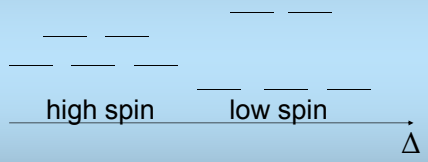
High-spin or low-spin ?

Octahedral d^4 – d^7 (aufbau &Hund)



P >< Δ

Spin pairing >< Orbital splitting

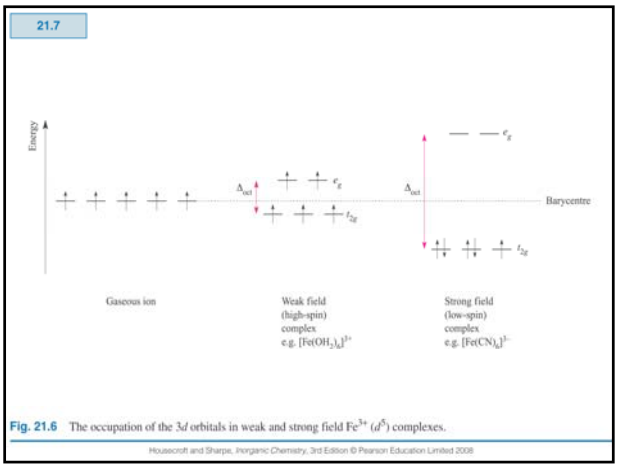
Spin pairing energies – Δ-values

- Pairing energies M^{z+}_{gas} : ~20% smaller in ML_n^{z+}

Energy $10^3 cm^{-1}$	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Δ from Maq_6^{2+}		12.2	13.9	7.7	10.4	9.7	8.5	12.5
Δ from Maq_6^{3+}	20.4	19	17.4	21	14	20		
P M^{2+}			23.5	25.5	17.6	22.5	27	
P M^{3+}				28	30	21		

Δ-values

Energy $10^3 cm^{-1}$	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
$M(H_2O)_6^{2+}$		12.2	13.9	7.7	10.4	9.7	8.5	12.5
$M(H_2O)_6^{3+}$	20.4	19.0	17.4	21.0	14.0	20		
MF_6^{3-}	17.0		15.0			13.1		
MF_6^{2-}				21.8				
$M(NH_3)_6^{3+}$			21.6			22.9		
$M(NH_3)_6^{2+}$						10.2	10.8	
$M(CN)_6^{3-}$			26.6		35.0			
Men_3^{3+}						24.0		
Men_3^{2+}							11.5	

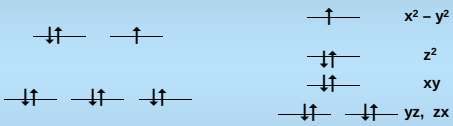


Low spin complexes:

- Strong field ligands
- Many d^6-systems in 1st row
  - All known Co(III)-complexes except CoF_6^{3-}
  - Several Fe(II)- complexes
- More frequent (in 2nd row) to dominating (in 3rd row)

Jahn Teller distortion

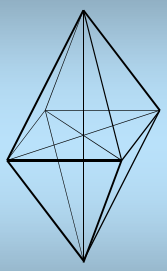
- d^9 (and d^4)



Singly occupied $x^2 - y^2$ less repulsive than z^2 (with 2 electrons)
⇨shorter distances in the X-Y plane

Jahn Teller distortion

Elongation



Case 1:
Look at K_1, K_2, and K_3 for Cu^{2+}.
Why is K_3 so small?

see next slide

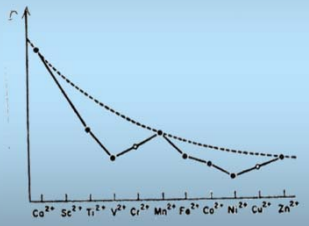
M^{2+} - 1,2-ethanediamine

Case study 1 ; the Cu^{2+} and the Cr^{2+} case

M^{2+}	$\log K_1$	$\log K_2$	$\log K_3$
Cr	5.15	4.04	-
Mn	2.77	2.10	0.92
Fe	4.34	3.31	2.05
Co	5.89	4.83	3.10
Ni	7.51	6.35	4.42
Cu	10.72	9.31	1.0
Zn	5.92	5.15	1.86
Cd	-	4.59	2.09

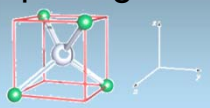
Sizes (cf. lattice energies)

- CFSE's reflected in bond lengths

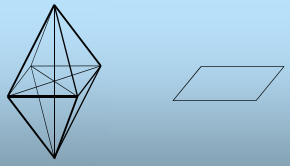


Other frequent geometries

- Tetrahedral



- Tetragonal (elongated or square planar)



21.9

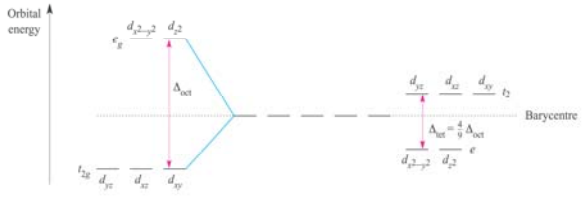


Fig. 21.8 Crystal field splitting diagrams for octahedral (left-hand side) and tetrahedral (right-hand side) fields. The splittings are referred to a common barycentre.

21.11

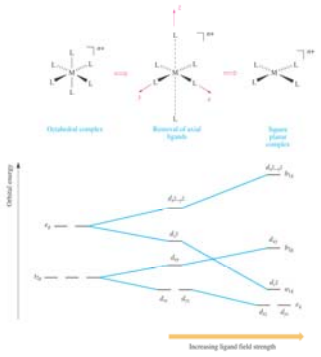


Fig. 21.10 A square planar complex can be derived from an octahedral complex by the removal of two ligands, e.g. those on the z axis; the intermediate stage is analogous to a Jahn–Teller distorted (elongated) octahedral complex.

21.12

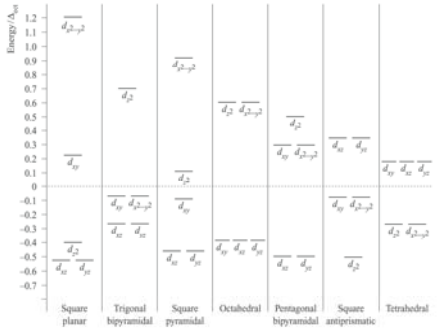


Fig. 21.11 Crystal field splitting diagrams for some common fields referred to a common barycentre; splittings are given with respect to Δ_{oct}

Magnetic behaviour

- An unpaired electron has a magnetic moment, which makes a species (molecule, ion…) paramagnetic by being attracted into a magnetic field.

  $\mu=2\sqrt{(S+1)}S$; $(S=\Sigma s)$ (spin-only)

- Measured as the magnetic susceptibility χ at a given temperature $\mu=k\cdot\sqrt{\chi}\cdot T$

21.28

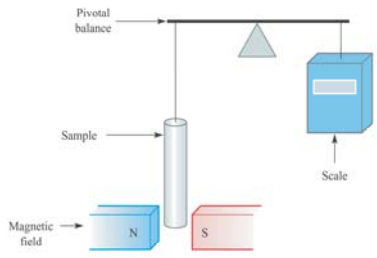
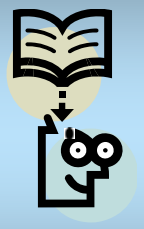


Fig. 21.25 Schematic representation of a Gouy balance.



End of chapter problems

End of chapter Problems

Ligands – structure donoratoms

bonding mode

- en, bipy, phen
- CN^- , CO
- N_3^-
- ox^{2-}
- NCS^-
- $P(Me_3)_3$

Increasing field strenght

Br^-, F^-, CN^-, OH^-, H_2O

End of chapter Problems

Δ_{oct} larger (why)

$Cr(H_2O)_6^{2+}$ or $Cr(H_2O)_6^{3+}$
CrF_6^{3-} or $Cr(NH_3)_6^{3+}$
$Fe(CN)_6^{3-}$ or $Fe(CN)_6^{4-}$
$Ni(H_2O)_6^{2+}$ or $Nien_3^{2+}$
MnF_6^{2-} or ReF_6^{2-}
$Coen_3^{3+}$ or $Rhen_3^{3+}$

Unpaired electrons ?

$Mn(CN)_6^{2-}$	3
$Mn(CN)_6^{4-}$	1
$Cren_3^{2+}$	4
$Feox_3^{3-}$	5
$Pd(CN)_4^{2-}$	0
$CoCl_4^{2-}$	3
$NiBr_4^{2-}$	2

End of chapter Problems

Diamagnetic ?	Structure
• $Co(H_2O)_6^{3+}$	$CoCl_4^{2-}$
• CoF_6^{3-}	
• NiF_6^{2-}	
• $Fe(CN)_6^{3-}$	$CuCl_4^{2-}$
• $Fe(CN)_6^{4-}$	
• $Mn(H_2O)_6^{2+}$	