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COORDINATION CHEMISTRY 2.3

by

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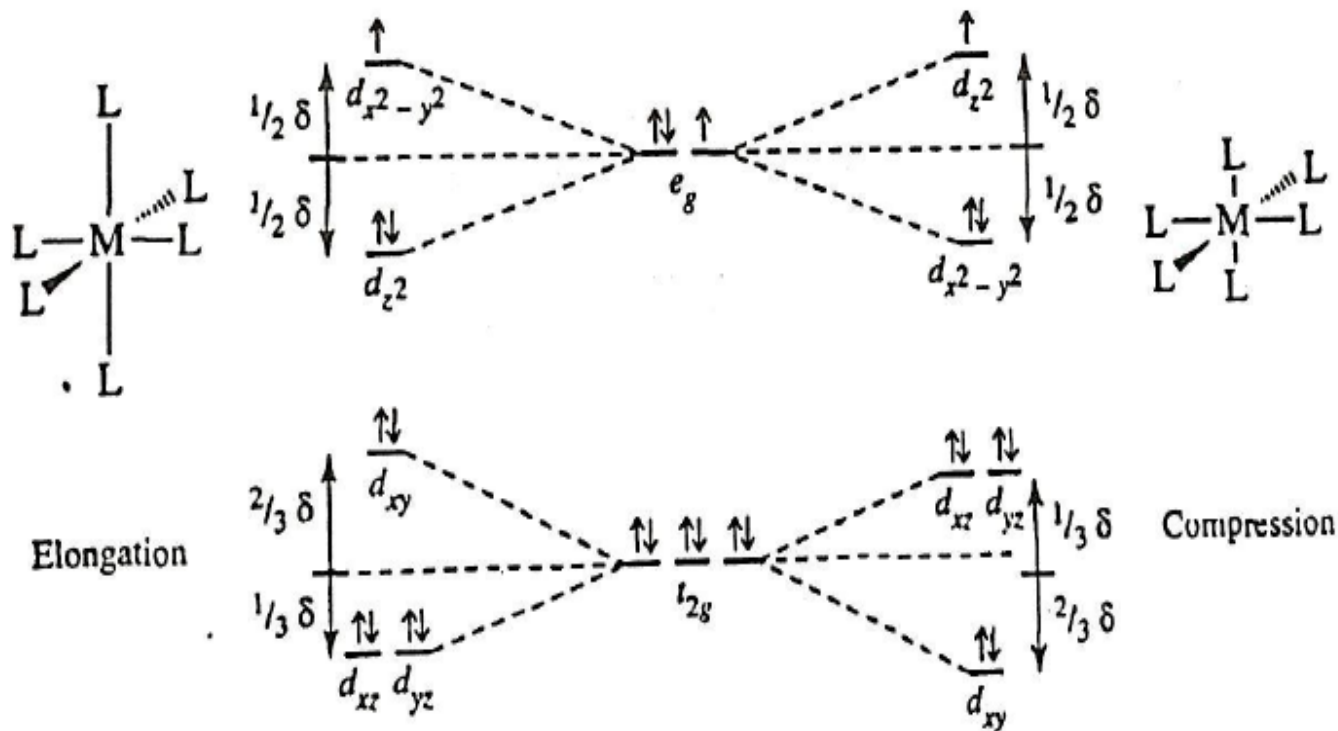
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Introduction

The Jahn-Teller Effect

The Jahn-Teller theorem states that there cannot be unequal occupation of orbitals with identical energies. To avoid such unequal occupation, the molecule distorts so that these orbitals are no longer degenerate. For example, octahedral Cu(II), a d^9 ion, would have three electrons in the two e_g levels without the Jahn-Teller effect, as in the center of the Figure below. The Jahn-Teller effect requires that the shape of the complex change slightly, resulting in a change in the energies of the orbitals. The resulting distortion is most often an elongation along one axis, but compression along one axis is also possible.

In octahedral complexes, where the e_g orbitals are directed towards the ligands, distortion of the complex has a larger effect on these energy levels and a smaller effect when the t_{2g} orbitals are involved.



Examples of significant Jahn-Teller are found in complexes : d^4 high spin (weak ligands) Cr(II) and Mn(III)

d^7 low spin (strong ligands) Co(II) and Ni(III)

d^9 (strong or weak ligands) Cu(II) and Ag(II)



Strong and Weak Jahn-Teller Distortion

- Configurations with e_g^1 or e_g^3 show pronounced Jahn-Teller distortions, because the orbitals are directed at ligands.
 - These configurations correspond to E_g terms.
- Configurations with $t_{2g}^1, t_{2g}^2, t_{2g}^4, t_{2g}^5$ have weaker Jahn-Teller distortions, because these orbitals lie between ligands.
 - These configurations correspond to T_{1g} or T_{2g} states.
- Jahn-Teller distortion causes splitting of E and T terms, whether ground- or excited-state.
 - Energy split for any E term is greater than the energy split for T terms of the same complex.



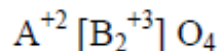
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Determination of the spinel structure

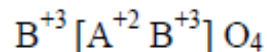
$Mg^{+2} Al_2^{+3} O_4$ is called as mineral spinel and accordingly all the mixed oxides having the general formula $A^{+2} B_2^{+3} O_4$ are known as spinels in which both the A^{+2} and B^{+3} cations can be same or different.

Oxide ion present in the spinel undergo cubic closed packing to construct two types of void's known as tetrahedral void and octahedral void.

(i) If all the +2 cations are occupied in the tetrahedral voids and all the +3 cation occupied in the octahedral voids then the spinel is known as simple or normal spinel, which can be represented as:-



(ii) If all the +2 cations and half of the +3 cations are occupied in the octahedral voids while the remaining half of the +3 cations are occupied in the tetrahedral voids then the spinel is known as inverse spinel, which can be represented as:



Now the nature of spinels can be determined with the help of CFSE for the A^{+2} & B^{+3} cations under weak field octahedral and tetrahedral conditions.



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Spinel Structure of Mn_3O_4

To determine the spinel structure of Mn_3O_4 , at first we have to consider the Mn^{+2} and Mn^{+3} ions in the octahedral and tetrahedral voids to construct the weak field octahedral and tetrahedral complexes. Then after that we can calculate the CFSE value under weak field octahedral and tetrahedral conditions.

	$\text{Mn}^{+2}(3d^5)$	$\text{Mn}^{+3}(3d^4)$
CFSE under strong field octahedral condition	0	$-0.9 \Delta_o$
CFSE under strong field tetrahedral condition	0	$-0.27 \Delta_o$

Since, the value of CFSE for Mn^{+3} under weak field octahedral condition is more –ve, which indicates that Mn^{+3} will have the tendency to occupied in the octahedral voids i.e. the Mn_3O_4 will have simple spinel (Normal spinel) structure.





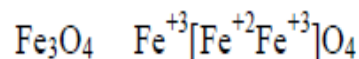
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Spinel structure of Fe_3O_4

Fe_3O_4 containing one of the Fe in the +2 oxidation states and 2Fe in the +3 oxidation state. To determine the spinel structure of Fe_3O_4 , at first we have to consider the Fe^{+2} and Fe^{+3} in the octahedral and tetrahedral voids to construct the weak field octahedral and tetrahedral complexes. Then after that we can determine the CFSE tetrahedral under the weak field octahedral and tetrahedral conditions.

	$\text{Fe}^{+2}(3d^6)$	$\text{Fe}^{+3}(3d^5)$
CFSE under strong field octahedral condition	$-0.4 \Delta_o$	0
CFSE under strong field tetrahedral condition	$-0.27 \Delta_o$	0

Since, the value of CFSE for the Fe^{+2} ion under weak field octahedral condition is more -ve, this indicates that the Fe^{+2} will have the tendency to occupied in the octahedral void i.e. the i.e. the Fe_2O_4 will have inverse spinel structure.





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SPIN ONLY FORMULA

Metal ion	d ⁿ configuration	S	μ_{eff} (spin only) BM	Observed values of μ_{eff} BM
Sc ⁺³ , Ti ⁺⁴	d ⁰	0	0	0
Ti ⁺³	d ¹	½	1.73	1.7- 1.8
V ⁺³	d ²	1	2.83	2.8–3.1
V ⁺² , Cr ⁺³	d ³	3/2	2.87	3.7–3.9
Cr ⁺² , Mn ⁺³	d ⁴	2	4.90	4.8–4.9
Mn ⁺² , Fe ⁺³	d ⁵	5/2	5.92	5.7–6.0
Fe ⁺² , Co ⁺³	d ⁶	2	4.90	5.0–5.6
Co ⁺²	d ⁷	3/2	3.87	4.3–5.2
Ni ⁺²	d ⁸	1	2.83	2.9–3.9
Cu ⁺²	d ⁹	½	1.73	1.9–2.1
Zn ⁺²	d ¹⁰	0	0	0



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TYPES OF THE ELECTRONIC TRANSITION

1. d- d transition

2. Charge transfer transition

1. **d-d transition:** In a d-d transition, an electron in a d orbital on the metal is excited to another d orbital of higher energy by a photon. In complexes of the transition metals, the d orbitals do not all have the same energy. In centrosymmetric complexes, d-d transitions are forbidden by the Laporte rule. According to Laporte rule states that, if a molecule is centrosymmetric, transitions within a given set of p or d orbitals will be forbidden. However, forbidden transitions become allowed if the center of symmetry is disrupted. Transitions that occur as a result of an asymmetrical vibration of a molecule are called vibronic transitions. Through such asymmetric vibrations, transitions that should be theoretically forbidden, such as a d-d transition, are weakly allowed.

d-d- Transition is the phenomena of excitation of the electrons of the splitted lower energy set of d-orbitals into the higher energy splitted set of d- orbitals by the absorption of electromagnetic radiation is known as phenomena.

Example: In the d^1 configuration containing octahedral complex i. E. $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ ion, the d-d transition phenomena is represented in



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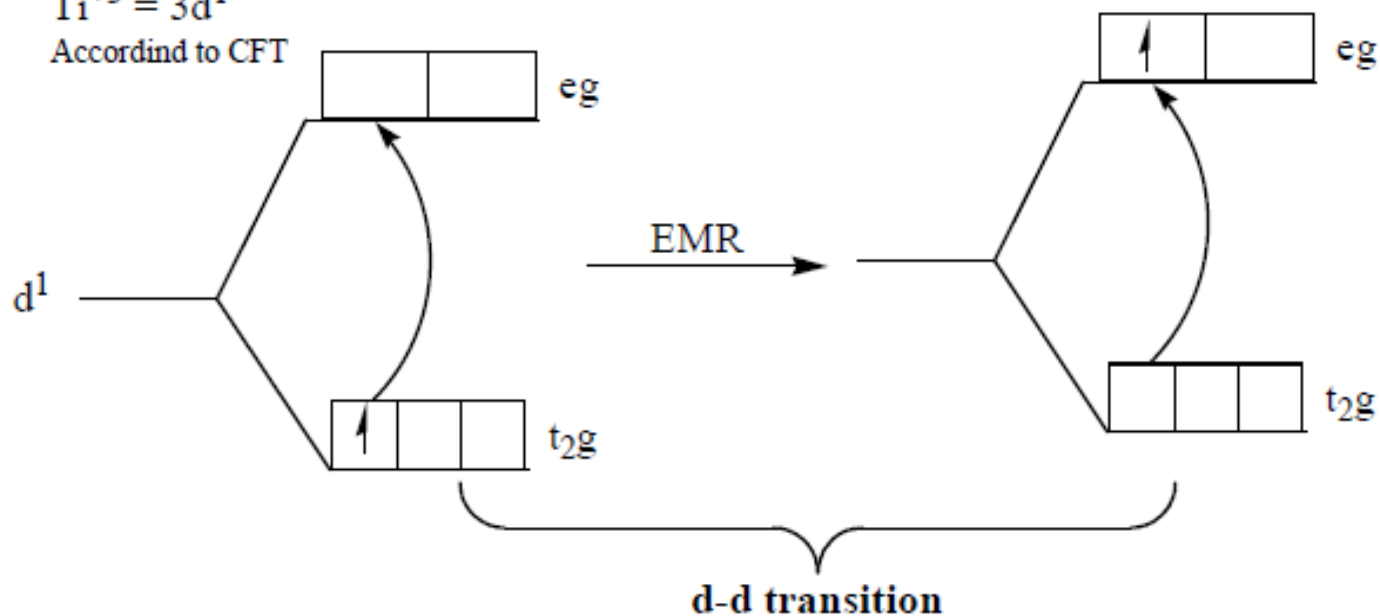
$[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$ ion

$\text{Ti} = 3d^2, 4s^2$

Oxidation state of Ti = +3

$\text{Ti}^{+3} = 3d^1$

According to CFT



d-d Transition in $[\text{Ti}(\text{H}_2\text{O})_6]^{+3}$



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SELECTION RULE FOR *d-d* TRANSITION

1. Spin selection rule

According to the spin selection rule, all the electronic transitions in the transition metal complexes which does not involve the change in the spin multiplicity are called as spin allowed transitions while on the other hand all the electronic transitions which can involve the change in the spin multiplicity are known as spin forbidden transitions. therefore,

$\Delta S = 0$ (Allowed transition)

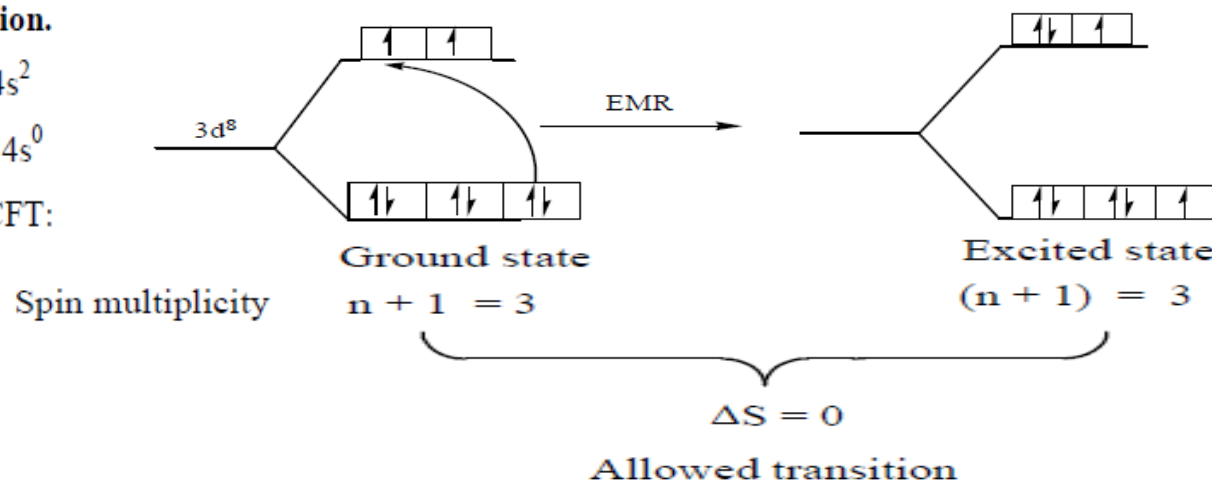
$\Delta S \neq 0$ (Forbidden transition)

(i) $[\text{Ni}(\text{H}_2\text{O})_6]^{+2}$ ion.

$\text{Ni} - 3d^8, 4s^2$

$\text{Ni}^{+2} - 3d^8, 4s^0$

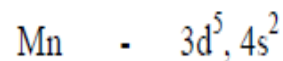
According to CFT:



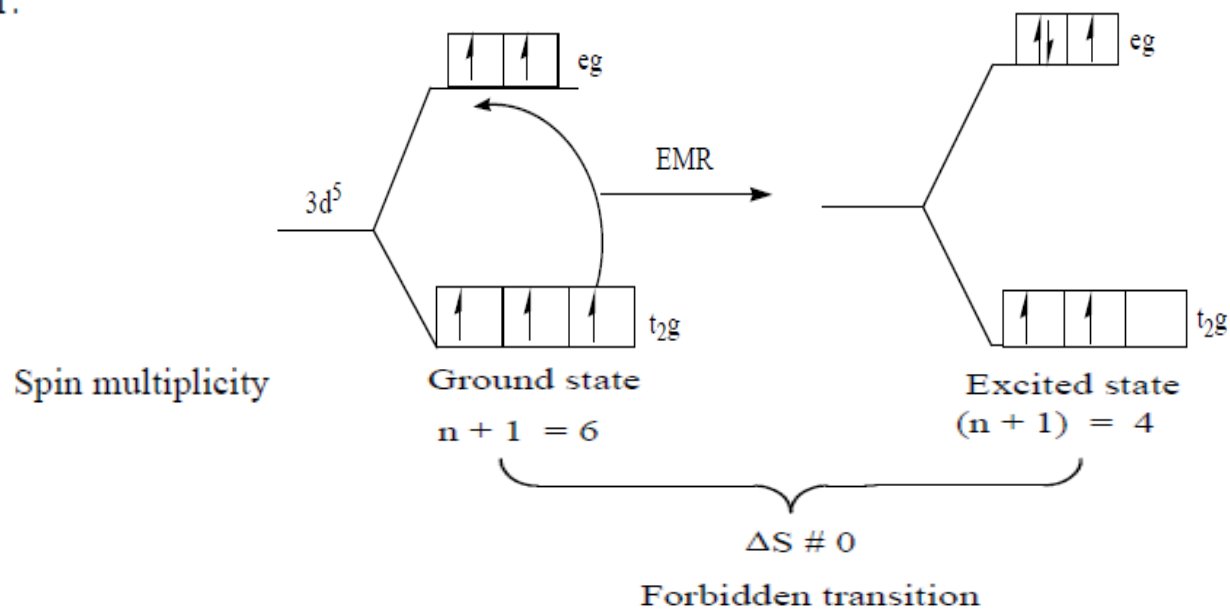


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(ii) $[\text{Mn}(\text{H}_2\text{O})_6]^{+2}$ ion.



According to CFT:

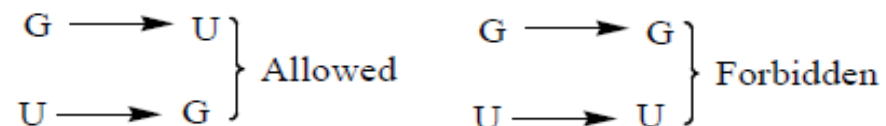




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2. Laporte selection rule

According to this rule, all the electronic transitions which occur from G (g) to U (u) (gerade to ungerade) or u to g orbitals, are known as Laporte allowed or symmetry allowed transitions while all the electronic transitions, which occur from g to g or u to u orbitals are known as Laporte forbidden transition or symmetry forbidden transition.



According to this selection rule all the d-d transition phenomena in the transition metal complexes are forbidden.

Therefore, according to the Laporte selection rule, all the electronic transitions in which there does not occur any change in the orbital quantum number (l) value are known as Laporte forbidden transition while all the electronic transitions which involve certain change in the orbital quantum number are known as Laporte allowed transition.

$$\Delta l = 0 \text{ (Laporte forbidden transitions)}$$

$$\Delta l \neq 0 \text{ (Laporte allowed transitions)}$$

Thus, according to this selection rule, it is observed that all the d-d transitions (g-g transitions) are Laporte forbidden. There are certain relaxations in Laporte selection rule due to the possibility of certain extent of d-p mixing.



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2. Charge transfer transition: In inorganic compounds, most of the charge-transfer complexes involve electron transfer between metal atoms and ligands. The charge-transfer bands of transition metal complexes result from shift of charge density between molecular orbitals (MO) that are predominantly metal like nature and those that are predominantly ligand like nature. If the transfer occurs from the MO with ligand character to the MO with metal-like character, the complex is called a ligand-to-metal charge-transfer (LMCT) complex and the transfer is LMCT. If the electronic charge shifts from the MO with metal character to the MO with ligand character, the complex is called a metal-to-ligand charge-transfer (MLCT) complex. Thus, oxidation of the metal center occurs as a result of MLCT, whereas a LMCT results in the reduction of the metal center.

Depending on the direction of charge transfer, these are classified as either ligand-to-metal (LM) or metal-to-ligand (ML) charge transfer

(a) Ligand-to-metal charge transfer (LMCT)

LMCT complexes arise from the transfer of electrons from MO having ligand character to those having metal character. This type of transfer occurs when complexes have ligands with relatively high-energy lone pairs and if the metal has low-lying empty orbitals. In such complexes, metals have higher uncommon oxidation states or less number of d-electrons (even d^0). These conditions suggest that the acceptor metal level is available which is of low energy.



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Examples:

MnO₄⁻: The permanganate ion with tetrahedral geometry is intensely purple coloured due to strong absorption involving charge transfer from MO of filled oxygen p orbitals to empty MO of manganese (VII).

CdS: The yellow color of cadmium sulphide is due to the transition of electrons from Cd²⁺ (5s) ← S²⁻ (π).

HgS: It is red due to Hg²⁺ (6s) ← S²⁻ (π) electronic transition.

(b) Metal-to-ligand charge transfer

Metal-to-ligand charge-transfer (MLCT) complexes arise as a result of transfer of electrons from MO with metal-like character to those with ligand-like character. These transitions are most common in complexes with ligands having low-lying π* orbitals, especially aromatic ligands. For these transitions to occur, metal should have low oxidation state with sufficient number of electrons and should be relatively high in energy.

Examples:

i. Tris (2,2'-bipyridyl)ruthenium(II): This is an orange-colour complex due to MLCT.

ii. W(CO)₄(phen)

iii. Fe(CO)₃(bipy)



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