



WILSON COLLEGE, MUMBAI

DEPARTMENT OF CHEMISTRY

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INORGANIC CHEMISTRY

MODULE II

TOPIC: THEORIES OF THE METAL - LIGAND BOND

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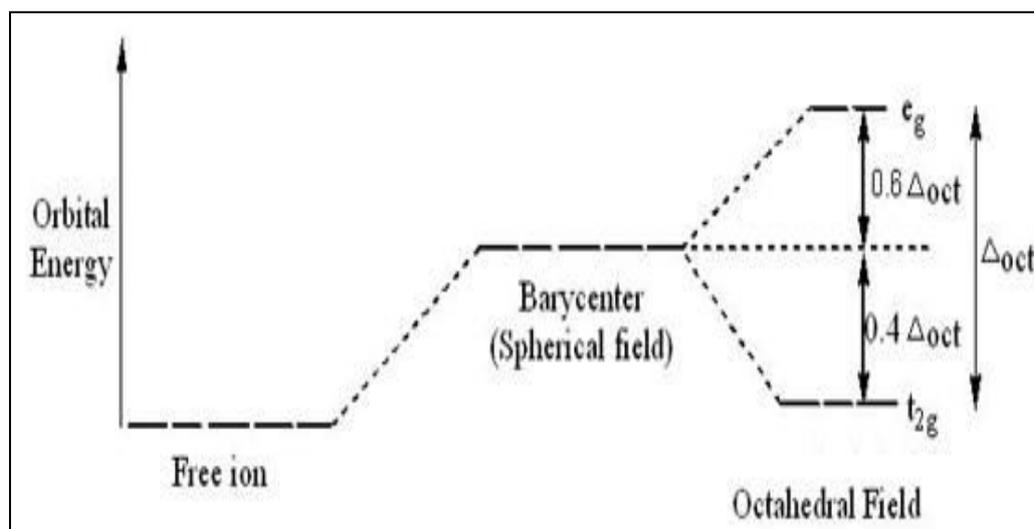
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LEARNING OUTCOMES

- Learners will know what is CFSE
- Learners will understand the distribution of electrons in d-orbitals in octahedral and tetrahedral complexes
- Learners will learn to calculate crystal field stabilisation energy in octahedral and tetrahedral complexes
- Learners will be able to understand when Distortions in Octahedral geometry takes place
- Learners will know Jahn-Teller theorem and different types of distortion

CRYSTAL FIELD STABILISATION ENERGY (CFSE) :

- a. The approach of six ligands towards the central metal can be considered as a two-step process.
- I. In the first step, the ligands just approach the metal and produce a hypothetical spherical field which repels all the *d-orbitals* to the same extent.
 - II. In the second step, the octahedral field brings out the splitting of *d* orbitals.
- b. The 'barycentre' or centre of gravity of the orbitals remains the same during the second step. That means, the energy of all the orbitals may be raised by the repulsion of the advancing ligands in step one but the arrangement of ligands from hypothetical spherical field to an octahedral field, will not alter the average energy of the set of *d-orbitals*.
- c. In other words, if the energy of the t_{2g} orbitals is $4Dq$ less, then to maintain barycentre constant the e_g orbitals should be $6Dq$ higher in energy than the hypothetical orbitals.



- d. For maintaining the average energy of the orbitals constant, the upper level must be $6Dq$ above the barycentre and the lower level $4Dq$ below it.
- e. In an octahedral complex with d^1 configuration, the d electron will occupy the orbital of lowest energy. Hence, it goes into one of the t_{2g} orbitals which have energy $4Dq$ less than the hypothetical degenerate orbitals.
- f. Thus, energy of the complex is lowered by $4Dq$ and subsequently it becomes more stable.
- g. This decrease in energy achieved by the preferential filling of the lower lying ' d ' levels, is called **crystal field stabilisation energy**. Hence for a complex with d^1 configuration the gain in CFSE is $4Dq$.
- h. CFSE is usually calculated by assigning a value of $-4Dq$ or $-0.4 \Delta_0$, for each electron placed in t_{2g} orbital and a value of $+6Dq$ or $+0.6 \Delta_0$, for each electron placed in e_g orbital. Thus, CFSE for a d^3 system is $3(-4Dq) = -12Dq$.
- i. The contribution of CFSE for stability of complex is very small compared to the larger stabilisation energy due to electrostatic forces of attraction in the ionic complex.
- j. The forces of attraction are so strong that when combined with electronic repulsions, the net energy of the system becomes lower than that of the isolated ions.

DISTRIBUTION OF ELECTRONS IN d orbitals & CFSE OCTAHADRAL COMPLEXES:

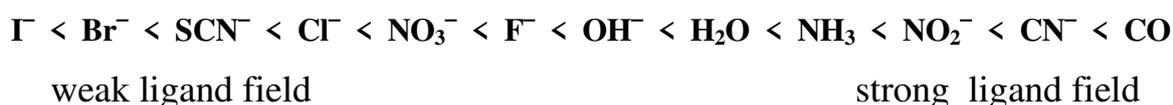
- a. Electrons prefer to occupy the orbitals of lower energy.
- b. Electrons obey Hund's rule, i.e. electrons pairing will not take place until all the available orbitals of a given set contain one electron each.

- c. If the energy to place an electron in the upper e_g level is greater than the energy to pair electrons (pairing energy = P) in the lower t_{2g} level, ($10 Dq > P$) then the electrons will pair up in t_{2g} orbitals.
- d. If the energy to place an electron in the upper e_g level is less than the pairing energy in the lower t_{2g} orbital ($10 Dq < P$), then the electrons will occupy e_g orbitals.

WEAK AND STRONG FIELD CASES :

- a. Ligands which cause only a small degree of splitting of d orbitals are **called weak field ligands**
- b. Ligands which cause a large splitting of d orbitals, are **called strong field ligands.**
- c. The magnitude of $10 Dq$ and hence the distribution of the electrons in d orbitals are very much influenced by the strength of the ligand field.

The crystal field splitting ability of ligands decreases in the following order.



- d. In a weak field, $10Dq$ is usually less than pairing energy, i.e., $10 Dq < P$. Hence electrons remain unpaired.
- e. But in the case of a strong field, $10 Dq > P$; hence electrons pair up in the lower energy orbitals.

CFSE and Electronic Arrangements in Octahedral Complexes

1. In octahedral complexes with d^1 configuration, the d electron will occupy the lower t_{2g} orbital, irrespective of the field strength and the crystal field stabilisation energy is $-4Dq$.

2. For d^2 configuration, the two electrons will occupy the lower two t_{2g} orbitals and CFSE is $-4 \times 2 = -8Dq$.
3. Similarly for d^3 configuration CFSE is $-12Dq$ and the t_{2g} level is just half filled.
4. Thus, complexes with d^1 , d^2 and d^3 configurations, irrespective of the ligand field strength, remain paramagnetic, with one, two and three unpaired electrons respectively.
5. For d^4 configuration, two possibilities arise, that is, the fourth electron can either enter the upper e_g level (Hund's Rule) or pair up in the lower t_{2g} level.
6. Which of these two arrangements occur depends upon the values of $10 Dq$ and P , which in turn depend upon the strength of the ligands.
7. In a weak field, $10 Dq < P$. Hence, the **fourth electron prefers to enter one of the e_g orbitals** rather than pairing in t_{2g} orbitals. This way, it loses somewhat less energy in the form of CFSE by entering the destabilised e_g level. The net CFSE energy is :

$$CFSE = (3 \times -4Dq) + (1 \times 6Dq) = -6Dq.$$

In a strong field, where $10 Dq > P$, **fourth electron prefers to pair up** in one of the three lower t_{2g} orbitals rather than entering the upper e_g orbitals. CFSE for this type of complex is $(4 \times -4Dq) = -16Dq + P$ because all the four electrons enter t_{2g} orbitals and some energy is used to pair up two electrons. The distribution of electrons in complexes with d^4 configuration is shown.:

8. Thus, for d^4 configurations the electronic arrangement differs in weak and strong fields. In the weak field there are four unpaired electrons while in the strong field, there are only two unpaired electrons. These two arrangements thus differ in the number of unpaired electrons. The arrangement with **maximum unpaired electrons** is called '**high spin**' or '**spin free**' and the

one with **minimum number of unpaired electrons** is called '**low spin**' or '**spin paired**' arrangement.

9. For d^5 configuration, in a weak field, three electrons occupy the t_{2g} orbitals and the other two, the two e_g orbitals (one in each). CFSE is zero because the presence of two electrons in the unfavourable level exactly balances the stabilisation from the three electrons in the t_{2g} level. In other words, the half filled shell (d^5) is physically symmetrical and no stabilisation can occur through the application of an external ligand field.

In case of strong field, the fifth electron will pair up in the t_{2g} orbital.

$$\therefore \text{CFSE} = -20Dq + 2P$$

10. For d^6 configuration in a weak field, the sixth electron will pair up in one of the lower t_{2g} orbitals because all the five d orbitals are already half filled. $\text{CFSE} = -4Dq + P$.

In case of strong field the sixth electron will pair up in the t_{2g} orbitals and all the three t_{2g} orbitals will have paired electrons.

$$\therefore \text{CFSE} = -24Dq + 3P$$

11. Similarly, for d^7 , d^8 , d^9 and d^{10} configurations, the d electrons of the metal can be distributed and their CFSE can be calculated.

12. From the table it is clear that for d^1 , d^2 , d^3 and d^8 , d^9 , d^{10} configurations, the distribution of electrons and CFSE are the same irrespective of the strength of the ligand field.

13. But for, configurations d^4 to d^7 , two arrangements (high spin and low spin) are possible depending upon the strength of ligand field.

14. The CFSE for the various EC can be calculated with the help of the general formula;

$$\text{CFSE} = [x(-4Dq) + y(+6Dq) + P]$$

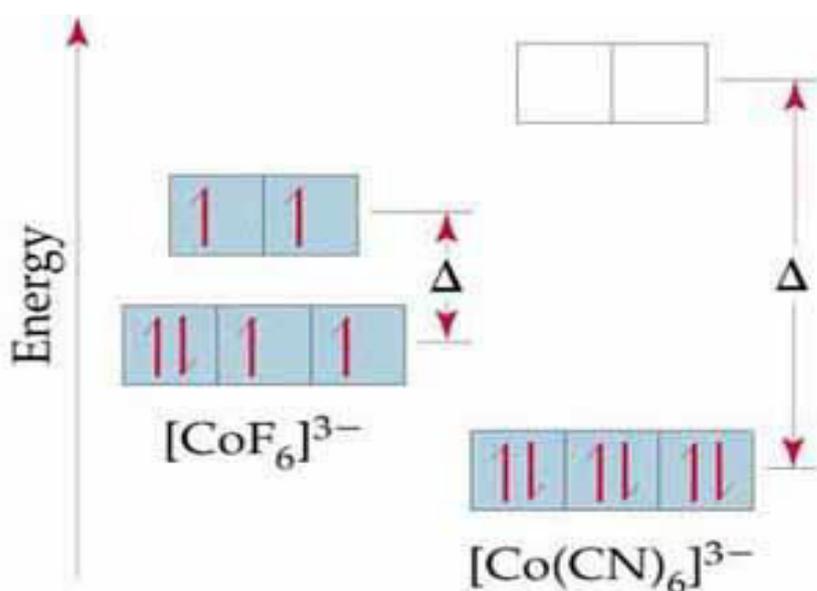
x = no. of electrons in t_{2g} orbitals

$y = \text{no. of electrons in } e_g \text{ orbitals}$

$P = \text{pairing energy}$

For example, the distribution of d electrons in Co^{3+} (d^6) complexes in presence of weak field $[\text{CoF}_6]^{3-}$ and strong field $[\text{Co}(\text{CN})_6]^{3-}$ can be shown

In $[\text{CoF}_6]^{3-}$ because $10Dq$ is less than P , electrons occupy even the higher e_g level and thus it has four unpaired electrons, i.e. high spin complex which is paramagnetic. In $[\text{Co}(\text{CN})_6]^{3-}$ since $10Dq$ is greater than P , the electrons pair up in the lower t_{2g} level and it has all paired electrons, i.e. low spin complex which is diamagnetic. Thus, on the basis of CFT, magnetic properties of complexes can be explained.

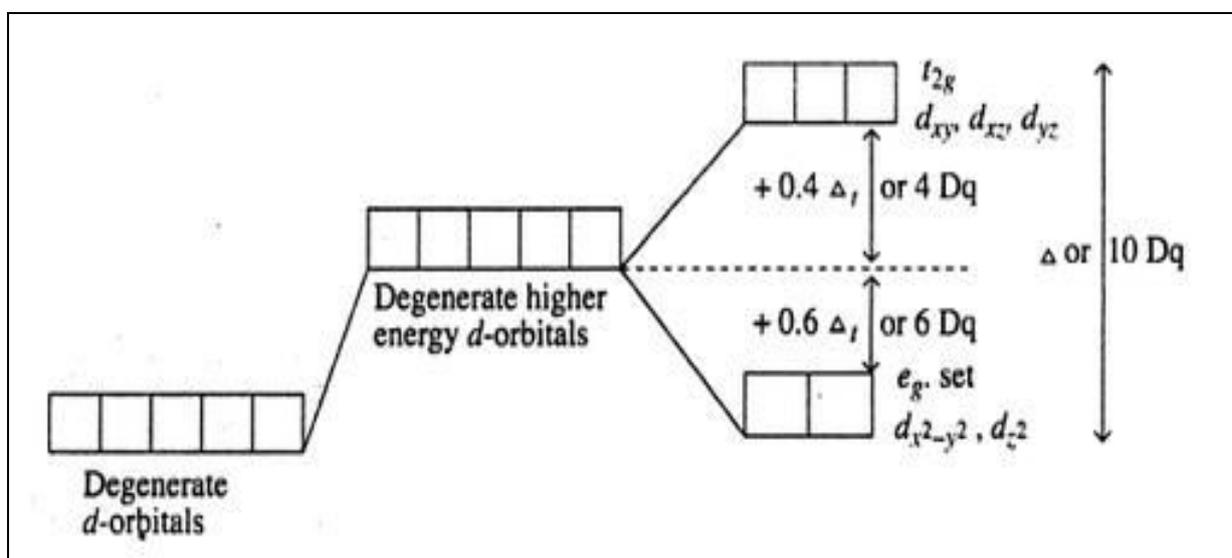


CRYSTAL FIELD SPLITTING IN TETRAHEDRAL COMPLEXES :

1. To visualise a tetrahedron placed inside a cube. Four ligands around the central metal atom are considered at the four appropriate corners of a

cube, in which the centre of the tetrahedron is taken as the centre of the cube.

2. X and Y axes emerge from the sides of the cube and the Z axis from the centre of the top face.
3. In this arrangement, the **ligands do not directly approach** any of the metal *d* orbitals.
4. They come closer to the t_{2g} orbitals, directed at the corners of the cube than to the e_g orbitals directed at the centres of the face of the cube.
5. Hence t_{2g} orbitals will be raised in energy while e_g orbitals will be lowered.
6. For maintaining the average energy constant, t_{2g} orbitals are raised by $4Dq$ while e_g orbitals are lowered by $6Dq$ from the barycentre.
7. Thus, the energy level scheme for the tetrahedral symmetry is exactly the reverse of that for octahedral symmetry.



8. It has been observed that the energy separation between the e_g and t_{2g} levels Δ_t , in tetrahedral symmetry is *smaller* than in octahedral symmetry Δ_o ($10Dq$).

9. This observation is as expected because the d orbitals are not directly affected by the ligands and moreover the number of approaching ligands is four as compared to 6 in octahedral complexes. For equivalent ligand charges and distances :

$$\Delta_t = -\Delta_o \frac{4}{9}$$

a) Where the minus sign means the reversal of the orbital levels.

b) Because of the low value of Dq in tetrahedral symmetry, crystal field favours the formation of octahedral complexes than tetrahedral complexes.

11. Low spin (strong field) tetrahedral complexes have not yet been obtained, probably because the crystal field stabilisation energies are never sufficient to bring out spin pairing.

12. Thus only high spin or weak field cases are to be considered for tetrahedral complexes. This simplifies the treatment of electron configuration and CFSE.

13. In a weak field, pairing energy (P) is more than Δ_t . Hence electrons enter even the higher levels and t_{2g} remain unpaired until the sixth electron forces pairing.

14. For example, in a complex with d^4 configurations two electrons occupy the lower e_g orbitals and two occupy the higher t_{2g} orbitals, all the four electrons remaining unpaired. Hence,

$$CFSE = -4Dq.$$

15. The CFSE for the various EC can be calculated with the help of the general formula;

$$CFSE = [y(-6Dq) + x(+4Dq) + P]$$

x = no. of electrons in t_{2g} orbitals :

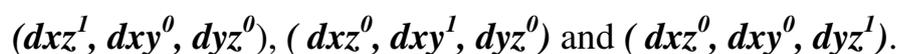
y = no. of electrons in e_g orbitals

P = pairing energy

Distortions in Octahedral geometry

The Jahn-Teller Theorem was published in 1937 and states: For a non-linear molecule in an electronically degenerate state, distortion must occur to lower the symmetry, remove the degeneracy and lower the energy.

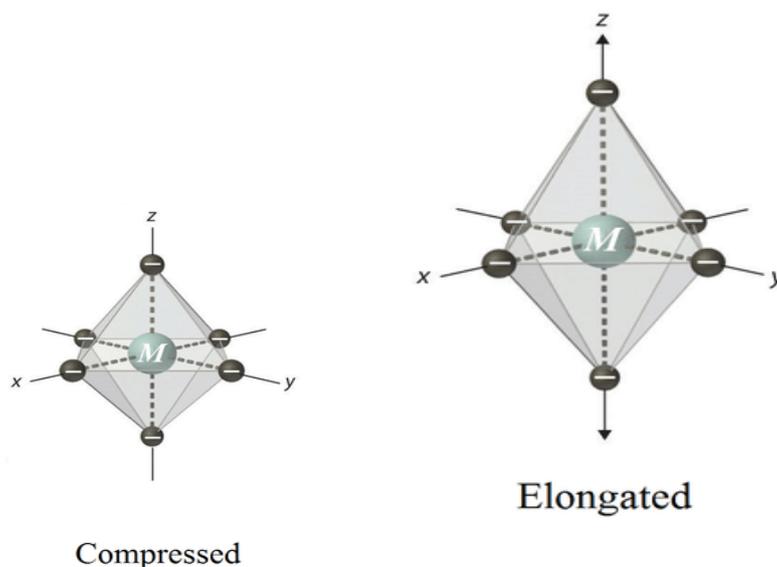
- a. Consider Ti^{3+} present in an octahedral environment. It is a d^1 system and the lone electron has the possibility of occupying any of the three d orbitals. Three electronic configurations are possible depending on which orbital is occupied



- b. Such a situation is called an electronically degenerate state.
- c. Similarly, for Cr^{3+} , that is d^3 system, there is only one way to fill the t_{2g} orbitals
- $$(dxz^1, dxy^1, dyz^1)$$
- hence it is an example of electronically non-degenerate state.
- d. The Jahn-Teller theorem predicts that a non-linear molecule that has an electronically degenerate state, distortion occurs so that the degeneracy is removed; the consequence is that the symmetry of the molecule is lowered and the system becomes more stable by losing energy.

Two types of distortions to be operating, z-in and z-out.

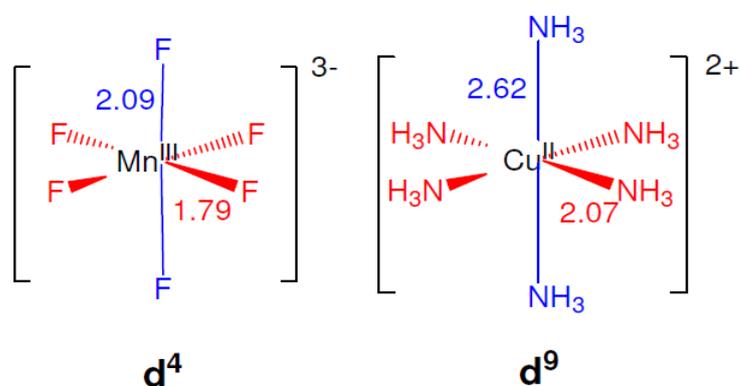
- a. In the case of octahedral complexes the tetragonal distortion reduces octahedral (O_h) symmetry of a complex to tetragonal (D_{4h}) structures producing either elongated (2-long, 4-short) compressed (4-long, 2-short) structures.



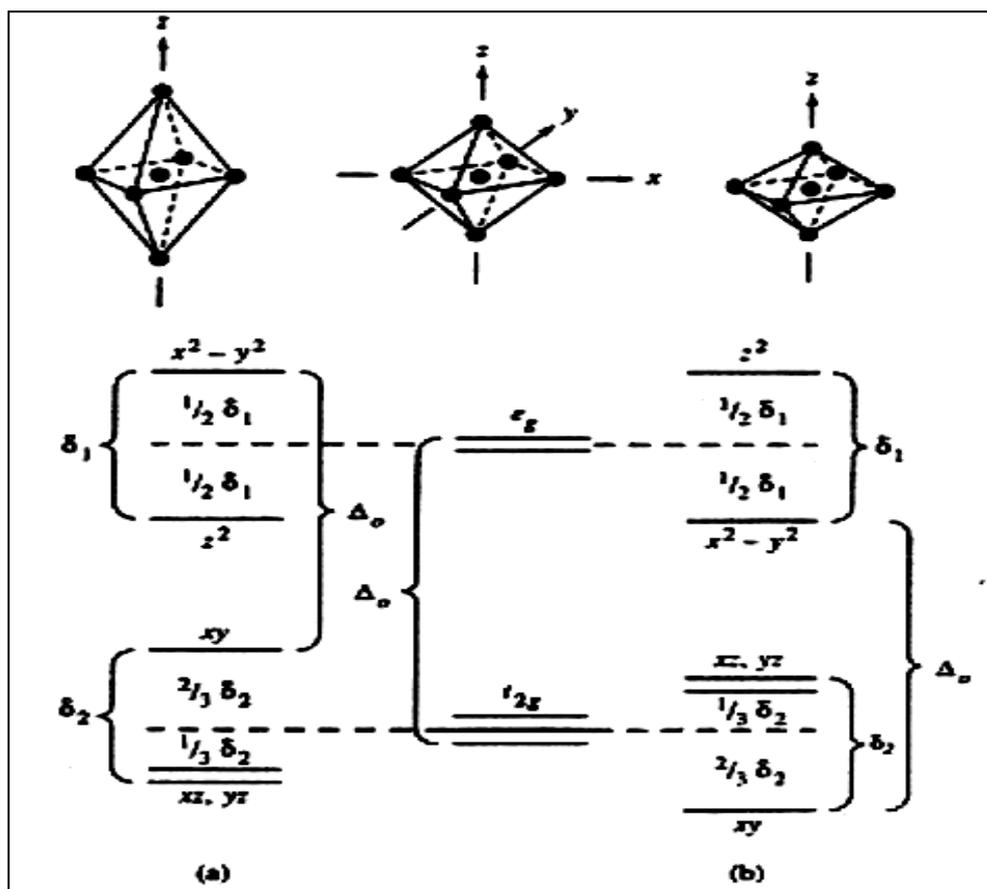
- b. Consider a case of $[\text{Ti}(\text{OH}_2)_6]^{3+}$, a d^1 system. To remove the electronic degeneracy, the t_{2g} orbital is split, the energy of d_{xz} and d_{yz} orbitals are raised in energy while the d_{xy} orbital is lowered. The separation let's say δ_2 . In the e_g set the dz^2 orbital is raised in energy in comparison to the dx^2-y^2 and the separation is δ_1 . In this way, the lone electron is on the d_{xy} orbital and the electronic degeneracy has been removed. The repulsion experienced in the orbitals containing the x,y component is more than the orbitals contain the z-component. The consequence of this is that four long (along x, y axis) and two short (along z axis) bonds. **This is known as Z-in case.**
- c. Consider the case of Cu(II), the d^9 system. The t_{2g} set is split, the d_{xz} and the d_{yz} orbitals are lowered in energy while the d_{xy} orbital is raised. In the e_g set, the d_{z^2} orbital is lowered in energy in comparison to the $d_{x^2-y^2}$. The odd electron resides in $d_{x^2-y^2}$ and the degeneracy in the system is removed. The consequence is that the four short (along x, y axis) and one long (along z axis) bonds. **This is known as Z-out case.**
- d. The Jahn-Teller effect is more pronounced when the former e_g level is not completely filled ($\delta_1 > \delta_2$), that is for configurations d^4 (high spin), d^7 (low spin) and d^9 . In these cases a static Jahn-Teller effect can be observed and

the species of D_{4h} symmetry can exist *in a solid phase*. We can now clearly see that Ti³⁺ with one d electron would prefer z-in as here the electronic degeneracy is removed and the energy is lowered (2/3 δ₂). In contrast V³⁺ with a d² configuration would prefer a z-out configuration. The Cr³⁺ has a d³ configuration and in an octahedral crystal field it is *not electronically degenerate*.

- e. Two further points need to be emphasized. One, the energy separations caused as a result of the distortion are much smaller in comparison to the original separation between *t_{2g}* and *e_g* levels and also naturally in comparison with pairing energies. Two, the distortions are better manifested when the electronically degenerate state occurs in the *e_g* levels rather than in the *t_{2g}* levels (because the effect of distortion is more *directly* felt). However, it is not possible to predict the type of distortion when the electronic degeneracy occurs in the *e_g* levels.



- f. Consequently a number of Cu²⁺ complexes in an octahedral environment show Jahn-Teller distortion. Although theoretically one is unable to predict the type of distortion that would occur in these molecules, experimentally it is found that elongation (z-out) is preferred.



g. Calculations of Jahn-Teller stabilization energy:

Let us consider example of d^9 i.e Cu(II) complex , Cu^{+2} generally form form Z-out(elongated complex)

The EC is $(t_{2g})^6 (d_{z^2})^2 (d_{x^2-y^2})^1$. Let δ_1 be the distortion of e_g orbital and δ_2 be the distortion of t_{2g} .the magnitude of splitting δ_1 and δ_2 is very small compared to Δ_o .

The two e_g orbitals separate in such a way that $d_{x^2-y^2}$ goes up as much as the d_{z^2} goes down. The doubly degenerate pair d_{xz} and d_{yz} goes down only half as far as the single orbital d_{xy} goes up.

$$\text{Hence net stabilisation energy } t_{2g} = [4 \times (-1/3 \delta_2)] + [2 \times (+2/3 \delta_2)] = 0$$

$$\text{net stabilisation energy } e_g = [2 \times (-1/2 \delta_1)] + [1 \times (+1/2 \delta_1)] = -1/2 \delta_1$$

this net energy $-1/2 \delta_1$ is called Jahn-Teller stabilization energy and it provide driving force for the distortion

Summary:

- Crystal field stabilisation energy (CFSE)
- Distribution of electrons in d-orbitals and CFSE in octahedral complexes
- Crystal field splitting in tetrahedral complexes
- Distortions in octahedral geometry
- Jahn-Teller Theorem

QUESTIONS

1. What is crystal field splitting? Discuss the splitting of d-orbitals of the central metal in octahedral complexes.
2. Define and explain crystal field stabilization energy.
3. State the factors on which CFSE depends. Explain any two in detail.
4. Calculate the C.F.S.E values for the octahedral complexes for weak ligand and strong ligand for metal ion with electronic configuration d^4 , d^5 , d^6 and d^7 .
5. Calculate the C.F.S.E values for the following octahedral complexes for weak ligand and strong ligand for metal ion (a) $[\text{Fe}(\text{CN})_6]^{4-}$, (b) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (c) $[\text{NiCl}_4]^{2-}$, (d) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, (e) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$