CONCEPT BOOSTER

Hello My family!! Wish you all enjoyed a lot in the festive season and side by side definitely have studied to keep the brain engine smooth and energetic. This is the time when you need a proper planning how to proceed in the forthcoming months with your preparation. Be convinced you will get me always beside you. I will start giving study plan and sequence of study in the forthcoming issues along with some off topics which you need to study. In the beginning, in this issue I have discussed JAHN-TELLER EFFECT, a very important but less discussed topic of COORDINATION CHEMISTRY. Keep your eyes intact on CHEMISTRY TODAY CONCEPT BOOSTER always for further guidance.

*Arunava Sarkar

SPECIAL TOPIC OF COORDINATION CHEMISTRY

At the beginning, know the fact that Jahn-Teller effect or Jahn-Teller theorem give an idea about the additional stabilisation of the system.

JAHN-TELLER THEOREM

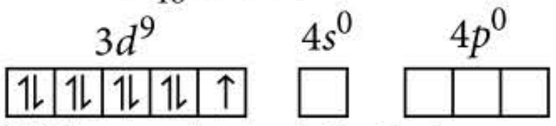
Any non-linear system in its orbitally degenerate electronic state will be unstable and therefore in order to attain stability this electronic state will undergo distortion in its geometry and thus will cause a splitting in its orbitally degenerate electronic state. This theorem was developed in the year 1937. Remember that orbitally degenerate electronic state is that state which represents more than one electronic arrangement with the same energy.

Jahn-Teller distortion is therefore that phenomena where distortion in the geometry of the non-linear system takes place in order to gain more stability.

Jahn-Teller distortion lowers the symmetry of the system in such a way that it lowers the energy of the system. It also takes place automatically.

The best example to understand Jahn-Teller distortion is Cu^{2+} :

$Cu^{2+} \rightarrow {}_{18}[Ar]3d^9$



With a perfect octahedral geometry, this configuration can be given as :

e_g^3 : ↿⇂ ↑

t_{2g}^6 : ↿⇂ ↿⇂ ↿⇂

(Ground state)

Now, two options are here :

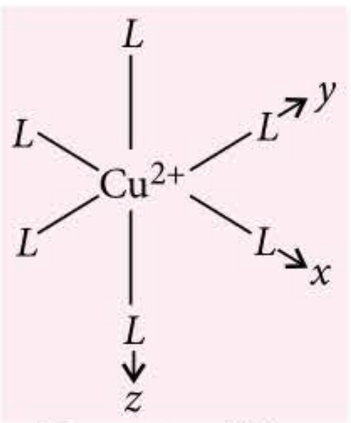
$$\left.\begin{array}{l}\text{Option-1 : } t_{2g}^6\ d_{z^2}^2\ d_{x^2-y^2}^1 \\ \text{Option-2 : } t_{2g}^6\ d_{z^2}^1\ d_{x^2-y^2}^2\end{array}\right\} \text{equal energy}$$

OPTION 1

The *d*-electron charge density will be higher in *z*-direction than in *x*- or *y*-direction. So, the nuclear charge of Cu^{2+} rather the positive charge of Cu^{2+} will be more in *z*-direction rather in *x*- or *y*-direction. As a result, the negative charge of the ligands along the *z*-direction will be less attractive than that of along *x*- or *y*-direction.

Now think the scenario! Due to lesser attraction, ligands along *z*-direction will move away from the metal ion whereas ligands along *x*- and *y*-directions will move nearer to the metal ion.

Obviously, now the octahedral geometry will get distorted to tetragonal geometry and it will be with the elongation along *z*-directions and compression along *x*- and *y*-directions.

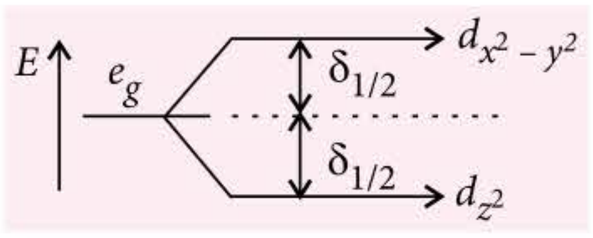


(Distortion of the octahedral geometry to tetragonal geometry due to Jahn-Teller effect)

So, what we found ultimately? There is elongation of metal-ligand bonds along *z*-direction. That is why the *d*-electrons of the metal ion experience lesser electrostatic repulsion force from the negative charge on the ligands.

*Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

The similar repulsion force will be more felt at the x- and y-directions. So, due to all these d_{z^2} will be of lower energy and $d_{x^2-y^2}$ will be of higher energy. In this way the degeneracy gets disturbed and gets lifted.



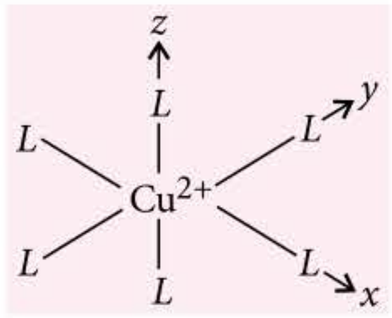
(Lifting of degeneracy of e_g orbitals due to Jahn-Teller effect when more electrons are there in d_{z^2} than $d_{x^2-y^2}$)

Now, there is a catch here. No external energy supply is required for the splitting here. It is automatic. Hence, overall energy of the split orbitals will be equal to the energy of the unsplit orbitals. So, if we assume that before the spliting, the energy of the orbitals was E, then after the spliting total energy of d_{z^2} and $d_{x^2-y^2}$ will be E. This is commonly known as 'Centre of gravity rule' according to which the centre of gravity of the split orbitals is maintained.

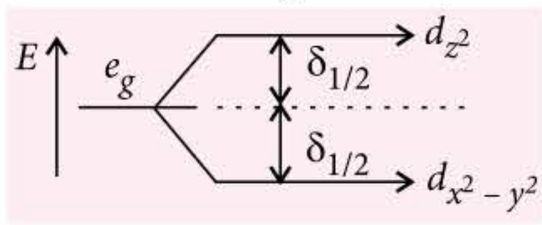
So, in a nut shell, when there are more electrons in d_{z^2} rather than in $d_{x^2-y^2}$ of an octahedral complex of any metal ion, distortion of octahedral geometry to tetragonal geometry will occur by elongation of metal-ligand bonds along z-direction.

OPTION 2

Here, $d_{x^2-y^2}$ has two electrons and d_{z^2} has one electron. This is why the negative charges on the ligands along x- and y- directions are less attracted by the nucleus or rather nuclear charge. This is of course because of the more effective screening. This screening is of course less along the z-direction as there is only one electron in d_{z^2}. As a consequence, there is elongation of metal-ligand bond along x- and y-directions whereas there is contraction of metal-ligand bond across z-direction. As a result the octahedral geometry of Cu^{2+} ion gets distorted and it takes tetragonal geometry.



Also, electrostatic repulsion experienced by d-electrons of Cu^{2+} from the negative charge on ligands along x- and y-direction will be less than the similar force experienced by the d-electron(s) from the negative charge along the z-direction. This is why $d_{x^2-y^2}$ becomes of lower energy and d_{z^2} becomes of higher energy. So degeneracy of two orbitals get lifted.



Now, we will take a few aspects which must be understood properly.

First of all, remember that apart from the $t_{2g}^6\ e_g^3$ configuration (ground state) resulting into the formation of octahedral complex, other ground state configuration which show Jahn-Teller effect is $t_{2g}^6\ e_g^1$. The point to be noted here is in both of these configurations t_{2g} is uniformly filled up and the type of distortion here depends upon e_g orbital *i.e.* whether the electron occupies $d_{x^2-y^2}$ or d_{z^2} orbital

Exam Update

JEE (Advanced) 2018

The Joint Entrance Examination (Advanced) 2018 will be conducted by the IITs . The performance of a candidate in this examination will form the basis for admission to the Bachelor's, Integrated Master's and Dual Degree programs (entry at the 10+2 level) in all the IITs. The decisions of the JAB 2018 will be final in all matters related to JEE (Advanced) 2018 and admission to IITs.

Candidates should be among the top 2,24,000 (including all categories) by scoring positive marks in Paper-1 of JEE (Main)-2018.

Examination will be held on May 20, 2018. The entire JEE (Advanced) 2018 Examination will be conducted in fully computer based test mode. The exam consists of two papers, Paper 1 and Paper 2, each of three hours' duration, and will be held in two sessions. Both the papers are compulsory.

For more information visit www.jeeadv.ac.in

MPP-7 CLASS XII ANSWER KEY

1. (a)	**2.** (c)	**3.** (d)	**4.** (c)	**5.** (a)
6. (b)	**7.** (d)	**8.** (c)	**9.** (a)	**10.** (b)
11. (c)	**12.** (b)	**13.** (b)	**14.** (a)	**15.** (c)
16. (a)	**17.** (c)	**18.** (b)	**19.** (d)	**20.** (a,c,d)
21. (b,c)	**22.** (a,b)	**23.** (b,d)	**24.** (4)	**25.** (4)
26. (3)	**27.** (d)	**28.** (b)	**29.** (b)	**30.** (c)