

The systematic naming of coordination compounds follow the following steps :

(1) Sequences of ligands and central atoms within names :

- (a) Ligand names are listed before the name(s) of the central atom(s).
- (b) No spaces are left between parts of the name that refer to the same coordination entity.
- (c) Ligand names are listed in alphabetical order (multiplicative prefixes indicating the number of ligands are not considered in determining that order).
- (d) The use of abbreviations of ligands are not applicable.

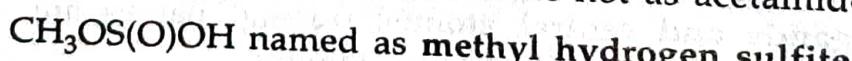
(2) Number of ligands in a coordination entity :

- (a) For simple ligands e.g. for monodentate ligands the prefixes di, tri, tetra, etc. are used for 2, 3, 4 etc. number of ligands. No enclosing marks are required.
- (b) For complicated ligands such as for polydentate or ambidentate ligands etc. the prefixes bis, tris, tetrakis, etc. are used instead of di, tri, tetra, etc. Here enclosing marks are to be used around the multiplicand.

For example the naming for  $(\text{NH}_3)_2$  will be diamine while for  $(\text{CH}_3\text{NH}_2)_2$  will be bis (methylamine) to make a distinction from dimethylamine. No hyphen will be used e.g. tetra-ammine a wrong statement, correct one is tetraammine, petaammine etc.

(3) Representation of the names of ligands :

- (a) For inorganic or organic anionic ligands if the name of the anions ends with 'ide', 'ite' or 'ate', the final 'e' is replaced by 'o' producing 'ido', 'ito' and 'ato' respectively. e.g. the halide ligands are named **fluorido**, **chlorido**, **bromido** and **iodido** and coordinated cyanide, hydride ( $\text{H}^-$ ) are named as **cyanido**, **hydrido** respectively.
- (b) Naming of neutral and cationic ligands including organic ligands are done without modification even if they carry the endings with 'ide', 'ite' or 'ate' e.g.



- (c) Enclosing marks are used for (i) naming of cationic and neutral ligands, (ii) naming of inorganic anionic ligands including multiplicative prefixes (such as triphosphato), (iii) naming of compositional names e.g. carbon disulfide, (iv) naming of substituted organic ligands and wherever necessary to avoid ambiguity. But for common ligand names such as aqua, ammine, carbonyl, nitrosyl, methyl, ethyl etc. no enclosing marks are required.

(4) Charge numbers, oxidation numbers in a complex entity :

- (a) The oxidation number of the central atom in a coordination entity is shown by Roman numeral in brackets immediately following its name. If the complex entity is negative then the ending will be with the 'ate'. When necessary a negative sign is placed before the number. Arabic zero indicates the oxidation number zero.

(b) Alternatively, the charge on a complex entity may be indicated. The net charge may be indicated by arabic number which is preceding with the charge sign and denoted in brackets. It is to be noted that the name of the central atom including the ending 'ate' must be written without the intervention of a space e.g.  $K_4[Fe(CN)_6]$  or tetrapotassium hexacyanidoferate(II), or potassium hexacyanidoferate (4-),

(5) **Specification of donor atoms—the kappa ( $\kappa$ ) convention :** In cases where coordination occurs through one of several possible donor atoms of a ligand, the specific indication of the donor atom is achieved through the use of kappa convention in which the Greek lower case kappa ( $\kappa$ ) is used to indicate the donor atom e.g. if glycinate anion ( $gly^-$ ) coordinates through the nitrogen atom, the abbreviation of the would be  $gly-\kappa N$  as in the complex  $[M(gly-\kappa N)_3X_3]$  where  $X$  = halide ligand.

The cases where specification of the donor atom is not necessary for a ligand that can bind the central atom in more than one way are :

- (a) monodentate O-bonded carboxylate groups
- (b) monodentate C-bonded cyanide ligand (name of the ligand is 'cyanido')
- (c) monodentate C-bonded carbon monoxide which is named as 'carbonyl'
- (d) monodentate N-bonded nitrogen monoxide which is named as 'nitrosyl'.

It is evident that in these cases the ligand names imply the binding modes as indicated above.

Single ligating atoms are indicated by a Greek kappa ( $\kappa$ ).  $\kappa$  symbols are placed after the portion of the ligand name that represents the ring, chain or substituent group in which the ligating atom is found. Multiplicative prefixes which apply to a ligand or portions of a ligand also apply to the donor atom symbols.

Simply the nitrogen bonded NCS is denoted by thiocyanato- $\kappa N$  while sulfur bonded NCS is named as thiocyanato- $\kappa S$ . Similarly nitrogen bonded nitrite is denoted by nitrito- $\kappa N$  and oxygen bonded nitrite is named as nitrito- $\kappa O$ . For example,

$[Co(NH_3)_5ONO]Cl_2$  named as pentaamminenitrito- $\kappa O$ cobalt(III) chloride and  $[Co(NH_3)_5NO_2]Cl_2$  is named as pentamminenitrito- $\kappa N$ cobalt(III) chloride.

1.  $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$   
pentaamminechloridocobalt(2+) chloride or  
pentaamminechloridocobalt(III) chloride
2.  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$   
hexaamminecobalt(III) chloride
3.  $[\text{CoCl}(\text{NH}_3)_4(\text{NO}_2)]\text{Cl}$   
tetraamminechloridonitrito- $\kappa$ N-cobalt(III) chloride
4.  $\text{K}_2[\text{PdCl}_4]$   
potassium tetrachloridopalladate(II)
5.  $\text{K}_2[\text{OsCl}_5\text{N}]$   
potassium pentachloridonitridoosmate(2-)
6.  $[\text{Co}(\text{en})_3]\text{Cl}_3$   
tris(ethane-1, 2-diamine)cobalt(III) chloride

## **7.9 ISOMERISM AMONG COORDINATION COMPOUNDS**

Isomerism is very common in organic chemistry e.g. ortho, meta and para substituted products, geometrical isomerism of maleic and fumaric acid, optical isomerism of lactic acid, conformational isomerism of cyclohexane etc. Since isomerism is a phenomena depending on the position and arrangement of atoms, so it cannot be limited to any particular class of compounds. A large number of inorganic complexes also exhibit the phenomena of isomerism. Compounds having the same molecular formula but having different structural arrangements are called isomers and the phenomena is called isomerism. (Greek, 'iso' means equal or the same and 'meros' means a part). Following are the types of isomerism exhibited by coordination compounds.

### **7.9.1 Hydrate isomerism or Solvate isomerism**

This isomerism arises due to the position of water molecules inside and outside the coordination sphere. Three isomers of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  are known :

- (1)  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  (violet) which has three ionic chloride ions, which can be precipitated by  $\text{AgNO}_3$  solution. The compound does not lose water over conc.  $\text{H}_2\text{SO}_4$  in a desiccator.



- (2)  $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$  (green) which loses one water molecule over conc.  $\text{H}_2\text{SO}_4$  and two ionic chlorides are precipitated by  $\text{AgNO}_3$  solution.
- (3)  $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$  (dark green) which loses two water molecules over conc.  $\text{H}_2\text{SO}_4$  and one ionic chloride is precipitated by  $\text{AgNO}_3$  solution.

These isomers can also be characterised by thermogravimetric analysis as also by conductance measurements. Conductance measurements of compounds (1), (2) and (3) behave as tri-uni, bi-uni and uni-univalent electrolytes respectively. Commercial  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  exist as a mixture of two green variety of isomers, the dark green dichloro variety exist as predominating trans form. The isomers may be separated by cation exchange resin with dilute  $\text{HClO}_4$  as eluting agent. Aqueous solution of commercial  $\text{CrCl}_3$  is green, but on standing for a week or more the green solution turns violet from which crystals of  $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$  may be obtained.

Other examples of this type of isomers are :

- $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})_2]\text{Br}_3$  and  $[\text{Cr}(\text{en})_2(\text{H}_2\text{O})\text{Br}]\text{Br}_2 \cdot \text{H}_2\text{O}$
- $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{O}\text{Cl}]\text{Cl}_2$  and  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$
- $[\text{Co}(\text{en})_2\text{H}_2\text{O}\text{Cl}]\text{Cl}_2$  and  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl} \cdot \text{H}_2\text{O}$
- $[\text{Cr}(\text{H}_2\text{O})_2\text{Cl}_2(\text{py})_2]\text{Cl}$  and  $[\text{Cr}(\text{H}_2\text{O})\text{Cl}_3(\text{py})_2]\text{H}_2\text{O}$
- $[\text{VO}(\text{Qui})_2\text{H}_2\text{O}]$  (olive green) and  $[\text{VO}(\text{Qui})_2]\text{H}_2\text{O}$  (cream)

where QuiH = quinaldinic acid

Thermogravimetric analysis indicates loss of water at  $170\text{-}180^\circ\text{C}$  for olive green variety while the cream variety loses water below  $100^\circ\text{C}$ .

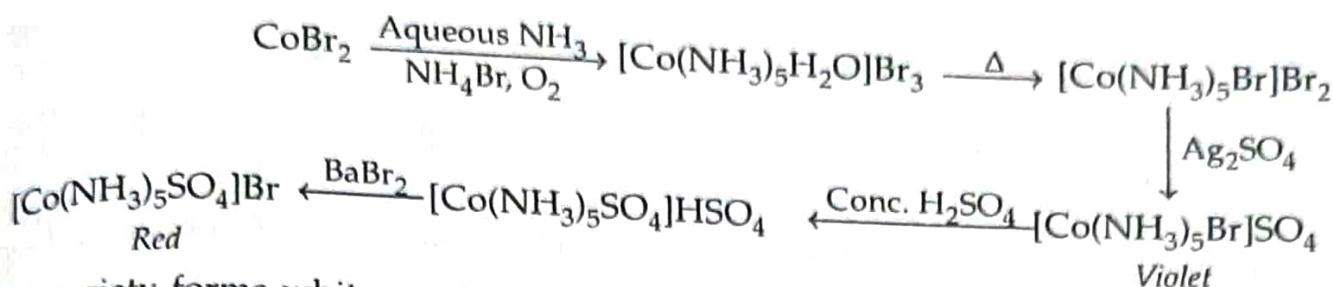
### 7.9.2 Ionisation isomerism

This isomerism arises when the coordinating ions/ligands exchange inside and outside the coordination entity. This can also be considered as the extension of hydrate isomerism because in case of hydrate isomerism also there are several examples where apart from the exchange of water molecules, the ions inside and outside the coordination sphere may change. Examples of ionisation isomers are :

- $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}$
- $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$
- $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2$  and  $[\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2$
- $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{SO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Cl}$
- $[\text{Co}(\text{en})_2\text{NO}_2\text{Cl}]\text{SCN}$  and  $[\text{Co}(\text{en})_2\text{NO}_2\text{SCN}]\text{Cl}$

These isomers are easily characterised by simple conductance measurements or by spectral studies and sometimes by simple analytical procedure.

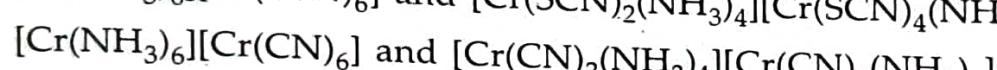
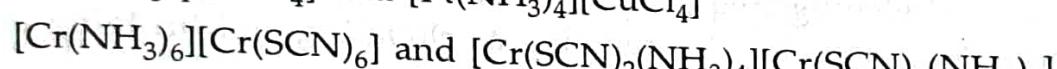
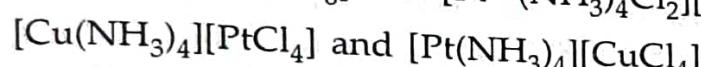
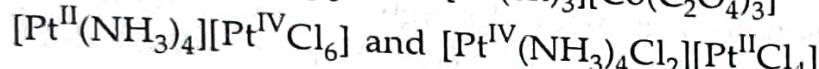
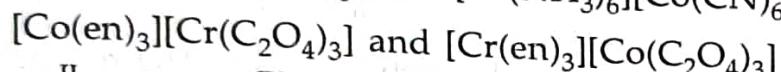
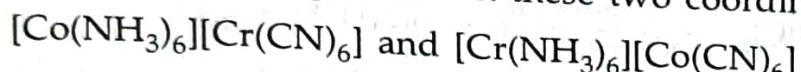
The following synthetic routes are followed for the preparation of violet and red variety of the isomer(a) :



The violet variety forms white precipitate of BaSO<sub>4</sub> on treatment with BaCl<sub>2</sub> solution while the red compound gives a pale yellow precipitate of AgBr with AgNO<sub>3</sub> solution. The violet one shows only one IR active stretching vibration while the red compound where SO<sub>4</sub><sup>2-</sup> coordinated, shows three IR stretching vibrations.

### 7.9.3 Coordination isomerism

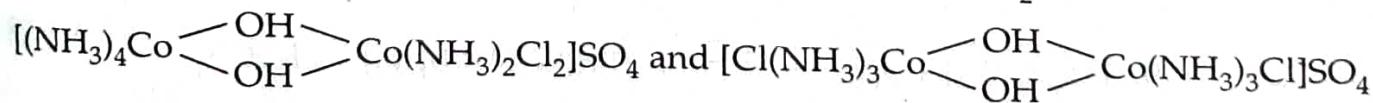
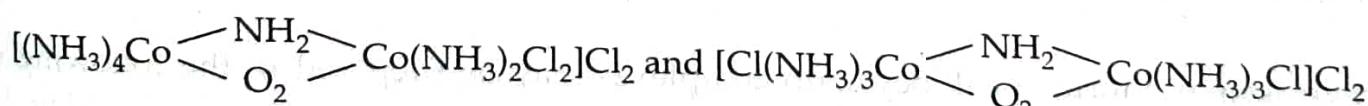
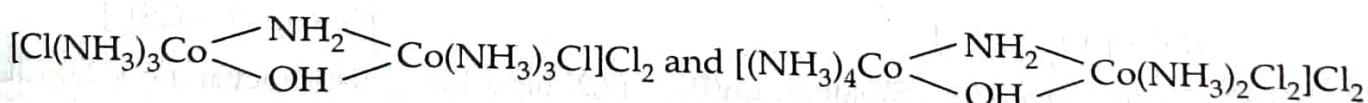
This type of isomerism is found in compounds where the cation and anion both are complex entity and ligands will interchange between these two coordination zones e.g.



Characterisation of these isomers are difficult. Complete elemental analysis as also different structural studies can give us the idea of the composition of these isomers.

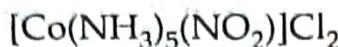
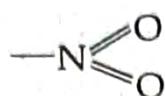
### 7.9.4 Coordination position isomerism

This type of isomerism arises in case of polynuclear complexes having bridging ligands. Isomers involve an exchange of ligands between the two metal atoms that are linked through one or more bridging groups e.g.



### 7.9.5 Structural, Salt or Linkage isomerism

Ambidentate ligands (Sec. 7.4.2) will exhibit this type of isomerism due to the different linking mode of the donor atoms of the ambidentate ligands. Thus the nitro group may be attached to the central atom through pentavalent nitrogen or may be attached through oxygen atom with trivalent nitrogen :

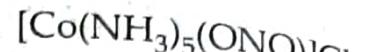
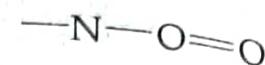


*Yellow brown*

pentaamminenitrito-Ncobalt(III) chloride

*or*

pentaamminenitrito- $\kappa$ Ncobalt(III) chloride

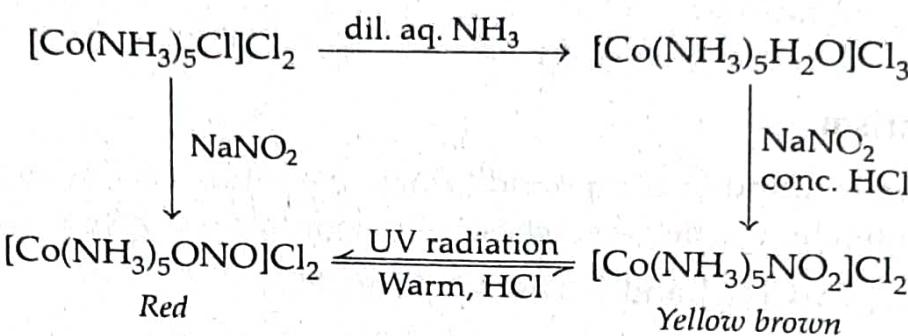


*Red*

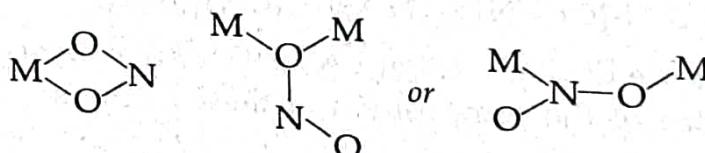
pentaamminenitrito-Ocobalt(III) chloride  
*or*

pentaamminenitrito- $\kappa$ Ocobalt(III) chloride

The above two variety of compounds may be prepared in the following schematic way



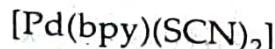
The characterisation of these isomers was made through IR study. The red compound having M-ONO bonding exhibits stretching frequency  $\sim 1060\text{cm}^{-1}$  while yellow brown compound (M- $\text{NO}_2$  bonding) shows stretching frequency  $\sim 820\text{ cm}^{-1}$ . The red isomer is less stable than the yellow brown form.  $\text{NO}_2^-$  ion can also function as **chelating and bridging modes** as shown below :



Another important ambidentate ligand is thiocyanate ion ( $\text{SCN}^-$ ) which can function as end on (EO) mode through coordination with S or N as :

$\text{M}-\text{SCN}$ , thiocyanato-S or

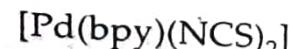
thiocyanato- $\kappa$ S



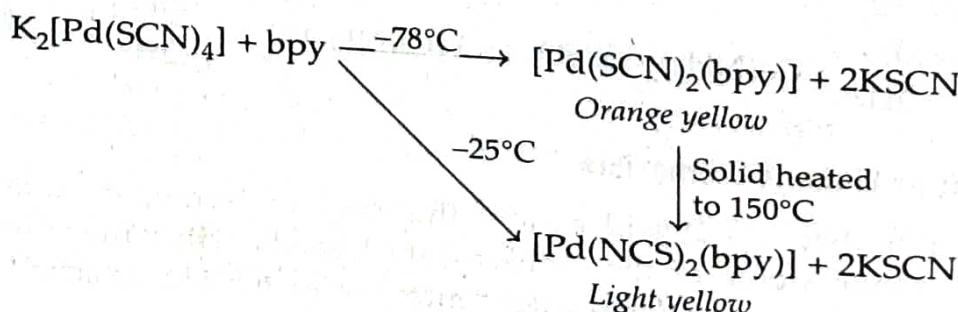
(2,2'-bipyridine)bis(thiocyanato- $\kappa^2\text{S}$ )palladium(II)      (2,2'-bipyridine)bis(thiocyanato- $\kappa^2\text{N}$ )palladium(II)

$\text{M}-\text{NCS}$ , thiocyanato-N or

thiocyanato- $\kappa$ N



The two isomeric forms of thiocyanato complexes may be prepared in the following way :



### 7.9.10 Stereoisomerism

Stereoisomerism is the isomerism which arises on account of the different arrangement of atoms or groups in space in a molecule. It is also known as space isomerism. It may be of two types : (a) Geometrical isomerism, (b) Optical isomerism.

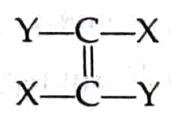
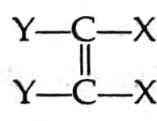
Both geometrical and optical isomerism are encountered among the coordination complexes. In the case of complexes the common coordination numbers are four and six and therefore we shall restrict our attention to tetrahedral, square planar and octahedral complexes only. A correlation between stereoisomerism and geometry is given in Table 7.4. The most significant aspect of Werner's theory is the directional property of secondary valencies of the central metal atoms and the prediction of stereoisomers. This is the new horizon of Werner's theory.

**Table 7.4 : Prediction of stereoisomers and geometry**

Coordination number	Geometry	Geometrical isomers	Optical isomers
4	Tetrahedral Square planar	Not possible Possible	Possible, but rare Not possible
6	Octahedral	Possible	Possible

### 7.9.11 Geometrical isomerism

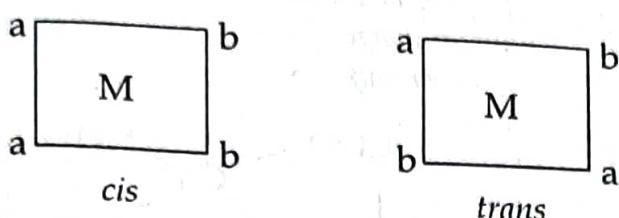
This isomerism is also called **cis-trans** isomerism. Cis means 'adjacent to' while trans means 'opposite to'. Thus when two similar ligands are adjacent, the isomer is named cis while if the ligands are in the farthest position in a specific geometry, the isomer is called trans. Geometrical isomerism with respect to metal has not been found among tetrahedral complexes. In organic chemistry, compound of the type  $C_2X_2Y_2$  exhibits geometrical isomerism and the two isomers may be represented as :



#### (A) Square planar complexes having coordination number 4

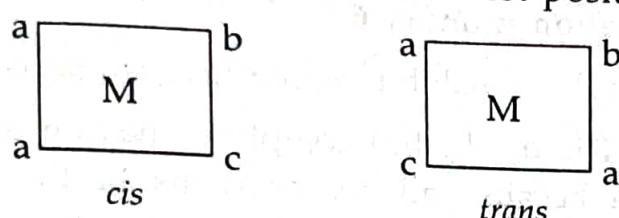
Square planar complexes of the following categories exhibit geometrical isomerism. Here M designates the central metal atom and a, b, c and d are ligands.

(i)  **$Ma_2b_2$  type shows two isomers :** The  $Ma_4$  type of square planar complex will not exhibit geometrical isomerism, but when two 'a' ligands are replaced by two 'b' ligands, the decomposition of the complex is  $Ma_2b_2$  which exhibits geometrical isomerism (cis-trans) of the following type :



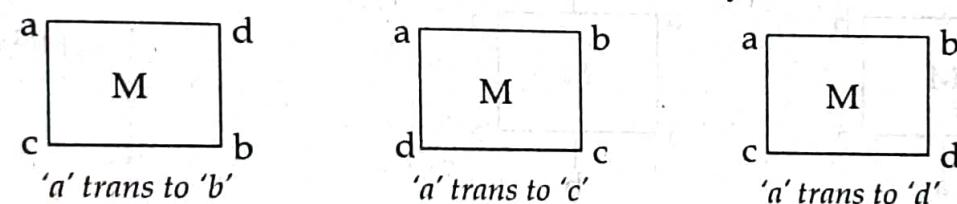
For example  $[Pt(NH_3)_2Cl_2]$

(ii)  **$Ma_2bc$  shows two isomers :** In this type when the two 'a's are nearest, the isomer is called **cis** while the two 'a's are in the farthest position\*, the isomer is called **trans**.

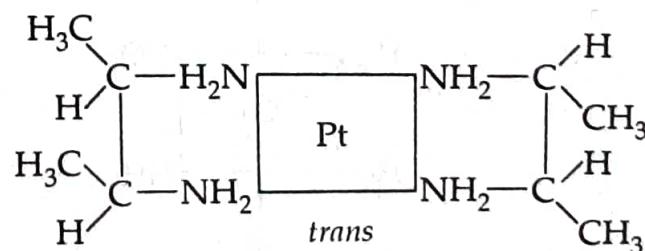
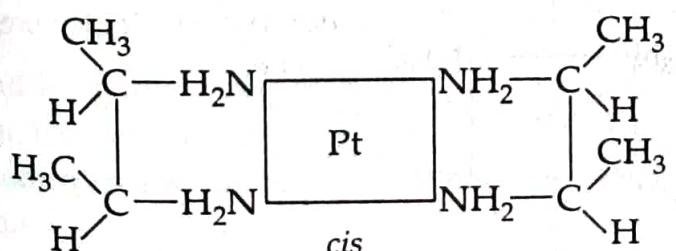


The example of this type of complex is  $[Pt(NH_3)_2ClBr]$ .

(iii) **Mabcd type of complex exhibits three isomers :** The example of this type of complex is  $[Pt(NH_3)(Br)(Cl)(py)]$ . In this case the position of any one ligand, say 'a' is fixed while the other ligands i.e. b, c and d are successively placed at the opposite end i.e. farthest end, then the remaining two positions in each structure are randomly filled with rest of the two ligands.

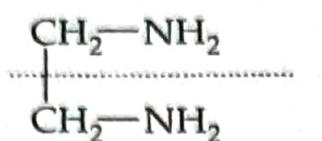


(iv)  **$Ma_4$  type chelate complex shows two isomers :** Normally  $Ma_4$  type of complexes will not show geometrical isomerism. But a chelate complex of the type  $Ma_4$  with substituents on the ring atoms may be expected to offer geometrical isomerism which are **cis** and **trans** with respect to the median plane of the molecule :

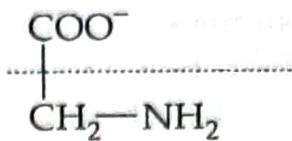


(v) **Complexes with unsymmetrical chelating ligands show two isomers :** Ethylenediamine is a symmetrical chelating ligand. If we divide it into two halves by an imaginary line, the upper half is a mirror image of the lower half. Such ligands do not show cis-trans isomerism. However unsymmetrical ligands such as glycinate ion in which the two halves are not the mirror image of each other may form cis-trans isomers of the following :

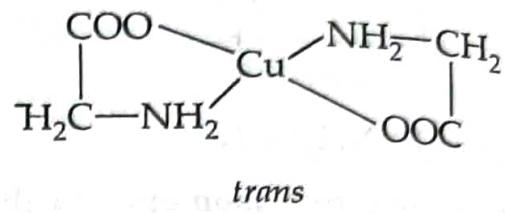
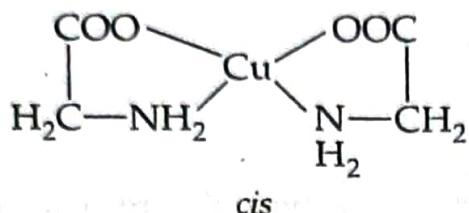
\* In square planar geometry the diagonal is the farthest position.



upper half is the mirror image of lower half



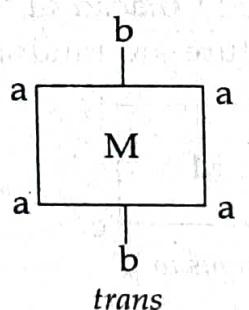
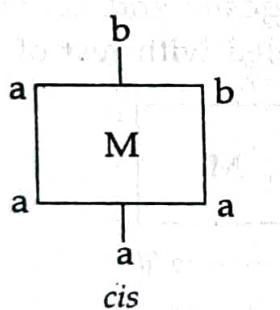
upper half is not the mirror image of lower half



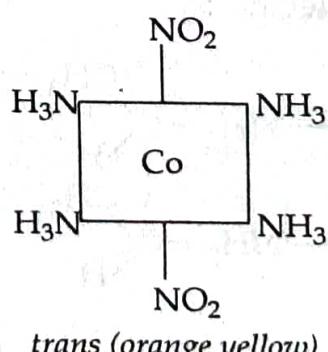
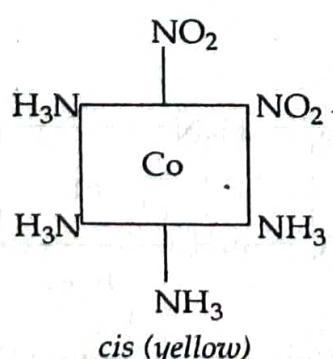
### (B) Octahedral complexes having coordination number 6

Following categories of octahedral complexes exhibit geometrical isomerism.

(i)  **$\text{Ma}_4\text{b}_2$  type shows two isomers :** The octahedral complexes having composition  $\text{Ma}_4\text{b}_2$  would not exhibit geometrical isomerism because all six positions of the octahedron are identical. But if the two 'a' ligands are substituted by two 'b' ligands then the composition will be  $\text{Ma}_4\text{b}_2$  and in that case cis-trans isomerism arises. When both the substituents occur in the edgewise position, the compound is called cis isomer. If the two substituents occur in the axial position, the compound is referred to as trans isomer i.e.

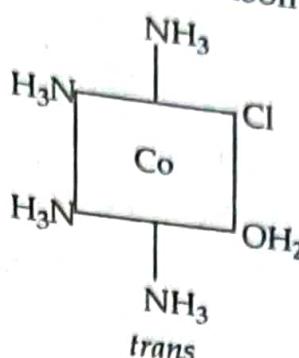
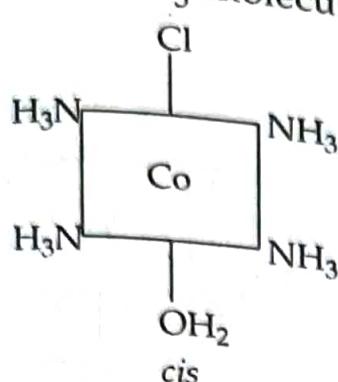


For example  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  has two isomers. Similarly  $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2]\text{NO}_3$  has two isomers which differ in colour :

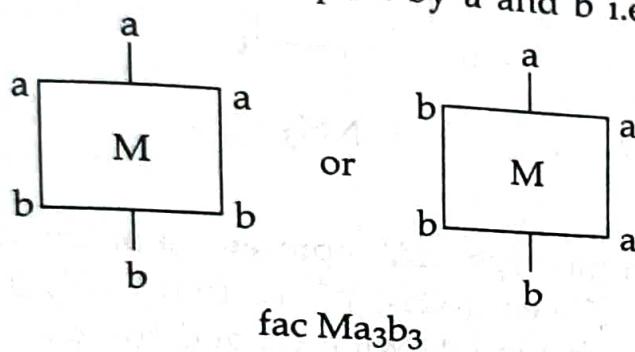


In this category large number of complexes are known e.g. cis  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  (violet) and trans  $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$  (green); cis  $[\text{CoCl}_2(\text{en})_2]\text{Cl}$  (purple) and trans  $[\text{CoCl}_2(\text{en})_2]\text{Cl}$  (green);  $[\text{Cr}(\text{en})_2(\text{NCS})_2]^+$  (orange red) and trans  $[\text{Cr}(\text{en})_2(\text{NCS})_2]^+$  (yellow orange);  $\text{NH}_4[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]$  etc.

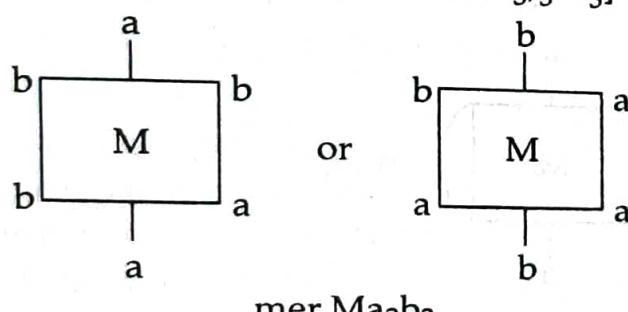
(ii)  $\text{Ma}_4\text{bc}$  shows two isomers : In this type for example  $[\text{Co}(\text{NH}_3)_4\text{H}_2\text{OCl}]^{2+}$  exists in two isomeric forms. When the four  $\text{NH}_3$  molecules exist in the nearest position the isomer is **cis** while when the four  $\text{NH}_3$  molecules are wide apart the isomer is **trans** i.e.



(iii)  $\text{Ma}_3\text{b}_3$  type exists in two isomers : This is one of the important type where the two isomers are designated as **facial** (cis) or **fac** and **meridional** (trans) or **mer**. In the **fac** form the three a's are all adjacent at one face of the octahedron while in case of **mer** isomer the two a's are placed opposite to each other, two b's are placed opposite to each other and the remaining two positions are randomly occupied by a and b i.e.

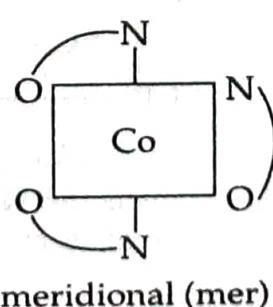
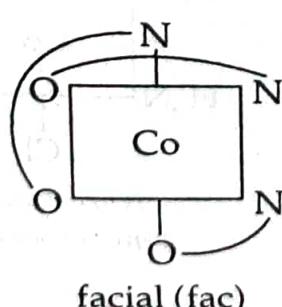


e.g. fac  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$  or fac  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

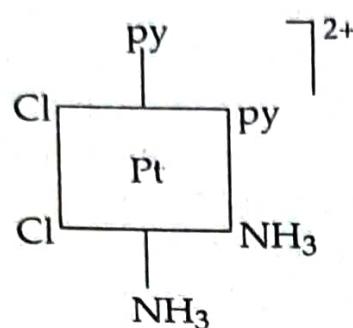


e.g. mer  $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3]$  or mer  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$

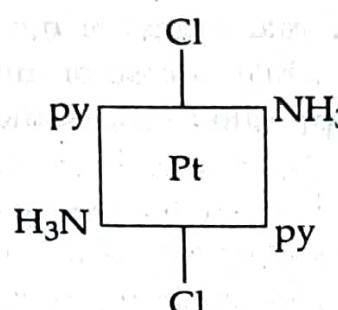
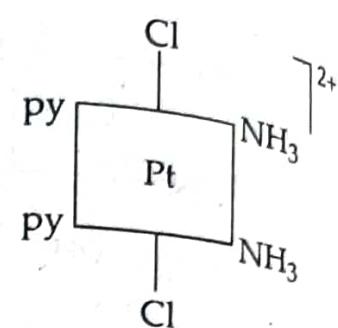
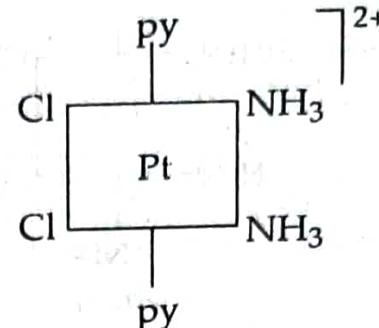
The a and b ligands are along the meridian plane of a sphere and so this isomer is called **mer**. In the **fac** isomer the three a ligands/atoms or the three b ligands/atoms are cis to each other. Other examples are  $[\text{RhCl}_3(\text{py})_3]$ ,  $[\text{Co}(\text{gly})_3]$  and  $[\text{IrCl}_3(\text{PMe}_3)_3]$ .  $[\text{Co}(\text{gly})_3]$  exists as following two forms :



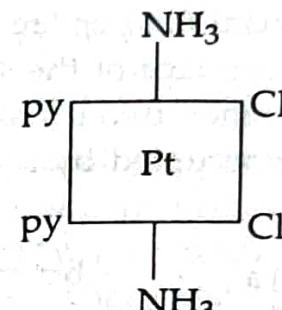
(iv)  $M_{a_2}b_2c_2$  type shows five isomers : In this type e.g.  $[Pt(NH_3)_2Cl_2(py)_2]^{2+}$  exhibit five geometrical isomers of the following type but only three isomers have been actually isolated.



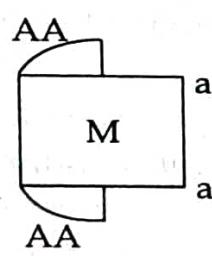
cis isomer



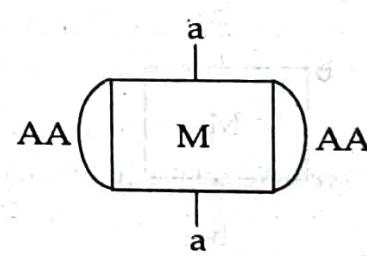
trans isomer



(v)  $M(AA)_2a_2$  type has two isomers : In this type 'AA' represents a bidentate ligand and 'a' is a monodentate ligand e.g.  $[Co(en)_2Cl_2]^+$ ,  $[Co(en)_2(NH_3)_2]^{3+}$ ,  $[Cr(en)_2Cl_2]^+$ ,  $[Co(en)_2(NO_3)_2]$ ,  $[Cr(C_2O_4)_2(H_2O)_2]^-$  etc. All these complexes exist in following **cis** and **trans** forms of which **cis** form may exhibit optical isomerism :

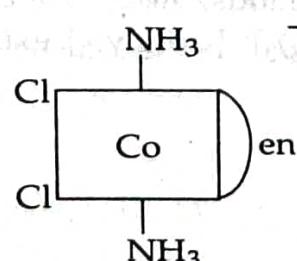
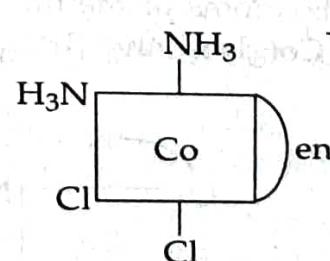
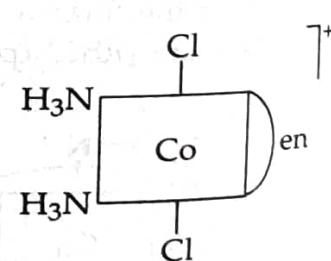


cis isomer



trans isomer

(vi)  $M(AA)a_2b_2$  type shows three isomers : The example of this type of complex is  $[Co(en)(NH_3)_2Cl_2]^+$  which has the following three isomers :

trans two  $NH_3$   
and cis two  $Cl^-$ cis two  $NH_3$   
and cis two  $Cl^-$ trans two  $Cl^-$   
and cis two  $NH_3$

### 7.14.2 Crystal Field Theory (CFT) : Theory of Crystalline Field (TCF)

To correlate the colour and magnetic properties of complexes and to obviate the defects of valence bond theory, the more plausible crystal field theory was developed. In crystal field theory the ligands are considered as point negative charges and metal ions are point positive charges so that there will be an electrostatic attraction between a metal ion and the ligands. Since this type of electrostatic attraction originally prevailing in case of ionic crystals e.g. KCl, NaCl etc., so that this model is termed as **electrostatic crystal field theory**. In this theory no consideration of overlap between ligand orbitals and metal ion orbitals have been made.

As transition metals are good complex former, therefore this electrostatic approach forces some perturbation or ordering of d-orbitals in different stereochemistries such as octahedral, tetrahedral square planar etc.

#### 7.14.2(A) Octahedral complexes

In octahedral complexes, the metal atom/ion is at the centre of an octahedron while six ligands are existing at the six corners of the octahedron along the arbitrarily chosen x, y and z axes (Fig. 7.4). Let us consider the metal has only s-orbital. For a given n value, the s-orbital is spherically symmetrical so that on interaction with six ligands, the energy of the s-orbital will be raised compared to field free state. Instead of s-orbital if there is a p-orbital which is three fold degenerate, similarly with s-orbital, the energy of the three p-orbitals i.e.  $p_x$ ,  $p_y$  and  $p_z$  will be raised, but the degeneracy will not be lifted. In place of octahedral field if we take a square planar arrangement, then degeneracy of p-orbitals will be lifted and two

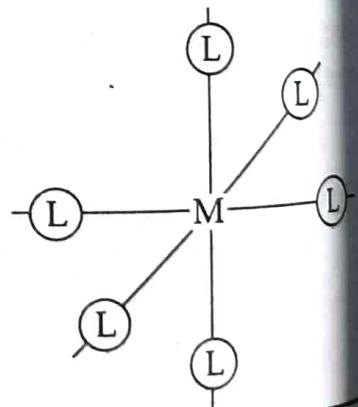


Figure 7.4 : The octahedral complex where the six ligands are along the three cartesian axes.

sets of orbitals are obtained—one having degenerate  $p_x$  and  $p_y$  orbitals of higher energy and the  $p_z$  orbital of lower energy because a square plane may be considered by taking  $x$  and  $y$  axes. These situations are less important in case of complex formation.

Now what happens when metal atom/ion have d-orbital which is of prime importance in our present discussion. The d-orbital is five fold degenerate and all the five d-orbitals are not alike. Three of these orbitals, viz.,  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  are similar in all respects but their spatial orientation are different. Since they occupy spaces between the three axes, their electron density is minimum along the axes and maximum along the diagonals between the axes. On the other hand the electron density of the remaining two orbitals i.e.  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals, is directed along the axes.

The six ligands initially surrounded the metal will create a spherically symmetrical field of negative charges. On the application of octahedral crystal field such a set of five d-orbitals will be no longer degenerate. The repulsion between metal and ligand electrons raises the energy of the five d-orbitals initially, although it does not lift the degeneracy. Finally since the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals are directed along the axes, there will be a strong interaction by the six ligands and their energy will be raised whereas the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  will experience lesser interacting force by the ligands and will be of lower energy. Thus there will be a splitting of d-orbitals between two sets of orbitals one having  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals designated as  $e_g$  of higher energy and the other having  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals classed as  $t_{2g}$  of lower energy (Fig. 7.5). The splitting will follow the the centre of gravity (barycentre) rule i.e. the amount of energy raised by  $e_g$  orbitals is equal to the amount of energy lowered by  $t_{2g}$  orbitals so that the total energy of the system is constant. If one electron of the metal ion are in the  $e_g$  set of orbitals, it will be experiencing more repulsion than the electron in  $t_{2g}$  set of orbitals in the case of octahedral complex than the hypothetical spherical complex. Figure 7.5 records an energy level diagram comparing the relative energies of d-orbitals that the d-electron(s) could occupy in these two

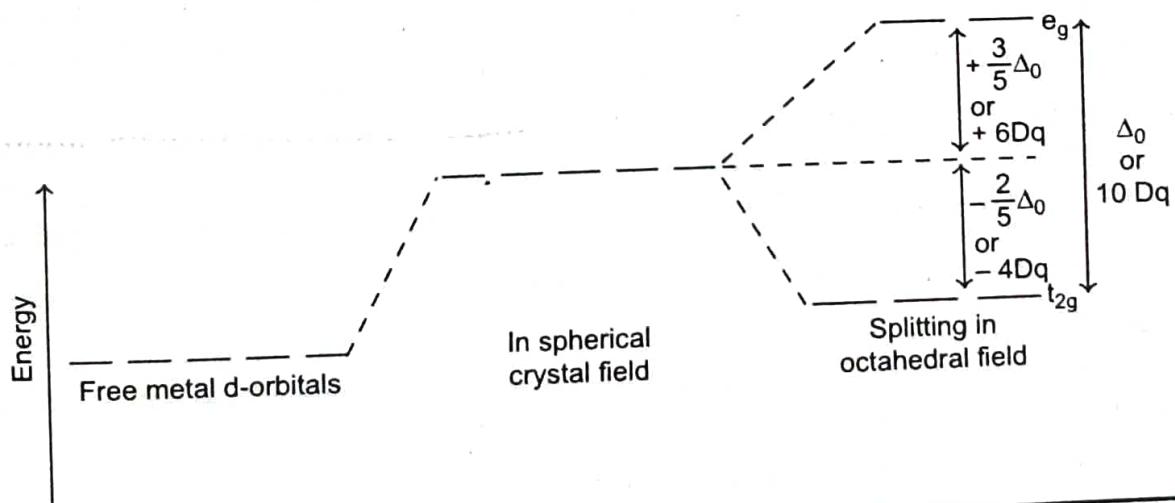


Figure 7.5 : Splitting (qualitative) of d-orbitals in an octahedral crystal field.

real octahedral and hypothetical spherical geometries. Any d-orbital in the spherical complex of the five degenerate d-orbitals in a uniformly smeared out field of six ligands is taken as the zero of energy while in the octahedral complex the energy is determined by the preferential filling of d-electrons in the  $e_g$  and  $t_{2g}$  sets of orbitals. The difference of energy between the two sets of

orbitals ( $e_g$  and  $t_{2g}$ ) is called the (octahedral) crystal field splitting or ligand field splitting and is represented as  $10Dq$  or  $\Delta_0$ . The subscript 'o' stands for octahedral. The terms D and q were obtained by the quantitative treatment of crystal field theory for d-orbital wave function. The potential energy and its effects on d-orbital wave function is related to the terms D and q in octahedral field as :

$$D = \frac{35Ze}{4a^5}, \quad q = \frac{2er^4}{105}$$

where Z = charge on the ligand, e = electronic charge, a = metal-ligand distance and r = distance of the electron from the nucleus. Electronic spectra of complexes give the experimental value of  $10Dq$ .

The symbol t denotes the triplet orbital degeneracy while e symbolise two fold degeneracy. The terms  $t_{2g}$  and  $e_g$  has the origin in group theory—the subscript 2 indicates particular symmetry operations. The subscript g stands for gerade or even (Sec. 3.4.4). In octahedral crystal field the metal is at the centre of inversion so g term is applied for centrosymmetric octahedral field while in tetrahedral field g term is omitted because the tetrahedron has no centre of inversion.

Now a question arises how the  $t_{2g}$  electrons are stabilised by the amount  $-\frac{2}{5}\Delta_0$  or  $-4Dq$

while  $e_g$  electrons are stabilised by  $+\frac{3}{5}\Delta_0$  or  $+6Dq$  with respect to the average energy of five degenerate d-orbitals in a spherical crystal field? When an electron in a complex resides on  $t_{2g}$  orbital which experiences less repulsive force by the ligands in an octahedral complex than in the hypothetical spherical complex. The ligands are able to move closer to the metal ion along the d-electron free x, y and z axis, thereby donating their electrons more effectively to the metal ion and produce a more stable complex. The extra energy evolved as a result of this non-spherical interaction is called the crystal field stabilisation energy (CFSE). Since this energy term arises due to the interaction of ligand d-orbital interaction so this is also called ligand field stabilisation energy (LFSE). The CFSE is also defined as the amount of energy gained by a  $d^n$  system due to the preferential filling of electrons in  $t_{2g}$  and  $e_g$  orbitals. Therefore the metal ion in spherical field has zero CFSE. The stabilisations resulting from the three  $t_{2g}$  orbitals must just balance the repulsions from the two  $e_g$  electrons. Naturally, the repulsion per  $e_g$  electron

is equal to  $\frac{3}{2}$  times the stabilisation per  $t_{2g}$  electron. This can also be stated in other way. Let each  $e_g$  electron will go up by an amount of energy  $\alpha$  and each  $t_{2g}$  electron will go down by an amount of energy  $\beta$  and if E is energy per electron in a hypothetical spherical field, then according to barycentre rule we can say,

$$10E = 4(E+\alpha) + 6(E-\beta) \quad \text{or} \quad 2\alpha = 3\beta$$

$$\text{again, } \alpha + \beta = \Delta_0 \text{ or } 10Dq, \text{ so that } \alpha = \frac{3}{5}\Delta_0 \text{ and } \beta = \frac{2}{5}\Delta_0.$$

Therefore taking the spherical field energy as zero, each  $e_g$  electron will be destabilised by an amount  $+\frac{3}{5}\Delta_0$  or  $+6Dq$  or  $+0.6\Delta_0$  and each  $t_{2g}$  electron will be stabilised by an amount of  $-\frac{2}{5}\Delta_0$  or  $-4Dq$  or  $-0.4\Delta_0$ .

### 7.14.2(B) Pairing energy : High and low spin electron configuration

CFSE primarily depends on the extent of crystal field splitting parameter  $\Delta_0$  and the number of electrons occupying  $t_{2g}$  and  $e_g$  orbitals. However it, also depends on whether pairing of electron(s) takes place or not. The CFSE is the sum of the energies of all the metal d-electrons of a particular  $d^n$  ion in an octahedral field compared to that of the hypothetical spherical field. Let a particular  $d^n$  ion has the configuration  $t_{2g}^x e_g^y$  where  $x$  and  $y$  are the electrons occupied by  $t_{2g}$  and  $e_g$  orbitals, so that,

$$\text{energy, } E = x\left(-\frac{2}{5}\Delta_0\right) + y\left(+\frac{3}{5}\Delta_0\right) + ZP \quad \dots(7.41)$$

where  $P$  denotes the pairing energy and  $Z$  is the number of electrons paired in the particular electron configuration.

For  $d^1, d^2, d^3, d^8, d^9$  and  $d^{10}$  systems, there will be no scope for alternative arrangements of electrons in  $t_{2g}$  and  $e_g$  orbitals (Fig. 7.6). So these systems have fixed  $E$  values.

$e_g$	---	---	---	$\uparrow\uparrow$	$\uparrow\downarrow$	$\uparrow\downarrow$
$t_{2g}$	$\uparrow$ --	$\uparrow\uparrow$ -	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow\uparrow$
$d^1=t_{2g}^1$	$d^2=t_{2g}^2$	$d^3=t_{2g}^3$	$d^8=t_{2g}^6 e_g^2$	$d^9=t_{2g}^6 e_g^3$	$d^{10}=t_{2g}^6 e_g^4$	

Figure 7.6 : Configurations of  $d^1$  to  $d^3$  and  $d^8$  to  $d^{10}$  systems in octahedral field.

For  $d^4, d^5, d^6$  and  $d^7$  systems alternative arrangements of the occupation of electrons in  $t_{2g}$  and  $e_g$  orbitals occur (Fig. 7.7). For a  $d^4$  metal ion e.g.  $\text{Cr}^{2+}$ , the fourth electron may be paired either to the three  $t_{2g}$  orbitals or may be promoted to the higher  $e_g$  orbitals depending upon the strength of the crystal field. There will operate two opposing forces in these configurations ( $d^4, d^5, d^6$  and  $d^7$ ). The crystal field splitting  $\Delta_0$  or  $10Dq$  will force to pair as many electrons into the lower  $t_{2g}$  orbitals while pairing energy ( $P$ ) will counter spin pairing. In fact when  $\Delta_0 > P$ , the electron(s)

High spin (a)	$e_g$	$\uparrow -$	$\uparrow\uparrow$	$\uparrow\uparrow$	$\uparrow\uparrow$
	$t_{2g}$	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow\uparrow$
	$d^4=t_{2g}^3 e_g^1$		$d^5=t_{2g}^3 e_g^2$	$d^6=t_{2g}^4 e_g^2$	$d^7=t_{2g}^5 e_g^2$
	$E = -0.6\Delta_0$		$E = 0$	$E = -0.4\Delta_0 + P$	$E = -0.8\Delta_0 + 2P$
Low spin (a)	$e_g$	---	---	---	$\uparrow -$
	$t_{2g}$	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow\uparrow$	$\uparrow\uparrow\uparrow$
	$d^4=t_{2g}^4$		$d^5=t_{2g}^5$	$d^6=t_{2g}^6$	$d^7=t_{2g}^6 e_g^1$
	$E = -1.6\Delta_0 + P$		$E = -2\Delta_0 + 2P$	$E = -2.4\Delta_0 + 3P$	$E = -1.8\Delta_0 + 3P$

Figure 7.7 : Energy level diagram of  $d^4, d^5, d^6$  and  $d^7$  metal ions (a) high spin configuration i.e. weak field ligand (b) low spin configuration i.e. strong field ligand.

is force to pair to the lower  $t_{2g}$  orbitals and we get low spin complex i.e. strong field ligand will produce low spin complex. Complexes in which the metal d-electrons would pair than fight the strong electric field of donor atoms are known as strong field complexes i.e. low spin complexes e.g.  $[\text{Cr}(\text{CN})_6]^{4-}$  ( $\text{Cr}^{2+}, d^4$  system). On the other hand when  $\Delta_0 < P$ , the electrons are free to move from lower  $t_{2g}$  to upper  $e_g$  orbitals and we get high spin complexes i.e. weak field ligands formed high spin complex. Complexes in which the metal d-electrons can more readily overcome the electric field of the ligands are known as weak field complexes i.e. high spin complexes e.g.  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ . It is to be noted that if we put  $\Delta_0 = P$ , the energy for both the high spin states are equal. We may generalise that in crystal field terminology the low spin and the high spin complexes correspond, respectively to the inner orbital and outer orbital complexes in valence bond theory.

### 7.14.2(C) Tetrahedral complexes

In a tetrahedral complex the splitting pattern of d-orbitals are just reverse to that of octahedral complexes. A tetrahedral arrangement can be considered by taking alternate corners of a cube (Fig. 7.9). In a tetrahedral complex none of the d-orbitals are directed along the metal-ligand bond axes but the orientation of the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals are such that their lobes are much closer to the metal-ligand bond axes than the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals. So the  $d_{xy}$ ,  $d_{yz}$  and  $d_{xz}$  orbitals ( $t_2$  set, here g subscript will be dropped) will experience greater repulsive force than the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals (e set). As a result maintaining the barycentre rule the  $t_2$  set will go up and e set will go down (Fig. 7.10). As the four ligands come closer to the metal, first a spherical field is operated (Fig. 7.10). Here the energy of the metal d-orbitals is raised but the degeneracy will not be lifted. Finally when the ligands are positioned at the four corners of the tetrahedron, the splitting occurs. The difference in energy between  $t_2$  and e sets of orbitals is called crystal field splitting for tetrahedral complexes and denoted by  $\Delta_t$ .

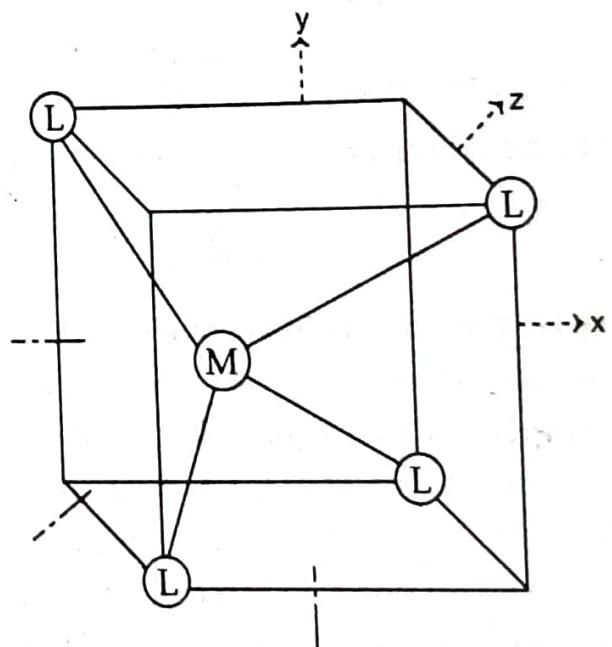
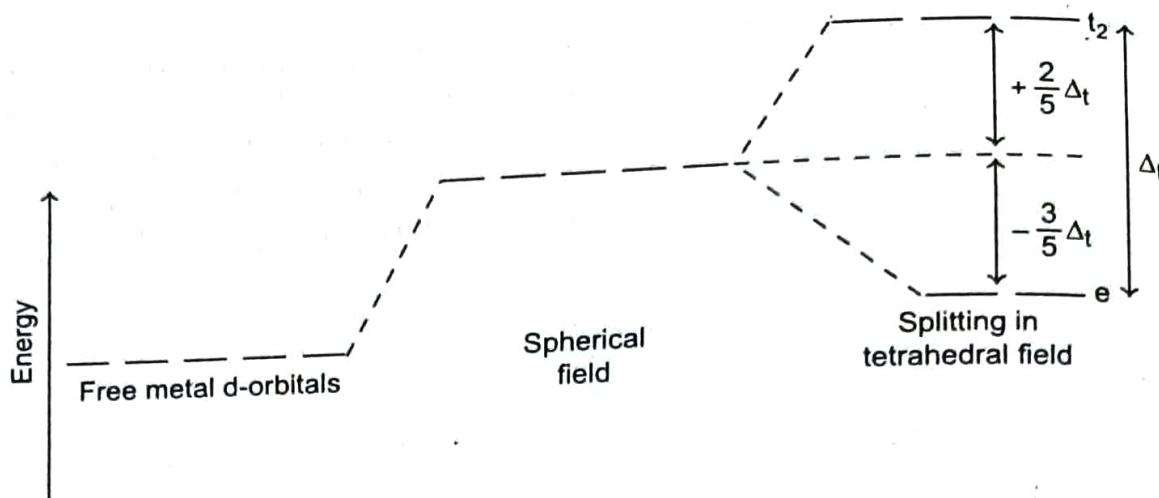


Figure 7.9 : A tetrahedral arrangements of four ligands in a cube.



**Figure 7.10 : Crystal field splitting (qualitative) in tetrahedral geometry.**

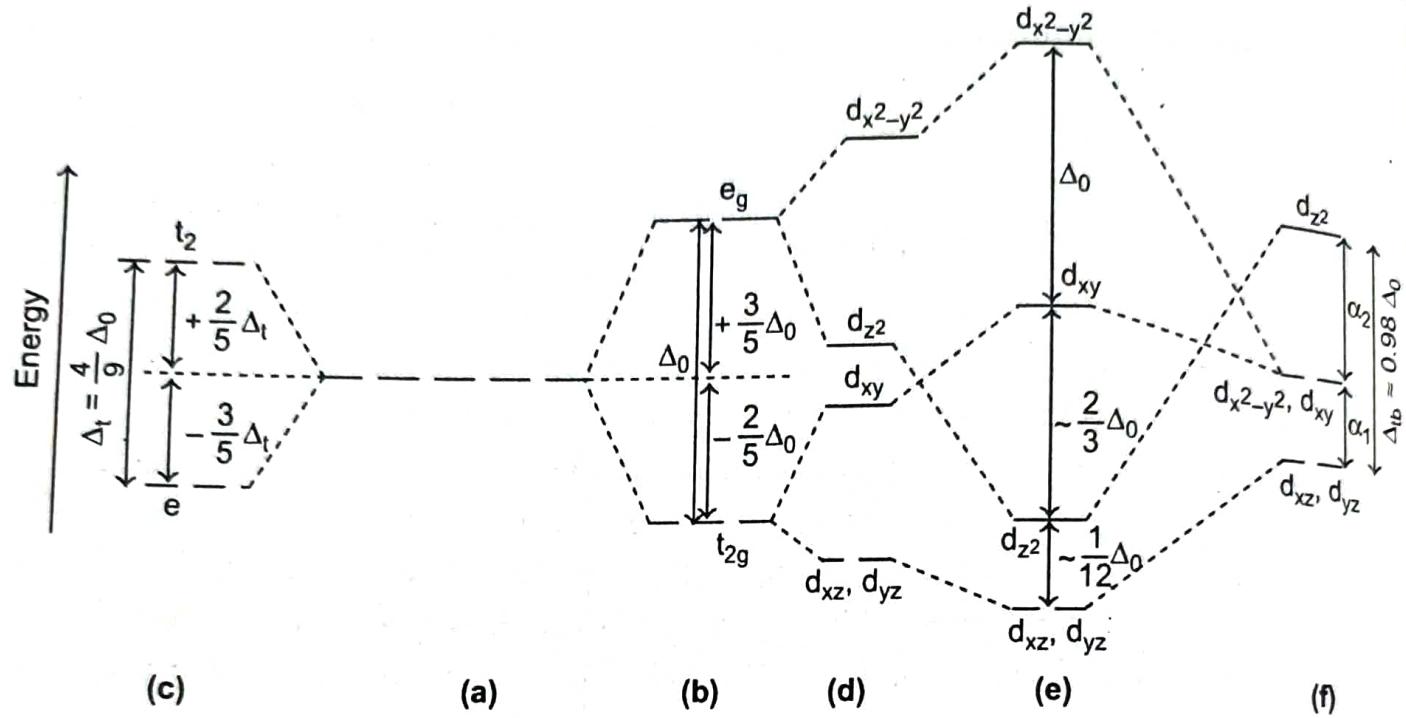
The magnitude of crystal field splitting  $\Delta_t$  is smaller than that of octahedral field ( $\Delta_0$ ). This is due to the following two reasons :

- There are only four ligands in tetrahedral complex compared to that of six ligands in octahedral one so that four ligands will create more weaker crystal field compared to that of six ligands. The crystal field splitting will therefore  $\frac{4}{6}$  times i.e.  $\frac{2}{3}$  times less in tetrahedral geometry.
- Unlike the octahedral geometry, none of the metal-ligand bonds are along the coordinate axes x, y and z. This reduces the crystal field splitting  $\Delta_t$  further by  $\frac{2}{3}$  times.

Therefore the crystal field splitting parameter  $\Delta_t$  is  $\frac{2}{3} \times \frac{2}{3}$  or  $\frac{4}{9}$  times that of octahedral crystal field i.e.

$$\Delta_t = \frac{4}{9} \Delta_0 \quad \dots(7.42)$$

This indicates that tetrahedral field always weaker than octahedral field i.e.  $\Delta_t < \Delta_0$  so that all tetrahedral complexes are weak enough to initiate spin pairing. Therefore **all tetrahedral complexes exist as high spin**. There is no longer any need of the weak-field/strong-field distinction in case of tetrahedral geometry. Moreover the CFSE for tetrahedral complexes is less than that of octahedral complexes so that octahedral complexes are more stable and more numerous compared to that of tetrahedral analogs. Equation (7.42) indicates tetrahedral splitting is less than half the octahedral splitting e.g.  $[\text{Co}(\text{NH}_3)_6]^{2+}$  and  $[\text{Co}(\text{NCS})_4]^{2-}$  have  $\Delta_0$  and  $\Delta_t$  values 10.1 and 4.9 kK respectively (1 kK = 1000 cm<sup>-1</sup>) (kK = kilo Keyser).



**Figure 7.12 :** Qualitative energy level diagram for the splitting of  $d$ -orbitals in different geometries :  
 (a) Hypothetical spherical field, (b) Octahedral geometry, (c) tetrahedral symmetry, (d) tetragonal distortion,  
 square pyramidal geometry, (e) square planar stereochemistry and (f) trigonal bipyramidal geometry.

### 7.14.3 Crystal field stabilisation energy

This is an important term used in modern coordination chemistry. Owing to the perturbation of d-orbitals in a complex, the extra stability gained by a  $d^n$  ion due to preferential filling of lower lying d-orbitals is called **crystal field stabilisation energy** or **ligand field stabilisation energy**, abbreviated as CFSE or LFSE. This can be calculated mainly for tetrahedral and octahedral complexes of different metal ions in terms of  $Dq$  values. Equation (7.41) denotes the calculation of energy in octahedral geometry where P indicates pairing energy. In the calculation of CFSE the pairing energy may be ignored but has to be considered to calculate the total energy (Fig. 7.7). Omission of P term in the expression for CFSE is justified from the fact that crystal field splitting tends to force as many electrons in the lower energy  $t_{2g}$  orbital while P tends to decouple the spin pairing and thus tends to put electrons in the upper  $e_g$  levels. Pairing of electrons is an unfavourable process. Pairing energy is the energy of repulsion between paired electrons in the same orbital and represents the price that we must pay in energy if we are to violate Hund's rule of maximum multiplicity. Thus P opposes the stabilisation energy due to perturbation of d-orbitals in crystal field. Appreciating this it is better to drop the term P in the

**Table 7.11 : CFSE/LFSE for tetrahedral and octahedral geometries**

$d^n$ system	Octahedral		Tetrahedral ( $\Delta_t = \frac{4}{9}\Delta_0 = 4.44 Dq$ )
	High spin	Low spin	
$d^1$	$-0.4\Delta_0/-4Dq$	$-0.4\Delta_0/-4Dq$	$-0.6\Delta_t = -0.266\Delta_0 = -2.66 Dq$
$d^2$	$-0.8\Delta_0/-8Dq$	$-0.8\Delta_0/-8Dq$	$-1.2\Delta_t = -0.532\Delta_0 = -5.32 Dq$
$d^3$	$-1.2\Delta_0/-12Dq$	$-1.2\Delta_0/-12Dq$	$-0.8\Delta_t = -0.355\Delta_0 = -3.55 Dq$
$d^4$	$-0.6\Delta_0/-6Dq$	$-1.6\Delta_0/-16Dq$	$-0.4\Delta_t = -0.177\Delta_0 = -1.77 Dq$
$d^5$	0	$-2\Delta_0/-20Dq$	0
$d^6$	$-0.4\Delta_0/-4Dq$	$-2.4\Delta_0/-24Dq$	$-0.6\Delta_t = -0.266\Delta_0 = -2.66 Dq$
$d^7$	$-0.8\Delta_0/-8Dq$	$-1.8\Delta_0/-18Dq$	$-1.2\Delta_t = -0.532\Delta_0 = -5.32 Dq$
$d^8$	$-1.2\Delta_0/-12Dq$	$-1.2\Delta_0/-12Dq$	$-0.8\Delta_t = -0.355\Delta_0 = -3.55 Dq$
$d^9$	$-0.6\Delta_0/-6Dq$	$-0.6\Delta_0/-6Dq$	$-0.4\Delta_t = -0.177\Delta_0 = -1.77 Dq$
$d^{10}$	0	0	0

expression of CFSE/LFSE in all the geometries of metal complexes (Table 7.11). The single electron energies of the different d-orbitals of a central metal ion for different geometries have been calculated assuming the same overall charge density and metal-ligand distance. These values are tabulated in terms of  $\Delta_0$  value for octahedral geometry (Table 7.12). These values are useful for calculating CFSE/LFSE for different types of complexes. It may be noted from Table 7.12 and Fig. 7.12 that square planar complexes have high CFSE so that square planar configuration is more stable than octahedral configuration. It should be memorised that :

**Table 7.12 : Energy of an electron ( $\Delta_0/Dq$ ) in different d-orbitals in different crystal fields**

Coordination number	Geometry	$d_{z^2}$	$d_{x^2-y^2}$	$d_{xy}$	$d_{xz}/d_{yz}^*$
2	Linear (along z axis)	1.028/10.28	-0.628/-6.28	-0.628/-6.28	0.114/1.14
3	Trigonal planar (in the xy plane)	-0.321/-3.21	0.546/5.46	0.546/5.46	-0.386/-3.86
4	Tetrahedral	-0.267/-2.67	-0.267/-2.67	0.178/1.78	0.178/1.78
4	Square planar (in the xy plane)	-0.428/-4.28	1.228/12.28	0.228/2.28	-0.514/-5.14
5	Trigonal bipyramidal	0.707/7.07	-0.082/-0.82	-0.082/-0.82	-0.272/-2.72
5	Square pyramid	0.086/0.86	0.914/9.14	-0.086/-0.86	-0.457/-4.57
6	Octahedral	0.600/6.00	0.600/6.00	-0.400/-4.00	-0.400/-4.00
7	Pentagonal bipyramidal	0.493/4.93	0.282/2.82	0.282/2.82	-0.528/-5.28
8	Cube	-0.534/-5.34	-0.534/-5.34	0.356/3.56	0.356/3.56
9	Tricapped trigonal prism	-0.225/-2.25	-0.038/-0.38	-0.038/-0.38	0.151/1.51
12	Icosahedral	0	0	0	0

\*  $d_{xz}/d_{yz}$  means the two orbitals have the same  $\Delta_0/Dq$  values.

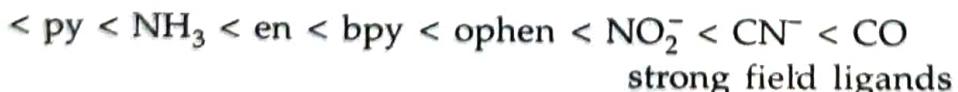
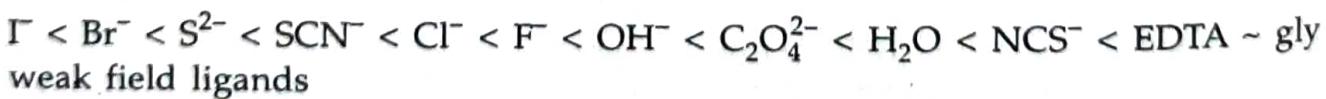
- (a) The  $10Dq$  or  $\Delta_0$  value is large for square planar geometry than for octahedral one.
- (b) Ligand-ligand repulsion is more in octahedral geometry compared to that of square planar configuration.
- (c) Total binding energy for six ligands are more compared to that of four ligands.

CFSE/LFSE value has an importance in assigning the stereochemistry and stability of complexes.

#### 7.14.4 Factors influencing the crystal field splitting

The following factors influence the variation of  $\Delta_0/10Dq$  values.

1. **Nature of the ligands and metal ions :** As mentioned earlier [Sec. 7.14.2(B)] the high and low spin states arises due to the character of ligands. In a particular geometry the magnitude of  $10Dq$  or  $\Delta_0$  depends on the following sequence of ligands irrespective of the nature of cations :



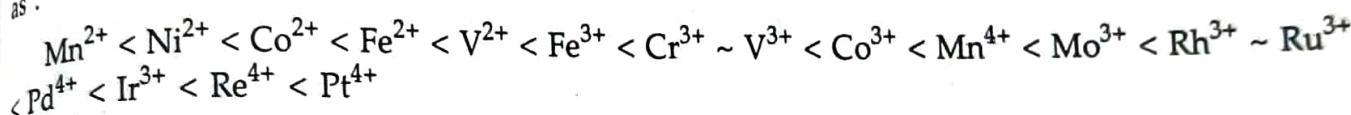
This is the well-known **spectrochemical series** or Fajans-Tsuchida series which is obtained from spectroscopic data. The C-bonded  $\text{CN}^-$  has the strongest crystal field strength and its  $Dq$  value

is about 1.7 times greater than that of water but N-bonded  $\text{CN}^-$  has the crystal field strength intermediate between that of  $\text{H}_2\text{O}$  and  $\text{NH}_3$ . The high crystal field strength of  $\text{CN}^-$  suggests that although  $\text{FeF}_6^{3-}$ ,  $\text{CoF}_6^{3-}$  are high spin,  $\text{Fe}(\text{CN})_6^{3-}$  and  $\text{Co}(\text{CN})_6^{3-}$  are low spin.

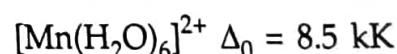
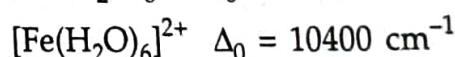
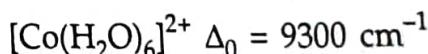
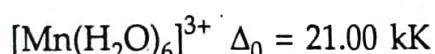
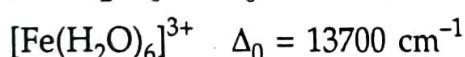
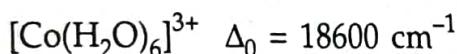
Similar with the spectrochemical series of ligands a spectrochemical series of metals can also be established. The approximate  $\Delta_0/10Dq$  can be estimated from the two independent parameters of metal and ligand i.e.

$$10Dq = f \times g$$

where  $f$  denotes the strength of the ligand relative to water ( $f=1$ ). The value of  $f$  generally in the range 0.7 to 1.7 and  $g$  values lie in the range 8.0 to 36.0 kK. All these results the variation of  $10Dq$  values of known octahedral complexes are in the range  $\sim 6000$  to  $\sim 45000 \text{ cm}^{-1}$ . As  $f$  and  $g$  values are valid for only octahedral geometry, so that significant variation of  $10Dq$  values may be observed (from the value of the product  $fg$ ) for other geometry of the complex. On the basis of  $g$  values metal ions are arranged which is known as **spectrochemical series of metals** as :



**2. Oxidation state of the metal ion :** Having the same ligand and same stereochemistry, the metal ion with higher oxidation state causes larger crystal field splitting than is done by the ion with lower oxidation state e.g.



With increase in oxidation state the metal-ligand bond length decreases due to the closer approach of ligands to metal and so  $\sigma$  bonding effect increases from ligand to metal. All these cause greater splitting of d-orbitals to a larger extent thereby larger values of  $10Dq$  is observed with increase of oxidation state of metals.

**3. Size of d-orbitals :** Given the same ligand, the same geometry, the same oxidation state  $\Delta_0$  values increases about 30-50% on going from first to second transition series and again by the same amount on going from second to third transition series i.e.

$$5\text{d} > 4\text{d} > 3\text{d}$$

This can be explained on the basis that 4d and 5d orbitals of second and third transition series respectively are bigger in size and spread out in space than the 3d orbital of first transition series. As a result the metal d-electrons in 5d orbital will experience smaller interelectronic repulsion compared to that of 4d electrons which in turn also experience less interelectronic repulsion than that of 3d electrons with that of the ligand orbitals. Since the interelectronic repulsion reduces as also nuclear charge increases from first to third transition series, so that there will be a closer approach of metal orbitals to ligand orbitals. This leads to highest perturbation of d-orbitals in case of third transition series (5d orbital) and will be less in case of 4d and also will be still less in case of 3d orbital. Thus the third transition series elements will register highest  $10Dq$  value and the first one will have a lowest value e.g.

### 7.14.5(C) Distortions from Regular geometry : The Jahn Teller Effect

In Sec. 7.14.2(D) we have seen how tetragonal distortion of an octahedral complex ( $ML_6$ ) leading to the formation of square planar ( $ML_4$ ) one (Fig. 7.12). In a regular octahedral complex splitting of the d-orbitals provide greater stability by CFSE. Further removal of degeneracy of upper  $e_g$  and lower  $t_{2g}$  level can sometimes result additional stabilisation of the system. The additional stabilisation is executed by a theorem which is well known Jahn-Teller theorem developed in 1937. This is actually the extension of tetragonal distortion leading to the formation of additional stabilisation. This states that *any nonlinear molecular system in degenerate electronic state will undergo some kind of distortion which will lower the energy and split the degenerate state.* This is also a case of wave mechanical phenomenon. This theorem only

*Limitations of Jahn-Teller theorem*

states the distortion of degenerate states but does not give any idea of geometrical nature of distortion as also the magnitude and direction of distortion. This does not state if the undistorted configuration has a centre of symmetry, whether it will be maintained or not after distortion. However this theorem can be applied with systems having unsymmetrically filled  $e_g$  level e.g.

$d^4$  (high spin) : Cr(II), Mn(III) ( $t_{2g}^3 e_g^1$ )

$d^7$  (low spin) : Ni(III), Co(II) ( $t_{2g}^6 e_g^1$ )

$d^9$  : Cu(II) ( $t_{2g}^6 e_g^3$ )

The reason behind this distortion is rather easy to understand. Let us begin with  $3d^9$  ( $Cu^{2+}$ ) octahedral complex where  $e_g$  orbitals ( $d_{x^2-y^2}$  and  $d_{z^2}$ ) have unequal population. The electrons in the  $d_{x^2-y^2}$  orbital repel the electrons donated by four ligands along the  $x$  and  $y$  axes, the electrons in the  $d_{z^2}$  orbital repel the electrons of two ligands along the  $z$  axis. If the two orbitals ( $d_{x^2-y^2}$  and  $d_{z^2}$ ) are equally populated then the repulsion would be same but practically the two orbitals ( $d_{x^2-y^2}$  and  $d_{z^2}$ ) are unequally populated so that we have to decide by physical reasoning which electronic configuration is permitted by which the repulsion is minimised :

- (1) Let the electronic configuration is  $d_{x^2-y^2}^2 d_{z^2}^1$ . The four ligands in the  $xy$  plane will be more screened from the electrostatic attraction of the  $Cu(II)$  ion than the two ligands along the  $z$  axis. Thus the two axial ligands will be drawn more closely than the other four equatorial ligands i.e. the ligands along the most populated axis will move farther away while the ligands along the less populated axis will move closer. These opposing motions will produce **tetragonally distorted octahedral geometry with a contraction along  $z$  axis**.
- (2) Let the electronic configuration is  $d_{x^2-y^2}^1 d_{z^2}^2$ . The four ligands along the  $xy$  plane will be less screened from the electrostatic attraction of the  $Cu^{2+}$  ion than the two ligands along the  $z$  axis and thus the four ligands along the  $xy$  plane will be drawn more closer than the other two ligands on the  $z$ -axis. In this case we get **tetragonally distorted octahedron with elongation along  $z$ -axis**.

In either case, the unequal bond lengths lower the symmetry below that expected for a regular octahedral structure. Experimentally for  $Cu(II)$  we find that elongation occurs along  $z$  axis with two long axial bonds and four short equatorial bonds along the  $xy$  plane. Therefore the orbitals having the  $z$  component among both the  $e_g$  and  $t_{2g}$  orbitals are stabilised with respect to orbitals having  $x$  and  $y$  components. As a result, the degeneracy of  $e_g$  orbital is lifted as also for  $t_{2g}$  orbital partly (Fig. 7.17). The centre of gravity rule is followed and we get a net stabilisation of the system equal to  $-\frac{1}{2}\delta_1$ . There will be no net change of stabilisation for the  $t_{2g}$  electrons. The electron configuration of  $Cu^{2+}$  is thus  $t_{2g}^6 d_{z^2}^2 d_{x^2-y^2}^1$ . Due to the net gain in stability by  $-\frac{1}{2}\delta_1$ , which motivates the system to undergo distortion. Mixed ligand complexes undergo this type of distortion due to the different types of crystal field strength of ligands.

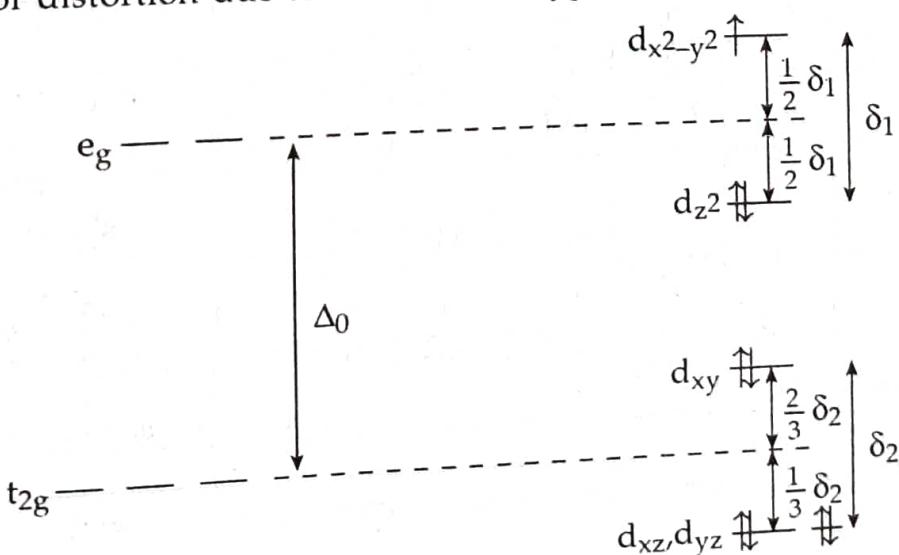


Figure 7.17 : Jahn-Teller distortion of an octahedral  $3d^9$  ( $Cu^{2+}$ ) complex ( $\delta_1, \delta_2 \ll \Delta_0$ ).