

Tetragonal Distortion of Octahedral Complexes

The shapes of the transition metal complexes are affected by whether the d -orbitals are symmetrically or asymmetrically filled

Symmetrical electronic configuration: d^0 , d^3 , d^5 (weak field),
 d^6 (strong field), d^8 , d^{10} .

d -electrons repel electrons of ligands equally






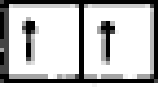






Asymmetrical electronic configuration: d^4 , d^7 (strong field),
 d^9 (in weak and strong field)

d -electrons repel electrons of ligands unequally and the structure gets **distorted**

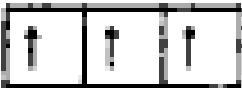





The effect is more for e_g orbitals (as they are directly facing ligands) than t_{2g} orbitals.

The distortion caused by asymmetric t_{2g} orbitals is usually small.

Symmetrical electronic arrangement

Electronic configuration	t_{2g}	e_g	Nature of ligand field	Examples
d^0			Strong or weak	$\text{Ti}^{\text{IV}}\text{O}_2$, $[\text{Ti}^{\text{IV}}\text{F}_6]^{2-}$ $[\text{Ti}^{\text{IV}}\text{Cl}_6]^{2-}$
d^3			Strong or weak	$[\text{Cr}^{\text{III}}(\text{oxalate})_3]^{3-}$ $[\text{Cr}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}$
d^5			Weak	$[\text{Mn}^{\text{II}}\text{F}_6]^{4-}$ $[\text{Fe}^{\text{III}}\text{F}_6]^{3-}$
d^6			Strong	$[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$
d^8			Weak	$[\text{Ni}^{\text{II}}\text{F}_6]^{4-}$ $[\text{Ni}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$
d^{10}			Strong or weak	$[\text{Zn}^{\text{II}}(\text{NH}_3)_6]^{2+}$ $[\text{Zn}^{\text{II}}(\text{H}_2\text{O})_6]^{2+}$

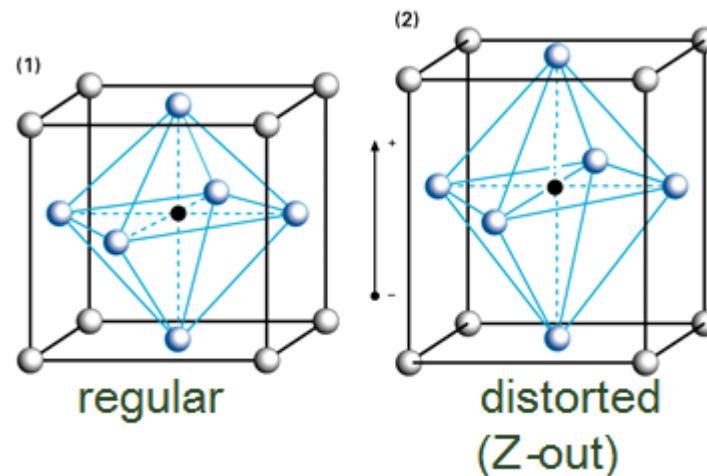
Asymmetrical electronic arrangement

Electronic configuration	t_{2g}	e_g	Nature of ligand field	Examples
d^3			Weak field (high-spin complex)	Cr(+II), Mn(+II)
d^7			Strong field (low-spin complex)	Co(+II), Ni(+II)
d^9			Either strong or weak	Cu(+II)

Tetragonal Distortion *contd...*

e_g orbitals if asymmetrically filled no longer remain degenerate

If d_{z^2} is filled, **two** ligands feel greater repulsion than the other four ligands. As a result these two bonds get elongated causing **tetragonal distortion** (Z-out)

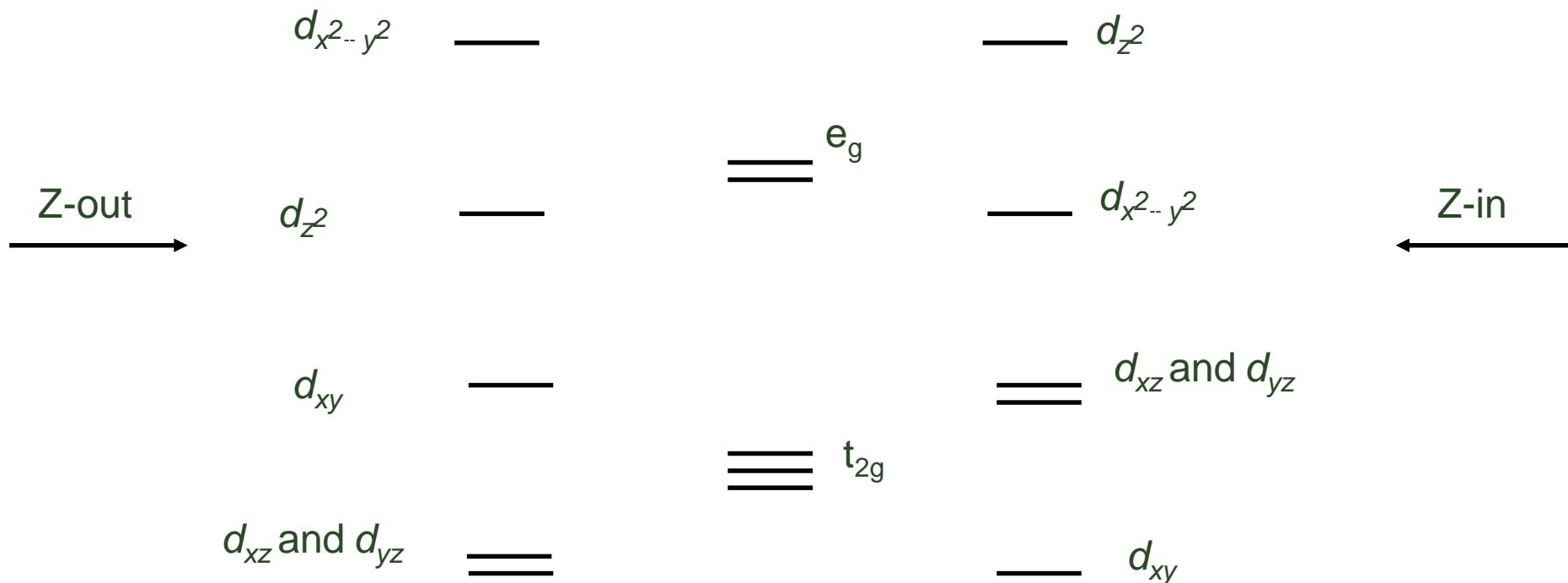


If $d_{x^2-y^2}$ is filled, **four** ligands feel greater repulsion than the other two ligands. As a result these four bonds get elongated and two bonds get shortened causing **Z-in distortion**; less stable condition and such cases are rare

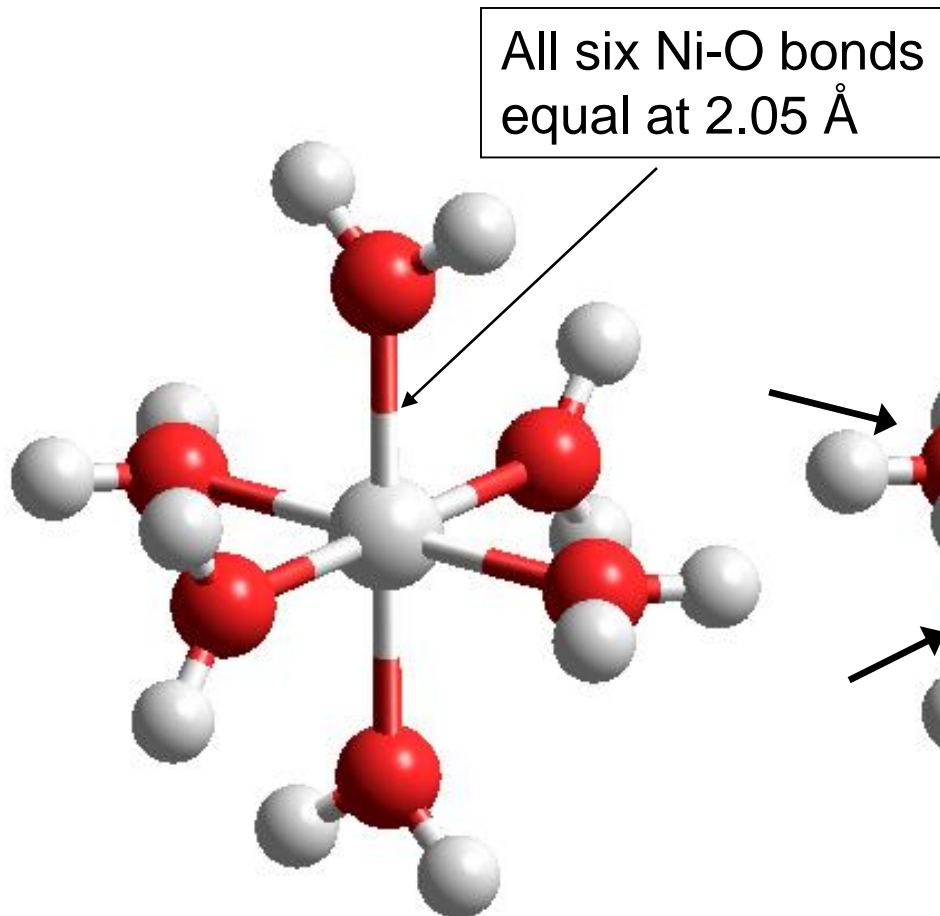
Jahn-Teller Theorem

Hermann Arther Jahn and Edward Teller stated that for a nonlinear molecule in an electronically degenerate ground state distortion must occur to lower the symmetry, remove degeneracy and lower energy– known as **Jahn-Teller Theorem**

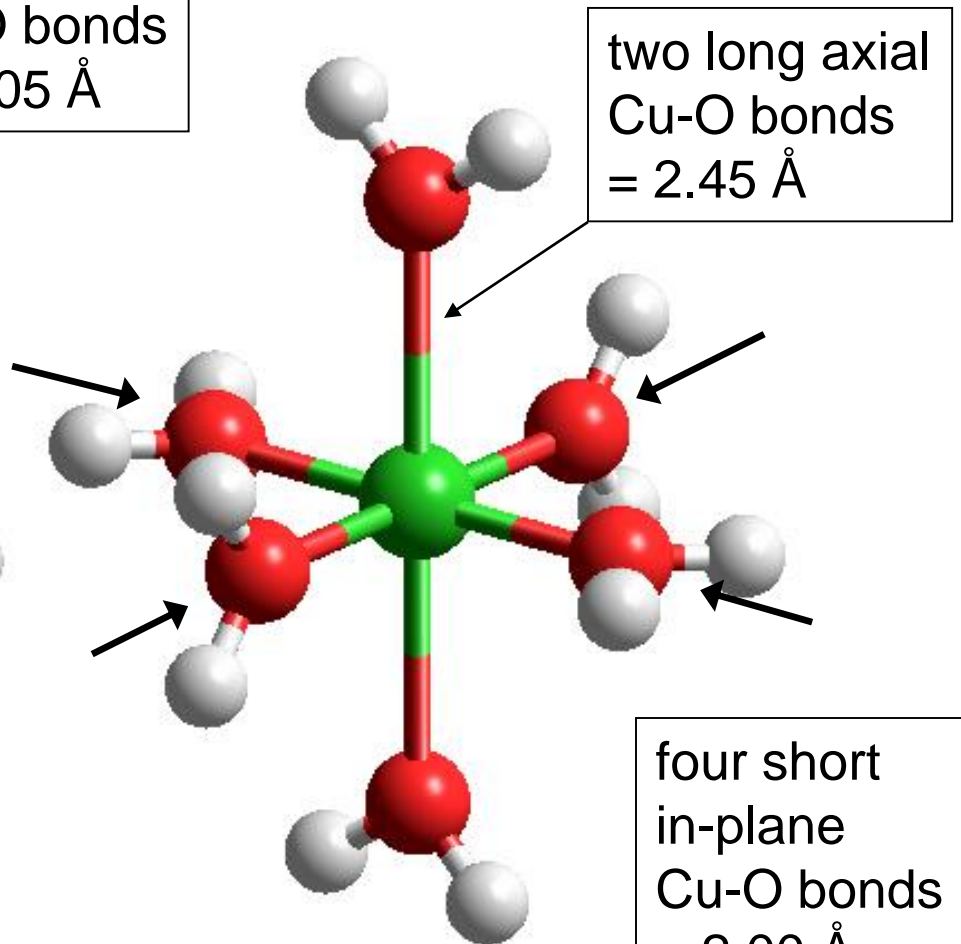
Octahedral Energy Level Diagram in a Tetragonal Field



Structural effects of Jahn-Teller distortion



$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
no J-T distortion



$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$
J-T distortion lengthens axial Cu-O

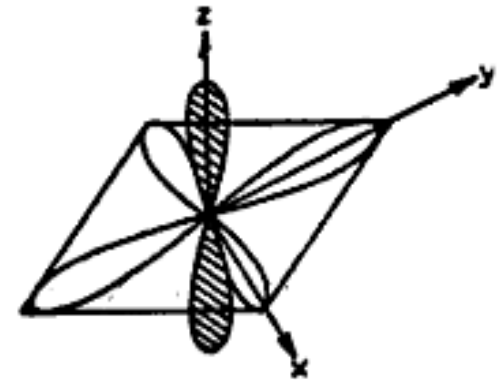
four short in-plane Cu-O bonds = 2.00 Å

Square planar complexes

d^8 configuration ($t_{2g}^6 e_g^2$) - the arrangement is symmetrical
BUT this is applicable **only for weak field cases** e.g. $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Ni}(\text{NH}_3)_6]^{2+}$

In strong field: An electron in $d_{x^2-y^2}$ gets repelled by four ligands
whereas an electron in d_{z^2} gets repelled by only two ligands
Thus e_g orbitals do not remain degenerate (Jahn-Teller distortion)

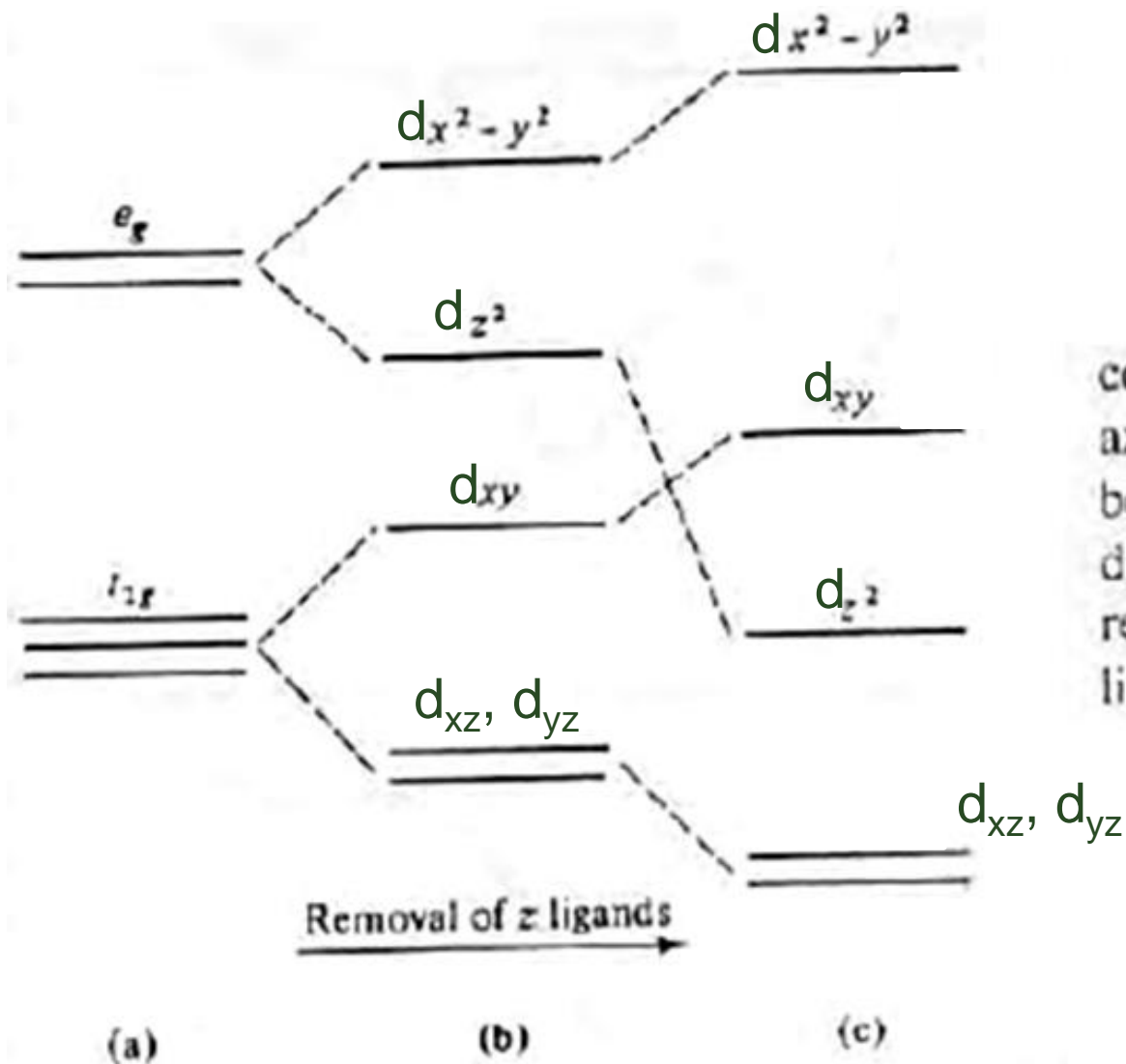
When the splitting of d_{z^2} and $d_{x^2-y^2}$ is more than the pairing energy of electrons, two electrons occupy d_{z^2} orbital and the $d_{x^2-y^2}$ will be empty.



The ligands along z-axis will experience more repulsion by two electrons.

These two ligands will not come to bonding distance with the metal — **leading to square planar complex**

Square planar arrangement



An octahedral complex (a) undergoing z axis elongation such that it becomes tetragonally distorted (b) and finally reaches the square planar limit (c).

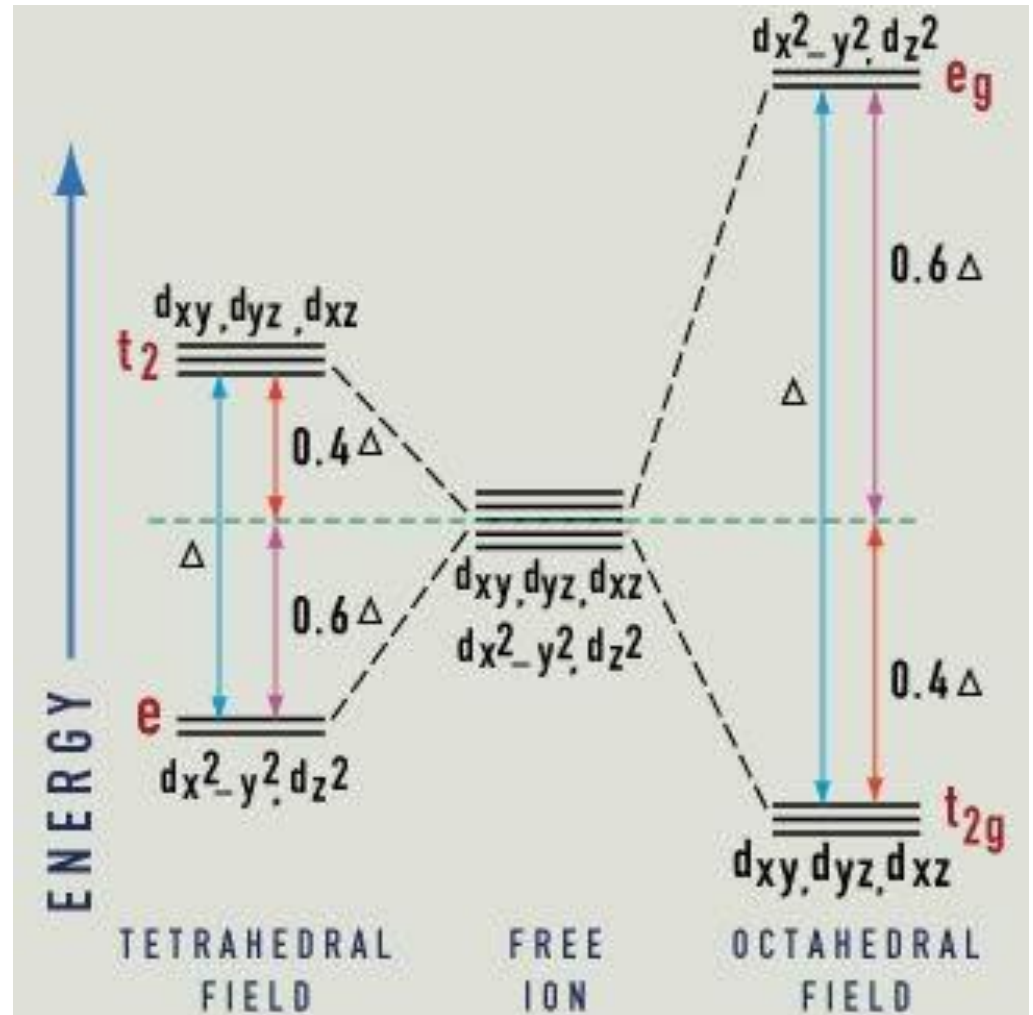
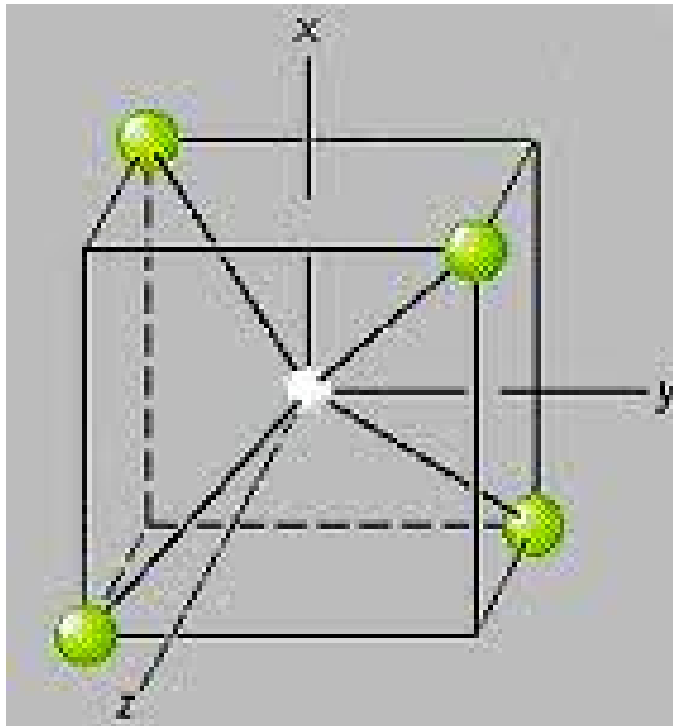
Square planar complexes *contd...*

Square planar complexes are formed

- ✓ With strong field ligands for 1st and other row elements
- ✓ Metals at higher oxidation state
- ✓ Even with weak field ligands for 2nd and 3rd row elements

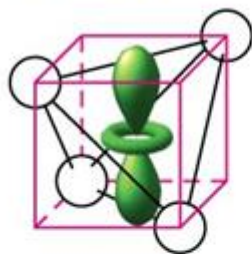
Mainly d^8 and d^9 systems form square planar complexes (e.g. Pt(II), Au(III))

Tetrahedral complexes



Tetrahedral complexes

54°44'



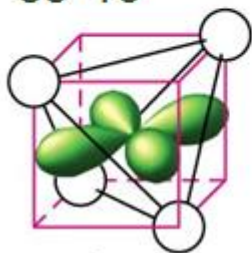
d_{z^2}



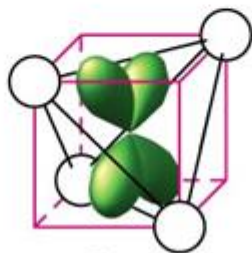
$d_{x^2-y^2}$

There are four ligands instead of six
The direction of the orbitals does not coincide with the direction of the ligands

35°16'



d_{xy}



d_{xz}



d_{yz}

$$\Delta_t = (4/9) \Delta_o \text{ (each point contribute } 2/3 \text{ factor to tetrahedral field)}$$

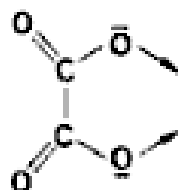
CFSE and electronic arrangement of tetrahedral complexes

Number of <i>d</i> electrons	Arrangement of electrons		Spin only magnetic moment	Tetrahedral CFSE	Tetrahedral CFSE scaled for comparison with octahedral values, assuming $\Delta_t = \frac{4}{9}\Delta_o$	Octahedral CFSE Δ_o	
	e_g	t_{2g}	$\mu(D)$	Δ_t		Weak field	Strong field
d^1			1.73	-0.6	-0.27	-0.4	-0.4
d^2			2.83	-1.2	-0.53	-0.8	-0.8
d^3			3.87	$-1.2 + 0.4 = -0.8$	-0.36	-1.2	-1.2
d^4			4.90	$-1.2 + 0.8 = -0.4$	-0.18	-0.6	-1.6
d^5			5.92	$-1.2 + 1.2 = 0.0$	0.00	0.0	-2.0
d^6			4.90	$-1.8 + 1.2 = -0.6$	-0.27	-0.4	-2.4
d^7			3.87	$-2.4 + 1.2 = -1.2$	-0.53	-0.8	-1.8
d^8			2.83	$-2.4 + 1.6 = -0.8$	-0.36	-1.2	-1.2
d^9			1.73	$-2.4 + 2.0 = -0.4$	-0.18	-0.6	-0.6
d^{10}			0.00	$-2.4 + 2.4 = 0.0$	0.00	0.0	0.0

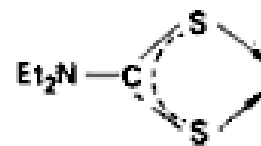
$$CFSE_{Td} = (-n_{(e)} \times 0.6 + n_{(t2)} \times 0.4) \times \Delta_t$$



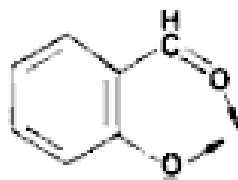
Acetylacetonato ion



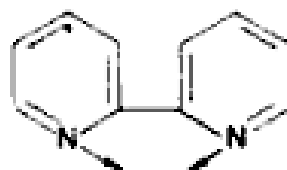
Oxalate ion



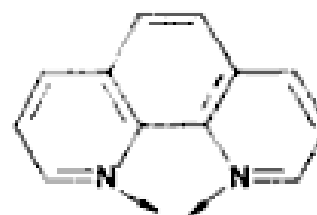
N,N'-Diethylthiocarbamate ion



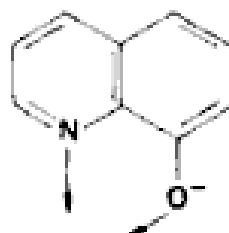
Salicylaldehyde anion



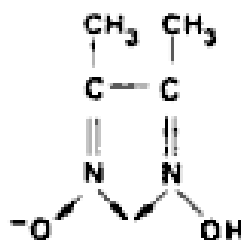
2,2'-Dipyridyl



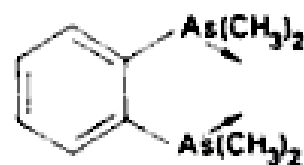
1,10-Phenanthroline
(o-phenanthroline)



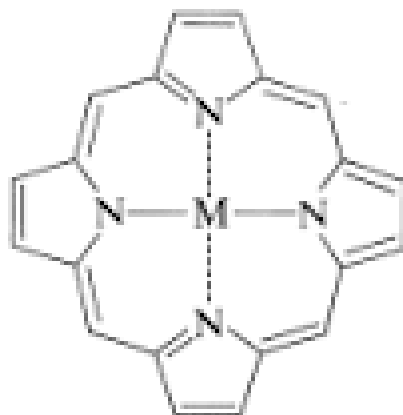
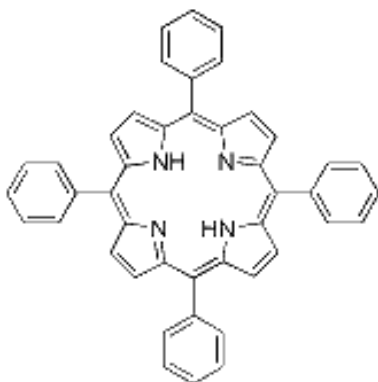
8-Hydroxyquinolinol ion
(oxine)



Dimethylglyoxime anion



o-Phenylenebisdimethylarsine (diarsine)



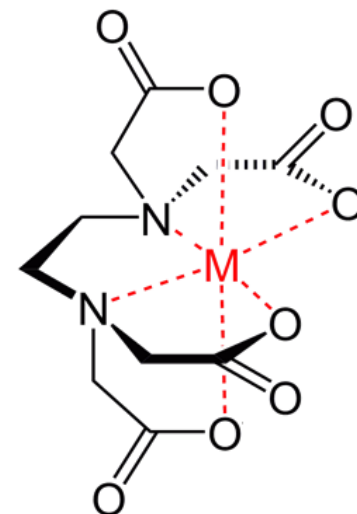
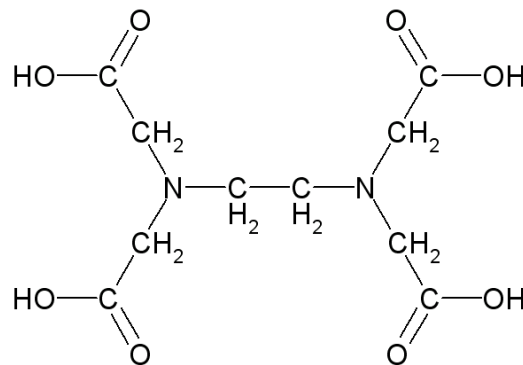
Tetradentate ligand

Several chelate compounds are of biological importance

Hemoglobin — Fe complex

Chlorophyll — Mg complex

Vitamin B₁₂ — Co complex



Hexadentate ligand

Isomerism

Structural isomerism

Stereoisomerism

polymerization

ionization

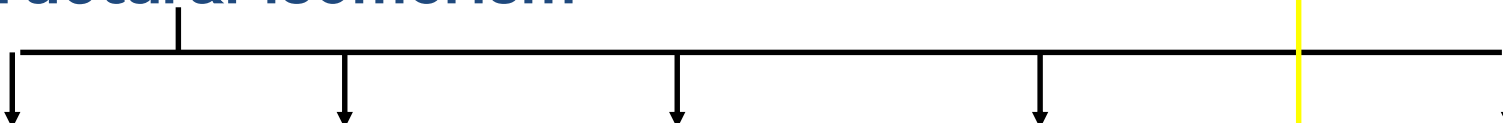
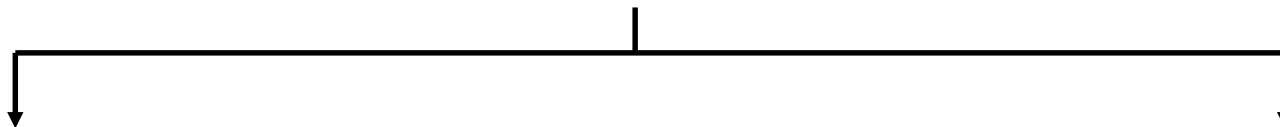
hydrate

linkage

coordination

geometrical

optical

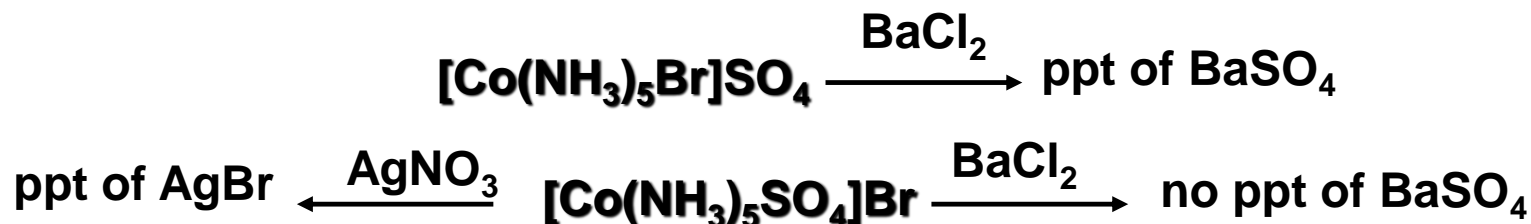


Structural isomerism

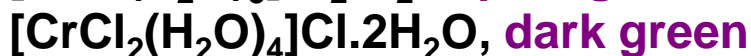
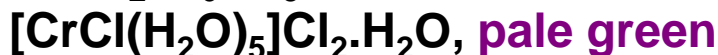
Polymerization isomerism: They are not true isomers but have same empirical formula



Ionization isomerism: This type of isomerism is due to the exchange of groups/ions between the complex ion and the ions outside it.



Hydrate isomerism: When there is different number of water molecule stay inside the coordination sphere and outside the coordination sphere to give same chemical formula.



Structural isomerism

Linkage isomerism: when there are ligands contain more than one atom which could donate electron pair ----- linkage to central metal ion through different atom.



Coordination isomerism: Coordination compounds made up of cationic and anionic coordination entities show isomerism due to the interchange of ligands between the cation and anion entities.



Stereoisomerism

Geometrical isomerism (cis-trans)



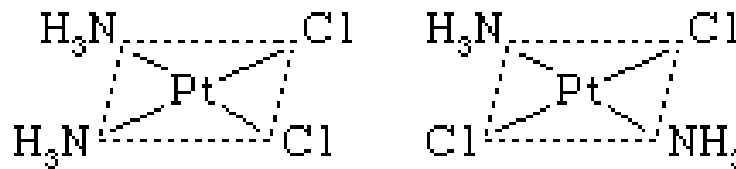
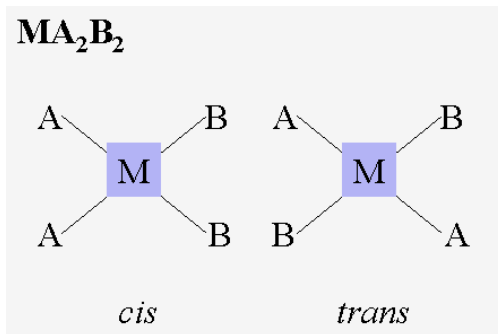
Optical isomerism: the isomers have opposite effects on plane-polarized light



Geometrical isomerism in square planar complexes



2 (cis- and trans-)



If the bidentate chelating ligand is not symmetrical,
2 isomers (cis and trans) can form

Geometrical isomerism in Octahedral complexes

Compound type



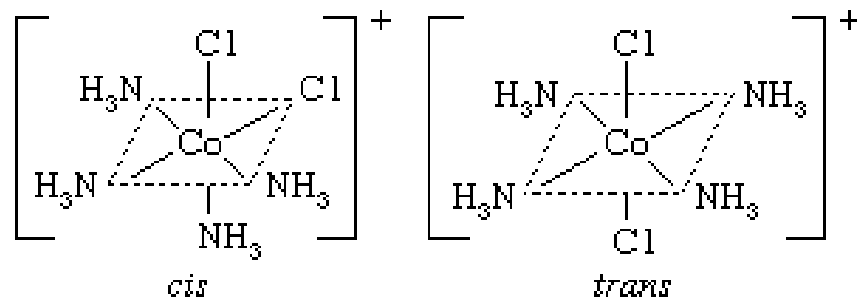
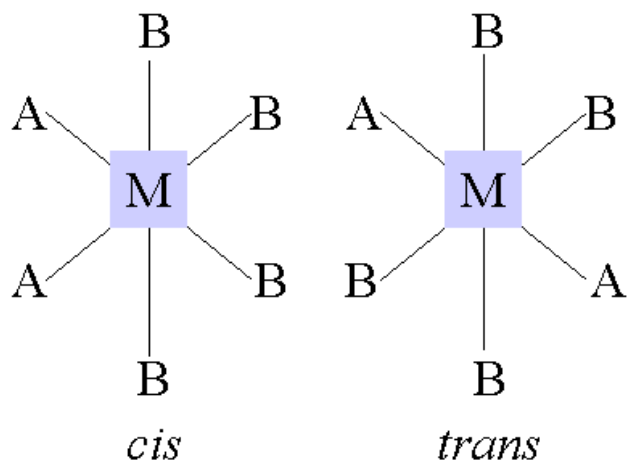
No. of isomers

2 (cis- and trans-)

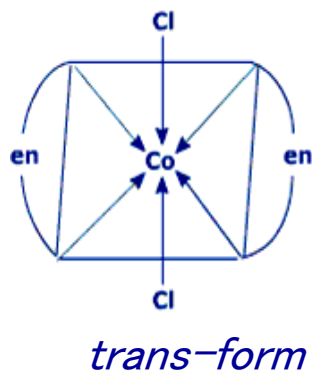
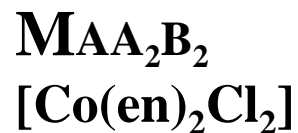
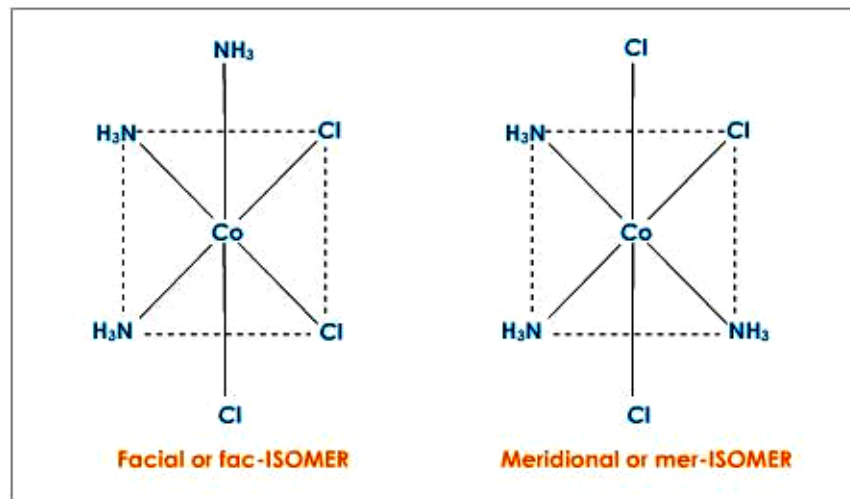
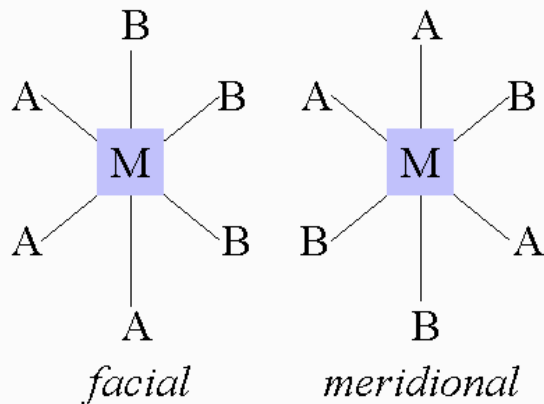
2 (fac- and mer-)

3 (2 cis- and 1 trans-)

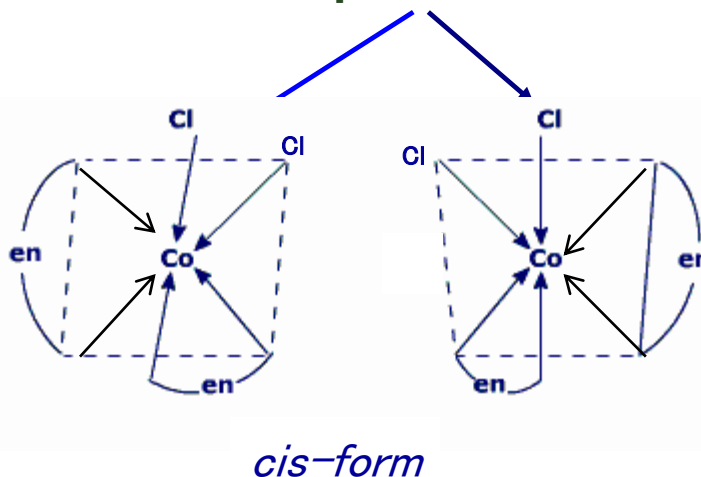
2 (fac- and mer-)



Geometrical isomerism in **Octahedral** complexes

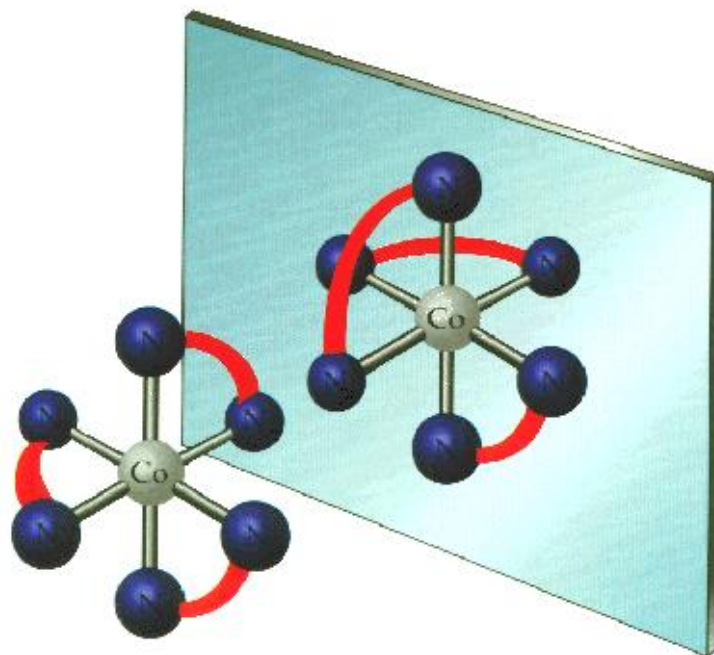


Optical isomers

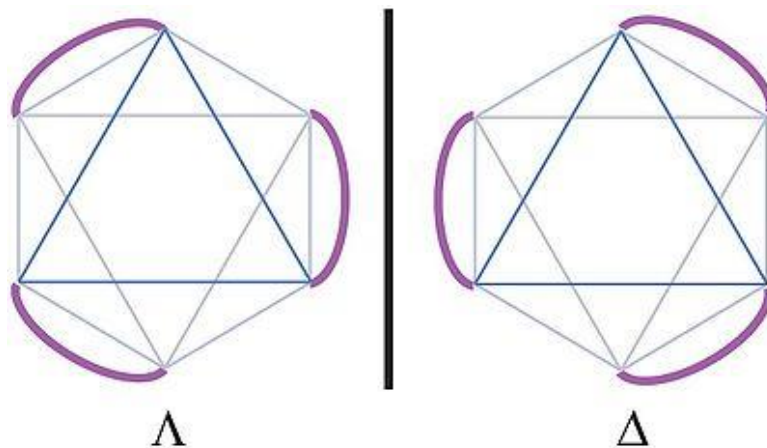


Tetrahedral symmetry does not show geometrical isomerism

Optical isomerism

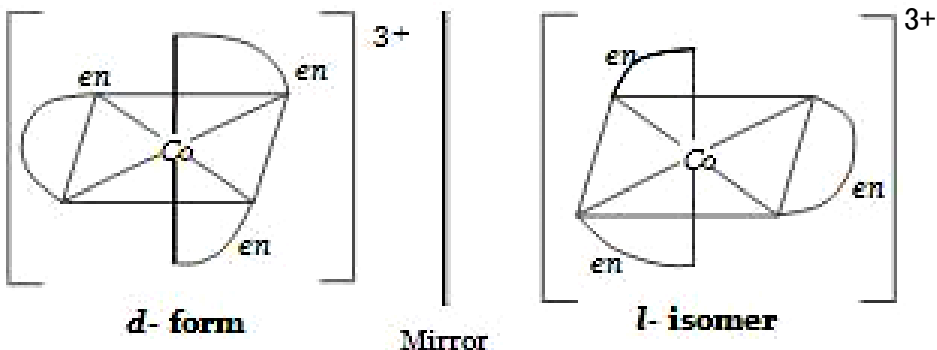


d or Δ – right hand rotation
l or Λ – right hand rotation

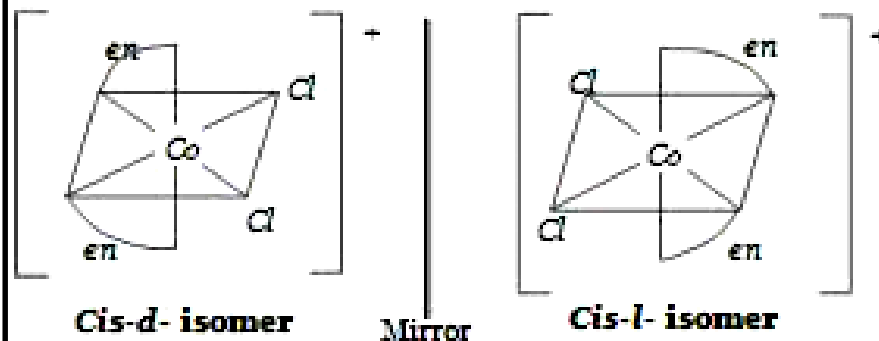


Optical isomerism in Octahedral complexes

MAA₃ e.g. [Co(en)₃]



MAA₂B₂ e.g. [Co(en)₂Cl₂]



MAA₂BC e.g. [Co(en)₂NH₃Cl]

