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Summary

Description	CFT was developed by physicists Hans Bethe and John Hasbrouck van Vleck in the 1930s. In this chapter, mnemonically, I have discussed the electronic configuration of coordination complexes in the light of CFT, their magnetic moments, and their spin state. Spin multiplicity value should be calculated innovatively by using the formula (n+1). Factors affecting the Crystal field splitting energy of different coordination compounds having CN=4 and CN=6 have also been discussed. Different examples have highlighted the relationship between pairing energy (P) and Crystal field splitting energy (Δ) for a high spin and low spin coordination complexes. How the wavelength (λ) of light absorbed by the coordination complexes is closely related to its Crystal Field Splitting Energy has also been conversed here. The relation between the enthalpy of atomization and the number of unpaired electrons in the metal atom has also been discussed in the 10th problem at the end of this chapter.
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Chapter-26

Coordination Chemistry: Crystal Field Theory (CFT)

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CFT was developed by physicists Hans Bethe and John Hasbrouck van Vleck in the 1930s. In this chapter, mnemonically, I have discussed the electronic configuration of coordination complexes in the light of CFT, their magnetic moments, and their spin state. Spin multiplicity value should be calculated innovatively by using the formula (n+1). Factors affecting the Crystal field splitting energy of different coordination compounds having CN=4 and CN=6 have also been discussed. Different examples have highlighted the relationship between pairing energy (P) and Crystal field splitting energy (Δ) for a high spin and low spin coordination complexes. How the wavelength (λ) of light absorbed by the coordination complexes is closely related to its Crystal Field Splitting Energy has also been conversed here. The relation between the enthalpy of atomization and the number of unpaired electrons in the metal atom has also been discussed in the 10th problem at the end of this chapter.

Main Objectives of CFT:

1.Draw electronic configuration (E.C.) of coordination compounds in presence of ligand field (LF).

2. From the E.C. predict magnetic properties by calculating the number of unpaired e^-s (n) and putting the value of 'n' in the formula $\mu_s=\sqrt{n(n+2)}$. If n = 0 then it will be diamagnetic and if $n\neq0$ then it will be paramagnetic in nature.

3. From the E.C. predict spin state from the spin multiplicity value (n+1).

4. Predict crystal field splitting energy (Δ_o or Δ_s or Δ_t) from the E.C. by putting the value of e^-s which are present in t_{2g} and e_g.

5. Predict crystal field stabilization energy (CFSE) from the E.C. by putting the value of e^-s which are present in t_{2g} and e_g. CFSE value is applicable for the determination of stability of coordination compounds.

Spectrochemical series:

Depending upon the ability of the ligands i.e. strength of ligands to cause crystal field splitting, ligands are arranged in increasing order of strength, the arrangements thus obtained is called Spectrochemical series as follows:

I^- < Br^- < S^{2-} < SCN^- (S–bonded) < Cl^- < N_3^- < F^- < NCO^- < OH^- < $C_2O_4^{2-}$ < O^{2-} < H_2O < $acac^-$ (acetylacetonate) < NCS^- (N–bonded) < CH_3CN < gly (glycine) < py (pyridine) < NH_3 < en (ethylenediamine) < bipy (2,2'-bipyridine) < phen (1,10-phenanthroline) < NO_2^- (N–bonded) < PPh_3 < CN^- < CO

Left →--→Right

Strength Increases

Weak field ligands: I^- to H_2O and **Strong field ligands:** $acac^-$ to CO

E.C. for the low spin and high spin octahedral complexes (coordination no 6) of first-row transition series elements ($3d^1$ to $3d^{10}$) in the light of CFT:

As per CFT, the five degenerate (same energy) d orbitals from octahedral complexes with a ligand field (LF) split into two set, t_{2g} and e_g. Three d orbitals (dxy, dyz, dxz) form a t_{2g} set and the other two (d_{x2-y2}, d_z^2) form an e_g set. In octahedral splitting, a t_{2g} set will be lower in energy than an e_g set. The energy difference between a t_{2g} and e_g set is to be treated according to the crystal field splitting energy of octahedral distortion and it is represented by Δ_o **(Fig.1)**.

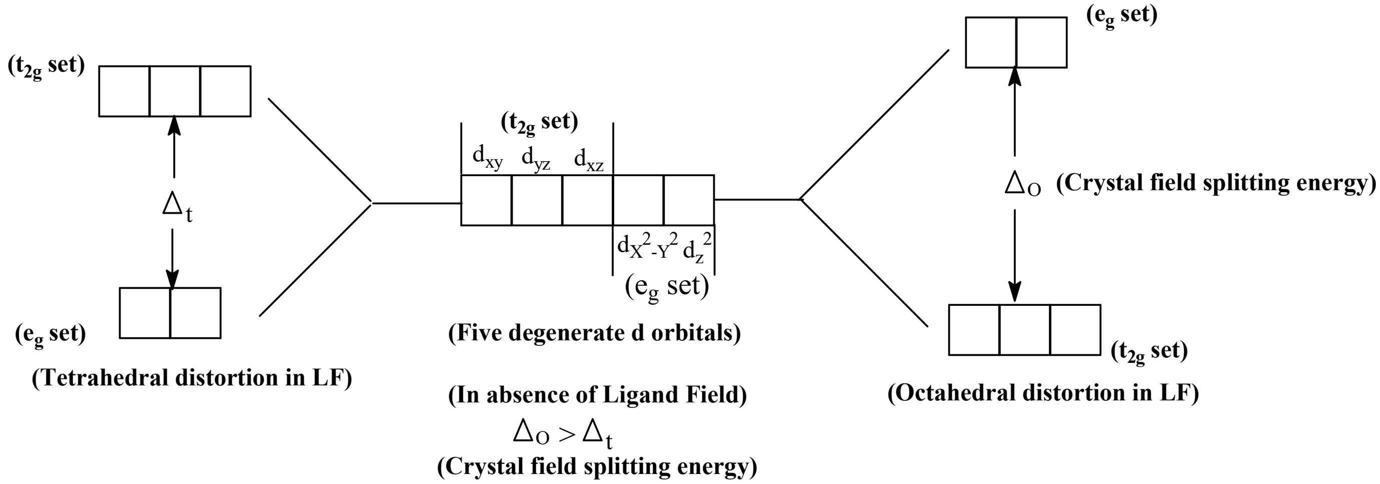


Fig.1: Splitting of d orbitals in Crystal Field Theory (CFT)

Relation between Δ_o and Δ_{tet}:

Δ_{tet} is approximately 4/9 Δ_o or Δ_{tet} is approximately 40/9 Dq (1Δ_0 = 10Dq)

Electronic Configuration for Low Spin (LS) Octahedral Complexes in the light of CFT:

- For $3d^1$(LS), electronic representation – (t_{2g}^1, e_g^0), EC – (t_{2g}^1, e_g^0), number of unpaired electrons (n) = 1, spin multiplicity value (n+1) = (1+1) = 2. The spin state is doublet.
- For $3d^2$(LS), electronic representation – ($t_{2g}^{1,\ 2}$, e_g^0), EC - t_{2g}^2, e_g^0, number of unpaired electrons (n) = 2, spin multiplicity value (n+1) = (2+1) = 3. The spin state is triplet.

- For $3d^3$(LS), electronic representation – ($t_{2g}{}^{1,2,3}$, $e_g{}^0$), EC - $t_{2g}{}^3$, $e_g{}^0$, number of unpaired electrons (n) = 3, spin multiplicity value (n+1) = (3+1) = 4. The spin state is quartet.
- For $3d^4$(LS), electronic representation – ($t_{2g}{}^{1,2,3,4}$, $e_g{}^0$), EC - $t_{2g}{}^4$, $e_g{}^0$, number of unpaired electrons (n) = 2, spin multiplicity value (n+1) = (2+1) = 3. The spin state is triplet.
- For $3d^5$(LS), electronic representation – ($t_{2g}{}^{1,2,3,4,5}$, $e_g{}^0$), EC - $t_{2g}{}^5$, $e_g{}^0$, number of unpaired electrons (n) = 1, spin multiplicity value (n+1) = (1+1) = 2. The spin state is doublet.
- For $3d^6$(LS), electronic representation – ($t_{2g}{}^{1,2,3,4,5,6}$, $e_g{}^0$), EC - $t_{2g}{}^6$, $e_g{}^0$, number of unpaired electrons (n) = 0, spin multiplicity value (n+1) = (0+1) = 1. The spin state is singlet (lowest spin state).
- For $3d^7$(LS), electronic representation – ($t_{2g}{}^{1,2,3,4,5,6}$, $e_g{}^7$), EC - $t_{2g}{}^6$, $e_g{}^1$, number of unpaired electrons (n) = 1, spin multiplicity value (n+1) = (1+1) = 2. The spin state is doublet.
- For $3d^8$(LS), electronic representation – ($t_{2g}{}^{1,2,3,4,5,6}$, $e_g{}^{7,8}$), EC - $t_{2g}{}^6$, $e_g{}^2$, number of unpaired electrons (n) = 2, spin multiplicity value (n+1) = (2+1) = 3. The spin state is triplet.
- For $3d^9$(LS), electronic representation – ($t_{2g}{}^{1,2,3,4,5,6}$, $e_g{}^{7,8,9}$), EC - $t_{2g}{}^6$, $e_g{}^3$, number of unpaired electrons (n) = 1, spin multiplicity value (n+1) = (1+1) = 2. The spin state is doublet.
- For $3d^{10}$(LS), electronic representation – ($t_{2g}{}^{1,2,3,4,5,6}$, $e_g{}^{7,8,9,10}$), EC - $t_{2g}{}^6$, $e_g{}^4$, number of unpaired electrons (n) = 0, spin multiplicity value (n+1) = (0+1) = 1. The spin state is singlet (lowest spin state).

Electronic Configuration for High Spin (HS) Octahedral Complexes in the light of CFT:

- For $3d^1$(HS), electronic representation – ($t_{2g}{}^1$, $e_g{}^0$), EC – ($t_{2g}{}^1$, $e_g{}^0$), number of unpaired electrons (n) = 1, spin multiplicity value (n+1) = (1+1) = 2. The spin state is doublet.
- For $3d^2$(HS), electronic representation – ($t_{2g}{}^{1,2}$, $e_g{}^0$), EC – ($t_{2g}{}^2$, $e_g{}^0$), number of unpaired electrons (n) = 2, spin multiplicity value (n+1) = (2+1) = 3. The spin state is triplet.
- For $3d^3$(HS), electronic representation – ($t_{2g}{}^{1,2,3}$, $e_g{}^0$), EC – ($t_{2g}{}^3$, $e_g{}^0$), number of unpaired electrons (n) = 3, spin multiplicity value (n+1) = (3+1) = 4. The spin state is quartet.
- For $3d^4$(HS), electronic representation – ($t_{2g}{}^{1,2,3}$, $e_g{}^4$), EC – ($t_{2g}{}^3$, $e_g{}^1$), number of unpaired electrons (n) = 4, spin multiplicity value (n+1) = (4+1) = 5. The spin state is quintet.
- For $3d^5$(HS), electronic representation – ($t_{2g}{}^{1,2,3}$, $e_g{}^{4,5}$), EC – ($t_{2g}{}^3$, $e_g{}^2$), number of unpaired electrons (n) = 5, spin multiplicity value (n+1) = (5+1) = 6. The spin state is sextet (highest spin state).
- For $3d^6$(HS), electronic representation – ($t_{2g}{}^{1,2,3}$, $e_g{}^{4,5}$, $t_{2g}{}^6$), EC – ($t_{2g}{}^4$, $e_g{}^2$), number of unpaired electrons (n) = 4, spin multiplicity value (n+1) = (4+1) = 5. The spin state is quintet.

- ▶ For $3d^7$(HS), electronic representation – ($t_{2g}{}^{1,2,3}$, $e_g{}^{4,5}$, $t_{2g}{}^{6,7}$), EC – ($t_{2g}{}^5$, $e_g{}^2$), number of unpaired electrons (n) = 3, spin multiplicity value (n+1) = (3+1) = 4. The spin state is quartet.
- ▶ For $3d^8$(HS), electronic representation – ($t_{2g}{}^{1,2,3}$, $e_g{}^{4,5}$, $t_{2g}{}^{6,7,8}$), EC – ($t_{2g}{}^6$, $e_g{}^2$), number of unpaired electrons (n) = 2, spin multiplicity value (n+1) = (2+1) = 3. The spin state is triplet.
- ▶ For $3d^9$(HS), electronic representation – ($t_{2g}{}^{1,2,3}$, $e_g{}^{4,5}$, $t_{2g}{}^{6,7,8}$, $e_g{}^9$), EC – ($t_{2g}{}^6$, $e_g{}^3$), number of unpaired electrons (n) = 1, spin multiplicity value (n+1) = (1+1) = 2. The spin state is doublet.
- ▶ For $3d^{10}$(HS), electronic representation – ($t_{2g}{}^{1,2,3}$, $e_g{}^{4,5}$, $t_{2g}{}^{6,7,8}$, $e_g{}^{9,10}$), EC – ($t_{2g}{}^6$, $e_g{}^4$), number of unpaired electrons (n) = 0, spin multiplicity value (n+1) = (0+1) = 1. The spin state is singlet (lowest spin state).

E.C. for the high spin and low spin tetrahedral complexes (coordination no 4) of first-row transition series elements ($3d^1$ to $3d^{10}$) in the light of CFT:

As per CFT, the five degenerate (same energy) d orbitals of tetra complexes in the presence of a ligand field (LF) will split into two sets, t_{2g} and e_g. Three d orbitals (dxy, dyz, dxz) form a t_{2g} set and the other two (d_{x2-y2}, $d_z{}^2$) form an e_g set. In tetrahedral splitting, a t_{2g} set will be higher in energy than an e_g set. The energy difference between an e_g and t_{2g} set should be treated using a crystal field splitting energy from a tetrahedral distortion and this is represented by Δ_t **(Fig. 1)**.

The electronic configuration (EC) for high spin (HS) tetrahedral complexes with CFT and their corresponding spin multiplicity value and spin state can be calculated as follows:

- ▶ For $3d^1$(HS), electronic representation – ($e_g{}^1$, $t_{2g}{}^0$), EC – ($t_{2g}{}^0$, $e_g{}^1$), number of unpaired electrons (n) = 1, spin multiplicity value (n+1) = (1+1) = 2. The spin state is doublet.
- ▶ For $3d^2$(HS), electronic representation – ($e_g{}^{1,2}$, $t_{2g}{}^0$), EC – ($t_{2g}{}^0$, $e_g{}^2$), number of unpaired electrons (n) = 2, spin multiplicity value (n+1) = (2+1) = 3. The spin state is triplet.
- ▶ For $3d^3$(HS), electronic representation – ($e_g{}^{1,2}$, $t_{2g}{}^3$), EC – ($t_{2g}{}^1$, $e_g{}^2$), number of unpaired electrons (n) = 3, spin multiplicity value (n+1) = (3+1) = 4. The spin state is quartet.
- ▶ For $3d^4$(HS), electronic representation – ($e_g{}^{1,2}$, $t_{2g}{}^{3,4}$), EC – ($t_{2g}{}^2$, $e_g{}^2$), number of unpaired electrons (n) = 4, spin multiplicity value (n+1) = (4+1) = 5. The spin state is quintet.
- ▶ For $3d^5$(HS), electronic representation – ($e_g{}^{1,2}$, $t_{2g}{}^{3,4,5}$), EC – ($t_{2g}{}^3$, $e_g{}^2$), number of unpaired electrons (n) = 5, spin multiplicity value (n+1) = (5+1) = 6. The spin state is sextet (highest spin state).
- ▶ For $3d^6$(HS), electronic representation – ($e_g{}^{1,2}$, $t_{2g}{}^{3,4,5}$, $e_g{}^6$), EC – ($t_{2g}{}^3$, $e_g{}^3$), number of unpaired electrons (n) = 4, spin multiplicity value (n+1) = (4+1) = 5. The spin state is quintet.

- For $3d^7$(HS), electronic representation – ($e_g^{1,2}$, $t_{2g}^{3,4,5}$, $e_g^{6,7}$), EC – (t_{2g}^3, e_g^4), number of unpaired electrons (n) = 3, spin multiplicity value (n+1) = (3+1) = 4. The spin state is quartet.
- For $3d^8$(HS), electronic representation – ($e_g^{1,2}$, $t_{2g}^{3,4,5}$, $e_g^{6,7}$, t_{2g}^8), EC – (t_{2g}^4, e_g^4), number of unpaired electrons (n) = 2, spin multiplicity value (n+1) = (2+1) = 3. The spin state is triplet.
- For $3d^9$(HS), electronic representation – ($e_g^{1,2}$, $t_{2g}^{3,4,5}$, $e_g^{6,7}$, $t_{2g}^{8,9}$), EC – (t_{2g}^5,e_g^4), number of unpaired electrons (n) = 1, spin multiplicity value (n+1) = (1+1) = 2. The spin state is doublet.
- For $3d^{10}$(HS), electronic representation – ($e_g^{1,2}$, $t_{2g}^{3,4,5}$, $e_g^{6,7}$, $t_{2g}^{8,9,10}$), EC – (t_{2g}^6, e_g^4), number of unpaired electrons (n) = 0, spin multiplicity value (n+1) = (0+1) = 1. The spin state is singlet (lowest spin state).

The electronic configuration (EC) for low spin (LS) tetrahedral complexes with CFT and their corresponding spin multiplicity value and spin state can be calculated as follows:

- For $3d^1$(LS), electronic representation – (e_g^1, t_{2g}^0), EC – (t_{2g}^0, e_g^1), number of unpaired electrons (n) = 1, spin multiplicity value (n+1) = (1+1) = 2. The spin state is doublet.
- For $3d^2$(LS), electronic representation – ($e_g^{1,2}$, t_{2g}^0), EC – (t_{2g}^0, e_g^2), number of unpaired electron (n) = 2, spin multiplicity value (n+1) = (2+1) = 3. The spin state is triplet.
- For $3d^3$(LS), electronic representation – ($e_g^{1,2,3}$, vt_{2g}^0), EC – (t_{2g}^0, e_g^3), number of unpaired electrons (n) = 1, spin multiplicity value (n+1) = (1+1) = 2. The spin state is doublet.
- For $3d^4$(LS), electronic representation – ($e_g^{1,2,3,4}$, t_{2g}^0), EC – (t_{2g}^0, e_g^4), number of unpaired electrons (n) = 0, spin multiplicity value (n+1) = (0+1) = 1. The spin state is singlet (lowest spin state).
- For $3d^5$(LS), electronic representation – ($e_g^{1,2,3,4}$, t_{2g}^5), EC – (t_{2g}^1, e_g^4), number of unpaired electrons (n) = 1, spin multiplicity value (n+1) = (1+1) = 2. The spin state is doublet.
- For $3d^6$(LS), electronic representation – ($e_g^{1,2,3,4}$, $t_{2g}^{5,6}$), EC – (t_{2g}^2, e_g^4), number of unpaired electrons (n) = 2, spin multiplicity value (n+1) = (2+1) = 3. The spin state is triplet.
- For $3d^7$(LS), electronic representation – ($e_g^{1,2,3,4}$, t $_{2g}^{5,6,7}$), EC – (t_{2g}^3, e_g^4), number of unpaired electrons (n) = 3, spin multiplicity value (n+1) = (3+1) = 4. The spin state is quartet.
- For $3d^8$(LS), electronic representation – ($e_g^{1,2,3,4}$, $t_{2g}^{5,6,7,8}$), EC – (t_{2g}^4, e_g^4), number of unpaired electrons (n) = 2, spin multiplicity value (n+1) = (2+1) = 3. The spin state is triplet.
- For $3d^9$(LS), electronic representation – ($e_g^{1,2,3,4}$, $t_{2g}^{5,6,7,8,9}$), EC – (t_{2g}^5, e_g^4), number of unpaired electrons (n) = 1, spin multiplicity value (n+1) = (1+1) = 2. The spin state is doublet.

- ▶ For $3d^{10}$(LS), electronic representation – ($e_g^{1,2,3,4}$, $t_{2g}^{5,6,7,8,9,10}$), EC – (t_{2g}^6, e_g^4), number of unpaired electrons (n) = 0, spin multiplicity value (n+1) = (0+1) = 1. The pin state is singlet (lowest spin state).

From this data, it is clear that both $3d^5$(HS) octahedral and tetrahedral complexes can exhibit the highest spin state, which is known as a sextet because it corresponds to spin multiplicity value of 6 with 5 unpaired electrons. However, $3d^6$ (LS) octahedral, $3d^{10}$ (LS) octahedral, $3d^{10}$ (HS) octahedral, $3d^{10}$ (HS) tetrahedral, $3d^4$ (LS) tetrahedral, and $3d^{10}$ (LS) tetrahedral complexes can exhibit the lowest spin state, which is known as a singlet because it corresponds to a spin multiplicity value of 1 and 0 unpaired electrons.

Relation between Pairing energy (P) with Crystal Field Splitting Energy (Δ_o):

i) For HS complexes: In the formation of **HS complexes $\Delta_o < P$**. When, pairing energy is greater than octahedral crystal field splitting energy (Δ_o) **then late pair occurs.**

Generally, octahedral crystal field splitting energy (Δ_o) tends to force electrons to pair-up in the t_{2g} set while P tends to prevent the electrons to pair-up in the t_{2g} set.

Eg. $[CoF_6]^{3-}$.

ii) For LS complexes: In the formation of **LS complexes $\Delta_o > P$.** When, pairing energy is lesser than octahedral crystal field splitting energy (Δ_o) then **quick pair occurs.**

Generally, octahedral crystal field splitting energy (Δ_o) tends to force electrons to pair-up in the t_{2g} set while P tends to prevent the electrons to pair-up in the t_{2g} set.

Eg. $[Co(NH_3)_6]^{3+}$.

Factors affecting the magnitude of Crystal Field Splitting Energy, Δo (10 Dq):

1. Nature of the metal cation:

i)Different Charges on same metal cations:

The cation with a higher oxidation state has a larger value of Δ_o (O.S. α Δ_o).

Eg. Δ_o for $[Fe(H_2O)_6]^{2+}$ ($3d^6$) -----------→ 10,400cm^{-1}

Δ_o for $[Fe(H_2O)_6]^{3+}$ ($3d^5$) -----------→ 13,700cm^{-1}

ii) Different Charges on different metal cations:

The cation with a higher oxidation state has a larger value of Δ_o (O.S. α Δ_o).

Eg. Δ_o for $[V(H_2O)_6]^{2+}$ ($3d^3$) -----------→ 12,400cm^{-1}

Δ_o for $[Cr(H_2O)_6]^{3+}$ ($3d^3$) -----------→ 17,400cm^{-1}

iii) Same Charges on the Cation but differ in the number of d electrons:

In this case, Δ_o (Δ_o α 1/ no of d electrons) decreases with the increase of the number of the d-electrons.

Eg. Δ_o for $[Co(H_2O)_6]^{2+}$ ($3d^7$) -----------→ 9,300cm^{-1}

Δ_o for $[Ni(H_2O)_6]^{2+}$ ($3d^8$) -----------→ 8,500cm^{-1}

iv) Principal Quantum number of metal d orbitals:

Δ_o increases about 30 to 50 % from $3d^n$ to $4d^n$ and by about the same amount again from $4d^n$ to $5d^n$ complexes.

Eg. Δ_o for $[Co(NH_3)_6]^{3+}$ ($3d^6$) -----------→ 23,000cm^{-1}
Δ_o for $[Rh(NH_3)_6]^{3+}$ ($4d^6$) -----------→ 34,000cm^{-1}
Δ_o for $[Ir(NH_3)_6]^{3+}$ ($5d^6$) -----------→ 41,000cm^{-1}

2. Strength of Ligands (as per Spectrochemical series):

The magnitude of crystal field splitting energy varies from stronger to weaker ligands as per spectrochemical series.

Stronger ligands (eg. CN^-) have higher splitting power give larger value of Δ_o where as weakerligands (eg. F^-) have relatively lower splitting power give smaller value of Δ_o.

Δ_o for $[Ni(H_2O)_6]^{2+}$ ($3d^8$)-----------→ 8,500cm^{-1}
Δ_o for $[Ni(NH_3)_6]^{2+}$ ($3d^8$)-----------→ 10,800cm^{-1}
Δ_o for $[Ni(en)_3]^{2+}$ ($3d^8$)-----------→ 11,500cm^{-1}

3. Geometry of the Complex:

$$\Delta_{sp}\ (=1.3\ \Delta_o) > \Delta_o > \Delta_t\ (= 0.45\ \Delta_o)$$

Eg. Δ of $[Ni(CO)_4]^{2+}$ (Square Planar, dsp^2) > Δ of $[Ni(CO)_6]^{2+}$ (Octahedral, sp^3d^2) > Δ of $[Ni(CO)_4]$ (Tetrahedral, sp^3)

Related Questions

Q.1. Which complex of the following pairs has the larger value of Δ_o

i) $[Co(CN)_6]^{3-}$ & $[Co(NH_3)_6]^{3+}$
ii) $[CoF_6]^{3-}$ & $[Co(NH_3)_6]^{3+}$
iii) $[Rh(H_2O)_6]^{3+}$ & $[Co(H_2O)_6]^{3+}$
iv) $[Co(CN)_6]^{3-}$ & $[Co(NH_3)_6]^{3+}$
v) $[Co(H_2O)_6]^{3+}$ & $[Co(H_2O)_6]^{2+}$

Q.2. The *d*-electron configuration of $[Ru(en)_3]Cl_2$ and $[Fe(H_2O)_6]Cl_2$, respectively are

a) $t_{2g}^6\ e_g^0$ and $t_{2g}^6\ e_g^0$ **(*b*) $t_{2g}^6\ e_g^0$ and $t_{2g}^4\ e_g^2$**
(c) $t_{2g}^4\ e_g^2$ and $t_{2g}^6\ e_g^0$ **(d) $t_{2g}^4\ e_g^2$ and $t_{2g}^4\ e_g^2$**

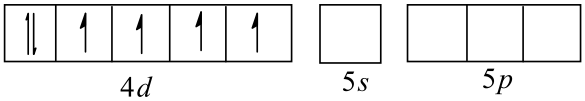
Ans. (*b*)

The *d*-electron configuration $[Ru(en)_3]Cl_2$ and $[Fe(H_2O)_6]Cl_2$ respectively are $t_{2g}^6 e_g^0$ and $t_{2g}^4 e_g^2$.

$[Ru(en)_3]Cl_2$

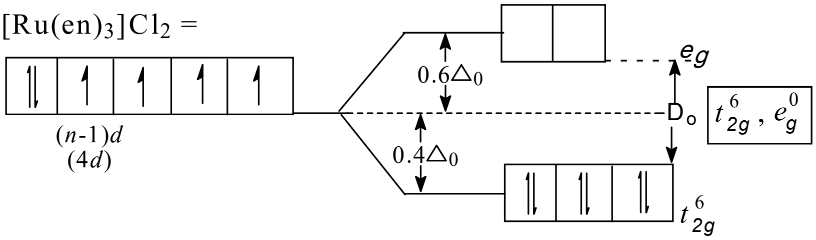
Ru = 4*d* series, en = bidentate ligand (strong field ligand), C.N. = 6 and Oxidation number = + 2
Ru^{2+} = [Kr] $4d^6 5s^0$

Ru^{2+} =



In presence of en, pairing should be done

$[Ru(en)_3]Cl_2$ =

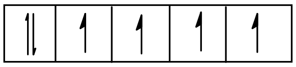


For $[Fe(H_2O)_6]Cl_2 \Rightarrow H_2O$ (weak field ligand)

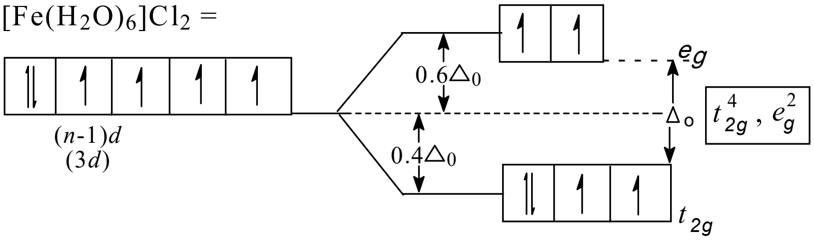
Oxidation number = + 2 ; C.N. = 6

$Fe^{2+} = 3d^6$

Fe^{2+} =



$[Fe(H_2O)_6]Cl_2$ =

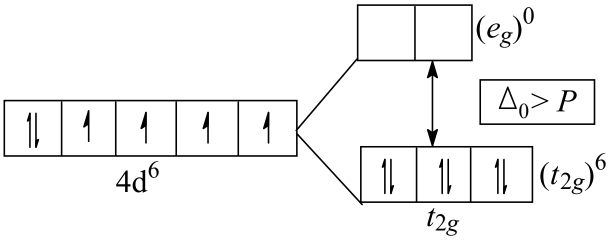


Q.3. Considering that $\Delta_0 > P$, the magnetic moment (in BM) of $[Ru(H_2O)_6]^{2+}$ would be ……..

Ans. (0)

Magnetic moment (in BM) of $[Ru(H_2O)_6]^{2+}$ would be; while considering that $\Delta_0 > P$, E.C. of $_{44}Ru$:-$[Kr]4d^7 5s^1$ (in ground state).

$\Rightarrow$ In Ru^{2+} $\Rightarrow$ $4d^6$ $\Rightarrow$ $(t_{2g})^6(e_g)^0$



$\Rightarrow$ Here, number of unpaired electrons in

$Ru^{2+} = (t_{2g})^6(e_g)^0 = 0$ and hence

$\mu = \sqrt{n(n+2)}BM = 0$ BM

Q.4. For a d^4 metal ion in an octahedral field, the correct electronic configuration is

(*a*) $t_{2g}^3\, e_g^1$ and $\Delta_0 < P$ (b) $t_{2g}^3\, e_g^1$ and $\Delta_0 > P$

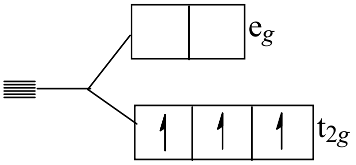
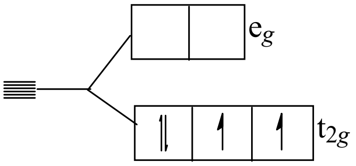
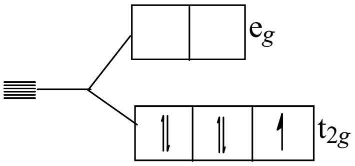
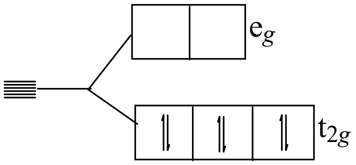
(c) $t_{2g}^4\, e_g^0$ and $\Delta_0 < P$ (d) $t_g^2\, e_{2g}^2$ and $\Delta_0 < P$

Exp. (*a*)

In octahedral complexes:
(i) If $\Delta_0 < P$ (weak field, high spin situation).
The fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^3\ e_g^1$.
(ii) If $\Delta_0 < P$ (strong field, low spin situation), pairing will occur in the t_{2g} level with e_g level remaining unoccupied giving configuration $t_{2g}^4\ e_g^0$.
Hence, for d^4 metal ion in an octahedral field, the correct, electronic configuration is $t_{2g}^3\ e_g^1$, when $\Delta_0 < P$.

Q.5. Among the statements (*A*) –(*D*), the incorrect ones are
(A) octahedral Co(III) complexes with strong, field ligands have very high magnetic moments
(B) When $\Delta_0 < P$, the *d*-electron configuration of Co(III) in an octahedral complex is t_{eg}^4, e_g^2
(C) Wavelength of light absorbed by $[Co(en)_3]^{3+}$ is lower than that of $[CoF_6]^{3-}$
(D) If the Δ_0 for an octahedral complex of Co(III) is 18,000 cm^{-1}, the Δ_t for its tetrahedral complex with the same ligand will be 16,000 cm^{-1}
a) *B* and *C* only b) *A* and *B* only
c) *C* and *D* only *d*) *A* and *D* only
Exp. (*d*)
(A) Co^{3+} has d^6 configuration with strong field ligands, the configuration becomest_{2g}^6, e_g^0.
As no unpaired electron is present in Co^{3+}, so it has zero magnetic moment.
∴ Statement is correct.
(B) When $\Delta_0 < P$ ***(Late pair occurs)***, pairing of *d*-electrons takes place only after filling every orbital with single electron.
∴ Configuration of $d^6 =\ t_{2g}^4, e_g^2$
Statement is correct.
(C) 'en' or ethane – 1, 2-diamine has greater field strength than F^-.
∴ Frequency of light absorbed in $[Co(en)_3]^{3+}$ is greater and wavelength is lower than $[CoF_6]^{3-}$
(E α strength of ligand α 1/λ). Thus, this statement is correct.
(D) $\Delta_t = \frac{4}{9}\ \Delta_0$ for complexes with same metal and ligand.
∴ Δ_t must be $\frac{4}{9} \times 18000 = 8000$ cm^{-1}.
This statement is incorrect.
Hence, among the given options, option (d) is incorrect.

Q.6. The correct order of the spin only magnetic moment of metal ions in the following low spin complexes, $[V(CN)_6]^{4-}$, $[Fe(CN)_6]^{4-}$, $[Ru(NH_3)_6]^{3+}$, and $[Cr(NH_3)_6]^{2+}$, is
a) $Cr^{2+} > Ru^{3+} > Fe^{2+} > V^{2+}$
***b*) $V^{2+} > Cr^{2+} > Ru^{3+} > Fe^{2+}$**
c) $V^{2+} > Ru^{3+} > Cr^{2+} > Fe^{2+}$
d) $Cr^{2+} > V^{2+} > Ru^{3+} > Fe^{2+}$
Exp. (b)
The correct order of the spin only magnetic moment of metal ions in the given low-spin complexes is $V^{2+} > Cr^{2+} > Ru^{3+} > Fe^{2+}$.
All the given complexes possess strong field ligands (CN, NH_3). Hence, readily form low spin complexes.

Complex	Oxidation state	Configuration	Orbital splitting	No. of unpaired electrons
$[V(CN)_6]^{4-}$	V^{2+}	$t_{2g}^3\ e_g^0$		3
$[Cr(NH_3)_6]^{2+}$	Cr^{2+}	$t_{2g}^4\ e_g^0$		2
$[Ru(NH_3)_6]^{3+}$	Ru^{3+}	$t_{2g}^5\ e_g^0$		1
$[Fe(CN)_6]^{4-}$	Fe^{2+}	$t_{2g}^6\ e_g^0$		0

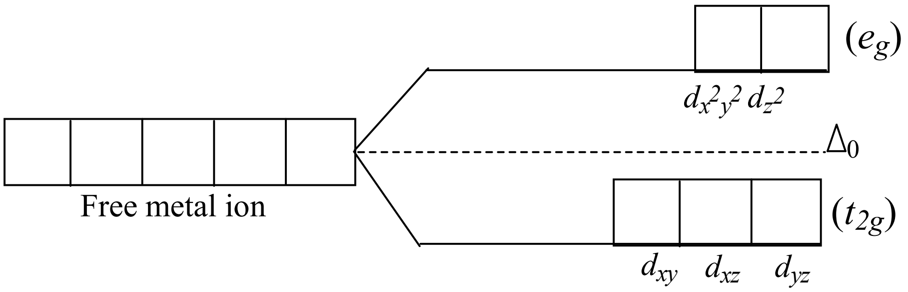
Q.7. The degenerate orbitals of $[Cr(H_2O)_6]^{3+}$ are

a) d_{z^2} and d_{xz} **b) d_{xz} and d_{yz}**

c) $d_{x^2-y^2}$ and d_{xy} **d) d_{yz} and d_{z^2}**

Ans. (*b*)

The degenerate orbitals of $[Cr(H_2O)_6]^{3+}$ are d_{xz} and d_{yz}. Electronic configuration of Cr^{3+} is $3d^5 4s^1$. The five *d*-orbitals in an isolated gaseous atom or ion have same energy, i.e. they are degenerate. This degeneracy has been removed due to the ligand electron-metal electron repulsions in the octahedral complex to yield three orbitals of lower energy, t_{2g} set and two orbitals of higher energy, e_g set.



Q.8. Three complexes,
$[CoCl(NH_3)_5]^{2+}$ (I), $[Co(NH_3)_5\ H_2O]^{3+}$ (II) and $[Co(NH_3)_6]^{3+}$ (III)
absorb light in the visible region. The correct order of the wavelength of light absorbed by them is

a) II > I > III **b) I > II > III**
c) III > I > II **d) III > II > I**

Ans. (*b*)

Key Idea The wavelength (λ) of light absorbed by the complexes is inversely proportional to its Δ_0 (Crystal Field Splitting Energy). $\Delta_0 \propto 1/\lambda$

The complexes can be written as:
I. $[CoCl(NH_3)_5]^{2+} = [Co(NH_3)_5(Cl)^{2+}]$
II. $[Co(NH_3)_5H_2O]^{3+} = [Co(NH_3)_5(H_2O)]^{3+}$
III. $[Co(NH_3)_5]^{3+} = [Co(NH_3)_5(NH_3)]^{3+}$

So, the differentiating ligands in the octahedral complexes of Co (III) in I, II and III are **Cl^-, H_2O and NH_3** respectively.

In the spectrochemical series, the order of crystal field splitting is $Cl^- < H_2O < NH_3$.

So, the crystal field splitting energy (Δ_0) order will be

$$\Delta_0\ (I) < \Delta_0\ (II) < \Delta_0\ (III)$$

and the order of wavelength (λ) of light absorbed by the complexes will be

$$\lambda\ (I) > \lambda\ (II) > \lambda\ (III) \qquad \left[\because \quad \text{Energy } (\Delta 0) \propto \frac{1}{\lambda}\right]$$

Q.9. The complex that has highest crystal field splitting energy (Δ), is

a) $[Co(NH_3)_5Cl]Cl_2$ **b) $[Co(NH_3)_5(H_2O)]Cl_3$**
***c*) $K_3[Co(CN)_6]$** **d) $K_2[CoCl_4]$**

Ans. (*c*)

All of the complex given are the octahedral complexes of Co (III) except $K_2[CoCl_4]$, which is a tetrahedral complex of Co (II) (sp^3-hybridised).

We know, $\Delta_t < \Delta_o \qquad \left[\because\ \Delta_t = \frac{4}{9}\ \Delta_o\right]$

So, the octahedral complexes (a, b, c) have higher Δ_o values than that of tetrahedral, $K_2[CoCl_4]$.

Now, for the complexes a, b and c, the magnitude of $\Delta_o \propto$ ligand strength, which is based on their positions in the spectrochemical series.

$$Cl^- < H_2O < NH_3 < CN^-$$

Hence, $K_3[Co(CN)_6]$ will have the highest Δ value.

Q.10. The transition element having least enthalpy of atomization is

a) Zn **b) V** **c) Fe** **d) Cu**

Ans. (*a*)

For transition metals.

$\Delta H^o_{\text{Atomisation}} \propto$ Number of unpaired electrons in the metal atom.

For the given 3*d*-transition metals.

V	Fe	Cu	Zn
$3d^3 4s^2$	$3d^6 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^0$
$n = 3$	$n = 4$	$n = 1$	$n = 0$

[$\because$ n = no. of unpaired electrons]

So, absence of unpaired *d*-electrons and larger size of Zn atoms, make the crystal lattice of Zn less closely packed.

Reference Books:

1. Introduction to Coordination Chemistry, Geoffrey A. Lawrance

2. Coordination chemistry, Joan Ribas Gispert

3. Coordination Chemistry, 20: Invited Lectures Presented at the 20th International Conference on Coordination Chemistry, Calcutta, India, 10-14 December 1979, D. Banerjea

4. Comprehensive Coordination Chemistry III, Gerard Parkin, Edwin C Constable, Lawrence Que Jr.

5. Evaluating Spin Multiplicity, Arijit Das, chem.libretexts.org, UC Davis, US, Link: https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Electronic_Structure_of_Atoms_and_Molecules/Evaluating_Spin_Multiplicity

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