# Tetragonal distortion

The six co-ordinated complexes in which all the six distances between the ligand electron clouds and central metal ion are not equal, they are said to be distorted octahedral complexes. The change in shape is called distortion.

Distorted octahedral complexes may be of the three types (a) Diagonally distorted octahedral complexes which are obtained when the distortion of a regular octahedron takes place along a two-fold axis.

(b) Trigonally distorted octahedral complexes in which the distortion takes place along a three-fold axis.

(c) Tetragonally distorted octahedral complexes which are also known as tetragonal complexes. These are obtained when the distortion of a regular octahedron takes place along a four-fold axis.

Tetragonal distortion may be obtained by any of the following two ways-

(i) If the two trans ligands lying along the z-axis in an octahedral complexes are moved away, the resulted tetragonal structure has two long bonds along the z-axis and four short bonds in xy-plane. The resulted distortion, termed as tetragonal elongation or z-out distortion.

(ii) If the two trans ligands lying along the z-axis in an octahedral complexes are moved in, the resultant tetragonal structure has two short bonds along the z-axis and four long bonds along the xy-plane. The resultant distortion, termed as tetragonal compression or z-in distortion.

However tetragonal distortion may arise from

(A) Unevenligation on the equatorial and axial sites of a six-coordinate complex e.g. trans $ML_4X_2$. Since the CF strengths of equatorial L and axial X are different the $t_{2g}$ and $e_g$ sets will split further. Taking X as weaker than L it can be seen that the $d_{z^2}$ orbital will be further stabilised while $d_{x^2-y^2}$ orbital will be destabilised. Again the $d_{xz}$ and $d_{yz}$ orbitals (with z components) will be stabilised while the $d_{xy}$ orbital will be destabilised. If the two trans ligands pulled

## Condition for distortion:

a) The d-orbitals which have both $t_{2g}$ and $e_g$ sets as symmetrical orbitals lead to perfectly symmetrical (i.e regular) octahedral complexes has no distortion. Thus ~~a~~ configs which have no distortions are:

LS complex:
- $d^0 (t_{2g}^0 e_g^0)$
- $d^3 (t_{2g}^3 e_g^0)$
- $d^6 (t_{2g}^6 e_g^0)$
- $d^{10} (t_{2g}^6 e_g^4)$

HS complex:
- $d^0 (t_{2g}^0 e_g^0)$
- $d^3 (t_{2g}^3 e_g^0)$
- $d^5 (t_{2g}^3 e_g^2)$
- $d^{10} (t_{2g}^6 e_g^4)$

(b) When d-orbitals of the central metal ion of an octahedral complex have $t_{2g}$ orbitals as unsymmetrical orbitals, there occurs slight distortions in the complex. Thus

HS complex:
- $d^1 (t_{2g}^1 e_g^0)$
- $d^2 (t_{2g}^2 e_g^0)$
- $d^6 (t_{2g}^4 e_g^2)$
- $d^7 (t_{2g}^5 e_g^2)$

and

LS complexes show slight distortion:
- $d^1 (t_{2g}^1 e_g^0)$
- $d^2 (t_{2g}^2 e_g^0)$
- $d^4 (t_{2g}^4 e_g^0)$
- $d^5 (t_{2g}^5 e_g^0)$

(c) whenever the $e_g$ orbitals which point directly towards the ligands, are unsymmetrical we expect strong distortions.

Thus.
- $d^4 (t_{2g}^3 e_g^1)$
- $d^9 (t_{2g}^6 e_g^3)$

} HS complex and

LS complexes show strong distortion & even to square planar geometry:
- $d^7 (t_{2g}^6 e_g^1)$
- $d^9 (t_{2g}^6 e_g^3)$
- $d^8 (t_{2g}^6 e_g^2)$

Examples: (i) $[Ti(H_2O)_6]^{3+}$ has a compressed octahedron with two short axial Ti-O bond while four long Ti-O equatorial bond.

(ii) $[Cu(H_2O)_6]^{2+}$ has two longer axial bond and four shorter bonds in xy-plane.

(iii) $[Cu(NH_3)_4]^{2+}$ is a perfect square planar.

(iv) Low spin complexes of $d^8$ ions i.e $Ni^{2+}$, $Pd^{2+}$, $Pt^{2+}$ form $[M(diars)_2I_2]$ square planar complex.

(iv) In $K_2CuF_4$, the $Cu^{2+}$ ion has two $F^{\ominus}$ at 1.95 Å and four at 2.08 Å

(v) In $FeF_2$, the $Fe^{2+}$ ion has two $F^{\ominus}$ at 1.99 Å and four at 3.12 Å

(vi) In $CuCl_2$ crystal each $Cu^{2+}$ ion is surrounded by six $Cl^{\ominus}$ ions four are at a distance of 2.30 Å and the other two are 2.95 Å away

(vii) In $CuF_2$ crystal Four $F^{\ominus}$ ions are 1.93 Å away from $Cu^{2+}$ ion while the two $F^{\ominus}$ ions are 2.27 Å apart.

## J-T distortion in $[Cu(H_2O)_6]^{2+}$

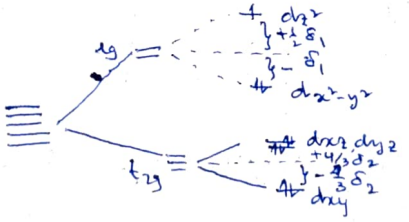
The central metal ion in the complex ion is $Cu^{2+}$; is a $d^9$ system.

Two alternative config$^{n}$ have been suggested

Case I = $t_{2g}^6 \, d_{x^2-y^2}^2 \, d_{z^2}^1$

Case II = $t_{2g}^6 \, (d_{z^2})^2 \, (d_{x^2-y^2})^1$

If the config$^{n}$ is CasI, then four ligand in the xy plane experiences much more repulsion compared to axial ligands Thus two bonds are shorter and four bonds are longer. The splitting of d-orbitals will be a 2-in distortion.




JTSE = JTSE in $t_{2g}$ set + JTSE in $e_g$ set

$= -\frac{1}{2}\delta_1$

If the config$^{n}$ is case II, then two axial ligand will experiences much more repulsion and moved away while four ligand in xy plane gets less repulsion. Thus four bonds will be short and two axial bond will be long. The splitting of 'd' orbitals will be a 2-out distortion.


JTSE = JTSE in $t_{2g}$ splitting + JTSE in $e_g$ splitting

$= \left[4(-\frac{1}{3}\delta_2) + 2\times(+\frac{2}{3}\delta_2)\right] + \left[2\times(-\frac{1}{2}\delta_1) + 1\times(+\frac{1}{2}\delta_1)\right]$

$= 0 - \frac{1}{2}\delta_1 = -\frac{1}{2}\delta_1$

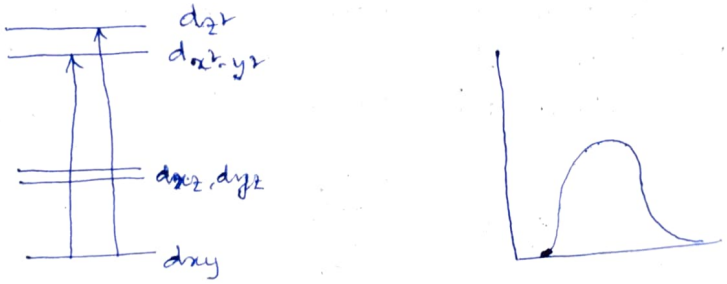
Thus from JTSE it can not be predicted that which config$^{n}$ is correct. However, experimental measurement found that two axial bonds are longer and four equatorial bonds are shorter, suggesting the second electronic config$^{n}$.

The systems gets extra stability of $\delta_{1/2}$ amount due to the unsymmetrical filling of $e_g$ orbitals. suggests the distorted $[Cu(H_2O)_6]^{2+}$ octahedral structure.

Evidence of J-T distortion:

① $Ti^{3+}$ (a $d^1$ ion) is sensitive to J-T distortion. For ligand out distortion, it gives the benifit of JTSE by an amount of $\frac{1}{3}\delta_2$ whereas for the ligand in distortion, the stabilisation energy is $\frac{2}{3}\delta_2$. Hence $O_h$ complexes of $Ti^{3+}$ will be compressed along z-axis.

The presence of J-T distortion is quite evident from the broadening of the absorption band. If there were no distortion a single band due to $t_{2g} \longrightarrow e_g$ should be observed. But due to the splitting of the orbitals caused by the distortion, atleast two close transition occurs which overlaps in a broad band.



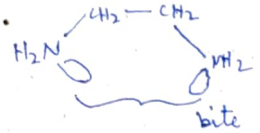

· The transition from $d_{xy} \rightarrow d_{xz}, d_{yz}$, falls in the IR region and hence not observed.

② HS $d^4$ complex e.g $[Mn(DMSO)_6]^{3+}$ having the $t_{2g}^3 e_g^1$ config$^{n}$ shows three closely associated band instead of a single absorption band ($t_{2g} \longrightarrow e_g^1$), which overlaps to a broad band.

③ $K_3CoF_6$ shows two broad peaks at around 15000 and 12000 $cm^{-1}$.

# Jahn- Teller distortion in chelates

Since, the chelate will have a preferred bite (the distance between the co-ordinating atoms) ↳ always spans to cis position the chelate ring tends to restrict the distortion of a complex from a regular octahedron (though trigonal distortion leading to prismitic complex is possible)




a chelating agent always spans cis position and for this it leads to restrict the distortion of $O_h$ complex.

However certain facts may be rationalized on the basis of the J-T distortion.

1) The trischelates of Cu (II) are very unstable. In general, the divalent transition metal ion form complexes with en by stepwise replacement of water.

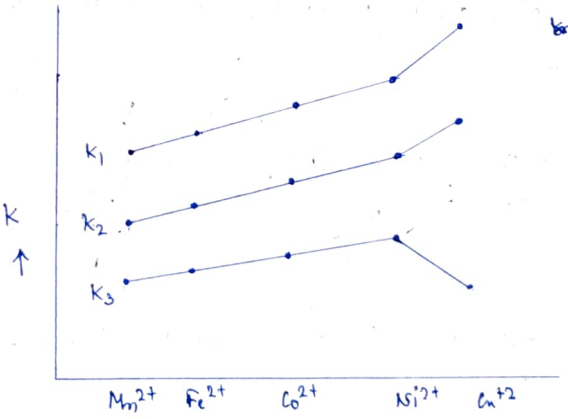
$$M(H_2O)_6]^{2+} + en \longrightarrow M(en)(H_2O)_4]^{2+} + 2H_2O$$

$$M(en)(H_2O)_4]^{2+} + en \longrightarrow M(en)_2(H_2O)_2]^{2+} + 2H_2O$$

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

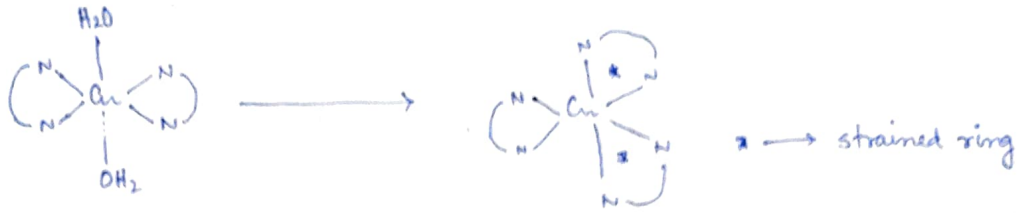
[ $RT \ln K = -\Delta G^\circ = -\Delta H^\circ + T\Delta S^\circ$
Higher the value of $\Delta S^\circ$ higher will be the value of K ]

The stepwise stability constant values show a regular increasing trend for the metal ion $Mn^{2+} \longrightarrow Cu^{2+}$. However, there is an exception for the $K_3$ value in case of $Cu^{2+}$. Though the $K_1$, $K_2$ values are highest for $Cu^{2+}$ but $Cu^{2+}$ complex has the lowest $K_3$ value indicating the remarkable instability of Cu(II) trischelates.




$K_1 > K_2 \gg K_3$

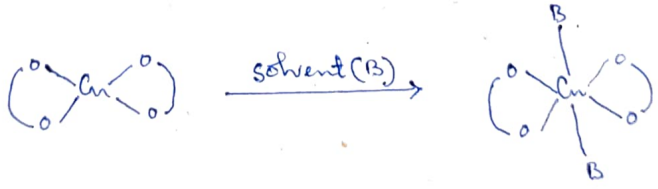
This lack of stability is evident due to the distortion necessary for a $d^9$ ion. The bischelate $[Cu(en)_2(H_2O)_2]^{2+}$ can distort by letting the two trans water molecules move out from the copper with the two ethylenediamine rings relatively unchanged. In contrast, the chelate can not distort tetragonally because it would introduce strain at least two of the chelate rings.



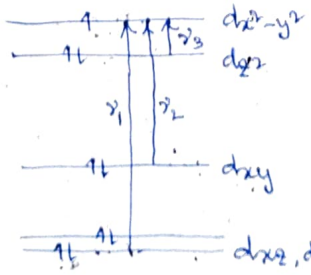

Alternatively, it may be said that the constraint of the chelate ring system will prevent tetragonal distortion and form a regular octahedron. But in this process the complex will lose the benifit of J-T stabilisation energy and the stability of the complex will be reduced.

The Cu(II) chelates with symmetrical structure e.g $Cu(en)_3]^{2+}$ are without any detectable stabilisation. On the otherhand, $[Cu(dipy)(hfacac)_2]$ ; hfacac = $CF_3$–C(=O)–CH–C(=O)–$CF_3$ , is known to be tetragonally distorted. It is not possible to predict, which complex will distort and which will not, although certainly a chelate ring system tends to inhibit distortion. This distortion in the chelates could not be explained on the basis of J-T distortion. Thus the theorm appears to be well suitated in simple systems - its predictive value in complex system is low.

2) The tetragonally distorted octahedral complexes of Cu(II) can give rise to three transitions. The frequencies of these transitions will depend upon the field experienced by the d-orbitals. $Cu(acac)_2$ has a sq. planar co-ordination (extreme tetragonal distortion). In basic solvents such as ethers, alcohols and amines, two solvent molecules co-ordinate along z-axis.



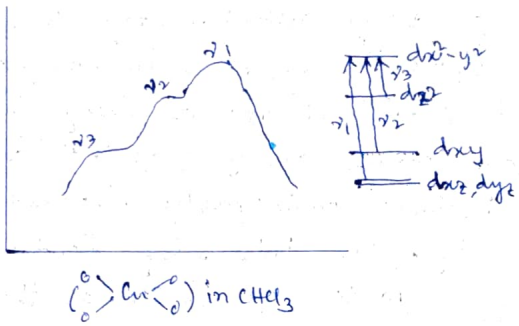

In tetragonal distortion is considerable, there will be evidently three transitions.



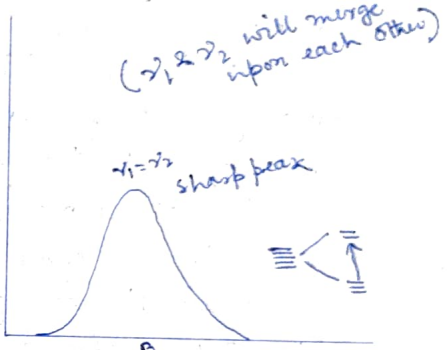

$\nu_2$ should remain constant at 10Dq for octahedral since neither the dxy or $dx^2-y^2$ has z-component.

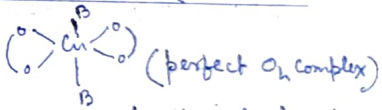
As the tetragonal field approaches the $O_h$ config$^n$, $\nu_1$ should diminish and approach $\nu_2$. The third transition $\nu_3$ will also

diminish and ultimately it will vanish (because in the $O_h$ config$^n$ $d_{x^2-y^2}$ and $d_{z^2}$ collapse to form degenerate $e_g$ orbital). Thus when the solvent in chloroform (extremely weak base), the complex will suffers the maximum J-T distortion. The analysis of the spectrum in $CHCl_3$ yields two major peaks ($\nu_1$, $\nu_2$) with a shoulder ($\nu_3$). As the basicity of the solvent is gradually increasing (dioxane, pentenol, pyridine, piperidine) it has been found that $\nu_2$ remains unaltered but $\nu_1$ gradually approaches to $\nu_2$ and the shoulder $\nu_3$ gradually vanishes (due to collapse of $d_{x^2-y^2}$ and $d_{z^2}$ orbitals). Thus when the solvent is piperidine, only a single transition ($\nu_2$) is observed, because the field is now almost regular octahedral.




($O_h$ Cu $O_h$) in $CHCl_3$




(perfect $O_h$ complex) in strongly basic medium

Types of J-T distortion.

i) Static Jahn-Teller distortion – results in a permanent distortion of the complex as in Cu(II), high spin Mn(III) and high spin Co(III). [measurable difference in bond length between two types of bond found]

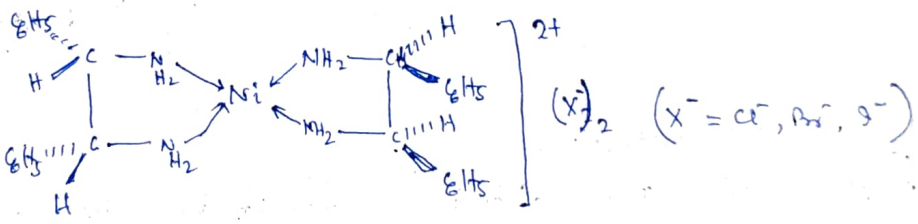
ii) Dynamic Jahn-Teller distortion – when the energy difference between the two possible distortions namely (i) four long equatorial bonds and two short axial bonds and (ii) four short equatorial bonds and two long axial bonds is minimal, the final time average structure may be close to an undistorted octahedron. Such a case is said to arise from dynamic Jahn-Teller distortion and is difficult to establish experimentally.

Thus $[Mn(H_2O)_6]^{3+}$ ($d^4$) and $[Cu(NO_2)_6]^{4-}$ assumes almost a perfect octahedral structure.

## Special case of distortion in Ni(II) Complex - structural equilib between spin state (Octahedral - square planar equilibrium in sol^n)

Ni(II) generally forms H.S $O_h$ complex, $[Ni(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$. This complexes are not expected to show distortion since both $t_{2g}$ and $e_g$ orbitals in these complex are symmetrically field as is evident form electronic config^n. $t_{2g}^6 e_g^2$ where the two electrons in $e_g$ level are distributed equally in the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals

However, some diamagnetic Ni(II) $O_h$ complexes e.g. $[Ni(diars)_4](ClO_4)_2$ have been isolated. Such diamagnetic complexes can only arise if the two electrons in the $e_g$ level pair up in $d_{z^2}$, leaving $d_{x^2-y^2}$ orbital empty. Thus the arrangement of two electrons in $e_g$ level is unsymmetrical and as a result the system will suffer a strong distortion. The two ligands along z-axis move away from $Ni^{2+}$ and as a result the $O_h$ complex becomes considerably distorted and assumes a square planar geometry. An interesting feature is observed with the Lifschitz salts, which are salts of the following cation -




Some of these are yellow and diamagnetic (sq. planar), Others are blue and paramagnetic $O_h$ ($\mu = 2.89$ BM) and still Others change from the the yellow to the blue form and black again upon heating and cooling, recrystallisation from certain solvents or removal or addition of solution of crystallisation. These observation be explained as due to structural change.

(Sq. planar diamagnetic yellow - i.e $d_{z^2}$ $d_{x^2-y^2}$) $\leftrightarrow$ distorted $O_h$ (diamagnetic yellow)

$\updownarrow$

$O_h$ (paramagnetic blue)

[This variation are caused by the approach of anion and/or solvent molecule to the central $Ni^{2+}$ ion in the crystal tending to complete an $O_h$, when the $O_h$ is not substaintially completed (tetragonal distortion of a high degree) the yellow diamagnetic form results, whereas when the field becomes $O_h$, the blue paramagnetic form appears]

[Situation is unfavourable and leads to square planar config$^n$ but the possibility of existance of LS $O_h$ (no doubt highly distorted) can not be ignored]

(b) Other diamagnetic, square complexes are also known to behave similarity e.g $[Ni(py)_4(ClO_4)_2]$ exist in two forms:

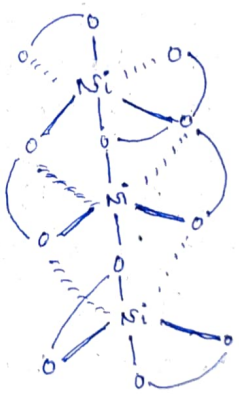
$[Ni(py)_4]^{2+}(ClO_4)_2$ — yellow, diamagnetic

$[Ni(py)_4(ClO_4)_2]$ — blue, paramagnetic

(c) monomer - polymer equilibria

monomer in non co-ordinating solvent

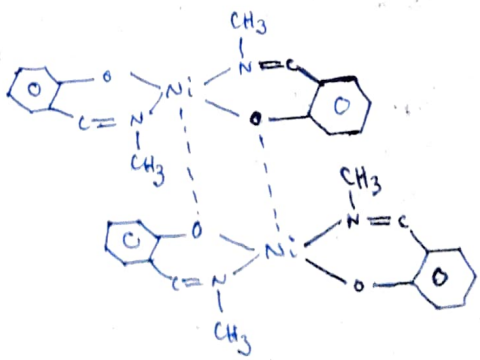
(red, diamagnetic)



acetylacetonate ion

(blue paramagnetic)

(d) N - methyl-salicylaldiminato complexes of Ni(II) in $CHCl_3$ or $C_6H_6$ show an equilibrium between diamagnetic monomer and the paramagnetic dimer with 5-coordinate high spin



(e) Square - tetrahedral equilibrium : Complexes of Ni(II) of the type $NiL_2X_2$ may have either square planar or tetrahedral structures depending on the nature of the ligand.

when L = $Ph_3P$ , complex is tetrahedral and

when L = $R_3P$ , complex is square planar

When L = alkyl aryl phosphine, the complex may exist in solution in an solution in an equilibrium mixture of both square planar and tetrahedral form.

e.g. $[NiBr_2(i\text{-}PrPPh_2)_2]$ is stable at 0°C (paramagnetic) isomerises to tetrahedral compd (paramagnetic) at 25°C at about 1 day.

John - Teller distortion in tetrahedral complex.

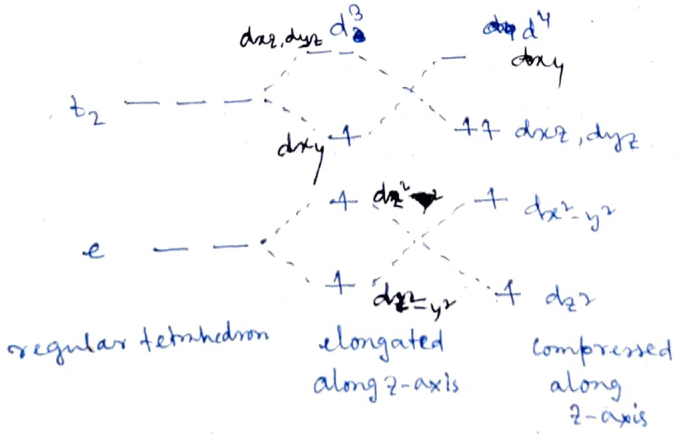
Td complexes are also expected to undergo J-T distortion with $d^3$, $d^4$, $d^8$ and $d^9$ config$^n$ where the $t_2$ orbitals are partially filled

$d^3$ ($e^2t_2^1$) and $d^8$ ($e^4t_2^4$) : elongation

$d^4$ ($e^2t_2^2$) and $d^9$ ($e^4t_2^5$) : flattening

In $d^3$ and $d^8$ config$^n$ one $t_2$ orbital has an additional electron than the other two ; this will provide better screening of the nuclear charge of the metal, ultimately resulting in a greater M-L distance i.e elongation. In $d^4$ and $d^9$, one $t_2$ orbital has one $e^\ominus$ less than the others and hence we expect contraction or flattening of the regular tetrahedral geometry.

Thus $[CuCl_4]^{2-}$ ion has a flattened tetrahedral structure while $[NiCr_2O_4]$ has an elongated tetrahedral co-ordination.




∴ J-T distortion in Td complexes of $d^3$ and $d^4$ ions.

$d^8$ metal ion will behave in the same manner as $d^3$ while $d^9$ metal ion will follow the pattern in $d^4$.