{(g)}$
Acid-base character	basic		amphoteric		acidic		

- based on bonding
 - metals
 - non-metals
 - metalloids

Basic Oxides

- dissolve in water to form a base
 - $\text{Na}_2\text{O}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow 2\text{NaOH}_{(aq)}$
 - $\text{MgO}_{(s)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{Mg}(\text{OH})_{2(aq)}$
- react with acid to form salt and water
 - $\text{Li}_2\text{O}_{(s)} + 2\text{HCl}_{(aq)} \rightarrow 2\text{LiCl}_{(aq)} + \text{H}_2\text{O}_{(l)}$
 - $\text{MgO}_{(s)} + 2\text{HCl}_{(aq)} \rightarrow \text{MgCl}_{2(aq)} + \text{H}_2\text{O}_{(l)}$

Acidic Oxides

- Non-metallic oxides react with water to produce acidic solutions
 - $\text{P}_4\text{O}_{10(s)} + 6\text{H}_2\text{O}_{(l)} \rightarrow 4\text{H}_3\text{PO}_{4(aq)}$
 - $\text{Cl}_2\text{O}_{7(l)} + \text{H}_2\text{O}_{(l)} \rightarrow 2\text{HClO}_{4(aq)}$

AMPHOTERIC OXIDES

- Al_2O_3 does not affect pH as it is added to water because it is insoluble
- behaves as a base as it reacts with acid
- behaves as an acid as it reacts with a base

First Row d-Block elements

(HL)

Electron Configurations

- Who has the unusual electron configurations across the first row of d-block elements?
- Cr and Cu
- Why?

Properties

- Physical
 - high electrical/thermal conductivity
 - high melting point
 - malleable
 - high tensile strength
 - ductile
- Chemical
 - form compounds with more than one oxidation number
 - form complex ions
 - form coloured compounds
 - can act as catalysts

Scandium and Zinc

- Form ions: Sc^{3+} and Zn^{2+}
- What is true about the electron configuration of these ions?
- Why might they not be considered transition metals?

Multiple Oxidation States

- Reasoning: ionization energies of transition metals allow for multiple oxidation states (graph on pg 122)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
								+1	
	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

Things to Notice...

- +2 and +3 are available for almost all TMs
 - M^{3+} is stable for Sc to Cr, but M^{2+} is more common for later elements because the increased nuclear charge makes it difficult to remove the 3rd electron
- Oxidation states above +3 show covalent character
 - $K_2Cr_2O_7$ - tend to be oxidizing agents

Complexes - Ligands

- ...Octahedral complex formed by Al^{3+} ...
- relatively high charge and small size allow transition metals to attract the lone pair of electrons from the ligand
- the number of dative bonds from the ligands to the central ion is called the coordination number
- shapes (page 125)

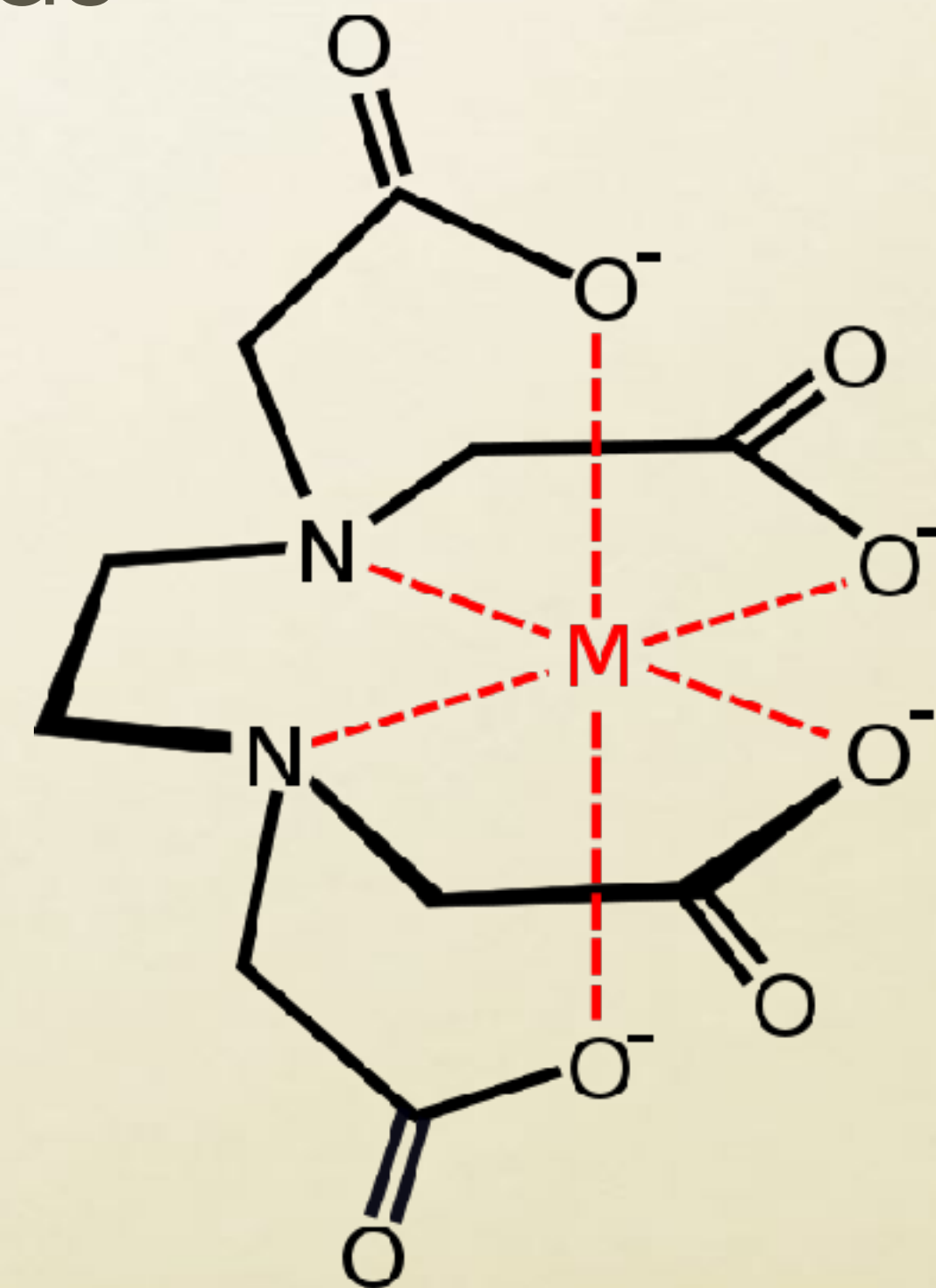
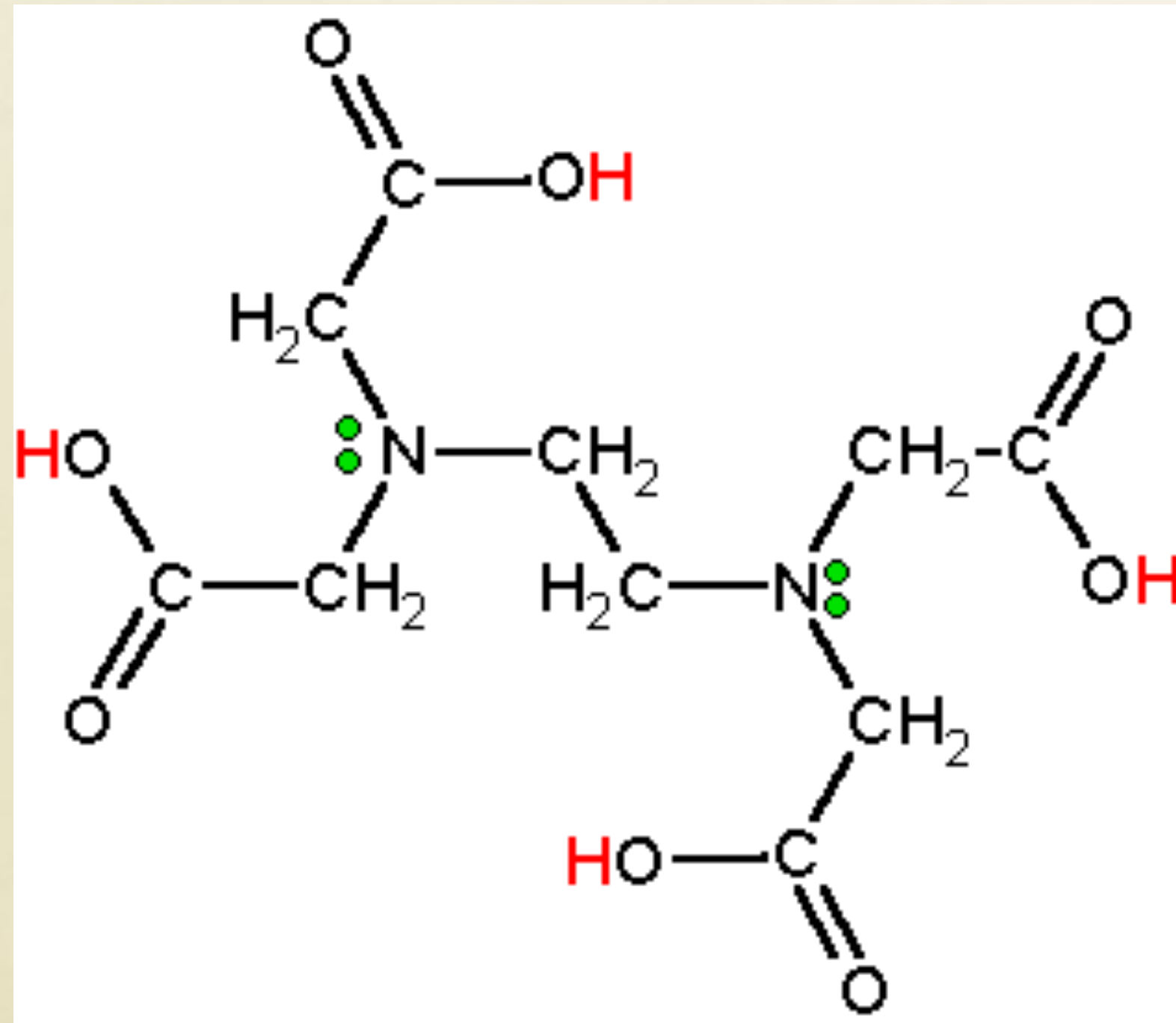
Complex	Ligand	Coordination number	Oxidation number of central ion	Shape
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	H_2O	6	+3	octahedral
$[\text{Co}(\text{NH}_3)_6]^{3+}$	NH_3	6	+3	octahedral
$[\text{CuCl}_4]^{2-}$	Cl^-	4	+2	tetrahedral
$[\text{Fe}(\text{CN})_6]^{3-}$	CN^-	6	+3	octahedral
$[\text{Ag}(\text{NH}_3)_2]^+$	NH_3	2	+1	linear
MnO_4^-	O^{2-}	4	+7	tetrahedral
$\text{Ni}(\text{CO})_4$	CO	4	0	tetrahedral
$\text{PtCl}_2(\text{NH}_3)_2$	Cl^- and NH_3	4	+2	square planar

Transition Metals as Catalysts

- heterogeneous catalyst - in a different state from the reactants - provide a surface for the reactants to come together with the correct orientation
- examples:
 - Iron in the Haber Process
 - Nickel in the conversion of alkenes to alkanes
 - Palladium and Platinum in catalytic converters
 - MnO_2 in the decomposition of hydrogen peroxide

Chelating agents

- Some species have more than one lone pair to bond as a ligand
- EDTA⁴⁻ is a polydentate ligand - 6 atoms with lone pairs to form coordinate covalent bonds

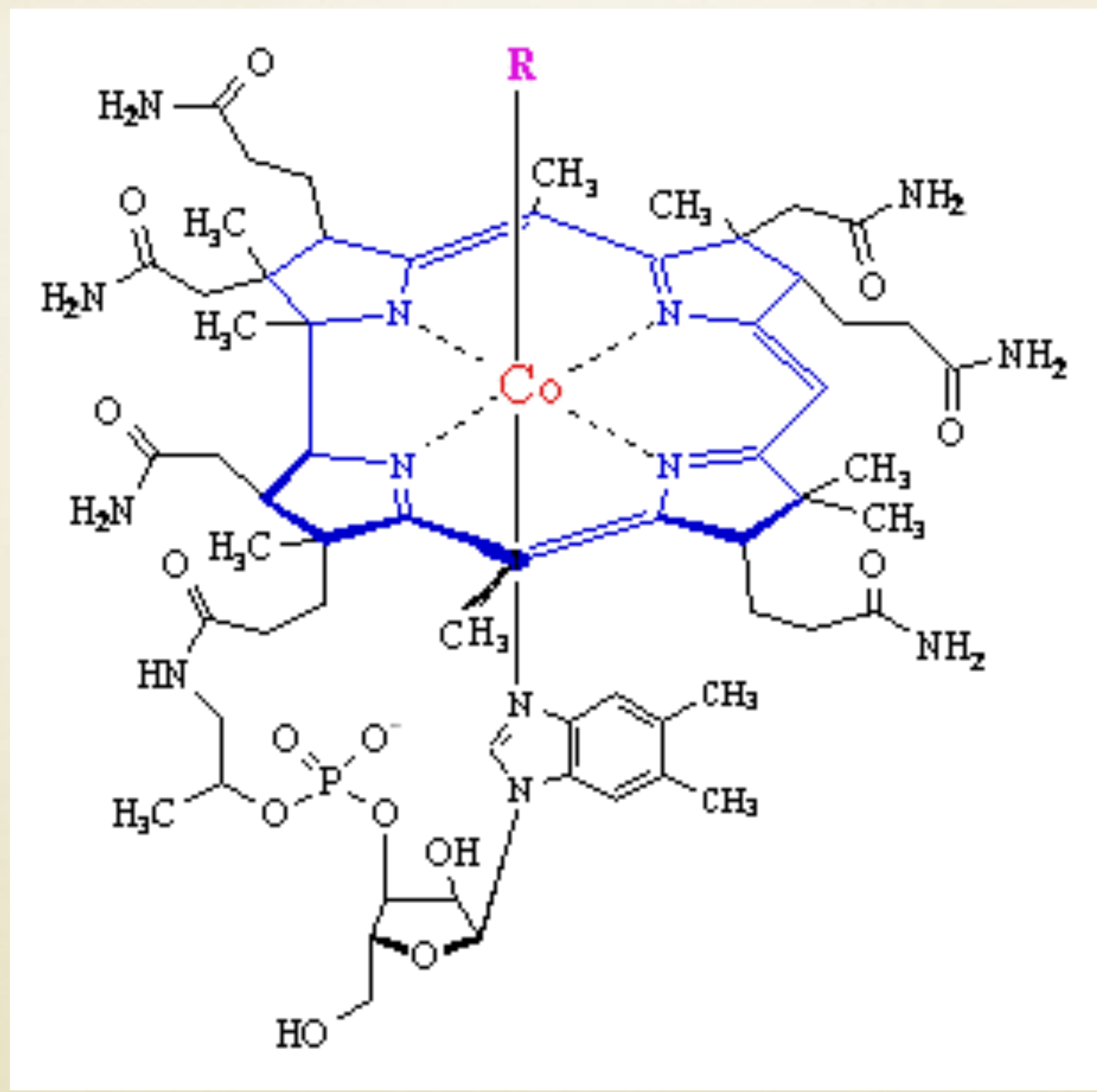


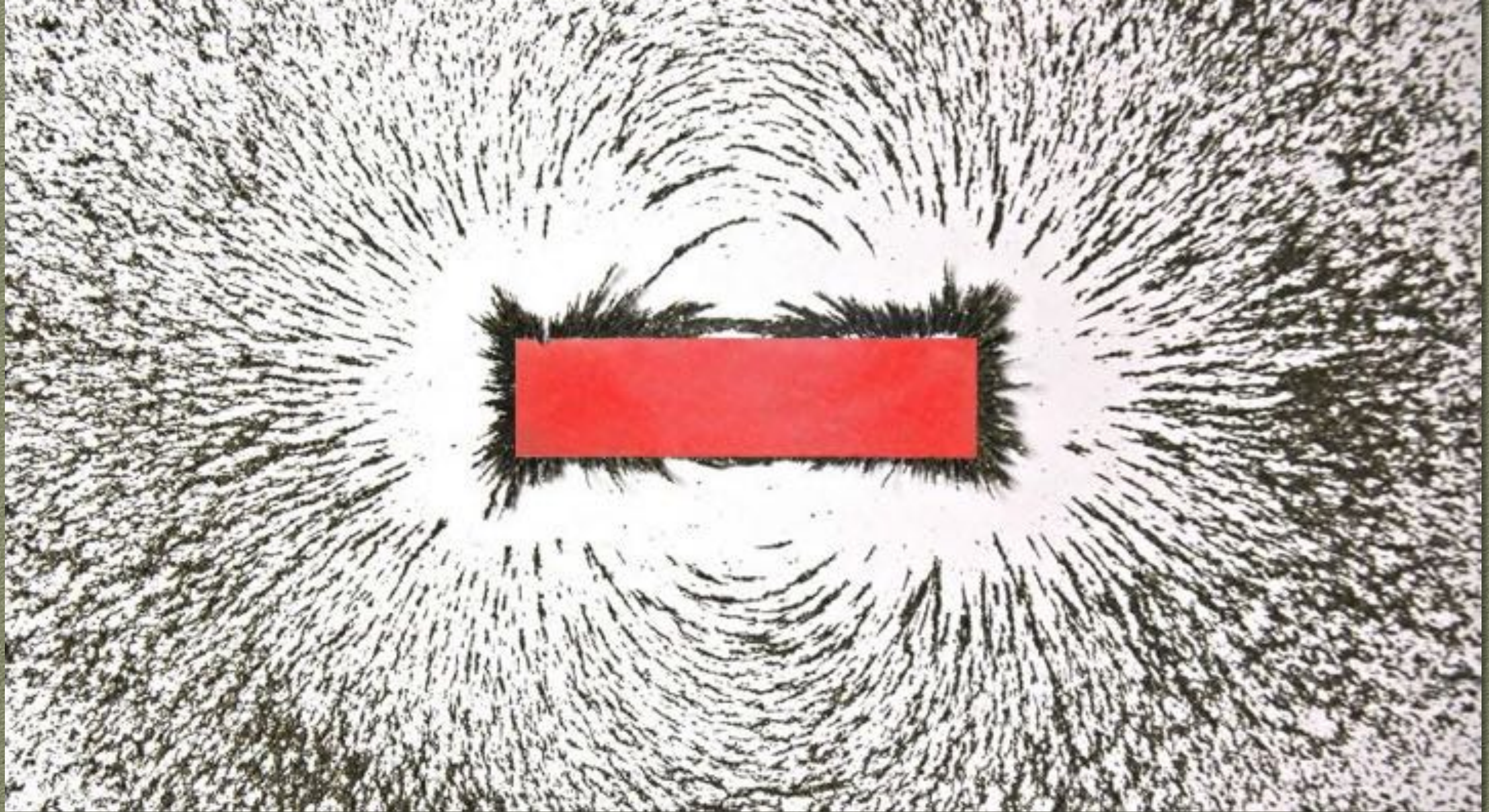
The "Contact Process"

- V_2O_5 is the catalyst
- $2SO_{2(g)} + O_{2(g)} \rightarrow 2SO_{3(g)}$
- sulfur trioxide is used in the manufacture of sulfuric acid, "the manufacturing world's most important chemical"

Ions of transition metals as Homogeneous Catalysts

- same state of matter as the reactants
- particularly effective in REDOX reactions because of the multiple oxidation states
- Examples:
 - Fe^{2+} in heme - transports O_2 in blood
 - Co^{3+} in vitamin B_{12} - 5 nitrogens attached leaving the 6th spot open for biological activity
 - (B_{12} is needed for red blood cell production and for a healthy nervous system)





Magnetic Properties of Transition Metals

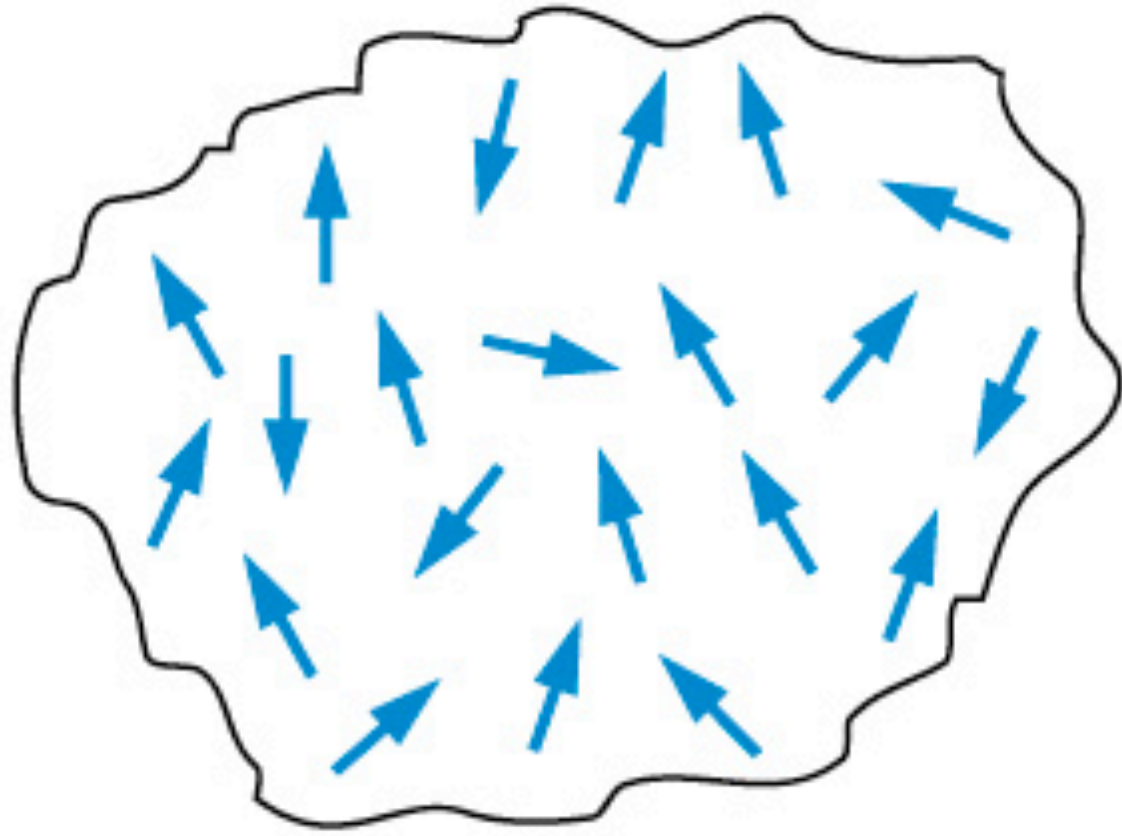
Magnetism

- **Diamagnetism** - property of all materials and produces a very weak opposition to an applied magnetic field
- **Paramagnetism** - only occurs with substances that have unpaired electrons. Produces magnetization proportional to the field and in the same direction

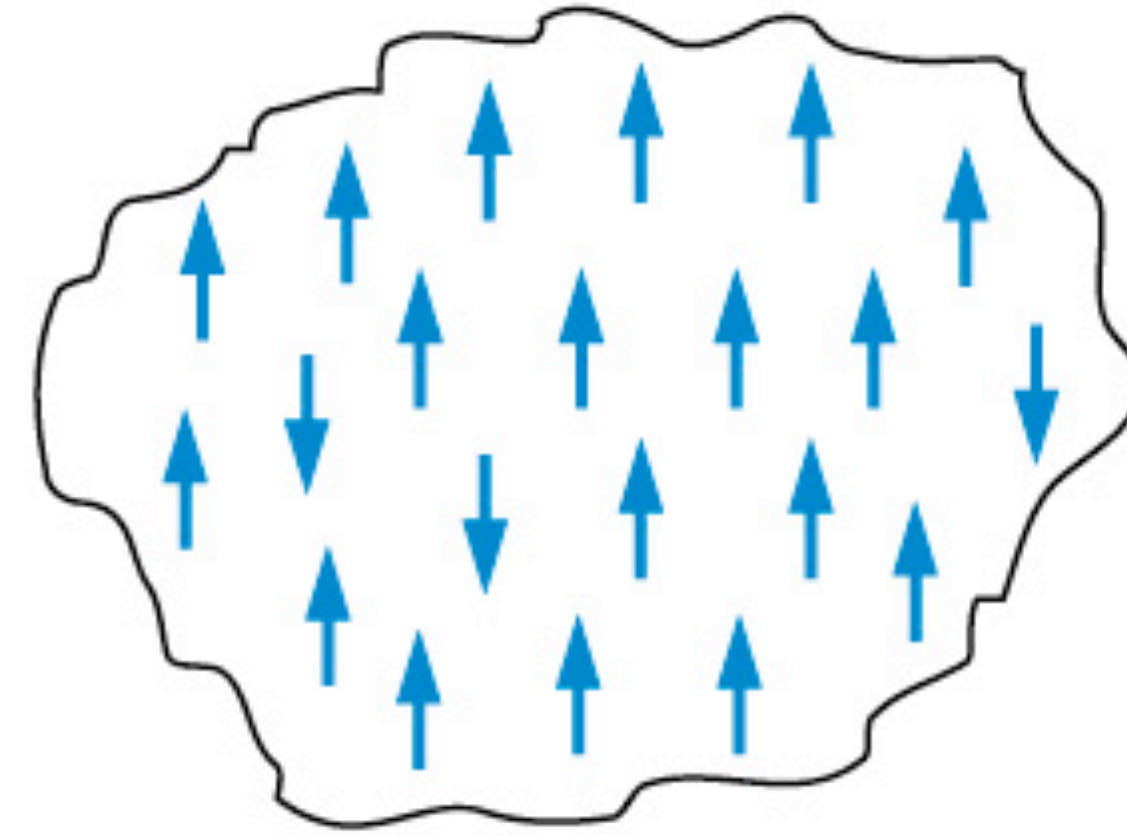
Ferromagnetism

- The largest effect, sometimes producing magnetism orders of magnitude bigger than the field applied
- Iron, cobalt and nickel - the unpaired d electrons will line up in parallel spins in **domains** which can orient themselves and become more ordered when exposed to a magnetic field
- These domains of magnetism will remain after the external magnetic field is removed

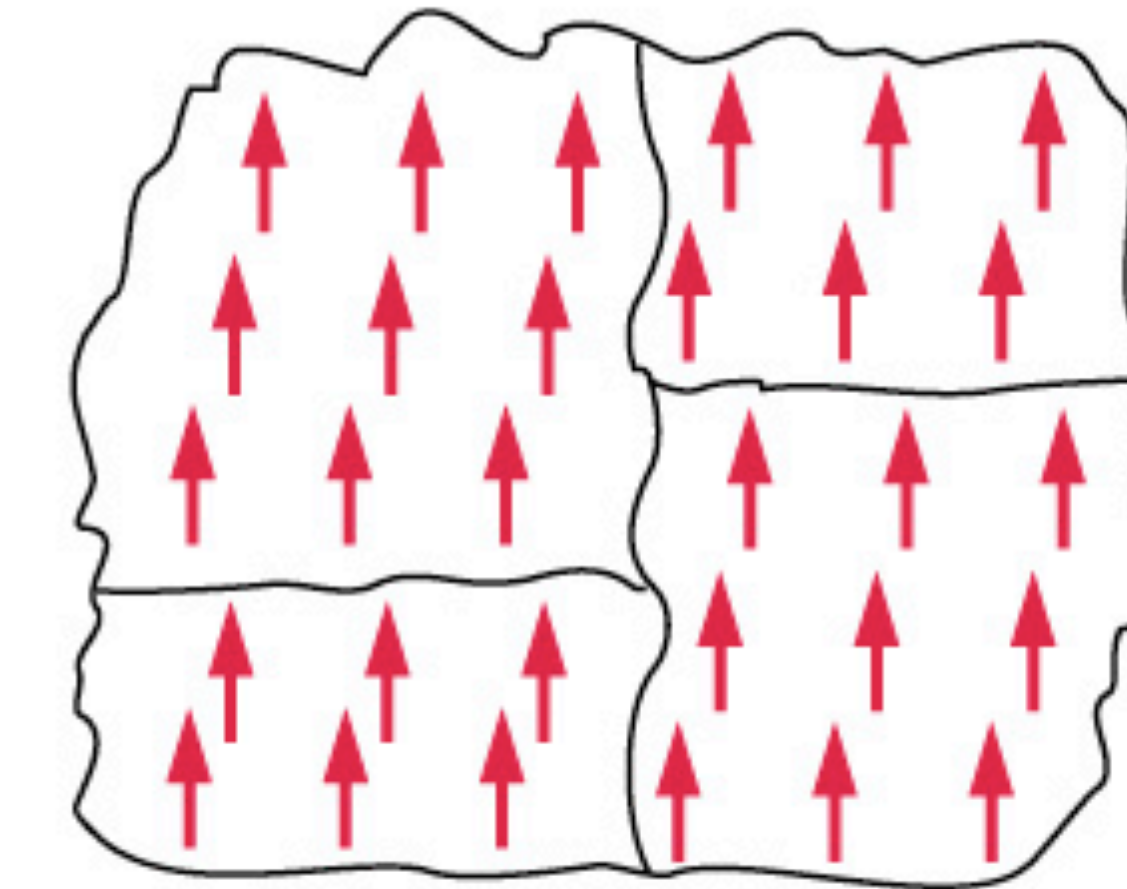
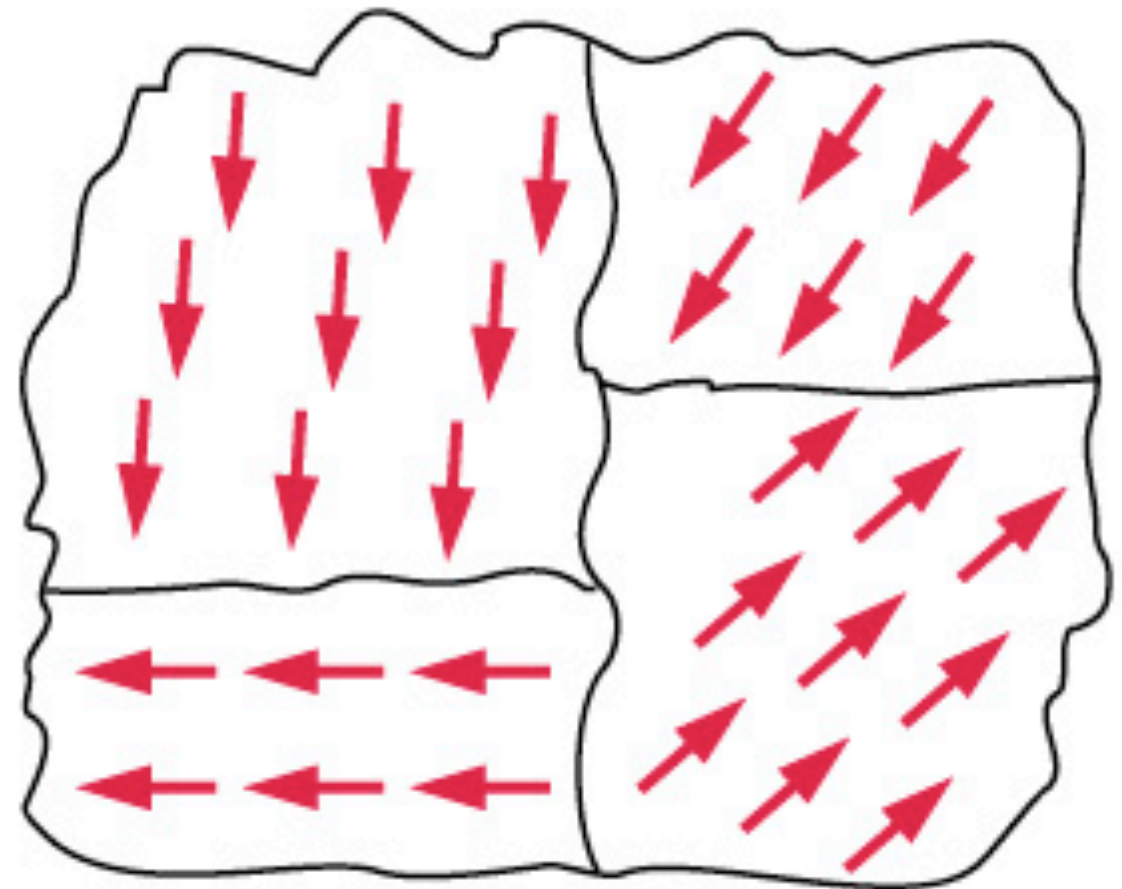
Magnetic field absent



In presence of magnetic field



Paramagnetism



Ferromagnetism

Other Transition metals...

- With unpaired electrons show paramagnetism
- Will increase with increase in unpaired d electrons
- Reaches a maximum at chromium (why?)



potassium dichromate



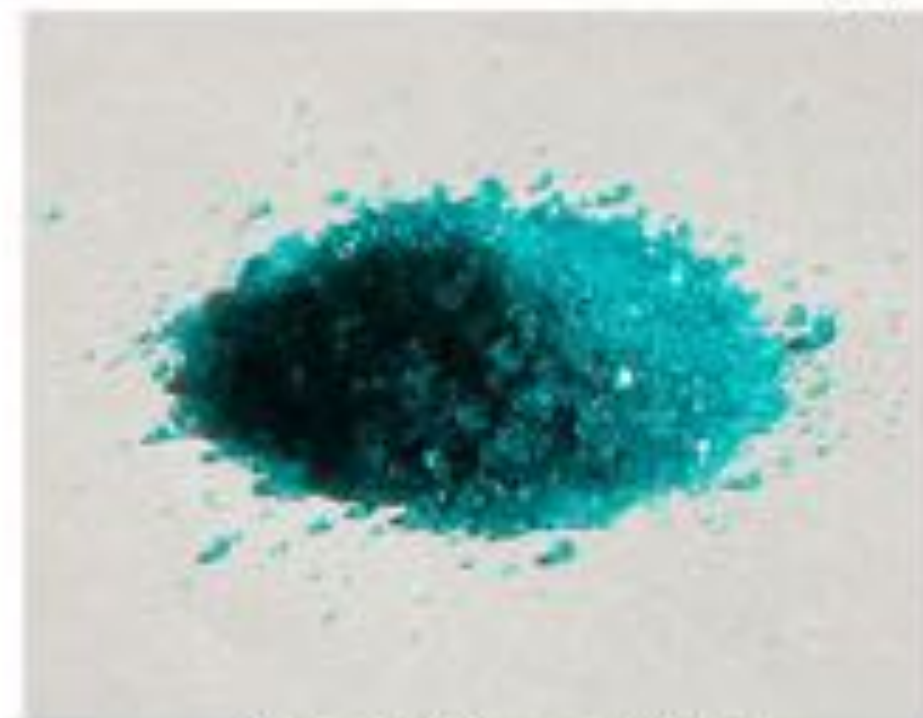
iron(II) sulfate



cobalt(II) chloride



copper(II) sulfate



nickel(II) sulfate

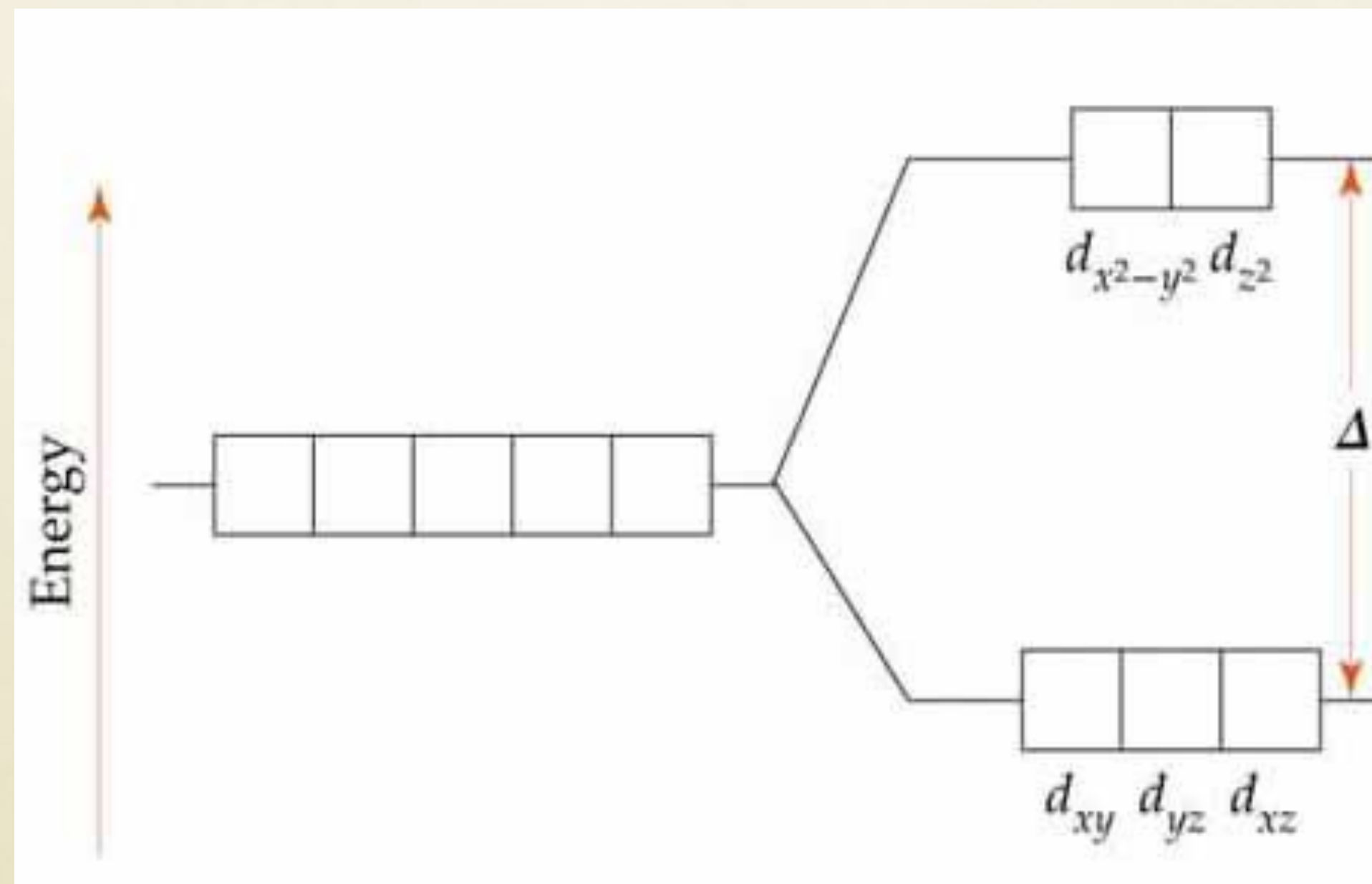
Coloured Complexes

Colour of Transition Metals

- related to the partially filled d-orbitals
- Which ions are colourless??
 - Sc and Zn
- they absorb visible light and depending on the colour, it is transmitted back as a complementary colour

Absorbing light

- The color transition metals appear are due to the light they absorb
- **Due to the split of d-orbitals into two sub levels**



Color depends on...

- Nuclear charge of the central ion
- Charge density of the ligand
- Geometry (shape) of the complex
- Number of d electrons present (oxidation state of central ion)
- More on pg 132-133