US05CCHE22 (SEM-V)

Unit-2: CRYSTAL FIELD THEORY

Calculation of CFSE from d^0 to d^{10}

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The CFSE value for each d^x ion ($x = 0$ to 10) having $t^p_{2g}e^q_g$ configuration $p + q = x$) for octahedral complex has been calculated as shown below:

1. d^0 ion

$t^p_{2g}e^q_g$ configuration of d^0 ion = $t^0_{2g}e^0_g$ (p=0, q=0, n=0, S=0, m=0)

∴ CFSE for d^0 ion $= (-0.4 \times p + 0.6 \times q)\Delta_0 + mP$

$= (-0.4 \times 0 + 0.6 \times 0)\Delta_0 + 0 \times P$

= **Zero**

2. d^1 ion

$t^p_{2g}e^q_g$ configuration of d^1 ion = $t^1_{2g}e^0_g$ (p=1, q=0, n=1, S=1/2, m=0)

∴ CFSE for d^1 ion $= (-0.4 \times p + 0.6 \times q)\Delta_0 + m \times p$

$= (-0.4 \times 1 + 0.6 \times 0)\Delta_0 + 0 \times p$

$= \mathbf{-0.4\ \Delta_0}$

$= -0.4 \times 10\ Dq$ (as $\Delta_0 = 10\ Dq$)

$= \mathbf{-4.0\ Dq}$

3. d^2 ion

$t^p_{2g}e^q_g$ configuration of d^2 ion = $t^2_{2g}e^0_g$ (p=2, q=0, n=2, S=2/2, m=0)

∴ CFSE for d^2 ion $= (-0.4 \times p + 0.6 \times q)\Delta_0 + mP$

$= (-0.4 \times 2 + 0.6 \times 0)\Delta_0 + 0 \times P$

$= \mathbf{-0.8\ \Delta_0}$

$= -0.8 \times 10Dq$

$= \mathbf{-8\ Dq}$

Note: The actual value of CFSE of d^2 metal ion in octahedral field environ ment is 6Dq which has been obtained by considering the effects of d-orbitals splitting and interelectronic repulsion amongst d-electrons. If the effects of d-orbitals splitting alone is considered and the effects of inter electronic repulsion amongst d electrons is ignored, then the value of CFSE for d^2 ion is 8Dq as shown above.

4. d^3 ion

$t^p_{2g}e^q_g$ configuration of d^3 ion = $t^3_{2g}e^0_g$ (p=3, q=0, n=3, S=3/2, m=0)

∴ CFSE for d^2 ion = $(-0.4 \times p + 0.6 \times q)\Delta_0 + mP$

= $(-0.4 \times 3 + 0.6 \times 0)\Delta_0 + 0 \times P$

= **$-1.2\ \Delta_0$**

= -1.2×10 Dq

= **-12 Dq**

5. d^4 ion in HS state (weak ligands)

$t^p_{2g}e^q_g$ configuration of d^4 ion = $t^3_{2g}e^1_g$ (p=3, q=1, n=4, S=4/2, m=0)

∴ CFSE for d^4 ion in HS state = $(-0.4 \times p + 0.6 \times q)\Delta_0 + mP$

= $(-0.4 \times 3 + 0.6 \times 1)\Delta_0 + 0 \times P$

= **$-0.6\ \Delta_0$**

= -0.6×10 Dq

= **-6.0 Dq**

6. d^4 ion in LS state (strong ligands)

$t^p_{2g}e^q_g$ configuration of d^4 ion in LS state ($\Delta_0 > P$)

= $t^4_{2g}e^0_g$ (p=4, q=0, n=2, S=2/2, m=1)

∴ CFSE for d^4 ion in LS state = $(-0.4 \times p + 0.6 \times q)\Delta_0 + mP$

= $(-0.4 \times 4 + 0.6 \times 0)\Delta_0 + 1 \times P$

= **$-1.6\ \Delta_0 + P$**

= -1.6×10 Dq + P

= **-16 Dq + P**

7. d^5 ion in HS state (weak ligands)

$t^p_{2g}e^q_g$ configuration of d^5 ion in HS state ($\Delta_0 < P$)

= $t^3_{2g}e^2_g$ (p=3, q=2, n=5, S=5/2, m=0)

∴ CFSE for d^5 ion in HS state = $(-0.4 \times p + 0.6 \times q)\Delta_0 + mP$

= $(-0.4 \times 3 + 0.6 \times 2)\Delta_0 + 0 \times P$

= **Zero**

8. d^5 ion in LS state (strong ligands)

$t^p_{2g}e^q_g$ configuration of d^5 ion in LS state ($\Delta_0 > P$)

= $t^5_{2g}e^0_g$ (p=5, q=0, n=1, S=1/2, m=2)

∴ CFSE for d^5 ion in LS state = $(-0.4 \times p + 0.6 \times q)\Delta_0 + mP$

= $(-0.4 \times 5 + 0.6 \times 0)\Delta_0 + 2 \times P$

$= \mathbf{-2.0\ \Delta_0 + 2P}$

$= -2 \times 10\ Dq + P$

$= \mathbf{-20\ Dq + P}$

9. d^6 ion in HS state (weak ligands)

$t^p_{2g}e^q_g$ configuration of d^5 ion in HS state ($\Delta_0 < P$)

$= t^4_{2g}e^2_g$ (p=4, q=2, n=4, S=4/2, m=1)

∴ CFSE for d^6 ion in HS state $= (-0.4 \times p + 0.6 \times q)\Delta_0 + mP$

$= (-0.4 \times 4 + 0.6 \times 2)\Delta_0 + 1 \times P$

$= \mathbf{-0.4\ \Delta_0 + P}$

$= -0.4 \times 10\ Dq + P$

$= \mathbf{-4\ Dq + P}$

10. d^6 ion in LS state (strong ligands)

$t^p_{2g}e^q_g$ configuration of d^6 ion in LS state ($\Delta_0 > P$)

$= t^6_{2g}e^0_g$ (p=6, q=0, n=0, S=0, m=3)

∴ CFSE for d^6 ion in HS state $= (-0.4 \times p + 0.6 \times q)\Delta_0 + mP$

$= (-0.4 \times 6 + 0.6 \times 0)\Delta_0 + 3 \times P$

$= \mathbf{-2.4\ \Delta_0 + 3P}$

$= -2.4 \times 10\ Dq + 3P$

$= \mathbf{-24\ Dq + 3P}$

11. d^7 ion in HS state (weak ligands)

$t^p_{2g}e^q_g$ configuration of d^7 ion in HS state ($\Delta_0 < P$)

$= t^5_{2g}e^2_g$ (p=5, q=2, n=4, S=3/2, m=2)

∴ CFSE for d^7 ion in HS state $= (-0.4 \times p + 0.6 \times q)\Delta_0 + mP$

$= (-0.4 \times 5 + 0.6 \times 2)\Delta_0 + 2 \times P$

$= \mathbf{-0.8\ \Delta_0 + 2P}$

$= -0.8 \times 10\ Dq + 2P$

$= \mathbf{-8\ Dq + 2P}$

Note: The actual value of CFSE of d^7 metal ion in weak octahedral ligand field environment is (-6Dq + 2P) which has been obtained by considering the effect of d-orbitals splitting and inter electronic repulsion amongst d electronic. If the effect of d-orbitals splitting alone is considered and the effects of interelectronic repulsion amongst d electrons is ignored, then the value of CFSE for d^7 ion (HS) is (-8Dq +2P) as shown above.

12. d^7 ion in LS state (strong ligands)

$t^p_{2g}e^q_g$ configuration of d^7 ion in LS state ($\Delta_0 > P$)

= $t^6_{2g}e^1_g$ (p=6, q=1, n=1, S=1/2, m=3)

$\therefore$ CFSE for d^7 ion in LS state = $(-0.4 \times p + 0.6 \times q)\Delta_0 + mP$

= $(-0.4 \times 6 + 0.6 \times 1)\Delta_0 + 3 \times P$

= $- 1.8\ \Delta_0 + 3P$

= -1.8×10 Dq + 3P

= - 18 Dq + 3P

13. d^8

$t^p_{2g}e^q_g$ configuration of d^8 ion = $t^6_{2g}e^2_g$ (p=6, q=2, n=2, S=2/2, m=3)

$\therefore$ CFSE for d^2 ion = $(-0.4 \times p + 0.6 \times q)\Delta_0 + mP$

= $(-0.4 \times 6 + 0.6 \times 2)\Delta_0 + 3 \times P$

= $- 1.2\ \Delta_0 + 3P$

= -1.2×10Dq + 3P

= - 12 Dq + 3P

14. d^9

$t^p_{2g}e^q_g$ configuration of d^9 ion = $t^6_{2g}e^3_g$ (p=6, q=3, n=1, S=1/2, m=4)

$\therefore$ CFSE for d^9 ion = $(-0.4 \times p + 0.6 \times q)\Delta_0 + mP$

= $(-0.4 \times 6 + 0.6 \times 3)\Delta_0 + 4 \times P$

= $- 0.6\ \Delta_0 + 4P$

= -0.6×10Dq + 4P

= - 6 Dq + 4P

15. d^{10}

$t^p_{2g}e^q_g$ configuration of d^{10} ion = $t^6_{2g}e^4_g$ (p=6, q=4, n=0, S=0, m=5)

$\therefore$ CFSE for d^9 ion = $(-0.4 \times p + 0.6 \times q)\Delta_0 + mP$

= $(-0.4 \times 6 + 0.6 \times 4)\Delta_0 + 5 \times P$

= 0 + 5P

= 5P

The CFSE value for each d^x ion (x = 0 to 10) having $t^p_{2g}e^q_g$ configuration p + q = x) for <u>tetrahedral complex</u> has been calculated as shown below:

1. d^0 ion

$e^p\ t^q_2$ configuration of d^0 ion = $e^0\ t^0_2$ (p=0, q=0,)

∴ CFSE for d^0 ion = $(-0.6 \times p + 0.4 \times q)\Delta_t$

= $(-0.6 \times 0 + 0.4 \times 0)\Delta_t$

= **Zero**

2. d^1 ion

$e^p t^q_2$ configuration of d^1 ion = $e^1 t^0_2$ (p=1, q=0,)

∴ CFSE for d^0 ion = $(-0.6 \times p + 0.4 \times q)\Delta_t$

= $(-0.6 \times 1 + 0.4 \times 0)\Delta_t$

= **$-0.6\ \Delta_t$**

= $-0.6 \times 0.45\ \Delta_0$

= $-0.270\ \Delta_0$

= $-0.270 \times 10Dq$

= -2.7Dq

3. d^2 ion

$e^p t^q_2$ configuration of d^2 ion = $e^2 t^0_2$ (p=2, q=0,)

∴ CFSE for d^0 ion = $(-0.6 \times p + 0.4 \times q)\Delta_t$

= $(-0.6 \times 2 + 0.4 \times 0)\Delta_t$

= **$-1.2\ \Delta_t$**

= $-1.2 \times 0.45\ \Delta_0$

= $-0.270\ \Delta_0$

= $-0.540 \times 10Dq$

= - 5.4Dq

4. d^3 ion

$e^p t^q_2$ configuration of d^3 ion = $e^2 t^1_2$ (p=2, q=1,)

∴ CFSE for d^0 ion = $(-0.6 \times p + 0.4 \times q)\Delta_t$

= $(-0.6 \times 2 + 0.4 \times 1)\Delta_t$

= **$-0.8\ \Delta_t$**

= $-0.8 \times 0.45\ \Delta_0$

= $-0.36\ \Delta_0$

= $-0.36 \times 10Dq$

= - 3.6Dq

5. d^4 ion

$e^p t^q_2$ configuration of d^4 ion = $e^2 t^2_2$ (p=2, q=2,)

∴ CFSE for d^0 ion = $(-0.6 \times p + 0.4 \times q)\Delta_t$

= $(-0.6 \times 2 + 0.4 \times 2)\Delta_t$

= **$-0.4\ \Delta_t$**

$= -\ 0.4 \times 0.45\ \Delta_0$

$\mathbf{= -\ 0.18}\ \Delta_0$

$= -\ 0.18 \times 10Dq$

$= -\ 1.8Dq$

6. d^5 ion

$e^p\ t^q_2$ configuration of d^5 ion $= e^2\ t^3_2$ (p=2, q=3,)

$\therefore$ CFSE for d^0 ion $= (-0.6 \times p + 0.4 \times q)\Delta_t$

$= (-0.6 \times 2 + 0.4 \times 3)\Delta_t$

$= \mathbf{0} \times \Delta_t$

= Zero

7. d^6 ion

$e^p\ t^q_2$ configuration of d^6 ion $= e^3\ t^3_2$ (p=3, q=3,)

$\therefore$ CFSE for d^0 ion $= (-0.6 \times p + 0.4 \times q)\Delta_t$

$= (-0.6 \times 3 + 0.4 \times 3)\Delta_t$

$= \mathbf{-\ 0.6\ \Delta_t}$

$= -\ 0.6 \times 0.45\ \Delta_0$

$\mathbf{= -\ 0.27}\ \Delta_0$

$= -\ 0.27 \times 10Dq$

$= -\ 2.7Dq$

8. d^7 ion

$e^p\ t^q_2$ configuration of d^7 ion $= e^4\ t^3_2$ (p=4, q=3,)

$\therefore$ CFSE for d^0 ion $= (-0.6 \times p + 0.4 \times q)\Delta_t$

$= (-0.6 \times 4 + 0.4 \times 3)\Delta_t$

$= \mathbf{-\ 1.2\ \Delta_t}$

$= -\ 1.2 \times 0.45\ \Delta_0$

$\mathbf{= -\ 0.54}\ \Delta_0$

$= -\ 0.54 \times 10Dq$

$= -\ 5.4Dq$

9. d^8 ion

$e^p\ t^q_2$ configuration of d^8 ion $= e^4\ t^4_2$ (p=4, q=4,)

$\therefore$ CFSE for d^0 ion $= (-0.6 \times p + 0.4 \times q)\Delta_t$

$= (-0.6 \times 4 + 0.4 \times 4)\Delta_t$

$= \mathbf{-\ 0.8\ \Delta_t}$

$= -\ 0.8 \times 0.45\ \Delta_0$

$\mathbf{= -\ 0.36}\ \Delta_0$

$= - 0.38 \times 10Dq$

$= - 3.6Dq$

10. d^9 ion

$e^p t^q_2$ configuration of d^9 ion $= e^4 t^4_2$ (p=4, q=5,)

∴ CFSE for d^0 ion $= (-0.6 \times p + 0.4 \times q)\Delta_t$

$= (-0.6 \times 4 + 0.4 \times 5)\Delta_t$

$= - 0.4 \Delta_t$

$= - 0.4 \times 0.45 \Delta_0$

$= - 0.18 \Delta_0$

$= - 0.18 \times 10Dq$

$= - 1.8Dq$

11. d^{10} ion

$e^p t^q_2$ configuration of d^{10} ion $= e^4 t^6_2$ (p=4, q=6,)

∴ CFSE for d^0 ion $= (-0.6 \times p + 0.4 \times q)\Delta_t$

$= (-0.6 \times 4 + 0.4 \times 6)\Delta_t$

$= 0 \times \Delta_t$

= Zero

Molecular Orbital Theory

In molecular orbital theory of complexes the AOs of central metal ions and ligands combine to form σ or π MO orbitals. These sets of MO have an equal number of bonding (lower energy level) and antibonding (higher energy level) orbitals. The non-participating AO of central metal ions is called a nonbonding MO and their energy remains unchanged.

Steps involved in σ MO in octahedral complex :

- Selection of the metal ion orbitals which are to overlap with ligand $p\sigma$ molecular orbitals.
- To determine the ligand p_σ orbital which may overlap with suitable metal ion orbitals to give σ MO orbitals.
- In this final step combination of metal ion orbitals and ligands orbitals of same symmetry overlap with each other and form σ-bonding molecular orbitals (s-BMO) and σ-antibonding molecular orbitals (*s-ABMO).

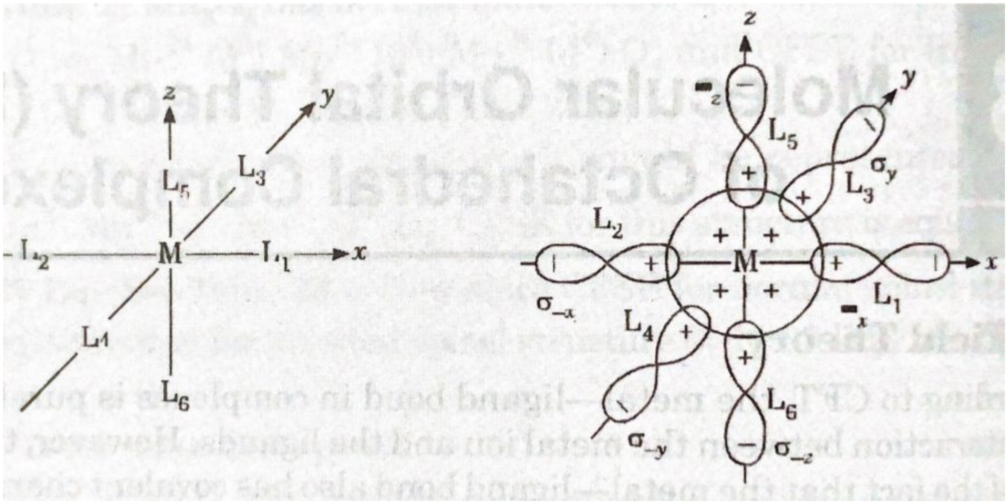


Fig (a) **Fig (b)**

(a) - Octahedral complexes in which the central metal atom (M) is surrounded octahedrally by 6 ligands.

(b) - Field p_s orbitals on 6 ligands.

Discussion of the above steps in detail.

1. **To make a selection of metal ion orbitals suitable for s-bonding :**

   Valence shell of 1st transition series metal ions has nine orbitals (one 4s, three 4p and five 3d). From these orbitals lobes of 4s, 4px, 4py, 4pz. $3d_{z2}$ and $3d_{x2-y2}$ have their lobes along the axes, and $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ orbitals have their lobes in between the axes. Therefore $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ orbitals are not capable of forming s-bonds.Since out of nine only six AOs are suitable to overlap with ligand orbitals to form σ-BMO and σ^*ABMO.

   According to group theory, the metal ion orbitals are designated by the following symmetry symbol:

Orbitals	Symmetry symbol
4s	a_{1g} or A_{1g} (single, gerade, symmetrical,non-degenerate)
$4p_x$, $4p_y$, $4p_z$	t_{1u} or T_{1u} (three, ungerade, degenerate)
$3d_{z2}$, $3d_{x2-y2}$	e_g or E_g (two, gerade, degenerate)
$3d_{xy}$, $3d_{yz}$, $3d_{xz}$	t_{2g} or T_{2g} (three, gerade, degenerate)

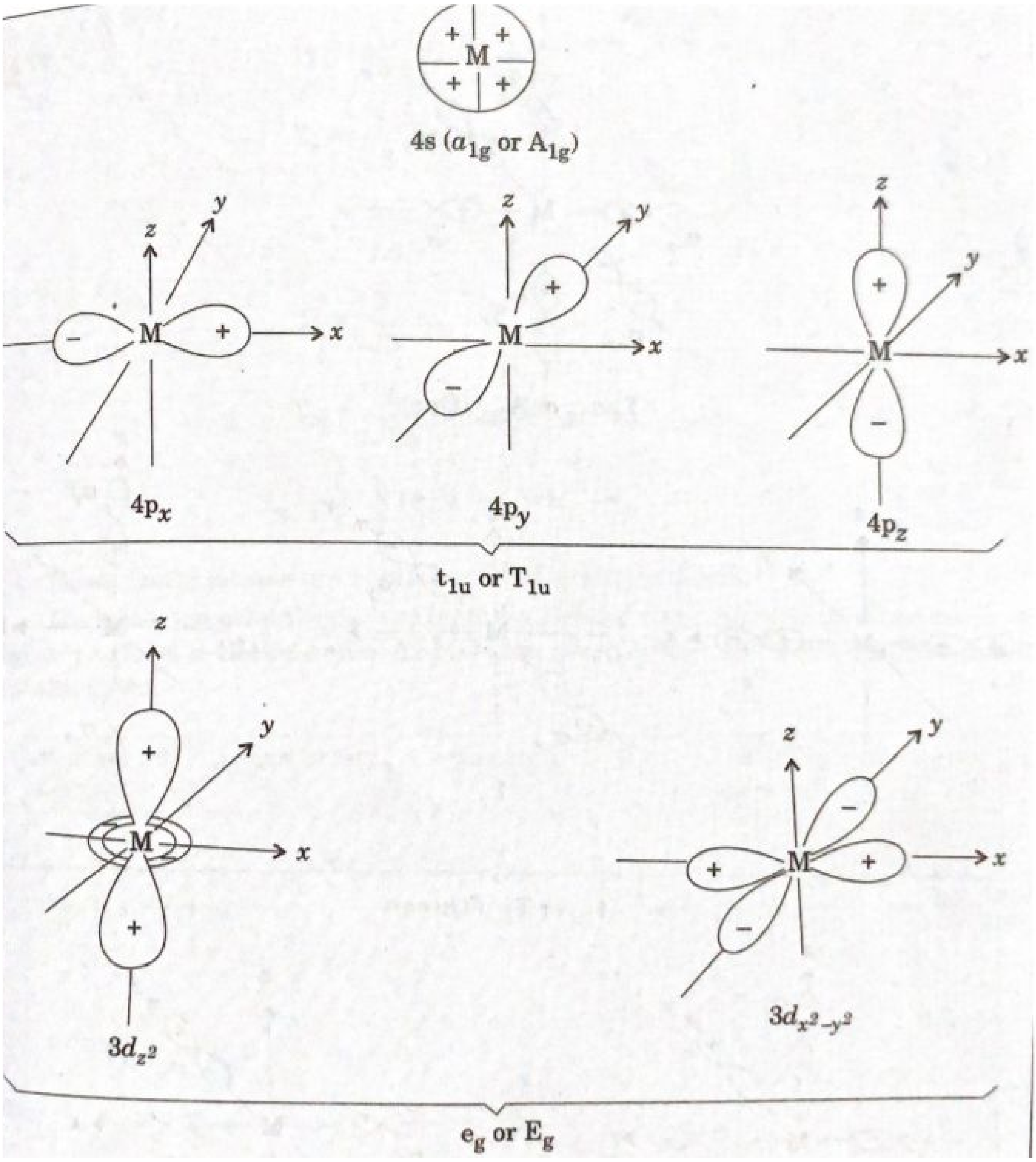
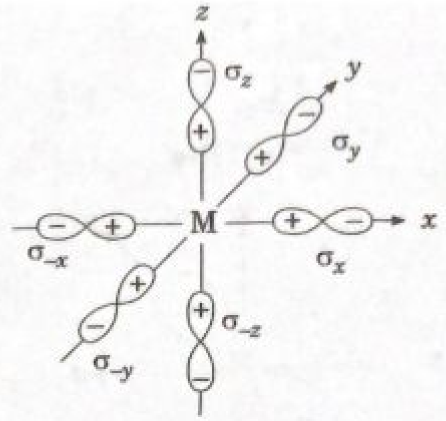


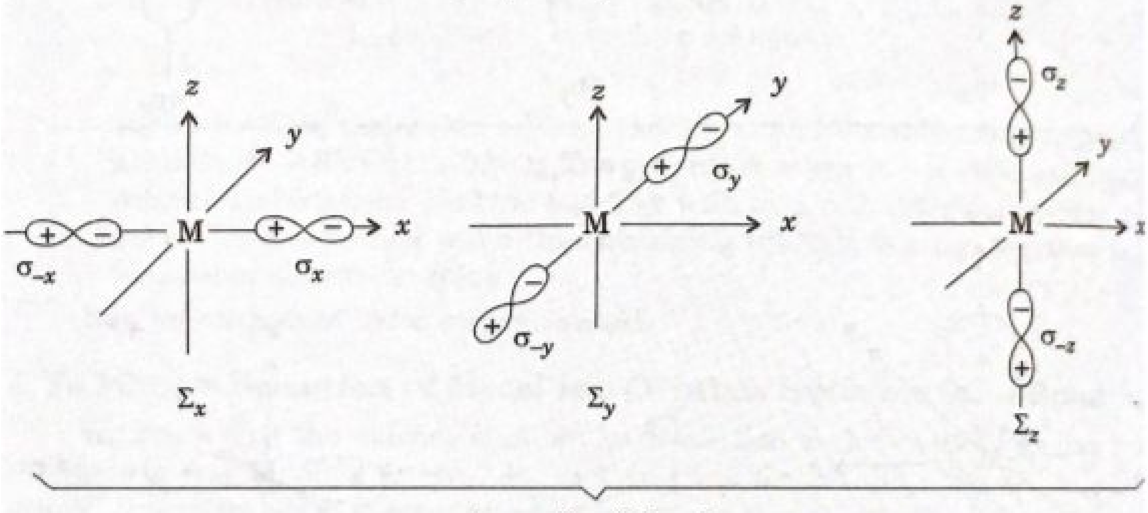
Fig: Six metal ion orbitals

2. To determine the ligand pσ orbital combinations :

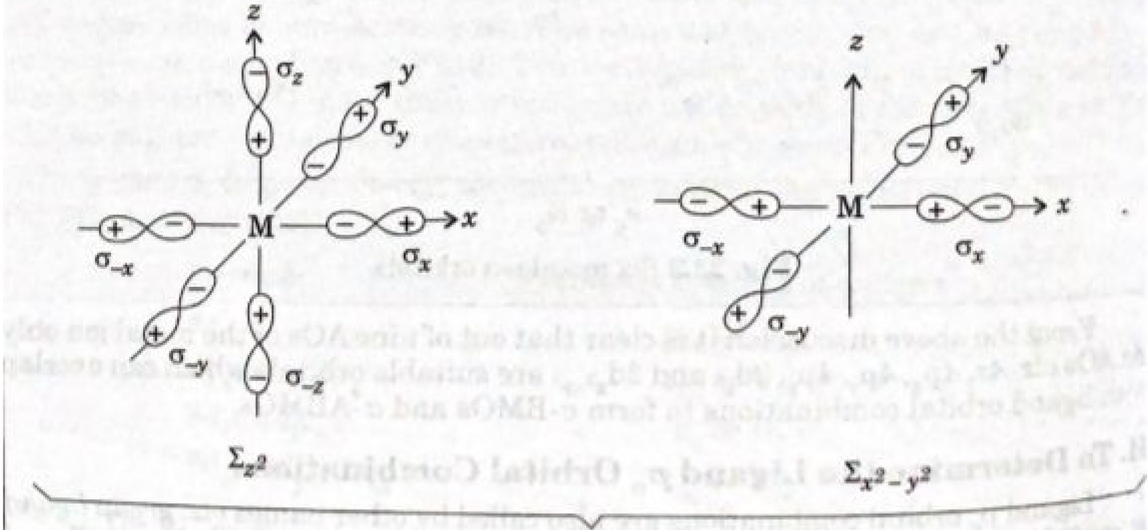
The six ligands p_σ orbitals viz. σ_x, σ_{-x}, σ_y, σ_{-y}, σ_z and σ_{-z} combine together linearly to form six ligand pσ orbital combination, designated as Σ_s Σ_x, Σy, Σ_z, Σ_{z2} and Σ_{x2-y2} have been shown in the figure:



Σ_s(a_{1g} or A_{1g}) (One)



t_{1u} or T_{1u} (Three)



e_g or E_g (Two)

Fig: Six ligand p_σ orbital combination

3. Formation of sigma (σ) molecular orbitals (MOs) in octahedral complexes :

Condition for effective combination for formation of MO

- The combining orbitals should have the same symmetry for the maximum overlap.
- The combining orbitals should not have large differences in their energies.
- In octahedral complexes, sigma MO are formed by the overlap of six ligand $p_\sigma(\Sigma_s)$ orbital with the six metal ion σ-orbitals(a_{1g}) along the axes.

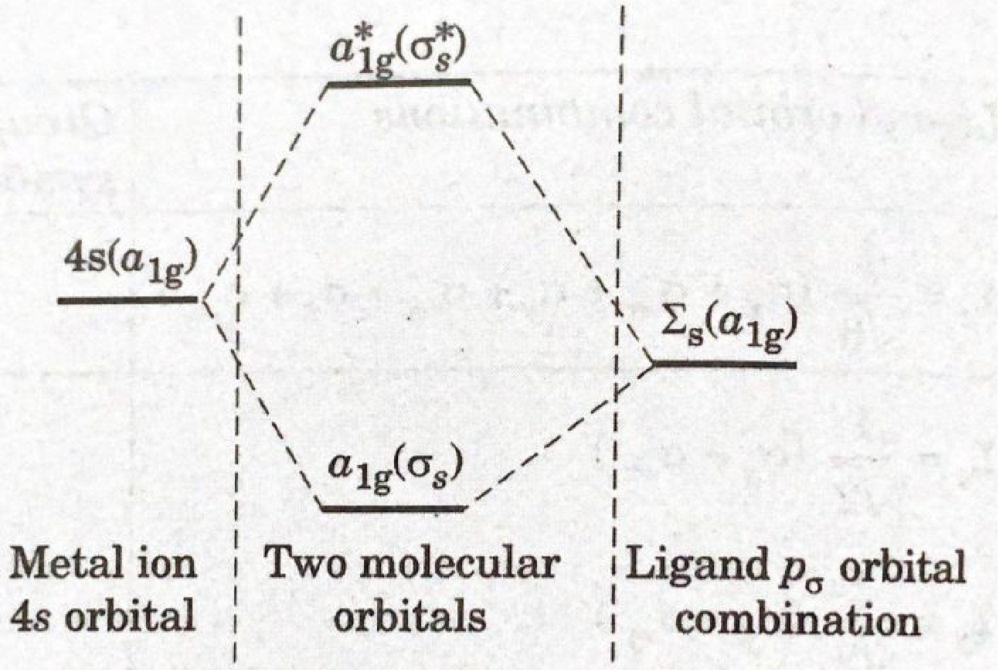


Fig: Formation of a_{1g} BMO (σ_s) and a_{1g}^* ABMO (σ_s^*) in an octahedral complex

- The three $4p(p_x, p_y, p_z)$ orbitals of metal ion(t_{1u}) and three ligand $p\sigma$-orbitals(Σ_x, Σ_y, Σ_z,) combine to form three t_{1u} BMOs(σ_p) and three t_{1u}^*ABMO(σ_p^*).

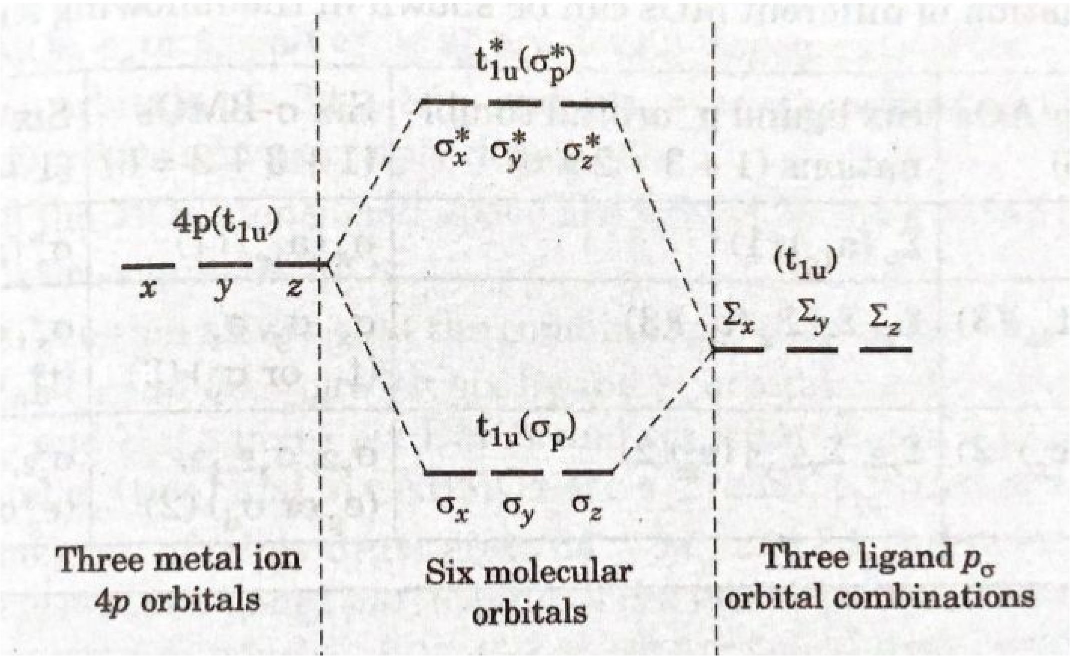


Fig: Formation of three t_{1u} BMO (σ_p) and three t_{1u}^* ABMOs (σ_p^*)

- Metal ion $3d_{x2}$ and $3d_{x2\text{-}y2}$ orbitals and two ligand pσ($\Sigma_{x2\text{-}y2}$, Σ_{z2}) orbitals combine to form two degenerate e_g BMO(σ_d) and two e_g^*ABMO(σ_d^*).

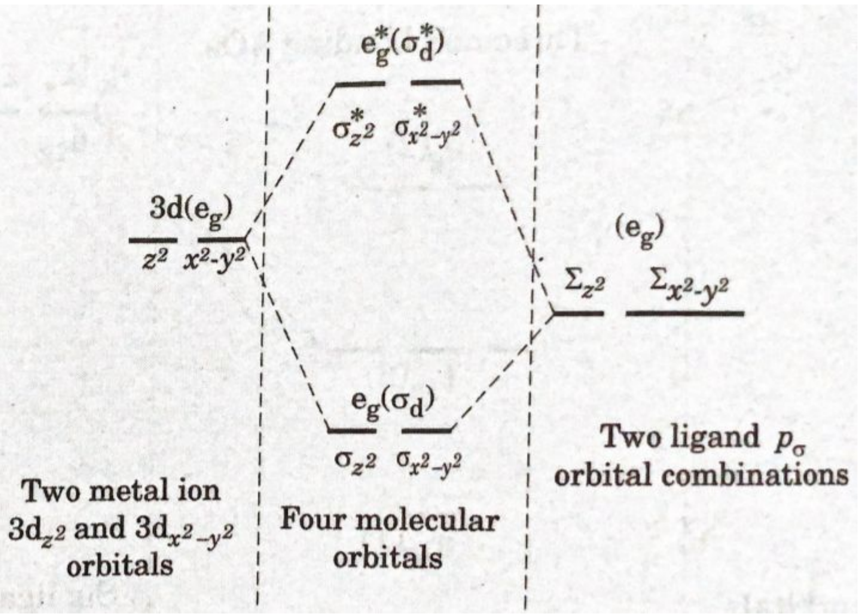
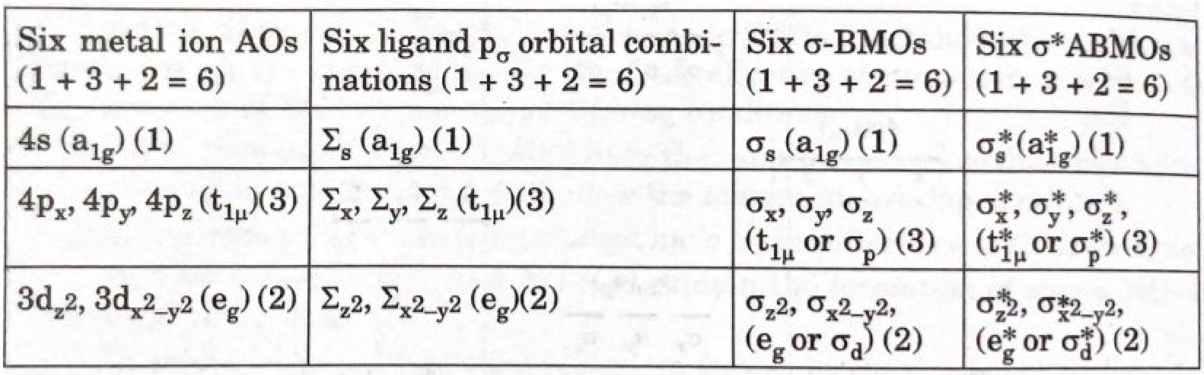


Fig: Formation of two e_g BMOs (σ_d) and two e_g^* ABMOs (σ_d^*)

The formation of different MOs can be shown in the following simple way:



Six metal ion AOs (1 + 3 + 2 = 6)	Six ligand p_σ orbital combinations (1 + 3 + 2 = 6)	Six σ-BMOs (1 + 3 + 2 = 6)	Six σ*ABMOs (1 + 3 + 2 = 6)
4s (a_{1g}) (1)	Σ_s (a_{1g}) (1)	σ_s (a_{1g}) (1)	σ_s^*(a_{1g}^*) (1)
$4p_x$, $4p_y$, $4p_z$ ($t_{1\mu}$)(3)	Σ_x, Σ_y, Σ_z ($t_{1\mu}$)(3)	σ_x, σ_y, σ_z ($t_{1\mu}$ or σ_p) (3)	σ_x^*, σ_y^*, σ_z^*, ($t_{1\mu}^*$ or σ_p^*) (3)
$3d_{z^2}$, $3d_{x^2-y^2}$ (e_g) (2)	Σ_{z^2}, $\Sigma_{x^2-y^2}$ (e_g)(2)	σ_{z^2}, $\sigma_{x^2-y^2}$, (e_g or σ_d) (2)	$\sigma_{z^2}^*$, $\sigma_{x^2-y^2}^*$, (e_g^* or σ_d^*) (2)

Energy level diagram of $[Co(NH_3)_6]^{3+}$ ion

In $[Co(NH_3)_6]^{3+}$ ion, Co is present as Co^{+3} ($3d^6\ 4s^0\ 4p^0$).This complex ion has 12 electrons from six NH_3 ligands and 6 electrons from d-orbitals of Co^{+3} ion. The distribution of 18 electrons accommodates in various orbitals can be written as :

$$\mathbf{(a_{1g})^2\ (t_{1u})^6\ (e_g)^4\ (t_{2g})^6 \ = \ (BMOs)^{12}\ (t_{2g})^6}$$

$$\mathbf{= \ (BMOs)^{12}\ (3d_{xy})^2\ (3d_{yz})^2\ (3d_{xz})^2}$$

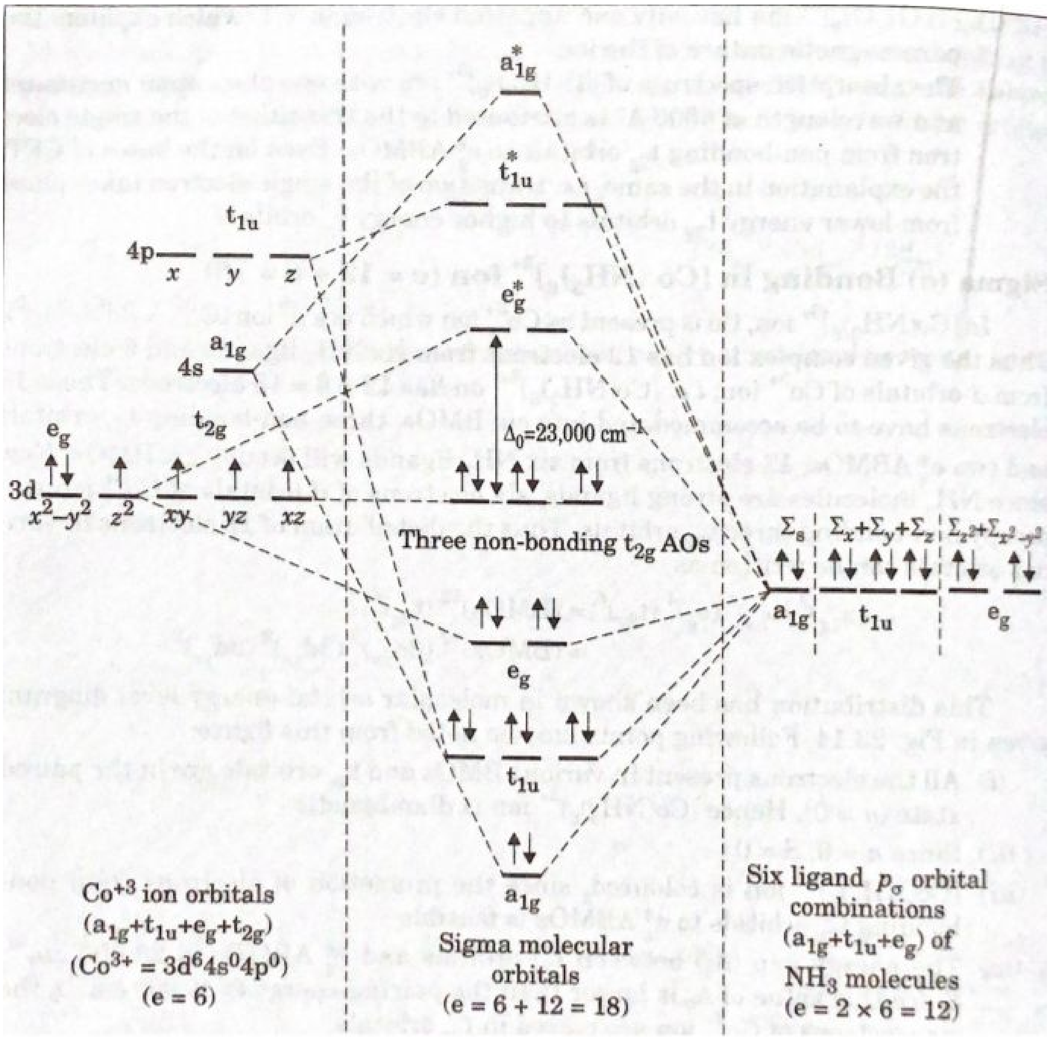


Fig: Molecular energy level diagram of $[Co(NH_3)_6]^{3+}$

Important point from the figure:

- All the electrons present in various BMOs and t_{2g} orbitals are in the paired state (n=0). Hence $[Co(NH_3)_6]^{3+}$ ion is diamagnetic.
- Since n = 0, S = 0
- $[Co(NH_3)_6]^{+3}$ ion is coloured, since the promotion of electrons from non-bonding t_{2g} orbitals to e_g^*ABMOs is feasible.
- The energy gap (Δ_0) between t_{2g} orbitals and e_g^*ABMOs is 23,000 cm^{-1}, is larger than pairing energy (= 19,000 cm^{-1}), the six electrons of Co^{+3} ion are paired in t_{2g} orbitals.
- Larger the value of Δ_0 is because of greater overlap between metal and ligand orbitals, it explains stronger covalent character of metal-ligand bond.

Energy level diagram of $[CoF_6]^{3-}$ ion

In $[CoF_6]^{3-}$ ion, Co is present as Co^{+3} ($3d^6\ 4s^0\ 4p^0$).This complex ion has 12 electrons from six F^- ligands and 6 electrons from d-orbitals of Co^{+3} ion. The distribution of 18 electrons accommodates in various orbitals can be written as :

$(a_{1g})^2\ (t_{1u})^6\ (e_g)^4$ = $(BMOs)^{12}$

$(t_{2g})^4$ $(3d_{xy})^2\ (3d_{yz})^1\ (3d_{xz})^1$

$(e^*_g)^2$ $(\sigma^*_{z2})^1(\sigma^*_{x2-y2})^1$

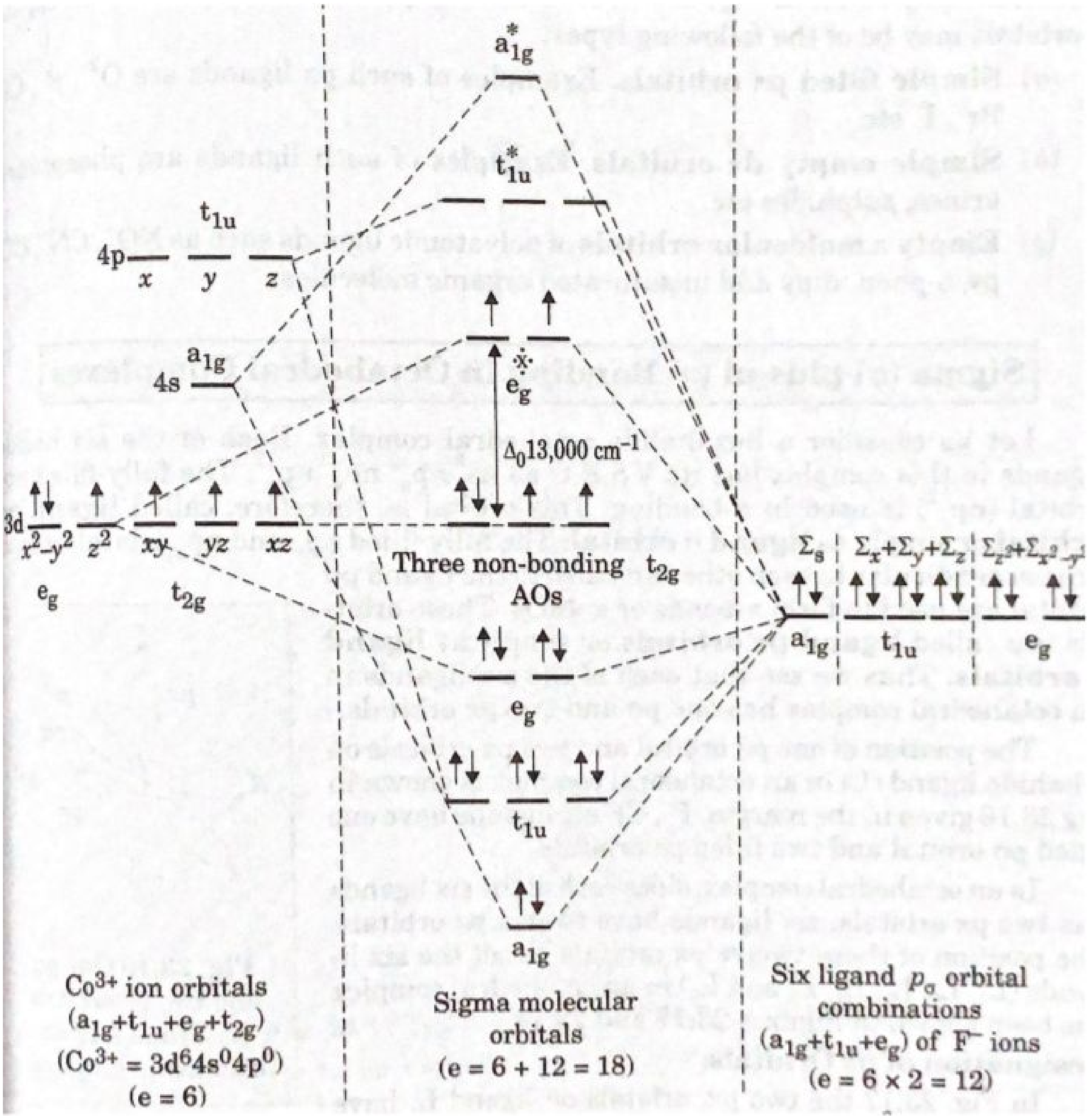


Fig: Molecular orbital energy level diagram of $[CoF_6]^{3-}$

Important point from the figure:

- Total number of unpaired electron (n) present in t_{2g} orbitals and e^*_g ABMOs is equal to 2+2 = 4. Thus $[CoF_6]^{3-}$ is paramagnetic.
- Since n = 4, S = 4/2 = 2
- The energy gap (Δ_0) between t_{2g} and e^*_g orbitals is 13000 cm^{-1} which is less than the pairing energy, P (= 19,000 cm^{-1}).Smaller the value of Δ_0 means lesser extent of overlap between metal and ligand orbitals.