Octahedral vs. Tetrahedral

ML_6 (O_h)

ML_4 (T_d)

d_{x2-y2} d_{z2}

e_g

Δ_o

t_{2g}

d_{xy} d_{yz} d_{xz}

d_{xy} d_{yz} d_{xz}

t_2

Δ_t

e

Not t_{2g} **and** e_g

d_{x2-y2} d_{z2}
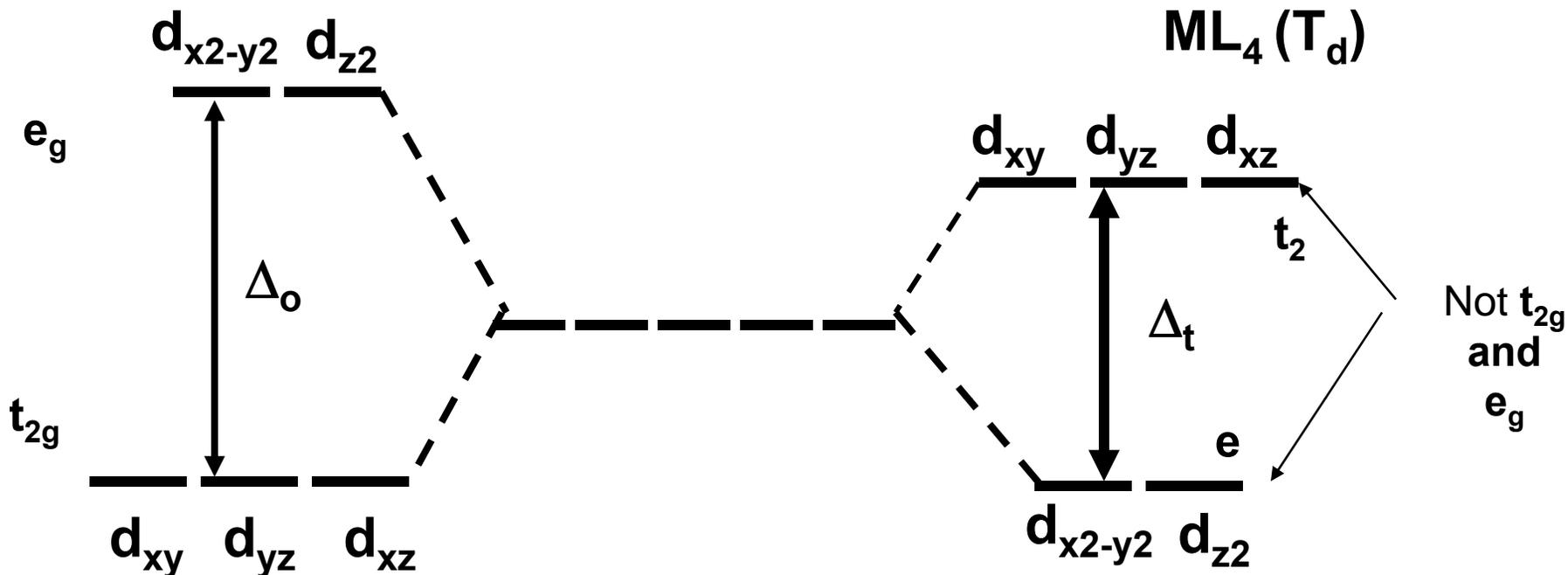
$\left(\begin{array}{c} \Delta_o \text{ is affected by no.} \\ \text{of} \\ \text{ligands} \end{array}\right)$

$\Delta_o \approx$ **4/9** Δ_t

$\left(\text{For same M and L}\right)$

$[Co(NH_3)_6]^{2+}$	O_h	Δ_o = 10200 cm^{-1}
$[Co(NH_3)_6]^{2+}$	T_d	Δ_t = 5900 cm^{-1}

Tetrahedral complexes are mostly high spin, since $\Delta_t < P$

Octahedral Coordination

❖ **6 ligands more stable**
❖ **6 M-L bonds (high Δ_o)**
❖ **Steric hindrance : larger for 6 ligands**

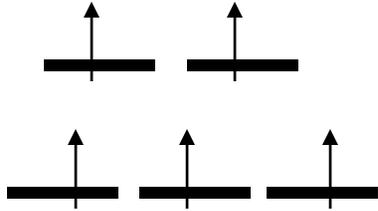**Bulky ligands** $\longrightarrow$ **Tetrahedral Coordination (if CFSE is not large)**

OSSE = E (CFSE of ML_6) – E (CFSE of ML_4)

OSSE : octahedral site stabilization energy

❑ **d^1. d^2, d^5, d^6, d^7 OSSE is small : steric factors become important**

❑ **d^3, d^8 : octahedral coordination is preferred (large CFSE, large OSSE)**

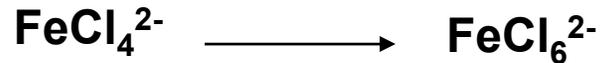**High charge (M^{n+}) favours octahedral coordination due to large Δ_o**

Case of Mn^{2+}(d^5)

$\uparrow$ $\uparrow$

$\uparrow$ $\uparrow$ $\uparrow$

CFSE = 0

With bulky ligands (e.g. Cl$^-$) MnCl$_4^{2-}$ (tetrahedral)

Case of Fe^{2+}(d^6)

FeCl$_4^{2-}$ $\longrightarrow$ FeCl$_6^{2-}$

Compare Mn^{2+}/ Fe^{2+} $\longrightarrow$ (CFSE ≠ 0)

Co^{2+} (d^7)   H.S. octahedral or
                 Tetrahedral [CoCl$_4$]$^{2-}$

Co^{3+} (d^6)   H.S. with F- [CoF$_6$]$^{3-}$
                 Low spin [Co(NH$_3$)$_6$]$^{3+}$

Site (Octahedral or Tetrahedral) preference in spinels

AB_2O_4

A (II) Mg^{2+} Zn^{2+} Fe^{2+} Ni^{2+}

B (III) Fe^{3+} Al^{3+} Mn^{3+}

AO_4 ⎤
BO_6 ⎦ Normal spinel

BO_4 ⎤
$A\backslash BO_6$ ⎦ Inverse spinel

AFe_2O_4 (Inverse spinel) ⟹ $Fe^{3+}(d^6)$, CFSE = 0

$NiFe_2O_4$ No preference (Fe^{3+}) for octahedral site

Ni^{2+}: OSSE = 86 kJ mol^{-1}

$(Fe)_{tet}\backslash (Ni\backslash Fe)_{oct}O_4$

Fe_3O_4 $Fe^{II}Fe_2^{III}O_4$ Inverse
Mn_3O_4 $Mn^{II}Mn_2^{III}O_4$ Normal
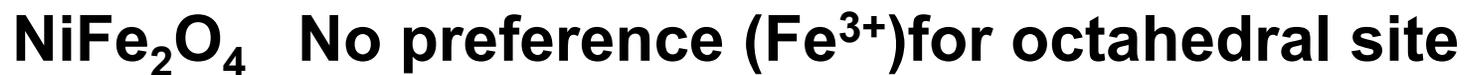
Evidence for crystal Field Stabilization

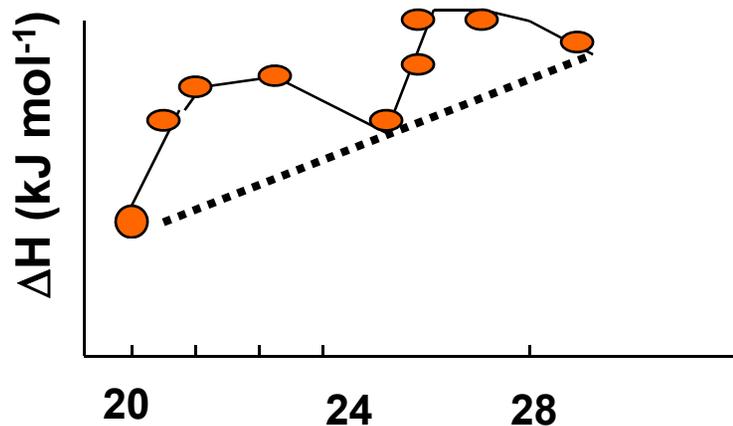❖ **Ability to predict magnetic and spectral (colour) properties.**
❖ **Correlation of the magnitude of 10Dq from spectral data.**
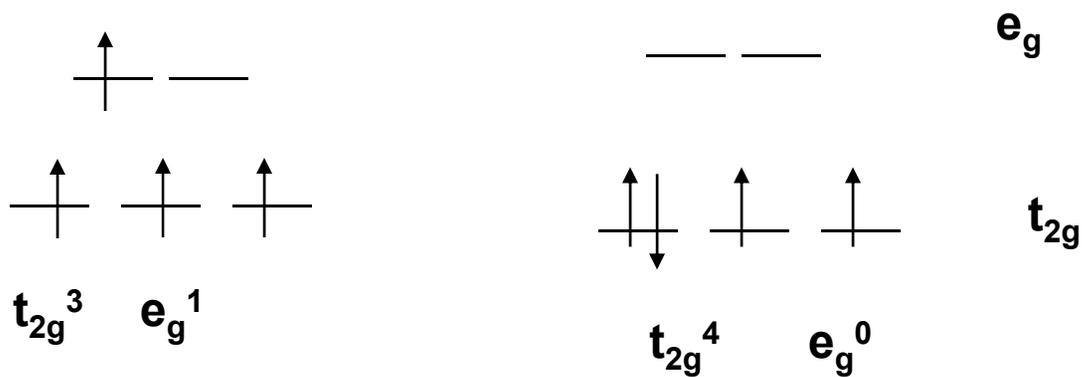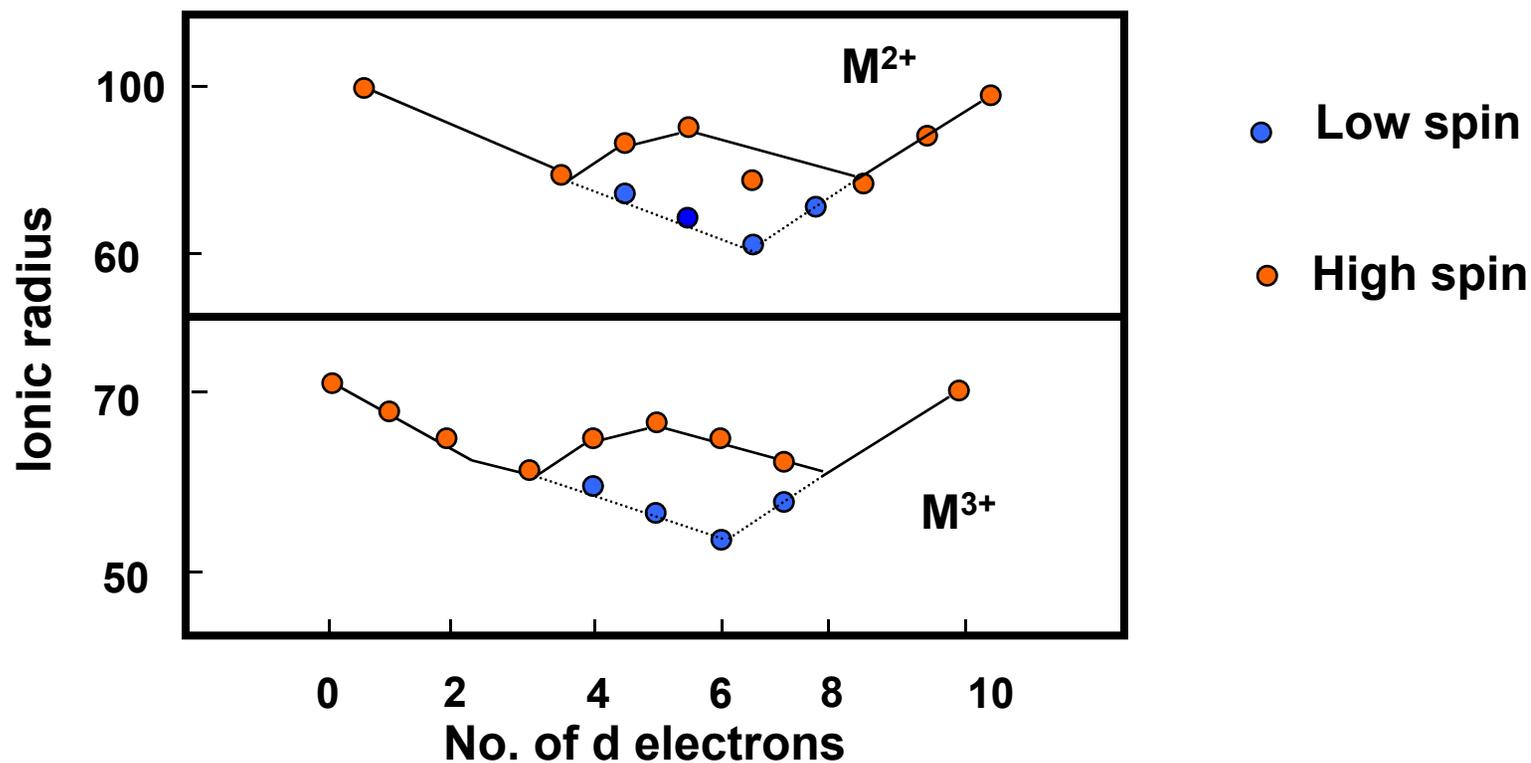❖ **Prediction of lattice energy.**

Born Lande Eqn.

$U_o \propto 1/r_o$ where, r_o is the radius of the ion

$$U_o = \frac{A \, N \, z^+z^- \, e^2}{4\pi \, \varepsilon_o r_o} \, (1-1/n)$$

❖ **Hydration energies**
(extrapolated to inf. dilution) $[M(H_2O)_6]^{2+}$

ΔH (kJ mol^{-1})

20   24   28

$-U$ (kJ mol^{-1})

M^{II} fluorides

M^{II} chlorides

20   23   26   29
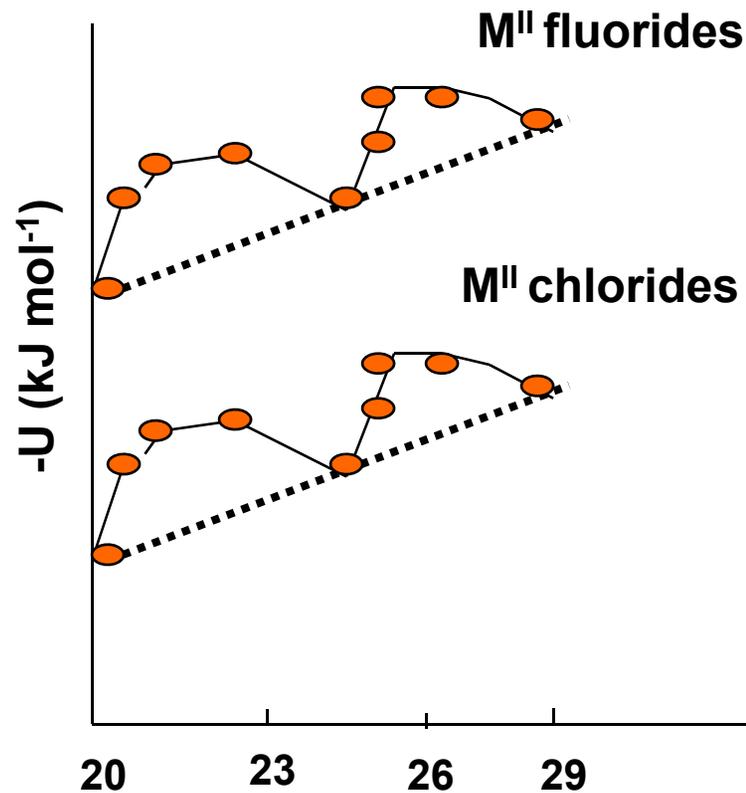
❖ **Ionic radii of 3d elements.**

Distortions of an ideal octahedron
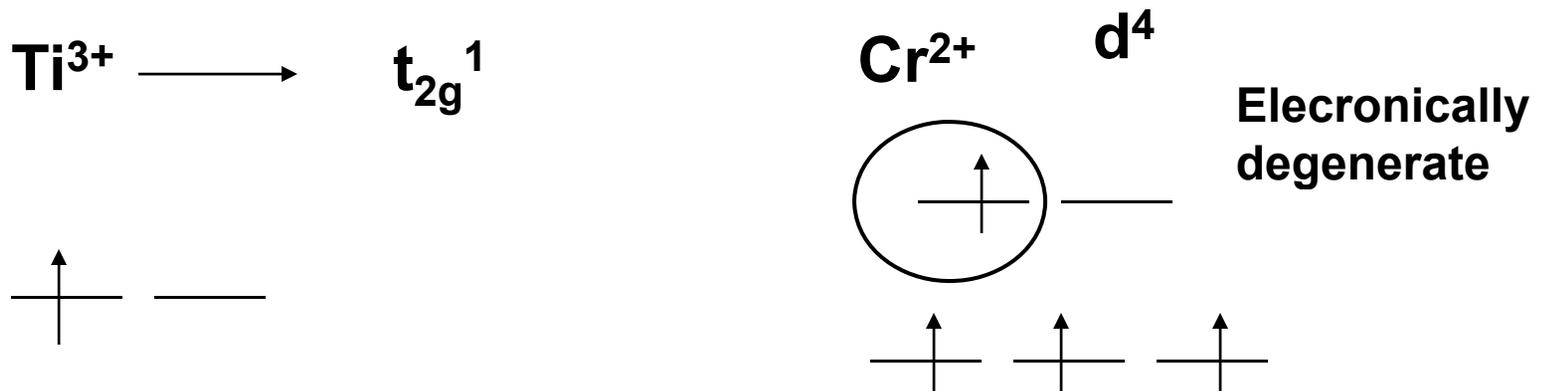

Tetragonal

Jahn - Teller / Tetragonal distortion
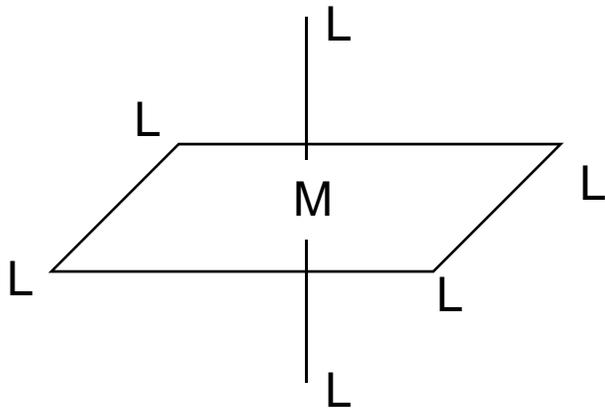
Rhombic

Trigonal
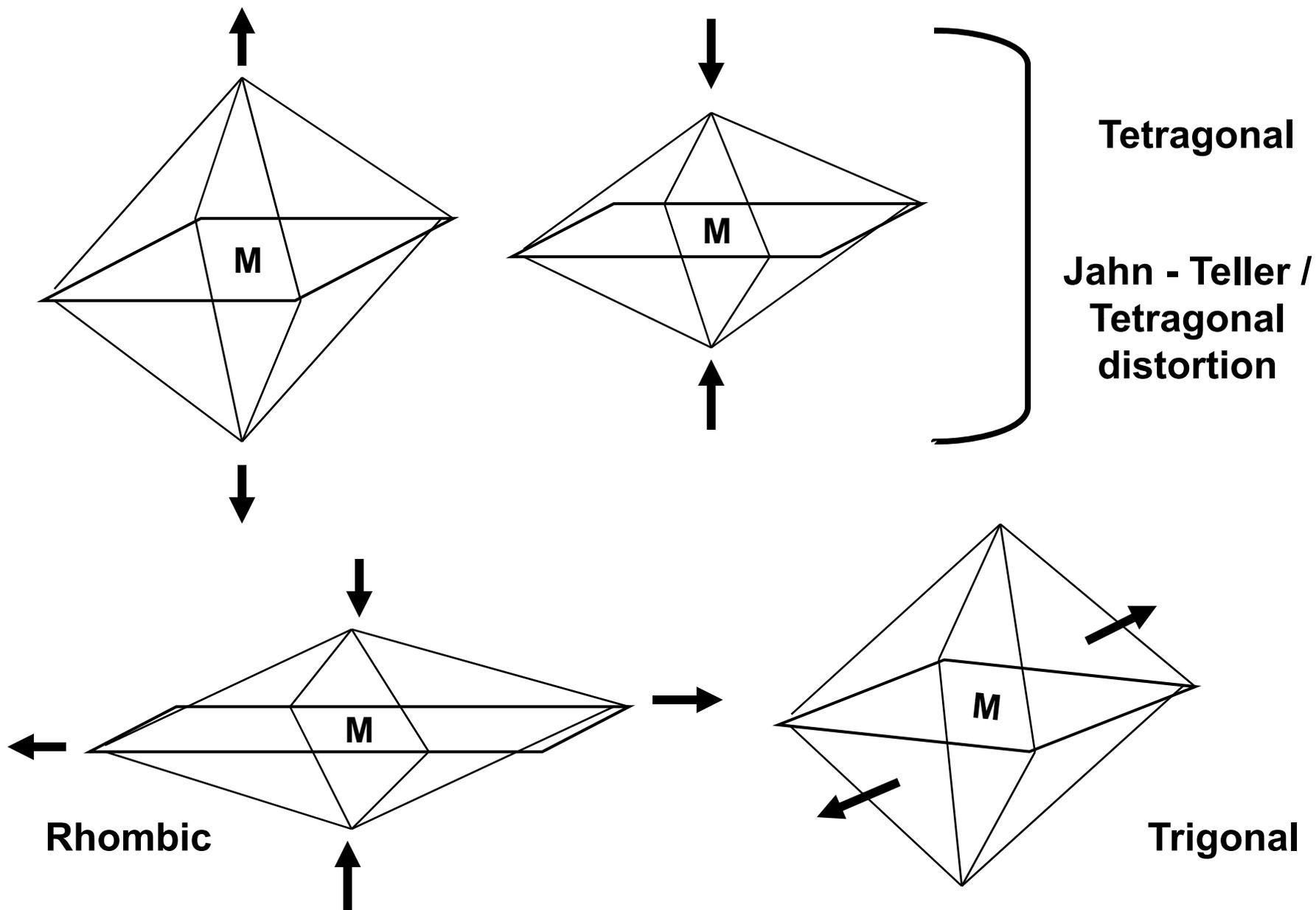
Jahn Teller Effect

For a non-linear molecule in an electromagnetically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy and lower the energy.
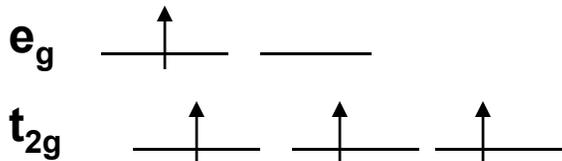
$Ti^{3+} \longrightarrow t_{2g}^{1}$

Cr^{2+} $\quad d^4$

Elecronically degenerate

Bond length in tetragonal distorted complexes

4 (M - L) bond lengths are long

2 (M -L) bond lengths are shorter

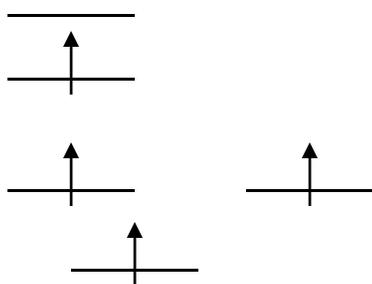[CrF_2 , MnF_3 etc.] Connected octahedras

Cr $^{2+}$ (d^4) – t$_{2g}^3$ eg^1 (F$^-$ is a weak field ligand)

Electronically degenerate
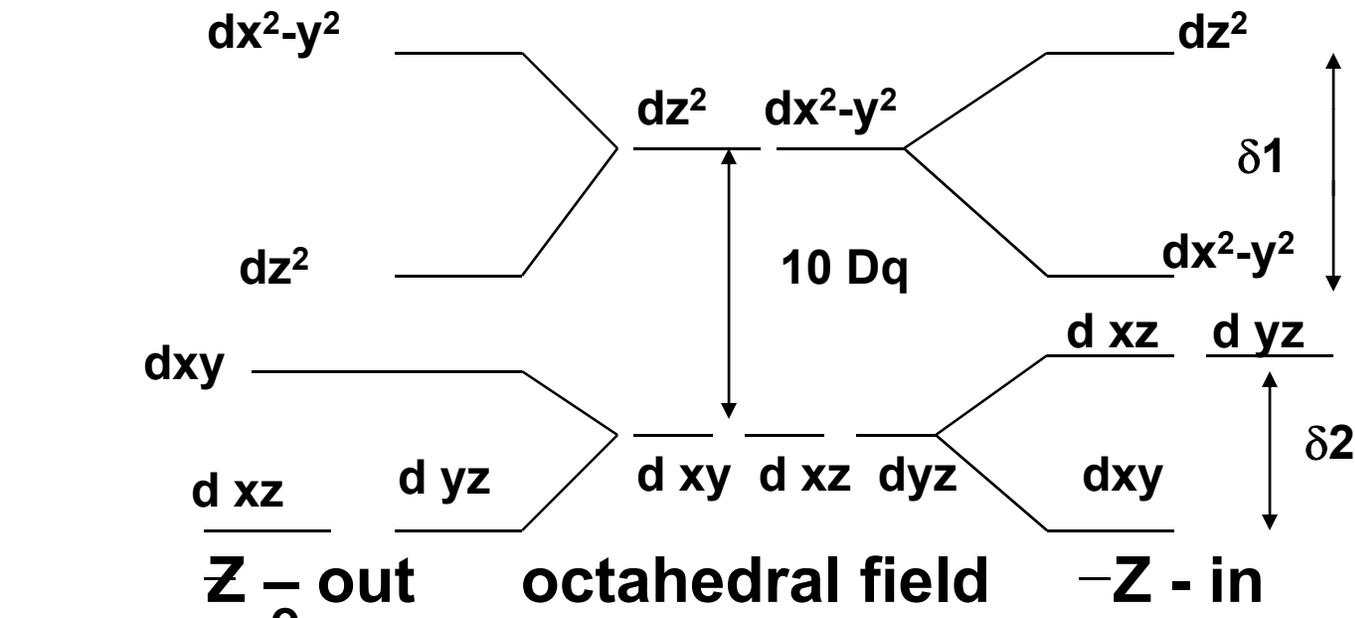
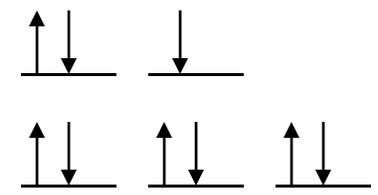Distort (J. T. effect)

Dynamic J.T. Effect

Lower temperature

To observe distortion

Large J.T. distortion
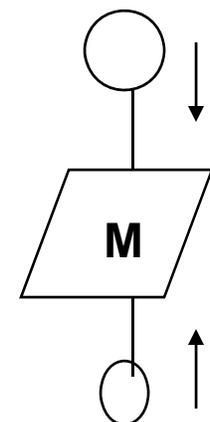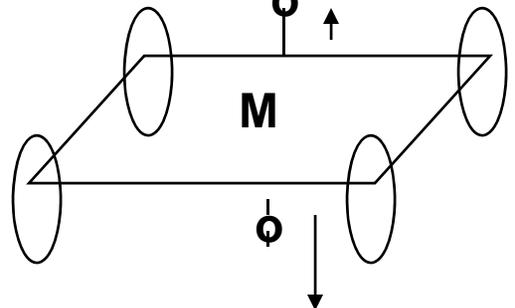
d^4 (Cr^{2+}) d^9 (Cu^{2+})   (Weak Field)

d^7 (Co^{2+}) and d^9 (Cu $^{2+}$)   (Strong field)

Partially / unequal filled orbitals eg. dx^2-y^2, dz^2

dx^2-y^2 dz^2

dz^2 dx^2-y^2 dz^2

δ1

dz^2 10 Dq   dx^2-y^2

δ1 > δ2

d xz   d yz

dxy   d xy d xz dyz   dxy

δ2

d xz   d yz

Z – out   octahedral field $^-$Z - in

M

M

Why Au(II) is unstable?

Cu²⁺ (d⁹) – Stable

Au²⁺ (d⁹) - Unstable

Octahedral Field

Tetragonal dist.

Cu⁺²

Δ_O **increases**

Cu

Ag

Au

VERY HIGH ENERGY

Au⁺²

Δ_O **: V. HIGH**

(d⁹)

Au ³⁺ (d⁸)

$2Au^{2+} \longrightarrow Au^{3+} + Au^{+}$
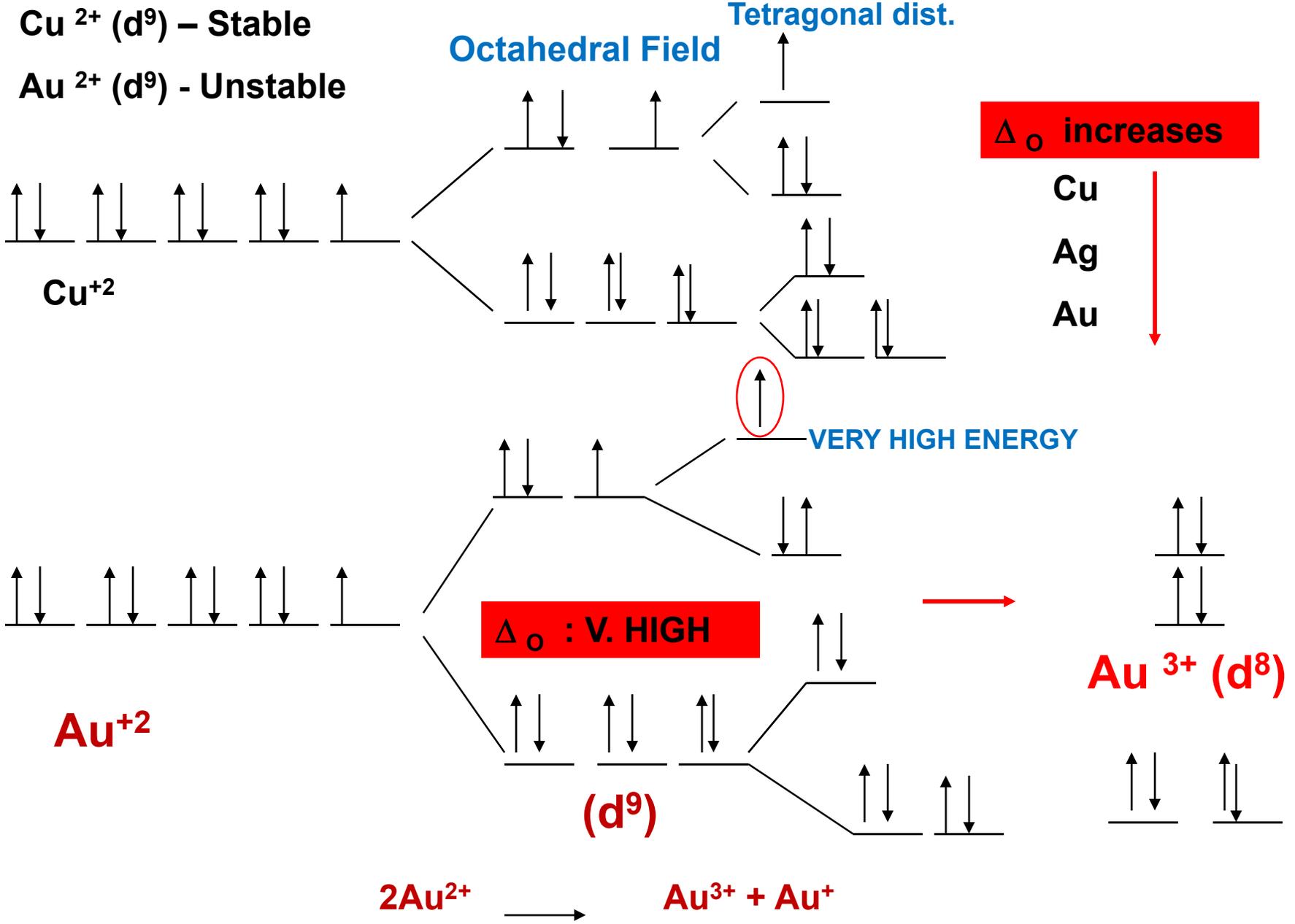
Jahn Teller effect in chelate complexes
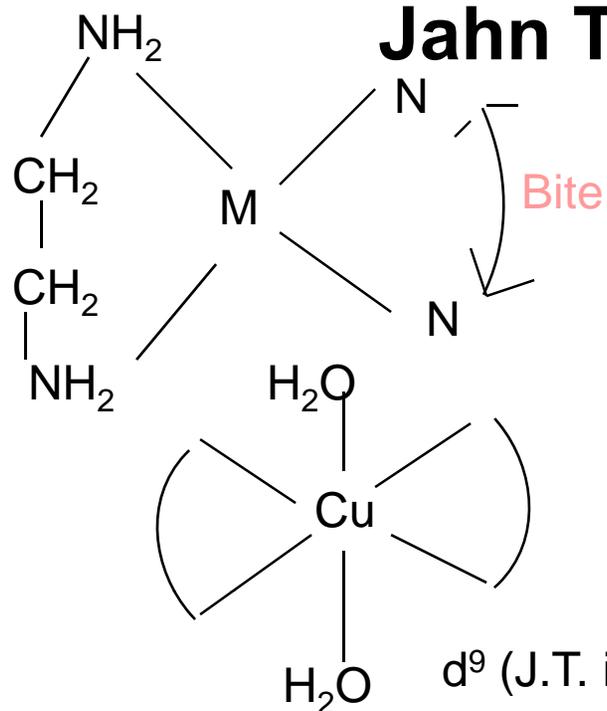
Chelates have preferred distances

Resist distortion

$[M(H_2O)_6]^{2+}$ + en $\xrightarrow{k1}$ $[M(H_2O)_4en]^{2+}$

$[M(H_2O)_4en]^{2+}$ + en $\xrightarrow{k2}$ $[M(H_2O)_2(en)_2]^{2+}$

$[M(H_2O)_2(en)_2]^{2+}$ + en $\xrightarrow{k3}$ $[M(en)_3]^{2+}$
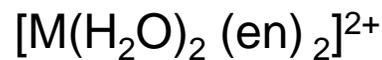
Cu + en $\longrightarrow$ Unstable

d^9 (J.T. ion)

Large ⟶   ⟵ Strain
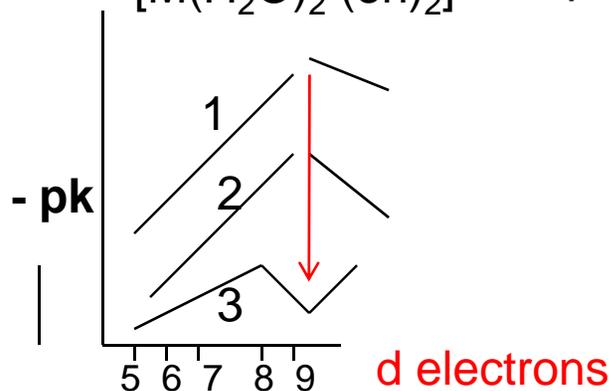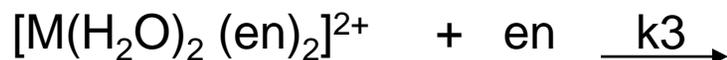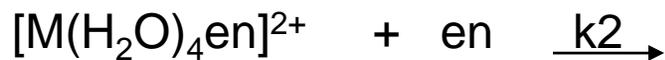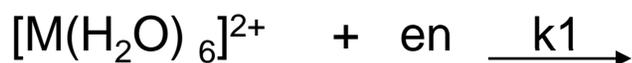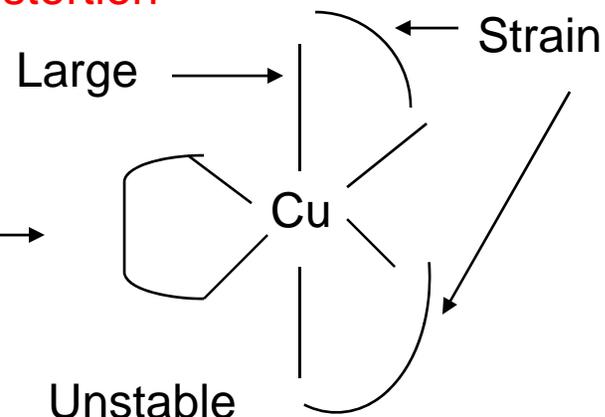
d5 – d9   k1, k2   increases

Irving – Williams series

- pk

d electrons

Crystal Field Splitting in square - planar Coordination

$d_{x^2-y^2}$ becomes very high in energy

Only four orbitals available (d^8 – ideal case)

Oct. field

Tetragonal distortion

Square planar

$[Ni(CN)_4]^{4-}$ $[PdCl_4]^{2-}$ $[PtCl_4]^{2-}$ $[Pt(NH_3)_4]^{2+}$

COLOUR OF COMPLEXES

$[Co(H_2O)_6]^{2+}$ **Why is it pink?**

$[CoCl_4]^{2-}$ **Why is it blue?**

$[Ni(H_2O)_6]^{2+}$ $\xrightarrow{\quad NH_3 \quad}$ $[Ni(NH_3)_6]^{2+}$

$[Cr(H_2O)_6]^{3+}$ $\xrightarrow{\quad e^- \quad}$ $[Cr(H_2O)_6]^{2+}$
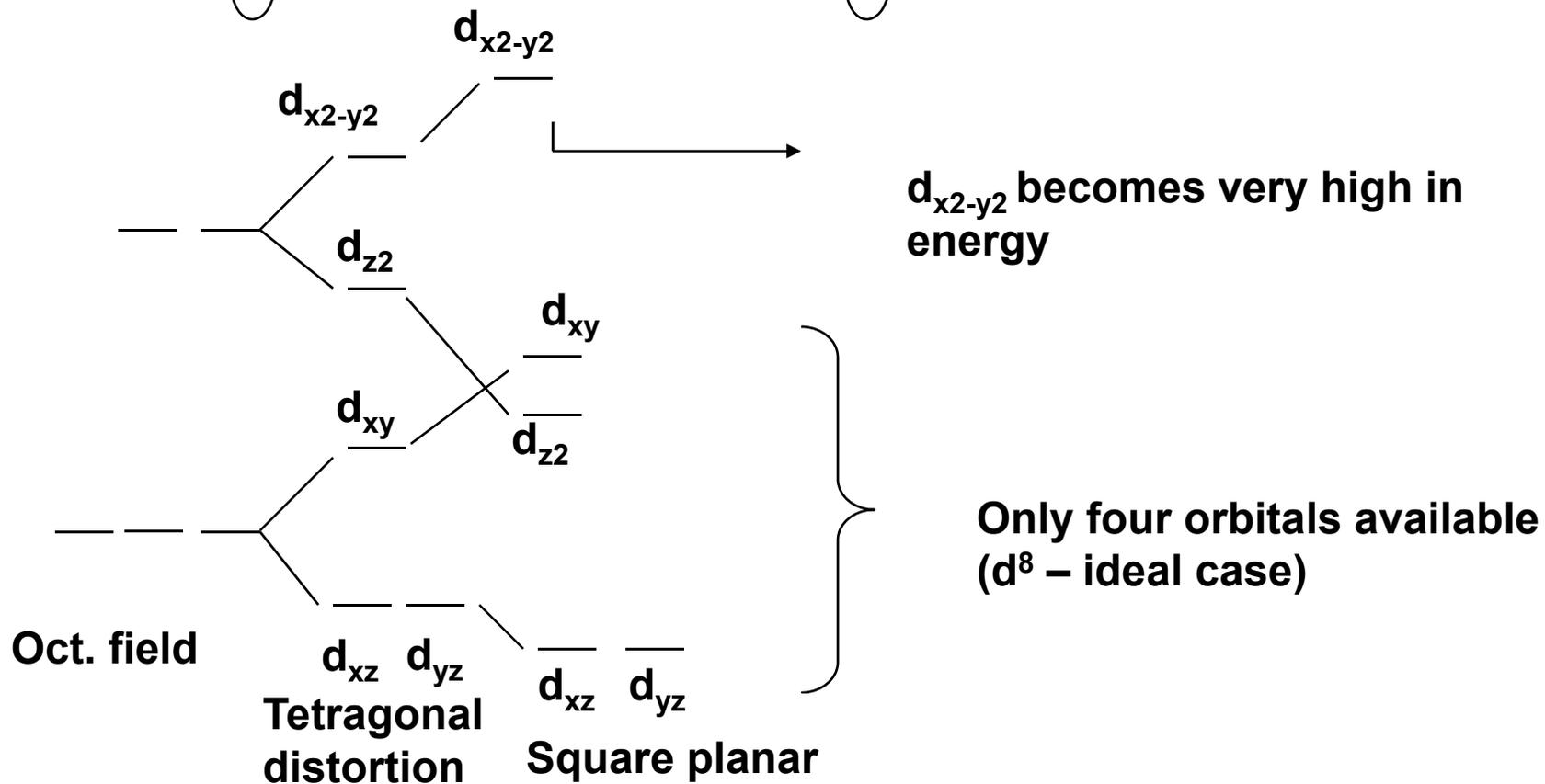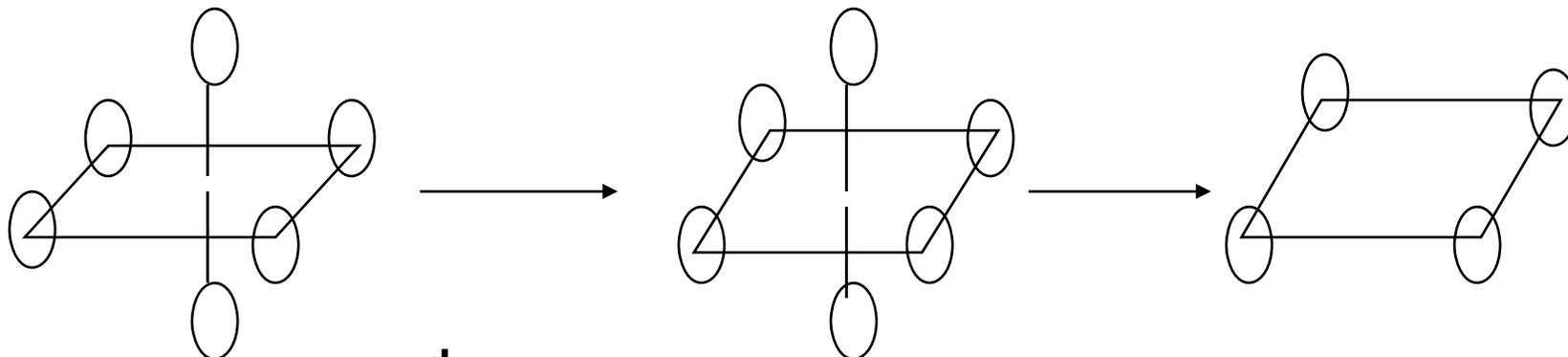
Electronic Transition

$h\nu$ (visible region)
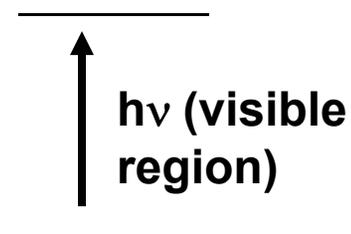
Observed color of molecule	Color of light absorbed	Wavelength of light absorbed in nm (approx.)
Green	Purple	680-780 nm
Blue-Green	Red	620-680 nm
Blue	Orange	580-620 nm
Violet	Yellow	520-580 nm
Purple	Green	500-520 nm
Red	Blue-green	470-500 nm
Orange	Blue	440-470 nm
Yellow	Violet-blue	420-440 nm
Green-yellow	Violet	380-420 nm
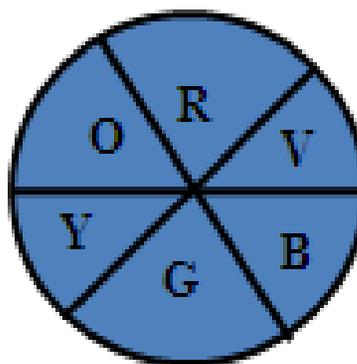
Colour of Complexes
Electronic / optical spectra

Radiation

Visible

Solution of complexes

Radiation (without the absorbed frequency)

Eye (complementary Colour)

Detector

14000 cm^{-1} (red) – 25000 cm^{-1} (violet) – 50000 cm^{-1} (UV)
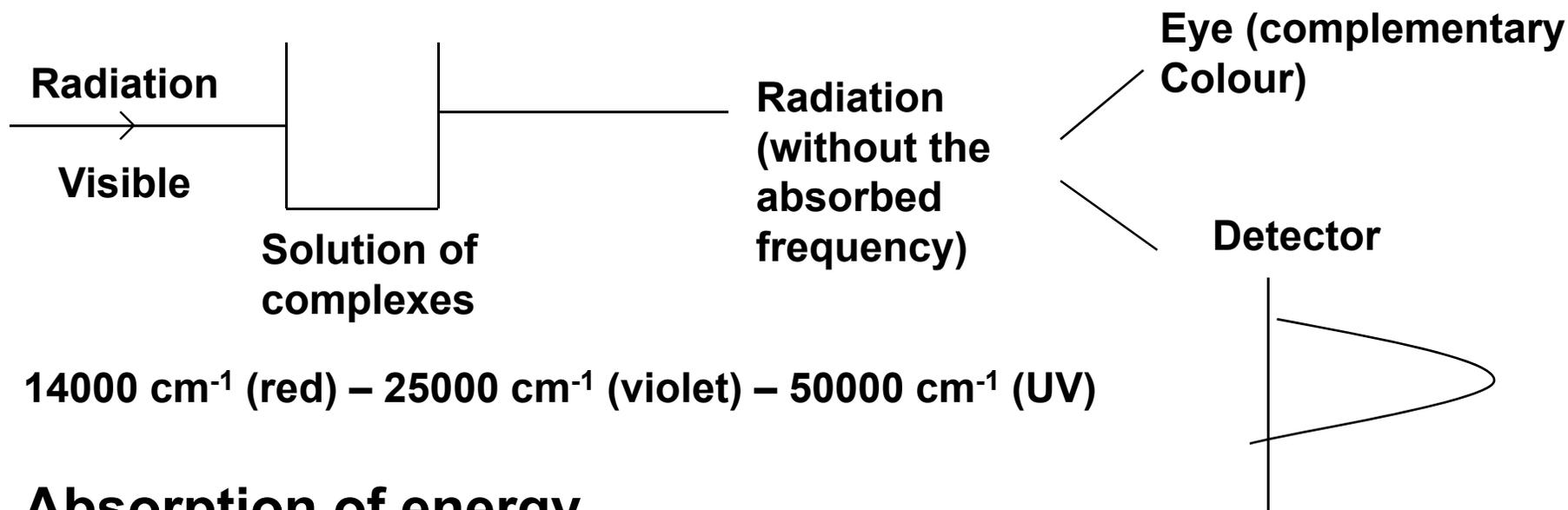
Absorption of energy

1. d-d Transitions

$\Delta o = h\nu$

e_g

t_{2g}

$t_{2g} \longrightarrow e_g$
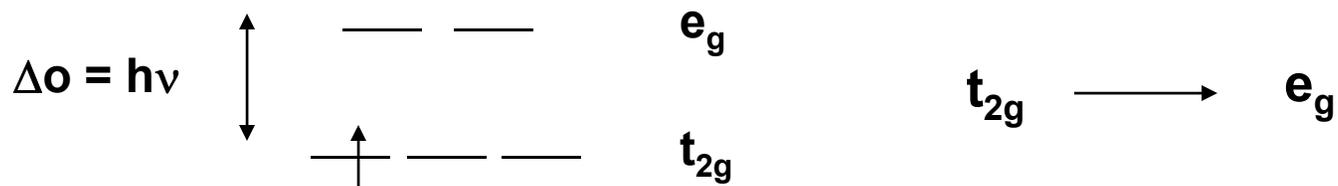
Selection rules for intensity of transition

2. Charge-Transfer Spectra

Metal ⟶ ligand   or   Ligand ⟶ Metal
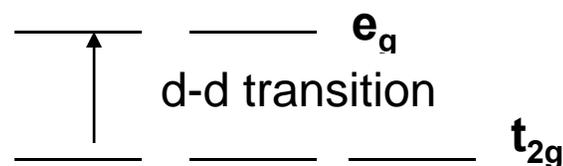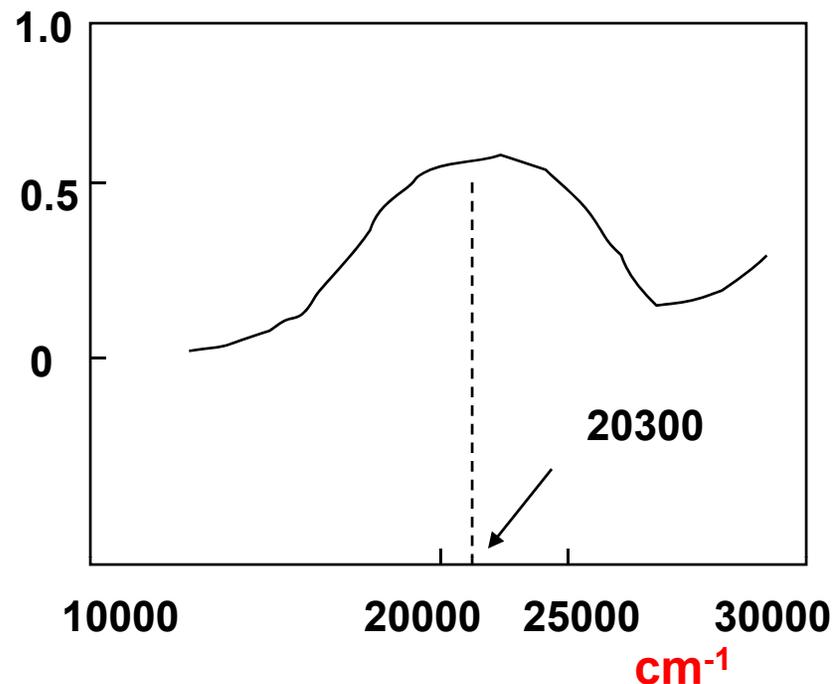
No selection rules / Intense

$$\left[Ti(H_2O)_6 \right]^{3+} \qquad (d^1)$$
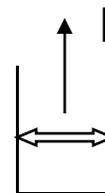
Colour absorbed = Green

Colour observed = purple / violet   (Complementary to green)

Intensity of absorption

$A = -\log I / Io = \epsilon c\, l$,   Where ϵ = Molar extinction coeff.

Beer – lambert's law   c = Molar conc.   l = path length

- 1.0
- 0.5
- 0
- 20300
- 10000 20000 25000 30000
- cm^{-1}

e_g

d-d transition

t_{2g}

Selection rules for d-d transition

d-d transition are allowed if :

ΔS = 0   (Spin multiplicity rule)

Ground state   Excited state S = 1/2   Δ S = 0

                                                    Spin allowed transition

S= 1/2

$S = 0$ $S = 1$ Δ S≠ 0

                                Spin forbidden

2   Δ l = ± 1   l = Orbital quantum number   For d orbital   l = 2

Laporte rule

d → d transition   Δ l = 0   Therefore Laporte forbidden in octahedral field

d → f

l = 2   l = 3   l = 1   (allowed)
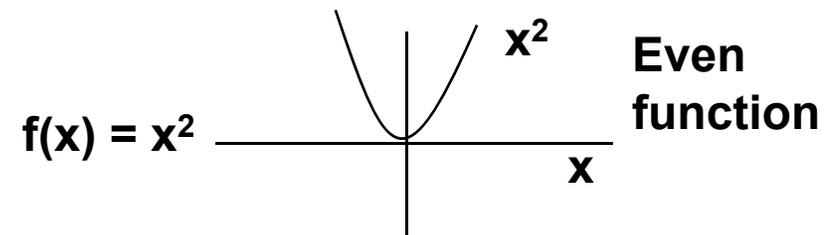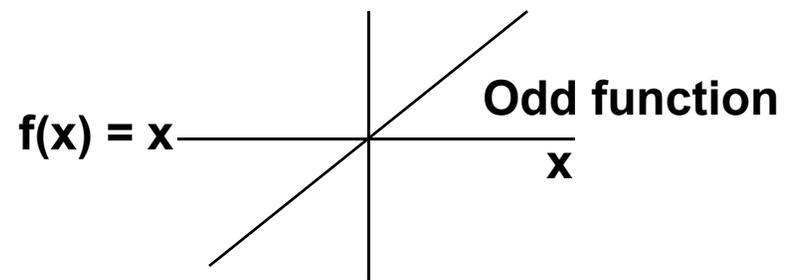
Origin   ∫ Ψ1ûΨ2 dτ ≠ 0

Transition probability is directly proportional to $\int \Psi_1 \, \mu \Psi_2 \, dT$

Ψ_1 = Wave function of ground state

Ψ_2 = Wave function of excited state

$\hat{U}$ = Electric dipole moment operator

$\hat{U}$ = e.x , where x = displacement

f(x) = x ———— Odd function / x

f(x) = x² ———— x² Even function / x

Therefore $\hat{U}$ is an odd function

$\int \Psi_1 \, \hat{u} \Psi_2 \, dT \neq 0$ If $\Psi_1 * \hat{u} * \Psi_2$ is g (symmetric to inversion)

i.e. if ψ_1 is a d-orbital and if d $\rightarrow$ d then ψ_1 is g and ψ_2 is g

then g * u * g is u (antisymmetric)

$\int \Psi_1 \, \hat{u} \Psi_2 \, dT = 0$: forbidden transition

Tetrahedral complexes are normally bright in colour

There is no center of symmetry and Laporte rule does not hold good for d-d transition.

Type of electronic transition (d-d)	Є (l mol-1 mm-1)
Spin forbidden, Laporte Forbidden	0.01
Spin allowed , Laporte Forbidden	1.00
Spin allowed , Laporte Forbidden with d-p mixing	10.0
Spin allowed , Laporte allowed	1000

For Charge transfer spectra there is no selection rules Ligand $\xrightarrow{e-}$ Metal

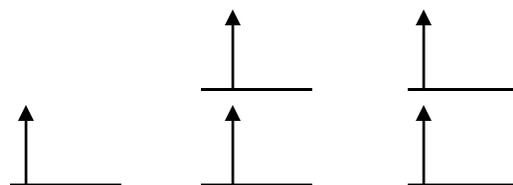Bright coloured solutions contain eg. MnO_4^- , CrO_4^{2-} etc..

Breakdown of selection rules

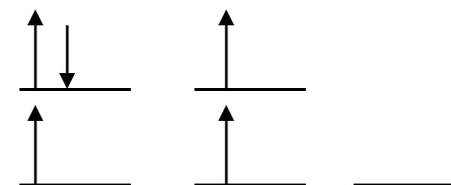1) **SPIN MULTIPLICITY RULE ($\Delta S = 0$)**

   a) **Spin orbit compling (l-s)**

   b) **Mixing of states**

     Mn^{2+} (d^5)

Ground state

S = 5/2

Excited stae

S = 3/2

     $\Delta S \neq 0$

But Mn^{2+} complexes are pink in colour and weak (Due to mixing of G. state with excited states)

2) **LAPORTE RULE ($\Delta l = \pm 1$)**

   a) **Mixing of orbitals d-p , d-f**

   b) **Vibronic coupling removes the centre of symmetry by an asymmetrical vibration**

Charge – Transfer spectra

LMCT / MLCT

LMCT → Ligand to metal charge transfer

Metal with empty orbitals at relatively low energy (Transition metals with highoxidising state)

Ligands are non metals with low electron affinity (S^{2-}, Se^{2-} or heavier halides)
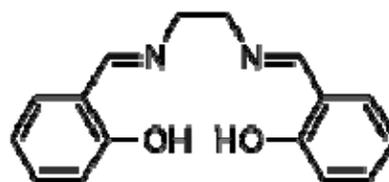
MnO_4^- (Mn^{+7})   Purple

$CrO_4^{\ 2-}$ (Cr^{+6})   Yellow

HgI_2 (Red)

PbI_2 (Yellow)

MLCT → Ligands with empty π* orbitals examples CO, py, bpy , phen etc.

|	Complex	Colour	λ
1.	$[Cr(H_2O)_6]^{2+}$	Greenish-blue	
2.	$[Mn(H_2O)_6]^{2+}$	Pale pink/nearly colourless	
3.	$[FeCl_4]^-$	Yellow bright	
4.	$Co(H_2O)]^{2+}$	pink	
5.	$[Ni(H_2O)_6]^{2+}$	Green	
6.	$[Ni(NH_3)_6]^{2+}$	Blue	
7.	$[Cu(H_2O)_6]^{2+}$	Blue	
8.	Mn(salen)	brown	
9.	$K_2Cr_2O_7$	orange	
10.	$KMnO_4$	purple	

Salen : tetradentate ligand

Magnetic properties of complexes

Diamagnetism   **(Paired electrons)**

Paramagnetism   **(Unpaired electrons)**   **(attracted towards a magnetic field)**
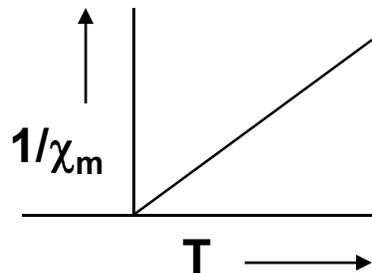

Magenitic field   **Align**

Temperature   **Ho**

Random
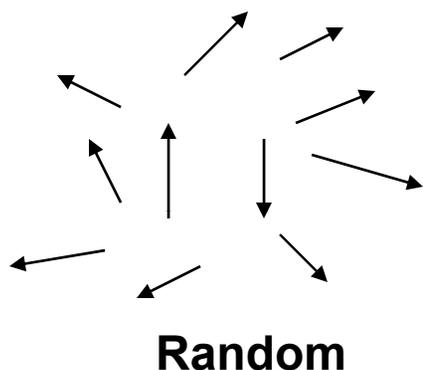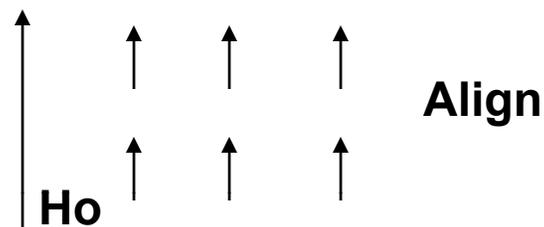
$$\chi = I / Ho$$

Magnetic moment   **(Spin only)** $= 2\sqrt{S(S+1)} = \sqrt{n(n+2)}$

S = Total Spin   **n = Number of unpaired electrons**

Curie law $\rightarrow \chi_M = C/T = N^2\mu^2/ 3RT$, **Where** χ_M **= Molar Susceptibility**

$1/\chi_m$

Slope = 1/C = 3R/N²µ²   **⌈Dilute Spins⌉**

No interaction between spins

T $\longrightarrow$

Failures of C.F. theory

1)   Absence of metal- ligand orbital overlap – strictly ionic complexes

2)   Intensities of forbidden d-d transitions not fully explained without taking metal ligand overlap.

3)   Nephelauxetic effect (Cloud - expanding). It is due to ligand influence in expanding the d electron clouds which is not explained.

4)   Evidence for superexchange (Spin) interaction M-O-M exist Ferromagnetism, Antiferromagnetism are not explained by CFT.
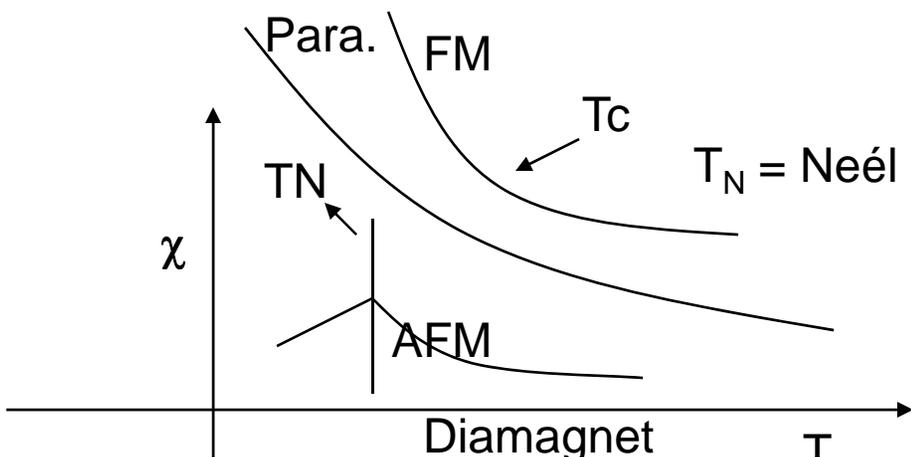
μ

μ

1

100   200   300

T (k) ⟶
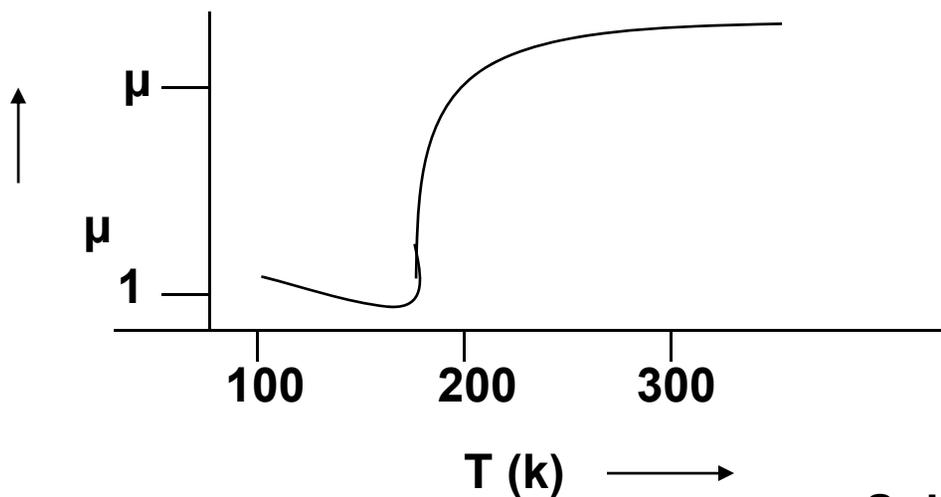
Fe (phen)$_2$ (NCS)$_2$

d^6 (H.S → L,S)   ~ 185°C

Spin Crossover

Solids

Spin – Spin interaction

(Exchange)

Antiferromagenitism

Ferromagnetism

Para. FM

Tc

T$_N$ = Neél

TN

χ

1/χ

AFM

χ$_m$ = C / T-θ

Diamagnet   T

T