## **Quadrant II – Transcript and Related Materials**

Programme: Bachelor of Science (Second Year) Subject: Chemistry Paper Code: CHC 104 Paper Title: Physical Chemistry and Inorganic Chemistry Unit: Unit 3 – Crystal field Theory Module Name: Comparison of CFSE for octahedral (O<sub>h</sub>) and tetrahedral (T<sub>d</sub>) complexes Module No: 22 Name of the Presenter: Mithil Fal Desai, Ph. D.

## Notes

The five d orbitals are oriented in different directions in space. These orbitals split into two sets with incoming ligands in octahedral ( $O_h$ ) and tetrahedral ( $T_d$ ) field. The three orbitals  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  are considered as  $t_2$  and  $t_{2g}$  set in tetrahedral ( $T_d$ ) and octahedral ( $O_h$ ) fields, respectively. While two orbitals  $d_x^2 \cdot y^2$  and  $d_z^2$  are considered as doubly degenerate e and  $e_g$  set in tetrahedral ( $T_d$ ) and octahedral ( $O_h$ ) fields, respectively. The  $d_{xy}$ ,  $d_{yz}$ , and  $d_{xz}$  orbitals are oriented in-between the axis while the  $d_x^2 \cdot y^2$  and  $d_z^2$  are along the axis. In an octahedral complex, the ligands approach along the axis while in tetrahedral complexes ligands approaches in between the axis. This result in a different kind of splitting pattern. The e set is lower in energy while  $t_2$  set is higher in energy for tetrahedral complexes. This is observed opposite for octahedral complexes than octahedral complexes.

The CFSE can be calculated using the following formulas,

$$CFSE_{oct} = [-0.4 n_{(t_{2g})} + 0.6 n_{(e_g)}] \Delta_o$$
$$CSFE_{tet} = [-0.6 n_{(e)} + 0.4 n_{(t_2)}] \Delta_t$$

\* n= number of electrons

Here  $\Delta_o$  and  $\Delta_t$  are the unit of crystal field stabilisation energy in tetrahedral (T<sub>d</sub>) and octahedral (O<sub>h</sub>) fields, respectively. The electrons in t<sub>2g</sub> set in octahedral complex stabilise the complex by 0.4 factor, while electrons present in e<sub>g</sub> set destabilise by 0.6 factor. Similarly in a tetrahedral complex, the electrons in e set would stabilise by 0.6 factor while electrons in t<sub>2</sub> set would destabilize by 0.4 factor.

It is observed that CFSE for tetrahedral complexes is less than that of the octahedral complexes by a factor of 0.44 due to two reasons. One reason is that there are only four ligands in the tetrahedral complex while there are six ligands in the octahedral complex. This would give a ratio of ligand field 4:6 that is tetrahedral to the octahedral field, so empirically this factor is 2/3. Also, none of the four ligands is directly facing the metal d orbitals in a tetrahedral complex. That is from six sides these ligands are approaching the metal centre in the octahedral field, while only by four sides ligands are approaching the metal centre in a tetrahedral field, so the ratio is again 4/6.

To compare the crystal field stabilisation energy of octahedral and tetrahedral field CFSE need to be expressed with the same unit. Thus, we have CFSE for tetrahedral complex expressed in the unit of  $\Delta_0$  in the following formula.



As the magnitude of crystal field splitting is less for tetrahedral complexes, these complexes are usually high spin. In the following table, the high spin complexes of octahedral splitting are compared to that of tetrahedral splitting.

E.C.	Octahedral complex		Tetrahedral complex		
dn	t <sub>2g</sub> <sup>n</sup> e <sub>g</sub> <sup>n</sup>	$CFSE_{oct} (\Delta_o)$	e <sup>n</sup> , t <sub>2</sub> <sup>n</sup>	$CFSE_{tet}(\Delta_t)$	$CFSE_{tetra}(\Delta_o)$
d1	$t_{2g}^{1}, e_{g}^{0}$	-0.4	e <sup>1</sup> , t <sub>2</sub> <sup>0</sup>	-0.6	-0.27
d <sup>2</sup>	$t_{2g}^{2}, e_{g}^{0}$	-0.8	$e^2, t_2^0$	-1.2	-0.53
d <sup>3</sup>	$t_{2g}^{3}, e_{g}^{0}$	-1.2	e <sup>2</sup> , t <sub>2</sub> <sup>1</sup>	-0.8	-0.36
d <sup>4</sup>	$t_{2g}^{3}, e_{g}^{1}$	-0.6	$e^2, t_2^2$	-0.4	-0.18
d5	$t_{2g}^{3}, e_{g}^{2}$	0	$e^2, t_2^3$	0	0.00
d <sup>6</sup>	$t_{2g}^{4}, e_{g}^{2}$	-0.4	$e^{3}$ , $t_{2}^{3}$	-0.6	-0.27
d <sup>7</sup>	$t_{2g}^{5}, e_{g}^{2}$	-0.8	e <sup>4</sup> , t <sub>2</sub> <sup>3</sup>	-1.2	-0.53
d <sup>8</sup>	$t_{2g}^{6}, e_{g}^{2}$	-1.2	e <sup>4</sup> , t <sub>2</sub> <sup>4</sup>	-0.8	-0.36
d <sup>9</sup>	$t_{2g}^{6}, e_{g}^{3}$	-0.6	$e^4, t_2^5$	-0.4	-0.18
d <sup>10</sup>	$t_{2g}^{6}, e_{g}^{4}$	0	$e^4, t_2^6$	0	0.00

Table 1. Comparison of CFSE for octahedral (Oh) and tetrahedral (Td) complexes

It is evident from the values of the above table that the CFSE for  $d^0$ ,  $d^5$  and  $d^{10}$  systems would be insignificant. The difference in CFSE is more between these two types of high spin complexes for  $d^2$ ,  $d^3$  and  $d^7$ ,  $d^8$  systems. As these values are expressed in terms of stability, more the negative value means more is the stabilisation energy. It can be understood that  $d^1$ ,  $d^2$ ,  $d^6$ , and  $d^7$  systems, the difference in energy is small so

the transition metals with such electronic configuration may like to prefer a tetrahedral geometry.

The Zn complexes with d<sup>10</sup> system or Mn compound with d<sup>0</sup> system have a tetrahedral structure as observed for tetrachlorozincate(II) and paramagnet ions.

The octahedral structures would be favoured due to high CFSE, but overcrowding of bulky ligands may result in tetrahedral structures. The magnitude of crystal field splitting in the tetrahedral field is 4/9 times the crystal field splitting in the octahedral field. This is related to the number of ligands and their direction to approach the metal centre.