

❖ Calculation of Dq , B and β Parameters

The Orgel diagrams explain how the magnitude of the splitting energy exerted by the ligands on d -orbitals vary when a free metal ion is approached by a ligand field; and can also act as deciding factor for governing the placement of electrons, just like the inter-electronic repulsion energy. However, if the ligand field splitting energy is greater than the inter-electronic repulsion energy, then Orgel diagrams fail in determining the placement of electrons. In that case, Orgel diagrams are restricted only to the high-spin complexes. Tanabe-Sugano diagrams do not have this restriction and can be applied to the situations when Δ is significantly greater than inter-electronic repulsion. Thus, the Tanabe-Sugano diagrams can be utilized in determining electron placements for high-spin and low-spin metal complexes. However, they are limited in the sense that they have only qualitative significance.

Despite that, Tanabe-Sugano and Orgel diagrams are fairly valuable in interpreting UV-vis spectra and can be used to determine the value of crystal field splitting energy (Dq), Racah parameter (B) and also the nephelauxetic ratio (β).

➤ d^1 Complexes

Metal complexes with d^1 -configuration do not have any inter electronic repulsion and the single electron resides in the t_{2g} orbital ground state. When t_{2g} orbital set holds the single electron, six microstates will have ${}^2T_{2g}$ state energy of $-4 Dq$; and when the electron is promoted to the e_g orbital, the four microstates will have 2E_g state energy of $+6 Dq$. Thus, the only parameter that is needed to be calculated is the magnitude of crystal field splitting energy ($10 Dq$); and the single absorption band in a UV-vis experiment is exactly what we are looking for. Hence, the energy of the transition ${}^2T_{2g} \rightarrow {}^2E_g$ gives the value of Δ directly.

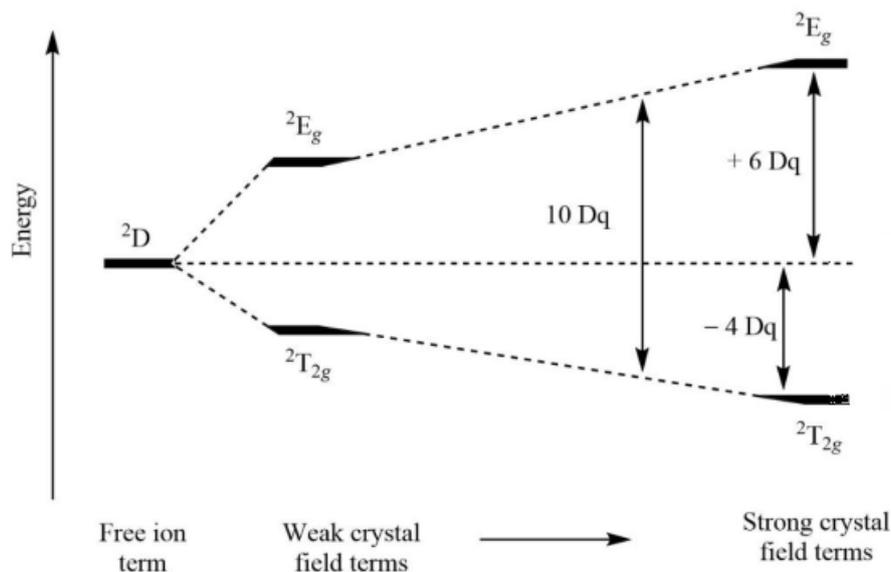


Figure 36. The splitting pattern of free ion term for d^1 complexes in the octahedral crystal field.

Consider the example of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

1. Calculation of B: No need to calculate the Racah parameter.

2. Calculation of Δ_0 : The purple color of the complex ion $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is due to a broad absorption band at 20300 cm^{-1} arising from ${}^2\text{T}_{2g} \rightarrow {}^2\text{E}_g$ transition. Hence, 10 Dq for this complex is 20300 cm^{-1} .

3. Calculation of β : No need to calculate the nephelauxetic ratio.

➤ **d^0 Complexes:**

In d^0 octahedral metal complexes, the ground state filling of electrons ($t_{2g}^6 e_g^3$) has only four microstates that have ${}^2\text{E}_g$ energy state with -6 Dq . When the electron from t_{2g} is promoted to the e_g orbital set; the new configuration will have six microstates that have ${}^2\text{T}_{2g}$ energy state with $+4 \text{ Dq}$. This could also be described as a positive "hole" that moves from the e_g to the t_{2g} orbital set. The sign of Dq is opposite that for d^1 , with a ${}^2\text{E}_g$ ground state and a ${}^2\text{T}_{2g}$ excited state. Like the d^1 case, the only parameter that is needed to be calculated in d^0 complexes is the magnitude of crystal field splitting energy (10 Dq); and the single absorption band in a UV-vis experiment is exactly what we are looking for. Hence, the energy of the transition ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ gives the value of Δ directly.

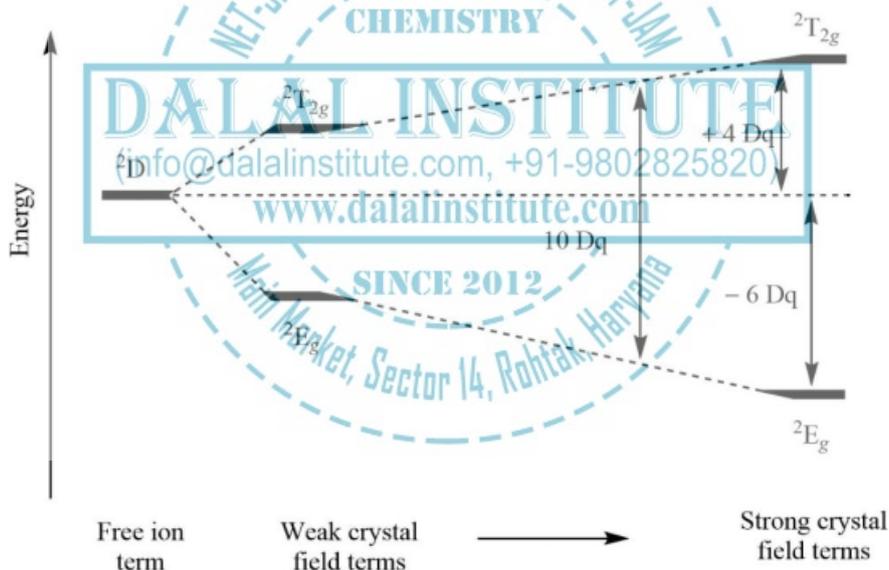


Figure 37. The splitting pattern of free ion term for d^0 complexes in the octahedral crystal field.

Consider the example of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$.

1. Calculation of B: No need to calculate the Racah parameter.

2. Calculation of Δ_0 : In the UV-visible spectra of $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, the broad band at 12000 cm^{-1} is due to spin-allowed ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition; and hence, 10 Dq for this complex is 12000 cm^{-1} .

3. Calculation of β : No need to calculate the nephelauxetic ratio.

➤ d^2 Complexes

Metal complexes with d^2 -configuration have 3F ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes ${}^3T_{1g}$ and remains as such in weak as well as in strong ligand fields. The Orgel and Tanabe-Sugano diagram for d^2 -configuration can be used to estimate the value of crystal field splitting energy for these transition metal complexes.

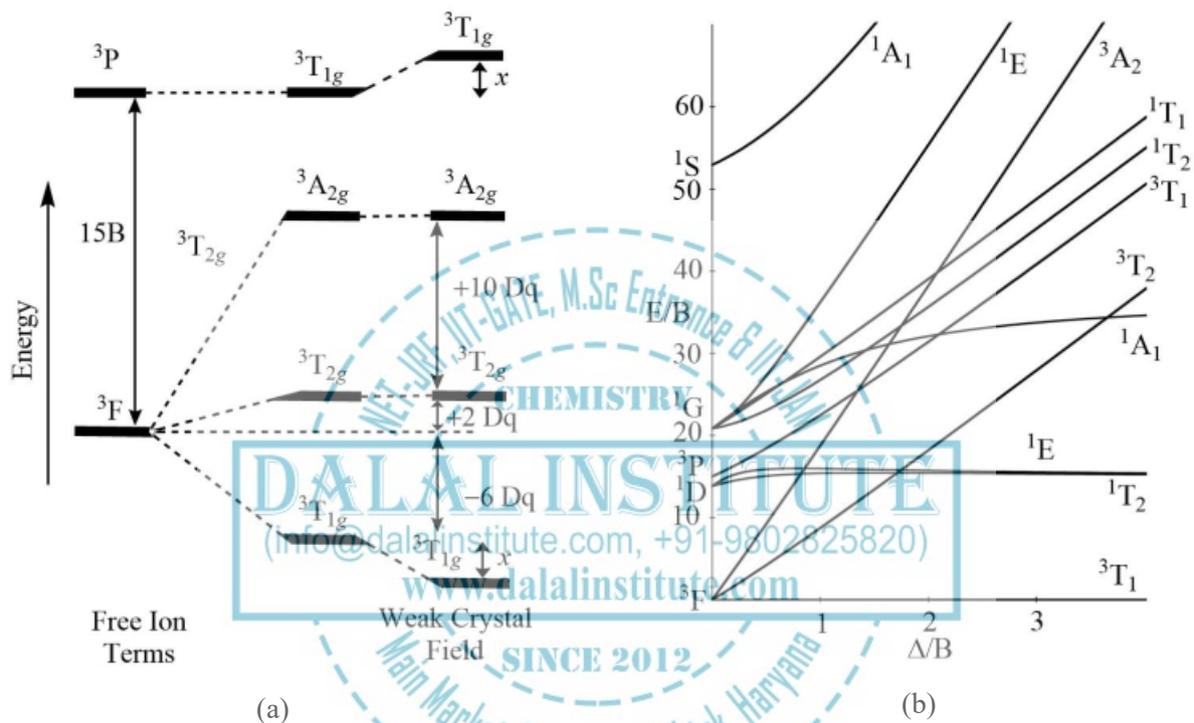


Figure 38. The (a) Orgel and (b) Tanabe-Sugano diagrams for d^2 complexes in the octahedral crystal field.

Consider the example of $[V(H_2O)_6]^{3+}$.

1. Calculation of B: From the Orgel diagram, it can be clearly seen that the ground state for d^2 -octahedral complexes is ${}^3T_{1g}$ and there are three main transitions before the crossover point. Moreover, it is worthy to note down that the order of second and third transitions is reversed after the crossover point and only two bands will be observed at or near the crossover point. As the magnitude of the crystal field splitting energy increases, the ${}^3T_{1g}(F)$ and ${}^3T_{1g}(P)$ states repel each other more and more with a magnitude of x energy value.

$$\nu_1 = {}^3T_{1g} \rightarrow {}^3T_{2g}$$

$$\nu_2 = {}^3T_{1g} \rightarrow {}^3A_{2g}$$

$$\nu_3 = {}^3T_{1g} \rightarrow {}^3T_{1g}(P)$$

Which gives

$$v_1 = 8 Dq + x \quad (1)$$

$$v_2 = 18 Dq + x \quad (2)$$

$$v_3 = 15 B + 6 Dq + 2x \quad (3)$$

Adding equation (1) and (2), we get

$$v_2 + v_1 = 18 Dq + x + 8 Dq + x$$

$$v_2 + v_1 = 26 Dq + 2x \quad (4)$$

Subtracting equation (1) and (2), we get

$$v_2 - v_1 = 18 Dq + x - 8 Dq - x$$

$$v_2 - v_1 = 10 Dq \quad (5)$$

Putting the value of $2x$ from equation (4) in equation (3), we get

$$v_3 = 15 B + 6 Dq + v_2 + v_1 - 26 Dq$$

$$v_3 = 15 B + v_2 + v_1 - 20 Dq \quad (6)$$

Multiplying equation (5) by 2 and putting the value of $20 Dq$ from equation (5) in equation (6), we get

$$v_3 = 15 B + v_2 + v_1 - 20 Dq$$

$$v_3 = 15 B + v_2 + v_1 - 2v_2 + 2v_1$$

$$15 B = v_3 + v_2 - 3v_1$$

$$B = \frac{v_3 + v_2 - 3v_1}{15} \quad (7)$$

However, only two transitions are observed, this method is difficult to apply in a precise manner and only gives approximations.

From the Tanabe-Sugano diagram, in the UV-visible spectra of $[V(H_2O)_6]^{3+}$, two bands are observed with maxima at around 17500 and 26000 cm^{-1} . There are three possible transitions expected, which include: $v_1 = {}^3T_{1g} \rightarrow {}^3T_{2g}$, $v_2 = {}^3T_{1g} \rightarrow {}^3T_{1g}(P)$, and $v_3 = {}^3T_{1g} \rightarrow {}^3A_{2g}$; but only two are observed. The ratio of experimental band energies is:

$$\frac{v_2}{v_1} = \frac{E_2}{E_1} = \frac{E_2/B}{E_1/B} = \frac{26000}{17500} = 1.49$$

Now slide a ruler across the printed diagram (perpendicular to the abscissa) until the ratio of E_2/B to E_1/B between lines becomes equivalent to 1.49. In this particular example, this ratio becomes 1.49 when $\Delta_o/B = 31$. Stop the ruler movement and find out the values of E_2/B and E_1/B

$$\frac{E_2}{B} = 43; \quad \frac{E_1}{B} = 27$$

Thus, on the T-S diagram, where $\Delta_o/B = 31$; the value of ${}^3T_{1g} \rightarrow {}^3T_{2g}$ and ${}^3T_{1g} \rightarrow {}^3T_{1g}(P)$ i.e. E_1/B and E_2/B , are 27 and 43, respectively. The Racah parameter can be found by calculating B from both ν_2 and ν_1 .

$$\frac{26000}{B} = 43; \quad \frac{17500}{B} = 27$$

$$B = \frac{26000}{43} = 604 \text{ cm}^{-1}; \quad B = \frac{17500}{27} = 648 \text{ cm}^{-1}$$

$$\text{Average value of Racah parameter (B)} = \frac{604 + 648}{2} = 626 \text{ cm}^{-1}$$

2. Calculation of Δ_o : Being a weak-complex, the theoretical value of lowest-energy absorption band given by the Orgel diagram is $8 Dq$ (${}^3T_{1g} \rightarrow {}^3T_{2g}$); and the experimental value for lowest-energy absorption band is 17500 cm^{-1} . Hence, the value of $10 Dq$ or Δ_o can be calculated as:

$$8 Dq = 0.8 \Delta_o = 17500 \text{ cm}^{-1}$$

$$\Delta_o = \frac{17500 \text{ cm}^{-1}}{0.8}$$

$$\Delta_o = 10 Dq = 21875 \text{ cm}^{-1}$$

However, this is just the approximation and a more precise and refined calculation should be carried out using the Tanabe-Sugano diagram. From the average value of the Racah parameter, the ligand field splitting parameter can be found as follows.

$$\frac{\Delta_o}{B} = 31; \quad \frac{\Delta_o}{626 \text{ cm}^{-1}} = 31; \quad \Delta_o = 19406 \text{ cm}^{-1}$$

3. Calculation of β : In order to calculate the nephelauxetic ratio, we must have the value of Racah parameter for a free metal ion in its gaseous state. For free d^2 ion like V^{3+} , it has been observed that 3P state lies 12925 cm^{-1} above to the 3F state. Hence, $15B = 12925 \text{ cm}^{-1}$ or $B = 862 \text{ cm}^{-1}$. Now, the value of nephelauxetic ratio can be calculated as

$$\text{Nephelauxetic ratio} = \beta = \frac{B_{\text{complex}}}{B_{\text{free ion}}} = \frac{626 \text{ cm}^{-1}}{862 \text{ cm}^{-1}} = 0.726$$

Hence, inter-electronic repulsion has been decreased during the process of complexation.

➤ d^8 Complexes

Metal complexes with d^8 -configuration have 3F ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes $^3A_{2g}$ and remains as such in weak as well as in strong ligand fields. The Orgel and Tanabe-Sugano diagram for d^8 -configuration can be used to estimate the value of crystal field splitting energy for these transition metal complexes.

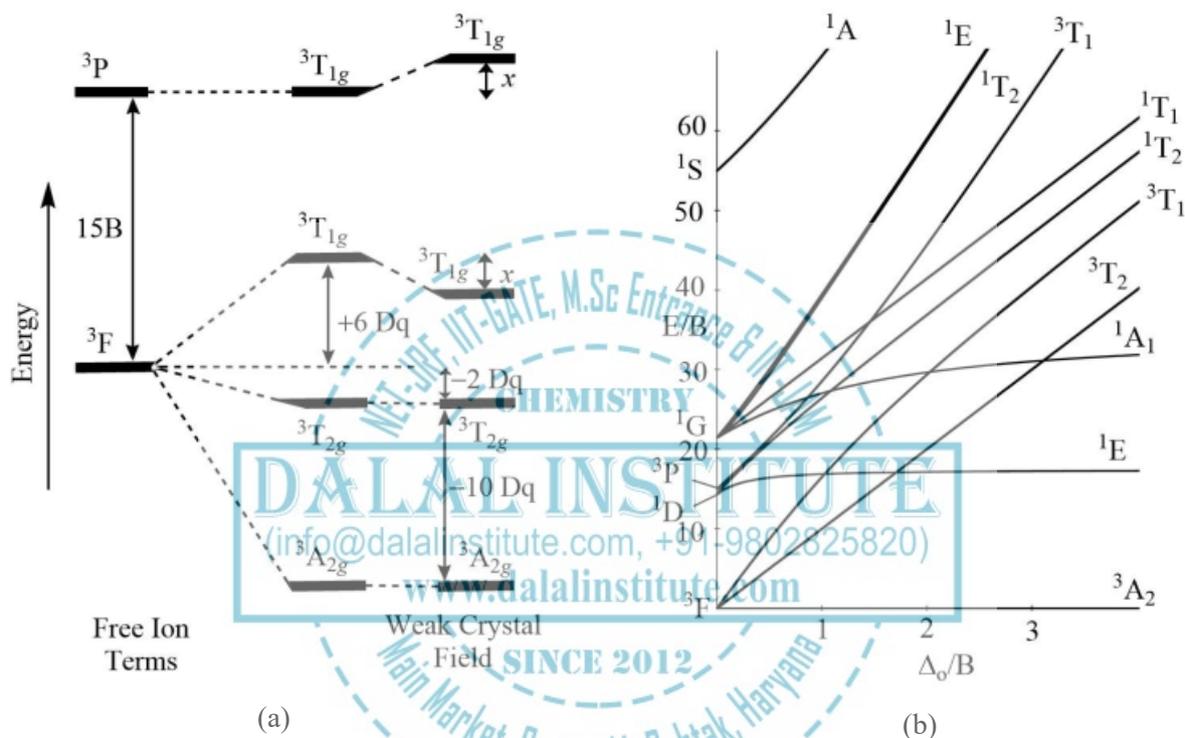


Figure 39. The (a) Orgel and (b) Tanabe-Sugano diagrams for d^8 complexes in the octahedral crystal field.

Consider the example of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$.

1. Calculation of B: From the Orgel diagram, it can be clearly seen that the ground state for d^8 -octahedral complexes is $^3A_{2g}$ and there are three main transitions. As the magnitude of the crystal field splitting energy increases, the $^3T_{1g}(\text{F})$ and $^3T_{1g}(\text{P})$ states repel each other more and more with a magnitude of x energy value owing to the non-crossing rule of the same symmetry states.

$$\nu_1 = {}^3A_{2g} \rightarrow {}^3T_{2g}$$

$$\nu_2 = {}^3A_{2g} \rightarrow {}^3T_{1g}$$

$$\nu_3 = {}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$$

Which gives

$$v_1 = 10 Dq \quad (1)$$

$$v_2 = 18 Dq - x \quad (2)$$

$$v_3 = 15 B + 12 Dq + x \quad (3)$$

Putting value of x from equation (2) in (3), we get

$$v_3 = 15 B + 12 Dq + 18 Dq - v_2$$

$$v_3 = 15 B + 30 Dq - v_2 \quad (4)$$

Multiplying equation (1) by 3 and putting the value of $30 Dq$ from equation (1) in (4), we get

$$v_3 = 15 B + 3v_1 - v_2$$

$$15 B = v_3 + v_2 - 3v_1$$

$$B = \frac{v_3 + v_2 - 3v_1}{15} \quad (5)$$

However, this method is applicable only when three transitions are observed. Moreover, this method is difficult to apply in a precise manner and only gives approximations.

From the Tanabe-Sugano diagram, in the UV-visible spectra of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, three bands are observed with maxima at around 8500, 14500 and 25300 cm^{-1} . There are three possible transitions expected, which include: $v_1 = {}^3A_{2g} \rightarrow {}^3T_{2g}$, $v_2 = {}^3A_{2g} \rightarrow {}^3T_{1g}$, and $v_3 = {}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$. The ratio of experimental band energies of v_3 to v_2 is:

$$\frac{v_3}{v_2} = \frac{E_3}{E_2} = \frac{E_3/B}{E_2/B} = \frac{25300}{14500} = 1.74$$

Now slide a ruler across the printed diagram (perpendicular to the abscissa) until the ratio of E_2/B to E_1/B between lines becomes equivalent to 1.74. In this particular example, this ratio becomes 1.74 when $\Delta_o/B = 10$. Stop the ruler movement and find out the values of E_3/B and E_2/B as:

$$\frac{E_3}{B} = 28; \quad \frac{E_2}{B} = 16$$

Thus, on the T-S diagram, where $\Delta_o/B = 10$; the value of ${}^3A_{2g} \rightarrow {}^3T_{1g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(\text{P})$ i.e. E_2/B and E_3/B , are 28 and 16, respectively. The Racah parameter can be found by calculating B from second and third i.e. from v_3 and v_2 transitions.

From v_3 , we get

$$\frac{25300}{B} = 28$$

$$B = \frac{25300}{28} = 904 \text{ cm}^{-1}$$

Similarly

$$\frac{14500}{B} = 16$$

$$B = \frac{14500}{16} = 906 \text{ cm}^{-1}$$

Therefore,

$$\text{Average value of Racah parameter (B)} = \frac{904 + 906}{2} = 905 \text{ cm}^{-1}$$

2. Calculation of Δ_o : Being a weak-complex, the theoretical value of lowest-energy absorption band given by the Orgel diagram is $10 Dq$ (${}^3A_{2g} \rightarrow {}^3T_{2g}$); and the experimental value for lowest-energy absorption band is 8500 cm^{-1} . Hence, the value of $10 Dq$ or Δ_o can be calculated as

$$10 Dq = 8500 \text{ cm}^{-1}$$

$$\Delta_o = 8500 \text{ cm}^{-1}$$

However, this is just the approximation and a more precise and refined calculation should be carried out using the Tanabe-Sugano diagram. From the average value of the Racah parameter, the ligand field splitting parameter can be found as follows.

$$\frac{\Delta_o}{B} = 10$$

$$\frac{\Delta_o}{905 \text{ cm}^{-1}} = 10$$

$$\Delta_o = 9050 \text{ cm}^{-1}$$

3. Calculation of β : In order to calculate the nephelauxetic ratio, we must have the value of the Racah parameter for a free metal ion in its gaseous state. For free d^8 ion like Ni^{2+} , it has been observed that 3P state lies 16200 cm^{-1} above to the 3F state. Hence, $15B = 16200 \text{ cm}^{-1}$ or $B = 1080 \text{ cm}^{-1}$. Now, the value of nephelauxetic ratio can be calculated as

$$\text{Nephelauxetic ratio} = \beta = \frac{B_{\text{complex}}}{B_{\text{free ion}}} = \frac{905 \text{ cm}^{-1}}{1080 \text{ cm}^{-1}} = 0.838$$

Hence, inter-electronic repulsion has been decreased during the process of complexation.

➤ d^3 Complexes

Metal complexes with d^3 -configuration have 4F ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes ${}^4A_{2g}$ and remains as such in weak as well as in strong ligand fields. The Orgel and Tanabe-Sugano diagram for d^3 -configuration can be used to estimate the value of crystal field splitting energy for these transition metal complexes.

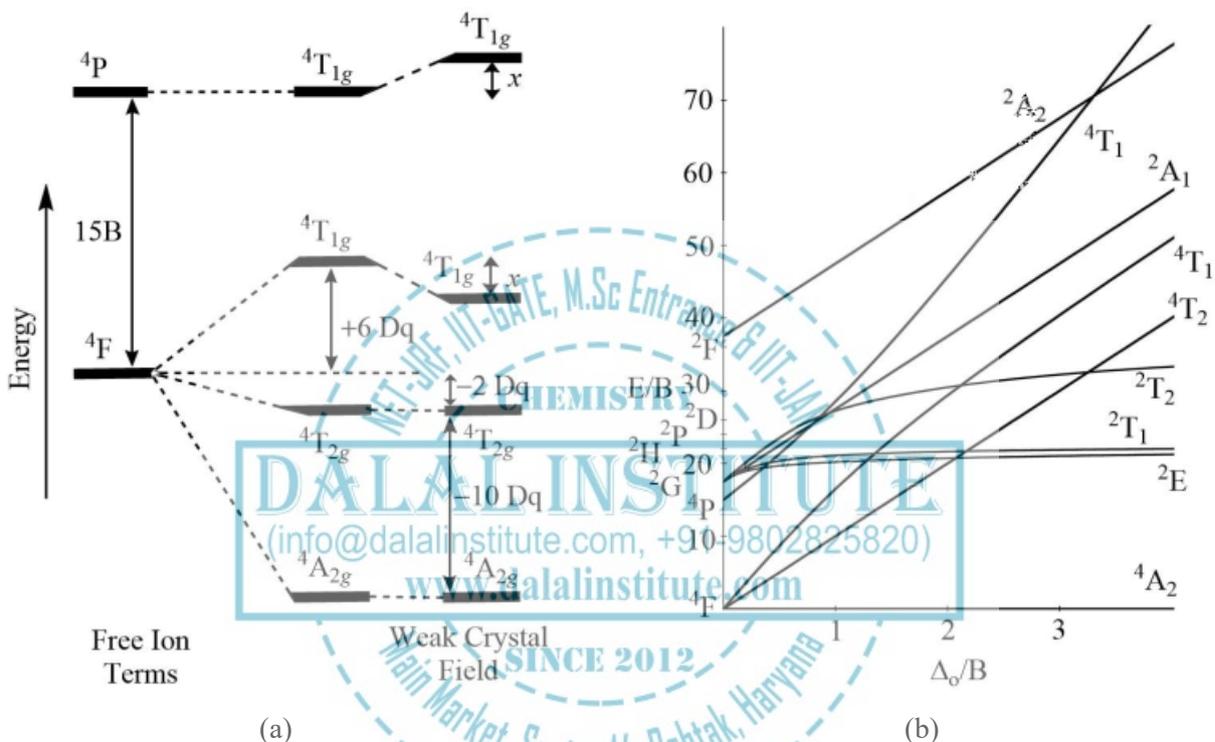


Figure 40. The (a) Orgel and (b) Tanabe-Sugano diagrams for d^3 complexes in the octahedral crystal field.

Consider the example of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$.

1. Calculation of B: From the Orgel diagram, it can be clearly seen that the ground state for d^3 -octahedral complexes is ${}^4A_{2g}$ and there are three main transitions. As the magnitude of the crystal field splitting energy increases, the ${}^4T_{1g}(\text{F})$ and ${}^4T_{1g}(\text{P})$ states repel each other more and more with a magnitude of x energy value owing to the non-crossing rule of the same symmetry states.

$$v_1 = {}^4A_{2g} \rightarrow {}^4T_{2g}$$

$$v_2 = {}^4A_{2g} \rightarrow {}^4T_{1g}$$

$$v_3 = {}^4A_{2g} \rightarrow {}^4T_{1g}(\text{P})$$

Which gives

$$v_1 = 10 Dq \quad (1)$$

$$v_2 = 18 Dq - x \quad (2)$$

$$v_3 = 15 B + 12 Dq + x \quad (3)$$

Putting the value of x from equation (2) in (3), we get

$$v_3 = 15 B + 12 Dq + 18 Dq - v_2$$

$$v_3 = 15 B + 30 Dq - v_2 \quad (4)$$

Multiplying equation (1) by 3 and putting the value of $30 Dq$ from equation (1) in (4), we get

$$v_3 = 15 B + 3v_1 - v_2$$

$$15 B = v_3 + v_2 - 3v_1$$

$$B = \frac{v_3 + v_2 - 3v_1}{15} \quad (5)$$

However, this method is applicable only when three transitions are observed. Moreover, this method is difficult to apply in a precise manner and only gives approximations.

From the Tanabe-Sugano diagram, in the UV-visible spectra of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$, three bands are observed with maxima at around 17000, 24000 and 37000 cm^{-1} . There are three possible transitions expected, which include: $v_1 = {}^4A_{2g} \rightarrow {}^4T_{2g}$, $v_2 = {}^4A_{2g} \rightarrow {}^4T_{1g}$, and $v_3 = {}^4A_{2g} \rightarrow {}^4T_{1g}(\text{P})$. The ratio of experimental band energies of v_2 to v_1 is:

$$\frac{v_2}{v_1} = \frac{E_2}{E_1} = \frac{E_2/B}{E_1/B} = \frac{24000}{17000} = 1.41$$

Now slide a ruler across the printed diagram (perpendicular to the abscissa) until the ratio of E_2/B to E_1/B between lines becomes equivalent to 1.41. In this particular example, this ratio becomes 1.41 when $\Delta_o/B = 24$. Stop the ruler movement and find out the values of E_2/B and E_1/B as:

$$\frac{E_2}{B} = 33.90; \quad \frac{E_1}{B} = 24$$

Thus, on the T-S diagram, where $\Delta_o/B = 24$; the value of ${}^4A_{2g} \rightarrow {}^4T_{1g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}(\text{P})$ i.e. E_2/B and E_3/B , are 33.90 and 24, respectively. The Racah parameter can be found by calculating B from first and second i.e. from v_2 and v_1 transitions.

From v_2 , we get

$$\frac{24000}{B} = 33.90$$

$$B = \frac{24000}{33.90} = 708 \text{ cm}^{-1}$$

Similarly

$$\frac{17000}{B} = 24$$

$$B = \frac{17000}{24} = 708 \text{ cm}^{-1}$$

Therefore,

$$\text{Average value of Racah parameter (B)} = \frac{708 + 708}{2} = 708 \text{ cm}^{-1}$$

2. Calculation of Δ_o : Being a weak-complex, the theoretical value of lowest-energy absorption band given by the Orgel diagram is $10 Dq$ (${}^4A_{2g} \rightarrow {}^4T_{2g}$); and the experimental value for lowest-energy absorption band is 17000 cm^{-1} . Hence, the value of $10 Dq$ or Δ_o can be calculated as

$$10 Dq = 17000 \text{ cm}^{-1}$$

$$\Delta_o = 17000 \text{ cm}^{-1}$$

However, this is just the approximation and a more precise and refined calculation should be carried out using the Tanabe-Sugano diagram. From the average value of the Racah parameter, the ligand field splitting parameter can be found as follows.

$$\frac{\Delta_o}{B} = 24$$

$$\frac{\Delta_o}{708 \text{ cm}^{-1}} = 24$$

$$\Delta_o = 16992 \text{ cm}^{-1}$$

3. Calculation of β : In order to calculate the nephelauxetic ratio, we must have the value of the Racah parameter for a free metal ion in its gaseous state. For free d^3 ion like Cr^{3+} , it has been observed that 3P state lies 15450 cm^{-1} above to the 3F state. Hence, $15B = 15450 \text{ cm}^{-1}$ or $B = 1030 \text{ cm}^{-1}$. Now, the value of nephelauxetic ratio can be calculated as:

$$\text{Nephelauxetic ratio} = \beta = \frac{B_{\text{complex}}}{B_{\text{free ion}}} = \frac{708 \text{ cm}^{-1}}{1030 \text{ cm}^{-1}} = 0.687$$

Hence, inter-electronic repulsion has been decreased during the process of complexation.

➤ d^7 Complexes

Metal complexes with d^7 -configuration have 4F ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes $^4T_{1g}$ in the weak field; and becomes 2E_g when the ligand field becomes sufficiently strong. The Orgel and Tanabe-Sugano diagram for d^7 -configuration can be used to estimate the value of crystal field splitting energy for these complexes.

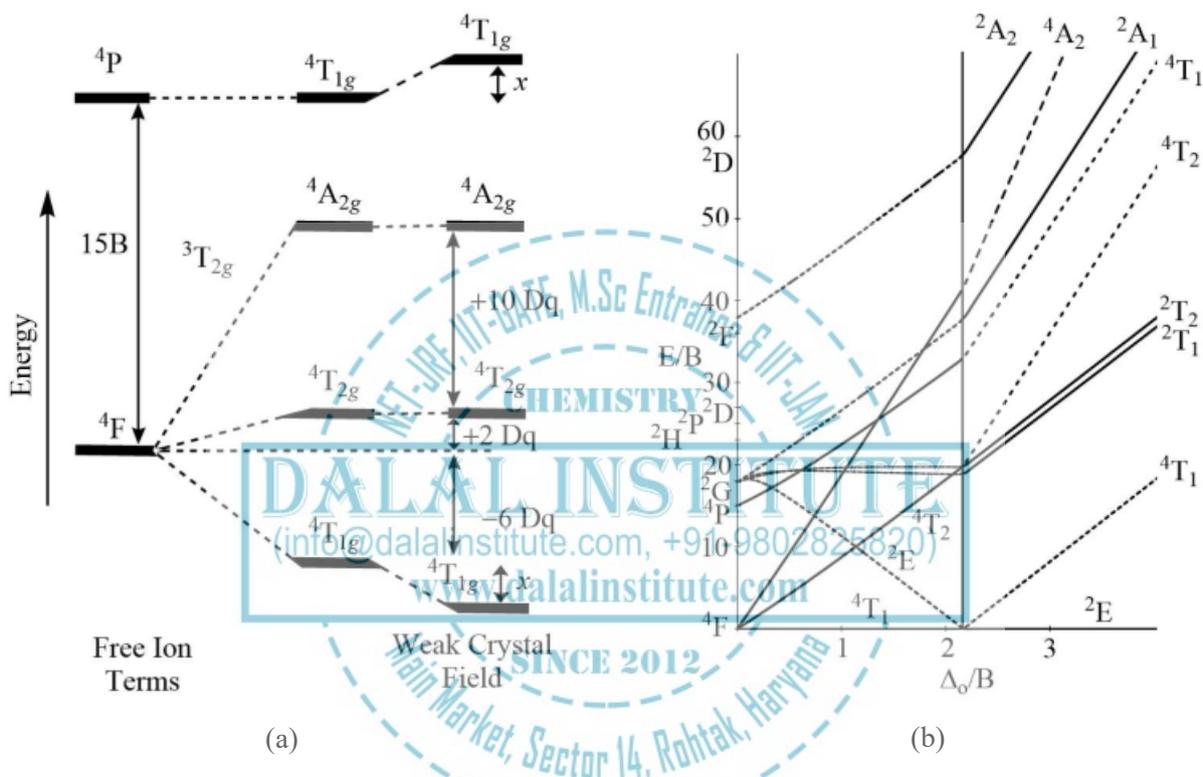


Figure 41. The (a) Orgel and (b) Tanabe-Sugano diagrams for d^7 complexes in the octahedral crystal field.

Consider the example of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$

1. Calculation of B: From the Orgel diagram, it can be clearly seen that the ground state for d^7 -octahedral complexes is $^4T_{1g}$ and there are three main transitions before the crossover point. Moreover, it is worthy to note down that the order of second and third transitions is reversed after the crossover point and only two bands will be observed at or near the crossover point. As the magnitude of the crystal field splitting energy increases, the $^4T_{1g}(\text{F})$ and $^4T_{1g}(\text{P})$ states repel each other more and more with a magnitude of x energy value.

$$\nu_1 = ^4T_{1g} \rightarrow ^4T_{2g}$$

$$\nu_2 = ^4T_{1g} \rightarrow ^4A_{2g}$$

$$v_3 = {}^4T_{1g} \rightarrow {}^4T_{1g}(P)$$

Which gives

$$v_1 = 8 Dq + x \quad (1)$$

$$v_2 = 18 Dq + x \quad (2)$$

$$v_3 = 15 B + 6 Dq + 2x \quad (3)$$

Adding equation (1) and (2), we get

$$v_2 + v_1 = 18 Dq + x + 8 Dq + x$$

$$v_2 + v_1 = 26 Dq + 2x \quad (4)$$

Subtracting equation (1) and (2), we get

$$v_2 - v_1 = 18 Dq + x - 8 Dq - x$$

$$v_2 - v_1 = 10 Dq \quad (5)$$

Putting the value of $2x$ from equation (4) in equation (3), we get

$$v_3 = 15 B + 6 Dq + v_2 + v_1 - 26 Dq$$

$$v_3 = 15 B + v_2 + v_1 - 20 Dq \quad (6)$$

Multiplying equation (5) by 2 and putting the value of $20 Dq$ from equation (5) in equation (6), we get

$$v_3 = 15 B + v_2 + v_1 - 20 Dq$$

$$v_3 = 15 B + v_2 + v_1 - 2v_2 + 2v_1$$

$$15 B = v_3 + v_2 - 3v_1$$

$$B = \frac{v_3 + v_2 - 3v_1}{15} \quad (7)$$

However, only two transitions are observed, this method is difficult to apply in a precise manner and only gives approximations.

From the Tanabe-Sugano diagram, in the UV-visible spectra of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$, two bands are observed with maxima at around 8000, 19600 and 21600 cm^{-1} . There are three possible transitions expected, which include: $v_1 = {}^4T_{1g} \rightarrow {}^4T_{2g}$, $v_2 = {}^4T_{1g} \rightarrow {}^4A_{2g}$ and $v_3 = {}^4T_{1g} \rightarrow {}^4T_{1g}(P)$. The ratio of experimental band energies is:

$$\frac{v_3}{v_1} = \frac{E_3}{E_1} = \frac{E_3/B}{E_1/B} = \frac{21600}{8000} = 2.70$$

Now slide a ruler across the printed diagram (perpendicular to the abscissa) until the ratio of E_3/B to E_1/B between lines becomes equivalent to 2.70. In this particular example, this ratio becomes 2.70 when $\Delta_o/B = 9.5$. Stop the ruler movement and find out the values of E_2/B and E_1/B as:

$$\frac{E_3}{B} = 22; \quad \frac{E_1}{B} = 8.2$$

Thus, on the T-S diagram, where $\Delta_o/B = 31$; the value of ${}^3T_{1g} \rightarrow {}^3T_{2g}$ and ${}^3T_{1g} \rightarrow {}^3T_{1g}(P)$ i.e. E_1/B and E_3/B , are 8.2 and 22, respectively. The Racah parameter can be found by calculating B from both ν_2 and ν_1 .

$$\frac{21600}{B} = 22; \quad \frac{8000}{B} = 8.2$$

$$B = \frac{21600}{22} = 982 \text{ cm}^{-1}; \quad B = \frac{8000}{8.2} = 976 \text{ cm}^{-1}$$

$$\text{Average value of Racah parameter (B)} = \frac{982 + 976}{2} = 979 \text{ cm}^{-1}$$

2. Calculation of Δ_o : Being a weak-complex, the theoretical value of lowest-energy absorption band given by the Orgel diagram is $8 Dq$ (${}^3T_{1g} \rightarrow {}^3T_{2g}$); and the experimental value for lowest-energy absorption band is 8000 cm^{-1} . Hence, the value of $10 Dq$ or Δ_o can be calculated as

$$8 Dq = 0.8 \Delta_o = 8000 \text{ cm}^{-1}$$

$$\Delta_o = \frac{8000 \text{ cm}^{-1}}{0.8}$$

$$\Delta_o = 10 Dq = 10000 \text{ cm}^{-1}$$

However, this is just the approximation and a more precise and refined calculation should be carried out using the Tanabe-Sugano diagram. From the average value of the Racah parameter, the ligand field splitting parameter can be found as follows.

$$\frac{\Delta_o}{B} = 9.5; \quad \frac{\Delta_o}{979 \text{ cm}^{-1}} = 9.5; \quad \Delta_o = 9300 \text{ cm}^{-1}$$

3. Calculation of β : In order to calculate the nephelauxetic ratio, we must have the value of the Racah parameter for a free metal ion in its gaseous state. For free d^7 ion like Co^{2+} , it has been observed that 3P state lies 16755 cm^{-1} above to the 3F state. Hence, $15B = 16755 \text{ cm}^{-1}$ or $B = 1117 \text{ cm}^{-1}$. Now, the value of nephelauxetic ratio can be calculated as:

$$\text{Nephelauxetic ratio} = \beta = \frac{B_{\text{complex}}}{B_{\text{free ion}}} = \frac{979 \text{ cm}^{-1}}{1117 \text{ cm}^{-1}} = 0.876$$

Hence, inter-electronic repulsion has been decreased during the process of complexation.

➤ *d⁴ Complexes*

Metal complexes with d^4 -configuration have 5D ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes 5E_g in the weak field; and becomes $^3T_{1g}$ when the ligand field becomes sufficiently strong. The Orgel and Tanabe-Sugano diagram for d^4 -configuration can be used to estimate the value of crystal field splitting energy for these complexes.

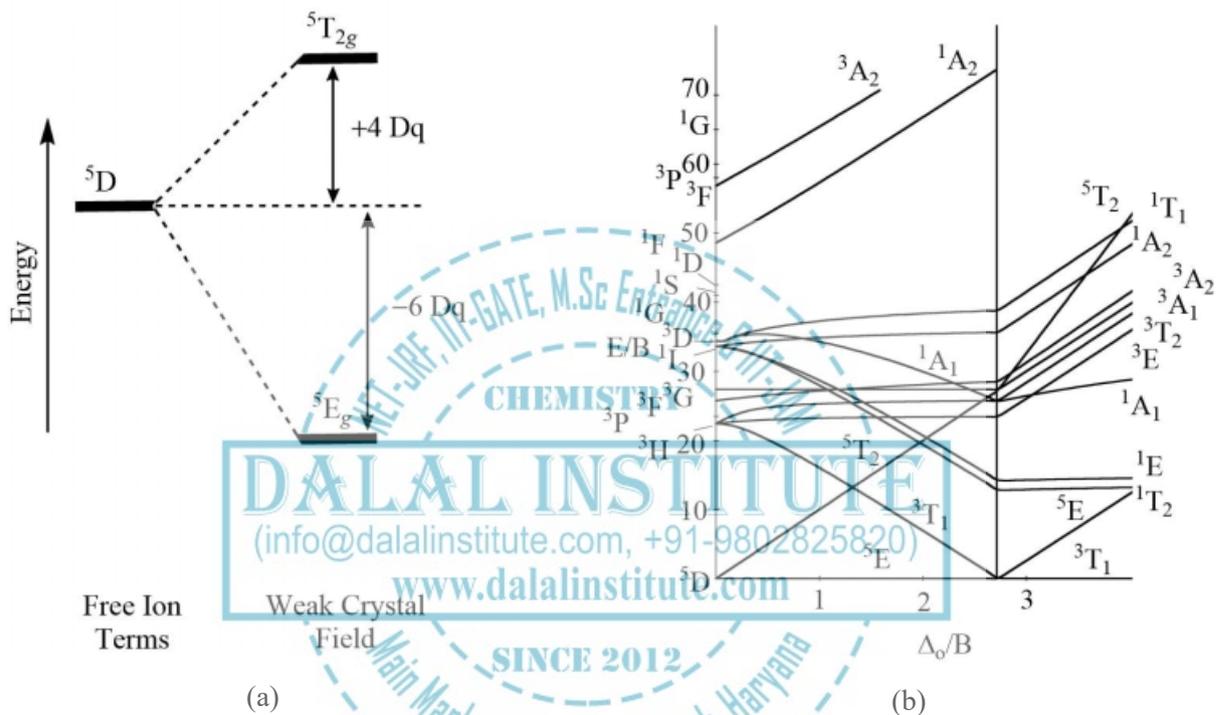


Figure 42. The (a) Orgel and (b) Tanabe-Sugano diagrams for d^4 complexes in the octahedral crystal field.

Consider the example of $[\text{Mn}(\text{CN})_6]^{3-}$

1. Calculation of B: From the Tanabe-Sugano diagram, it can clearly be seen that the spin-allowed $d-d$ transitions in low-spin d^4 metal complexes are $^3T_{1g} \rightarrow ^3E_g$, $^3T_{1g} \rightarrow ^3T_{2g}$, $^3T_{1g} \rightarrow ^3A_{1g}$ and $^3T_{1g} \rightarrow ^3A_{2g}$. In the UV-visible absorption spectra of $[\text{Mn}(\text{CN})_6]^{3-}$, three bands are observed; one strong band with maxima at around 27000 and other two bands at 29000 and 34000 cm^{-1} . Moreover, the bands at 21800 and 43500 cm^{-1} can be ignored as they correspond to charge transfer transitions. Thus, the ratio of experimental energies is

$$\frac{\nu_2}{\nu_1} = \frac{E_2}{E_1} = \frac{E_2/B}{E_1/B} = \frac{29000 \text{ cm}^{-1}}{27000 \text{ cm}^{-1}} = 1.07$$

Now slide a ruler across the printed diagram (perpendicular to the abscissa) until the ratio of E_2/B to E_1/B i.e. the ratio between the lines corresponding to the first two spin-allowed transitions becomes equivalent

to 1.07. In this particular example, this ratio becomes 1.07 when $\Delta_o/B = 40$. Stop the ruler movement and find out the values of E_2/B and E_1/B .

$$\frac{E_2}{B} = 38; \quad \frac{E_1}{B} = 35$$

Thus, on the T-S diagram, where $\Delta_o/B = 40$; the value of ${}^3T_{1g} \rightarrow {}^3T_{2g}$ and ${}^3T_{1g} \rightarrow {}^3E_g$ i.e. E_2/B and E_1/B , are 38 and 35, respectively. The Racah parameter can be found by calculating B from both ν_2 and ν_1 .

$$\frac{29000 \text{ cm}^{-1}}{B} = 38; \quad \frac{27000 \text{ cm}^{-1}}{B} = 35$$

$$B = \frac{29000 \text{ cm}^{-1}}{38} = 763 \text{ cm}^{-1}; \quad B = \frac{27000 \text{ cm}^{-1}}{35} = 771 \text{ cm}^{-1}$$

$$\text{Average value of Racah parameter (B)} = \frac{763 \text{ cm}^{-1} + 771 \text{ cm}^{-1}}{2} = 767 \text{ cm}^{-1}$$

2. Calculation of Δ_o : The only parameter that is needed to be sought for the calculation of the magnitude of crystal field splitting energy (10 Dq) in weak field complexes is the single absorption band in a UV-vis experiment. Hence, the energy of the transition ${}^5E_g \rightarrow {}^5T_{2g}$ should give the value of Δ directly. In other words, the lowest energy absorption band in d^4 high-spin complexes is equal to the crystal field splitting energy. However, the magnitude of crystal field splitting energy for high-spin d^4 complexes cannot be obtained accurately from the Orgel diagram as the Jahn-Teller distortion reduces the symmetry from perfectly octahedral to a tetragonal geometry. The effect of Jahn-Teller distortion will be discussed later in this chapter. Furthermore, the practical applicability of the Tanabe-Sugano diagram in the high-spin region (before $\Delta_o/B = 27$) is strongly doubted because only one spin allowed transition is present, and it is a fact that two minimum spin-allowed transitions are required for the ratio calculation.

Being a strong-field complex, the theoretical value of crystal field splitting energy in $[\text{Mn}(\text{CN})_6]^{3-}$ cannot be given by the Orgel diagram; hence, we are bound to use Tanabe-Sugano diagram. From the average value of the Racah parameter, what we have deduced earlier, the ligand field splitting parameter can be found as follows.

$$\frac{\Delta_o}{B} = 40; \quad \frac{\Delta_o}{767 \text{ cm}^{-1}} = 40; \quad \Delta_o = 30680 \text{ cm}^{-1}$$

3. Calculation of β : In order to calculate the nephelauxetic ratio, we must have the value of the Racah parameter for a free metal ion in its gaseous state. For free d^4 ion like Mn^{3+} , the value of B is found to be 1140 cm^{-1} . Now, the value of nephelauxetic ratio can be calculated as

$$\text{Nephelauxetic ratio} = \beta = \frac{B_{\text{complex}}}{B_{\text{free ion}}} = \frac{767 \text{ cm}^{-1}}{1140 \text{ cm}^{-1}} = 0.673$$

Hence, inter-electronic repulsion has been decreased during the process of complexation.

➤ d^6 Complexes

Metal complexes with d^6 -configuration have 5D ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes $^5T_{2g}$ in the weak field; and becomes $^1A_{1g}$ when the ligand field becomes sufficiently strong. The Orgel and Tanabe-Sugano diagram for d^6 -configuration can be used to estimate the value of crystal field splitting energy for these complexes.

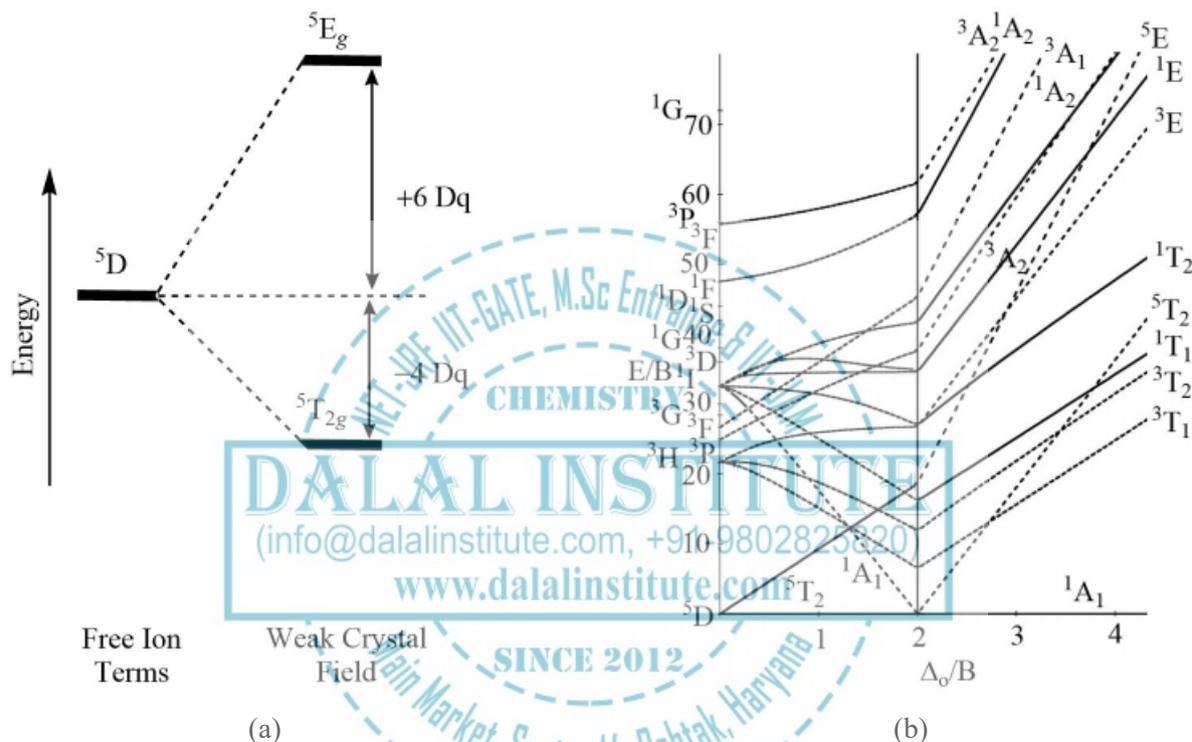


Figure 42. The (a) Orgel and (b) Tanabe-Sugano diagrams for d^6 complexes in octahedral crystal field.

Consider the example of $[\text{Co}(\text{en})_3]^{3+}$

1. Calculation of B: From the Tanabe-Sugano diagram, it can clearly be seen that the spin-allowed $d-d$ transitions in low-spin d^6 metal complexes are $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$. In the UV-visible absorption spectra of $[\text{Co}(\text{en})_3]^{3+}$, two bands are observed; one strong band with maxima at around 21450 and the other band at 29450 cm^{-1} . Therefore, the ratio of experimental band energies is

$$\frac{\nu_2}{\nu_1} = \frac{E_2}{E_1} = \frac{E_2/B}{E_1/B} = \frac{29450 \text{ cm}^{-1}}{21450 \text{ cm}^{-1}} = 1.37$$

Now slide a ruler across the printed diagram (perpendicular to the abscissa) until the ratio of E_2/B to E_1/B i.e. the ratio between the lines corresponding to the first two spin-allowed transitions becomes equivalent

to 1.37. In this particular example, this ratio becomes 1.37 when $\Delta_o/B = 40$. Stop the ruler movement and find out the values of E_2/B and E_1/B .

$$\frac{E_2}{B} = 52; \quad \frac{E_1}{B} = 38$$

Thus, on the T-S diagram, where $\Delta_o/B = 40$; the value of ${}^1A_{1g} \rightarrow {}^1T_{2g}$ and ${}^1A_{1g} \rightarrow {}^1T_{1g}$ i.e. E_2/B and E_1/B , are 52 and 38, respectively. The Racah parameter can be found by calculating B from both ν_2 and ν_1 .

$$\frac{29450 \text{ cm}^{-1}}{B} = 52; \quad \frac{21450 \text{ cm}^{-1}}{B} = 38$$

$$B = \frac{29450 \text{ cm}^{-1}}{52} = 566 \text{ cm}^{-1}; \quad B = \frac{21450 \text{ cm}^{-1}}{38} = 564 \text{ cm}^{-1}$$

$$\text{Average value of Racah parameter (B)} = \frac{566 \text{ cm}^{-1} + 564 \text{ cm}^{-1}}{2} = 565 \text{ cm}^{-1}$$

2. Calculation of Δ_o : The only parameter that is needed to be sought for the calculation of the magnitude of crystal field splitting energy (10 Dq) in weak-field d^6 -complexes is the single absorption band in a UV-vis experiment. Hence, the energy of the transition ${}^5T_{2g} \rightarrow {}^5E_g$ should give the value of Δ directly. In other words, the lowest energy absorption band in d^6 high-spin complexes is equal to the crystal field splitting energy. However, the magnitude of crystal field splitting energy for high-spin d^6 complexes cannot be obtained accurately from the Orgel diagram as the Jahn-Teller distortion reduces the symmetry from perfectly octahedral to a tetragonal geometry. The effect of Jahn-Teller distortion will be discussed later in this chapter. Furthermore, the practical applicability of the Tanabe-Sugano diagram in the high-spin region (before $\Delta_o/B = 20$) is strongly doubted because only one spin allowed transition is present, and it is a fact that two minimum spin-allowed transitions are required for the ratio calculation.

Being a strong-field complex, the theoretical value of crystal field splitting energy in $[\text{Co(en)}_3]^{3+}$ cannot be given by the Orgel diagram; hence, we are bound to use Tanabe-Sugano diagram. From the average value of the Racah parameter, what we have deduced earlier, the ligand field splitting parameter can be found as follows.

$$\frac{\Delta_o}{B} = 40; \quad \frac{\Delta_o}{565 \text{ cm}^{-1}} = 40; \quad \Delta_o = 22600 \text{ cm}^{-1}$$

3. Calculation of β : In order to calculate the nephelauxetic ratio, we must have the value of the Racah parameter for a free metal ion in its gaseous state. For free d^6 ion like Co^{3+} , the value of B is found to be 1100 cm^{-1} . Now, the value of nephelauxetic ratio can be calculated as

$$\text{Nephelauxetic ratio} = \beta = \frac{B_{\text{complex}}}{B_{\text{free ion}}} = \frac{565 \text{ cm}^{-1}}{1100 \text{ cm}^{-1}} = 0.514$$

Hence, inter-electronic repulsion has been decreased during the process of complexation.

➤ d^5 Complexes

Metal complexes with d^5 -configuration have 6S ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes ${}^6A_{1g}$ in the weak field; and becomes ${}^2T_{2g}$ when the ligand field becomes sufficiently strong. The Tanabe-Sugano diagram for d^5 -configuration can be used to estimate the value of crystal field splitting energy for these complexes.

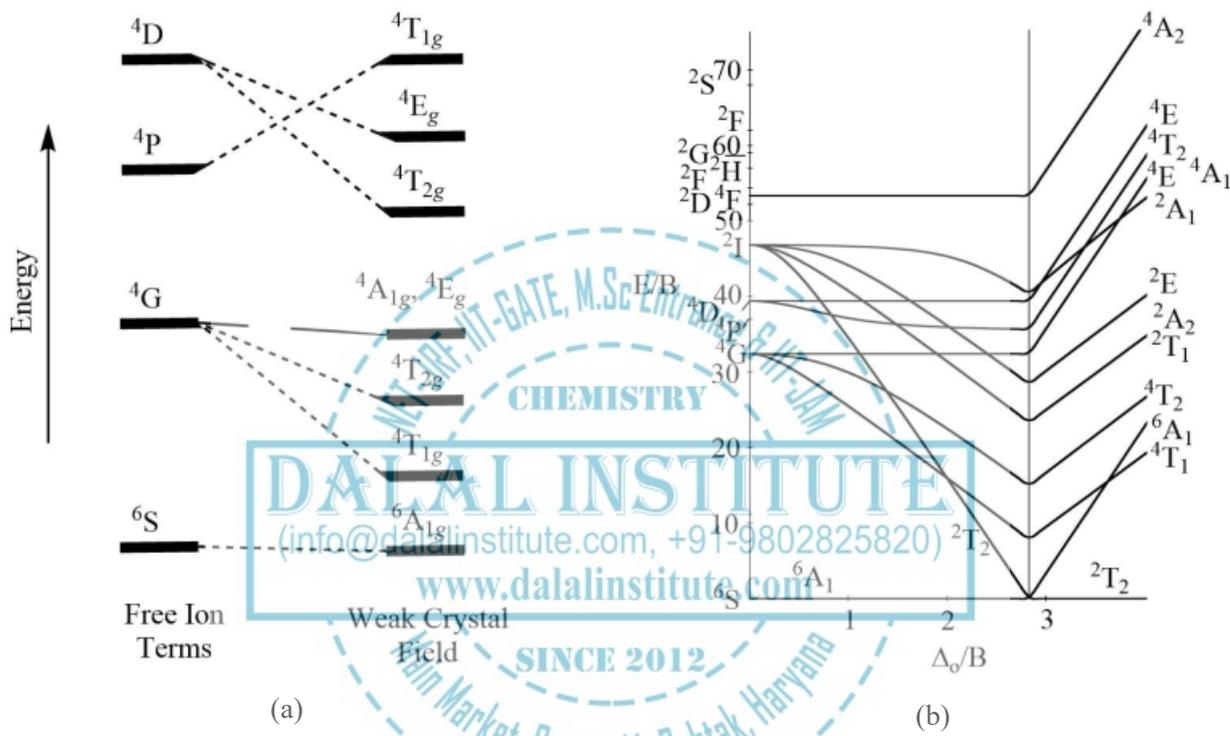


Figure 42. The (a) Orgel and (b) Tanabe-Sugano diagrams for d^5 complexes in the octahedral crystal field.

Consider the example of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

1. Calculation of B: From the Tanabe-Sugano diagram, it can clearly be seen that there is no spin-allowed $d-d$ transitions in high-spin d^5 metal complexes. However, main spin-forbidden transitions are ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$, ${}^6A_{1g} \rightarrow {}^4A_{1g}(G)$, ${}^6A_{1g} \rightarrow {}^4E_g(G)$, ${}^1A_{1g} \rightarrow {}^4T_{2g}(D)$ and ${}^1A_{1g} \rightarrow {}^4E_g(D)$. In the UV-visible absorption spectra of $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, the first two bands are observed at around 18600 and the other band at 22900 cm^{-1} . Therefore, the ratio of experimental band energies is

$$\frac{\nu_2}{\nu_1} = \frac{E_2}{E_1} = \frac{E_2/B}{E_1/B} = \frac{22900 \text{ cm}^{-1}}{18600 \text{ cm}^{-1}} = 1.23$$

Now slide a ruler across the printed diagram (perpendicular to the abscissa) until the ratio of E_2/B to E_1/B i.e. the ratio between the lines corresponding to the first two spin-allowed transitions becomes equivalent

to 1.23. In this particular example, this ratio becomes 1.23 when $\Delta_o/B = 11$. Stop the ruler movement and find out the values of E_2/B and E_1/B .

$$\frac{E_2}{B} = 29$$

$$\frac{E_1}{B} = 24$$

Thus, on the Tanabe-Sugano diagram, where $\Delta_o/B = 11$; the value of ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$ i.e. E_2/B and E_1/B , are 29 and 24, respectively. The Racah parameter can be found by calculating B from both ν_2 and ν_1 .

$$\frac{22900 \text{ cm}^{-1}}{B} = 29$$

$$\frac{18600 \text{ cm}^{-1}}{B} = 24$$

$$B = \frac{22900 \text{ cm}^{-1}}{29} = 789 \text{ cm}^{-1}; \quad B = \frac{18600 \text{ cm}^{-1}}{24} = 775 \text{ cm}^{-1}$$

$$\text{Average value of Racah parameter (B)} = \frac{789 \text{ cm}^{-1} + 775 \text{ cm}^{-1}}{2} = 782 \text{ cm}^{-1}$$

2. Calculation of Δ_o : The magnitude of crystal field splitting energy for high-spin d^5 complexes cannot be obtained accurately from the Orgel diagram as the degeneracy of the ground state term is only one and does not split at all in the octahedral field. Therefore, we are bound to use the Tanabe-Sugano diagram. From the average value of the Racah parameter, what we have deduced earlier, the ligand field splitting parameter can be found as follows.

$$\frac{\Delta_o}{B} = 11$$

$$\frac{\Delta_o}{782 \text{ cm}^{-1}} = 11$$

$$\Delta_o = 8602 \text{ cm}^{-1}$$

3. Calculation of β : In order to calculate the nephelauxetic ratio, we must have the value of Racah parameter for a free metal ion in its gaseous state. For free d^5 ion like Mn^{2+} , the value of B is found to be 960 cm^{-1} . Now, the value of nephelauxetic ratio can be calculated as

$$\text{Nephelauxetic ratio} = \beta = \frac{B_{\text{complex}}}{B_{\text{free ion}}} = \frac{782 \text{ cm}^{-1}}{960 \text{ cm}^{-1}} = 0.814$$

Hence, the inter-electronic repulsion has been decreased during the process of complexation.

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