

Metal-Ligand Binding in Transition Metal Complexes

LIMITATIONS OF VALENCE BOND THEORY

1. It is qualitative in its approach; qualitative interpretation of the stability of complexes is not possible.
2. It cannot predict as to which of the five *d*-orbitals, the metal will provide for hybridization.
3. No satisfactory explanation for the existence of inner and outer orbital complexes.
4. It cannot account for the dependence on the nature of ligands.
5. It cannot account for the field strength of ligands as strong and weak field ligands.
6. Since the *d*-orbitals are considered to be degenerate, it cannot account for the colour and electronic spectra of complexes.
7. It cannot account for the preference of a particular geometry over other geometries, e.g., the square planar geometry of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex.
8. And many more to be discussed at higher level.

CRYSTAL FIELD THEORY

An explanation of colour and paramagnetism is readily given by crystal field theory. This theory, first introduced by Bethe and Van Vleck, was extended mainly by Orgel to cover transition metal chemistry. The theory starts with the assumption that, as far as transition metal complexes are concerned, the central transition metal ion can be regarded as a point charge, i.e., a charge concentrated into a very small volume, and that the surrounding ligands, be they anions or neutral molecules containing lone pairs of electrons, can likewise be represented as point charges. The bonding between the central metal ion and the surrounding ligands is assumed to be ionic.

The $3d$ levels are split into an upper group of two (doubly degenerate and labelled e_g) and a lower group of three (triply degenerate and labelled t_{2g}); the splitting of the levels is represented by the symbol Δ . If we reckon the zero of energy as the state of affairs that would obtain if each of the five $3d$ orbitals had interacted equally with the six ligands, then each of the upper two orbitals is raised by $3/5\Delta$ (or $6/5\Delta$ collectively) while each of lower three orbitals is lowered by $2/5\Delta$ (or $6/5\Delta$ collectively). As the diagram shows, the degree of splitting depends upon the strength of the crystal field.

If we now consider the example of a transition metal ion with only one $3d$ electron surrounded octahedrally by six ligands, e.g., $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, then this single $3d$ electron will normally occupy one of the three degenerate lower levels (t_{2g}). In order to transfer this electron into an upper level (e_g) radiation of the appropriate frequency must be supplied. Transition metal ions are coloured because radiation in the visible spectrum is of the right frequency to promote this electronic transition; and in particular $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ions are purple because green light (wavelength about 500 nm) is absorbed; i.e., white light minus green light gives purple light. The relationship between Δ and the frequency of light absorbed is given by the usual expression:

$$\Delta = h\nu$$

where h is Planck's constant and ν is the frequency of light absorbed.

FACTORS AFFECTING THE MAGNITUDE OF CRYSTAL FIELD SPLITTING (Δ_0)

The energy level splitting depends on four factors.

1. The Identity of the Metal

The crystal field splitting Δ is about 50 per cent greater for the second transition series compared to the first, whereas the third series is about 25 per cent greater than the second. There is small increase in the crystal field splitting along each series (Table 2.1).

Table 2.1 Crystal field splitting in the complexes of one group elements.

	in cm^{-1}	in kJ mol^{-1}
$[\text{Co}(\text{NH}_3)_6]^{3+}$	24800	296
$[\text{Rh}(\text{NH}_3)_6]^{3+}$	34000	406
$[\text{Ir}(\text{NH}_3)_6]^{3+}$	41000	490

2. The Oxidation State of the Metal

Generally, the higher the oxidation state of the metal, the greater the crystal field splitting. Thus, most cobalt (II) complexes are high spin as a result of the small

crystal field splitting. Whereas almost all the cobalt (II) complexes are low spin as a result of the much large splitting by the $3+$ ion. Some examples are given in Table 2.2.

Table 2.2 Crystal field splittings for hexa-aqua complexes of M^{2+} and M^{3+}

Oxidation state	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
+II Electronic configuration	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
$\Delta_0 \text{ cm}^{-1}$	–	12600	13900	7800	10400	9300	8500	12600
$\Delta_0 \text{ kJ mol}^{-1}$	–	151	(166)	93	124	111	102	(151)
+III Electronic configuration	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8
$\Delta_0 \text{ cm}^{-1}$	20600	18900	17830	21000	13700	18600	–	–
$\Delta_0 \text{ kJ mol}^{-1}$	243	226	213	251	164	222	–	–

3. The Number of the Ligands

The crystal field splitting is greater for the large number of ligands. For example, splitting of Δ_{octa} is larger as compared to Δ_t for four ligands in a tetrahedral environment.

$$\Delta_0 = 4/9 \Delta_t$$

4. The Nature of the Ligands

The common ligands can be ordered on the basis of the effect that they have on the crystal field splitting. This ordered listing is called the spectrochemical series. Among the common ligands, the splitting is the largest with carbonyl and cyanide and smallest with iodide. The ordering for the most metal is



Thus, for a particular metal ion, it is the ligand that determines the value of the crystal field splitting energy. There are two spin possibilities high spin (weak field) with four unpaired electrons and low spin (strong field) with all electrons paired. We find that the hexa-aquairon(II) ion $[\text{Fe}(\text{OH}_2)_6]^{2+}$ possesses four unpaired electrons. The water ligands being low in the spectrochemical series, produce a small Δ_{oct} , hence the electrons adopt a high-spin configuration. Conversely, the hexacyanoferrate(II) ion, $[\text{Fe}(\text{CN})_6]^{4-}$, is found to be diamagnetic (zero unpaired electrons). Cyanide is high in the spectrochemical series and produces a large Δ_{oct} , hence the electrons adopt a low-spin configuration.

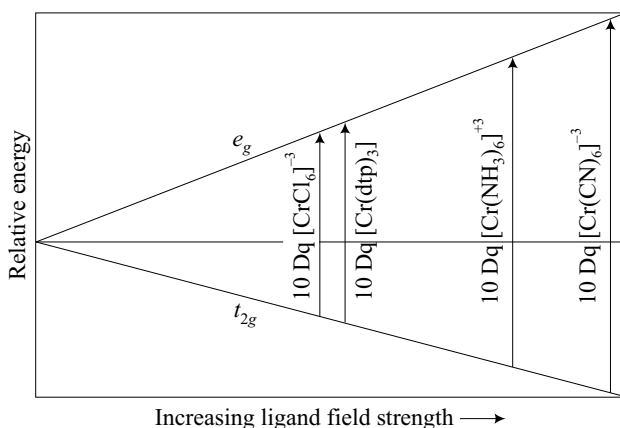
Crystal field splitting of chromium (III) complex with different ligands is given in Table 2.3.

The spectrochemical series is an experimentally determined series. It is difficult to explain the order as it incorporates both effects of σ and π bonding. The halides are in order expected from electrostatic effects. In other case, we consider

Table 2.3 Crystal field splittings by various ligands

Complex	Absorption peak	
	cm^{-1}	KJ mol^{-1}
$[\text{CrCl}_6]^{3-}$	13640	163
$[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$	17830	213
$[\text{Cr}(\text{NH}_3)_6]^{3+}$	21680	259
$[\text{Cr}(\text{CN})_6]^{3-}$	26280	314

covalent bonding to explain the order. A pattern of increasing σ donating is followed halide donors $< O$ donors $< N$ donors $< C$ donors (Fig. 2.3). The crystal field splitting produced by the strong CN^- is about double that of weak field ligands like halide ions.

**Fig. 2.3** Effect of ligand on magnitude of $10 Dq$.

CRYSTAL FIELD STABILIZATION ENERGY: WEAK FIELD CASE

As we have seen, the energy difference between the t_{2g} and e_g orbitals is defined as $10Dq$ and the energy of the t_{2g} level relative to the barycenter of unperturbed d -orbitals is $-4Dq$. In the d^1 case the crystal field stabilization energy (CFSE) is $-4Dq$. For d^2 , the CFSE = $-8Dq$ and for d^3 , CFSE = $-12Dq$. In these configurations the electrons enter the degenerate orbitals upon reaching the d^3 configuration, however, the t_{2g} level becomes half filled and without pairing. When one electron is added to form the d^4 case, two possibilities arise. In the weak field limit the splitting of the orbitals is small with respect to energy necessary to cause electron pairing in single orbital (the pairing energy, p). Since $P > 10Dq$, the fourth electron enters the e_g level rather than the "pay the price" of the pairing with one of the electrons in the t_{2g} orbitals. Instead, it loses somewhat less energy (in the form of CFSE) by entering the destabilized e_g level. Therefore the net CFSE for d^4 is

For d^4 (Fig. 2.4) $CFSE = (3 \times -4Dq) + (1 \times +6Dq)$

$$t_{2g}^3 e_g^1 \text{ the } = -6Dq$$

or

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

$$= -1.2\Delta_0 + 0.6\Delta_0 = 0.6\Delta_0.$$

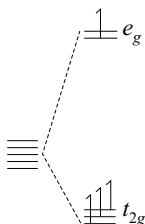


Fig. 2.4 Electron configuration of a d^4 ion in a weak octahedral field.

The electron configuration for d^5 may be written $t_{2g}^3 e_g^2$, the addition of a fifth electron results in a half-filled d subshell and an electron configuration $t_{2g}^3 e_g^2$. The crystal field stabilization energy is zero. The presence of two electrons in the unfavourable e_g level exactly balances the stabilization resulting from the three electrons in the t_{2g} level. In other words, the half-filled subshell (d^5) is spherically symmetrical and no stabilization can occur through the application of an external ligand field, octahedral or otherwise. In the same way, the configuration for d^6 to d^{10} may be obtained. The configurations and their resultant CFSEs are listed in Table 2.4 together with the number of unpaired electrons expected for each configuration.

Table 2.4 Crystal field effect for weak strong octahedral fields

Weak field				Strong field			
d^n	Configuration	Unpaired electron	CFSE	d^n	Configuration	Unpaired electrons	CFSE
d^1	$t_{2g}^1 g$	1	$-4Dq$	d^1	$t_{2g}^1 g$	1	$-4Dq$
d^2	$t_{2g}^2 g$	2	$-8Dq$	d^2	$t_{2g}^2 g$	2	$-8Dq$
d^3	$t_{2g}^3 g$	3	$-12Dq$	d^3	$t_{2g}^3 g$	3	$-12Dq$
d^4	$t_{2g}^3 e_g^1$	1	$-6Dq$	d^4	$t_{2g}^3 e_g^1$	1	$-6Dq$
d^5	$t_{2g}^3 e_g^2$	5	$0Dq$	d^5	$t_{2g}^3 e_g^2$	5	$-0Dq$
d^6	$t_{2g}^4 e_g^2$	4	$-4Dq$	d^6	$t_{2g}^4 e_g^2$	4	$-4Dq$
d^7	$t_{2g}^5 e_g^2$	3	$-8Dq$	d^7	$t_{2g}^5 e_g^2$	3	$-8Dq$
d^8	$t_{2g}^6 e_g^2$	2	$-12Dq$	d^8	$t_{2g}^6 e_g^2$	2	$-12Dq$
d^9	$t_{2g}^6 e_g^3$	1	$-6Dq$	d^9	$t_{2g}^6 e_g^3$	1	$-6Dq$
d^{10}	$t_{2g}^6 e_g^4$	0	$0Dq$	d^{10}	$t_{2g}^6 e_g^4$	0	$0Dq$

This Table 2.3 is somewhat oversimplified being based on one electron energy levels. In other words, configuration interaction or electron-electron effects have been neglected.

CRYSTAL FIELD STABILIZATION: STRONG FIELD CASE

If the splitting of the d -orbitals is large with respect to its pairing energy ($10Dq > P$), it is more favourable for the electrons to pair up in the t_{2g} level than to enter the strongly unfavourable e_g level. This situation is known as the strong field case. In the strong field case, the first three electrons remain unpaired in the degenerate t_{2g} orbitals, but the fourth pairs in order to remain in the t_{2g} level rather than enter the strong unfavourable e_g level (Fig. 2.5). As a result, the crystal field stabilization energy of configuration with more than 3 electrons will in general be greater for the strong field case. For d^4 , the configuration is t_{2g}^4 and the CFSE is $-16Dq + P$; for d^5 , CFSE = $-20Dq + 2P$; and for d^6 CFSE = $-24Dq + 2P$. But for d^7 the seventh electron enters the destabilizing e_g level and CFSE decreases:

$$\begin{aligned}\text{CFSE} &= (6 \times -4Dq) + (1 \times 6Dq) \times P \\ &= -18Dq + P\end{aligned}$$

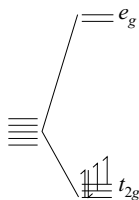


Fig. 2.5

A Summary

If $10Dq > P_1$	Complexes will be of low-spin type
If $10Dq < P_1$	Complexes will be of high-spin type
If $10Dq = P$	High-spin \rightleftharpoons Low-spin will be in an equilibrium

TETRAHEDRAL COMPLEXES

The second most common stereochemistry is tetrahedral. Fig. 2.6 shows the tetrahedral arrangement of four ligands around the metal ion.

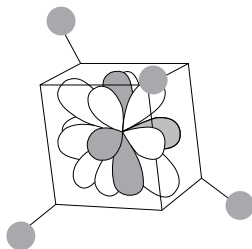


Fig. 2.6 The orientation of four ligands with respect to the metal d -orbitals.

In this case, it is the d_{xy} , d_{xz} and d_{yz} orbitals that are more in line with the approaching ligands than the $d_{x^2-y^2}$ and d_{z^2} orbitals. As a result it is $d_{x^2-y^2}$ and d_{z^2}

orbitals that are lower in energy and the tetrahedral energy diagram is inverted relative to the octahedral diagram (2.7).

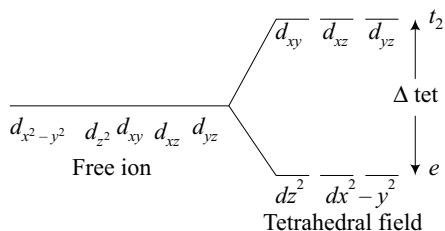


Fig. 2.7 The splitting of the d -orbitals energies that occur when the metal ion is surrounded by tetrahedral array of ligands.

With only four ligands instead of six ligands and the ligands are not quite pointing directly at the three orbitals, the crystal field splitting is much less than that in the octahedral case, in fact, as we mentioned earlier it is about four-ninths of Δ_{oct} ($\Delta_t = 4/9 \Delta_0$). As a result of the small orbital splitting almost all tetrahedral complexes are of high spin type. **Example:** tetrachlorocobalate(II) ion $[\text{CoCl}_4]^{2-}$ and for the oxyanions, such as the tetraoxomolybdate(VI) ion, MoO_4^{2-} (commonly called molybdate). Crystal field stabilization energy for tetrahedral complexes are given in Table 2.5.

Table 2.5 Crystal field effects for weak cubic and tetrahedral field







d^n	Configuration	Number of unpaired electrons	CFSE
d^1	e_g^1	1	$-6Dq$
d^2	e_g^2	2	$-12Dq$
d^3	$e_g^2 t_{2g}^1$	3	$-8Dq$
d^4	$e_g^2 t_{2g}^2$	4	$-4Dq$
d^5	$e_g^2 t_{2g}^3$	5	$0Dq$
d^6	$e_g^3 t_{2g}^3$	4	$-6Dq$
d^7	$e_g^4 t_{2g}^3$	3	$-12Dq$
d^8	$e_g^4 t_{2g}^4$	2	$-8Dq$
d^9	$e_g^4 t_{2g}^5$	1	$-4Dq$
d^{10}	$e_g^4 t_{2g}^6$	0	$0Dq$

Since tetrahedral fields do not have a centre of symmetry, the g subscripts are inappropriate for that symmetry.

TETRAGONAL DISTORTION OF OCTAHEDRAL COMPLEXES (JAHN-TELLER DISTORTION)

Jahn-Teller theorem states that in a non-linear molecule distortion must occur to lower symmetry to lower the energy and to remove degeneracy.

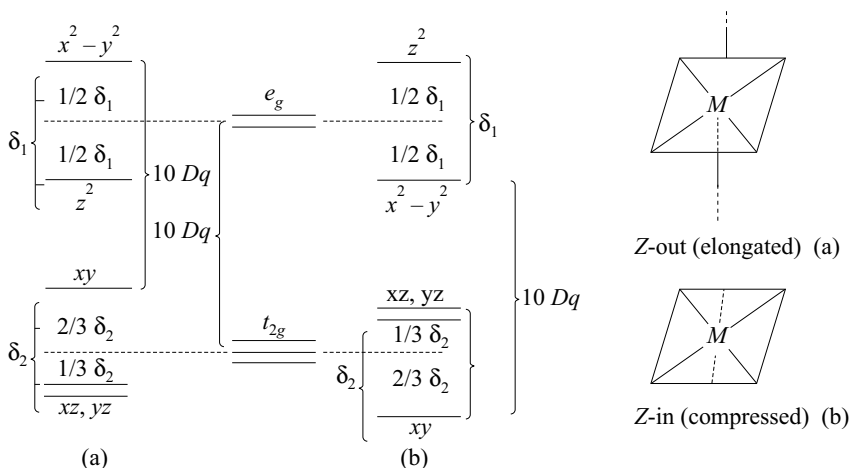
Table 2.7 Asymmetrical electronic arrangements

Electronic configuration	t_{2g}	e_g	Nature of ligand field	Examples
d^4			Weak field (high-spin complex)	Cr(+II), Mn(+III)
d^7			Strong field (low-spin complex)	Co(+II), Ni(+III)
d^9			Either strong or weak	Cu(+II)

The two e_g orbitals, $d_{x^2-y^2}$ and d_{z^2} are normally degenerate. However, if they are asymmetrically filled then this degeneracy is destroyed, and the orbitals are no longer equal in energy.

If the d_{z^2} orbital contains one electron more than the $d_{x^2-y^2}$ orbital, then the ligands approaching $+z$ and $-z$ will encounter greater repulsion than the other four ligands. The repulsion and distortion occurs along the z -axis. This is called tetragonal distortion. Strictly it should be called tetragonal elongation. This form of distortion is commonly observed.

If the $d_{x^2-y^2}$ orbital contains the extra electron, then elongation will occur along the x and y -axes. This means that the ligands approach more closely along the z -axis. Thus, there will be four long bonds and two short bonds. This is equivalent to compressing the octahedron along the z -axis and is called tetragonal compression. Tetragonal elongation is much more common than tetragonal compression, and it is not possible to predict which will occur (Fig. 2.8).


Fig. 2.8 Orbital energy diagram for a tetragonal field : z ligands out; (b) z ligands in

For example, the structure of CrF_2 is a distorted rutile (TiO_2) structure. Cr^{2+} is octahedrally surrounded by six F^- , and there are four $\text{Cr}-\text{F}$ bonds of length 198–201 pm and two longer bonds of length 243 pm. The octahedron is said to be tetragonally distorted. The electronic arrangement in Cr^{2+} is d^4 . F^- is a weak field ligand, and so the t_{2g} level contains three electrons and the e_g level contains one electron. The $d_{x^2-y^2}$ orbital has four lobes whilst the d_{z^2} has only two lobes pointing at the ligands. To minimize repulsion with the ligands, the single e_g electron will occupy the d_{z^2} orbitals. This is equivalent to splitting the degeneracy of the e_g level so that d_{z^2} is of lower energy, i.e., more stable, and $d_{x^2-y^2}$ is of higher energy, i.e., less stable. Thus, the two ligands approaching along the $+z$ and $-z$ directions are subjected to greater repulsion than the four ligands along $+x$, $-x$, $+y$ and $-y$. Thus, causes tetragonal distortion with four short bonds and two long bonds. In the same way MnF_3 contains Mn^{3+} with a d^4 configuration and forms a tetragonally distorted octahedral structure.

Now consider another example of Jahn-Teller distortion, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. The $\text{Ti}(\text{III})$ is a d^1 species and in an octahedral field the configuration is t_{2g}^1 . The t_{2g} level is triply degenerate, however the Jahn-Teller theorem forbids it to be (Fig. 2.9) occupied by a single electron without undergoing distortion. (Note that the $\text{Cr}(\text{III})$ ion, d^3 would be acceptable since no degeneracy occurs.) If distortion occurs, the odd electron can occupy a lower energy level. Note, however, that the Jahn-Teller theorem per se does not predict, which way the distortion will occur. In this case, however, it is easy to see that the stabilization of the added electron in the ‘z-in’ distortion is twice that of the ‘z-out’ distortion, and we would therefore expect the $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion to be distorted, compressed along the z-axis. The CFSE energy will be $2/3 \delta_2$ larger than it would have been in a regular octahedron. Although the upper e_g levels are split as well, there is no energetic effect since they are unoccupied in the ground state. The excited state, $t_{2g}^0 e_g$ subject to distortion of the same type. The spectrum of the ion (Fig. 2.10) shows the result of this splitting. Instead of a single, Gaussian curve the absorption peak shows a shoulder resulting from the superposition of the two peaks: one from the ground state to the lower of the two e_g levels and the other to the upper (Fig. 2.9). In some species, such as the $(\text{CoF}_6)^{3-}$ ion, the splitting of the two bands is sufficient to cause two distinct peaks to be found in the spectrum (Fig. 2.11).

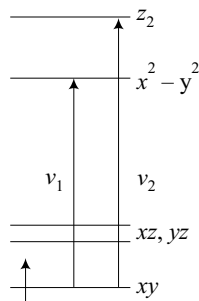


Fig. 2.9 Energy level in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ and transitions to excited states.

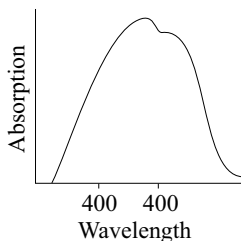


Fig. 2.10 Spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$.

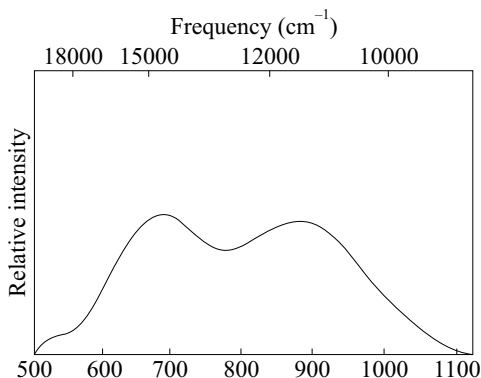


Fig. 2.11 Absorption spectrum of K_3CoF_6 illustrating transitions from the ground state to the Jahn-Teller split excited state.

The best evidence for the presence of Jahn-Teller effects in transition metal compounds comes from structural studies of solids containing Cu(II). The latter is a d^9 configuration and in an octahedral field the ninth electron has the option of entering the d_{z^2} or the $d_{x^2-y^2}$ orbital. The octahedral complex is therefore degenerate and not expected to exist in an undistorted form. Alternatively, the d^{10} system may be viewed by means of the “hole formalism” which would describe Cu(II) as the spherically symmetrical d^{10} system with a hole, or missing electron. From this point of view, the hole behaves exactly the way the electron does, but instead of finding the lowest orbital available to it, the hole tends to “float” to the top. Jahn-Teller distortion thus lets it float somewhat higher than it would in the undistorted complex (Fig. 2.12). An analogous scheme for viewing such systems is to consider a d^n system as an inverted d^{10-n} system as shown in Fig. 2.13. All these schemes are useful, and they will be encountered again in the following discussion.

Experimentally, we find that in the Cu(II) series of compounds the distortion is usually elongation along the z -axis. Table 2.8 lists some distances found in crystal containing hexacoordinate Cu(II) ions. Each compound has both “short” and “long” bonds. It is of interest to note that the “short” bonds represent a nearly constant radius for the Cu^{2+} ion, whereas the “long” bonds show no such constancy. This might be expected since the distortion or lengthening of the long bonds can proceed to various degrees.

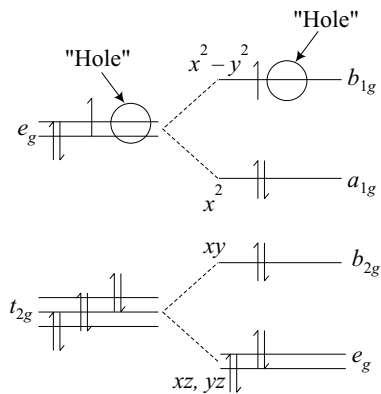


Fig. 2.12 Energy level diagram for d^9 configuration in an octahedral and a tetragonal field illustrating the tendency of the "hole" to "float".

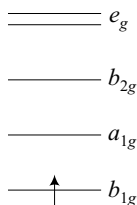


Fig. 2.13 The configuration of Cu(II) represented as an inverted d^1 case.

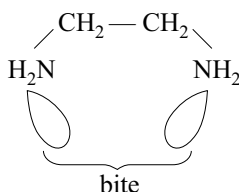
Orbital degeneracy will occur only when the e_g or t_{2g} level is partially filled. Since the splitting of the e_g level is somewhat greater than the splitting of the t_{2g} level, we would therefore expect weak-field d^4 and d^9 and strong field d^1 and d^9 to show the greatest effects. Cu(II) is an excellent example of a d^9 species undergoing Jahn-Teller distortion. We have fewer data to support Jahn-Teller distortion in high-spin d^4 or low-spin d^7 . Cr(II) and Mn(III) are d^4 , and both have been found to be distorted Table 2.9 in some compounds. Furthermore, extensive studies of the spectra of Mn(III) compounds are readily interpreted in terms of elongation along the z -axis. The d^7 configuration of Co^{2+} is less satisfying. Only the cyanide ion can provide a sufficiently strong field to induce spin pairing. The expected cyano complex, $[\text{Co}(\text{CN})_6]^{-4}$, is not found, however, but instead the principal species in solution has five cyano groups per cobalt, probably $[\text{Co}(\text{CN})_5\text{H}_2\text{O}]^{3-}$. One might suggest that this is the "ultimate" in Jahn-Teller distortion, namely, complete dissociation of one cyanide.

In case of Cu(II) , distortion via either elongation or compression will lead to a stabilization of $1/2 \delta_1$. Again, the Jahn-Teller theorem provides us with no clue as to which way the distortion will occur, but simply says that such distortion will lower the energy of the system. Undoubtedly there has been in the past too much

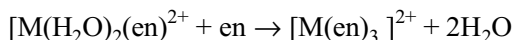
Table 2.9 Metal-ligand distances in Cr(II) and Mn(II) compounds

Compound	Short distance	r_M	Long distance	r_M
CrF ₂	4F at 200	129	2F at 243	172
KCrF ₃	2F at 200	129	4F at 214	143
MnF ₃	2F at 179	108	2F at 191	120
			2F at 209	138
γ -MnO(OH)	4O at 188	115	2O at 230	157

The nature of the chelate ring tends to restrict the distortion of complex and form a perfect octahedral. Since the chelate will have a preferred “bite” or distance between the coordinating atoms.



An example of the conflict between stabilization from the Jahn-Teller effect and chelate geometrical requirement is found in the ethylenediamine complexes of Cu(II). Most divalent transition metal ions form complexes with ethylenediamine (en) by stepwise replacement of water:



The stepwise stability constants, K_1 , K_2 , K_3 , measure the tendency of ethylenediamine to displace two, four, and six molecules of water with the formation of the mono, bis, and tris-(ethylenediamine) complexes. The value for these constants for the ions Mn^{2+} to Zn^{2+} show a rather uniform trend of slightly increasing stability of all the ethylenediamine complexes toward the end of the series the Irving-Williams order). Cu(II) provides a striking exception, however, the tris (ethylenediamine) copper(II) complex, $[Cu(en)_3]^{2+}$ is remarkably unstable. At one time its existence was questioned and although it has subsequently been prepared, the value of K_3 (a measure of the tendency to add the third ethylenediamine ligand) is the lowest of the ions discussed even though the K_1 and K_2 value are the highest (Fig. 2.14). The lack of stability can be traced directly to the distortion necessary in a $d^9 Cu^{2+}$ ion. The bis(ethylenediamine) complex, $[Cu(en)_2(H_2O)]^{2+}$, can distort readily by letting the two trans-water molecules more out from the

copper with the two ethylenediamine rings relatively unchanged. In contrast, the tris (ethylenediamine) complex cannot distort tetragonally without straining at least two of the chelate rings:

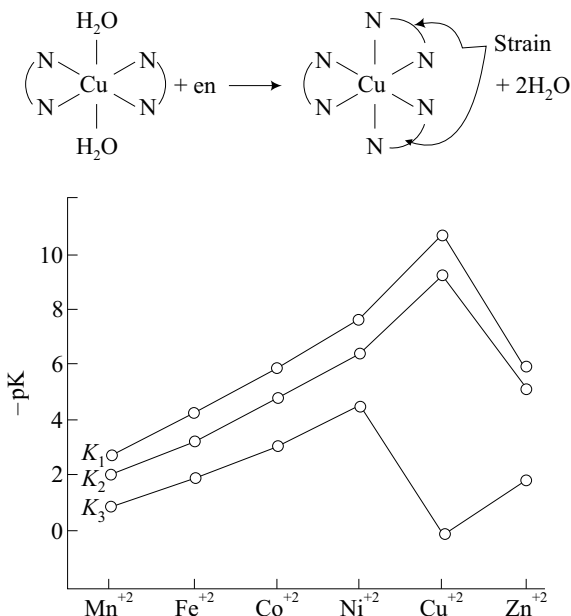
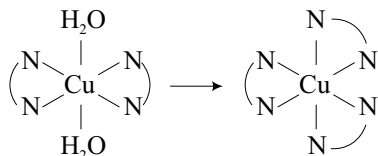


Fig. 2.14 Step-wise stability constant K_1 , K_2 , and K_3 of ethylenediamine complexes in aqueous solution at 25°C.

Alternatively, it is possible that the constraint of the chelate ring system can prevent tetragonal distortion and form an undistorted octahedron, but the resulting complex would lack the stabilization inherent in Jahn-Teller distortion:



SQUARE PLANAR COMPLEXES

For the 3d-transition metals, it is only nickel that tends to form square planar complexes, such as the tetracyanonickelate(II) ion, $[\text{Ni}(\text{CN})_4]^{2-}$. These complexes are diamagnetic. We can develop a crystal field diagram to see why it is so, even though both octahedral and tetrahedral geometries result in two unpaired electrons for the d^8 configuration.

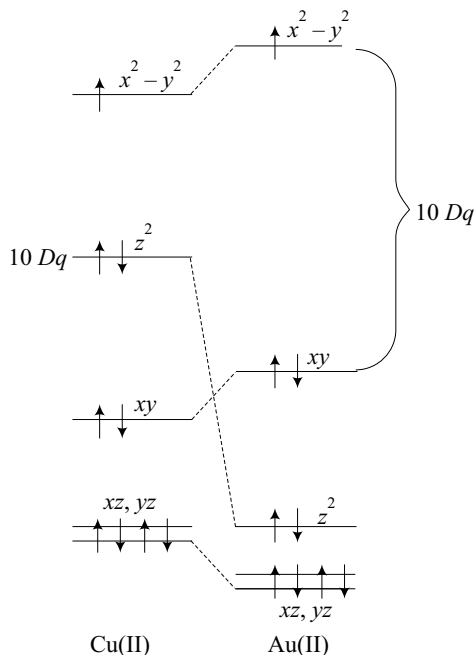


Fig. 2.16 Comparison of Cu(II) and Au(II) in tetragonal and square planar fields to illustrate the instability of Au(II) towards the removal (oxidation) of the odd electron.

1. Magnetic Properties

Any theory of transition metal ions has to account for the paramagnetism of many of the compounds. The degree of paramagnetism is dependent on the identity of the metal. Its oxidation state, its stereochemistry and nature of the ligand. Crystal field theory explains the paramagnetism very well in terms of the splitting of d -orbital energy, at least for the $3d$ -transition metals. For example, we have just seen that crystal field theory can explain the diamagnetism of the square planar nickel (II) ion, which contrasts with the paramagnetism of the tetrahedral and octahedral geometries.

2. Colours of Transition Metal Complex

The most striking feature of transition metal complexes is the range of colours that they exhibit. These colours are the result of absorptions in the visible region of the electromagnetic spectrum. For example, Fig. 2.17 shows the visible absorption spectrum of the purple hexaaquatitanium (III) ion, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. This ion absorbs light in the green part of the blended purple colour.

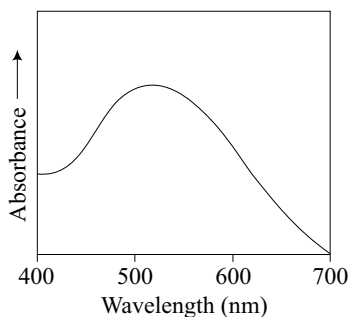


Fig. 2.17 The visible absorption spectrum of the hexaaquatitanium (III) ion.

The visible absorption spectrum of the hexaaquatitanium(III) ion

The titanium(III) ion has a d^1 electron configuration and with six water molecules as ligands. We can consider the ion to be in an octahedral field. The resulting d -orbital splitting is shown on the left-hand side of Fig. 2.18. An absorption of electromagnetic energy causes the electron to shift to the upper d -orbital set, as shown on the right-hand side Fig. 2.18.

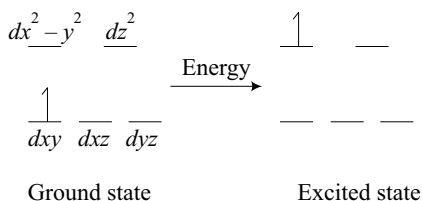


Fig. 2.18 The electron transition corresponding to the visible absorption of the titanium (III) ions.

The electron subsequently returns to the ground state and the energy is released as thermal motion rather than as electromagnetic radiation. The absorption maximum is about ~ 520 nm, which represents the energy difference, i.e., the value of Δ (the crystal field splitting energy).

As it is apparent from the figure that the electronic absorption bands are very broad (for d^1 and d^9 configuration). These bands are broad because the electron transition time is much shorter than the vibration occurring within the molecules. When the ligands are farther away from the metal than the mean bond length, the field is weaker and the splitting is less, hence the transition energy is smaller than the normal value. Conversely when the ligands are closer to the metal, the field is stronger, the splitting is greater and the transition energy is larger than normal value. We can confirm this explanation by cooling the complex to close to absolute zero, thereby reducing the molecular vibrations. When we do as predicted, the bands in the visible absorption spectrum become much narrower.

and Zn^{2+} represents zero stabilization. The heights of other points above this line are the crystal field stabilization energies.

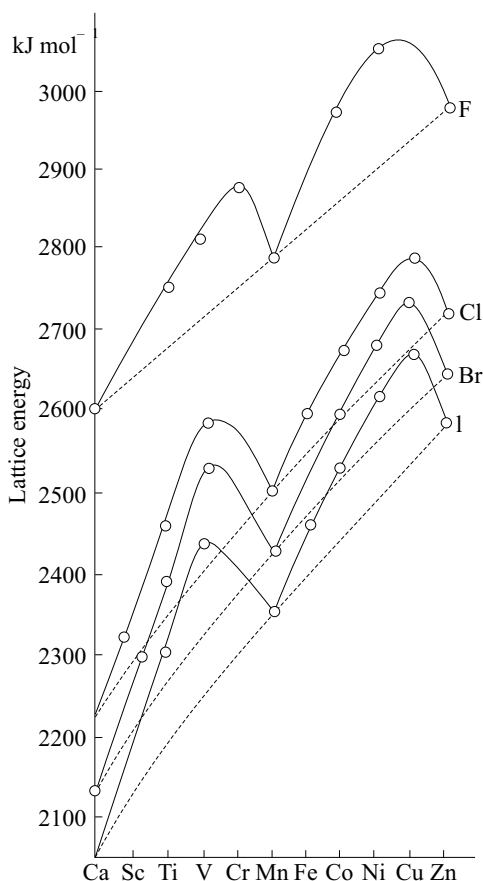
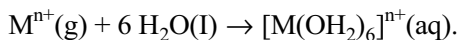


Fig. 2.19 CFSE of dihalides of the first transition series.

4. Hydration Enthalpies

Another parameter that can be explained by crystal field theory is the enthalpy of hydration of transition metal ion. This is the energy released when gaseous ions are hydrated.



As the effective nuclear charge of metal ions increases across a period, we expect the electrostatic interaction between the water molecule and the metal ions to increase regularly along the transition metal ions to series. In fact, we can find deviations from the linear relationship Fig. 2.20.

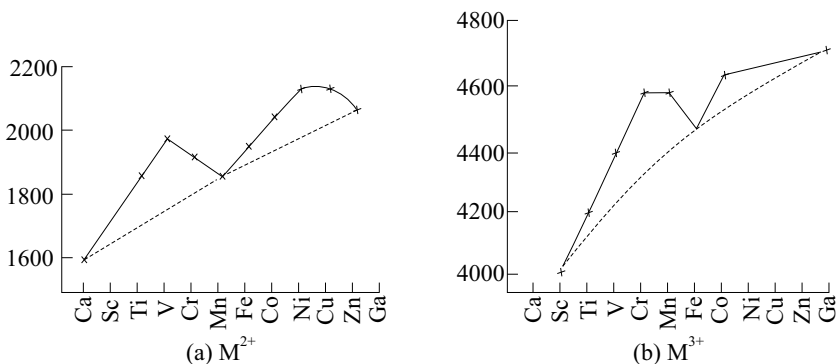


Fig. 2.20(a) Experimental hydration enthalpies of the dipositive ions of the 3d transition metal.

To explain this observation, we assume that greater enthalpy is the result of the crystal field stabilization energy which can be calculated in terms of Δ_{oct} (the crystal field splitting). Recall that for an octahedral field that d_{xy} , d_{xz} and d_{yz} orbitals are lowered in energy by $2/5 \Delta_{\text{oct}}$ and the $d_{x^2-y^2}$ and d_{z^2} orbitals are raised in energy by $3/5 \Delta_{\text{oct}}$. Thus, for a particular electron configuration, it is possible to calculate the crystal field to the hydration energy. Fig. 2.20(b) illustrates the situation for the d^4 high spin ion. This ion would have a net stabilization energy of

$$- [3(2/5 \Delta_{\text{oct}})] + [1(3/5 \Delta_{\text{oct}})] = -0.6 \Delta_{\text{oct}}$$

$$\begin{array}{ccccccc} \frac{1}{+3/5 \Delta} & & \dots & & & & \\ & & & & & & \\ \frac{1}{-2/5 \Delta} & & \frac{1}{-2/5 \Delta} & & \frac{1}{-2/5 \Delta} & & \end{array}$$

Fig. 2.20(b) the crystal field stabilization energy of the d^4 high electron configuration. The complete set of crystal field stabilization energies is listed in Table 2.11

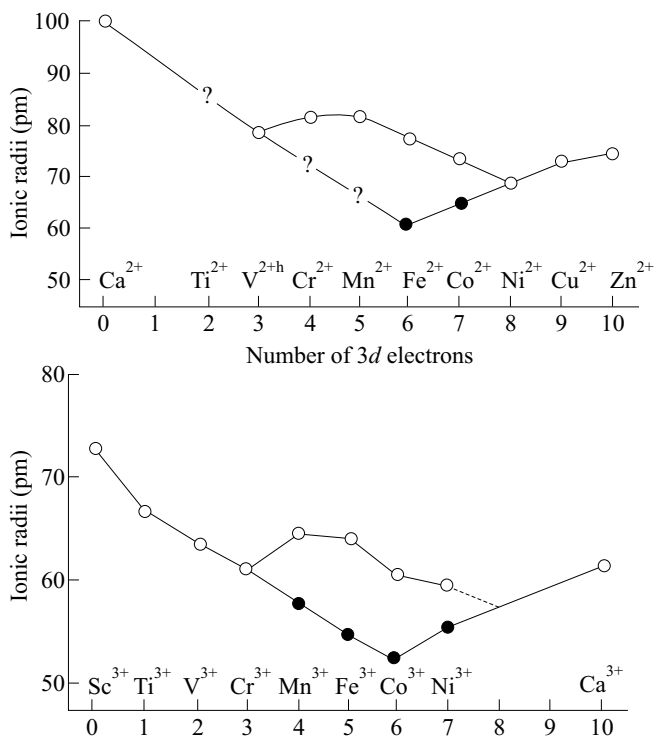
These values correspond remarkably well with the derivations of the hydrogen enthalpies of particular note, it is only the d^0 , d^5 (high spin) and d^{10} ions that fit the expected near-linear relationships and these all have zero crystal field stabilization energy.

5. Ionic Radii

A slightly different form of the typical two-humped curves is shown by the ionic radii of the 3d divalent metals. These are plotted in Fig. 2.21 for both dipositive and tripositive ions. There is a steady decrease in radius for the strong field case until t_2g^6 configuration.

Table 2.11 Crystal field stabilization energies (CFSE) for the divalent, high-spin ions

<i>Ion</i>	<i>Configuration</i>	<i>CFSE</i>
Ca ²⁺	<i>d</i> ⁰	-0.0 Δ _{oct}
-	<i>d</i> ¹	-0.4 Δ _{oct}
Ti ²⁺	<i>d</i> ²	-0.8 Δ _{oct}
V ²⁺	<i>d</i> ³	-1.2 Δ _{oct}
Cr ²⁺	<i>d</i> ⁴	-0.6 Δ _{oct}
Mn ²⁺	<i>d</i> ⁵	-0.0 Δ _{oct}
Fe ²⁺	<i>d</i> ⁶	-0.4 Δ _{oct}
Co ²⁺	<i>d</i> ⁷	-0.8 Δ _{oct}
Ni ²⁺	<i>d</i> ⁸	-1.2 Δ _{oct}
Cu ²⁺	<i>d</i> ⁹	-0.6 Δ _{oct}
Zn ²⁺	<i>d</i> ¹⁰	-0.0 Δ _{oct}

**Fig. 2.21** Radii of the divalent ions Ca²⁺ to Zn²⁺ (above) and trivalent ions Sc³⁺ to Ca³⁺.

At this point the next electron enters the e_g level, into an orbital directed at the ligands, repelling them and causing an increase in the effective radius of the metal. In the case of high-spin ions the increase in the effective radius of the metal. In the case of high-spin ions the increase in radius occurs with the $t_{2g}^3 e_g^1$ configuration for the same reason (Table 2.12).

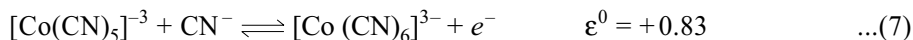
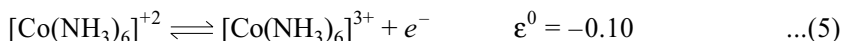
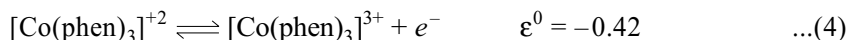
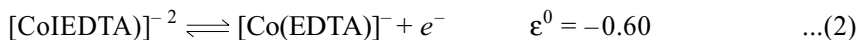
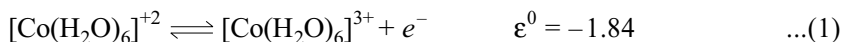
Table 2.12 Electronic configuration of divalent metal ion

d^n	Strong field	Trend in radii	Weak field	Trend in radii
d^1	$t_{2g}^1 e_g^0$	↓ Decrease	$t_{2g}^1 e_g^0$	↓ Decrease
d^2	$t_{2g}^2 e_g^0$		$t_{2g}^2 e_g^0$	
d^3	$t_{2g}^3 e_g^0$		$t_{2g}^3 e_g^0$	↑ Increase
d^4	$t_{2g}^4 e_g^0$		$t_{2g}^3 e_g^1$	
d^5	$t_{2g}^5 e_g^0$		↑ Increase	$t_{2g}^3 e_g^2$
d^6	$t_{2g}^6 e_g^0$	$t_{2g}^4 e_g^2$		
d^7	$t_{2g}^6 e_g^1$	$t_{2g}^5 e_g^2$		↓ Decrease
d^8	$t_{2g}^6 e_g^2$	$t_{2g}^6 e_g^2$		
d^9	$t_{2g}^6 e_g^3$	↑ Increase		$t_{2g}^6 e_g^3$
d^{10}	$t_{2g}^6 e_g^4$		$t_{2g}^6 e_g^4$	

6. Stability of Complexes

Further evidence of the importance of CFSE comes from the stability of particular oxidation states. In aqueous solution Co(III) is unstable with respect to reduction by water to form Co(II). Although, there are several terms involved, this may be viewed as a reflection of the high third ionization enthalpy of cobalt. If various moderate to strong field ligands are present in the solution, however, the Co(III) ion is perfectly stable, in fact, in some cases it is difficult or impossible to present the spontaneous transformation of Co(II) to Co(III).

For example, the appropriate oxidation *emfs* are:



Note that the order of ligands in Eqs. 1-7 is approximately that of the spectrochemical series and, hence, that of increasing crystal field stabilization energies. The oxidation of Co(II) to Co(III) results in change from high to low spin. We think of the oxidation as taking place in two steps, the first being the rearrangements of electrons to the low spin state and the second the removal of the seventh electron to produce Co(III):

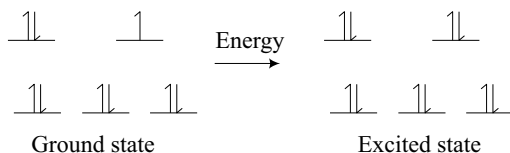


Fig. 2.22 The electron transition for the d^9 electron configuration.

For d^2 ions, we might expect two absorption peaks, corresponding to the excitation of one or both of the electron. However, a total of three fairly strong absorptions are observed.

We have to consider inter-electronic in the ground state, a d^2 ion. Such as the hexaaquavanadium (II) ion, has three electrons in d_{xy} , d_{xz} and d_{yz} orbitals. When one electron is excited, the resulting combination can have different energies, depending on whether the two electrons are occupying overlapping orbitals and therefore repelling each other. For example, the excited configuration of $(d_{xy})^1(d_{z^2})^1$ will be lower in energy because the two electrons occupy very different space, whereas the $(d_{xy})^2(d_{x^2-y^2})^0$ configuration will be higher in energy because both electrons occupy space in the x and y planes.

By calculation, it can be shown that the combination $(d_{xy})^1(d_{z^2})^1$, $(d_{xz})^1(d_{x^2-y^2})^1$, all have the same lower energy, and $(d_{xy})^2$, $(d_{x^2-y^2})^2$ all have the same higher energy.

This accounts for two transitions, and the third transition corresponds to the excitation of both electrons into the upper level to give the configuration $(d_{x^2-y^2})^2$, $(d_{z^2})^2$ Fig. 2.23.

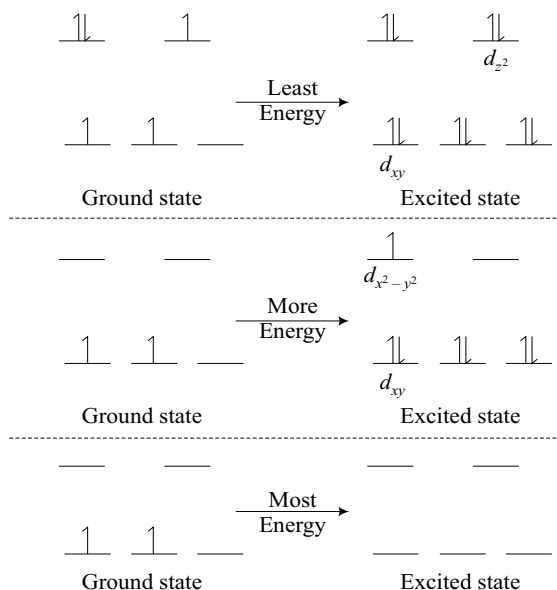


Fig. 2.23 The possible electron transitions for the d^2 electron configuration.

Q.3 Predict the colours of $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. The energy difference between the d -levels Δ in $[\text{Co}(\text{NH}_3)_6]^{3+}$ is 22900 cm^{-1} , in $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ it is 17400 cm^{-1} .

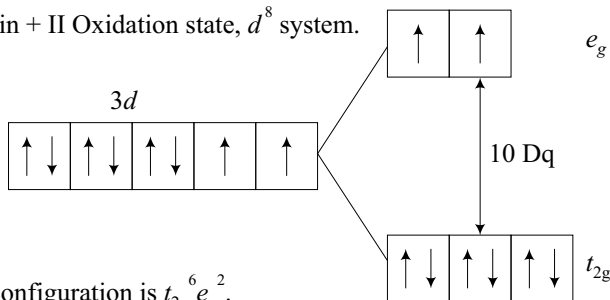
Ans. $\Delta = 1/\bar{\nu} = 1/22900 = 4.37 \times 10^{-5} \text{ cm} = 4370 \text{ \AA}$. An absorption band is expected at about 4400 \AA , which corresponds to the absorption of blue light. The observed colour of the complex is orange, as expected. In $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ the value of Δ corresponds to the absorption light is about 5750 \AA . The expected colour is violet, however, the actual colour is green. In this case an additional absorption occurs at 4050 \AA hence the colour cannot be predicted. Consideration of Δ alone.

Q.4 Write down the electronic configuration of the following complexes by using CFT (crystal field theory).

- (i) $[\text{Ni}(\text{NH}_3)_6]^{2+}$ paramagnetic (ii) $[\text{Cr}(\text{CN})_6]^{3-}$
 (iii) $[\text{NiCl}_4]^{2-}$ tetrahedral

Ans. (i) $[\text{Ni}(\text{NH}_3)_6]^{2+}$. Octahedral

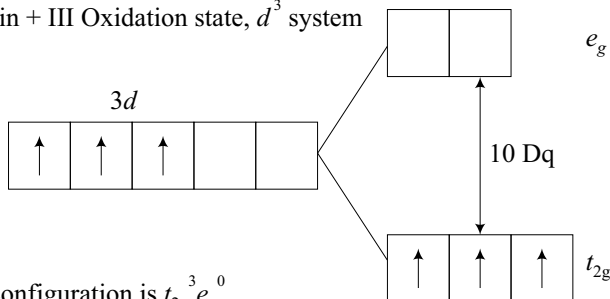
Ni is in + II Oxidation state, d^8 system.



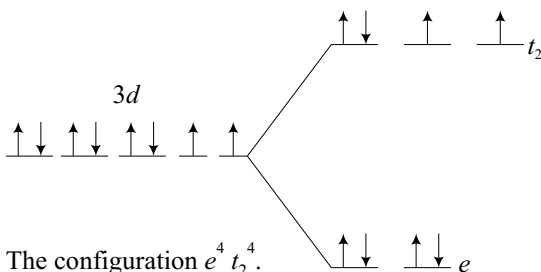
The configuration is $t_{2g}^6 e_g^2$.

(ii) $[\text{Cr}(\text{CN})_6]^{3-}$ Octahedral

Cr is in + III Oxidation state, d^3 system



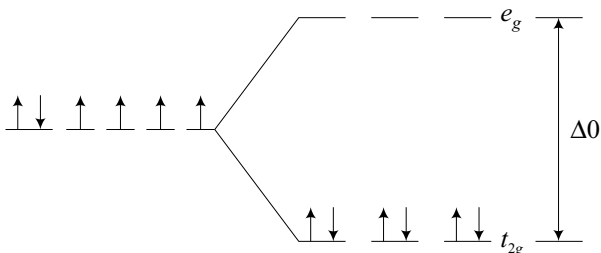
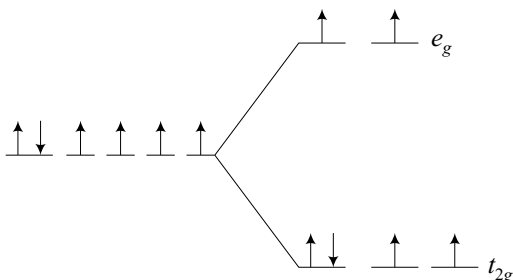
The configuration is $t_{2g}^3 e_g^0$.

(iii) $[\text{NiCl}_4]^{2-}$ tetrahedralCr is in + II oxidation state and Cl^- is weak field ligand.The configuration is $e^4 t_2^4$.

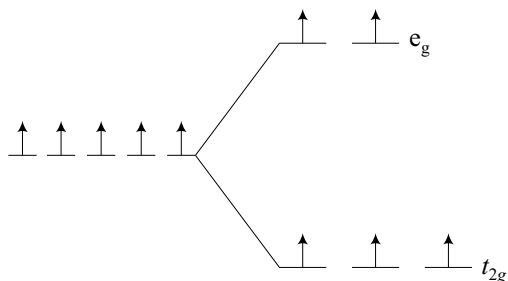
Q.5 Draw the energy level diagram indicating the number of electrons in each level for the following complexes.

(a) $[\text{Co}(\text{CN})_6]^{3-}$ $\Delta_0 > p$ (b) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$ $\Delta_0 < p$ (c) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ $\Delta_0 < p$ (d) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ $\Delta_0 < p$ (e) $[\text{Mn}(\text{CN})_6]^{3-}$ $\Delta_0 > p$ (f) $[\text{Fe}(\text{CN})_6]^{3-}$ $\Delta_0 > p$

Ans. (a) $[\text{Co}(\text{CN})_6]^{3-}$, Cobalt in (+III) oxidation state, d^6 system $\Delta_0 > p$.

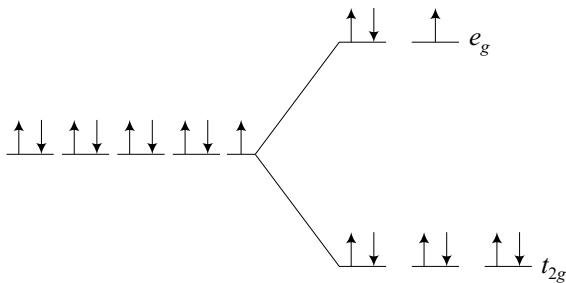
(b) $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $\Delta_0 < p$, d^6 system

(c) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$, $\Delta_0 < p$, It is a d^5 system



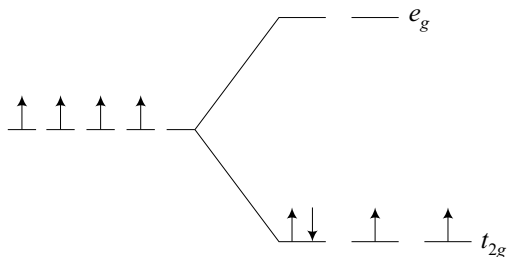
Configuration is $t_{2g}^3 e_g^2$

(d) $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$, it is a d^9 system.



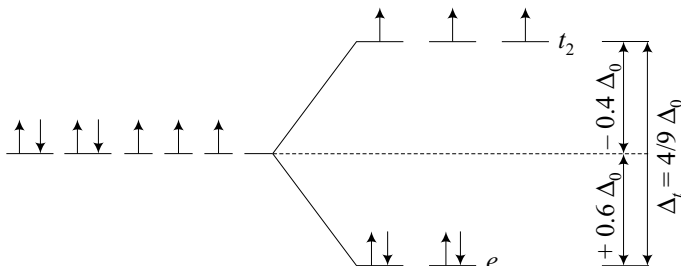
Configuration is $t_{2g}^6 e_g^3$.

(e) $[\text{Mn}(\text{CN})_6]^{3-}$, $\Delta_0 > p$, it is a d^4 system.



Configuration is $t_{2g}^4 e_g^0$.

Tetrahedral complexes are generally of high spin type complexes because Δ_t being very low as compared to Δ_0 (octahedral). Hence, the electrons do not pair up and follow Hund's rule of maximum multiplicity.



$$\begin{aligned} \text{CFSE (tetrahedral)} &= (-0.6 \times ne + 0.4 \text{ mt}) \\ &= (-0.6 \times 4 + 0.4 \times 3) \\ &= -1.2 \end{aligned}$$

$$\begin{aligned} \mu_{\text{eff}} &= \sqrt{n(n+2)} = \sqrt{3 \times 5} \\ &= 3.87 \text{ B.M.} \end{aligned}$$

and the complex is paramagnetic due to the presence of three unpaired electrons.

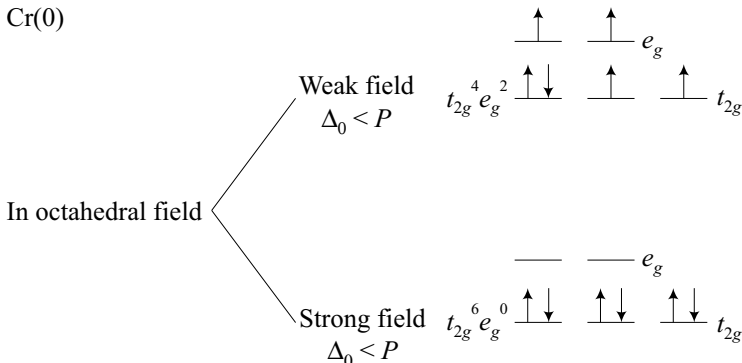
Q.7 Draw the energy level diagram depicting the occupation of energy levels for weak and strong fields around Cr(0), Cr(II) and Cr(III) in an octahedral field.

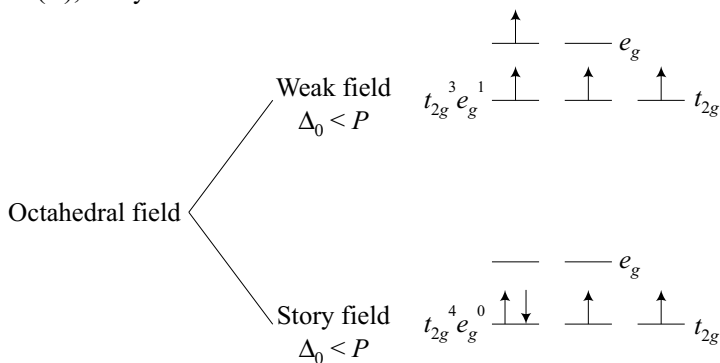
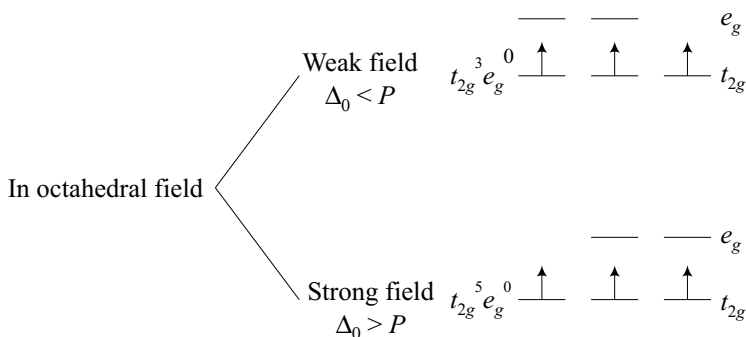
Ans. Cr(0), d^6 system or d^5s^1 $t_{2g}^6 e_g^0$ (SF) $t_{2g}^4 e_g^2$ (WF)

Cr(II), d^4 system $t_{2g}^4 e_g^0$ (SF) $t_{2g}^3 e_g^1$ (WF)

Cr(III), d^3 system $t_{2g}^3 e_g^0$ (SF) $t_{2g}^3 e_g^0$ (WF)

Cr(0)

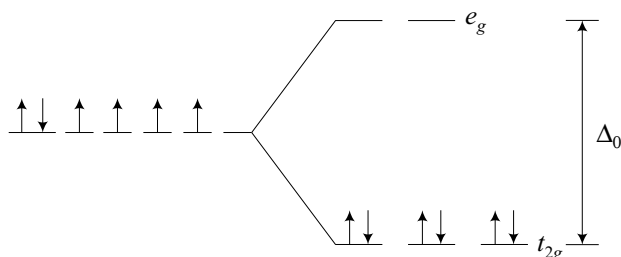


Cr(II), d^4 systemCr(III), d^3 system

Q.8 Calculate the relative energies as a function of Δ_0 and p for high spin and low spin complexes of Fe(II) and Co(II).

Ans. Low spin Fe(II) is a d^6 system

In strong field $\Delta_0 > p$, hence pairing has taken place to form low spin complex. The filling of t_{2g} and e_g orbitals takes place as shown below.



The CFSE = $(-0.4nt_{2g} + 0.6 me_g)\Delta_0$

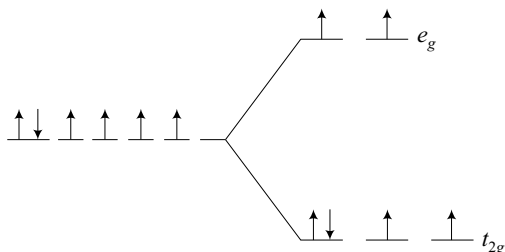
where nt_{2g} is the number of electrons in t_{2g} orbitals, while me_g is the

number of electrons in e_g orbitals.

$$\begin{aligned} \text{CFSE Fe(II) strong field} &= -0.4 \times 6 \Delta_0 \\ &= -2.4 \Delta_0 \end{aligned}$$

and the complex is diamagnetic:

High spin Fe(II) complex is formed with weak field ligands where $\Delta_0 < p$, hence Hund's rule is obeyed.



$$\begin{aligned} \text{CFSE. Fe(II) weak field} &= (0.4 \times 4 \times 0.6 \times 2) \Delta_0 \text{ (octahedral)} \\ &= -0.4 \Delta_0 \end{aligned}$$

and its complex is paramagnetic due to four unpaired electrons.

low spin (Co(II) d^7 system, $t_{2g}^6 e_g^1$)

Strong field ligand $\Delta_0 > p$

$$\text{CFSE (octahedral)} = (-0.4 \times 6 + 0.6 \times 1) \Delta_0 = -1.8 \Delta_0$$

and the complex is paramagnetic due to the presence of one unpaired electron.

High spin Co(II) d^7 system, weak field $\Delta_0 < p$, $t_{2g}^5 e_g^2$

$$\text{CFSE (octahedral)} = (0.4 \times 5 \times 0.6 \times 2) \Delta_0 = -0.8 \Delta_0$$

and the complex is paramagnetic due to the presence of 3 unpaired electrons.

Q.9 Which of the following complex amongst the following pairs, has high $10Dq$ or Δ_0 value and why?

- (i) $[\text{Co}(\text{NH}_3)_6]^{3+}$ or $[\text{Rh}(\text{NH}_3)_6]^{3+}$
- (ii) $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{4-}$ or $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
- (iii) $[\text{Cr}(\text{en})_3]^{3+}$ or $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$

Ans. (i) $[\text{Co}(\text{NH}_3)_6]^{3+}$ or $[\text{Rh}(\text{NH}_3)_6]^{3+}$
 $[\text{Rh}(\text{NH}_3)_6]^{3+}$ has higher Δ_0 or $10Dq$.

It is because Rhodium (III) belongs to $4d$ transition series and is considerably bigger than cobalt (III) which belongs to $3d$ series.

It has been found that Δ_0 values are 30-50% higher for $4d^n$ complexes as compared to $3d^n$ complexes.

$$3d^6 \Delta_0 \text{ for } [\text{Co}(\text{NH}_3)_6]^{3+} = 23000 \text{ cm}^{-1}, \Delta_0 = 275 \text{ kJ mol}^{-1}$$

$$4d^6 \Delta_0 \text{ for } [\text{Rh}(\text{NH}_3)_6]^{3+} = 34000 \text{ cm}^{-1}, \Delta_0 = 406 \text{ kJ mol}^{-1}$$

Q.11 Low spin tetrahedral complexes are not known. Explain why?

Ans. It is because Δt , i.e., the tetrahedral crystal field splitting energy is always much smaller than the octahedral Δ crystal field splitting energy being $\Delta t = 4/9 \Delta_0$ and it is never energetically favourable to pair electrons. Hence, all tetrahedral complexes are high spin.

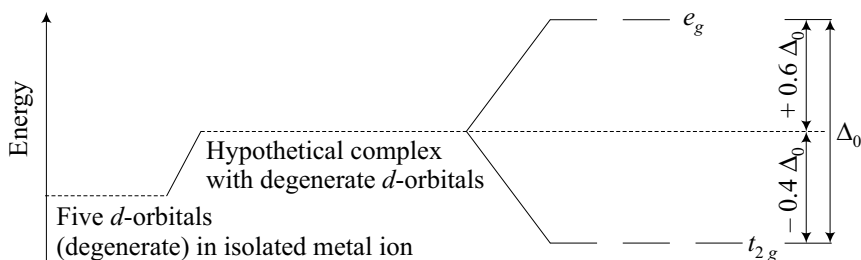
Q.12 Calculate CFSE in kJ mol^{-1} for an $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ octahedral complex for which $d-d$ transition is the single broad absorption peak with a maximum at 20300 cm^{-1} . Draw the splitting diagram also. ($1 \text{ kJ mol}^{-1} = 83.7 \text{ cm}^{-1}$).

Ans. The crystal field splitting energy in kJ mol^{-1}

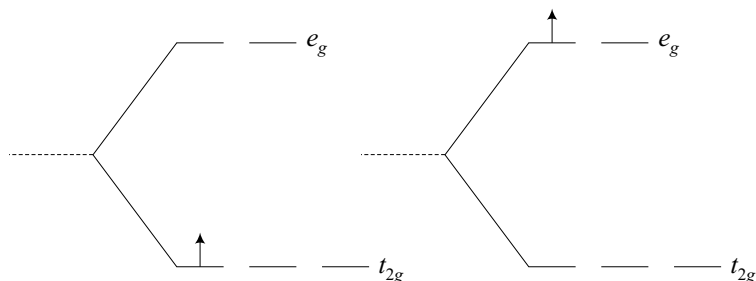
$$\Delta_0 = \frac{20300}{83.7} \text{ kJ mol}^{-1}$$

i.e., $\Delta = 243 \text{ kJ mol}^{-1}$

and is represented in the diagrams below.



In $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, Ti is in (III) oxidation state d^1 system. The $d-d$ transition is represented below:



$$\text{CFSE (octahedral)} = (-0.4nt_{2g} + 0.6 me_g)\Delta_0$$

In d^1 system, $\text{CFSE (octahedral)} = -0.4 \Delta_0$ the one electron occupies lower energy t_{2g} orbitals. nt_{2g} = no. of electrons occupying t_{2g} orbitals
 me_g = no. of electrons occupying e_g orbitals.

Hence, $\text{CFSE} = -0.4 \Delta_0 = 0.4 \times 233 \cong -97 \text{ kJ mol}^{-1}$

- Q.13** Assuming that light of only one specific wavelength is absorbed by a coordination compound, utilize the following relationship of the visible spectrum to determine.

Colour	violet	blue	green	yellow	orange	red
λ cm ⁻¹	4.0×10^{-5}	4.5×10^{-5}	5.0×10^{-5}	5.5×10^{-5}	6.0×10^{-5}	7.0×10^{-5}
Absorbed						
Colour seen	yellow	orange	red	violet	blue	green

- (i) The colour of the complex as observed upon its absorption of 42.9 kcal per mole of light radiation energy.
- (ii) The colour of the visible light radiation absorbed by the complex if it is found that the frequency of radiation corresponding to the observed colour of the complex is 5.30×10^{14} sec⁻¹.
- (iii) [TiX₆]³⁻ complex is violet, what change in colour would you expect if the ligand X, in this complex was replaced by a ligand, y, that produces a stronger field?

Ans. (i) $E = Nh\nu$ $N = \text{Avogadro's number} = 6.02 \times 10^{23}$

$$E = Nh \frac{C}{\lambda} \quad h = \text{Planck's constant} = 6.6 \times 10^{-27} \text{ erg sec}^{-1}$$

$$C = \text{velocity of light cm sec}^{-1}$$

$$1 \text{ calorie} = 4.18 \times 10^7 \text{ erg.}$$

The energy absorbed per mole is 42.9 k cal.

$$\text{or } 42.9 \times 4.18 \times 10^{10} \text{ ergs}$$

Putting the value of E , N , h and C , we get

$$\frac{1}{\lambda} = \frac{E}{NhC} = \frac{42.9 \times 4.18 \times 10^{10}}{6.023 \times 10^{26} \times 6.6 \times 10^{-27} \text{ erg sec.} \times 3.8 \times 10^{10} \text{ cm sec}^{-1}}$$

$$\lambda = \frac{6.023 \times 10^{23} \times 6.6 \times 10^{-27} \times 3.0 \times 10^{10}}{42.9 \times 4.18 \times 10^{10}}$$

$$= 6.65 \times 10^{-5} \text{ cm}$$

The colour absorbed is red and the complex will be green in colour.

(ii) $\nu = 5.30 \times 10^{14}$ sec⁻¹

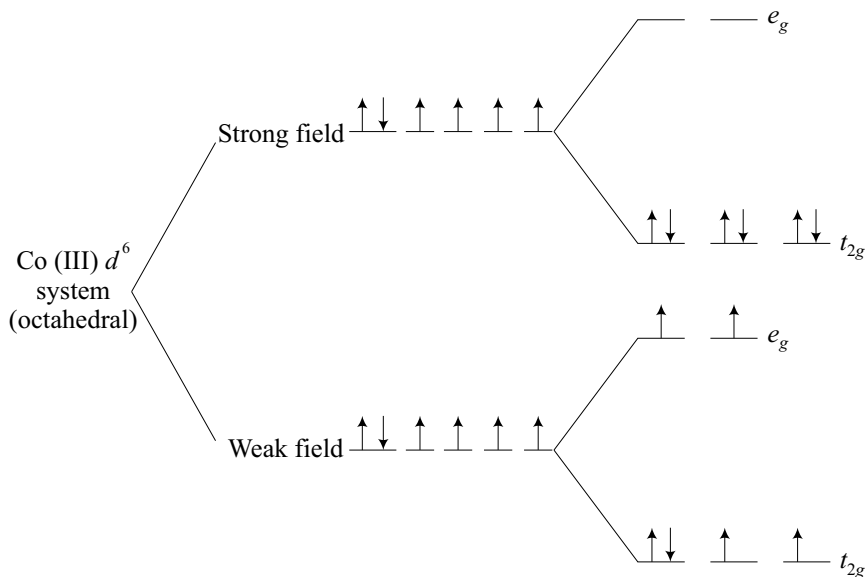
$$\therefore \lambda = \frac{c}{\nu} = \frac{3.0 \times 10^{10} \text{ cm sec}^{-1}}{5.30 \times 10^{14} \text{ sec}^{-1}}$$

$$= 5.66 \times 10^{-5} \text{ cm.}$$

The colour absorbed is violet so the complex will appear yellow.

Q.15 Co(III) is stabilized in the presence of strong field ligands while Co(II) is stabilized in the presence of weak field ligands. Explain with the help of crystal field theory.

Ans. Co(III) is a d^6 system while Co(II) is a d^7 system.



In strong field, d^6

$$\begin{aligned} \text{CFSE (octahedral)} &= (0.4 \times n_{t_{2g}} + 0.6 \times m_{e_g})\Delta_0 \\ &= 0.4 \times 6 \Delta_0 = 2.4\Delta_0 \end{aligned}$$

In weak field, d^6

$$\begin{aligned} \text{CFSE (octahedral)} &= (0.4 \times n_{t_{2g}} + 0.6 \times m_{e_g})\Delta_0 \\ &= (0.4 \times 4 + 0.6 \times 2)\Delta_0 \\ &= -1.6\Delta_0 + 1.2\Delta_0 \\ &= -0.4\Delta_0 \end{aligned}$$

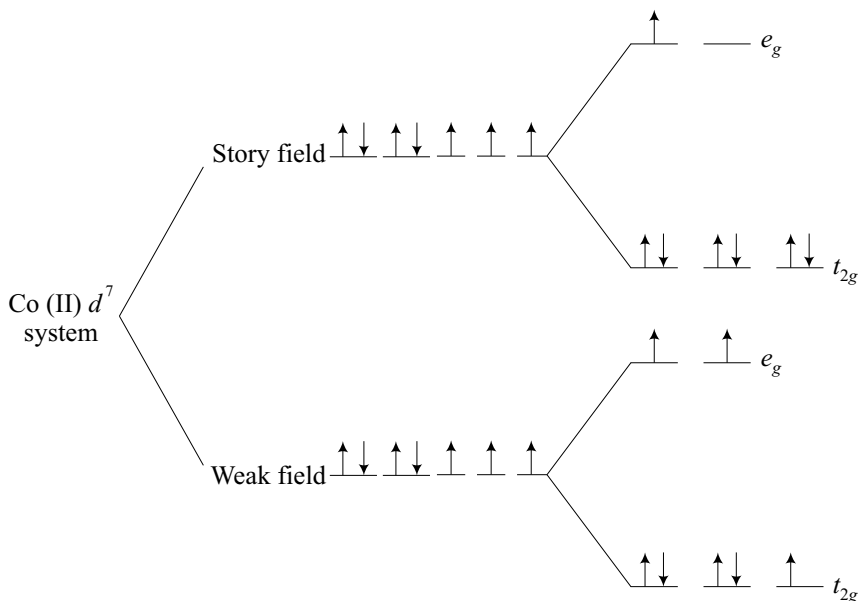
In strong field, Co(II), $3d^7$

$$\begin{aligned} \text{CFSE (octahedral)} &= (-0.4 \times n_{t_{2g}} + 0.6 \times m_{e_g})\Delta_0 \\ &= (-0.4 \times 6 + 0.6)\Delta_0 \\ &= -1.8\Delta_0 \end{aligned}$$

In weak field d^7 ,

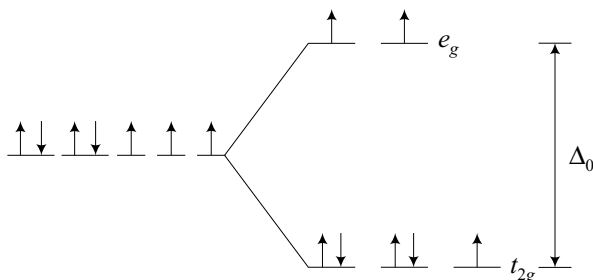
$$\begin{aligned} \text{CFSE (octahedral)} &= (-0.4n_{t_{2g}} + 0.6 m_{e_g})\Delta_0 \\ &= (-0.4 \times 5 + 0.6 \times 2)\Delta_0 \\ &= -0.8\Delta_0. \end{aligned}$$

If we compare the crystal field stabilization energy in weak field Co(III) complexes, the energy released in Co(III) is only $0.4 \Delta_0$ while in case of Co(II), it is more, i.e., $0.8 \Delta_0$ while the release in case of strong field ligands, Co(III) CFSE = $-2.4 \Delta_0$ while that of Co(II) is $-1.8 \Delta_0$.

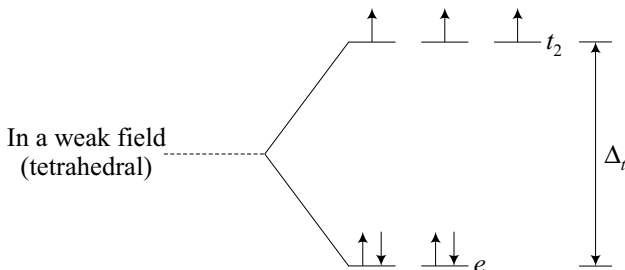
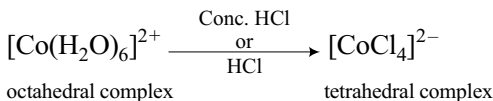


Q.16 If conc HCl or excess of KCl is added to an aqueous of cobaltous chloride, there is colour change from light pink to dark blue. The pink colour is restored by diluting with water. Explain in terms of CFT and also write the structure of the complex species in solution under above condition.

Ans. Cobaltous chloride solution contains aqua complex of Co(II). It is $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ light pink in colour.
Octahedral complex.



when KCl or conc. HCl is added



Δ_0 is more than Δt .

As we know that crystal field splitting energy in case of an octahedral field is more than that of tetrahedral field and H_2O is a stronger ligand than Cl ion. $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ absorbs higher energy radiation, i.e., blue and will appear as pink while $[\text{CoCl}_4]^{2-}$ absorbs lower energy radiation, absorbs red and appear as blue.

Q.17 Explain why Δ_0 increases in the order $[\text{CrCl}_6]^{3-}$, $[\text{Cr}(\text{NH}_3)_6]^{3+}$ and $[\text{Cr}(\text{CN})_6]^{3-}$.

Ans. Despite the $-ve$ charge on Cl^- , Δ_0 in $[\text{CrCl}_6]^{3-}$ is less than for NH_3 in $[\text{Cr}(\text{NH}_3)_6]^{3+}$ because of the repulsion between the non-bonding electrons of it and $d\pi$ electrons of $\text{Cr}(\text{III})$. In $[\text{Cr}(\text{CN})_6]^{3-}$ the value of Δ_0 for CN is very high because of back bonding $p\pi - d\pi$ type. This back bonding results in shifting of electron density from the $d\pi$ orbitals of $\text{Cr}(\text{III})$ to $p\pi$ orbitals of CN^- . This interaction leads to increase in Δ_0 in case of $[\text{Cr}(\text{CN})_6]^{3-}$.

Q.18 In a square planar complex, the CFSE of the d -orbitals of a central ion decreases in square $d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz} > d_{yz}$.

Give an explanation for the same.

Ans. In a square planar complex, it is assumed that the four ligands approach along $+X$, $-X$ and $+Y$ and $-Y$ direction.

Since the $d_{x^2-y^2}$ orbital will be repelled most strongly by the four ligands approaching from $+X$, $-X$, $+Y$ and $-Y$ direction, $d_{x^2-y^2}$ which lies on the X and Y axes will be having maximum energy.

The next most affected orbital will be d_{xy} which lies in between X and X -axes and will have less energy than $d_{x^2-y^2}$.

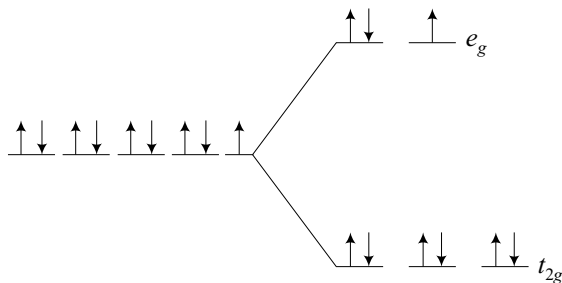
Then comes d_{z^2} , and then d_{xz} and d_{yz} will be affected least by the approaching ligands and hence the order is

$$d_{x^2-y^2} > d_{xy} > d_{z^2} > d_{xz}, d_{yz}$$

along $+Z$ and $-Z$ direction meet very strong repulsive forces from the filled d_{z^2} orbital. Thus, only four ligands succeed in bonding to the metal and a square planar complex is formed, resulting from an unsuccessful attempt to form an octahedral complex, e.g., $[\text{Ni}(\text{CN})_4]^{2-}$.

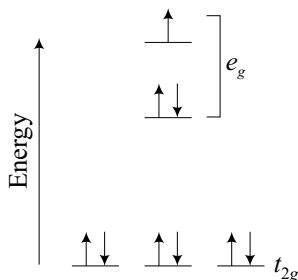
Q.20 The octahedral copper(II) complexes, even in the situation when all the six ligands attached are symmetrical and generally distorted. Explain why?

Ans. Cu(II) has a d^9 configuration is a octahedral complex.



whenever d_{z^2} and $d_{x^2-y^2}$ orbitals are unequally occupied distortion (known as Jahn-Teller distortion) occurs. The Jahn-Teller theorem states that any non-linear molecule system in a degenerate electronic state will be unstable and will undergo some sort of distortion to lower its symmetry and remove the degeneracy and to lower the energy. In an octahedral complex, distortion occurs mainly from unequal filling of the e_g orbitals, because these orbitals lie on the axes unlike t_{2g} orbitals which lie in between the axes.

The minimize repulsion with the ligands, two electrons occupy the d_{z^2} orbital and one electron occupy the $d_{x^2-y^2}$ orbital. Thus, the two ligand along $+z$ and $-z$ direction are repelled more strongly than the other four ligands given rise to a distorted octahedral structure.

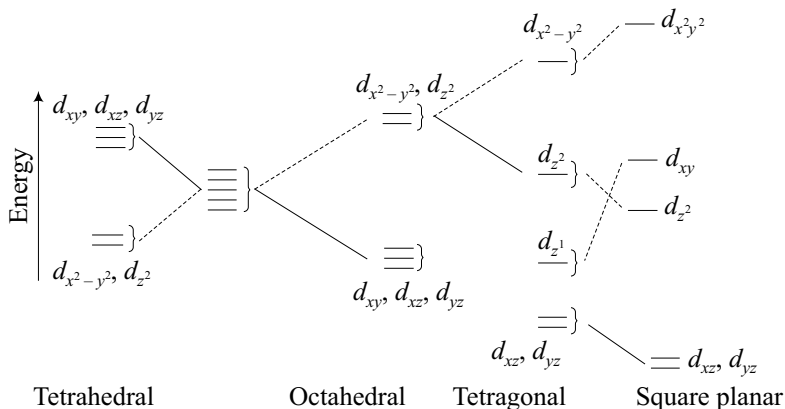


Q.21 Diagrammatically represent for the splitting of the orbitals for the following geometries:

- (i) Tetrahedral (ii) Octahedral
 (iii) Tetragonal (iv) Square planar

Ans. Splitting of the d -orbitals for various geometries no. (i) \rightarrow (iv) is shown below.

Tetrahedral, spherical octahedral, tetrahedral, square planar splitting of the d -orbitals for the various geometries.



Q.22 How many unpaired electrons are there in Cr^{2+} , Cr^{3+} , Fe^{2+} , Co^{3+} and Co^{2+} in

- (i) a strong octahedral field and
 (ii) a weak octahedral field?

Ans. Unpaired electron in the ions in (i) strong and (ii) weak octahedral field are given in the following table.

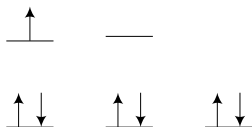
Ion	No. of electrons in d -orbitals	Electronic configuration		No. of unpaired electrons	
		Strong field	Weak field	Strong field	Weak field
Cr^{3+}	3	$t_{2g}^3 e_g^0$	$t_{2g}^3 e_g^0$	3	3
Cr^{2+}	4	$t_{2g}^4 e_g^0$	$t_{2g}^3 e_g^1$	2	4
Mn^{2+}	5	$t_{2g}^5 e_g^0$	$t_{2g}^3 e_g^2$	1	5
Fe^{2+}	6	$t_{2g}^6 e_g^0$	$t_{2g}^4 e_g^2$	0	4
Co^{3+}	6	$t_{2g}^6 e_g^0$	$t_{2g}^4 e_g^2$	0	4
Co^{2+}	7	$t_{2g}^6 e_g^1$	$t_{2g}^5 e_g^2$	1	3

- Q.23**
- (i) Which are Cu^+ or Cu^{2+} , is colourless and why?
 - (ii) Which one, Ti^{3+} or Ti^{2+} is coloured and why?
 - (iii) Which one, Co^{2+} or Co^{3+} , has lower magnetic moment.
 - (iv) Which one Fe or Zn is higher melting and why?
 - (v) Which one Fe Sc or Mn, exhibits more variations in oxidation states and why?
 - (vi) Which one, Cu^{+2} or Zn^{+2} is diamagnetic and why?
 - (vii) Which one, Ti^{4+} or V^{4+} is paramagnetic and why?
 - (viii) Which one, Fe^{2+} or Fe^{5+} has higher magnetic moment and why?

- Ans.**
- (i) Cu^+ with electronic configuration $3d^{10}$ is colourless because no unpaired electron is present whereas Cu^{2+} ($3d^9$) is coloured because it contains one unpaired electron.
 - (ii) Ti^{3+} with electronic configuration $3d^1$ is coloured because of the presence of one Unpaired electron in its $3d$ -orbitals. On the other hand, Ti^{4+} is colourless, because it has no unpaired electron.
 - (iii) The outer electronic configuration of Co^{2+} and Co^{3+} are $3d^7$ and $3d^6$, respectively. Obviously, Co^{2+} with d^7 configuration has 3 unpaired electron while Co^{3+} and d^6 configuration has 4 unpaired electron. Because the magnetic moment is related to the number of unpaired electrons, Co^{2+} has lower magnetic moment.
 - (iv) Fe is higher melting than the Zn because number of unpaired electrons available for metallic bonding is more in the former case.
 - (v) Mn exhibits more variations in oxidation states because 1-7 electrons can be involved in bonding as is apparent from its configuration $3d^5 4s^2$. Thus, we have Mn(II) in MnSO_4 , Mn(III) in $\text{Mn}(\text{CH}_3\text{COO})_3$, Mn (IV) in MnO_2 , Mn (VI) in K_2MnO_4 and Mn (VII) in KMnO_4 . On the other hand, Sc with the outer electronic configuration $3d^1 4s^2$ can exhibit + I and + III oxidation states.
 - (vi) Zn^{2+} is diamagnetic because it has the configuration $3d^{10}$ (no unpaired electron). Magnetic moment is related to number of unpaired electron Cu^{2+} shown paramagnetism corresponding to the presence of one unpaired electron in the configuration $3d^9$.
 - (vii) V^{4+} is paramagnetic because it has one electron in d shell ($3d^1$). On the other hand, in the Ti^{4+} configuration is $3d^0$, therefore, it has no unpaired electron ($3d^0$). Hence, it is diamagnetic.
 - (viii) The outer electronic configuration of Fe^{2+} and Fe^{3+} are $3d^6$ and $3d^5$ respectively. Obviously, Fe^{3+} with d^5 configuration has 5 unpaired electrons while Fe^{2+} with d^6 configuration has 4 unpaired electrons. Because the magnetic moments is related to the number of unpaired electrons, so Fe^{3+} has higher magnetic moments.

- Q.27** (a) Using crystal field theory depict the electronic configuration of the rhodium (11) ion (Rh^{2+}) in an octahedral field for which the crystal field splitting Δ is greater than the pairing energy P .
- (b) Calculate the crystal field stabilization energy for the configuration (in terms of Δ and P).

Ans. (a) $\text{Rh(II)}, t_{2g}^6 e_g^1$



- (b) $\text{CFSE} = -1.8\Delta + P$ (even in a spherical field, the complex must have two pairs of electrons, one additional pair is formed in the octahedral field).

- Q.28** Which of the following d^n ion will have the smallest crystal stabilization energy if Δ is greater than P the pairing energy $d^6, d^7, d^8, d^9, d^{10}$.

Ans. d^{10} (It has $\Delta = 0$ CFSE no matter whichever the value of P)

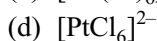
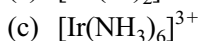
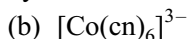
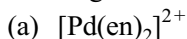
- Q.29** A coordination compound in an octahedral field has five electrons in d -orbital. If the mean pairing energy P is 20500 cm^{-1} and Δ is 15500 cm^{-1} . This complex will of high spin or low spin?

Ans. Since $P > \Delta$, the complex will be of high spin.

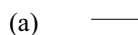
- Q.30** What factors determine whether the crystal field in an octahedral complex is strong or weak? How many d -electrons must be present in orbitals of the central atom for there to be an abrupt change in crystal field stabilization energy between strong or weak fields.

Ans. Strong field or weak field depends on the relative magnitude of Δ and P . Abrupt change in crystal field stabilization energies occurs with d^4, d^5, d^6 and d^7 configuration.

- Q.31** Explain the electronic configuration of the central atom of each of the following from the viewpoint of crystal field theory diagrammatically.



Ans.



Ans. The orbital with the highest energy is $d_{x^2-y^2}$ and the lowest energy are the degenerate pairs, d_{xz} and d_{yz} .

Q.37 Construct a table of crystal field stabilization energies for square planar complexes. Assume that only the energy difference between the $d_{x^2-y^2}$ and d_{z^2} orbital is sufficiently large to cause pairing in some cases.

Ans.

No. of <i>d</i> electrons	CFSE (Strong field)
1	-0.514Δ
2	-1.028Δ
3	-1.456Δ
4	-1.228Δ
5	$-1.742\Delta + P$
6	$-2.256\Delta + P$
7	$-2.684\Delta + P$
8	$-2.456\Delta + P$
9	-1.228Δ
10	-0Δ

Note that the only splitting large enough to be classified in Δ difference and next to highest energy orbital.

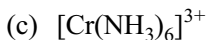
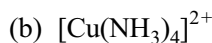
Q.38 Explain why crystal field theory is not applied to complexes of main group metals.

Ans. The main group metals have no incomplete *d*-subshells and for empty or completely filled *d* subshells CFSE = 0.

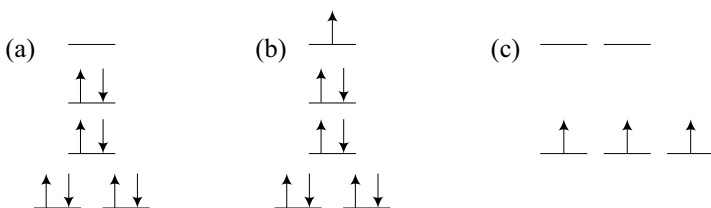
Q.39 Explain why d^8 complexes are more likely than other complexes to have a square planar geometry.

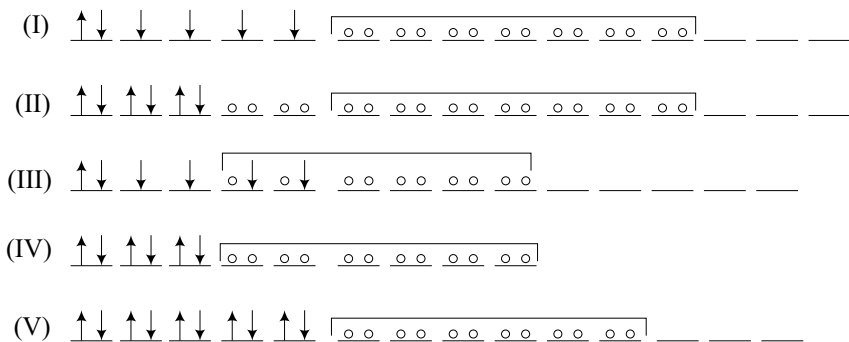
Ans. CFSE is much greater for square planar complexes than for octahedral complexes only in the d^8 and d^9 cases.

Q.40 Write down the electronic configuration of the central metal of each of the following ions from the viewpoints of the crystal field theory.



Ans.





A has all six metal electrons paired so it matches structure *IV*. *B* has four electrons unpaired of the six *d*-electrons present as shown in *I*.

Q.44 The enthalpy of hydration of the Fe^{2+} ion is $11.4 \text{ kcal mol}^{-1}$ higher than would be expected if there were no crystal field stabilization energy. Assuming the aqua complex to be high spin, estimate the magnitude of Δ for $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$.

Ans. CFSE for the d^6 weak field ion is -0.40Δ the ΔH is higher because the energy of the complex is lowered by that much -11.4 kcal/mol .

$$\text{CFSE} = -11.4 \text{ kcal mol}^{-1} = -0.40\Delta$$

$$\Delta = 28.5 \text{ kcal mol}^{-1}$$

UNSOLVED PROBLEMS

Q.1 Both Mn^{2+} and Fe^{3+} have d^5 configuration whereas most of octahedral complexes of Mn^{2+} are high-spin the large number of octahedral complexes of Fe^{3+} are of low-spin. Explain.

Q.2 The enthalpy of hydration of Cr^{2+} is $-460 \text{ kcal mol}^{-1}$. In the presence of crystal field stabilization energy (CSFE), the value for ΔH would be $-435 \text{ kcal mol}^{-1}$. Estimate the value of Δ_0 for $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$.

Q.3 DMSO reacts with $\text{Co}(\text{ClO}_4)_2$ in absolute ethanol to form pink colored product that has a magnetic moment of 4.9 B.M. However, when DMSO reacts with CoCl_2 a dark blue coloured product is formed which shows magnetic moment of 4.6 B.M:

- Identify the geometry of pink and coloured compound
- Rationalize the colour of these complexes in view of your structural choice.

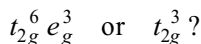
Q.4 $4d$ and $5d$ elements usually form low-spin complex why?

Q.5 Calculate the CFSE of a d^6 octahedral ion (high spin and low spin) having $\Delta_0 = 25000 \text{ cm}^{-1}$ and $P = 15000 \text{ cm}^{-1}$.

- (b) The crystal field splitting in tetrahedral complexes is about one half of that in octahedral complexes.

$$\left(\Delta t = \frac{4}{9} \Delta_0 \right)$$

- Q.18** (a) On the basis of crystal field theory explain the variation in the ionic radii of divalent metals of the first transition series.
 (b) State Jahn-Teller theorem which configuration will show Jahn-Teller distortion:



- Q.19** Taking the example of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex explain the drawback of crystal field theory.

- Q.20** (a) How can you explain a high spin Cr^{2+} complex in terms of Jahn-Teller effect?
 (b) The crystal field stabilization energy for an octahedral complex is 18000 cm^{-1} . Calculate the CFSE in tetrahedral arrangement.
 (c) In the crystal field splitting of d -orbital energies the $d_{x^2-y^2}$ orbitals of the central ion have the highest energy in a square complex. Explain.

- Q.21** (a) "The complex $\text{Ni}(\text{CN})_4^{2-}$ is diamagnetic" but NiCl_4^{2-} is paramagnetic with two unpaired electron. Likewise, $\text{Fe}(\text{CN})_6^{3-}$ has only one unpaired electron whereas $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ has five unpaired electron. Explain on the basis of both—valance bond theory and crystal field theory.
 (b) Complex of Co(III) like $\text{Co}(\text{NH}_3)_6^{3+}$, $\text{Co}(\text{en})_3^{3+}$ and $\text{Co}(\text{NO}_2)_6^{3-}$ are diamagnetic and orange, yellow in colour. Explain these properties. Explain why?

- Q.22** Explain in the following:

- (a) Low-spin tetrahedral complexes are not known.
 (b) Fe^{3+} usually form octahedral complexes that are low spin.
 (c) Ni^{2+} gives a low-spin square planar complex with CN^- only whereas Pt^{2+} , Pd^{2+} or Au^{3+} form low-spin complexes with NH_3 and even Cl^- .

- Q.23** Calculate in kJ/mole^{-1} the crystal field stabilization energy (CSFE) attained by Fe^{2+} in an octahedral oxide environment. Given Δ_0 for Fe^{2+} in an oxide environment is 124 kJ/mole . What will be the CFSE in a tetrahedral environment of oxide ion?

- Q.24** (a) on the basis of crystal field theory explain the following:

- I. CuSO_4 (anhydrous) is colours.
- II. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue
- III. $\text{Cu}(\text{NH}_3)_4^{2+}$ is violet
- IV. $\text{Cu}(\text{CN})_4^{2-}$ is colourless.

- Q.36** Which complex in each of the following pairs will have higher Δ_0 value? Explain.
 (I) $[\text{PtCl}_4]^{2-}$ and $[\text{PdCl}_4]^{2-}$
 (II) $[\text{CoF}_6]^{2-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$
- Q.37** Which of the following pairs of complexes will have higher Δ_0 . Explain.
 (I) $[\text{Cr}(\text{en})_3]^{2+}$ and $[\text{Cr}(\text{CN})_6]^{3-}$
 (II) $[\text{PtCl}_6]^{2-}$ and $[\text{PdCl}_4]^{2-}$
- Q.38** Crystal field stabilization energy for an octahedral complex is 18000 cm^{-1} calculate the CFSE in tetrahedral arrangement.
- Q.39** In the crystal field splitting of orbital energies the $dx^2 - y^2$ orbitals of the central ion have the highest energy in a square planer complex. Explain.
- Q.40** Represent the electronic configuration of the central metal ion (in terms of $t_{2g} \cdot e_g$ notation) in each of the following complex ions on the basis of CFT.
 $[\text{Pt}(\text{NH}_3)_4]^{2+}$, $[\text{CoCl}_4]^{2-}$, $[\text{CoF}_6]^{3-}$ and $[\text{Ni}(\text{CO})_4]$
- Q.41** Calculate CFSE of a d^6 octahedral ion (high spin and low spin having $\Delta = 25000 \text{ cm}^{-1}$ and $P = 15000 \text{ cm}^{-1}$).
- Q.42** Which complex ion would show the greatest crystal field splitting?
 (i) $\text{Co}(\text{H}_2\text{O})_6^{2+}$
 (ii) $\text{Co}(\text{H}_2\text{O})_6^{3+}$
- Q.43** Which complex ion would show greater crystal field splitting and why?
 (I) $[\text{Fe}(\text{CN})_6]^{3-}$ or $[\text{Ru}(\text{CN})_6]^{3-}$
 (II) $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ or $[\text{Fe}(\text{CN})_6]^{3-}$
 (III) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ or $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$
 (IV) $[\text{Rh}(\text{NH}_3)_6]^{3+}$ or $[\text{Ir}(\text{NH}_3)_6]^{3+}$.
- Q.44** (a) Represent the electronic configuration of the following complexes by using CFT (crystal field theory)?
 (i) $[\text{Ni}(\text{NH}_3)_6]^{2+}$ paramagnetic (ii) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 (iii) $[\text{Cr}(\text{CN})_6]^{3-}$ (iv) $[\text{NiCl}_4]^{2-}$ tetrahedral.
 (b) Which would you expect to be disturbed in case of the above-mentioned complexes? Comment.
 (c) Calculate the relative energies as a function of ΔP for high-spin and low-spin octahedral of $\text{Fe}(\text{II})$ and $\text{Co}(\text{II})$.
- Q.45** How does the crystal theory explain the structure of spinals.
- Q.46** $\text{K}_2[\text{NiF}_6]$ is diamagnetic while $\text{K}_3[\text{CoF}_6]$ is paramagnetic. Both have same d^6 configurations. Explain on the basis of CFT.