

Transition Metal Coordination Chemistry

Prof S.M.Draper

2.05 SNIAMS Building
smdraper@tcd.ie

Recommended books

M.J. Winter, d-block Chemistry, Oxford Chemistry Primers, OUP, 2001

M.S. Silberberg, Chemistry, 3rd Ed, McGrawHill, 2003 (chapter 23)

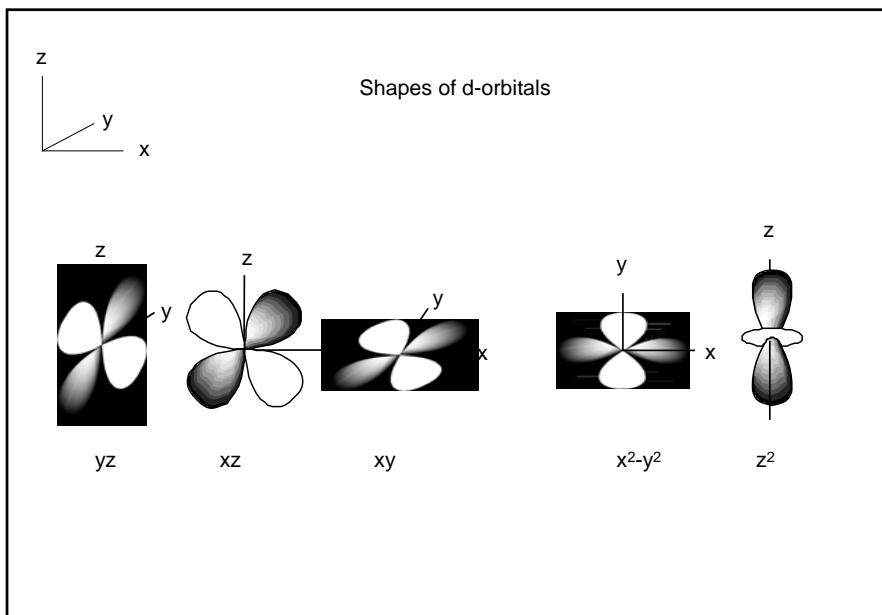
C.E. Housecroft, A.G. Sharpe, Inorganic Chemistry, 1st Ed, PrenticeHall, 2001

J.E. Huheey, E.A. Keiter, R.L. Keiter, Inorganic Chemistry, 4th Ed., HarperCollins, 1993

What is a transition metal?

Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

Period	1A (1)	2A (2)	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8)	1B (9)	2B (10)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
1																
2																
3			3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8)	1B (9)	2B (10)						
4			21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn				
5			39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd				
6			57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg				
7			89 Ac	104 Rf	105 Dy	106 Sg	107 Bh	108 Hs	109 Mt	110 No	111 Lr	112				



Electrons in atoms

	4s	3d	4p
Sc	1↑	1	
Ti	1↑	1 1	
V	1↑	1 1 1	
Cr	1	1 1 1 1 1	
Mn	1↑	1 1 1 1 1	
Fe	1↑	1↑ 1 1 1 1	
Co	1↑	1↑ 1 1 1 1	
Ni	1↑	1↑ 1↑ 1↑ 1↑ 1	
Cu	1	1↑ 1↑ 1↑ 1↑ 1	
Zn	1↑	1↑ 1↑ 1↑ 1↑ 1	1 1

Working out numbers of d-electrons from oxidation states:

1st: how many electrons are there in the shell?

- count along the periodic table

e.g. Mn = 7 electrons Cu = 11 electrons

2nd: how many electrons are lost?

- oxidation state

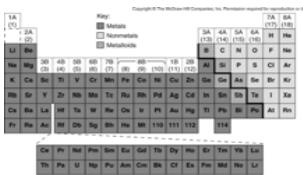
e.g. Mn(VII) = 7 electrons lost Cu(II) = 2 electrons lost

3rd: how many electrons left over?

- subtract

e.g. Mn(VII) = Cu(II) =

Hence the only valence electrons available in a transition metal ion are d-electrons



How many d-electrons has the metal?



1 2												B	C	N	O	F	H	
Li	Be											Al	Si	P	S	Cl	A	
Na	Mg	3	4	5	6	7	8	9	10	11	12	Zn	Ga	Ge	As	Se	R	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Sn	Ge	As	Br	Cl	I	X	
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	In	Sn	Ge	As	Se	Br	I	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	R	
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	110	111	112		114					
			Ca	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr		

complex

complex O.S. of L

complex O.S. of L O.S. of M

complex O.S. of L O.S. of M no. d electrons

$$[\text{Cr}_2\text{O}_7]^{2-}$$

$$[\text{MnO}_4]^- \quad -2$$

$$[\text{Ag}(\text{NH}_3)_2]^+$$

$$[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$$

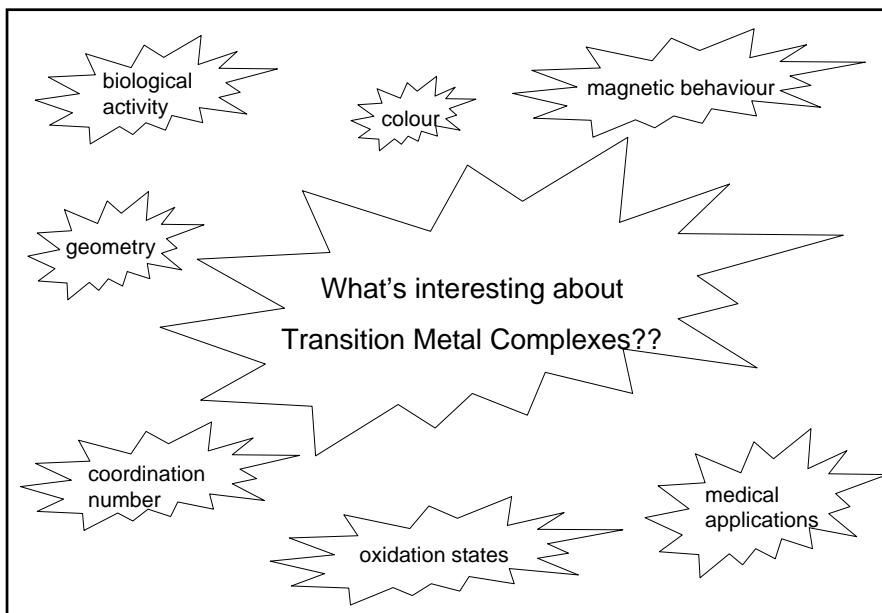
$$[\text{Co}(\text{en})_3]^{3+}$$

$$[\text{PtCl}_2(\text{NH}_3)_2] \quad -1, 0$$

$$[\text{V}(\text{CN})_6]^{4-}$$

[Fe(ox)₃]³⁻ -2

[View Details](#)



Colour of transition metal complexes



Ruby
Corundum
 Al_2O_3 with

impurities



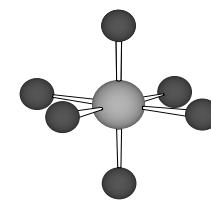
Sapphire
Corundum
 Al_2O_3 with

and impurities

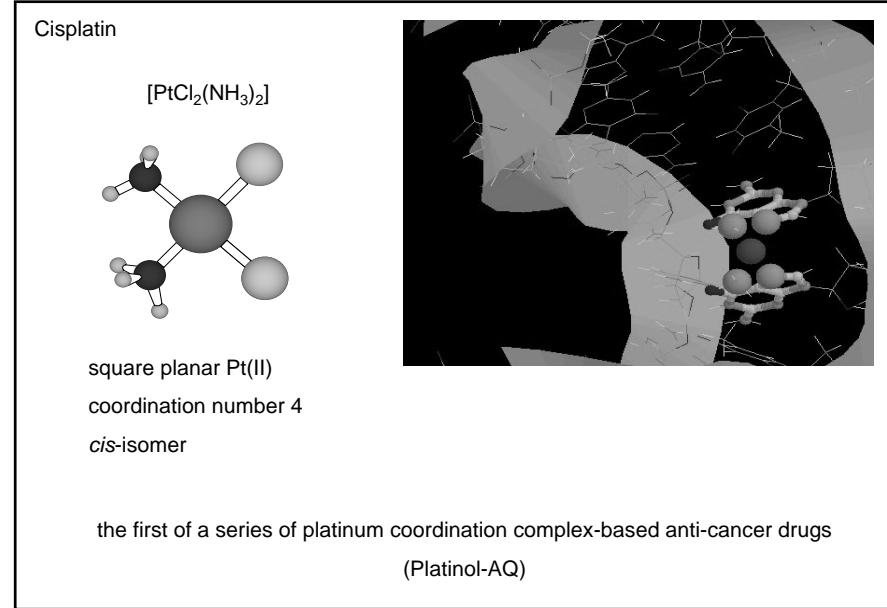
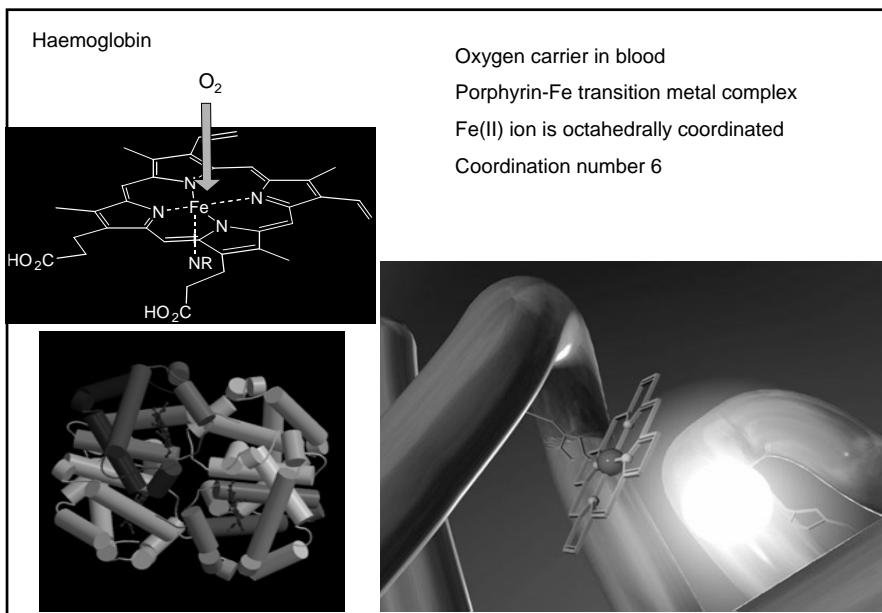


Emerald
Beryl
 AlSiO_3 containing Be with

impurities



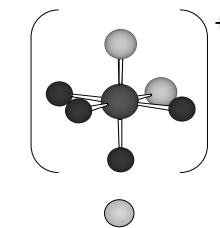
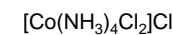
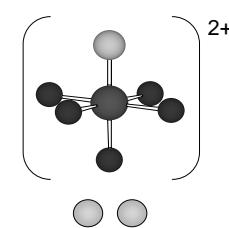
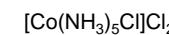
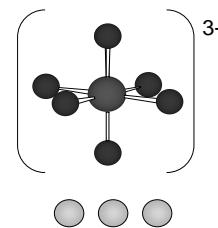
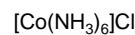
octahedral metal centre
coordination number 6



Alfred Werner - Nobel Prizewinner 1913



$\text{CoCl}_3 \cdot 6\text{NH}_3$	yellow	x s Ag^+	3 moles AgCl
$\text{CoCl}_3 \cdot 5\text{NH}_3$	purple	x s Ag^+	2 moles AgCl
$\text{CoCl}_3 \cdot 4\text{NH}_3$	green	x s Ag^+	1 mole AgCl
$\text{CoCl}_3 \cdot 3\text{NH}_3$		x s Ag^+	0 moles AgCl

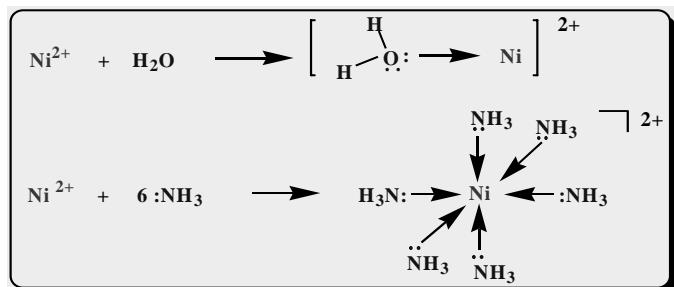


Werner's conclusions

1. The metal is in a particular (primary valency)
2. The complex has a fixed (secondary valency)
3. The ligands are bound to the metal via a bond which resembles a covalent bond

Lewis Acid-Base Concept: parallel with main group chemistry

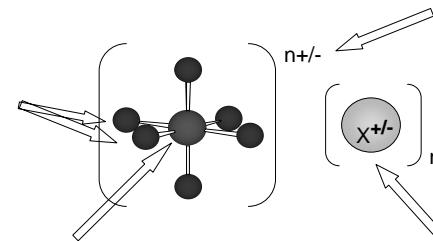
- Adducts formed by the reaction of metal ions (Lewis acids) with several ligands (Lewis bases).



- Properties of products differ from those of separate reactants (*i.e.*, colour, composition, magnetic properties, *etc.*).

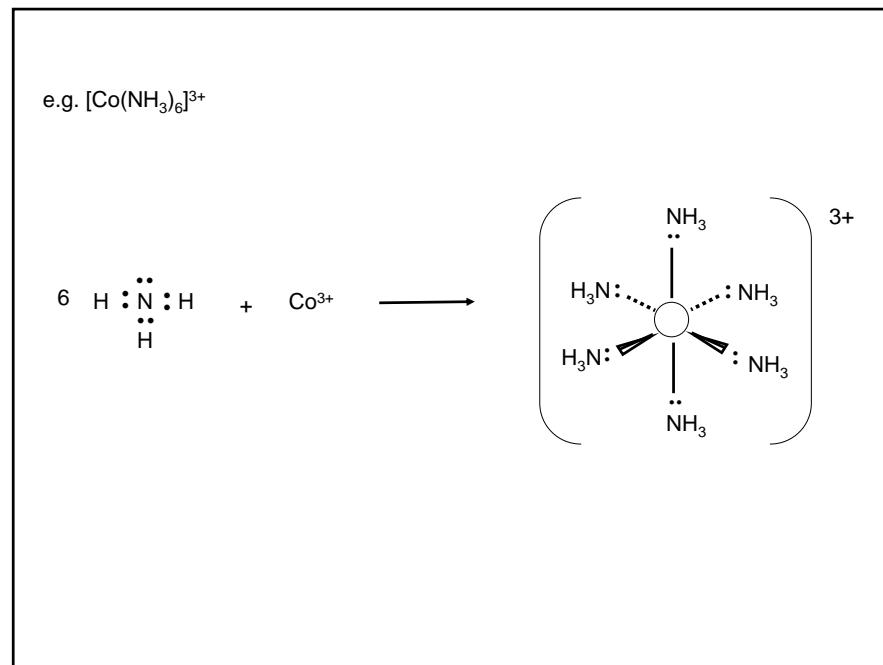
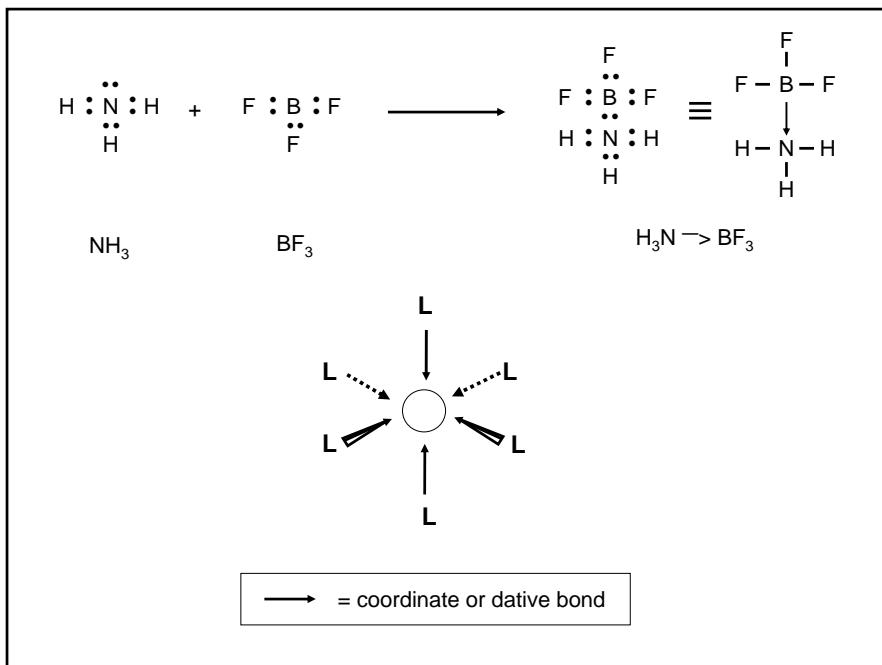
1

What is a coordination complex?

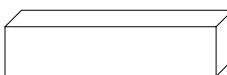


Central metal ion or atom surrounded by a set of ligands

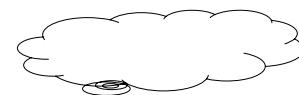
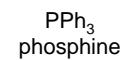
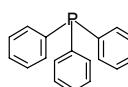
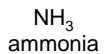
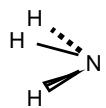
The ligand donates two electrons to the d-orbitals around the metal forming a



Group 14



Group 15



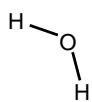
e.g. NH_3 , H_2O , OH^- , CO_3^{2-}

Small donor atoms

Electronegative

Not very polarisable

Group 16

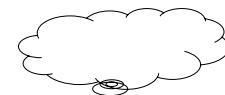


CO, PPh_3 , C_2H_4 , SRH , CN^- , SCN^-

Larger donor atoms

Less electronegative

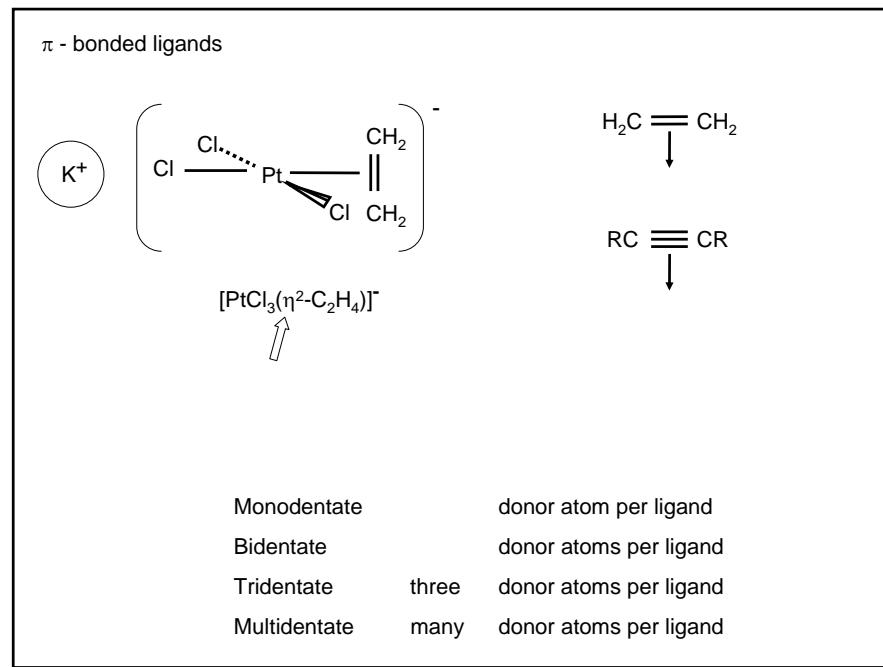
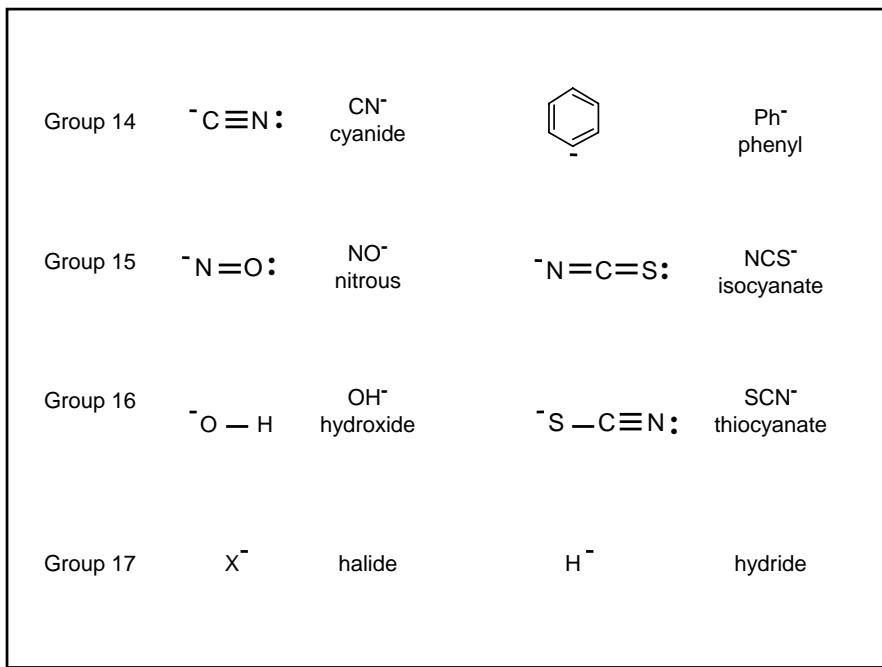
Easily polarisable



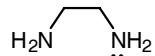
e.g. $\text{Ag}(\text{I})$, $\text{Cu}(\text{I})$

Larger metals (2nd + 3rd row)

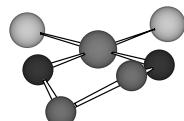
Low oxidation state



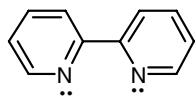
Neutral bidentate ligands: 2 donor atoms



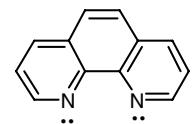
e.g. $[\text{PtCl}_2(\text{en})]$



1,2-diaminoethane = ethylene diamine = en



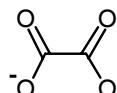
1,2-diphenylphosphineethane
dppe



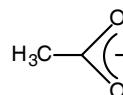
2,2'-bipyridine
bpy

1,10-phenanthroline
phen

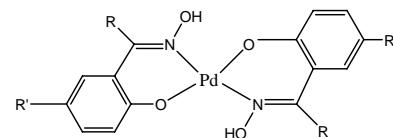
Anionic bidentate ligands



oxalate = ox^{2-}

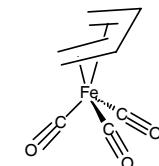


acetate = ac^-

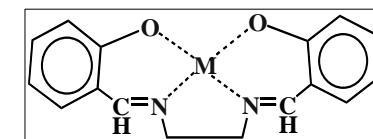


Pd(II)-oxime complex

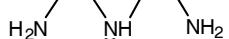
π -donor bidentate ligand



$[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_6)]$

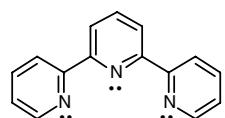
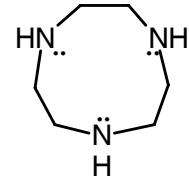


Tridentate ligands: three donor atoms



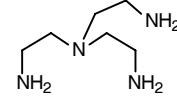
dien

1,2,4-triazacyclonane
macrocyclic ligand

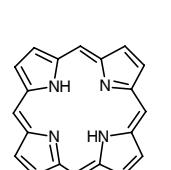


2,2':6',2''-terpyridine
tpy

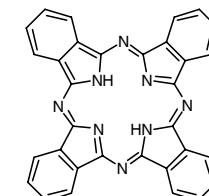
Tetradentate ligands



tris(2-aminoethyl)amine
tren



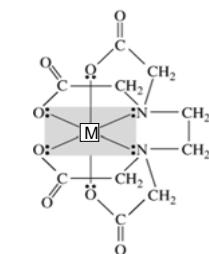
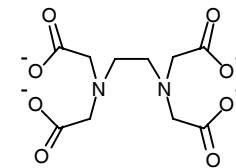
porphyrin



phthalocyanin

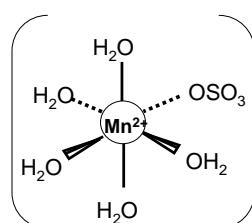
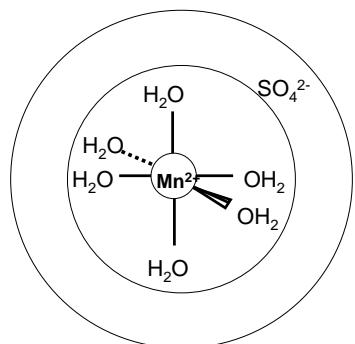
Hexadentate ligand

tetraanion of
ethylenediaminetetraacetic acid
EDTA



Inner coordination sphere =

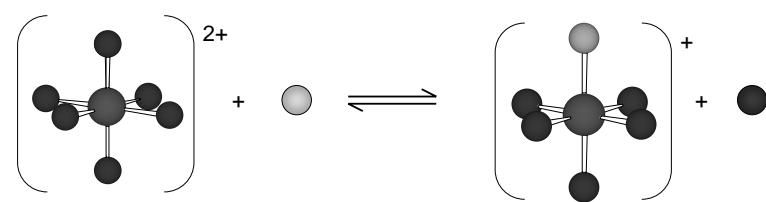
Outer coordination sphere =



Copyright © The McGraw-Hill Companies, Inc. Permission required for reproduction or display.

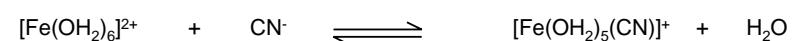
		Periodic Table of the Elements																									
		1A (1)		2A (2)		TRANSITION ELEMENTS d block												8A (18)									
1		3B (3)		4B (4)		5B (5)		6B (6)		7B (7)		8B (8) (9) (10)		1B (11)		2B (12)											
2		Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd						
3		La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg																
4		Ac	Rf	Db	Sg	Bh	Hs	Mt																			
5																											
6																											
7																											
Period																											
INNER TRANSITION ELEMENTS f block																											
58	59	60	61	62	63	64	65	66	67	68	69	70	71	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
90	91	92	93	94	95	96	97	98	99	100	101	102	103	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Ligand Exchange Reactions



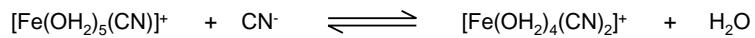
hexaaquo iron(II)
complex

cyanide
ion



$$K_1 = \frac{\text{const}}{[\text{H}_2\text{O}]} = \frac{[\text{Fe}(\text{OH}_2)_5(\text{CN})^+] \cancel{[\text{H}_2\text{O}]}}{[\text{Fe}(\text{OH}_2)_6^{2+}] [\text{CN}^-]}$$

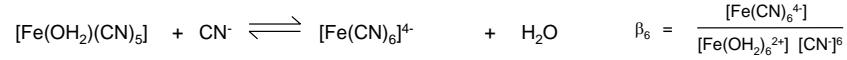
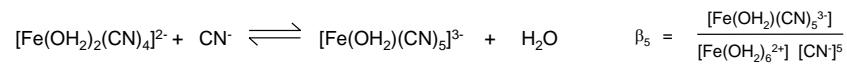
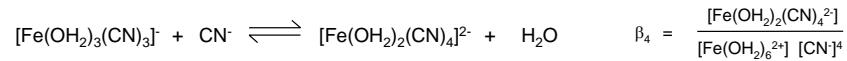
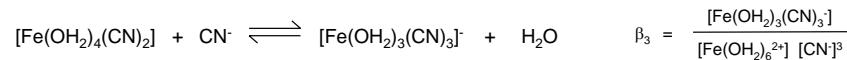
The reaction continues....



$$K_2 = \frac{[\text{Fe}(\text{OH}_2)_4(\text{CN})_2]}{[\text{Fe}(\text{OH}_2)_5(\text{CN})^+] [\text{CN}^-]}$$

$$K_1 K_2 = \beta_2 = \frac{\cancel{[\text{Fe}(\text{OH}_2)_5(\text{CN})^+]}}{[\text{Fe}(\text{OH}_2)_6^{2+}] [\text{CN}^-]} \times \frac{[\text{Fe}(\text{OH}_2)_4(\text{CN})_2]}{\cancel{[\text{Fe}(\text{OH}_2)_5(\text{CN})^+] [\text{CN}^-]}}$$

The reaction continues....

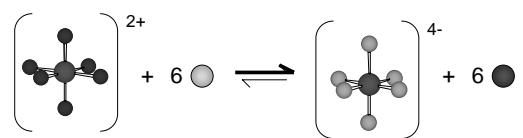


Overall Stability Constant

$$\beta_n = \frac{[\text{ML}_n]}{[\text{M}] [\text{L}]^n}$$

Stability constants are often expressed in log form ie $\log \beta_n$

Values of β_n

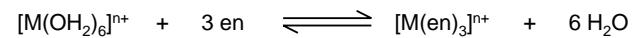
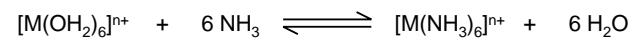
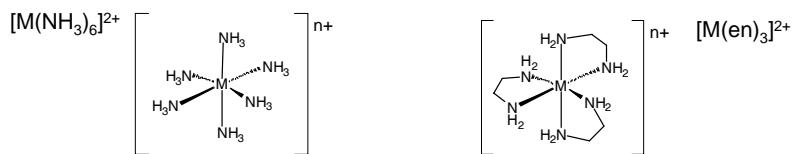


$$\beta_6 = \frac{[\text{Fe}(\text{CN})_6]^{4-}}{[\text{Fe}(\text{OH}_2)_6]^{2+} [\text{CN}]^6} \sim 10^{35}$$

$$\log \beta_6 = 35$$

$$K_n < \dots < K_3 < K_2 < K_1$$

The Chelate Effect



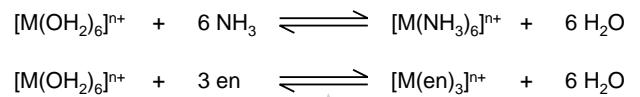
Entropy of chelate formation

$$\Delta G^\circ = -RT \ln K$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Enthalpy changes similar

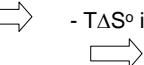
Entropy changes differ



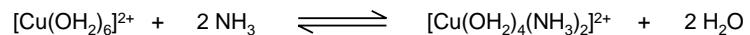
ΔS° is large and positive



$-T\Delta S^\circ$ is large and negative



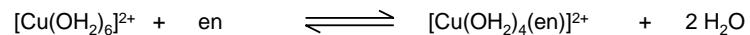
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$



$$\beta_2 10^{7.7} \log \beta_2 = 7.7$$

$$\Delta H^\circ = -46 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = -8.4 \text{ J K}^{-1}\text{mol}^{-1}$$



$$\beta_2 10^{10.6} \log \beta_1 = 10.6$$

$$\Delta H^\circ = -54 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = +23 \text{ J K}^{-1}\text{mol}^{-1}$$

The Macrocyclic Effect

Complexes containing macrocyclic rings have enhanced stability compared to acyclic ligands

$$\log K_1 = 23.9$$

acyclic chelating ligand

$$\log K_1 = 28.0$$

macrocyclic ligand

ΔG always favours formation of macrocyclic complex

Thermodynamic vs Kinetic Stability

e.g. $[\text{Cr}(\text{OH}_2)_6]^{3+}$ d³ kinetically inert slow substitution of Ls

cf. $[\text{Fe}(\text{OH}_2)_6]^{3+}$ hs d⁵ kinetically labile rapid substitution of Ls

(thermodynamic stability similar)

Tour of Coordination Numbers and their Geometries

The Kepert Model

The shape of a complex is usually dictated by the number of coordinated atoms. The coordinated atoms are as far away from each other as possible. Non-bonding electrons are ignored.

Note:

- regular geometries are often distorted
- structural features of multinuclear complexes are described in terms used for individual metal centres
- when energy differences between different structures are small, fluxional behaviour may be observed

Most Common Geometries of Transition Metal Complexes

Tetrahedral $109^\circ 28'$ C.N. 4



Square Planar 90° C.N. 4



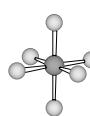
Trigonal bipyramidal $120^\circ + 90^\circ$ C.N. 5



Square based pyramidal 90° C.N. 5

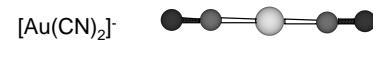


Octahedral 90° C.N. 6



Coordination number 2

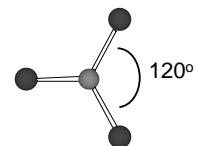
Cu(I), Ag(I), Au(I), Hg(II)



Coordination number 3

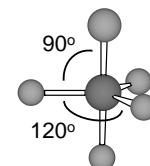
$[\text{Cu}(\text{CN})_2]^-$

$[\text{HgI}_3]^-$

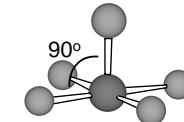


Coordination number 5

trigonal bipyramidal

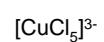


square-based pyramid

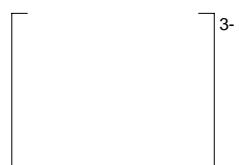


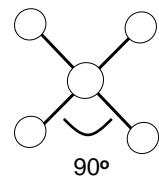
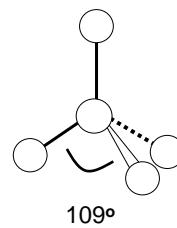
The two structures have very similar energy

trigonal bipyramid

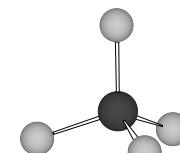


square-based pyramid





Tetrahedral complexes



$[\text{CoCl}_4]^{2-}$
 $[\text{MnO}_4]^-$
 $[\text{NiCl}_4]^{2-}$

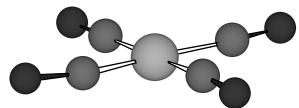
Favoured by steric requirements

optical isomerism



non-superimposable mirror images

Square planar geometry



e.g. $[\text{PtCl}_4]^{2-}$
 $[\text{AuBr}_4]^-$
 $[\text{Co}(\text{CN})_4]^{2-}$

Square planar complexes are formed by

i.e. group 10 Ni^{2+} , Pd^{2+} , Pt^{2+}
 Au^{3+}

Square planar complexes are formed by

e.g. CN^-

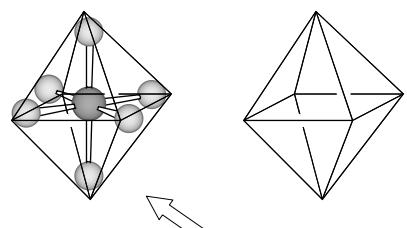
Square Planar Geometry

cisplatin

cis- $[\text{PtCl}_2(\text{NH}_3)_2]$
cis-diamminedichloroplatinum(II)

trans- $[\text{PtCl}_2(\text{NH}_3)_2]$
trans-diamminedichloroplatinum(II)

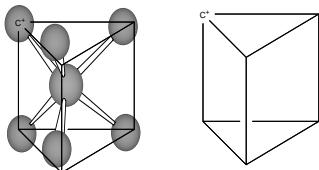
Coordination number 6



e.g. $[\text{Mn}(\text{OH}_2)_6]^{2+}$
 $[\text{Cr}(\text{CO})_6]$

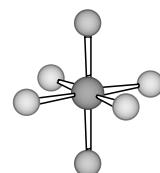
Staggered ligands vs. Eclipsed ligands

d^0 metals
e.g. WMe_6



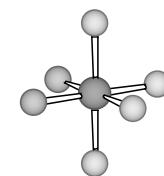
Octahedral geometry

$[\text{ML}_4\text{X}_2]$



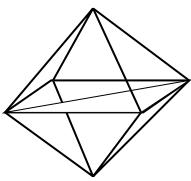
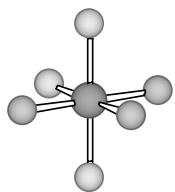
trans- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
green

Geometrical Isomerism

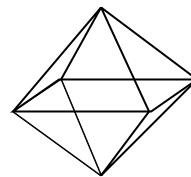
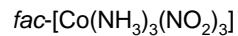
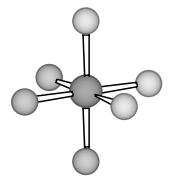


cis- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
violet

Octahedral geometry
[ML₃X₃]



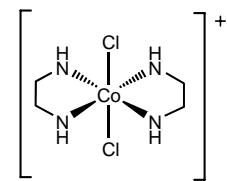
Geometrical Isomerism



Octahedral geometry

[M(K²L)₂X₂] e.g. [Co(en)₂Cl₂]⁺

trans geometrical isomer



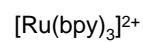
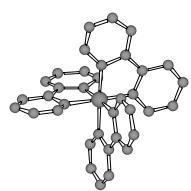
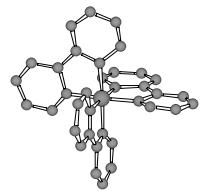
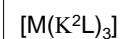
cis geometrical isomer $\xrightarrow{}$ two optical isomers

Geometrical and Optical Isomerism

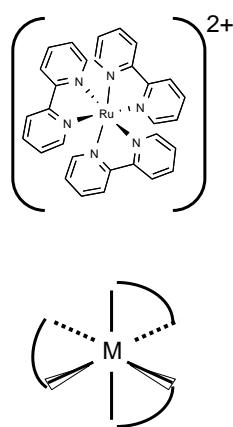
Non-superimposable mirror images = Δ and Λ enantiomers



Octahedral geometry



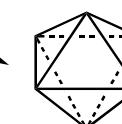
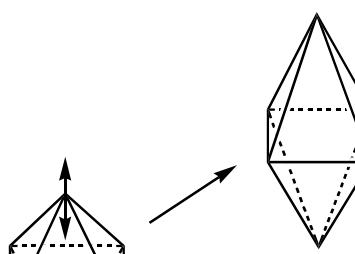
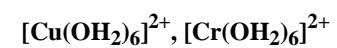
Optical Isomerism



Tetragonal Distortion:

Tetragonal elongation z-axis

2 long axial & 4 shorter equatorial bonds



Tetragonal compression z-axis

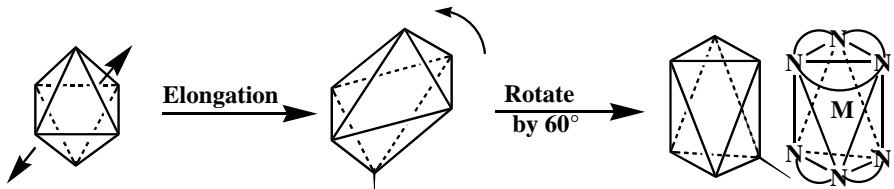
2 short axial & 4 longer equatorial bonds



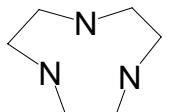
* Small distortion but symmetry lower than octahedral.

Trigonal Distortion:

- Two faces on opposite sides of octahedron move either towards or away from each other



Complexes of tacn can show this type of distortion $[M(tacn)_2]^{2+}$



tacn = 1,3,7-triazacyclononane

Isomerism

Structural Isomerism

Isomers have the same empirical formula but the atoms connectivities differ

Stereoisomerism

Isomers have the same M-L bonds, but the atoms are arranged differently in space

Ionisation isomerism

Hydration isomerism

Coordination isomerism

Linkage isomerism

Polymerisation isomerism

Geometrical isomerism

cis/trans

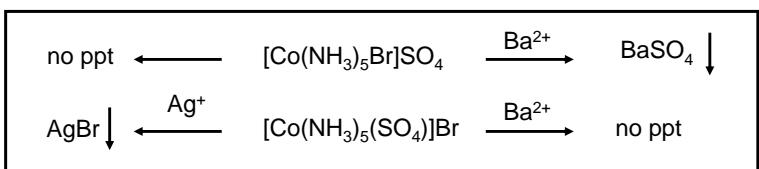
mer/fac

Optical isomerism

Δ and Λ

Ionisation isomerism

Exchange of a ligated anion with a counterion

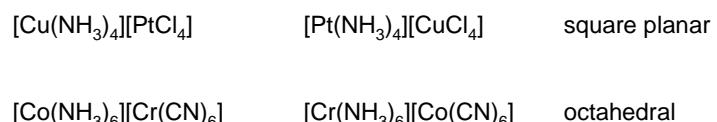


Solvate isomerism

Exchange of a neutral ligand for an anionic ligand

e.g. $[\text{Co}(\text{OH}_2)_6]\text{Cl}_3$ violet
 $[\text{Co}(\text{OH}_2)_5\text{Cl}]\text{Cl}_2$ light green
 $[\text{Co}(\text{OH}_2)_4\text{Cl}_2]\text{Cl}$ dark green

Coordination isomerism

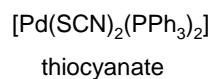
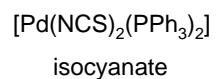
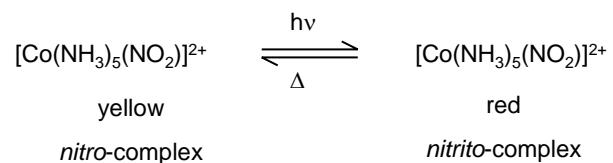


Polymerisation isomerism

e.g. $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$ $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

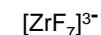
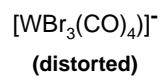
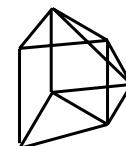
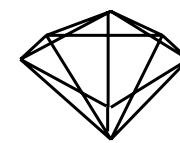
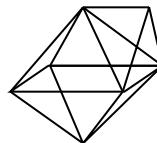
Both polymers have the empirical formula $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]_n$

Linkage isomerism

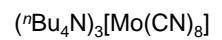
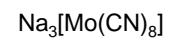
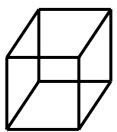
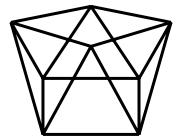


Higher Coordination Numbers

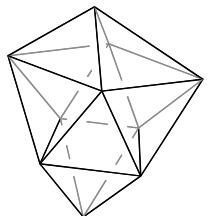
Coordination Number 7

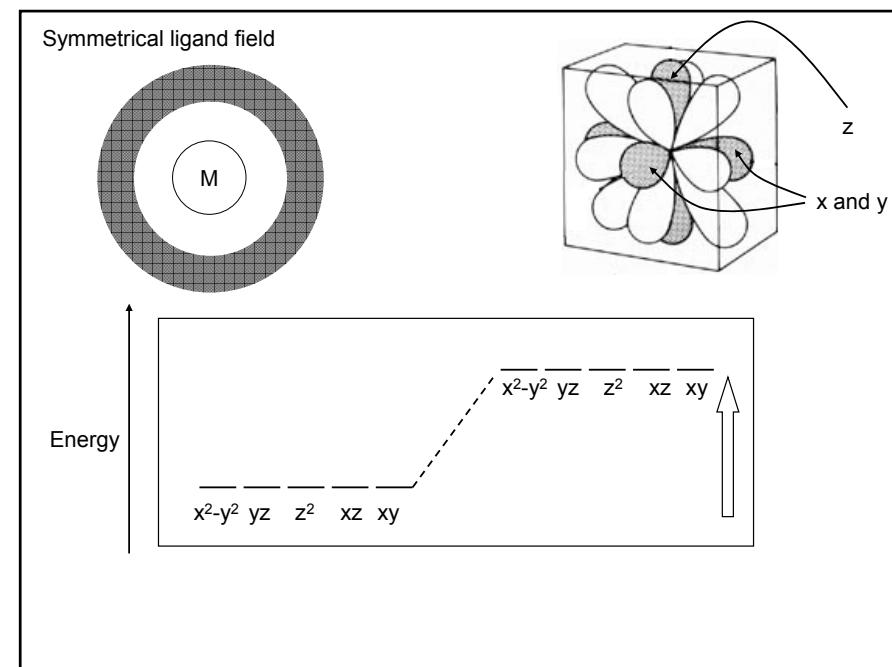
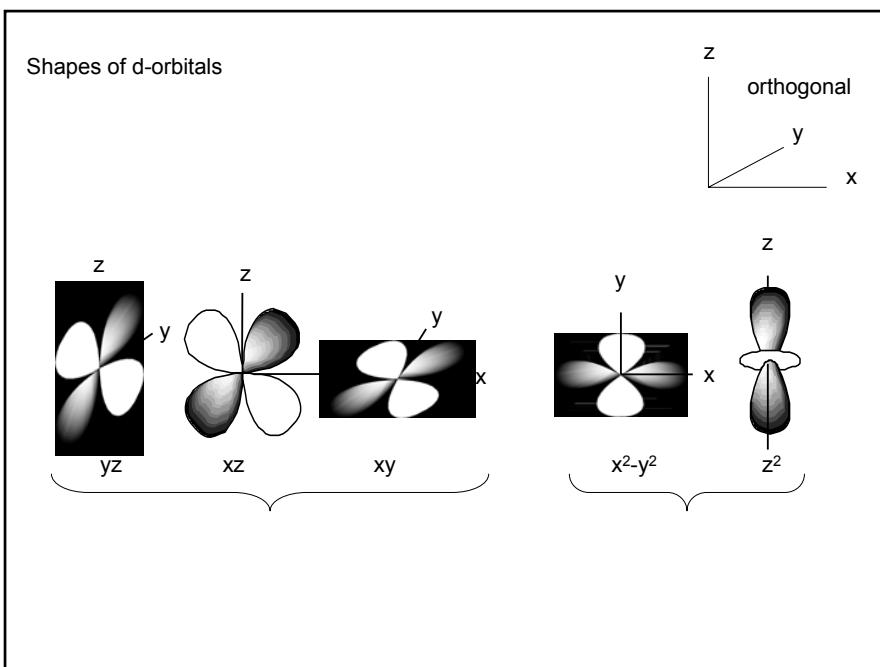


Coordination Number 8

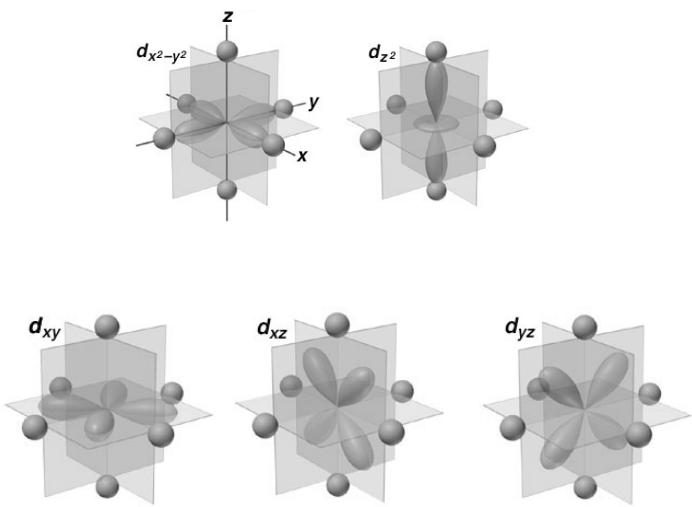


Coordination Number 9



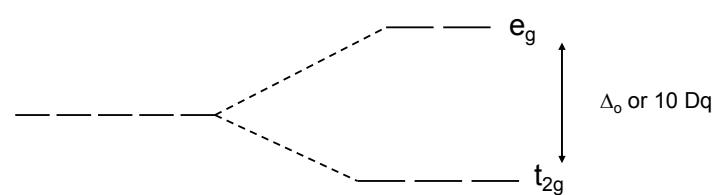


Effect of ligand field on metal d-orbitals



The difference in energy between the e_g and the t_{2g} energy levels is the . This is given the value 10 Dq.

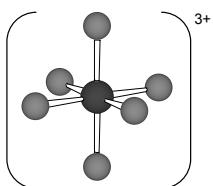
symmetrical field octahedral ligand field



Electron configurations: d¹ ion



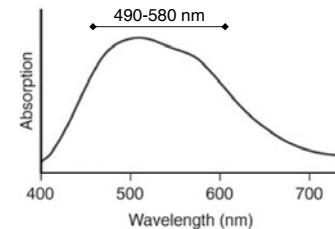
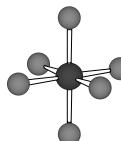
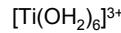
violet solution in water



one d-electron in a t_{2g} orbital

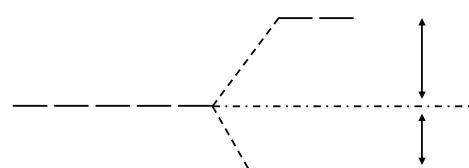
the complex has a Crystal Field Stabilisation Energy (CFSE) of - 0.4 Δ_{oct}

The nature of Δ_{oct}

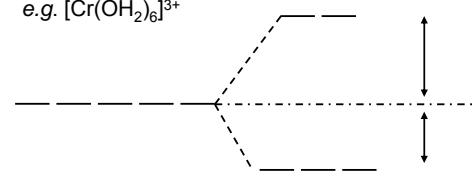


Absorption spectrum: λ_{max} = 510 nm = 243 kJ mol⁻¹

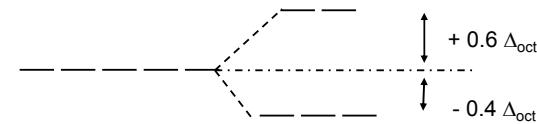
e.g. $[\text{V}(\text{OH}_2)_6]^{3+}$



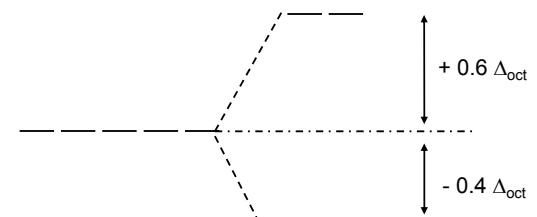
e.g. $[\text{Cr}(\text{OH}_2)_6]^{3+}$



d^4 ions



$$\begin{aligned} \text{CFSE} &= \\ &= - 0.6 \Delta_{\text{oct}} \end{aligned}$$



$$\begin{aligned} \text{CFSE} &= \\ &= - 1.6 \Delta_{\text{oct}} + P \end{aligned}$$

High and Low spin Complexes

High spin complex

Low spin complex

Δ is small

electrons occupy e_g and t_{2g} orbitals singly before pairing

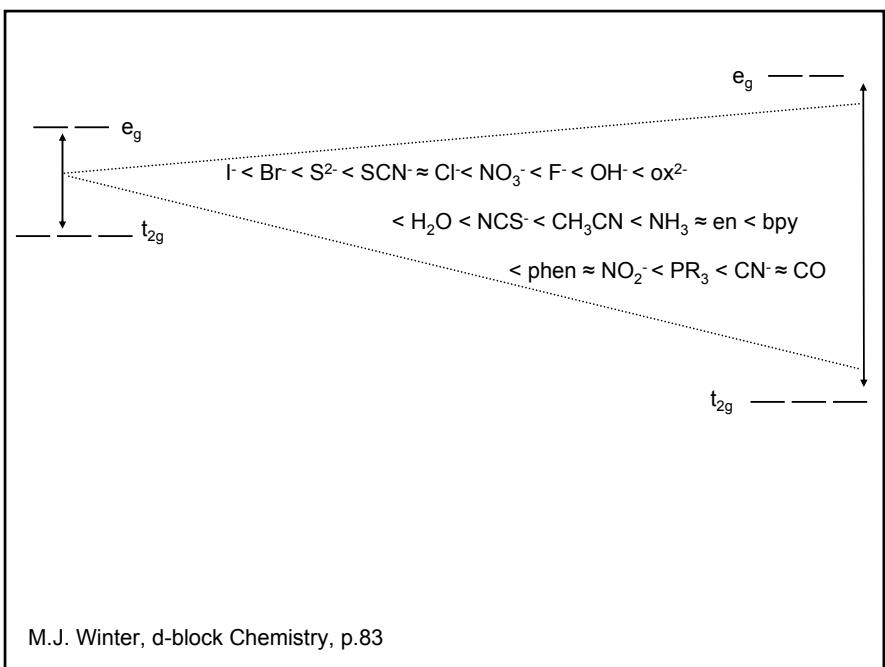
Δ is large

electrons pair in t_{2g} orbitals before occupying e_g orbitals

Factors affecting the magnitude of Δ_{oct}

e.g. $[\text{Fe}(\text{OH}_2)_6]^{2+} \quad \Delta_{\text{oct}} = 10\ 000 \text{ cm}^{-1}$ $[\text{Fe}(\text{OH}_2)_6]^{3+} \quad \Delta_{\text{oct}} = 14\ 000 \text{ cm}^{-1}$
 $[\text{Co}(\text{OH}_2)_6]^{2+} \quad \Delta_{\text{oct}} = 9\ 700 \text{ cm}^{-1}$ $[\text{Co}(\text{OH}_2)_6]^{3+} \quad \Delta_{\text{oct}} = 18\ 000 \text{ cm}^{-1}$

e.g. $[\text{Co}(\text{NH}_3)_6]^{3+} \quad \Delta_{\text{oct}} = 22\ 900 \text{ cm}^{-1}$
 $[\text{Rh}(\text{NH}_3)_6]^{3+} \quad \Delta_{\text{oct}} = 34\ 100 \text{ cm}^{-1}$
 $[\text{Ir}(\text{NH}_3)_6]^{3+} \quad \Delta_{\text{oct}} = 41\ 000 \text{ cm}^{-1}$



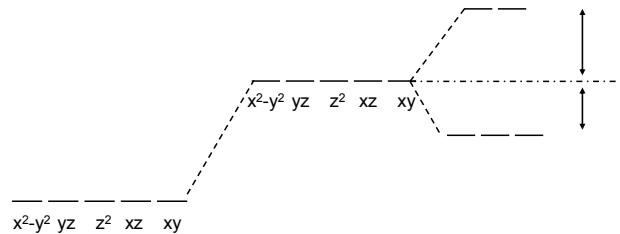
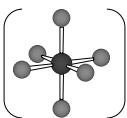
Octahedral Crystal Field

d-orbital energies in...

free ion

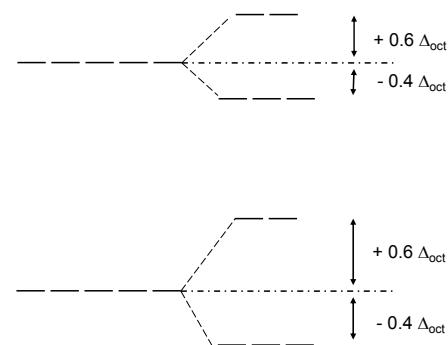
spherical ligand field

octahedral ligand field

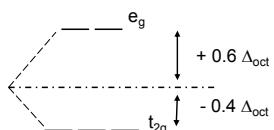
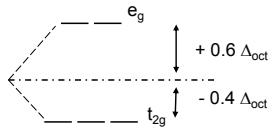


the complex has a Crystal Field Stabilisation Energy (CFSE)

ions, O_h field

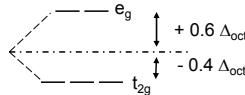


ions, O_h field

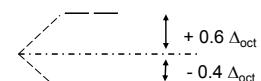


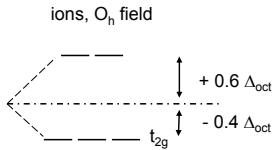
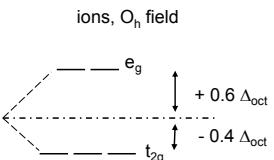
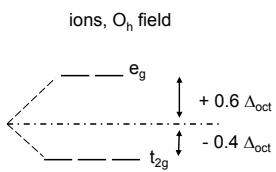
ions, O_h field

High Spin



Low Spin



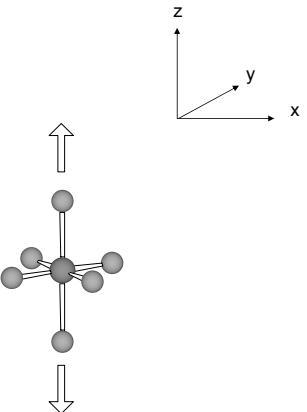
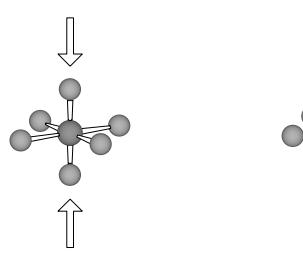


Only configurations
can be high or low spin

eg 1. What is the CFSE of $[Fe(CN)_6]^{3-}$?

eg. 2. If the CFSE of $[Co(H_2O)_6]^{2+}$ is $-0.8 \Delta_{oct}$,
what spin state is it in?

Jahn-Teller Distortion

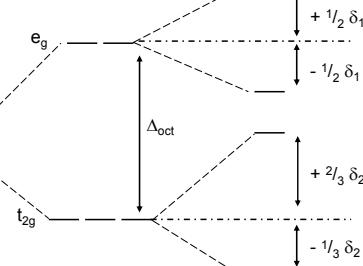
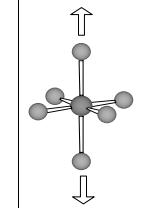


The ligands contract or elongate giving a complex

Jahn-Teller Distortion

z -out: d-orbitals with z-component are stabilised

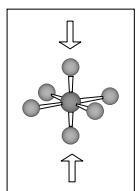
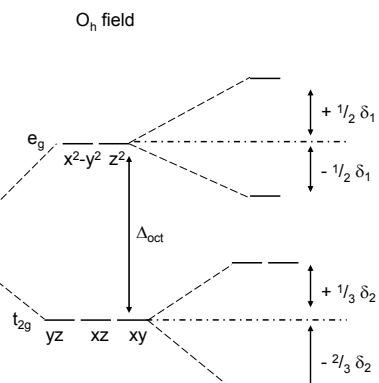
O_h field



Jahn-Teller Distortion

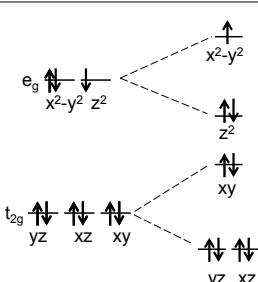
z-in: d-orbitals with z-component are destabilised

O_h field



Jahn-Teller Theorem

"For a nonlinear molecule in an electronically degenerate state distortion must occur to lower the symmetry, remove the degeneracy and lower the energy"



e.g. $K_2[CuF_4]$ O_h z-in
 $Na_2[CuF_4]$ O_h z-out

Cr_2F_5 O_h z-out
 $Cr(II)$ = high spin d^4

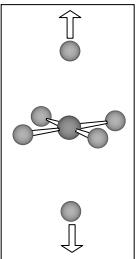
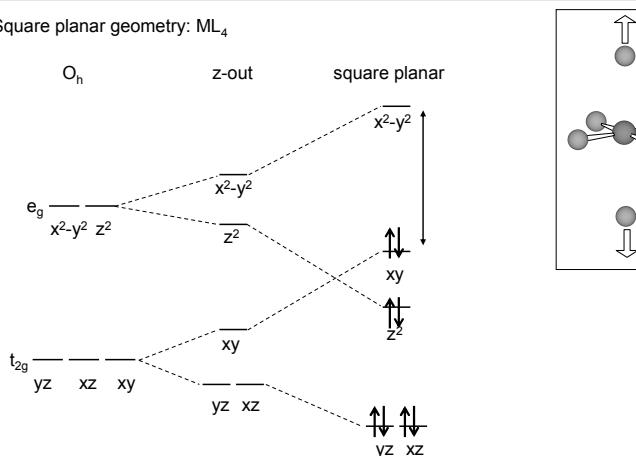
e.g. $[Cu(OH_2)_6]^{2+}$
 $Cu(II)$ = d^9
z-out

Square planar geometry: ML_4

O_h

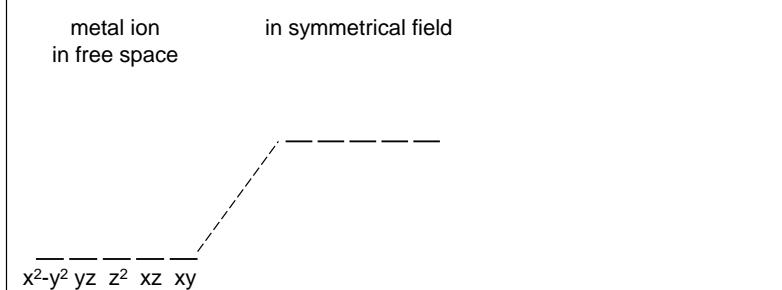
z-out

square planar

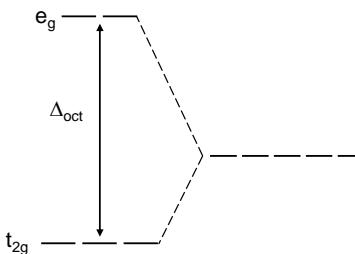


d^8 complexes: some $Ni(II)$, and $Pd(II)$, $Pt(II)$

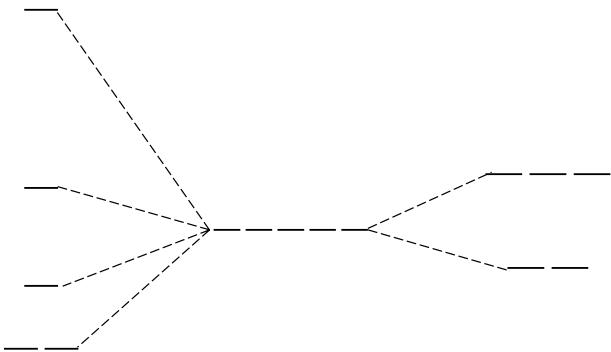
Tetrahedral crystal field splitting



Splitting of d-orbitals in a tetrahedral crystal field



Effect of crystal fields on complex geometry



Spin orbit coupling is particularly significant for metals lower in the periodic table but for 1st row transition metal complexes the formula can be used in a simplified form because:

"The spin contribution outweighs the orbital angular momentum contribution to μ_{eff} "

→ Spin only magnetic moment, μ_{SO}

$$\mu_{\text{SO}} = \sqrt{n(n+2)}$$

where n = number of unpaired electrons

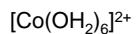
$$\mu_{\text{SO}} = 2 \sqrt{S(S+1)}$$

where S = total spin quantum number = $n / 2$

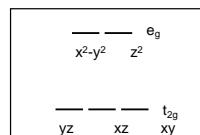
Spin only magnetic moment, μ_{SO}

$$\mu_{SO} = \sqrt{n(n+2)}$$
 where n = number of unpaired electrons

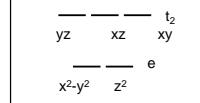
What is the spin only magnetic moment of?



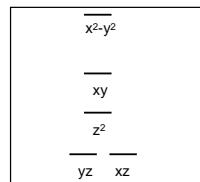
$$n = \mu_{SO} = \sqrt{\quad} =$$



$$n = \mu_{SO} = \sqrt{\quad} =$$

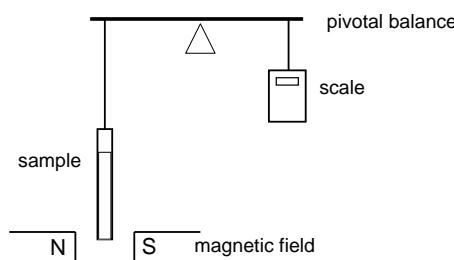


$$n = \mu_{SO} = \sqrt{\quad} =$$



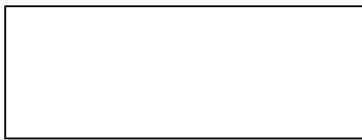
Measurement of magnetic susceptibility

Gouy Balance



Effective magnetic moment, μ_{eff}

From experimentally measured molar magnetic susceptibility, χ_m



μ_{eff} in Bohr Magnetons:

$$\mu_B = \frac{e h}{4 \pi m_e} = 9.27 \times 10^{-24} \text{ J T}^{-1}$$

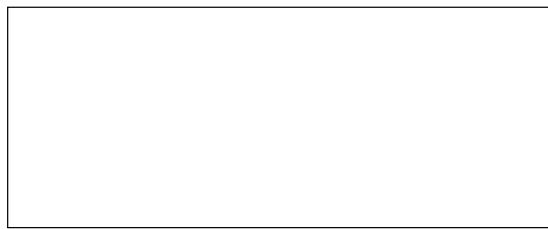
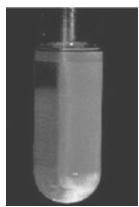
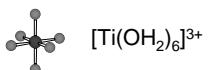
2.83 is the magnetogyric ratio

T is temperature in Kelvins

Values of μ_{eff} for high spin O_h complexes

M ion	d^n	S	$\mu_{\text{SO}}(\text{BM})$	$\mu_{\text{obs}}(\text{BM})$
Sc ³⁺ , Ti ⁴⁺	d^0	0	0	0
Ti ³⁺	d^1	$1/2$	1.73	1.7 - 1.8
V ³⁺	d^2	1	2.83	2.8 - 3.1
V ²⁺ , Cr ³⁺	d^3	$3/2$	3.87	3.7 - 3.9
Cr ²⁺ , Mn ³⁺	d^4	2	4.90	4.8 - 4.9
Mn ²⁺ , Fe ³⁺	d^5	$5/2$	5.92	5.7 - 6.0
Fe ²⁺ , Co ³⁺	d^6	2	4.90	5.0 - 5.6
Co ²⁺	d^7	$3/2$	3.87	4.3 - 5.2
Ni ²⁺	d^8	1	2.83	2.9 - 3.9
Cu ²⁺	d^9	$1/2$	1.73	1.9 - 2.1
Zn ²⁺	d^{10}	0	0	0

Colour in TM complexes



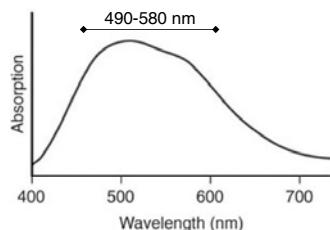
Absorption spectrum: $\lambda_{\text{max}} = 510 \text{ nm}$

white light
400-800 nm

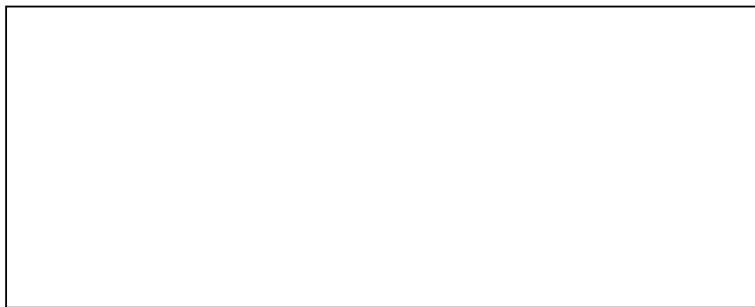
Blue: 400-490 nm

yellow-green: 490-580 nm

Red: 580-800 nm



Colour of d-d transitions depends on magnitude of Δ



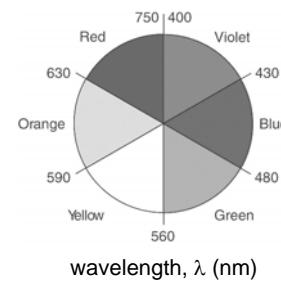
The Colour Wheel

If red light is absorbed

⇒ the complex appears green

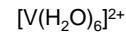
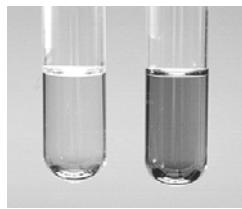
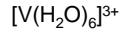
If purple light is absorbed

⇒ the complex appears yellow

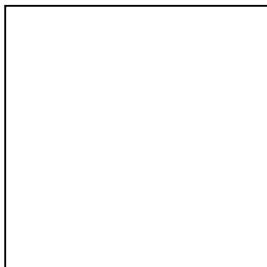


Effect of magnitude of Δ on colour

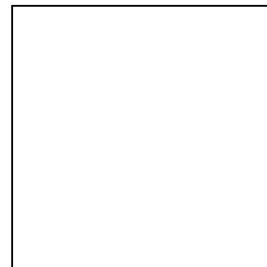
1. For a given ligand, the colour



violet light absorbed
complex appears yellow

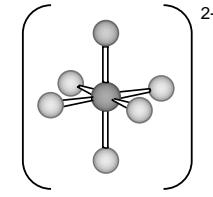
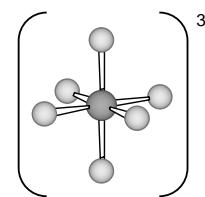
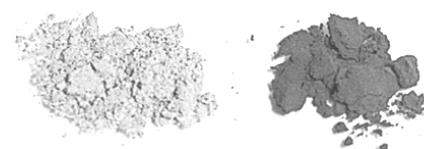


yellow light absorbed
complex appears violet



Effect of magnitude of Δ on colour

2. For a given metal ion, the colour depends on



Colour and the Spectrochemical Series

Weak Field Ligands

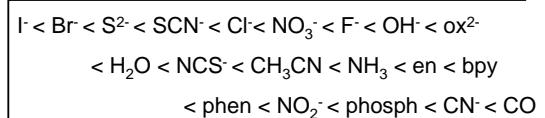
High Spin Complexes

Strong Field Ligands

Low Spin Complexes

small Δ

large Δ



Transition Metal Coordination Chemistry

Professor Sylvia Draper

smdraper@tcd.ie

WHERE HAVE WE BEEN ?

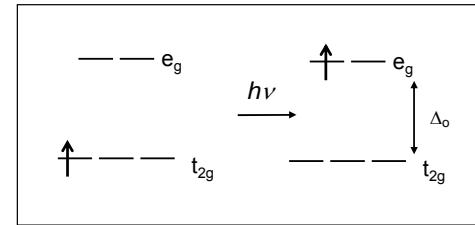
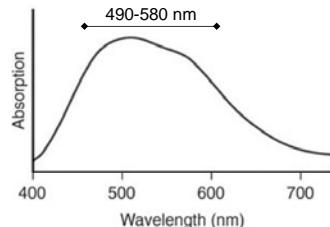
Lecture 7: Magnetism and Colour
Tetrahedral crystal field
Magnetism
Spin only magnetic moment
Magnetism measurements
Absorption of light
d1 complexes and colour
Effect of Δ on colour

WHERE ARE WE GOING ?

Lecture 8:
Colour continued, and Ligand Field Theory
Selection rules
Limitations of CFT
LFSE and Δ
Thermodynamic aspects of LFT

[Ti(H₂O)₆]³⁺

Absorption spectrum: $\lambda_{\text{max}} = 510 \text{ nm}$



Factors affecting magnitude of Δ

1. Oxidation state of metal e.g.
2. Position of metal in periodic table
3. Type of ligand in spectrochemical series

Intensity of colour depends on

1. Laporte Selection Rule
2. Spin Selection Rule

The Intensity of the colour depends on Selection Rules and is measured by the absorbance

Absorbance is defined by the Beer-Lambert equation: $A = \log_{10}(I_0/I) = \varepsilon \cdot c \cdot l$

where A = absorbance

I_0 = intensity of incident light; I = intensity of light after passing through the cell;

ε = molar absorption coefficient; c = concentration; l = cell pathlength.

Typical Spectrum: Octahedral Cr(III) complex

$[Cr] = 0.002M$

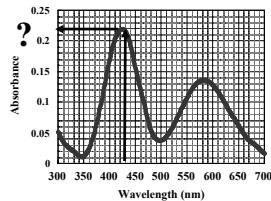
Calculation of ε : At 590 nm, $A = 0.138$

$$A = \varepsilon \cdot c \cdot l$$

$$0.138 = \varepsilon \times 0.002M \times 1 \text{ cm}$$

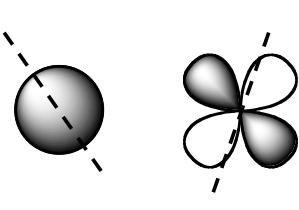
$$\varepsilon = 0.138 / 0.002 \times 1$$

$$\varepsilon = 69 \text{ M}^{-1} \text{ cm}^{-1}$$



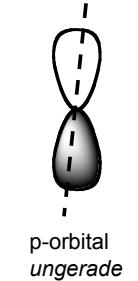
Transitions allowed by the selection rules (high ε values $> 1000 \text{ M}^{-1} \text{ cm}^{-1}$).

Laporte Selection Rule



s-orbital
gerade

d-orbital
gerade



p-orbital
ungerade

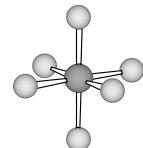
e.g. p-orbital to d-orbital
 d-orbital to d-orbital

by the Laporte selection rule
by the Laporte selection rule

Transitions between d-orbitals (g) forbidden by the Laporte selection rule

Octahedral complexes

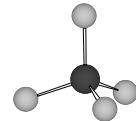
Centrosymmetric: t_{2g} and e_g orbitals



Selection rule lifted by molecular vibration

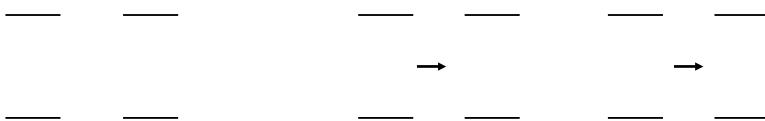
Tetrahedral complexes

non-Centrosymmetric: t_2 and e orbitals



Tetrahedral complexes are usually more strongly coloured than analogous octahedral complexes

The Spin Selection Rule



Assumptions made in CFT

1. The ligands are
2. Interactions are purely

Explains

1. Geometry
2. Magnetism
3. Colour

Limitations

Does not allow for in M-L bonding

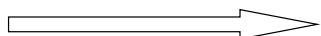
Doesn't explain

Order of ligands in the Spectrochemical Series

Nephelauxetic Effect

The Spectrochemical Series

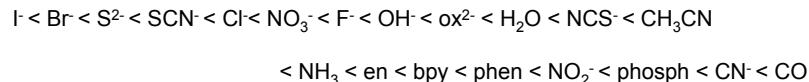
Weak Field Ligands



Strong Field Ligands

High Spin Complexes

Low Spin Complexes



CFT does not explain why some ligands with charges are
than analogous ligands which are not charged

The Nephelauxetic Effect

"there is

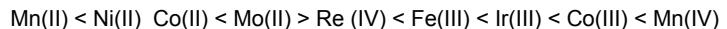
in complexes than in the free ion"

- some in M-L bonds – M and L share electrons
- effective size of metal orbitals
- electron-electron repulsion

Nephelauxetic series of ligands



Nephelauxetic series of metal ions



LFT is identical to CFT, except that it allows for some

in M-L bonding.

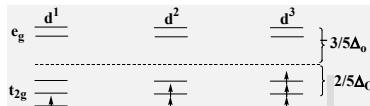
LFT is based on

parameters.

LFSE:-

the EXTRA stabilisation of complexes that occurs as a result of the splitting of orbitals in a ligand field
(cf. to CFSE: it is always positive and no account of P is taken)

LFSE Octahedral (always greater than tetrahedral) high/low spin options d^4 to d^7 only



d^1 : LFSE 0.4

d^2 : LFSE $0.4 \times 2 = 0.8$

d^3 : LFSE $0.4 \times 3 = 1.2$ maximum

d^4 hs : LFSE $0.4 \times 3 - 0.6 = 0.6$

d^4 ls : LFSE $0.4 \times 4 = 1.6$

d^5 hs : LFSE $0.4 \times 3 - 0.6 \times 2 = 0$ minimum

d^5 ls : LFSE $0.4 \times 5 = 2.0$ highest

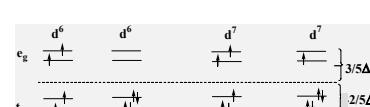
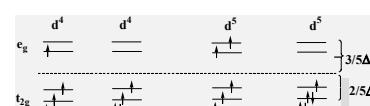
d^6 hs : LFSE $0.4 \times 4 - 0.6 \times 2 = 0.4$

d^6 ls : LFSE $0.4 \times 6 = 2.4$

d^7 hs : LFSE $0.4 \times 5 - 0.6 \times 2 = 0.8$

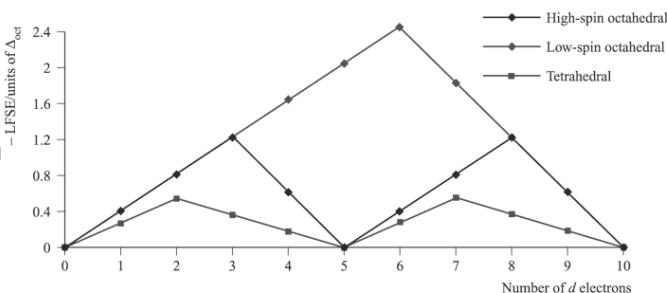
d^7 ls : LFSE $0.4 \times 6 - 0.6 = 1.8$

d^8 : LFSE $0.4 \times 6 - 0.6 \times 2 = 1.2$ maximum



ls gives higher LFSE than hs option

Variation in LFSE with Δ_{ex} (excluding P)



Is d^6 :

LFSE

hs d^0, d^5, d^{10} :

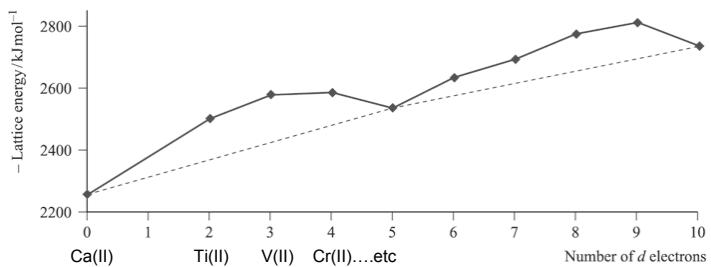
LFSE

hs $O_h d^3, d^8$:

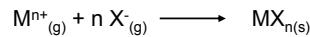
LFSE

Lattice Energies (from Born Haber cycle)

For 1st row M(II) chlorides: hs, O_h



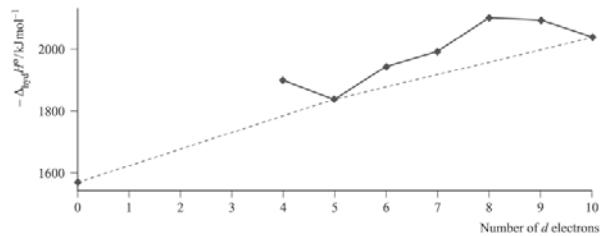
The energy
separation to form a crystal



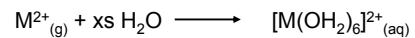
Discrepancies in lattice energies are a result of

when ions come together from infinite

Variation in Hydration Enthalpies



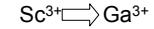
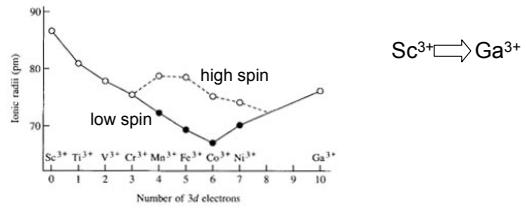
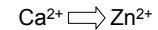
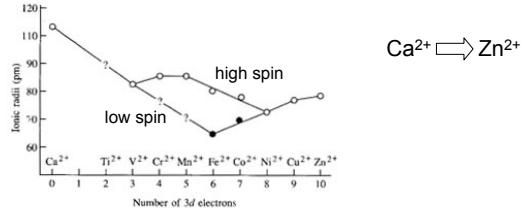
Enthalpy of hydration:



Last Lecture
9 lecture course on Coordination Chemistry
Prof. Sylvia Draper

So..... CFSE, LFE and MO theory agree !
- each one building upon and improving the other

Variation in Ionic Radii



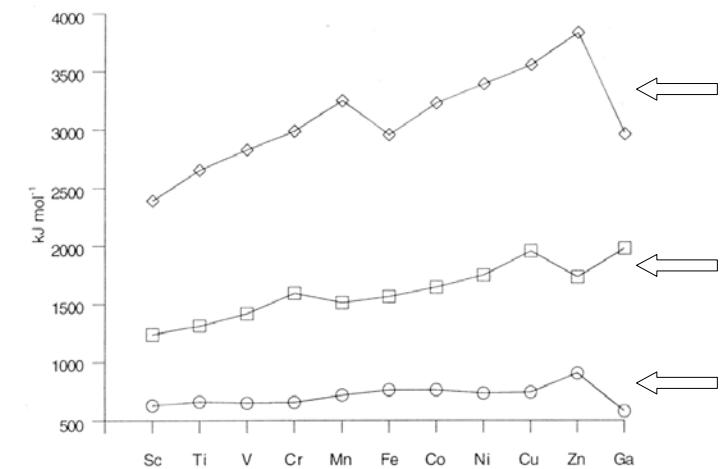
low spin: steady

high spin: steady

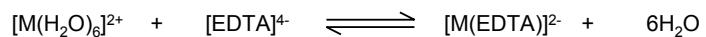
followed by increase from $t_{2g}^6 e_g^1$

followed by increase from $t_{2g}^3 e_g^1$

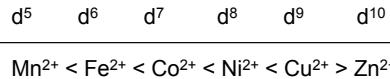
Ionisation Energies of first row TM ions, hs, O_h



Irving-Williams series



Position of equilibrium depends on



Valence Bond Theory

Ligand = Lewis base

Metal = Lewis acid

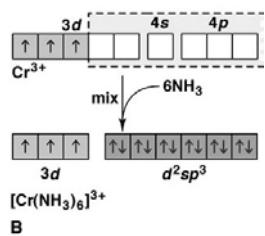
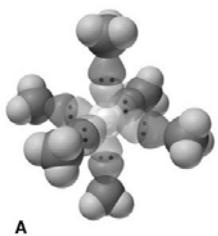
s, p and d orbitals give

with specific geometries

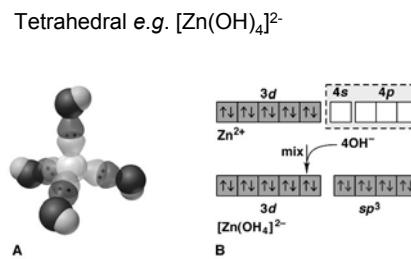
Number and type of M-L hybrid orbitals determines geometry of the complex

Octahedral Complex

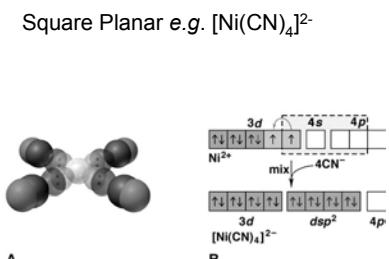
e.g. $[\text{Cr}(\text{NH}_3)_6]^{3+}$



Tetrahedral e.g. $[\text{Zn}(\text{OH})_4]^{2-}$



Square Planar e.g. $[\text{Ni}(\text{CN})_4]^{2-}$



Limitations of VB theory

Assumes bonding is

Does not account for

Can predict

wrongly

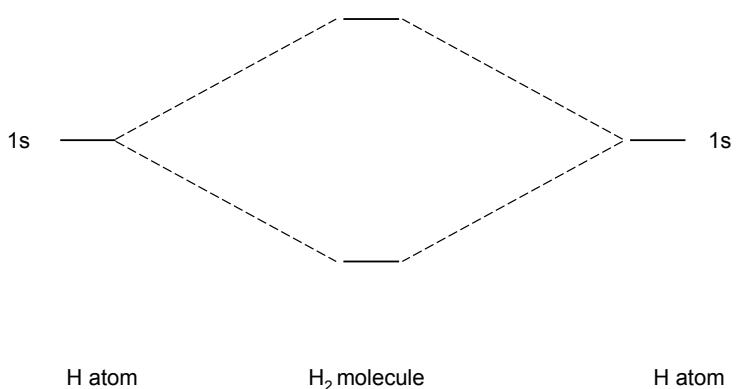
Does not account for

Molecular Orbital (MO) theory

MO theory considers covalent interactions

e.g. molecular hydrogen

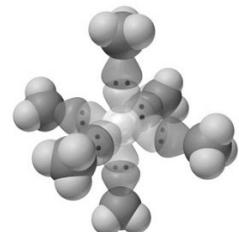
Linear Combination of Atomic Orbitals (LCAO)



Ligand Group Orbitals

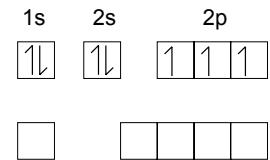
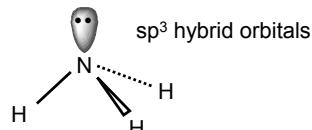
Metal valence shell orbitals =

Ligand valence shell orbitals =



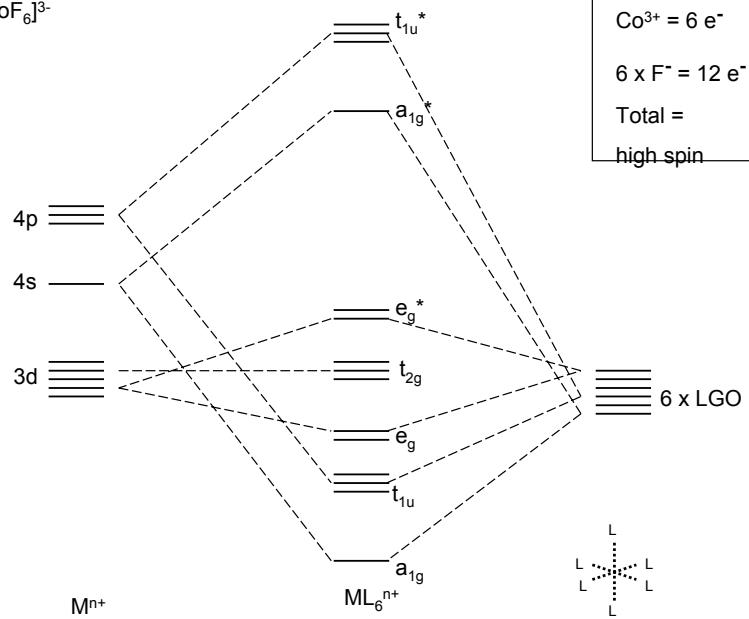
LCAO approach

e.g. [Co(NH₃)₆]³⁺ = sigma-bonded complex



Six sp³ hybrid ligand orbitals form a set of

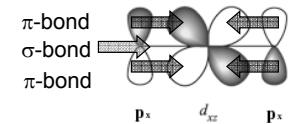
e.g. $[\text{CoF}_6]^{3-}$



Complexes with M-L π -bonding

e.g. H₂O, OH⁻, lower halides Cl⁻, Br⁻, I⁻

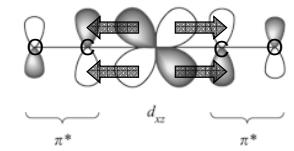
electron density to the metal centre
ligand orbital and metal orbital



of electron density from filled p orbitals

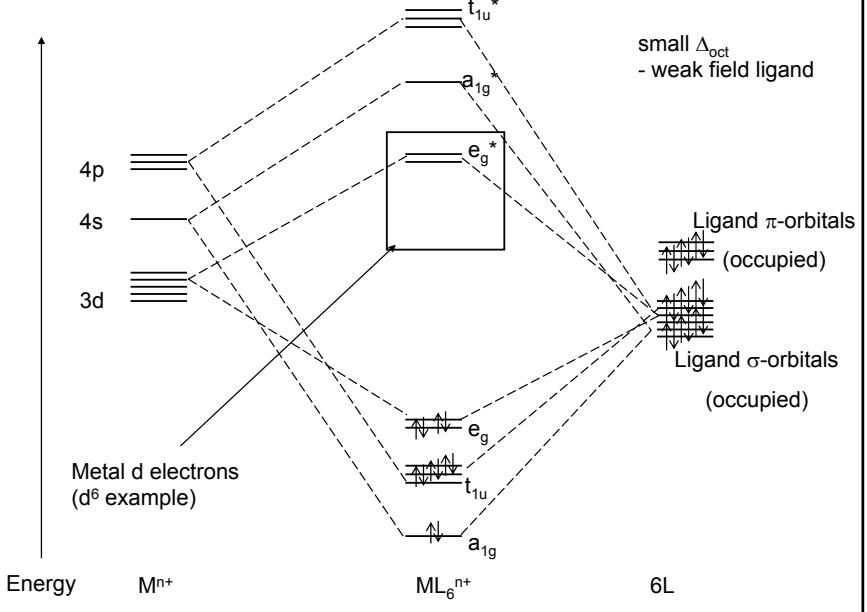
π -acceptor ligands e.g. CO, N₂, NO, alkenes

electron density from the metal centre
metal orbital and ligand orbitals



of electron density into empty π^* -antibonding orbitals

π -donor ligands: filled ligand orbitals and empty metal orbitals



π -acceptor ligands: back-donation to empty ligand antibonding orbitals

