Electronic Spectra And Colour of Transition Metal Complexes

Colouration is an important property of transition metal complexes. When white light is allowed to fall on a complex, then the following cases may arise —

i) The complex may absorb whole of the white light, then the complex appears as black.

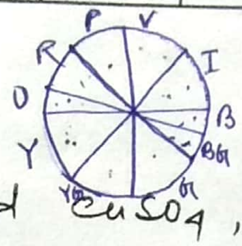
ii) Whole of the white light may be reflected or transmitted by the complex. Then the complex is white or colourless.

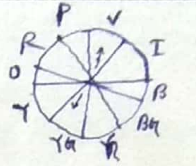
iii) The complex may absorb some part of the incident white light and may refect or transmit some part of the incident light. In this case the complex appears as coloured. The colour of the transmitted light is the colour of the complex. The coloured complexes absorb the light in the visible region (4000 Å – 7000 Å) of the spectrum. The colour of the absorbed light is different from the colour of transmitted light. The colour of the transmitted light is known as the complementary colour of the colour of absorbed light. The absorbed colours and corresponding transmitted colours are as follows —

4000 A° Energy Decreases ⟶ 7000 A°

Absorbed colour	Violet	Blue	Green-Blue	Blue-Green	Green	Yellow-Green	Yellow	Orange	Red
Complementary colour	↓ Yellow-Green	Yellow	Orange	Red	Purple	Violet	Blue	Green	Blue-Green

For examples,





i> Hydrated $CuSO_4$, $[Cu(H_2O)_4]^{2+}$ is blue in colour. It absorbs yellow light.
indigo

ii> Tetraamine copper sulphate containing $[Cu(NH_3)_4]^{2+}$ is violet in colour, because it absorbs yellow-green light.

iii> $[Cr(H_2O)_6]^{3+}$ is green coloured
↳ absorbs purple light.

iv> $[Ti(H_2O)_6]^{3+}$ is purple coloured
↳ absorbs green light.

If the complex absorbs light in the IR or UV region, then it appears as colourless.

(UV ⇒ λ is less than 4000 A°)
(IR ⇒ λ is greater than 7000 A°)

e.g. i> Anhydrous $CuSO_4$ is colourless because it absorbs light in IR region.

ii) $[Cu(CN)_4]^{2-}$ is colourless because it absorbs light from UV region.

The colour of the complex arises due to electronic transition between different energy levels present in the metal centre of the complex compounds. On the basis of mode of this transition, it is classified into two types —

a) d-d transition
b) Charge transfer.

a) **d-d transition** ⇒ The degeneracy of the metal d orbitals is lost in the complex. These are splitted into different energy levels. When this metal complex is exposed to the monochromatic light, then it absorbs light energy from visible region ($\lambda = 4000Å - 7000Å$) and its complementary colour is shown as the colour of the complex. (The transition energy depends on the spacing of the different energy levels and this spacing depends on the geometry of the complex, nature of the ligand and oxidation state of the central metal ion.) The colour of the complex can be designed by colour disc,, known as 'artist's wheel'.

As the transition occurs between d orbitals of different energy so it is called as d-d transition.

The electronic transition obey certain Selection rules. These are as follows—

1. Spin Selection Rule: According to this rule the transition is allowed if there is no change in spin state, i.e, $\Delta S = 0$. But the transition which results in a change in total no. of unpaired electrons are spin forbidden ($\Delta S \neq 0$). Thus transition from singlet to singlet and triplet to triplet are allowed. But the transition from singlet to triplet or vice versa is spin forbidden.

$$s^2 \longrightarrow s^1p^1 \left(+\tfrac{1}{2}, -\tfrac{1}{2}\right) \Rightarrow \text{Singlet}$$

Singlet ↙ $\pm 1/2$

$S = 0$

$2S+1 = 1$

This transition is allowed.

$s^2 \longrightarrow s^1 p^1 \quad (+\frac{1}{2}, +\frac{1}{2}) \Rightarrow$ Triplet.

$\downarrow$
Singlet $\qquad S = +\frac{1}{2} + \frac{1}{2} = 1 \quad 2S+1 = 3$

This transition is spin forbidden.

$t_{2g}^3 e_g^2 \longrightarrow t_{2g}^2 e_g^3$ (spin forbidden, $\Delta S \neq 0$)

$t_{2g}^3 e_g^1 \longrightarrow t_{2g}^2 e_g^2$ (spin allowed, $\Delta S = 0$)

The allowed transitions have high molar absorption co-efficient (ϵ), i.e, shows deep colour. The forbidden transitions are very weak and hence the colour of the complex is colourless or light coloured.

2. Laporte or Orbital Selection Rule: This rule states that the electronic transition occurs between the two energy levels which have different symmetry properties with respect to inversion. i.e, gerade (g) to ungerade (u) or vice versa transitions are allowed. But $g \rightarrow g$ or $u \rightarrow u$ transitions are Laporte forbidden. According to orbital selection rule, those transitions are allowed where $\Delta l = \pm 1$. i.e, $p \rightarrow d$, $d \rightarrow p$, $s \rightarrow p$, $p \rightarrow s$ etc. are allowed, Whereas $s \rightarrow s$, $p \rightarrow p$ or $d \rightarrow d$ or, $d \rightarrow s$, $s \rightarrow d$ are forbidden transitions according to this selection rule.

So the selection rules indicate that in the centrosymmetric octahedral complex, all the electronic transitions are Laporte forbidden and some cases are spin-forbidden. So, the metal complexes should to be colourless. But there are so many metal complexes which are coloured. This intense colour indicates that there must be some relaxation of selection rule.

* Breakdown of Spin Selection Rule ⇒

Spin orbit coupling relax the particular spin character of the orbital electron and this is mainly observed when the metal ion having higher charge and small size. The spin state of different energy levels are in this case are much closer and they further interact to mixed and then the transition mainly shift from forbidden to allowed, i.e, colour intensity of the complex increases. But this effect is very weak and it is mainly observed in case of 2nd and 3rd transition series metal complexes and for lanthanides.

Breakdown of Laporte Selection Rule ⇒

In the complex compounds metal ion vibrate in its position and vibrational modes may be symmetrical or unsymmetrical. As a result, there occurs a mixing in the vibrational and electronic parts of d and p orbitals. This mechanism is Known as vibronic coupling. So the electron lost its 'd' character and transition may be allowed.

In the unsymmetrical octahedral complexes due to vibronic coupling d-p mixing occurs in a large extent and the possibility of allowed transition becomes higher in compare to symmetric octahedral complexes.

Tetrahedral complexes have no centre of symmetry. As a result, vibronic coupling occurs in a large extent, i.e, metal electron ultimately looses its pure 'd' character. So the Laporte selection rule breaks down and the electronic transition mainly becomes allowed. Due to this reason tetrahedral complexes show intense colour.

According to MO theory, during complex formation metal and ligand orbitals mix together and metal e⁻ gets some character of ligand orbitals and then the transition may be allowed. The complex shows intense colour.

Complex	Splitting	Class of transition	Molar extinction co-efficient (ε) / Colour
$[Mn(H_2O)_6]^{2+}$ (d^5)	$t_{2g}^3\ e_g^2$	Spin forbidden Laporte forbidden.	0·1 (faint pink).
$[Fe(H_2O)_6]^{3+}$	$t_{2g}^3\ e_g^2$	Spin and Laporte forbidden	0·1 (faint yellow)
$[Co(H_2O)_6]^{2+}$	$t_{2g}^5\ e_g^2$	Spin allowed Laporte forbidden.	10 (pink)
$[Ti(H_2O)_6]^{3+}$	$t_{2g}^1\ e_g^0$	Spin allowed, Laporte forbidden.	10 (purple).
$[CoCl_4]^{2-}$	$e^4\ t_2^3$	Spin allowed, Laporte Breakdown	5×10^2 (Blue)
$[TiCl_6]^{2-}$	d^0 system	No d–d transition, charge transfer transition occurs here.	10^4

Russel- Saunders Term / State :

The electronic spectra of the complexes can be successfully explain by Russel- Saunders term or state. Russel- Saunders state arises due to the combination of resultant spin angular momentum (S) and resultant orbital angular momentum (L). This combination is Known as Russel- Saunders coupling or L-S coupling. In the multi-electronic system different states arise due to the interelectronic repulsion and spin-orbit coupling. The electronic transition between these states is responsible for the colouration of the metal complexes. The steps of formation of Russel- Saunders state are as follows—

i> Individual spin angular momentum of the electrons (s_i) combine to give a resultant spin angular momentum S. i.e, $S = \Sigma s_i$

$$\therefore S = (s_1 + s_2), (s_1 + s_2 - 1), \ldots\ldots\ldots, (s_1 - s_2).$$

ii> Individual orbital angular momentum of the electrons (l_i) combine to give a resultant orbital angular momentum (L). i.e, $L = \Sigma l_i$

$$\therefore L = (l_1 + l_2), (l_1 + l_2 - 1), \ldots\ldots, (l_1 - l_2).$$

iii> L and S couple together to give a total resultant angular momentum J. J is also quantised and may have the values

$(L+S), (L+S-1), (L+S-2), \ldots\ldots, (L-S)$.

These actually represent the different energy levels. Russel-Saunders state can be represented by the term symbol which can expressed as

$$^{2S+1}L_J \quad (2S+1 = \text{Spin multiplicity.})$$

The values of L is expressed by the letters S, P, D, F, G etc. as follows —

L =	0	1	2	3	4	5	6 ......
Symbol	S	P	D	F	G	H	I ......

* Ground Term & splitting Pattern ⇒

The number of microstates can be calculated as follows —

$$\text{No. of microstates} = \frac{\overset{\text{2× no. of Orbitals}}{n!}}{\underset{\text{no. of electrons present in the metal ion system.}}{r!(n-r)!}}$$

Where, $n = 2 \times$ number of orbitals.

r = number of electrons present in the metal ion system.

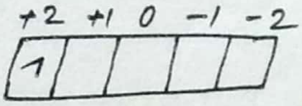
So for d^1 system the number of microstates is $= \frac{\lfloor 10}{\lfloor 1 \ \lfloor 9} = \frac{10 \times 9!}{9!} = 10.$

$\frac{n!}{r!(n-r)!}$

Among these 10 microstates the ground

level, i.e, ground term can be desired by considering Hund's rule and resultant orbital angular momentum quantum no. The ground state must have the highest spin multiplicity (2S+1) value. If two states have the same spin multiplicity then the higher L value indicates the ground term. Thus,

$d^1 \Rightarrow$



$$L = 2, \quad S = \frac{1}{2} \quad \therefore 2S+1 = 2$$

L = 2 so the symbol is D.

So, the ground state term may be

$$^2D_{2+\frac{1}{2}} \quad \text{or} \quad ^2D_{2-\frac{1}{2}}$$

$$\text{i.e,} \quad ^2D_{5/2} \quad \text{or} \quad ^2D_{3/2}.$$

Similar free ion terms can also arise in case of d^9 system. According to hole formalism in weak field, more than half filled sub-shell contains equal number of holes with the number of electrons present in the less than than half-filled configuration have the same ground term but only J value is different. More than half-filled configuration have the higher J value and the less than half-filled configuration has the lower J value in the ground term.

So, for d^1 system the ground term symbol is $^2D_{3/2}$ and the ground term symbol for d^9 is $^2D_{5/2}$.

$L-S$
$= 2-1/2$
$= 3/2$

$L+S = 2+1/2$
$= 5/2$

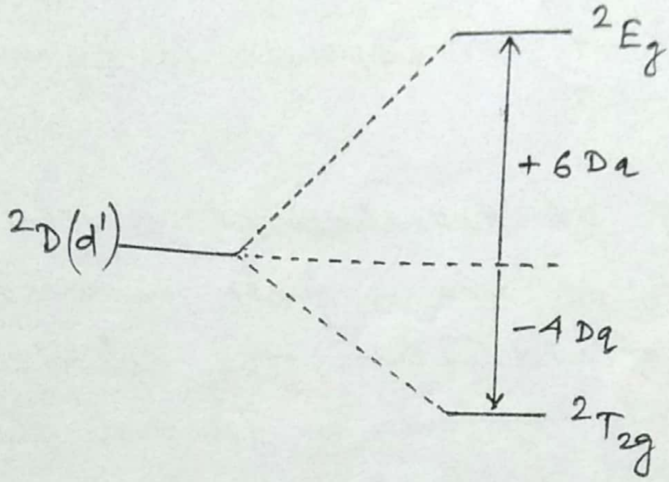
Similarly, in different d^n and d^{10-n} system have same ground term but only J values are different due to hole formalism.

The levels for split components of various electronic configurations in a particular field are derived from group theory and are used to express as much as possible about the degeneracy and the symmetry of this field. The degeneracy is expressed by A, B, E, T etc. A or B signifies to non-degenerate orbitals. E signifies to doubly degenerate orbitals and T signifies to triply degenerate orbitals. Thus, the terms arise for the splitting of a d^n system in octahedral field are as follows—

Terms of Free Ions	Terms arising in Crystal Field.
S	A_1
P	T_1
D	$T_2 + E$
F	$A_2 + T_1 + T_2$
G	$A_1 + E + T_1 + T_2$

(These are Known as Mulliken Symbols.)

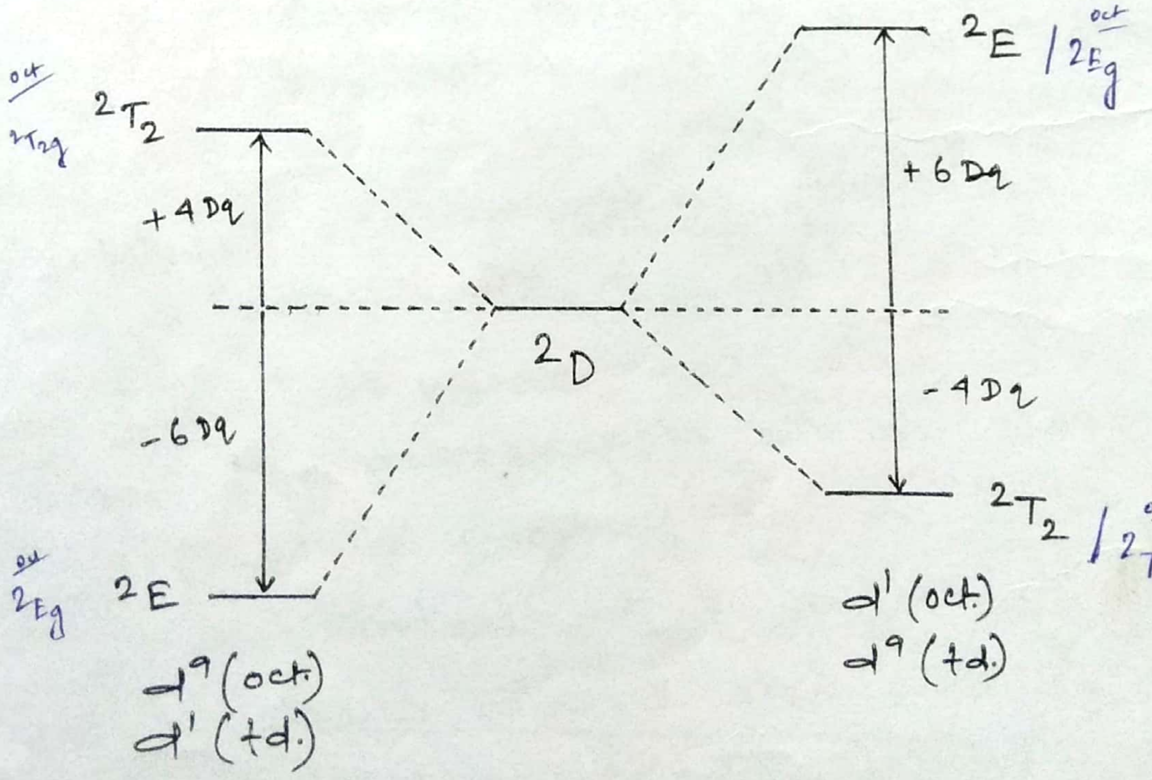
For a d^1 system, splitting of the free ion ^2D term in an octahedral field is as follows—



The splitting for a d^9 system is just inverse. This can be understood with the help hole formalism. For d^9 the ground state electronic configuration is $t_{2g}^6 e_g^3$, i.e, there is a 'hole' in the upper eg level. Since the hole can occupy the one of two eg levels, so the degeneracy is 2 which gives rise to an E-term in the ground state. Excitation of an electron from t_{2g} level to this hole creates another hole in t_{2g} orbitals. This new hole can be placed in any of the three t_{2g} orbitals. So the orbital degeneracy is 3. So the excited $t_{2g}^5 e_g^4$ configuration corresponds to a T-term. Thus d^9-system will have a splitting pattern which would be the inverse of d^1

system. When the electronic transition occurs in d^1 octahedral complex compound, $T_{2g} \rightarrow E_g$ transition represents to 10 Dq value. But in case of d^9 system (oct.) the ground level is E_g and 10 Dq corresponds to $E_g \rightarrow T_{2g}$ transition.

In case of tetrahedral crystal field, the splitting pattern is just reverse of the octahedral field. Thus, the splitting pattern of d^1 and d^9 system in td and octahedral field is given below—



For tetrahedral field, levels are $^2T_2$ and ^2E but for octahedral, these are $^2T_{2g}$ and ^2E_g (g = gerade, i.e, possesses centre of inversion.).

* d² and d⁸ system ⇒ According to hole formalism, d² and d⁸ have same term but different J values. For d² system,

+2	+1	0	-1	-2
↿	↿			

$L = 3\ (F)$, $S = \frac{1}{2} + \frac{1}{2} = 1$

$\therefore 2S+1 = 3$

$S = +1\ (+\frac{1}{2}, +\frac{1}{2})$

or, $S = 0\ (+\frac{1}{2}, -\frac{1}{2})$

or, $S = -1\ (-\frac{1}{2}, -\frac{1}{2})$

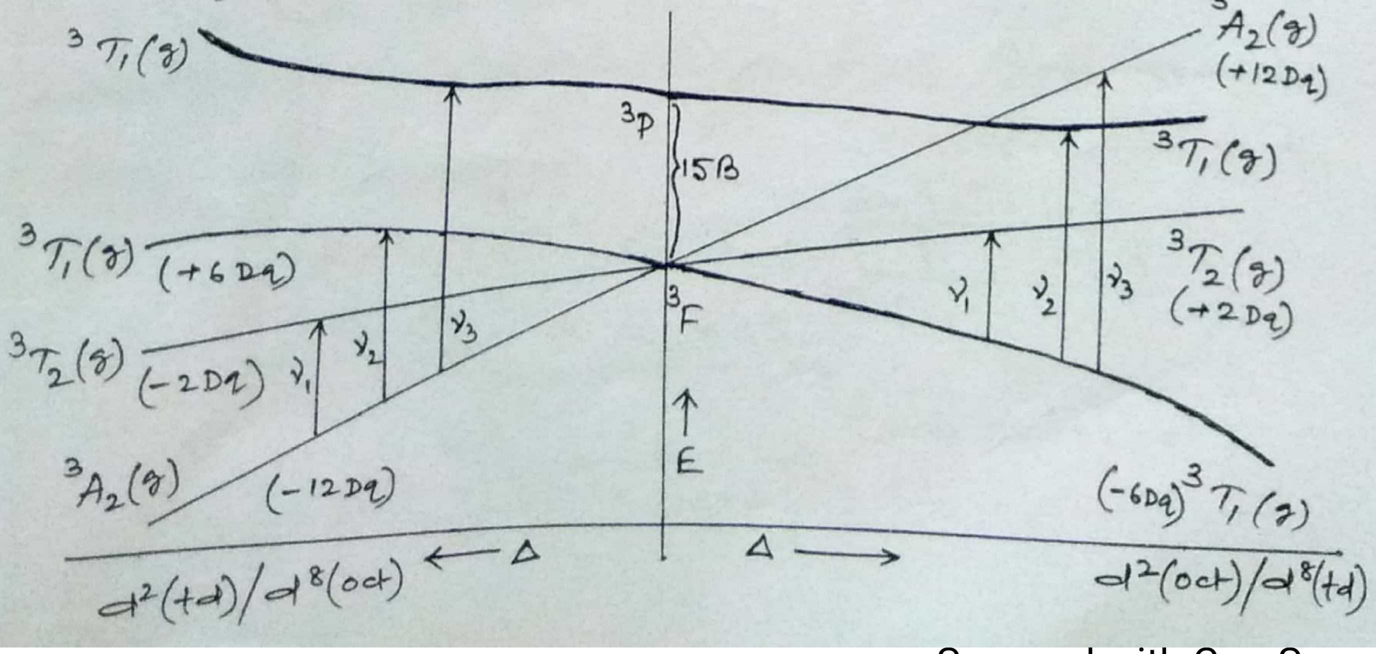
∴ The terms are

$^3F_{3-(-1)}$ $^3F_{3+1}$, $^3F_{3+0}$, $^3F_{3-1}$

or, $^3F_4$, $^3F_3$, $^3F_2$

∴ For d² system the groud term is $^3F_2$ and for d⁸ system the ground term is $^3F_4$.

In this case the next higher term is ^3P and both the term split in ligand field and hence the orgel diagram of d² and d⁸ system is as follows—



The energy gap between ground level ${}^3F$ and next higher level ${}^3P$ is represented by 15 B, where B is Racah parameter. This represents the interelectronic repulsion parameter.

For d^2 metal ion in octahedral field the electronic transitions are

$${}^3T_{1g} \longrightarrow {}^3T_{2g}\ (\nu_1)$$

$${}^3T_{1g} \longrightarrow {}^3T_{1g}(P)\ (\nu_2)$$

$${}^3T_{1g} \longrightarrow {}^3A_{2g}\ (\nu_3)$$

i.e, in this case ${}^3T_{1g}(F)$ is the ground level. ν_3 corresponds to 18 Dq and ν_1 represents the 8 Dq. So the 10 Dq can be calculated as $(\nu_3 - \nu_1)$.

* d^3 and d^7 system ⇒ The ground term of d^3 and $d7$ is same but J is different due to hole formalism.

For d^3 system,

+2	+1	0	-1	-2
↿	↿	↿		

$L = 3\ (F)$ $S = 3/2$

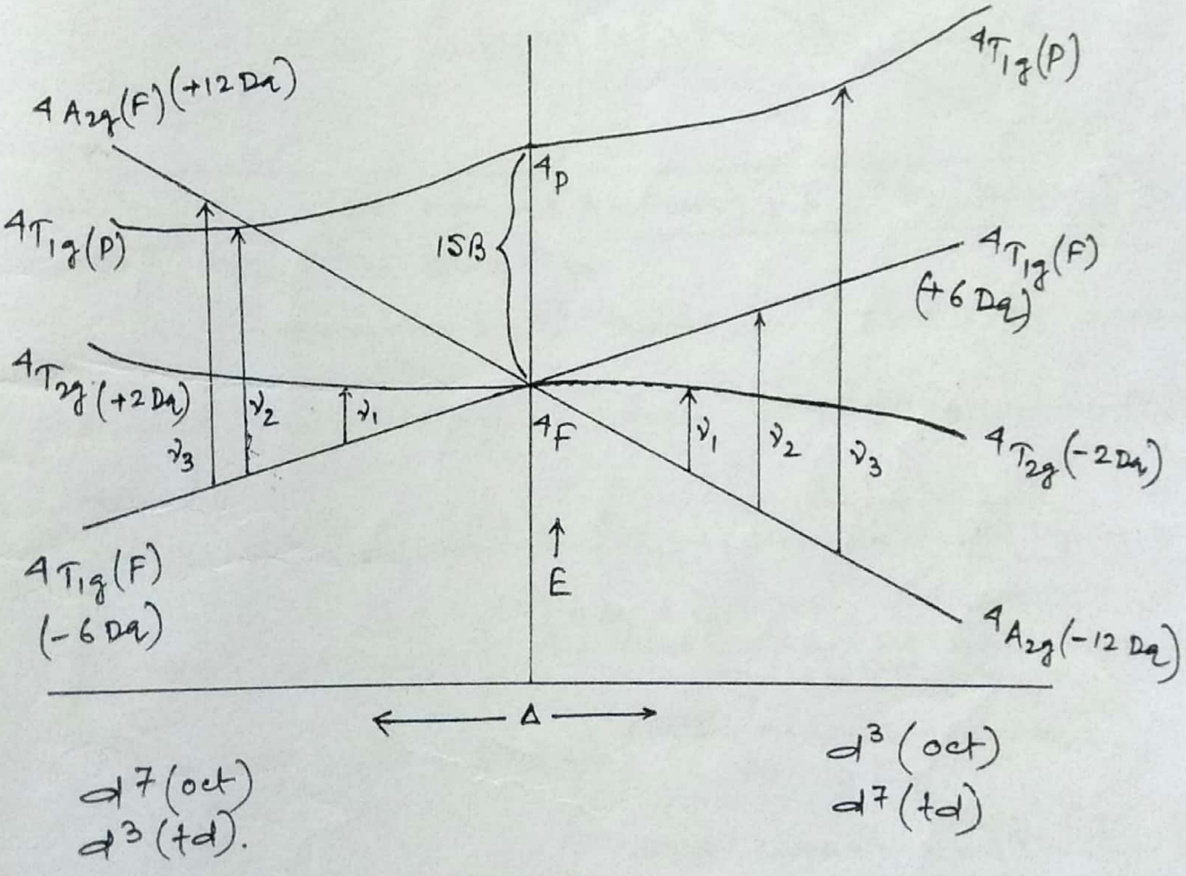
$2S+1 = 4$. $\therefore S = 3/2, \frac{1}{2}, -1/2, -3/2$

∴ The terms are ${}^4F_{3+3/2}$, ${}^4F_{3+1/2}$, ${}^4F_{3-1/2}$, ${}^4F_{3-3/2}$

or, $^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$, $^4F_{3/2}$.

∴ For d^3 system ground term is $^4F_{3/2}$ and for d^7 system ground term is $^4F_{9/2}$

The orgel diagram for d^3 and d^7 is as follows —



In d^3 octahedral system the possible transitions are

$$^4A_{2g} \xrightarrow{\nu_1} {}^4T_{2g}$$

$$^4A_{2g} \xrightarrow{\nu_2} {}^4T_{1g}(F)$$

$$^4A_{2g} \xrightarrow{\nu_3} {}^4T_{1g}(P)$$

But for d^7 octahedral system, the transitions are,

$$^4T_{1g} \xrightarrow{\nu_1} {}^4T_{2g}$$

$$^4T_{1g} \xrightarrow{\nu_2} {}^4T_{1g}\,(P)$$

$$^4T_{1g} \xrightarrow{\nu_3} {}^4A_{2g}$$

In case of d^3 (oct) system 10 Dq is represented by ν_1 and for d^7(oct) System 10 $Dq = \nu_3 - \nu_1$.

* <u>d^4 and d^6 System</u> ⇒ Due to hole formalism d^4 and d^6 both have same ground term but J is different.

For d^4 system,

+2	+1	0	-1	-2
↿	↿	↿	↿	

$L = 2\ (D)$

$S = 4 \times (+\frac{1}{2}) = 2$

$\therefore\ 2S+1 = 5$

$S = +2, +1, 0, -1, -2$

$\therefore$ The terms are

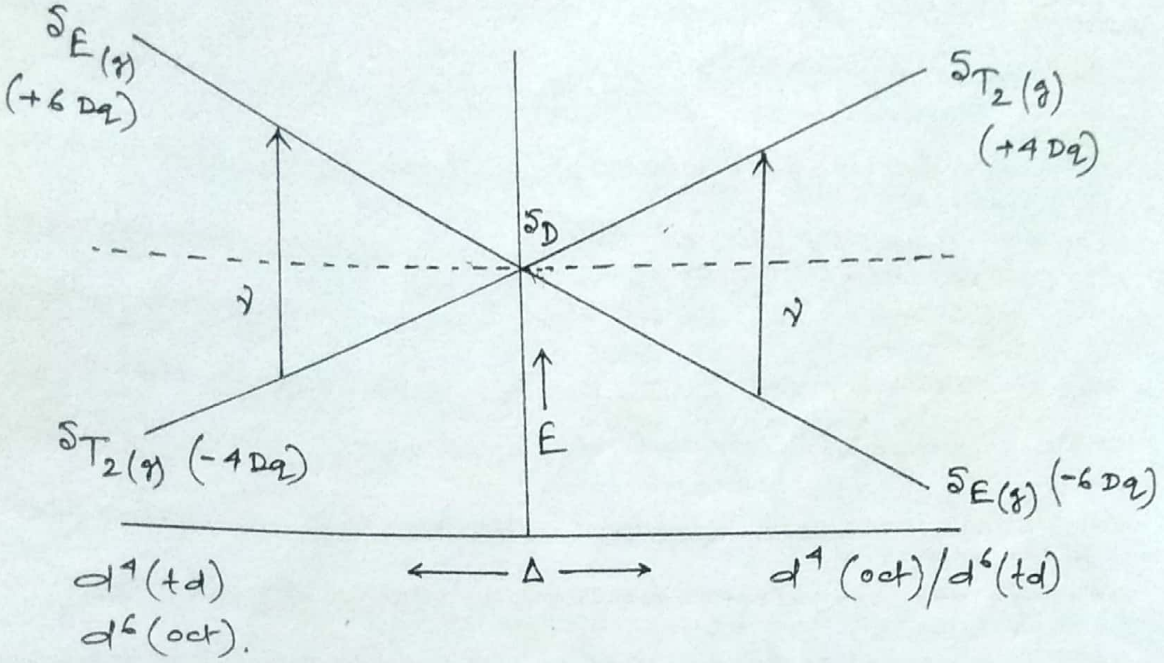
$$^5D_{2+2},\ {}^5D_{2+1},\ {}^5D_{2+0},\ {}^5D_{2-1},\ {}^5D_{2-2}$$

or, $^5D_4$, $^5D_3$, $^5D_2$, $^5D_1$, $^5D_0$.

$\therefore$ Ground term of d^4 is $^5D_0$

and for d^6, the ground term is $^5D_4$.

The orgel diagram for d^4 and d^6 is as follows —



In d^4 octahedral system the possible transition is

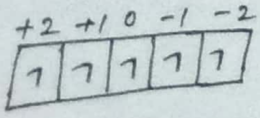
$$^5E_g \xrightarrow{\nu} {}^5T_{2g} \text{ (corresponds to 10 Dq)}$$

In d^6 octahedral system the possible transition is

$$^5T_{2g} \xrightarrow{\nu} {}^5E_g \text{ (This also corresponds to 10 Dq.)}$$

* Q. Why d^5 weak field metal complexes are colourless or of less intense colour?

For d^5 system,



L = 0 (S), S = 5/2

2S + 1 = 6

The term is ^6S.

In ligand field the ^6S term splits to $^6A_{1g}$ level which has the spin multiplicity 6. But the higher energy states arise are ^4G, ^4P, ^4D and ^2I, which have the spin multiplicity 4 or 2. So when electronic transition occurs from lower energy level $^6A_{1g}$ to higher energy level it becomes a spin forbidden transition. Again d-d transition is Laporte forbidden. Hence the probability of transition is very low. Due to this reason, molar extinction co-efficient for a d^5 system becomes very small. Hence the corresponding metal complexes becomes almost colourless.

2. Charge Transfer Transition :

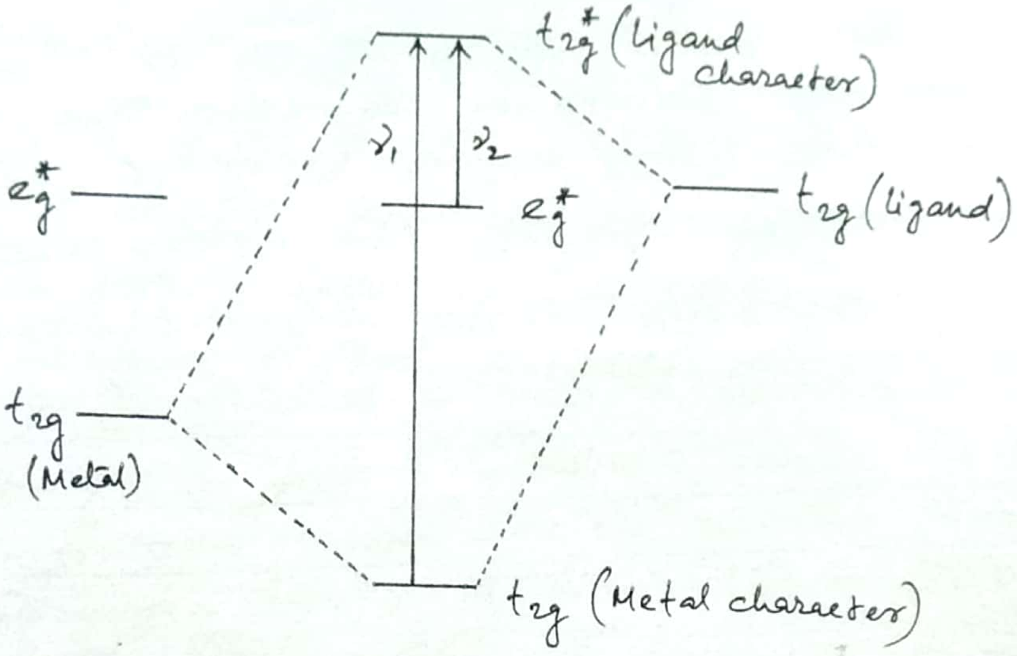
The metal ions having d^0 or d^{10} system can also show colours in complexes. These cases can be successfully explain with the help of charge transfer spectra. This arises due to electron transition of two different sites in the complex. So it can be considered as a internal redox process. This type of transition is totally allowed. So the molar extinction co-efficient (ε) varies in $10^3 - 10^4$ order and the metal complexes show intense colour. The transition region lies in visible and also in UV region.

On the basis of mode of transitions the charge transfer transition can be divided into three types as follows—

i) Metal to ligand charge transfer (MLCT)
ii) Ligand to metal charge transfer (LMCT)
iii) Metal to metal charge transfer (MMCT).

These are explain individually as follows-

i) Metal to Ligand charge transfer ⇒ This type of charge transfer spectra is observed when the metal ion present in low oxidation state and the ligand is a π-acid ligand. Metal 'd' electron is transferred to ligand vacant π^* orbital. This can be explain with the help of following diagram—



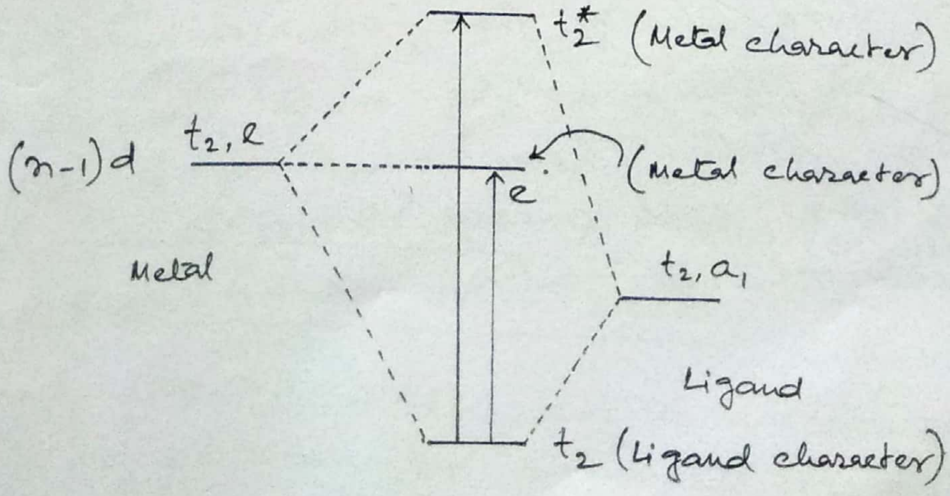
The complexes of π acid ligands such as CO, CN^-, bipyridine, o-phenanthrolene shows deep colour due to this type of charge transfer transition. For example, $[Fe(o\text{-}phen)_3]^{2+}$ is deep red in colour.

In case of octahedral metal complex $Cr(CO)_6$, it gives two intense bands at 35800 cm^{-1} and 44500 cm^{-1}. This occurs due to the transition of electron of metal orbital to ligand vacant orbital. $Mo(CO)_6$ gives two intense bands at 35000 cm^{-1} and 43000 cm^{-1}.

* Why [Cu(bipy)] shows intense colour?

Hint ⇒ Bipy or 2,2'-bipyridine is as π-acceptor ligand. The intense colour is due to charge transfer from metal to ligand as the ligands have empty π* orbital.

ii) Ligand To Metal Charge Transfer ⇒ When the electron transition takes place from a MO located primarily on the ligand (σ or π bonding orbitals) to a non-bonding or anti-bonding MO located primarily on the metal atom, then L → M charge transfer bands are observed. Generally oxide, chloride, bromide and iodide complexes show the L → M charge transfer bands. For d^0 system, where the d-d transition is not possible, the charge transfer bands are used to determine the value of 10 Dq. MnO_4^- shows the LMCT transition. From the MO diagram of tetrahedral complexes we can identify possible LMCT transitions.



These transitions are responsible for the deep purple colour of MnO_4^- because for these transitions it absorbs green colour.

The deep colour of $KMnO_4$. $K_2Cr_2O_7$, HgI_2, HgO etc. is observed due to LMCT transition.

Ligand to metal charge transfer is completely allowed process, so intense colour is observed. The transition energy depends on the following facts —

a) With increasing the oxidation states of metal, the transition energy decreases because with increasing charge metal behaves as strong oxidant.

b) Transition energy also depends on the ligand polarisability or reducing character. So larger ligands having high polarisability can transfer electron easily and so the energy required for transition decreases from lower size ligand to larger size ligands.

iii) Metal To Metal Charge Transfer ⇒

This type charge transfer mainly observed in the complexes having metal ions of mixed oxidation state. There must be a suitable pathway for such charge transfer, i.e, two different charge centres are bridged by a

Suitable Ligands such as halides, CN^- etc.

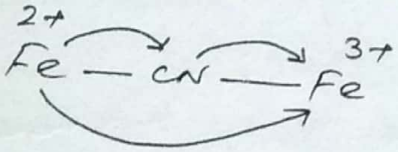
For example, prussian blue, turnbull's blue show MMCT transition. So these are deep blue in colour.

$$Fe^{3+} + K_4[Fe(CN)_6] \longrightarrow K\overset{+3}{Fe}[\overset{+2}{Fe}(CN)_6]$$

Prussian Blue.

$$Fe^{+2} + K_3[Fe(CN)_6] \longrightarrow K\overset{2+}{Fe}[\overset{+3}{Fe}(CN)_6]$$

Turnbull's Blue



$Cs_2[\overset{I}{Au}\overset{III}{Au}Cl_6]$ shows intense colour due to charge transfer from $[\overset{I}{Au}Cl_2]^-$ to $[\overset{III}{Au}Cl_4]^-$.

Molybdanum blue also show intense colour due to metal $(\overset{IV}{Mo})$ to metal $(\overset{VI}{Mo})$ charge transfer.

N.B. ⇒ $K_2\overset{II}{Fe}[\overset{II}{Fe}(CN)_6]$ ⇒ Colourless (charge transfer doesnot occur.)

* Why in the spectra of transition metal ions broad bands are shown?

The spectra arises due to electronic transition between two different energy levels.

when the energy differance between two levels is fixed then we get sharp band but when the energy difference is not fixed then we get broad bands. The change or variation of energy difference between two energy levels can be arise due to following reasons—

i> In the complex compounds, the metal ion vibrates continuously so the M-L distance always changes and hence Δ_o or Δ_t and different energy levels always flactuate. So, we can get broad bands.

ii> Due to variation of Ligand field and Jahn Teller distortion effect, the energy levels arenot fixed and transition between these levels gives broad band.

iii> Due to spin-orbit coupling the terms are splitted into different energy states. Broad bands can also be expected for this type of spin-orbit coupling.

* Which of the following should have more intense d-d transition?

Trans-$[CrCl_2(H_2O)_4]^+$ and cis$[CrCl_2(H_2O)_4]^+$.

The cis isomer has no centre of symmetry and the trans isomer has a centre of symmetry. The lowering of molecular symmetry relaxes the Laporte rule and increases the intensity of absorption of crystal field transition. So, for trans isomer the Laporte selection rule is more forbidden than similar transition in cis isomer. So, cis isomer gives more intense band and show deep colour.

* Which of the following complexes is of deep colour?

$Ni(CO)_4$ and $Fe(CO)_5$

Hints: $Ni(CO)_4 \Rightarrow sp^3$ hybridised ⇒ td ⇒ d-p mixing ⇒ laporte relaxed ⇒ intense colour

$Fe(CO)_5 \Rightarrow dsp^3$ ⇒ TBP ⇒ Laporte forbidden ⇒ less intense colour.

* $[Cr(H_2O)_6]^{3+}$ is green colour - explain.

$Cr^{3+} \Rightarrow d^3$ system $\Rightarrow t_{2g}^3 e_g^0 \Rightarrow$ Laporte forbidden Spin allowed.

Green Coloured. ← absorbs purple colour ←

* $FeCl_3$ and $FeBr_3$ are yellow coloured but FeF_3 or $[FeF_6]^{3-}$ is colourless – explain.

Hints: $FeCl_3$ and $FeBr_3$ ⇒ CT transition (L→M)

⇒ coloured

⇒ absorbs indigo colour

⇒ Yellow coloured.

FeF_3 ⇒ Absorbs UV light ⇒ Colourless.

* $TiCl_4$ solution is colourless but $TiCl_3$ is violet – explain.

Hints: $TiCl_4$ ⇒ $[Ti(H_2O)_6]Cl_4$ ⇒ d^0 ⇒ no scope of d-d transi^n ⇒ 3p → 4s transi^n ⇒ Absorbs UV light ⇒ Colourless.

$TiCl_3$ ⇒ $[Ti(H_2O)_6]Cl_3$ ⇒ d^1 ⇒ $t_{2g}^1 e_g^0$ ⇒ Break down of Laporte selection rule, spin allowed ⇒ absorbs Yellow-green light ⇒ Violet colour is observed.

* Co(II) chloride sol^n is faint pink colour but it turns deep blue colour on addition of HCl – explain.

Hints ⇒ $[Co(H_2O)_6]^{2+}$ ⇒ d^7 ⇒ $t_{2g}^5 e_g^2$ ⇒ Laporte forbidden spin allowed ⇒ less intense band ⇒ faint colour

$[Co(H_2O)_6]^{2+} \xrightarrow{HCl} [CoCl_4]^{2-}$ ⇒ td complex ⇒ d-p mixing due to absence of symmetry ⇒ laporte allowed and spin allowed ⇒ deep colour is observed.