Quadrant II – Transcript and Related Materials

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Unit: 3

Module Name: Crystal Field Splitting in Tetrahedral Complexes; Calculation of CFSE

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Notes

d- orbitals

Figure 1 shows shapes and orientations of the five d- orbitals (d_{xy}, d_{yz}, d_{xz}, d_{x2-y2} and d_{z2}). It can be seen that the lobes of d_{x2-y2} and d_{z2} lie along the axes whereas the lobes of d_{xy}, d_{yz} and d_{xz} lie on the respective planes but between the axes.

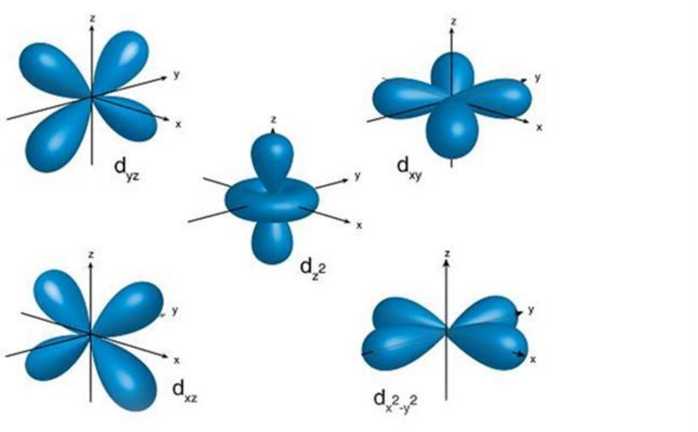

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Figure 1. Shapes and orientations of d orbitals.

Tetrahedral geometry

Figure 2 shows a cube with the three axes passing through the centres of opposite faces of the cube. These axes will intersect at the centre of the cube, we can place the central metal at this centre of the cube. Now the four ligands can be placed at the alternate vertices of the cube. Joining the central metal with the four ligands will end up giving a tetrahedral complex. Important point to notice over here is that the ligands in a tetrahedral complex are oriented between the axes. We know that the lobes of d_{xy}, d_{yz} and d_{xz} orbitals are also oriented between the axes. Thus, the d_{xy}, d_{yz} and d_{xz} orbitals of central metal will be closer to the ligands whereas the d_{x2-y2} and d_{z2} orbital of central metal will be farther from the ligands in a tetrahedral complex. As a result of this arrangement, according to Crystal Field Theory (CFT), the electrons in the d_{xy}, d_{yz} and d_{xz} orbitals of central metal will experience higher repulsions from the electrons on the ligands, whereas the electrons in d_{x2-y2} and d_{z2} orbital on central metal will experience comparatively smaller repulsions from the electrons on the ligands in a tetrahedral complex.

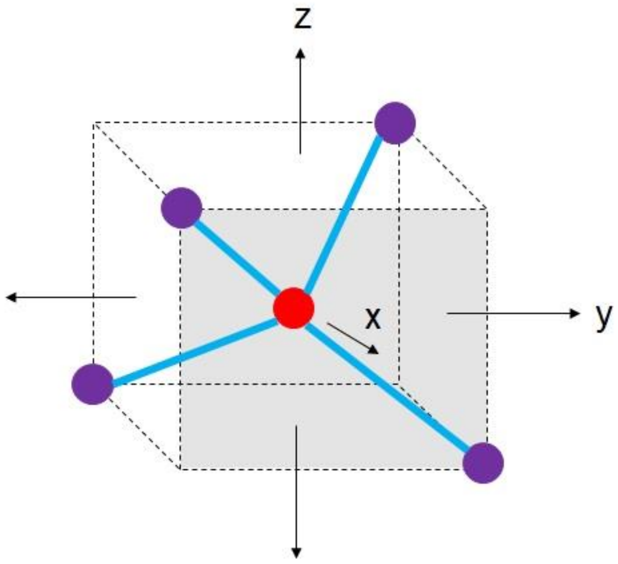


Figure 2. Tetrahedral complex

Crystal Field Splitting in tetrahedral complexes

The Crystal Field Splitting in a tetrahedral complex in depicted in figure 3. State I represent an isolated metal ion for which the five d orbitals are degenerate. State II represent the metal ion in a hypothetical spherical ligand field. Since the ligand field is spherical the energies of all the five d orbitals will be equally raised. State III represents the metal ion in a tetrahedral complex. In the tetrahedral complex the d_{x2-y2} and d_{z2} orbital of central metal will be stabilised with respect to the degenerate orbitals in the spherical field as these sets of orbitals (d_{x2-y2} and d_{z2})will experience less repulsions from the electrons on the ligands in a tetrahedral complex, as discussed earlier. d_{xy}, d_{yz} and d_{xz} orbitals of central metal on the other hand will be destabilised with respect to the degenerate orbitals in the spherical field as these sets of orbitals (d_{xy}, d_{yz} and d_{xz}) will experience more repulsions from the electrons on the ligands in the tetrahedral complex. This splitting of d orbital on central metal under the influence of ligand field is called as Crystal Field Splitting. The d_{x2-y2} and d_{z2} set of orbitals is called as *e* and the d_{xy}, d_{yz} and d_{xz} set of orbitals is called as t_2 for a tetrahedral complex. The energy difference between *e* and t_2 sets of orbitals is given as Δ_t (crystal field splitting parameter for a tetrahedral complex). The difference in energy between barycentre and the *e* orbitals and between the barycentre and the t_2 orbitals comes to be $0.6\Delta_t$ and $0.4\Delta_t$ respectively. For same central metal and ligand, $\Delta_t < \Delta_o$, as a matter of fact $\Delta_t = 0.45\ \Delta_o$. There are two reasons for this: 1) In octahedral complex the e_g orbitals are directly pointing at the ligands, whereas in a tetrahedral complex although the t_2 orbitals are close to ligands they are not directly pointing at the ligands. 2) In octahedral complex there are six ligands whereas there are only four ligands in tetrahedral complex.

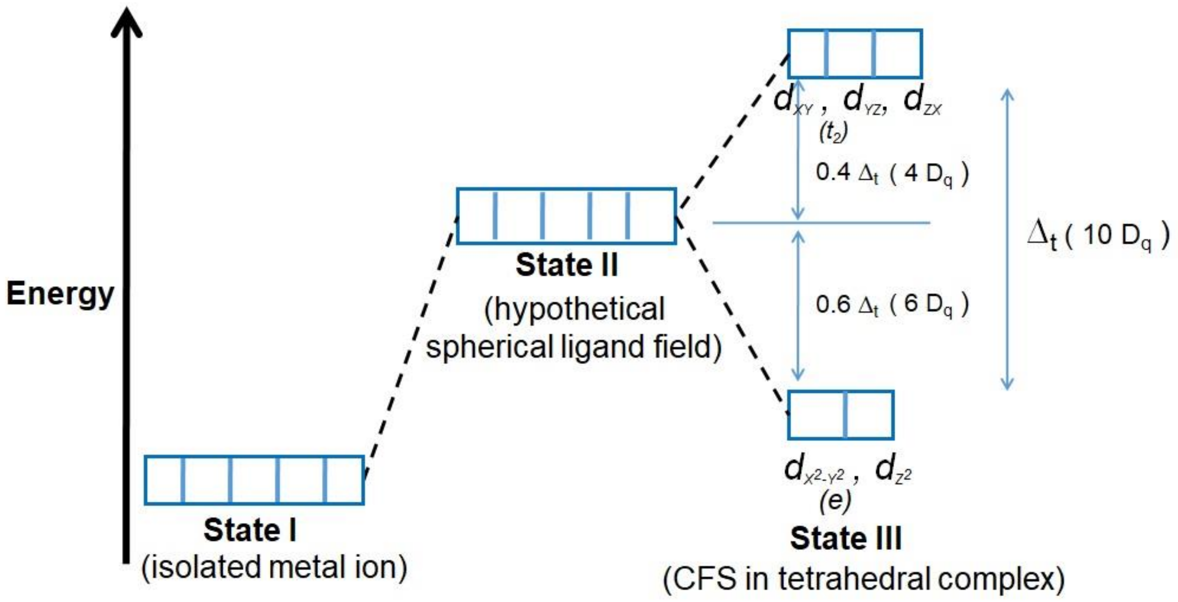
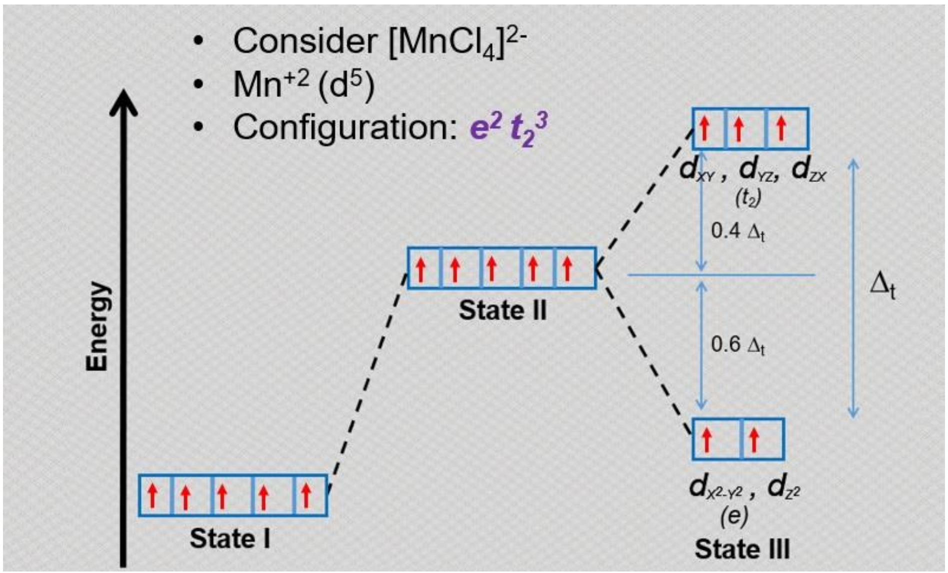


Figure 3. Crystal Field Splitting in tetrahedral complex.

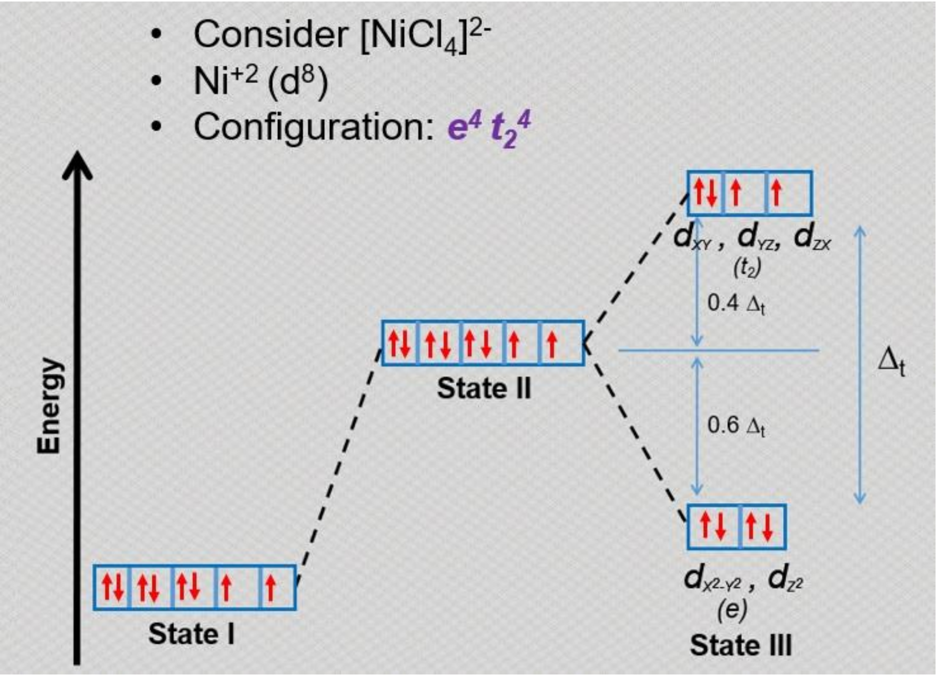
Examples of tetrahedral complexes

Refer figure 4 and figure 5. It should be noted that even in the state III for a tetrahedral complex the electrons are first filled singly in all the five d orbital, and only then the pairing takes place. This is because the value of Δ_t is small for a tetrahedral complex, and as a matter of fact the Δ_t is smaller than the energy required for pairing to take place initially.



- Consider $[MnCl_4]^{2-}$
- Mn^{+2} (d^5)
- Configuration: $e^2 t_2^3$

Figure 4. Crystal Field Splitting in $[MnCl_4]^{2-}$



- Consider $[NiCl_4]^{2-}$
- Ni^{+2} (d^8)
- Configuration: $e^4 t_2^4$

Figure 5. Crystal Field Splitting in $[NiCl_4]^{2-}$

Crystal Field Stabilization Energy (CFSE)

To understand CFSE let us consider an example (refer figure 6). In this complex the *e* orbitals have less energy by a value of 0.6 Δ_t compared to that of degenerate orbitals in the state II. This complex will be more stable by a value of (1x0.6 Δ_t) compared to the complex with no splitting. Evidently, the energy of the complex is now less due to splitting. This decrease in energy is the CFSE.

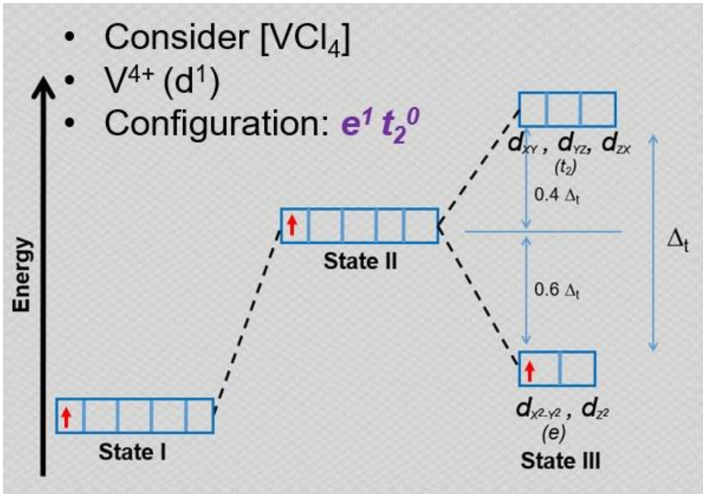


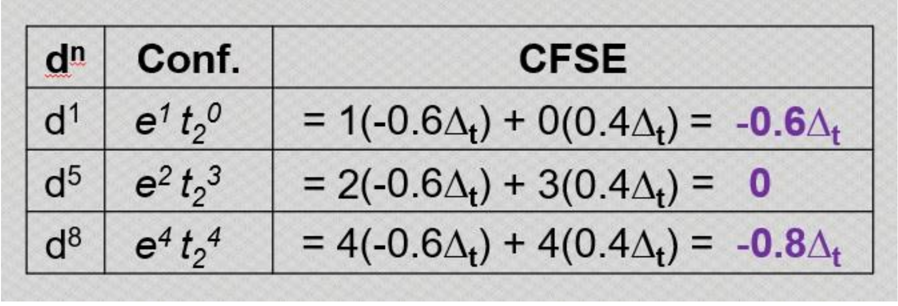
Figure 6. Crystal Field Splitting in [VCl$_4$]

Calculation of CFSE

General formula for calculation of CFSE for a tetrahedral complex is as follows:

$$\text{CFSE}_{\text{tetrahedral}} =$$
$$(\text{Number of elec. in } e \text{ orbitals})(-0.6\Delta_t) + (\text{Number of elec. in } t_2 \text{ orbitals})(0.4\Delta_t)$$

Table 1 shows the calculations of CFSE for the tetrahedral complexes considered earlier. Consider the tetrahedral complex with d^1 configuration for central metal. For this complex, the CFSE= $1(-0.6\Delta_t) + 0(0.4\Delta_t) = -0.6\Delta_t$. Similarly, CFSE can be calculated for other configurations.



d^n	Conf.	CFSE
d^1	$e^1\, t_2^0$	$= 1(-0.6\Delta_t) + 0(0.4\Delta_t) =$ **$-0.6\Delta_t$**
d^5	$e^2\, t_2^3$	$= 2(-0.6\Delta_t) + 3(0.4\Delta_t) =$ **0**
d^8	$e^4\, t_2^4$	$= 4(-0.6\Delta_t) + 4(0.4\Delta_t) =$ **$-0.8\Delta_t$**

Table 1. Calculations of CFSE for different configurations.