D.N.R. COLLEGE(A), BHIMAVARAM

DEPARTMENT OF P.G. CHEMISTRY

INORGANIC CHEMISTRY –I

PRESENTED BY

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Unit-1

Structurte And Bonding

VALENCE SHELL ELECTRON PAIR REPULSION (VSEPR) THEORY

The main postulates of this theory are:

1. according to Lewis structure of a given molecule or ion only the valence shell electrons of the central atom participate in bonding forming various bonds.

Based on the nature of central atom's valence shell surrounding the central atom, the various species can be grouped into following categories:

(a) Species whose central atom is surrounded by -bonding electrons pairs (-bps) only. Examples of such species are BeF_2,CH_4,PF_5,SF_6,IF_7, etc.

(b) Species whose central atom is surrounded by -bps as well as by lone pairs of electrons (lps). Examples of such species are $SnCl_2$,NH_3, H_2O, SF_4,SlF_3,XeF_2,IF_5,XeF_4,XeF_6, etc.

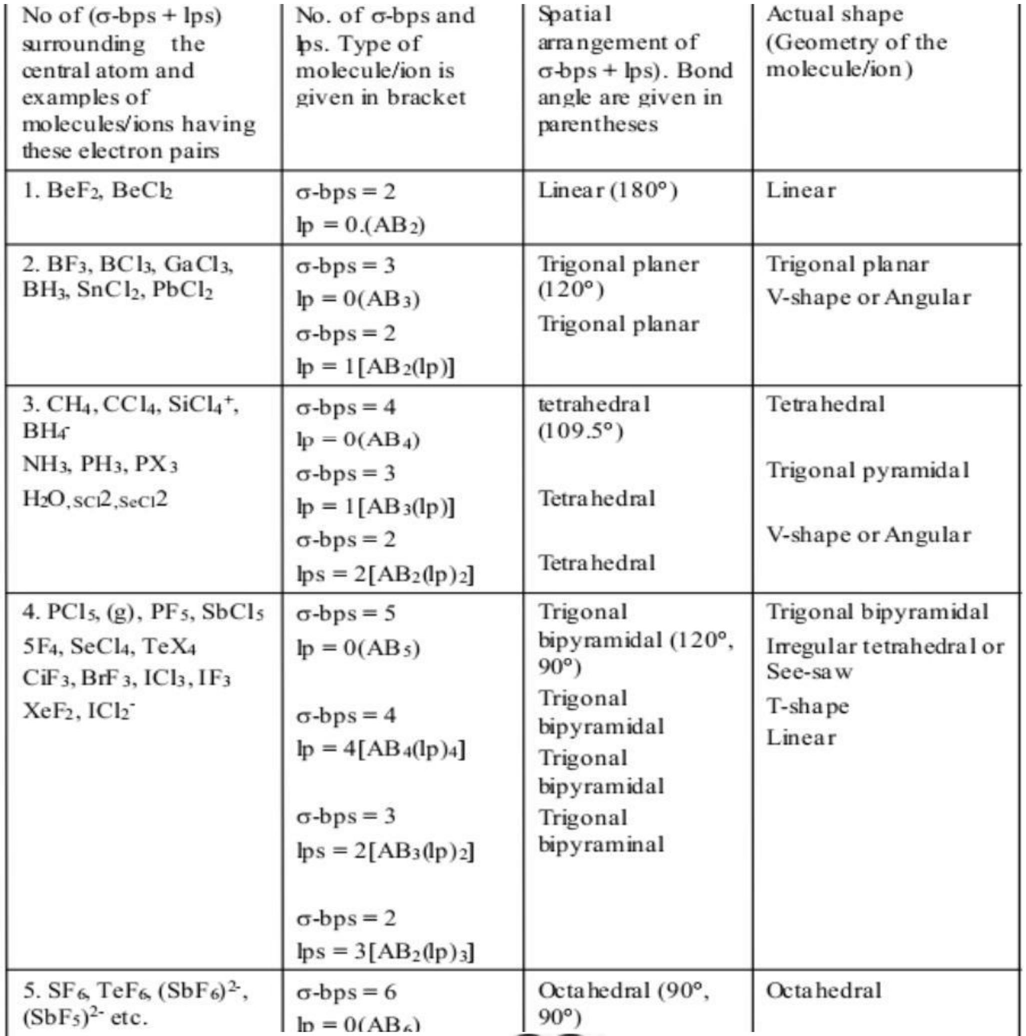
(c) Species whose central atom is surrounded by -bps as well as by - bps. lps are absent. Examples of such species are CO_2 (O = C = O), HCN (H-CN), H_2C_2 (H-CC-H), etc.

(d) Species whose central atom is surrounded by -bps, lps and ———————————————-bps.
Examples are SO_2 (O = SO) ClO_3 – | O Cl O O
the type of spatial arrangement (for example, linear, trigonal planar, tetrahedral, etc.) the electron pairs surrounding the central atom depends on the sum of -bps and lps surrounding the central atom. The presence of -bps does not influence the spatial arrangement of the electron pairs. The spatial arrangement takes place in such a way that the electron pairs occupy their positions in space as far away from each other as possible because in this case the electrostatic repulsion between the electron pairs is reduced to minimum. The system with minimum repulsive forces is the most stable. It has been observed that when (-bps + lps) is equal to 2, 3, 4, 5, 6 and 7, the spatial orientation of these electron pairs round the central atom is linear (angle – 180°), trigonal planar (angle = 120°), tetrahedral (angle – 109.5°), trigonal bipyramidal (angle = 120°, 90°), octahedral (angle = 90°) and pentagonal bipyramidal (angle – 72°, 90°). The orientation of -bps for the molecules whose central atom is surrounded only b -bps and no lps is shown in Figure 2.1

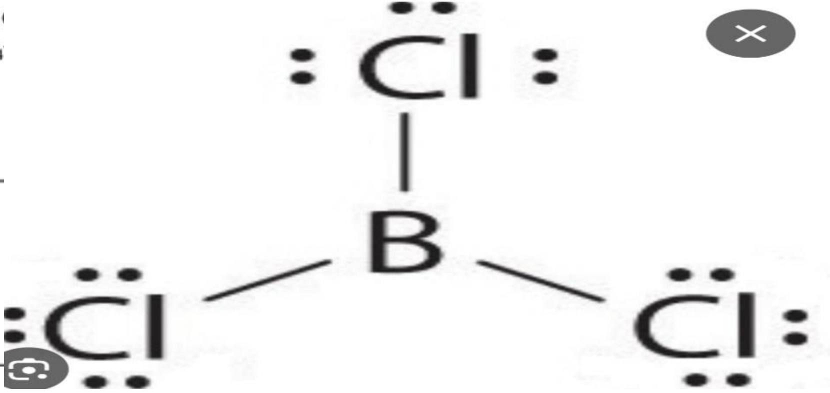
In which A is the central atom and B are the surrounding atoms with which a (central atom) is linked by -bps

2. While determining geometry of a given molecule or ion on the basis of VSPER theory, the presence of -bps surrounding the central atom of the species should not be considered, since these electron pairs do not influence the geometry of the molecule or ion. It is only-bps and lps surrounding the central atom which decide the shape of the species and hence only these electron pairs (i.e.,-bps and lps) should be considered.

3. If the central atom is surrounded purely a -bps, then the shape (geometry) of the molecule or ion is the same as the spatial arrangement of the -bps round the central atom. However, if the central atom is surrounded by - bps as well as by lps, then the geometry of the molecule or ion gets distorted from its expected geometry and becomes different from the spatial arrangement of (-bps + lps)(Refer Table 2.1). Due to the presence of lps, bond angle also becomes different from the expected bond angle between the-bps. For example since C-atom (central atom) in CH_4 molecule is surrounded only by four -bps, it has the expected tetrahedral shape with the expected H-C-H bond angle of 190.5° (expected angle). On the other hand, since N-atom (central atom) in NH_3 molecule is surrounded by three -bps and one lp, it does not have the tetrahedral shape; rather it has pyramidal shape with H-N-H bond angle = 107



No of (σ-bps + lps) surrounding the central atom and examples of molecules/ions having these electron pairs	No. of σ-bps and lps. Type of molecule/ion is given in bracket	Spatial arrangement of σ-bps + lps). Bond angle are given in parentheses	Actual shape (Geometry of the molecule/ion)
1. BeF_2, $BeCl_2$	σ-bps = 2 lp = 0.(AB_2)	Linear (180°)	Linear
2. BF_3, BCl_3, $GaCl_3$, BH_3, $SnCl_2$, $PbCl_2$	σ-bps = 3 lp = 0(AB_3) σ-bps = 2 lp = 1[AB_2(lp)]	Trigonal planer (120°) Trigonal planar	Trigonal planar V-shape or Angular
3. CH_4, CCl_4, $SiCl_4^+$, BH_4^- NH_3, PH_3, PX_3 H_2O, SCl_2, $SeCl_2$	σ-bps = 4 lp = 0(AB_4) σ-bps = 3 lp = 1[AB_3(lp)] σ-bps = 2 lps = 2[$AB_2(lp)_2$]	tetrahedral (109.5°) Tetrahedral Tetrahedral	Tetrahedral Trigonal pyramidal V-shape or Angular
4. PCl_5, (g), PF_5, $SbCl_5$ $5F_4$, $SeCl_4$, TeX_4 CiF_3, BrF_3, ICl_3, IF_3 XeF_2, ICl_2^-	σ-bps = 5 lp = 0(AB_5) σ-bps = 4 lp = 4[$AB_4(lp)_4$] σ-bps = 3 lps = 2[$AB_3(lp)_2$] σ-bps = 2 lps = 3[$AB_2(lp)_3$]	Trigonal bipyramidal (120°, 90°) Trigonal bipyramidal Trigonal bipyramidal Trigonal bipyraminal	Trigonal bipyramidal Irregular tetrahedral or See-saw T-shape Linear
5. SF_6, TeF_6, $(SbF_6)^{2-}$, $(SbF_5)^{2-}$ etc. IF_5, BrF_5, XeF_4, ICl_4	σ-bps = 6 lp = 0(AB_6)	Octahedral (90°, 90°)	Octahedral
6. IF_7 XeF_6			ral



4. sigma-bps are considered to be localized between the two atoms linked together by covalent bond while a lp is held by only one atom, i.e., bonding electron pair is under the influence of two atoms and a lp is under the influence of VSEPR Theory NOTES Self-Instructional Material 57 one atom only, viz., central atom. Thus we expect that the orbital containing an lp is more spread out in space in comparison to that (i.e., orbital) which contains a bonding electron pair. Consequently an lp will exert more

repulsion on the bonding electron pair as compared to the repulsion exerted by a bonding electron pair on the other bonding electron pair as, (lp – bp) > (bp – bp) ...(2.1) On similar lines of argument it can be shown that: lp – lp) > (lp – bp) ...(2.2) On combining the above two relations we get: (lp – lp) > (lp – bp) > (bp – bp) ...(2.3) Relation (2.3) gives us the order of the magnitude or repulsion between electron pairs. The repulsions between the electron pairs at 90° are stronger than that between the electron pairs at 120°. These repulsions are the weakest (lowest) when the electron pairs are at 180°.

1.3.1. Structure of beryllium chloride (BeCl2)

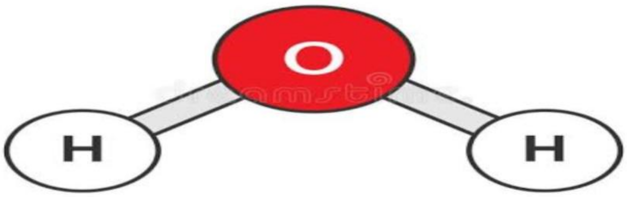
Beryllium chloride is a white colored hygroscopic solid substance with chemical formula BeCl2. Beryllium chloride has two bonding pairs and no lone pair of electrons around the beryllium atom as depicted in Figure 1.1. In order to minimize mutual repulsion, the bonding pairs of electrons orient far from each other which results in the linear geometry of the molecule. As per VSEPR considerations, the Cl-Be-Cl bond angle is 180° Figure 1.1.The linear geometry of BeCl2 molecule.

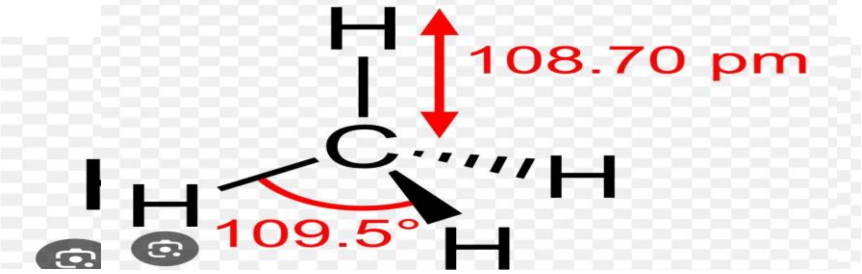
1.3.2. Structure of boron trichloride (BCl3)

Boron trichloride is a colorless gas with chemical formula BCl3. This molecule has three bonding pairs of electrons around the boron atom; hence, the molecule assumes trigonal planar geometry with Cl-B-Cl bond angle of 120° (Figure 1.2). Figure 1.

1.3.3. Structure of water (H2O), ammonia (NH3) and methane (CH4)

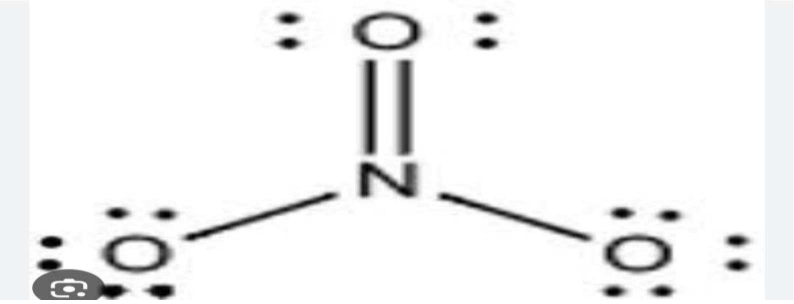
. Geometry and structural attributes of methane (left), ammonia (middle) and water (right). Each of the water, ammonia and methane molecules has four electron pairs around the respective central atom (Figure 1.3). However, the number of bonding and lone pairs of electrons is different. Methane with four bonding pair of electrons has a tetrahedral geometry (H-C-H bond angle = 109.5°). Ammonia has three bonding pairs and a lone pair of electron; therefore, the geometry reduces to trigonal pyramidal. Since, the lp-bp repulsion is stronger than the bp-bp repulsion; therefore, H-N-H bond angles of ammonia are contracted to 107°. In case of water, there are two lone pairs and two bonding pairs of electrons which surround the oxygen atom. Therefore, the geometry of molecule reduces to bent shape with H-O-H bond angle of 105°.





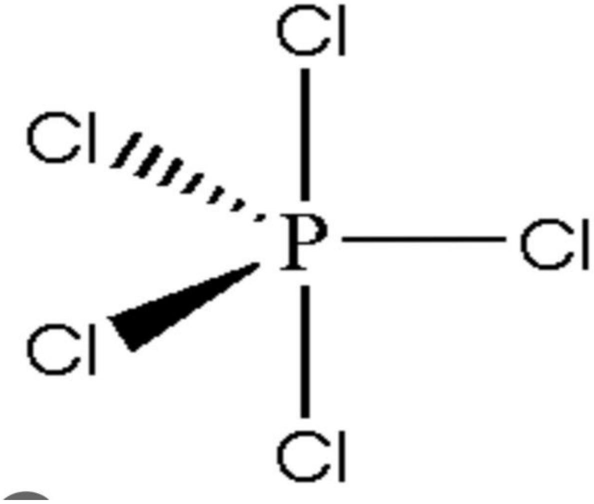
1.3.4. Structure of nitrate anion (NO3 -)

The Lewis structure of nitrate anion is presented in Figure 1.4 where formal charge on the anion is not depicted for the sake of clarity. Central nitrogen atom has one double bonded and two single bonded oxygen atoms around it. There is no lone pair of electron present around nitrogen atom. Hence, VSEPR theory suggests a trigonal planar geometry for nitrate ion (Figure 1.4). Figure 1.4.The trigonal planar shape of NO3 - anion.



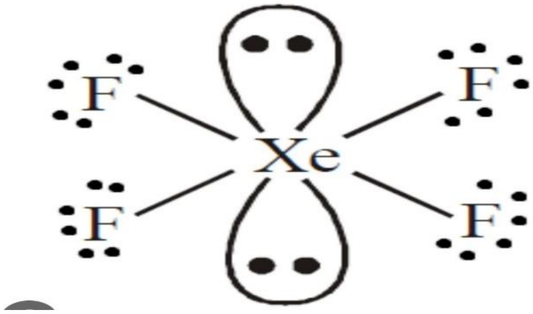
1.3.5. Structure of phosphorous pentachloride (PCl5)

Phosphorous pentachloride molecule has five bonding pairs of electrons around phosphorous atom and there is no lone pair of electrons on central atom. Therefore, VSEPR theory suggests the structure of PCl5 to be trigonal bipyramidal (Figure 1.5). Figure 1.5.The trigonal bipyramidal shape of PCl5 molecule.



Structure of xenon tetrafluoride (XeF4)

The Lewis structure of xenon tetrafluoride suggests that there are four bonding pairs and two lone pairs of electrons around the central xenon atom. Hence, the octahedral geometry for six coordinated central atom reduces to square planar in case of XeF4 (Figure 1.6).



1.3.7. Limitations of VSEPR theory

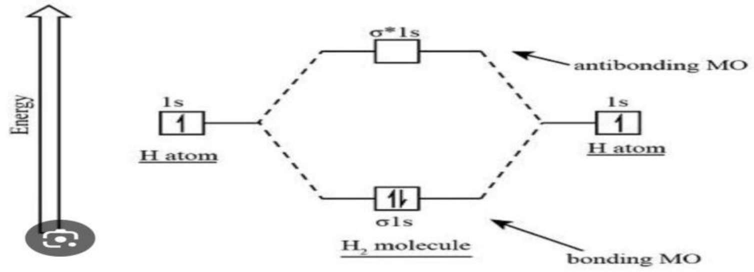
The VSEPR theory makes general statements about molecular geometry which is very useful in predicting the geometries of most of the molecules and ions. However, there are limitations to the theory as the predicted structures does not corroborate with those established by physical characterizations in some cases as discussed ahead. 1. IF_7 and TeF_7 - are isoelectronic with seven bonding pairs of electrons around the respective central atoms. Hence, VSEPR predicts pentagonal bipyramidal geometry for both of these structures. VSEPR theory does not predict different bond distances for axial and equatorial positions in pentagonal bipyramidal geometry. Physical characterization establishes that the axial bonds of these structures are slightly shorter than the respective equatorial bonds. Additionally, the geometry of TeF_7 - in their crystallographically characterized salts seems much distorted from the predicted pentagonal bipyramidal geometry as the equatorial fluorine atoms are not coplanar.

2. VSEPR theory successfully predicts the geometry of simple p-block molecules but it is not appropriate to predict structures of the d-block derivatives.

3. VSEPR theory does not take inert pair effect into account. Hence, it does not explain structures of molecules derived from heavy elements of periodic table. Crystallographic analyses have revealed that the species such as $[SeCl_6]$ 2- , $[TeCl_6]$ 2- and $[BrF_6]$ –

Molecular orbital theory:

Homonuclear Species 1. Hydrogen molecule: Hydrogen molecule is having two hydrogen atoms containing one electron each (1s1). Its mod is as given in Figure



(a) M.O. configuration of H_2 = (1s) 2 (1s *) 0 (b) Bond order = 1 2 [Nb - Na] = 1 2 [2 - 0] = 1 (single bond) (c) Stability = as bond order is one, the molecule is quite stable. (d) It is diamagnetic in nature as all the electrons in molecular orbital are paired.

H_2 ion: It is made up of H atom containing one electron and H+ ion containing no electron. M.O.

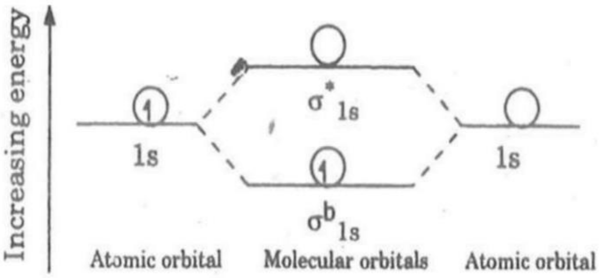


diagram for H2 ion is given in Figure 3.

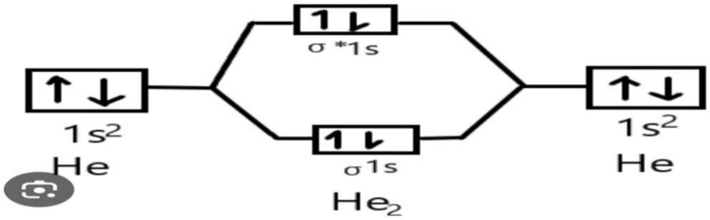
(a) M.O. configuration of H2 ion = (1s) 1 (1s *) 0

(b) Bond order = 1 2 [Nb - Na] = 1 2 [1 - 0] = 1 2

(c) Stability. Its bond order is less than the bond order for H2 molecule. Therefore, it is less stable than H2 molecule.

(d) It is paramagnetic in behavior as it possess one unpaired electron (1s) 1 .

Helium molecule (He2): Each helium atom contains 2 electrons. Therefore, He2 molecule will have 4 electrons. These 4 electrons will be arranged in M.O. diagram as given below in Figure 3.11.



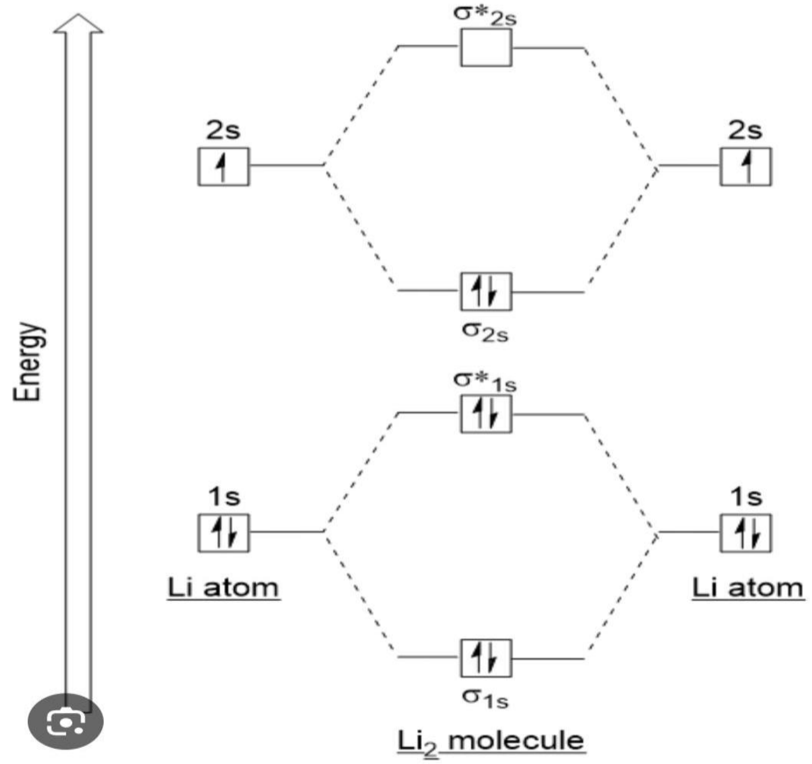
(a) M.O. configuration of He2 = (1s) 2 (1s *) 2

(b) Bond order = 1 2 [Nb - Na] = 1 2 [2 - 2] = zero Bond order zero indicates that there is no linkage between two atoms. Hence the He2 molecule does not exist.

(c) Stability. The molecule is highly unstable and there is no experimental proof for its existence.

(d) It is diamagnetic in nature as all the electrons in M.O. are paired.

Lithium molecule (Li2): Each lithium atom has electronic configuration of 1s2 2s1 and so the li2 molecule has total of six electrons. In the molecular orbital formation, the electrons of the inner shell (K shell) do not enter in bonding and so remain in their atomic orbitals. The orbitals which do not Molecular Orbital Theory of Covalent Bonding NOTES Self-Instructional Material 87 enter into bonding are called nonbonding orbitals. Thus we infer that only the valence electrons are involved in bond formation. The M.O. energy level diagram of Li2 is shown in Figure 3.12



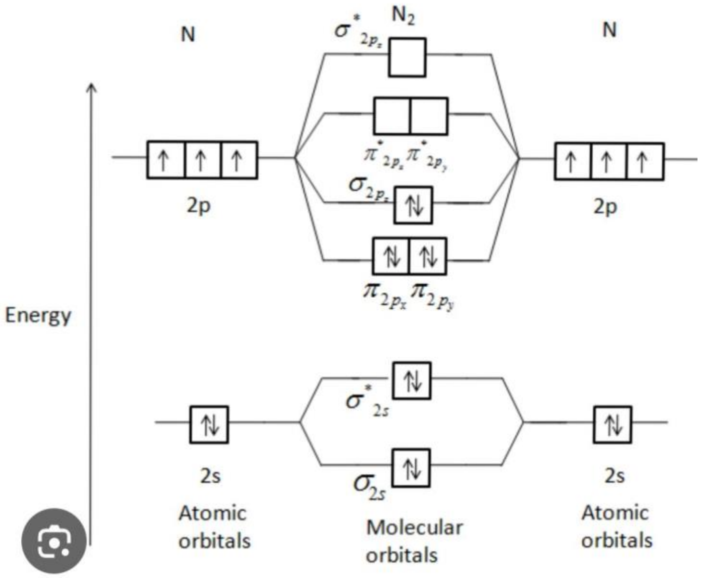
(a) M.O. configuration Li2 = (KK) (2s) 2 (2s *) 0

(b) Bond order = 1 2 [Nb - Na] = 1 2 [2 - 0] = 1

(c) Stability. The bond in lithium molecule is comparatively longer and weaker than that of H2 molecule as being formed by overlapping of 2s orbitals. Bond dissociation energy of Li2 kJ/mole which is less than that of H2 molecule (431.4 kJ/mole).

(d) It is diamagnetic in nature as all electrons in M.O. are paired.

Nitrogen molecule (N2): Nitrogen molecule has 14 electrons and thus its M.O. energy level diagram may be shown as in Figure 3.13.



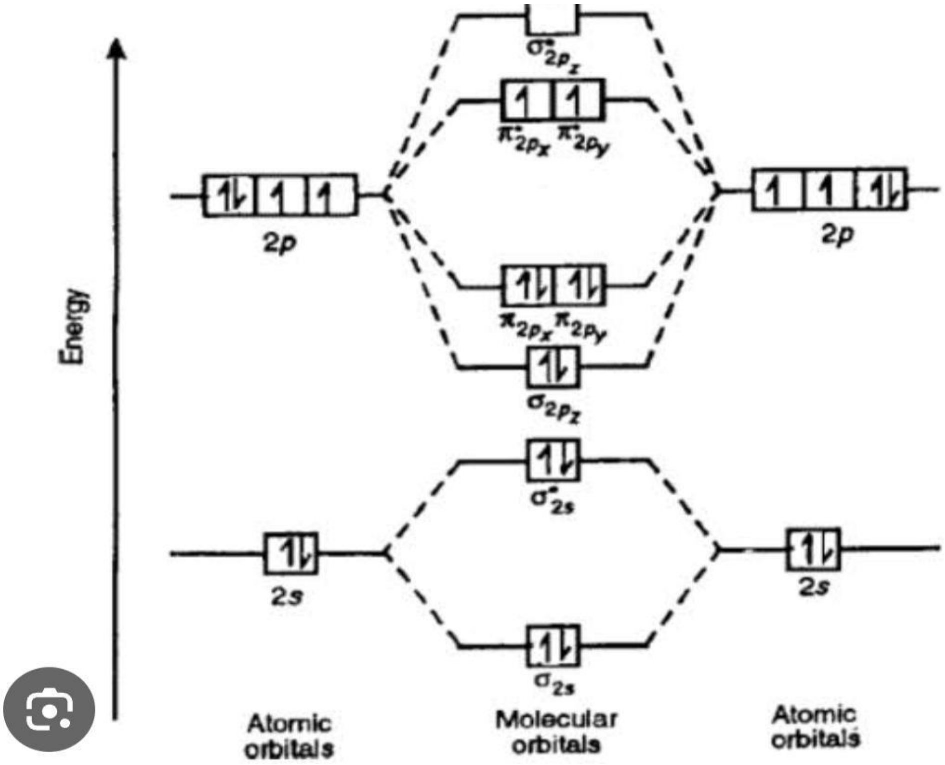
M.O. configuration of N2 = (KK) (2s) 2 (2s *) 2 (x 2p) 2 (y 2p) 2 (z 2p) 2

(b) Bond order = 1 2 [Nb - Na] = 1 2 [8 - 2] = 3 Molecular Orbital Theory of Covalent Bonding NOTES Self-Instructional 88 Material i.e. a triple bond exists between two nitrogen atoms. (Note: Electrons of K shell do not involve in M.O. formation. Therefore, these electrons remain as nonbonding electrons. Hence these are neither considered as bonding nor as anti-bonding.)

(c) Stability. Since the bond order of N2 molecule is 3, it is highly stable molecule. It is evident from its bond dissociation energy (940 kJ/mole).

(d) All the electrons in M.O. are paired so it is diamagnetic in nature. This has also been proved experimentally.

Oxygen molecule (O2): Oxygen molecule has 16 electrons in all, in which each oxygen atom has contributed 8 electrons. The molecular orbital energy level diagram of O2 molecule is as given below in Figure 3.14.



(a) M.O. electronic configuration. z x y x 2 2 2 2 1 2 1 KK 2s 2s 2p 2p2p2p 2py (b) Bond order. From M.O. diagram of O2 , the Nb = 8 and Na = 4. Therefore, bond order = 1 8 4 , 2
2 i.e. it has double bond. (c) Stability. Since the bond order of O2 molecule is 2, therefore the O2 molecule is quite stable. It is confirmed by its high dissociation energy (443 kJ/mole). (d) Magnetic character. From its M.O. diagram it is clear that the oxygen molecule has two unpaired electrons x y 1 1 2p 2p . So, it is paramagnetic in nature as confirmed by experiments.

O cation : 2 This cation is formed when one electron is ionized from the oxygen molecule. From the M.O. diagram of O2 molecule (Figure 3.14), if one electron is ionized x y 2p 2p or , then the M.O. electronic configuration will be: z x y 2 2 2 2 2 O KK 2 2s 2s 2p 2p2p 2px 1
(a) Bond order = b a 1 1 1 N N 8 3 2 2 2 2 (b) Stability. The bond order of O2 cation is higher than that of O2 molecule. Therefore, its stability will be more than that of O2 molecule [i.e. O2 > O2]. (c) Bond length. Bond length being inversely proportional to bond order, it decreases with increase of bond order. Therefore, O2 has lower bond length than O2 molecule. (d) Magnetic parameter. M.O. configuration has one unpaired electron x 2p ( ). Thus, it is paramagnetic in nature. 12.

– O2 ion (Superoxide ion): This ion is formed when O2 molecule gains one electron. This new electron pairs with either of the two half-filled antibonding orbitals x py 2p 2 or . Therefore, its electronic configuration becomes z x y x y 2 2 2 2 1 2 2 O KK 2 2s 2s 2p 2p2p2p2p

(a) Bond order = b a 1 1 1 N N 8 5 1 2 2 2

(b) Stability. As the bond order of superoxide ion is less than that of O2 molecule, it is less stable than O2 molecule O O .

(c) Bond length. Higher the bond order, shorter is the bond length. Thus, the bond length of O2 ion is more than O2 molecule O O . 2 2 (d) Magnetic nature. O2 shows paramagnetic character due to the presence of one unpaired electron y 1 2p . 13. 2

- O ion Peroxide ion. 2: Addition of two electrons (one each in x y 2p 2p&) to O2 molecule gives 2 O2 ion. So, its M.O. electronic configuration will be: z x y x y 2 2 2 2 2 2 2 2 O KK 2 2s 2s 2p 2p2p2p2p Diagram

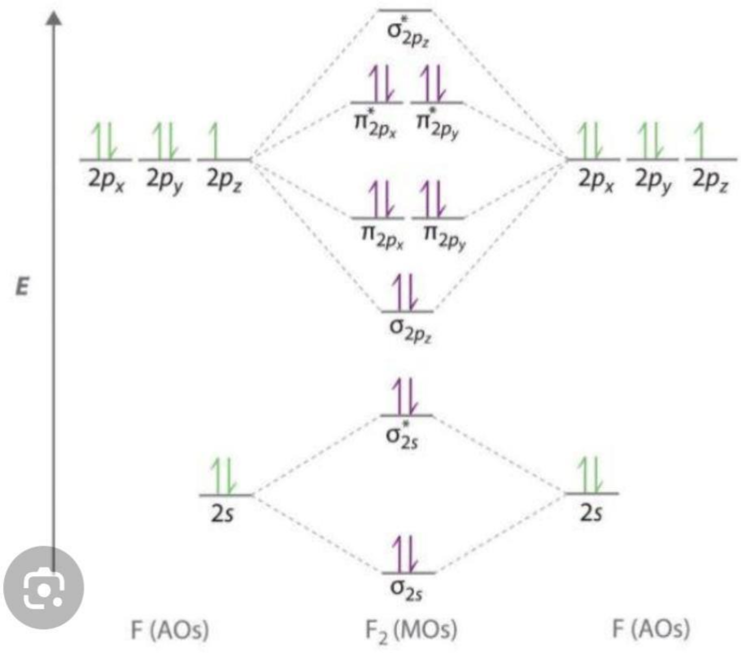
(a) Bond order b a 1 1 N N 8 6 1 Single bond 2 2

(b) Stability. It is less stable than O2 molecule. The order of stability of O2 and its various ionic species is 2 O O O O 2 2 2 2

(c) Bond length. Bond length is inversely proportional to bond order its bond length will be greater than O2 molecule 2 O O 2 2

(d) Magnetic effect. As expected 2 O2 shows diamagnetic behaviour when placed in a magnetic field. The complied list of the properties of these ions and oxygen molecule is presented below.

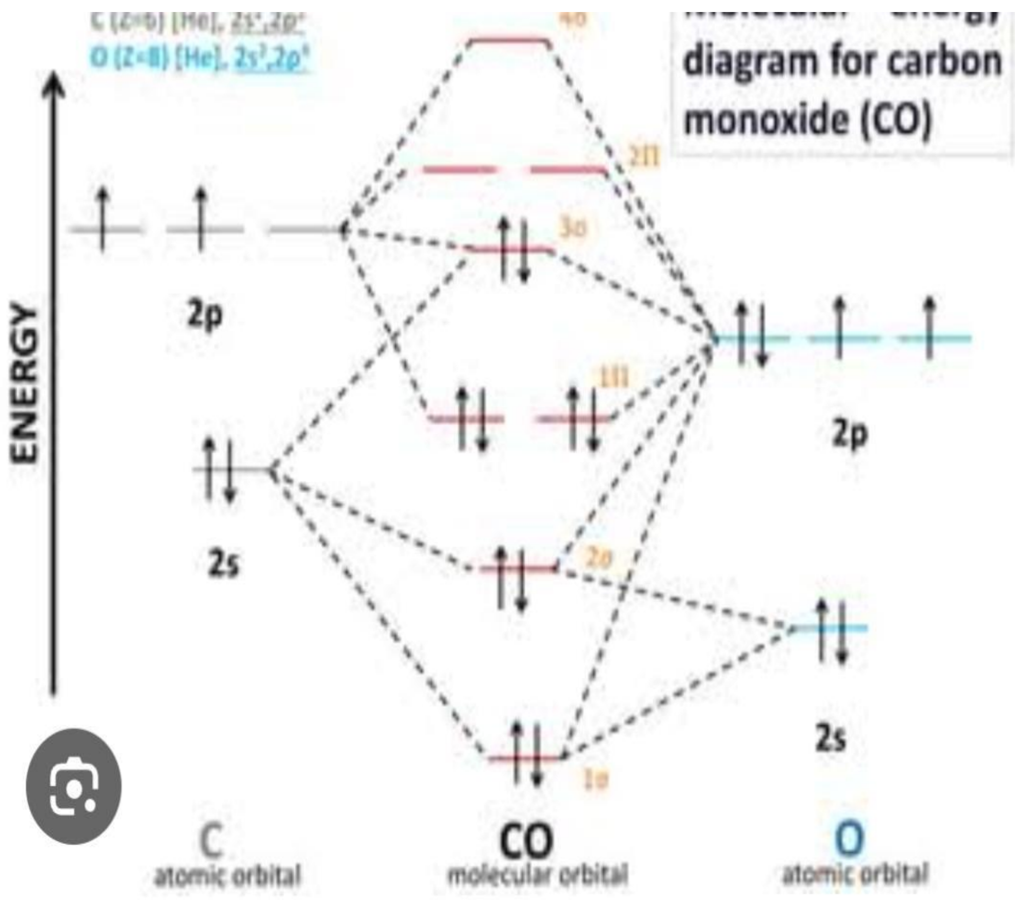
Fluorine molecule (F2): When two fluorine atoms (each having 9 electrons) combine to give F2 molecule then the total 18 electron occupy the molecular orbitals according to Aufbau’s rule. It results in the following M.O. electronic configuration (Refer Figure 3.15)



(a) M.O. configuration (b) Bond Order b a 1 1 N N 8 6 1 2 2
(i.e. single bond between two fluorine atoms). (c) Stability. Since the bond order of F2 molecule is one therefore, it is a stable molecule. (d) Magnetic Nature: Itshows diamagnetic behaviour as all the electrons in F2 molecule are paired

Heteronuclear Molecules In the foregoing discussion, we have studied the M.O. diagrams for homonuclear diatomic molecules and their related properties. We may now apply the same Molecular Orbital Theory of Covalent Bonding NOTES Self-Instructional Material 93 method to heteronuclear diatomic species such as CO, *NO+ , CN– , NO. Due to difference in electronegativities of the two hetero atoms, the molecular orbitals become polarized. It results in higher stabilization of MO’s of more electronegative atom compared to other atom. This can best be illustrated taking the example of CO.

Carbon Monoxide: It possesses 10 valence electrons (4 contributed by carbon and 6 by oxygen atom) which may be accommodated in five M.O. The M.O. energy level diagram of CO is as given in Figure 3.16.



(a) Electronic configuration. x y x 2 2 2 2 2 KK 2s 2s 2p 2p2p

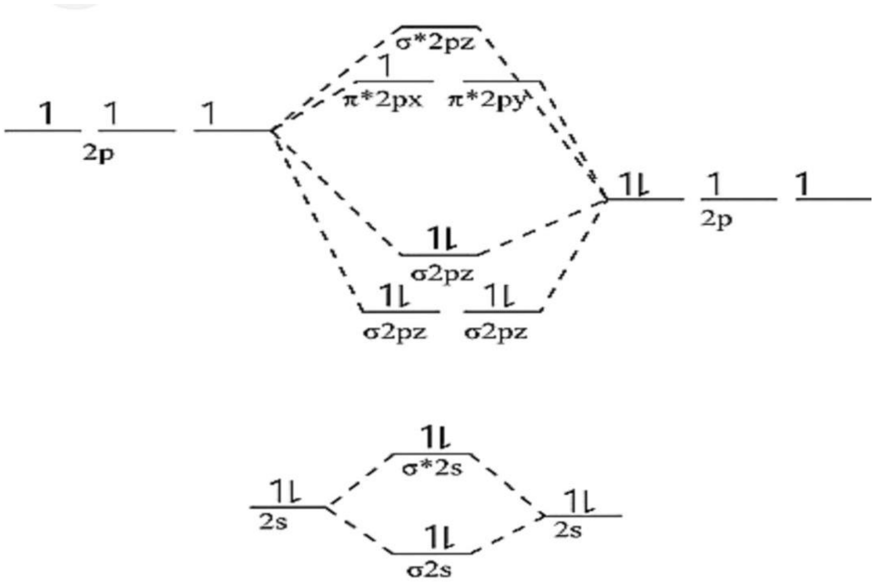
(b) Bond order. b a 1 1 N N 8 2 3 2 2
(Triple bond)

(c) Stability. As the bond order is three, the CO molecule is highly stable molecule. (d) Magnetic properties. All electrons in M.O. are paired. Hence CO is diamagnetic in nature.

Nitric Oxide (NO):

Nitric oxide has 11 valence electrons and so its M.O. electronic configuration will be x y x 2 1 2 2 2 NO KK
Diagram

2s 2s 2p 2p2p (a) Bond order b a 1 1 1 N N 8 3 2 2 2 2 (b) Stability. It is less stable than NO^+ ion (bond order = 3) because bond order of NO is smaller than that of NO^+ ion. This is manifested by quick oxidation of NO to NO^+ iron by the loss of one x 2p electron. (c) Magnetic nature. It is paramagnetic, as it possesses one x 2p unpaired electron



MO Diagram of Octahedral Complexes

According to molecular orbital theory,

The six σ-orbitals of the ligands overlap with the suitable atomic orbitals of the central metal ion. The six σ-orbitals of the ligands are shown in Figure 4.1. These orbitals are denoted by σx , σ-x, σ y , σ -y, σz and σ-z indicating σ-orbitals on +x, –x, +y, –y, +z and –z axes, respectively. The nine valence shell atomic orbitals 4s, 4px , 4py 4pz , 3d xy, 3d yz, 3dzx, 3dx2-y2 and 3dz2 of the central metal ion are grouped into four symmetry classes, as follows: 4s → A1g or a1g

4px , 4py 4pz → T1u or t 1u 3dx 2 -y 2, 3dz 2→ E g or e g 3d xy, 3d yz, 3dxz→ T2g or t 2g

Now let us consider the distribution of electrons in the molecular orbitals of the complex ion, $[Co(NH_3)_6]^{3+}$. We known that NH_3 is a strong ligand and it forms low spin complexes.

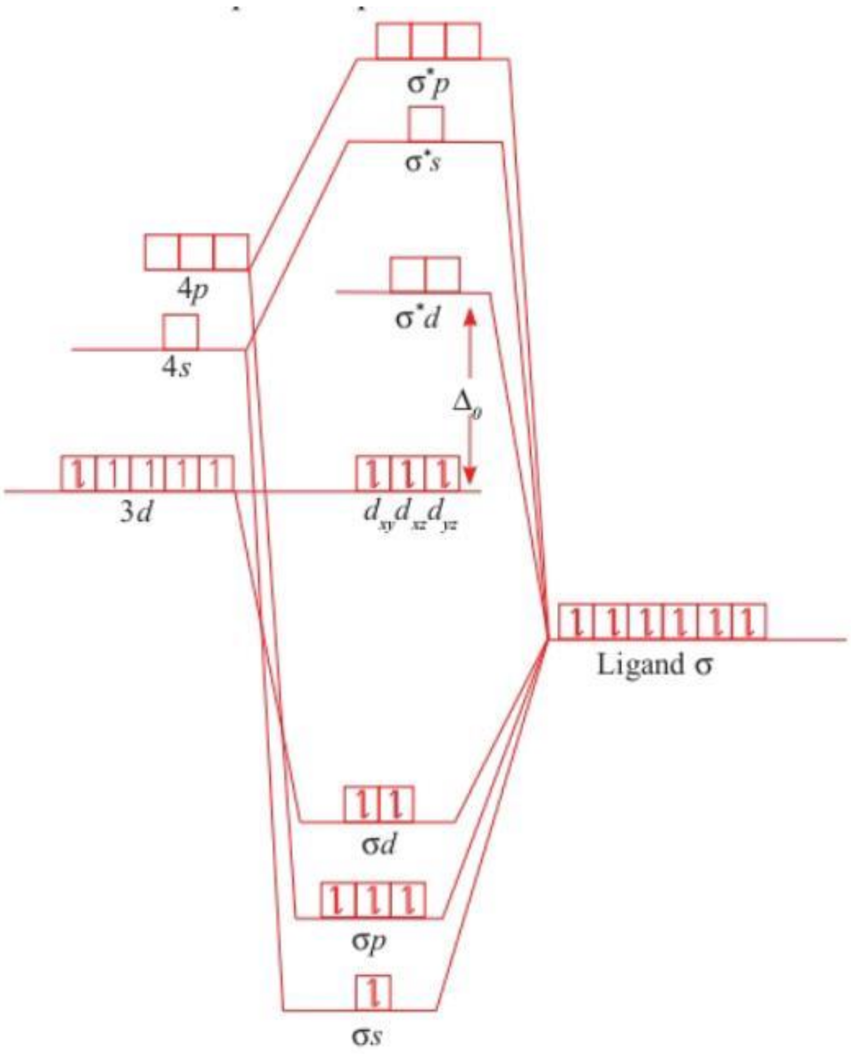


Fig. 4.2 *The MO Diagram for Low Spin* $[Co(NH_3)_6]^{3+}$ *Ion*

Filling of the molecular orbitals occur according to Aufbau's principle. In [Co(NH3)6]3+ complex, there is a total of 18 electrons (12 from six metalligand orbitals and six from metal d orbitals). These electrons are to be accommodated. The distribution of these electrons in different molecular orbitals in shown in Figure 4.2. Now take the example of the complex ion [CoF6] 3–. We known that F– ion is a weaker ligand, i.e., it forms high spin complex. In this complex ion also, 18 electrons are to be distributed in molecular orbitals. There are four unpaired electrons in complex ion and hence this ion is paramagnetic. The distribution of electrons between T2g and E* g in this complex occurs as t4 2g , E*2 g . This makes it a high spin complex. This distribution also explains why the Co−F bonds in the complex are not very strong. The reason for this is that the presence of two electrons in the antibonding orbitals reduces the strength of Co−F bonds. Also, the high spin complexes contains electrons in the antibonding orbitals, so these are less stable

MO Diagram of Tetrahedral Complexes

Consider the distribution of electrons in the molecular orbitals of a tetrahedral complex like [CoCl4]2–. The electrons are distributed in different molecular orbitals as shown in Figure 4.3. sb -orbitals p-orbitals 3d 4s s* s 4p p*zx px2–y2 p* z2 t p*yz p*xy s+ x s+ y s+ z s p Co2+ orbitals CoCl2– 4 orbitals Cl– orbitals Energy Fig. 4.3 The MO Diagram for High Spin [CoCl4]2- Ion

There a seven electrons in 3d-orbitals of Co2+ ion and eight electrons in four ligand ions (Cl–). So, 15 electrons are to be distributed in different molecular orbitals. There are three unpaired electrons in t2g ,

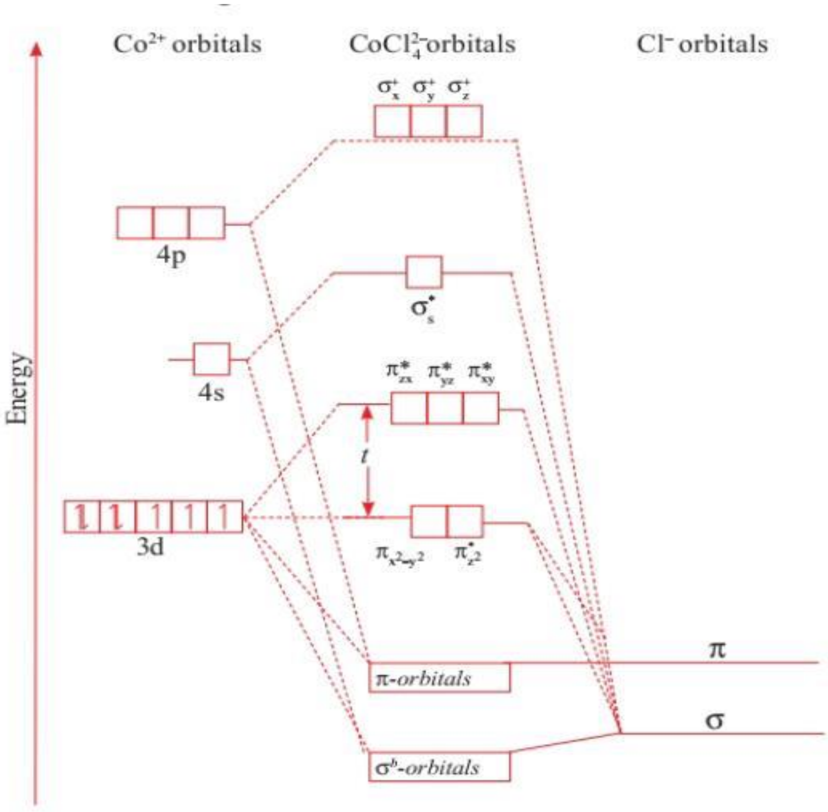


Fig. 4.3 The MO Diagram for High Spin $[CoCl_4]^{2-}$ *Ion*

hence this complex ion is paramagnetic

MO Diagram of Square Planar Complexes Consider the case of [PtCl4]2- ion. In this complex ion, total of 16 electrons, 8 electrons belonging to 5d-orbitals of Pt and 8 electrons of 4Cl– ion are to be distributed in different molecular orbitals as shown in Figure 4.4. Since all the electrons are paired, so this complex ion is diamagnetic in nature.

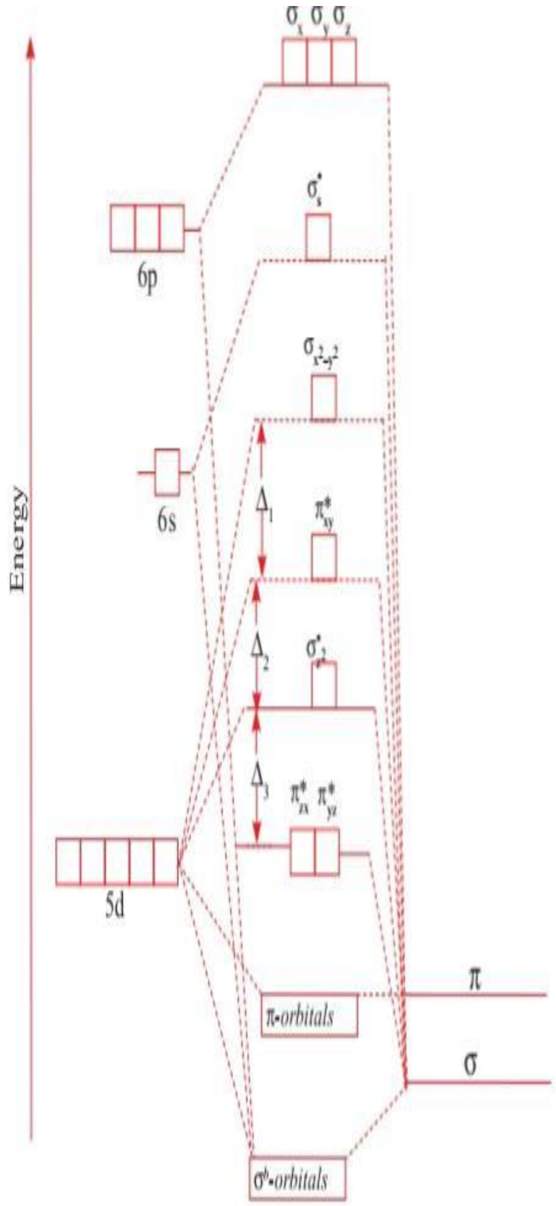
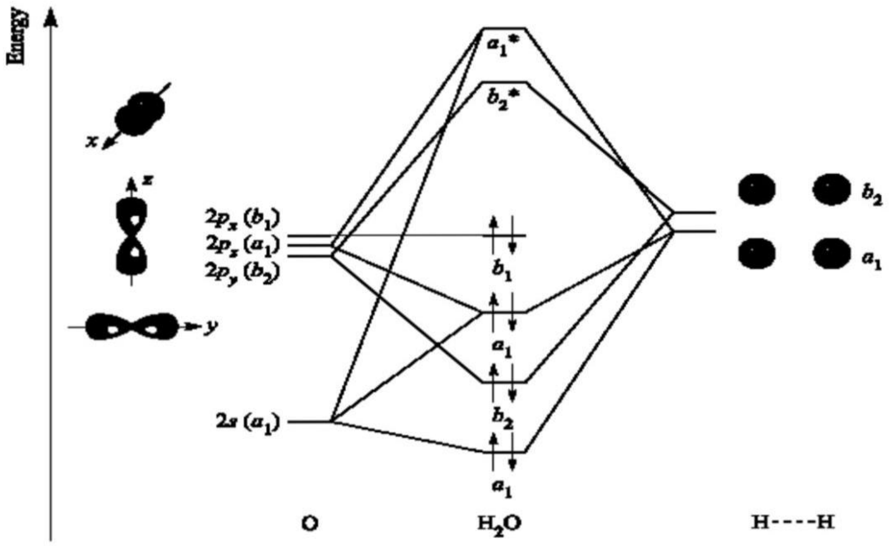
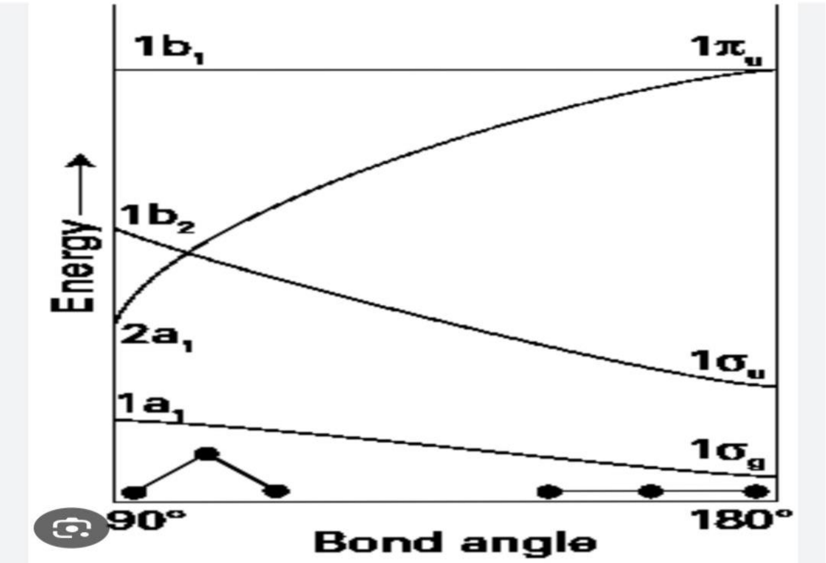


Fig. 4.4 The MO Diagram for $[PtCl_4]^{2-}$ Ion

WALSH DIAGRAMS

Walsh diagram for tri-atomic molecules Simplified Walsh diagram for a triatomic molecule is depicted in Figure 1.7, which is energy versus bond angle plot. It should be noted that the depicted energy levels are qualitative and for actual system should be calculated by a suitable simulation. MO levels drawn on the left are for the bent configuration with bond angle of 90° whereas those on right are for the linear configuration with bond angle 180°.





The correlation lines joining the energy levels on left and right extreme depict the energy levels for bond angle θ defined by the range 90° ≤ θ < 180°. The plot offers quick comparison of the energies for bent and linear geometries with a given bond angle, θ. It is evident that the molecule prefers the geometry with lower HOMO levels.

dπ-pπ BOND

Formation of inorganic molecules is different than that of organic molecules in many aspects, one of which is the occurrence of dπ-pπ bonds. Generally, π bonds, as in case of organic molecules, formed by lateral overlapping of p orbitals present on two atoms such as carbon, nitrogen or oxygen. Bonding interactions between two d orbitals resulting in δ bonds in inorganic molecules are also prevalent. However, bonding interactions in inorganic molecules can also make use of suitably available d and porbitals at once. When a bond forms by lateral overlapping of p (or p*) and d orbitals present on two different atoms, it is called dπ-pπ bond. Such bonds are frequently observed in metal complexes such as carbonyls and nitrosyls. A simple example is sulfur trioxide (SO3). Main group compounds such as

phosphine oxides and disiloxane can also feature the dπ-pπ bonds. Presence of dπ-pπ bonding interactions usually result in shortening of bond length and planar configuration of involved atoms. However, observing such molecular features should not always be attributed to dπ-pπ bonds as several other factors may also be playing role. Hence, a careful evaluation of electronic and orbital symmetries must be made.

Diagram

Phosphine Oxide ( ) offers an example of dπ-pπ bond in molecules comprising of nonmetallic elements (Figure 1.9). In this case, all the p orbitals present on phosphorous are utilized in hybridization and hence, not available for lateral overlapping. Empty d orbital on phosphorous accepts electron density from filled p orbital available with oxygen atom. This dπ-pπ bond causes tighter binding of both involved atoms which is reflected in short bond distance (150 pm) and stability (bond energy 544 kJ/mol) of the bond.

Diagram

Bonding in metal carbonyls is classical example of dπ-pπ bond, where empty π* orbital present of oxygen atom accepts electron density from the filled d orbital of metals which results in the increase in bond order of metal-carbon bond (Figure 1.10).

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DEPARTMENT OF P.G. CHEMISTRY

INORGANIC CHEMISTRY –I

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Unit-II

INORGANIC CASE AND RING COMPOUNDS

Boron hydrides or boranes Boron forms several hydrides known as Boranes, composed solely of boron and hydrogen bonds and may be neutral or ionic. They are electron deficient species possess fewer valence electrons than are required for a localized bonding scheme. Their chemistry was first studied by Alfred Stock. Typical boranes are B_2H_6, B_4H_{10}, B_9H_{15}, $B_{10}H_{14}$, and $B_{20}H_{16}$. 7.3.2.1.

Nomenclature The nomenclature of boranes is somewhat simple. As mentioned before boranes exist as neutral and ionic species. Neutral Boranes: For neutral boranes, prefix di, tri etc. are used before 'borane' to indicate the number of boron atoms. The number of hydrogen atoms are indicated by writing the Arabic numeral in the parentheses at the end. For example:

BH_3 borane (3)

B_2H_6 diborane (6)

B_3H_7 triborane (7)

B_4H_{10} tetraborane (10)

B_5H_9 pentaborane (9)

B_5H_{11} pentaborane (11)

B_6H_{10} hexaborane (10)

$B_{10}H_{14}$ decaborane (14)

$B_{10}H_{16}$ decaborane (16)

$B_{20}H_{16}$ icosaborane (16)

It is to be noted that these names are based on the molecular formula and not on their structures. Generally, the numbers in the bracket are not written

Classification Higher boranes or borane clusters possess deltahedral structures which are somewhat complex in terms of their 3c-2e bonding (Figure 7.1). A deltahedron is a polyhedron that possesses only triangular faces, e.g., an octahedron. The boranes are mainly classified as:

1. closo-B_nH_{n+2} (closo-Greek for cage), Closo pertains to the most symmetrical form that is a closed polyhedra

2. nido-B_nH_{n+4} (nido-Greek for nest), nido has one of the vertexes removed from a regular polyhedral; (n + 1)-cornered polyhedron.

3. arachno-BnHn+6 (arachno-Greek for spider web). Arachno is a higher version of nido, with most highly connected boron vertex on the open face removed. Thus, the arachno form has two vertices missing; (n + 2)-cornered polyhedron.

4. Hypho- BnHn+8 (Greek: net like): They have the most open clusters in which the B atoms occupy n corners on an (n + 3)-cornered polyhedron.

5. Conjuncto- BnHn+10 (Latin: join together): They have structures formed by linking together of two or more of the above-mentioned type of clusters. They can also be written as having the general formula BnHn 2–, BnHn 4¯, BnHn 6¯, BnHn 8¯, BnHn 10¯ for closo, nido, arachno, hypho and conjuncto respectively. That is formally subtracting the number of H+ ions from the formula to make the number of boron and hydrogen atoms equal.

Diborane(6) Synthesis Diborane(6), B2H6 is a gas and like most boranes it is air-sensitive and catches fire. It is spontaneously hydrolyzed by water into hydrogen and boric acid.

One of the simplest methods is hydride abstraction from

BH4 - . BH4 - + BX3→ ½ B2H6 + HBX3 - (X = Cl, Br)

3 NaBH4 + 4 BF3 →2 B2H6 + 3 NaBF4

2 NaBH4 + I2→ B2H6 + 2 NaI + H2

At industrial scale, diborane is prepared by reduction of BF3 with sodium hydride

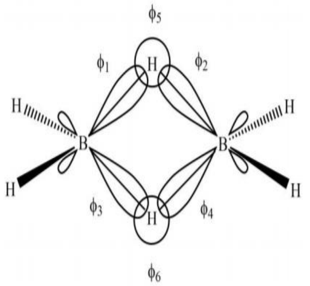
2 BF3 + 6 NaH→B2H6 + 6 NaF

Diborane acts as a very versatile reagent in synthesis of organoboranes. It also acts as a reducing agent for certain functional groups such as nitriles and aldehydes. Synthesis of some higher borane and their ions Most of the higher boranes can be prepared from diborane by controlled pyrolysis reactions.

B10H14 + R3N→ 2(R3NH)+ + B10H10 2¯ + H2

6 B2H6 + R3N →2(R3NH)+ + B12H12 2¯ + 11 H2

Structure and bonding In the earliest stages of decoding the structure of diborane, many errors and contradictions led to the establishment of the structure known today. The imminent deficiency of electrons in their structural formula indicates that there cannot be conventional 2c-2e (two center-two electron, two electrons are shared between two atoms) bonds. Thus, in the efforts to rationalize the structure of boranes, earliest concepts of multicenter bonding were developed. Languet-Higgins proposed the theory of 3c-2e (three center-two electron) bonds which greatly helped in the understanding of bonding in boranes. This implies that a pair of electrons can share more than two atomic centers.



The simplest borane i.e. diborane B2H6, is two electron short species for bonding when compared with its electron-precise analogue C2H6. Thus, diborane is two electron short of conventional 2c-2e bonding. It was proposed that BH3 exists as dimer to form B2H6. This was later confirmed by X-ray diffraction studies. These studies revealed the presence of terminal and bridging hydrogen atoms. The two-terminal hydrogen atoms present on each boron atom form the conventional 2c-2e bonds; thus, utilizing eight electrons out of the total of 12 electrons. The remaining two H atoms are bridging in nature. They link together the two boron centers (B-H-B) as shown in Figure 7.2. The bridging bonds are electron deficient utilizing only 4 electrons and form 3c-2e bonds. Thus, the deficiency of two electrons is compensated by the formation of the electron deficient B–Hμ–B bridging bonds (Figure 7.2). The higher boranes acquired a deltahedral structure and involve formation of several 3c-2e bonds.

Reactions Diborane

1. Reaction with oxygen

B2H6 + 3 O2 →B2O3 + 3 H2O; Exothermic reaction ΔH= -2160 kJ/mol

2.**Reaction with water**

B2H6 + 6 H2O →2 B(OH)3 + 6 H2

3. Reaction with acids • Diborane is hydrolyzed by weak acids such as alcohols.

B2H6 + 6 ROH (weak acid) →2 B(OR)3 + 6 H2 •

With HCl, a terminal hydrogen is replaced with chlorine

B2H6 + HCl→B2H5Cl + H2

4. **Reaction with chlorine**

$B_2H_6 + 6\ Cl_2 \rightarrow 2BCl_3 + 6\ HCl$

CARBORANES

Carboranes are large family of clusters which contain boron and carbon atoms. They are mixed hydrides of carbon and boron having electron deficient molecular structure. The carboranes are considered to be derived from $B_nH_n^{2-}$ by replacement of BH^- unit(s) with isoelectronic (since C atom has one more electron than B so CH moiety is isoelectronic with BH^-) and isostructural CH unit(s).

Each C-H group is regarded as donating 3 electrons to the framework electrons. So, a replacement of two BH^- will give a neutral molecule having general formula $B_{n-2}C_2H_n$. Carboranes having n =5 to n = 12 are known. They have delocalized electrons in the boron framework having one or more carbon atoms. Carboranes with higher boron content are dominant. The most studied boranes are $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$;thus, for carboranes, the best studied system is $C_2B_{10}H_{12}$ that is isoelectronic with $[B_{12}H_{12}]^{2-}$. Some other boranes and their corresponding carboranes are listed below:

Pentaborane(5) $B_5H_5^{2-}$ $[C_2B_3H_5]$, Hexaborane(6)$B_6H_6^{2-}$ $[C_2B_4H_6]$

Heptaborane(7) $B_7H_7^{2-}$ $[C_2B_5H_7]$, Octaborane(8) $B_8H_8^{2-}$ $[C_2B_6H_8]$, Nonaborane(9)$B_9H_9^{2-}$ $[C_2B_7H_9]$, Decaborane(10) $B_{10}H_{10}^{2-}$ $[C_2H_8H_{10}]$ Dianions $B_{11}H_{11}^{2-}$ $[C_2B_9H_{11}]$. Similar to boranes, carboranes are also classified as closo, nido and arachno which can be regarded as derivatives of B_nH_{n+2} (or related anion $B_nH_n^{2-}$), B_nH_{n+4} and B_nH_{n+6} respectively.

i. Closocarboranes: General formula is $C_xB_{n-x}H_{n-x+2}$ bonded by n+1 skeletal pair of electrons. Eg. Most common with x=2, $C_2B_{n-2}H_n$. One or both C atoms can be replaced by isoelectronic B^- ion to give $CB_{n1}H_{n+1}$.

ii. Nidocarboranes: General formula is $C_xB_{n-x}H_{n-x+4}$ bonded by n+2 skeletal pair of electrons. Here also C can be replaced by B^- or BH to give compounds that have their skeleton isostructural with B_nH_{n+4}

iii. Arachnocarboranes: General formula is $C_xB_{n-x}H_{n-x+6}$ bonded by n+3 skeletal pair of electrons. These are structurally related to B_nH_{n+6} (i.e. x =0); for example $C_2B_7H_{13}$ is related to B_9H_{15} and $B_9H_{14}^-$

Synthesis and reactions

. Synthesis

$$B_{10}H_{10} + 2Et_2s \rightarrow B_{10}H_{12}(Et_2s)_2$$

$$B_{10}H_{12}(Et_2s)_2 \rightarrow C_2B_{10}H_{12}$$

Reactions

1. Pyrolysis

$$C_2B_nH_{n+4} \rightarrow C_2B_nH_{n+2} + H_2$$

METALLOBORANES

Compounds in which metal atom bound with boron hydride group form the class of compounds known as metalloboranes. They can be classified into following categories: 1. Ionic hydroborates: Such as $NaBH_4$, $Ba(BH_4)_2$ 2. Metal hydroborates: Contain hydrogen bridge bonds, M–H–B. Eg: $Al(BH_4)_3$, $(Ph_3P)_2CuBH_4$. 3. Metal Carbaboranes: Include π-bonded 'sandwich compounds'. 4. Compounds containing metal-boron bonds except those in the above category (3). Like boranes and carboranes, metalloboranes can also be structurally classified as closo, nido, arachno, crypto and commo.

METALLACARBORANES

Metallacarboranes or metallacarboboranes are metal complexes where carboranes or heteroboranes act as ligands with at least one metal atom incorporated in the cage framework. They are inorganic polyhedral clusters which contain carbon, boron, hydrogen and metal ion in different combinations. Hawthorne and co-workers first synthesisedmetallacarboranes in the mid-1960s. A typical example of metallacarborane is the $[C_2B_9H_{11}]^{2-}$ (dicarbollide) cluster having a metal atom sandwiched between two dicarbollide units. Here, the dicarbollide, binds as η^5 and thus, considered to be isolobal with cyclopentadienyl ligand, somewhat similar to ferrocene. Hawthrone suggested that $[C_2B_9H_{11}]^{2-}$is isoelectronic with $C_5H_5^-$ and therefore, it should be capable of acting as the π ligand in similar metallocenes compounds. The other highly investigated metallacarborane is nido-$[2,3\text{-}R_2C_2B_4H_4]^2$(R=H or a cage carbon substituents), having pentagonal bipyramidal structure.

There are two different types of metallacarboranes, endo- and exo. In endo- type, the metal centre is sandwiched between two carborane clusters. Whereas, in exo- type, a metal fragment is linked to the periphery of the carborane skeleton, generally through B-H···M interactions.

$$B_{10}C_2H_{12} + CH_3O^- + 2CH_3OH \rightarrow B_9C_2H_{12}^- + B(OCH_3)_3 + H_2$$

$$B_9C_2H_{12}^- + NaH \rightarrow B_9C_2H_{11}^{2-} + H_2 + Na^+$$

$$2B_9C_2H_{11}^{2-} + FeCl_2 \rightarrow [(B_9C_2H_{11})_2Fe]^{2-} + 2Cl^-$$

WADE'S RULE

A set of rules were laid down by Kenneth Wade to predict the shape of boron clusters. These rules correlate skeletal structures of boranes, carboranes, heteroboranes and their anions (closo, nido, arachno, hypho) with the number of skeletal electron pairs present in them. According to the rule, suppose a cluster has say 'n' skeletal atoms (that is the vertices) then it will adopt closo structure if it contains n+1 skeletal bonding electron pairs. Similarly, nido if n+2, arachno if n+3 and hypho if n+4 skeletal bonding electron pairs respectively and so on. To determine this, one needs to know the number of skeletal electron pairs in a cluster which can be determined by following the electron count for various donating units as given below. Each BH unit gives 2 skeletal bonding electrons. B as such gives three skeletal electrons. Each C-H unit of a carboranecontributes 3 skeletal bonding electrons.

Each additional H furnishes 1 skeletal bonding electron. Ionic charges must be included in the electron count. For borane clusters with other hetero-elements, C, Si, Ge and Sn of a cluster is replaced with a BH unit; N, P and As with a BH2 unit and S andSe with a BH3 unit for counting purpose

Examples

B5H9	**C2B10H12**
5BH=5x2=10e	2CH=3x2=6e
4H=4x1=4e	10BH=2x10=20e
14e=7Pair	26e=13Pair
n=5,n+2=nido	n=12,n+1=closo

PHOSPHORUS-NITROGEN cyclic compounds

PHOSPHAZENES (PHOSPHONITRILIC / P–N COMPOUNDS)

The term phosphazene or phosphonitrile includes those compounds which have phosphorous and nitrogen atom joined alternatively by single or double bonds. Overall, they may constitute a ring or a chain motif in which nitrogen is trivalent and phosphorous is pentavalent. The empirical formula for very first phosphazene N3P3Cl6 (white crystalline product obtained by reaction of ammonia with phosphorous pentachloride) was derived after some errors. It was first considered to be NPCl2 but later found out to be a trimer having a cyclic structure (proposed by H.N. Stokes). The trimer on heating yielded an elastomer known as the “inorganic rubber”.

The cross linked ‘inorganic rubber ‘was formed by the reaction of [NPCl2]n with trace amounts of H2O. Thus, if the reaction is carried out in the absolute absence of atmospheric moisture, non-crosslinked and soluble macromolecules of [NPCl2]n could be prepared. Reaction of organic nucleophiles with [NPCl2]n can result in the replacement of chlorine atom and hence generate stable poly(organo)phosphazenes. A wide range of polymers with mixed substituents having varied properties can be generated if two different nucleophiles are used on the same molecule i. Poly(dichloro)phosphazene [NPCl2]n is a key precursor in the synthesis of almost all polymeric phosphazenes (Scheme 1.1)

Preparation

nPCl5+nNH4Cl→(NPCl2)n+4nHCl

Reactions

NPCl6+6NaOR→N3P3(OR)6+6NaCl

STRUCTURE AND BONDING IN PHOSPHAZENES

Structure of $(NPCl_2)_3$ It has a planar six-membered ring. The bond angles are consistent with sp^2 hybridization (118° for P–N–P) of nitrogen and sp^3 hybridization of phosphorous (108° for Cl–P–Cl angle). See Figure 2.2 below in which all bond lengths are reported in angstrom (Å) unit. Two of the sp^2 hybrid orbitals of nitrogen lone pair of electrons. Thus, the remaining one electron is left in the unhybridizedpz orbital.

In case of phosphorous, the four sp^3 hybridized orbitals accommodate four electrons and are used in σ bonding. The remaining one (fifth) electron occupies a vacant d orbital. The resonance structures similar to benzene can also be drawn for $(NPCl_2)_3$. However, the nature of bonding here does not follow the same resonancedelocalization and aromaticity in these inorganic cyclic molecules has been a matter of debate since long. Despite the presence of delocalization in some phosphazenes, not all molecules maintain the planarity of ring. This factor does not make them unstable. The ultra violet spectra of phosphazenes does not show structural features similar to those of aromatic organic compounds and also it is very difficult to reduce their unsaturated bonds. Furthermore, unlike benzene, the π bonds in cyclophosphazene have contribution from both p and d orbitals. Several theories have been suggested for the dπ-pπ bonding.

Structure of tetrameric phosphazenes Tetrameric phosphazenes have a more flexible structure than their trimeric analogues. They may have a planar structure or tub, boat, chair, crown and saddle conformations. The presence of a definite structure is not very obvious, intermolecular forces play a major role in any structure. The structure of $(NPF_2)_4$ is planar and $(NPCl_2)_4$ is known to exist in two forms. The most stable is the 'chair form' also called as the T form (Figure 2.5). The other form has a tub conformation. The nonplanar structures do not prevent extensive delocalization in the rings. Organic analogue of tetrameric phosphazene is the cyclooctatetraene. It is a nonaromatic compound because of lack of planarity and secondly, it does not obey the Hückel's rule of $(4n+2)\pi$ electrons. Huckle's rule was formulated on pπ-pπ bonding and hold well for organic compounds having n=1 to n=4. Now, these inorganic compounds do not hold organic rules for aromaticity. Here, the d orbitals are involved which overrules the Hückel's rule. The diffused nature of d orbitals is suitable for bonding in nonplanar systems providing greater flexibility to the ring.

Diagram

SULFUR NITROGEN COMPOUNDS

2.7.1 Significance

The electron rich $(SN)_X$ compounds can serve as donors in charge transfer complexes and unlike phosphonitriles, the cyclic $(SN)_X$ compounds follow Hückel's rule of aromaticity. These factors have attracted much interest to their synthesis, bonding and exploration of their overall chemistry. The S-N compounds have been explored for their bonding with transition metals and also for their magnetic and conducting properties. A variety of acyclic and cyclic S-N compounds are known. S_2N_2, even though a strained structure, is the smallest homoleptic ring known to exist. It is the most important precursor for the synthesis of several polythiazyl $(SN)_X$

Preparation

SO2Cl2+4NH3=SO2(NH2)2+2NH4Cl

3SO2(NH2)2=[(SO2N)3]3-+NH4+

Structure and bonding Some S–N compounds show planar ring structure. It has been found that they follow Hückel's rule of (4n+2)π electrons. If we consider that in these planar cyclic S–N compounds each atom contributes one electron to the σ bond and two electrons to a lone pair, then sulfur has two π electrons and nitrogen has one π electron. Or we can also explain the electron distribution as follows. At each S–N unit, two electrons are allocated for sigma bonds and two electrons for each S and N atom for non-bonding lone pairs. Thus, one electron at N at two electrons at S are left which can be used in the cyclic π-system of the ring. Considering these electron's distribution, we can say that S2N2 has 6π electrons; S3N3$^-$ has 10π electrons; S4N3 + has 10π electrons and S5N5 + has 14π electrons. However, in contrast to the stable π-organic molecules, the S–N compounds mentioned above have electrons in the antibonding (π*) molecular orbitals which has a weakening effect on S–N bond. The stability of these compounds can be ascribed to the following factors:

(a) The higher electronegativity of nitrogen compared to sulfur or oxygen lowers the energy of antibonding (π*) orbitals thus bringing them closer to bonding region. (b) The longer S–N bond lengths reduces the mutual repulsion between any other pair of electrons, this lowers the energy of the π-system. i) Disulfurdinitride (S2N2): It is cyclic square planar molecule with S–N bond length of 1.65Å. The N–S–N angle is 89.6° while the S–N–S angle is 90.4° (Figure 2.8). ii) Trisulfurtrinitride anion (S3N3$^-$): The structure of [nBu4N]+ [S3N3 -] is well established. It has a planar six membered ring with S–N bond length in the range

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COORDINATION COMPOUNDS

Crystalfieldtheory:-

PostulatesofCrystalFieldTheory

(i) The central metal cation is surrounded by ligands which contain one or more lone pairs of electrons.

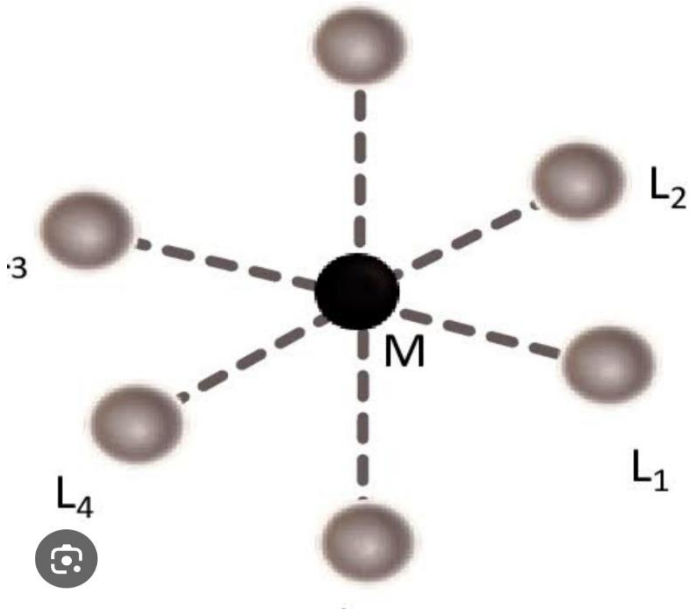
(ii) The ionic ligands (e.g., F-, Cl-, CN-, etc.) are regarded as negative point charges (also called point charges) and the neutral ligands (e.g., H_2 O, NH,, etc.) are regarded as point dipoles or simply dipoles, i.e., according to this theory neutral ligands are dipolar. If the ligand is neutral, the negative end of this ligand dipole is oriented towards the metal cation.

(iii) The CFT does not provide for electrons to enter the metal orbitals. Thus the metal ion and the ligands do not mix their orbitals or share electrons, i.e., it does not consider any orbital overlap.

(iv) According to CFT, the bonding between the metal cation and ligand is not covalent but it is regarded as purely electrostatic or coulombic attraction between positively-charged (i.e., cation) and negatively- charged (i.e., anions or dipole molecules which act as ligands) species. Complexes are thus presumed to form when centrally situated cations electrically attract ligands which may be either anions or dipole molecules. The attraction between the cations and the ligands is because the cations are positively charged and the anions are negatively charged and the dipole molecules, as well, can offer their negatively incremented ends of such electrostatic attractions.

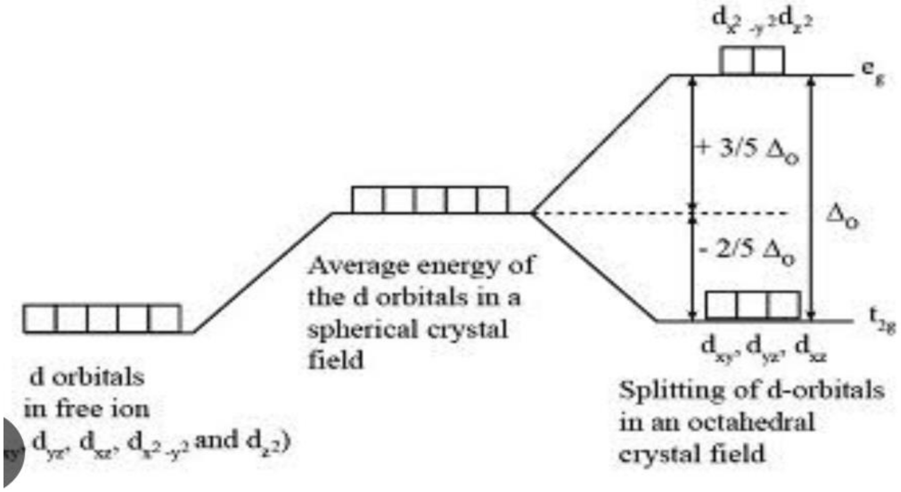
2.3 **CRYSTALFIELDSPLITTINGINOCTAHEDRALCOMPLEXES**

Consider an octahedral complex, [ML]ot in which the central metal cation, M™ is palced at the centre of the octahedron and is surrounded by six ligands which reside at the six corners of the octahedron as shown in Figure 2.1 The three axes, viz. x, y and z-axes which point along the corners have also been shown

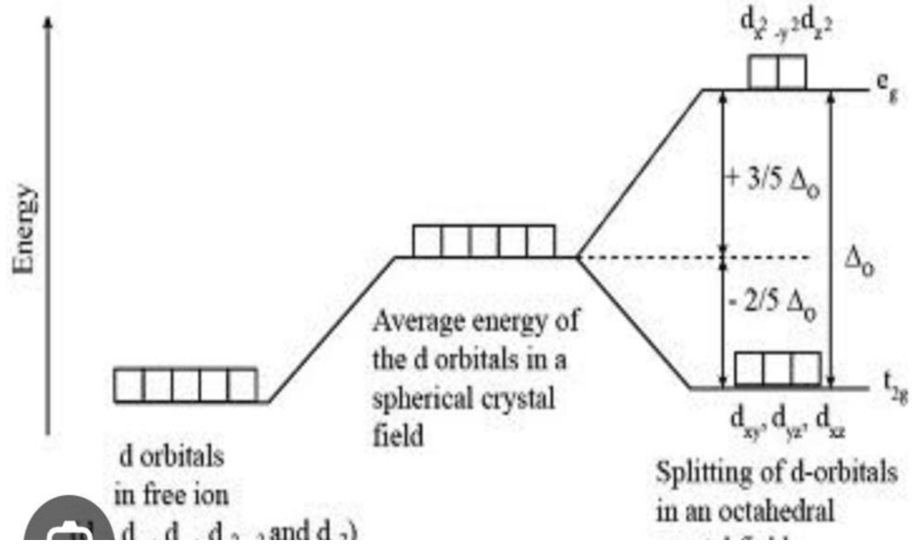


Now suppose both the ligands on each of the three axes are allowed to approach towards the metal cation, M" from both the ends of the axes. In this process the electrons in d-orbitals of the metal cation are repelled by the negative point charge or by the negative end at the dipole of the ligand. This repulsion will raise the energy of all the five d-orbitals. If all the ligands approaching the metal ion are at equal distance, the energy of each of the five d-orbital will raise by same amount. But this is not the case, since the takes of the two e orbitals lie directly in the path of the approaching ligands, the electrons in these orbitals will experience greater for of repulsion than those in three t orbitals (i.e., d d and d orbitals) whose lobes are directed in space between the path of the approaching ligands, i.e., the energy of e orbitals is increased while that tof t is decreased. Thus we find that under the influence of approaching ligands, the five d-orbitals which were originally degenerate in the free metallic cation are now split (or resolved) into two levels, viz., t, level which is triply degenerate and is of lower energy, and e level which is doubly degenerate and is of higher energy (see Figure 2.2). In other words the degeneracy of the five d-orbitals is removed under the influence of the ligands. The separation of five d-orbitals of the metal ion into two sets having different energies is called crystal field splitting or energy level splitting. This concept of crystal field splitting makes the basis of CFT

The energy gap between t_2 and e sets is denoted by A, or 10 2g where 0 in A, indicates an octahedral arrangement of the ligands round central metal cation. This energy difference arises because of the differe in electrostatic field exerted by the ligands on t, and e, sets of orbital 2g the central metal cation. A or 10Dq is called crystal field splitting ene With the help of simple geometry it can be shown that the energy o orbitals is 0.4 A (=4Dq) less than that of hypothetical degenerate d-orbi (No splitting state shown by dotted line in Figure 2.2) and, hence, that c orbitals is 0.64 (=6Dq) above that of the hypothetical degenerate d-orbit Thus, we find that 1, set loses an energy equal to 0.44 (= 4Dq) while e 28 gains an energy equal to 0.6A (= 6Dq). In Figure 2.2 the loss and gai energies of t and e orbitals is shown by negative (-) and positive (+) sig respectively. A is generally measured in cm^1.



CRYSTALFIELDSPLITTINGINTETRAHEDRALCOMPLEXES: In tetrahedral complexes [ML] the form ligands occupy the alternate corners of a cube, in the centre of which is placed the metal cation (Refer Figure 2.4). The four ligands are lying between the three axes, viz., x, y and z which pass through the centre of the six faces of the cube and hues go through the centre of the cube. So, the t, orbital (d, d, d) are lying between the axes, i.e., directly in the path of the ligands. Hence these orbitals will experience greater repulsive force from the ligands. e (d2/d22) orbitals lie along the axes, i.e., along the space between the ligands, thus will experience lesser repulsive force



Unsequently the d orbitals again split into two sets as shown in Figure 2.5. The order of energy of t, and e orbitals is reverse as observed in case of octahedral complexes. The energy difference between 1, and e orbitals for 28 tetrahedral complexes is designated as At. It is shown that Ar< A, because the orbitals do not point directly at the ligands and also there are only four ligands in tetrahedral complexes against six ligands in octahedral complexes, for the same metal and ligands and the same inter nuclear distances. It is also shown that,

∆t = 0.45 A. Thus the energy of the 1, set is raised by 0.4 ∆t= 0.18 Δ while that of e set is lowered by 0.6 ∆t=0.27 A. The relation namely At = 0.45 A, also shows that, other things being equal, the crystal field splitting in a tetrahedral complex will be about half the magnitude of that in an octahedral complex.

In case of tetrahedral complex, since At is generally less than P (At < P), the electrons tend to remain unpaired and hence only high spin tetrahedral complexes are known, i.e., low complexes.

3.2 **ORIGINOFTETRAGONALANDSQUAREPLANARSYMMETRIES**

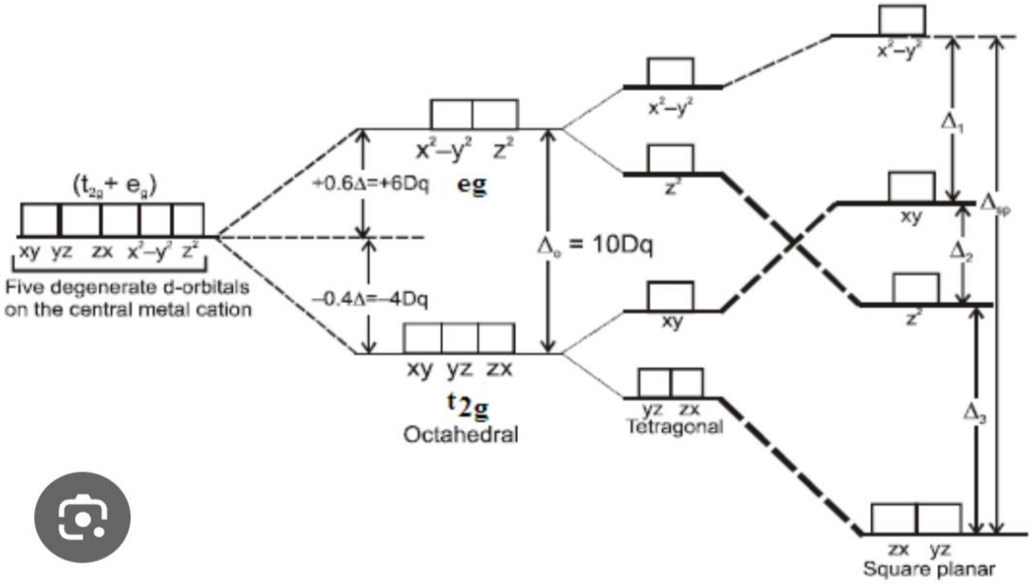
Crystal Field Theory (CFT) describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. CFT qualitatively describes the strength of the metal-ligand bonds. Based on the strength of the metal-ligand bonds, the energy of the system is altered. This may lead to a change in magnetic properties as well as colour. In CFT, it is assumed that the ions are simple point charges (a simplification). When applied to alkali metal ions containing a symmetric sphere of charge, calculations of bond energies are generally quite successful. The approach taken uses classical potential energy equations that take into account the attractive and repulsive interactions between charged particles (that is, Coulomb's Law interactions).

In a tetrahedral complex, there are four ligands attached to the centralmetal. The d orbitals also split into two different energy levels. The top threeconsist of the do, d and d orbitals. The bottom two consist of the dx2-y2and dz2 orbitals. The reason for this is due to poor orbital overlap betweenthe metal and the ligand orbitals. The orbitals are directed on the axes, whilethe ligands are not. d-orbital splitting for tetrahedral coordination can beexplained by considering a cube, an octahedron, and a tetrahedron that arerelated geometrically. Octahedral coordination results when ligands are placedin the centers of cube faces. Tetrahedral coordination results when ligandsare placed on alternate corners of a cube.

Square planar molecular geometry describes the spatial arrangement of atoms that is adopted by certain chemical compounds. The molecules of this geometry have their atom positioned at the corners of a square on the same plane about a central atom. In square planar molecular geometry, a central atom is surrounded by constituent atoms, which form the corners of a square on the same plane. The geometry is prevalent for transition metal complexes.with d8 configuration. In principle, square planar geometry can be achieved by flattening a tetrahedron. As such, the inter-conversion of tetrahedral and square planar geometries provides a pathway for the isomerization of tetrahedral compounds.

Firstly we shall consider the origin of tetragonal and square planar geometries from the regular octahedral geometry of complexes. Consider a regular (symmetrical) octahedral ccomplex

[M(L), (L),] in which M is the central metallic cation, L are two trans- ligands (i.e., L are the ligands lying along the z-axis) and L are the basal equatorial ligands lying in xy plane. In this complex all the six bond distances (four M-L, and two M-L, distances) are equal [Refer Figure 3.1(a)]. Now if two L, ligands are moved slightly longer from the central metal cation, M so that each of the two M-L distances becomes slightly longer than each of the four co-planar M-L, distance, the symmetrical shape of octahedral complex gets distorted and becomes distorted octahedral shape [Refer Figure 3.1 (b)]. In this shape, since the two trans ligand have elongated, the distorted octahedral shape is also called elongated distorted octahedral shape. Elagnated distorted octahedral geometry is also called tetragonally distorted octahedral shape or simple tetragonal shape. Obviously the elongation of two trans ligands takes place along +z and-z axis. Elangated distorted octahedral geometry is also called tetragonally distorted octahedral shape or simply tetragonal shape. Now if the two L ligands are completely removed away from the axis, the tetragonally distorted octahedral shape becomes square planar which is a four-coordinated complex.



Thus, for n = 0, μ = 0.0 (diamagnetic); n = 1, μ = 1.73 B.M; n = 2, = 2.83 B.M;

η = 3, μ = 3.87 B.M; n = 4, μ = 4.90B.M; η = 5, μ = 5.92 B.M.

(ii) Whether the give complex ion is high spin or low spin.

(iii) Whether the ven complex ion is paramagnetic or diamagnetic.

3.6 LIMITATIONS OF CRYSTAL FIELD THEORY

Some of the Limitations of CFT are:

(i) The CFT ignores the attractive forces between the d-electrons o the metal ion and nuclear charge on the ligand atom. Therefore, al properties are dependent upon the ligand orbitals and their interaction with metal orbitals are not explained.

(ii) In CFT model partial covalency of metal-ligand bonds are not taken into consideration. According to CFT metal-ligands **bonding is purel electrostatic.**

(iii) In CFT only d-electrons of the metal ion are considered, the othe orbitals, such as s, p, p, and p, are not taken into considered.

(iv) In CFT π orbitals of ligand are not considered.

(v) This theory can not explain the relative strength of the ligands, i.e., i

can not explain that why H,O is a stronger ligand than OH according

to spectrochemical series.

(vi) It does not explain the charge transfer spectra on the intensities of the absorption bands.

FactorsAffecting crystal field theory:

ThemagnitudeofA**,** dependsonmanyfactorsdiscussedbelow**.**

A. Nature of Metal Cation

Theeffectofthenatureofmetalcationcanbestudiedas**:**1.DifferentChargesonthe*Cation*ofthe SameMetal**:** TheA**,** valueofthecationofthesamemetalhavingsameoxidationstateisalmostsamebutthecationhavinghigheroxidationstatehas **a** largervalueof **Δ.** Forexample

(a) $\Delta°$for $[Fe^{2}(H_2O)]^{2}$ = 10,400 cm^{21}….3d6

Δ° for $[Fe(H_2\ O)]+$ = 13,700 cm^{21} ….3d5

(b) Δ° for $[Co(H_2\ O)]+$ = 9,300 cm….3d7

Δ° for $[Co(H_2\ O)]$ = 18,200 cm… 3d6

This is because the central ion with higher oxidation state (i.e., with higher charge) will polarise the ligands more effectively and thus the ligands would approach such a cation more closely than they can do the cation of lower oxidation state, resulting in larger splitting.

2. Different Charges on the Cation of the Different Metals: The cation with higher oxidation state has a larger value of A, than with that of lower oxidation state. For example,

Δ° for $[V(H_2\ O)]$ = 12400 cm^{21}
Δ° for $[Cr(H_2\ O),]$ = 17400 cm-^{1}

3. In case of complexes having same cations with the same charges but with different number of d-electron, A, decrease with the increase of the number of d-electrons. For example,

$\Delta^\circ$for $[Co(H_2\ O)]+$= 9,300 cm …..3d7
$\Delta^\circ$for $[Ni(H_2\ O)]+$ = 8,500 cm^{21}…..3d8

From the combination of 1, 2 and 3 mentioned above it can be concluded

that:

(a) For the complexes having the same geometry and the same ligands but having different number of d-electrons, the magnitude of A decreases with the increase of the number of d-electrons in the central metal cation (No. of d-electrons
(b) In case of complexes having the same number of d-electrons the magnitude of A, increases with the increase of the charges (i.e. oxidation state) on the central metal cation (oxidation state Δ).

4. Quantum Number (n) of the d-Orbitals of the Cation: The A, increase about 30-50% form 3d to 4d and by about the same amount from 4d" to 5d complexes.

Δ° for $[Co^3\ (NH)]$ = 23,000 cm^{1} ….3d6
Δ° for $[Rh^3\ (NH)]$ = 34,000 cm…….4d6
Δ° for $[Ir^3\ (NH)]$ = 41,000 cm^{2}. ….5d6B.

SpectrochemicalSeries:

Aspectrochemical series is a list of ligands ordered on ligand strength and a list of metal ions based on oxidation number, group and its identity. In Crystal Field Theory or CFT, the ligands modify the difference in energy between the d orbitals (A) called the ligand-field splitting parameter for ligands or the crystal-field splitting parameter, which is mainly reflected in differences in colour of similar metal-ligand complexes.

We have seen earlier that stronger ligands are those which exert a stronger field on the central metal ion and hence have higher splitting power while weaker ligands have comperatively lower splitting power as they exert weak field on the central metal cation. This can be shown in Figure 2.3 where strong ligand CN- give larger value of Δ and weaker ligand F- yield a smaller value of Δ°.

(a) Five d-Orbitals in the Free Metal Ion

(b) Splitting of d-Orbitals in Presence of Strong(er) Ligands

(c) Splitting of d-Orbitals in Presence of Weak(er) Ligands.

Figure shows that not only A, which represents the energy difference between the t_2 and e-sets of orbitals, is smaller in the weak(er) 2g g field complex than in the strong(er) field, but also that both the t_2 and e- 2g levels of the weak(er) field are correspondingly closer to the level of the degenerate five d-orbitals of the free isolated metallic ion than are those, respectively, of the strong(er) field.

The common ligands can be arranged in the order of their increasing splitting power to cause d-orbitals splitting. This series is called spectrochemical series and is given below:

I-< Br< Cl- - SCN- - N-3< $(C_2 H_2 O)$, PS-2< F- < (NH2)2CO < OH- <CO^2- - $H_2 O$ < NCS- - H- < CN- <$NH_2 CH_2 CO_3$ < NH_1 - $C_2 H_2 N$ <en 2 SO2- 3<$NH_2 OH$ <NO-2 <phen< H-<CH-3< CN-, CO.

This series shows that the value of A in the series also increase from left to right.

The order of field strength of the common ligands shown above is, in fact, independent of the nature of the central metal ion and the geometry of the complex.

The increase in the value of A, on proceeding from left to right in the spectrochemical series is quite evident from the values of A for some octahedral complexes given in Table 2.3 which clearly shows that since on proceeding from 6Br→ 3 en, the field strength of the ligands increases, the value of A, also correspondingly increases.

Mean Pairing Energy (P):

The energy which is required for pairing of two electrons against electron-electron repulsion in the same orbital is called the mean pairing energy far one electron pair. It is generally expressed in cm^1. Pairing energy depends on the principal energy level (n) of the d-electrons.

If m is the total number of paired electrons in t_2 and e, orbitals, then, 2g Total pairing energy for m electron pairs = mP cm-^{1}. g

Predicting Spin State of an Octahedral Complex:

The spin state of an octahedral complex can be predicted by comparing the values of A, and P. A, tends to force as many electrons to occupy t_2 orbitals 2g while P tends to prevent the electrons to pair in t2g orbitals

(i) When A_1 >P, the electrons tend to pair and hence low spin octahedral complex is obtained.

(ii) When A<P, the electron tends to remains unpaired and hence high spin octahedral complexes are obtained.

C. Crystal Field Stabilization Energies:

From Figure 2.3 it is clear that electrons will tend to occupy the lower energy (12) orbitals in order to achieve stability. Each electron entering the t2g orbital stabilizes the complex ion by 0.4 A units and each electron entering the higher energy (e) orbital destabilizes the complex ion by 0.6 A i.e., stabilization energy in the two cases is 0.4 A and 0.6 A, respectively. The gain is energy achieved by preferential filling up of orbitals by electrons is known as Crystal Field Stabilization Energy (CFSE). Creater the amount of CFSE of the complex, greater is the stability of the complex. The derivation far CFSE is discussed below.

Consider a d ion containing to Pe configuration in which p is the 2gg number of electrons in t_2 set, q is the number of electrons in e, set and x = p + q. So,

Change in energy (in terms of A) for te configuration: 2g g = Loss in Energy due to p Electrons in t in Energy due to q Electrons in e Set g =-0.4 A, xp + 0.64 × q = [-0.4 p+0.6q] Δo 12 Set + Gain 2g (2.1) Now, since A= 10Dq, the above expression can also be written as: Change in energy (in terms of Dq) for t2g g configuration.

= [-0.4p+0.6q] × 10 Dq = [-4p + 6q] Dq ... (2.2)

Thus Equations (2.1) and (2.2) give the energies of d* ion containing t Pe configuration. The change in energy for d* ion containing to Pe 2gg 2gg configuration calculated as above is called Crystal Field Stabilization Energy

(CFSE) of d* ion, since it stabilizes d-orbitals by lowering their energy which results from their splitting into t_2 and e orbitals. 2g

In the derivation of Equations (2.1) and (2.2) we have not considered the pairing energy, P, of d* ion which is the energy required to pair two electrons against electron-electron repulsion in the same orbital. If the pairing energy of the ion is also involved in the t, Pe configuration of a given d* ion, then 2g 2g g CFSE of the ion is given by the expression:

CFSE = [-0.4p + 0.6q] A + mP 0 = [-4p + 6q] Dq + mP (A = 10Dq) ... (2.3) (2.4) ...

Here m is the total number of paired electrons in 12g t and eg orbitals. Equations (2.3) and (2.4) have been used to calculate the CFSE values (in terms of A, and Dq, respectively).

For do to d^{1o} ions of high spin and low spin octahedral complexes. The values calculated from above equations are listed in Table 2.5 and Table 2.6.

In Table 2.5, the CFSE values (in the units of A, and Dq) for d configuration (x = 0 to 10) of the central metal ion in weak field (spin free or high spin) octahedral complexes. m = Total number of paired electrons in t t2 and e 2g orbitals, P = Mean pairing energy, p + q = x = 0, 1, 2, ..., 8, 0 or 10.

Jahn-Teller Effect:

The Jahn-Teller theorem essentially states that any nonlinear molecule system possessing electron degeneracy will be unstable and will undergo distortion to form a system of lower symmetry as well as low- energy and thus the degeneracy will be removed.

This effect describes the geometrical distortion of molecules and ions that is associated wi electronically degenerate configurations. A configuration is said to be electronically degenerate if more tha one sites are available for the filling of a single electron. The Jahn-Teller effect is generally encountered octahedral transition metal complexes. The phenomenon is much more common in hexacoordinated complex of bivalent copper. The de configuration of Cu2+ ion yields three electrons in the doubly degenerate e orbita set, leading to a doubly degenerate electronic state as well. Such complexes distort along one of the molecul four-fold axis (always labeled the z-axis), which has the effect of removing the orbital and electron. degeneracies and lowering the overall energy. The distortion usually occurs via the elongation the metal-ligand bonds along the z-axis, but sometimes also occurs as a shortening of the same bonds instead. Moreover, thJahn-Teller theorem predicts the presence of an unstable geometry

only and not the direction of the distortio When distortion involving elongation occurs to decrease the electrostatic repulsion between the electron-pa on the ligand-attached and any extra electrons in metal orbitals with a z-component; and hence lowering th energy of the metal complex. Inversion center is retained after z-out as well as z-in the distortion. Symmetric configurations possess electronic degeneracy while the unsymmetrical ones do not. Various symmetrical an unsymmetrical configurations are given below.

Table 10. Symmetrical and Unsymmetrical 12g and eg orbitals.

Symmetrical configurationsUnsymmetrical configurations

t2g0,t2g3,t2g6t2g1,t2g2,t2g4,t2g5

eg0,eg4,eg2 (high-spin)eg1, eg3, eg^2 (low-spin)

Now, the conditions for different kinds of distortion can be summed up as:

Table 11. Conditions for Jahn-Teller distortion.

Type of distortionConfiguration required

No distortiont2g (symmetrical) + eg (symmetrical)

Slight distortiont2g (unsymmetrical)

Strong distortioneg (unsymmetrical)

Let the case of the low-spin Cot octahedral complex. The corresponding electronic configuration is 12g eg^1. Owing to the electronically degenerate state, the Jahn-Teller distortion is expected. Now suppose that the single electron of eg set is present in d^2 orbital; the ligands approaching from z-axis will feel more repulsion than the ligands coming from x and y-axis. Therefore, the bonds along z-axis will be weaker in comparison to the bond along x and y-axis. This in a tetragonal elongation about z-axis with two longer and four dalalinstitute.co 19-9002025820) shorter bonds. This is formally called as z-out distortion. On the other hand, if the single electron of eg set is e.com present in d_1 2-2 orbital; the ligands approaching from x and y-axis will feel more repulsion than the ligands coming from z-axis. Therefore, the bonds along x and y-axis will be weaker in comparison to the bond along z-axis. This results in a tetragonallyflattened octahedral geometry with two shorter and four longer bonds. This is formally called as about z-axis z-in distortion., Consider the following examples

1. [Co(CN)6]: It is a low-spin complex with 12g eg electronic configuration and will undergo strong Jahn- Teller distortion.

2. [Cr(NH3)6]3+: It is a high-spin complex with 12g^3 ex electronic configuration which is completely symmetrical; and therefore, will not show any Jahn-Teller distortion.

3. [FeF6]: It is a high-spin complex with 12g eg^2 electronic configuration and will undergo slight Jahn-Teller distortion.

➤ Energetics of Jahn-Teller Distortion

The Jahn-Teller distortion results in a system of lower symmetry and lower energy. This is actually the opposite of what is expected. Generally, symmetry leads to stability; but the Jahn-Teller effect is actually an exception to this statement. Therefore, it is necessary to discuss the driving force responsible for this behavior. The magnitude of Jahn-Teller effect is larger where the electron density associated with the

degenerate set orbitals is more concentrated. Hence, Jahn-Teller effect plays a significant role in determining the structure of transition metal complexes with active 3d-orbitals. The whole energetics of the Jahn-Teller can be understood by the case study of d and d' complexes.

1. Cu2+ complexes: The electronic configuration of free Cu2+ ion is d'; and in an octahedral environment, it is 12g eg^3. Before we put any conclusive remark on the direction or nature of the distortion, we shall find the crystal field stabilization energy for z-out as well as for z-in case.

i) Crystal field stabilization energy for z-out distortion:

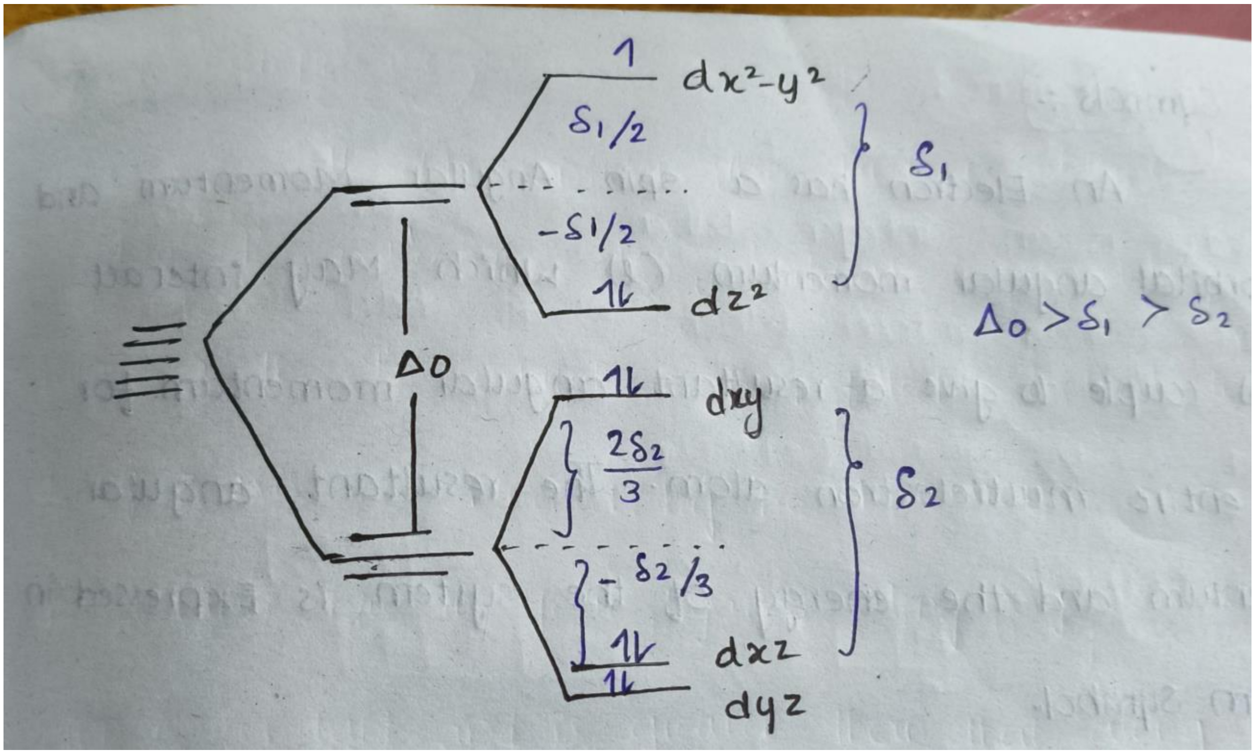


Figure 58. The splitting pattern and filling of d-orbital set of Cu2+ in octahedral and subsequently in the tetragonally elongated complex due to Jahn-Teller effect.

CFSE due to distortion = Energy of the distorted complex (E2) - Energy of the complex without distortion (E1)

E_1 = 6(-0.44%) + 3(+0.64o)

E_1 = -0.64

E2=4(0.4082/3)+2(0.44+282/3)+2(+0.60 – 81/2) +1(+0.64, +81/2)

E2 = -0.64. – 81/2

CFSE due to distortion = E2-E1 = -81/2

Hence, the crystal field stabilization due to z-out distortion is -δı/2.

ii) Crystal field stabilization energy for z-in distortion:

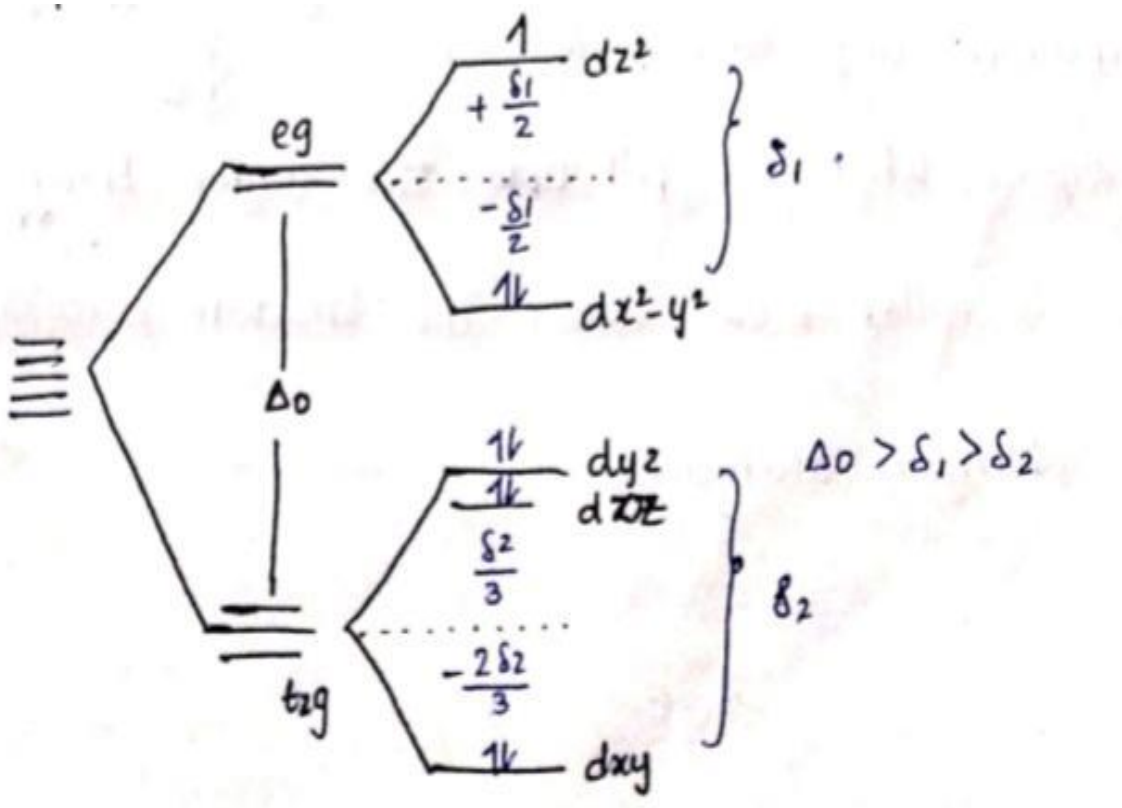


Figure 59. The splitting pattern and filling of d-orbital set of Cu^2+ in octahedral and subsequently in theTetragonally compressed complex due to Jahn-Teller effect.

CFSE due to distortion = Energy of the distorted complex (E2) Energy of the complex without distortion (E1)

E2 = 4(-0.440 – 282/3) + 2(-0.44 + 82/3)+2(+0.60 – 81/2) + 1(+0.64, +81/2) E2 = -0.64 - 81/2

CFSE due to distortion = E2 - E_1 = -81/2

Hence, the crystal field stabilization due to z-in distortion is -81/2.

Hence, the magnitude of crystal field stabilization in z-out case is same as that is present in z-in complex. This implies that Jahn-Teller effect cannot predict the direction of the distortion. However, it has been observed that it is the z-out case that dominates in most of the cases. It may depend on the repulsive forces between the d-electrons and the ligands, so the odd electron will prefer d-2-orbital more than dx2-y2 due to the lesser number of ligands it will repel with. Moreover, when a z-in distortion occurs, one can also view it terms of equatorial elongation while z-out will mean the weakening of two axial metal-ligand bonds. In other words, it is easier to weaken two bonds rather stretching four metal-ligand bonds.

Static and Dynamic Jahn-Teller Distortion:

On the basis of the observed geometry, the Jahn-Teller distortion can be classified in two types given below.

1. Static Jahn-Teller distortion: Some molecules show tetragonal shape under all conditions i.e., in so state and in solution state; at lower and relatively higher temperatures. This is referred to as static Jahn-Tel distortion. Hence the distortion is strong and permanent. For example, in CuF2 lattice

2. Dynamic Jahn-Teller distortion: If the energy gap between z-out and z-in is smaller than the availa thermal energy, the complex ions tend to attain both states, i.e., compressed and elongated. This is known Som Market, Sector 14 the "Dynamic Jahn Teller Effect". consider complex: For examples, K_2 Pb[Cu(NO3)6].

Consequences of Jahn-Teller Distortion

Some of the main consequences of the Jahn-Teller effect in the field of chemical science are given below.

1. Irving-William series: Stability of metal complexes with a given ligand follows the order Mn2+ < Fe2+ < Co2+ < Ni2+ < Cu2+ > Zn2+. The increase in the stability of the complexes from Mn^{2} to Zn^{2} is the increase effective nuclear charge. However, the exceptionally greater stability of Cu^{21} complexes is the Jahn-Teller distortion.

Diagram:

The sequence is generally quoted only for Mn(11) to Zn(II) as there is little or no data available for SINCE 2012 the other 3d series transition metal ions as their

M(11) oxidation states are not very much stable. Crystal field Ha theory is based on the idea that the interactions between the metal centre and the ligands-attached are purely ionic in nature; this suggests that the stability of the complexes should be related to the charge to radius ratio (ionic potential).

2. Disproportionation of Au^{1}t salts: Bivalent gold is less stable and undergoes disproportionation to form Au and Au^{3}. On the other hand, bivalent salts of Cu and Ag ions are quite common and relatively more stable. However, as far as the electronic configuration is concerned, all of the three belong to the same group and are d systems.

Thus, a strong Jahn-Teller distortion is expected. The disproportion of Au^{2} can be explained in terms of increasing A value down the group. Therefore, bivalent salts of gold would have the maximum magnitude of crystal field splitting, which results high destabilization associated with the filling of last electron (in d,^{22}). This makes Aut to undergo either to form Au^{31}, a d system; or reduction to Au^{1}t, a d^{10} system. The a system (Au^{3}+) is usually square-planar in geometry and quite stable as the electron from the d^{2}-2 is removed. The do system (Au^{11}) is of linear geometry and stable due to fully filled configuration

3. Stabity order of ethylenediamine complexes of Cu^{2}: Jahn-Teller distortion is responsible for the stability order of [Cu(en)3]2+, cis-[Cu(en),(H$_2$ O)2]".

Bivalent copper cannot form [Cu(en)3]2+ because the Jahn-Teller distortion induces strain into the ethylenediamine molecule that is added along z-axis. Therefore, the only complex that exists is [Cu(en)2(H2O)2]2+. Similarly, cis-[Cu(en)2(H2O)2]2+ is less stable in comparison than trans-[Cu(en)2(H2O)2]2+. The extra stability of trans-[Cu(en)2(H2O)2]2+ is because of the non-involvement of longer bonds in chelation.

The NephelauxeticSeries:

The nephelauxetic series is a list of ligands or metal ions ordered on the basis of the strength of their nephelauxetic effect.

In the inorganic studies, the term "nephelauxetic effect" is very frequently used for transition metal complexes. This refers to a decreasing Racah parameter (B), a measure of inter-electronic repulsion, that occurs when a free transition-metal ion forms a complex with different types of ligands. The label "nephelauxetic" is for cloud-expanding in the Greek language. The presence of the nephelauxetic effect brings out the drawbacks of crystal field theory, as this suggests a somewhat covalent character in the metal-ligand bonding.

The declining value of the Racah parameter hints that in a metal complex, there is less repulsion between the two electrons in a given doubly occupied metal d-orbital than what is in the free ion counterpart, M"; which consecutively implies that the orbital size is larger after complexation. Two reasons for electron- cloud-expansion effect may be given; one is that the effective positive charge on the metal is reduced by any negative charge on the ligands, the d-orbitals can expand a slight manner; the second is the considers the overlapping with ligand orbitals and creation of covalent bonds increases the size of the orbital.

The reduction of B from parameter, ß, as: its free ion value is normally reported in terms of the nephelauxetic parameter B is

B=B'(complex)÷B (free ion)

Moreover, it is also observed experimentally that the magnitude of the nephelauxetic parameter always follows a certain order with respect to the nature of the ligands attached. However, there are many ligands which do not form complexes with a particular metal ion and the vice-versa is also true. It clearly means that the value of the Racah parameter for these complexes cannot be calculated experimentally. Therefore, an empirical method must be used to find out their B yalues. In this method, two empirical parameters have been suggested for metal ions and ligands.

Table 13. Values of parameters k and h for different metal centers and ligands.

Metal ion k Ligandsh

Co2+0.246CN-2.0

Co3+0.35. 3en1.5

Cr+0.216H_2 O1.0

Mn2+0.076NH31.4

Ni2+0.126F0.8

The empirical formula to calculate the magnitude of the Racah parameter for any metal ion in complexation is given below.

B' = B(1-kh) cm-1

Where, B and B' are the Racah parameters for free ion and metal center in complexation, respectively.

i) For [Ni(H2O)6]2+

B' =1080(10.12 x 1.0) cm-1

B’= 950 cm-1

This value is pretty close to what has been observed experimentally (905 cm^{-1}).

ii) For [Co(en)3]3+

B' = 1400(1 0.35 x 1.5) cm-1

This experimental value of B for is 568 cmhy For [Co(en)3

The values of Racah parameter (B) for transition metal ion in the gaseous state can be noted from the table given below.

1. Nephelauxetic series of ligands: The list is shown below list commons ligands (with increasing nephelauxetic effect):

F<H_2 O NH3 <en< NCS (N-bonded) <Cl-<CN <Br< N; <I

Although parts of this series may seem quite similar to the spectrochemical series of ligands, that is not true. for instance; the fluoride, ethylenediamine and cyanide seem to occupy almost similar positions; Some other ligands such as chloride, iodide and bromide, are arranged very differently. Roughly, we can say that the ordering reflects the capability of the ligands to form batter covalent bonds with metals; means ligands at the end of the series i.e. with large nephelauxetic effect have batter tendency to for covalent bond than the ligands present at the start of the series.

2. Nephelauxetic series of metal ions: The nephelauxetic effect does not only depend upon the ligand type but also upon the central metal ion. These too can be arranged in order of increasing nephelauxetic effect as follows:

Mn2+ Ni2+Co2+Mo2+Re+ < Fe3+ <Ir3+ <Co^3+Mn+

It is obvious that as the oxidation number for the metal ion increases, the nephelauxetic effect also increases

Atomic Term Symbols:

Atomic term symbols may be defined as the symbolic representations of various electronic states having different resultant angular momentums resulting from spin-spin, orbital-orbital or spin-orbital interactions and the transitions between two different atomic states may also be represented using their term symbols, to which certain rules apply.

The general form of any atomic term symbol that is used to represent any electronic state resulting from inter-electronic repulsion is: (2S+1)Lj

Where,2S+1= spinmultiplicity

S = resultant spin angular momentum quantum number

L = resultant orbital angular momentum

resultant total angular momentum quantum number Just like in the case of atomie orbitals, where / represents the individual orbital angular momentums; L represents the resultants orbital angular momentum of an electronic state and gives the base designation of any atomic term symbol.

L =01234567

State =S P DFGHIK

The calculation of resultant spin and orbital angular momentum involves the concepts of space quantization and vector interactions. A somewhat simplified approach for the calculation of resultant orbital angular momentum quantum number (L), resultant spin angular momentum quantum number S and resultant total angular momentum quantum number (J) can be given by understanding the spin-spin, orbital-orbital and spin- orbital couplings schemes.

1. Orbital-orbital coupling (/-/1 interaction): Consider a multielectron system, then the resultant orbital angular momentum quantum number can be deduced as:

L=(l1+l2), (l1+l2-1) (l1+l2-2)…..(l1+l2-n)

Where 11 and 12 are the individual orbital angular momentum quantum numbers for electrons and modulus sign shows that the value of resultant orbital angular momentum quantum number is always positive. Given the eigenstates of / and /2, the construction of eigenstates of L (which still is conserved) is the coupling of the angular momenta of electrons 1 and 2.

i) For p'p'-configuration, 1 and 12 = 1, therefore L=(1+1), (1+1-1), (1-1)
ii) L=2, 1,0 States D, P, S

Similarly,

ii) For d'd'-configuration, 2 and 12 = 2, therefore

L=(2+2), (2+2-1)....... (2-2)

L = 4, 3, 2, 1, 0

States G. F, D, P, S

Although the above-mentioned procedure provides the resultant orbital angular momentum quantum number (L) quite easily, the exact concept of orbital-orbital coupling can be understood only after knowing the concepts of space quantization. One thing that is totally clear is that these symbols are nothing but the mathematical shorthand of the electronic arrangements around the nucleus. The quantization of individual orbital angular momentums can be used to calculate the resultant value as follows:

For i) For p'p'-configuration, 4=1 and 1, therefore orbital angular momentum for each of the electron is √2 alalin and it is a well-known fact from from the quantum mec mechanics that v2 angular momentum can be oriented in space with three different ways (+1, 0 and 1) The different combinations of orbital angular momentum can be calculated as

L1(z)+1+1+1000-1-1-1

L2(z)+10-1 +1 0 -1 +1 0

Lz. +2+1 0 +1. 0 -1 0 -1

Hence, the orbital angular momentums of two p-electrons can interact in nine ways, creating nine combinations; out of which, three quantum-mechanically allowed series can be fashioned.

L=(+2, +1, 0, -1,-2),(+1, 0, -1), (0)

L=2, 1,0

Hence States D, P, S

Therefore, we can say that there are nine ways in which the orbital motion can interact.

2. Spin-spin coupling (s-s interaction): Consider a multielectron system, then the resultant spin angular momentum quantum number can be deduced as:

S=(S1+S2), (S1+S2-1).... $1-$21

Where s_1 and s2 are the individual spin angular momentum quantum numbers for electrons and modulus sign shows that the value of resultant spin angular momentum quantum number is always positive.

i) For p'p' or d'd'-configuration, s_1 = 1/2 and $2 1/2, therefore S=(1/2+1/2), (1/2-1/2)

or

Which means

S = 1,0

Multiplicity (2S + 1) = 3 and 1

The aforementioned procedure offers the resultant spin angular momentum quantum number (S) quite easily but the exact concept of spin-spin interaction can be understood only after knowing the concepts of space quantization. The quantization of individual spin angular momentums can be used to calculate the resultant value as follows:

i) For p'p' or d'd'-configuration, si 1/2 and 1/2, therefore spin angular momentum for each of the electrons is V0.75 and it is a well-known fact from the quantum mechanics that V0.75 angular momentum can be oriented in space with two different ways (+1/2 and -1/2). The different combinations of spin angular momentum can be calculated as:

Hence, the spin angular momentums of two por d-electrons can interact in four ways, creating four combinations; out of which, two quantum-mechanically allowed series can be fashioned.

S:=(+1,0,-1), (0)

S=1,0

Multiplicity (2S+1) = 3 and 1

The multiplicity actually represents the number of orientations possible for the total spin relative to the total orbital angular momentum L, and thus to the number of near-degenerate levels that differ only in their spin- orbit coupling energy. For example, the ground state of the carbon atom is a 'P state. The superscript of three specifies that the multiplicity 2S+13 i.e. triplet, so that the total spin S = 1. This spin is due to two unpaired electrons, as a result of Hund's rule which favors the single filling of degenerate orbitals. The spin multiplicity is a primary factor in governing the overall energy of an electronic state and maybe summarised for different electron combination.

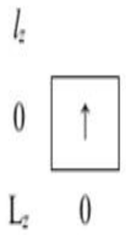
3. Spin-orbital coupling (L-S interaction): In a multi-electron system, the resultant orbital angular momentum (L) and resultant spin angular momentum (S) interact with each other to give total angularmomentum which is defined by the quantum number J.

Where L and S are the quantum numbers for resultant orbital angular momentum and resultant spin angular momentum, respectively. The modulus sign shows that the value of the resultant total angular momentum quantum number is always positive. The value of J is assigned as the subscripts of the overall term symbol.

i) For p'p'-configuration, 9 combinations given by orbital-orbital coupling (L = 2, 1, 0) and 4 combinations given by spin-spin coupling (S = 1,0) combine to create a total of 36 microstates. therefore

L = 0, 1, 2 and S = 1. States = S, P, D.

Term symbols for various configurations :

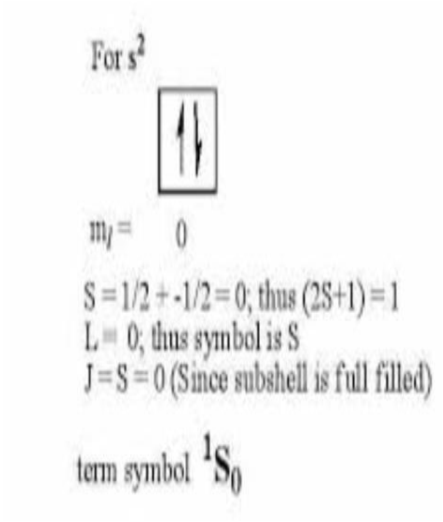


1. s¹-configuration:

As L = 0, the value of resultant orbital momentum quantum number L = 0. There is only one unpaired electron, therefore S = 1/2.

From L = 0, the state TIRE GATE, M.Sc Entrance & IIT-JAM is S; and from S = 1/2, the Thus, the overall term symbol is 2S.

2. s^2-configuration:-


For s^2

m_l = 0

S = 1/2 + -1/2 = 0; thus (2S+1) = 1

L = 0; thus symbol is S

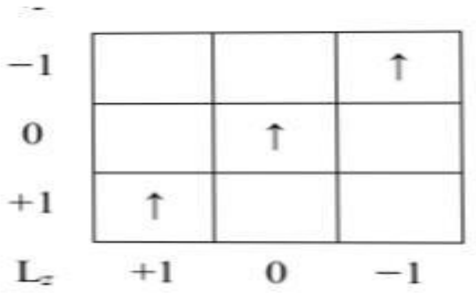
J = S = 0 (Since subshell is full filled)

term symbol $^1S_0$

electrons From L = = 0, the state is S; and from S = 1. Thus, the overall term symbol is 'S

As L = 0, the value of resultant orbital angular momentum quantum number L = 0. There are no unpaired , therefore S = 0. Haryana

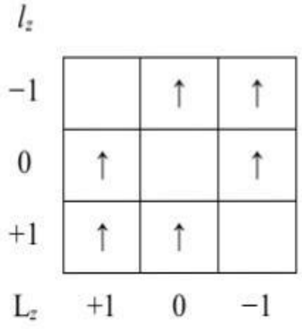
3. p^1 and p5-configuration:



As L. +1, 0, -1; the value of resultant orbital angular momentum quantum number L = 1. There is one unpaired electron, therefore S = 1/2.

From L = 1, the state is P; and from S = 1/2, the multiplicity is 2. Thus, the overall term symbol is 2P. Hence, all the 6 microstates for p^1 and p^3-configurations are distributed in 2P term symbol.

4. p^2 and p4-configuration:For parallel arrangements,



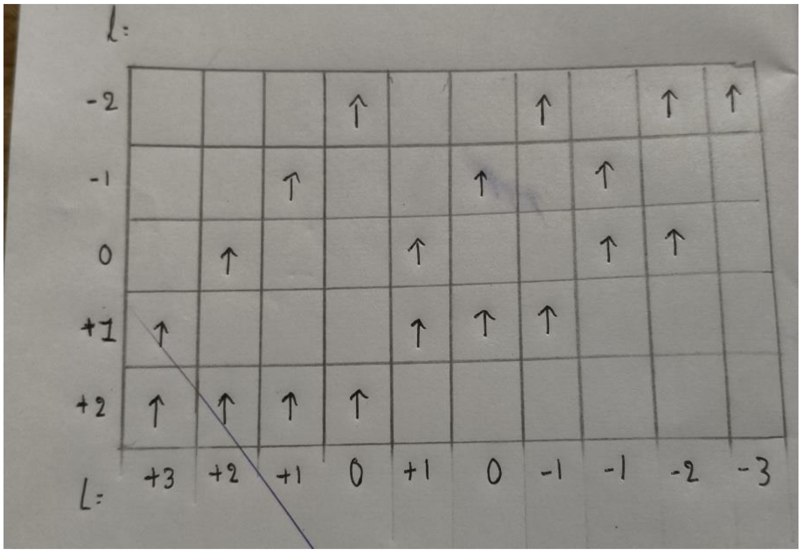
As L.+1, 0, -1; the value of resultant orbital angular momentum quantum number L = 1.

There are two unpaired electrons, therefore S=1.

From L 1, the state is P.

From S = 1, the multiplicity is 3.

Thus, the overall term symbol is P.



Out of six values of L. (resultant orbital angular momentum in reference direction), two quantum-mechanically allowed series can be setup. One with L. +2, +1, 0, -1, -2; giving resultant orbital angular momentum quantum number L = 2. The second series with L. = 0; giving resultant orbital angular momentum quantum number L = 0.

There are zero unpaired electrons, therefore S = 0.

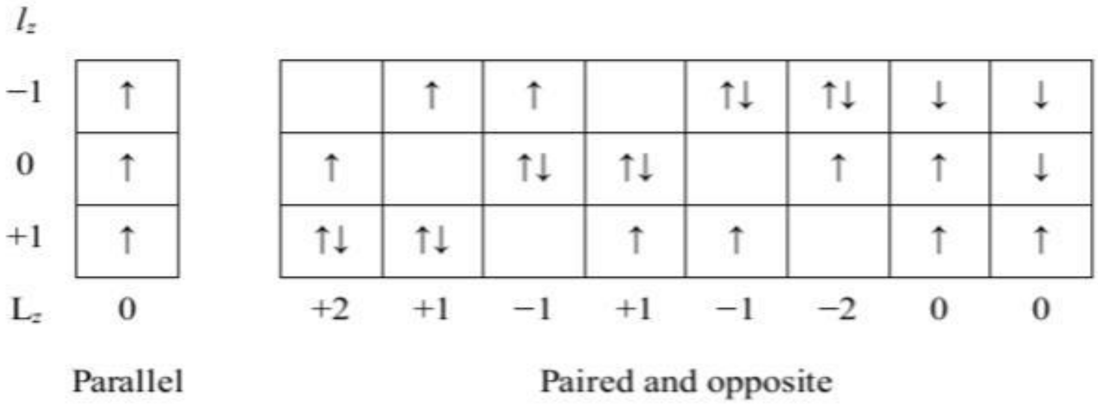
From L = 2 and 0; the states are D and S, respectively.

From S = 0, the multiplicity is 1.

Thus, the overall term symbols are 'D and 'S.

Hence, all the 15 microstates for p^2 and p^3 electronic configurations which can be distributed in 1S, 3P and 1D term symbols.

5. p^3-configuration:



For parallel arrangements,

As L. = 0; the value of resultant orbital angular momentum quantum number L = 0. There are three unpaired electrons, therefore S = 3/2.

From L = 0, the state is S; and from S = 3% , the multiplicity the overall term symboli is 'S.

For paired and opposite arrangemes

Out of eight values of L., two quantum-mechanically allowed series can be setup. One with L. =+2, +1, 0, -1, -2; giving resultant orbital angular momentum quantum number L-2. The second series with L. =+1, 0, -1;

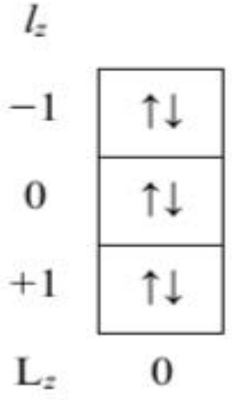
giving resultant orbital angular momentum quantum number L = 1. There is one unpaired electron, therefore S=1/2.

From L = 2 and 1 the states are D and P. respectively.

From S = 1/2, the multiplicity is 2.

Thus, the overall term symbols are D and Market Sector 4. Hence, all the 20 microstates for p-configurations are distributed in 'S, P and 'D term symbols.

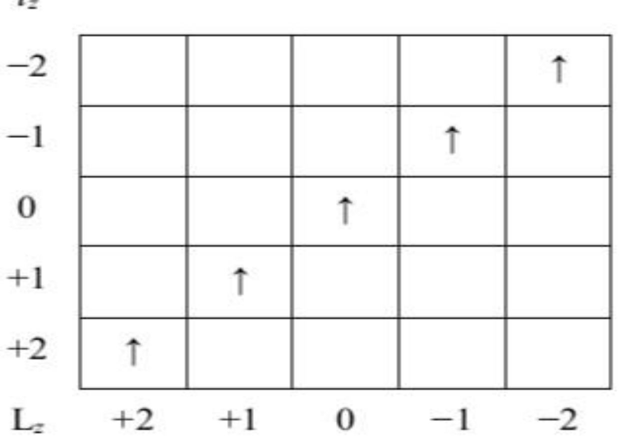
6. p6-configuration:



As L. =0, the value of resultant orbital angular momentum quantum number L = 0; and zero unpaired electrons, therefore S = 0. Thus, the overall term symbol is 'S which contains the one and only microstate of p^o-electronic configuration.

7. d' and d9-configuration:

As L_2 +2, +1, 0, -1, -2; the value of resultant orbital angular momentum quantum



number L = 2.

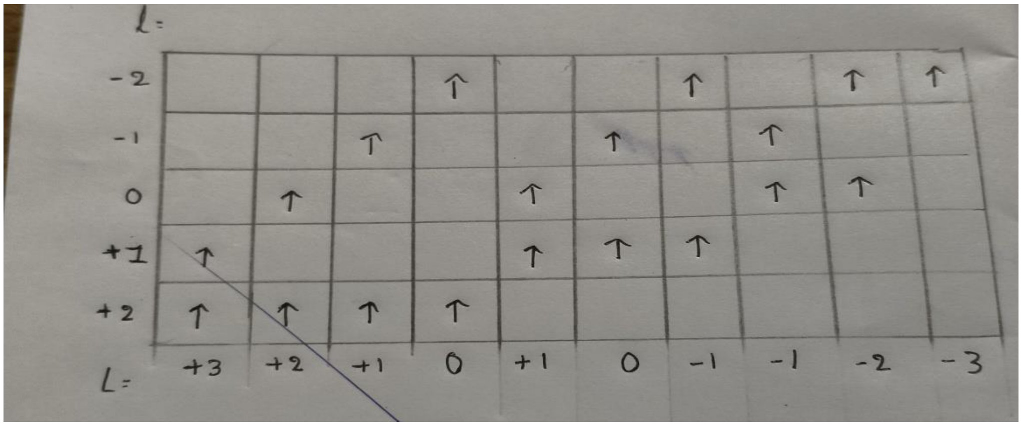
There isonly one unpaired electron, therefore S1

From L=2, the state is D; and from S = 1/2, the multiplicity is isalso 2

Thus, the overall term symbol is 2D

Hence, all the 10 microstates for d and d-configurations are distributed in D term symbols.

8.d2and d8-configuration,



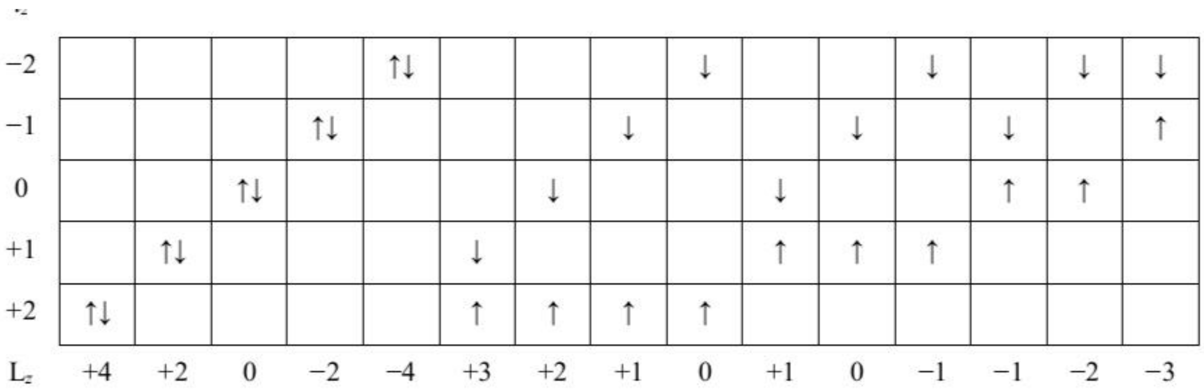
l =										
-2				↑			↑		↑	↑
-1			↑			↑		↑		
0		↑			↑			↑	↑	
+1	↑				↑	↑	↑			
+2	↑	↑	↑	↑						
L =	+3	+2	+1	0	+1	0	-1	-1	-2	-3

For parallel arrangements,

Out of ten values of L., two quantum-mechanically allowed series can be setup. One with L. +3, +2, +1, 0, -1, -2, -3; giving resultant orbital angular momentum quantum number L 3. The second series with L. = +1, 0, -1; giving resultant orbital angular momentum quantum number L = 1. There are two unpaired electrons, therefore S=1.

From L=3 and 1, the states are F and P, respectively. From S = 1, the multiplicity is 3. Thus, the overall term symbols are 'F and P.

For paired and opposite arrangements,



−2					↑↓				↓			↓		↓	↓
−1				↑↓				↓			↓		↓		↑
0			↑↓				↓			↓			↑	↑	
+1		↑↓				↓				↑	↑	↑			
+2	↑↓					↑	↑	↑	↑						
L_z	+4	+2	0	−2	−4	+3	+2	+1	0	+1	0	−1	−1	−2	−3

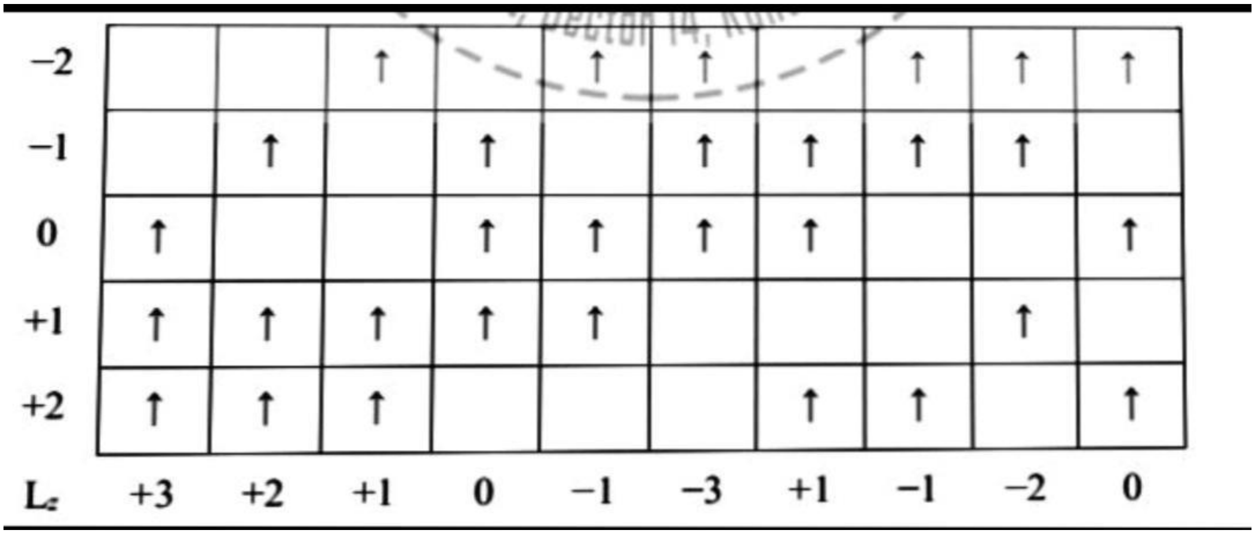
Out of fifteen values of L., three quantum-mechanically allowed series can be setup. First with L. = +4, +3, +2, +1, 0, -1, -2, -3, -4; giving resultant orbital angular momentum quantum number L = 4. Second series with L = +2, +1, 0, -1, -2; giving resultant orbital angular momentum quantum number L = 2. The third series with L. = 0; giving resultant orbital angular momentum quantum number L = 0. There are zero unpaired electrons, therefore S = 0

From L=4, 2 and 0 the states are G, D and S, respectively. From S = 0, the multiplicity is 1. Thus, the overall term symbols are 'G, ‘D,1S

Hence, all the 45 microstates for de and de-configurations are distributed in 'S, P, 'D, F and 'G term symbols.

9. d3and d7-configuration:

For parallel arrangements,



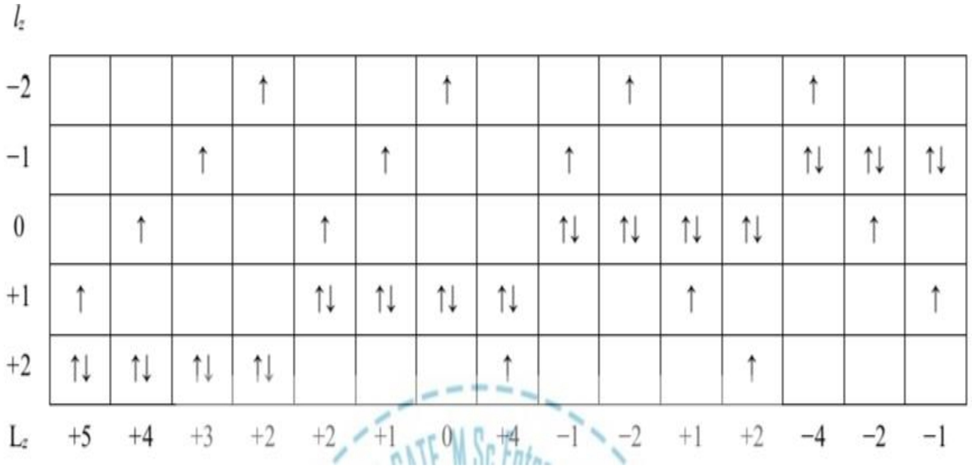
−2			↑		↑	↑		↑	↑	↑
−1		↑		↑		↑	↑	↑	↑	
0	↑			↑	↑	↑	↑			↑
+1	↑	↑	↑	↑	↑				↑	
+2	↑	↑	↑				↑	↑		↑
L_z	+3	+2	+1	0	−1	−3	+1	−1	−2	0

Out of ten values of L., two quantum-mechanically allowed series can be setup.

One with L = +3, +2, +1, 0, -1, -2, -3; giving resultant orbital angular momentum quantum number L = 3.

The second series with L. = +1, 0, -1; giving resultant orbital angular momentum quantum number L = 1. There are three unpaired electrons, therefore S = 3/2.

From L3 and 1; the states are F and P, respectively. From S = 3/2, the multiplicity is 4. Thus, the overall term symbols are 4F and P. For paired and opposite arrangements,



l_z															
−2				↑			↑			↑			↑		
−1			↑			↑			↑				↑↓	↑↓	↑↓
0		↑			↑				↑↓	↑↓	↑↓	↑↓		↑	
+1	↑				↑↓	↑↓	↑↓	↑↓			↑				↑
+2	↑↓	↑↓	↑↓	↑↓				↑				↑			
L_z	+5	+4	+3	+2	+2	+1	0	+4	−1	−2	+1	+2	−4	−2	−1

Out of thirty values of L., six quantum-mechanically allowed series can be setup. First with L. +5, +4, +3, +2, +1, 0, -1, -2, -3, -4, -5; giving resultant orbital angular momentum quantum number L = 5. Second series with L. +4, +3, +2, +1, 0, -1, -2, -3, -4; giving resultant orbital angular momentum quantum number L = 4. The third series with L. +3, +2, +1, 0, -1, -2, -3; giving resultant orbital angular momentum quantum number L3. Fourth and fifth series with L. = +2, +1, 0, -1, -2; giving resultant orbital angular momentum quantum number L = 2 and 2, respectively. The sixth series is consisted of L. +1, 0, -1; giving resultant orbital angular momentum quantum number L = 1.

There is one unpaired electron, therefore S = 1/2.

From L5, 4, 3, 2, 2 and 1; the states are H, G, F, D, D and P, respectively.

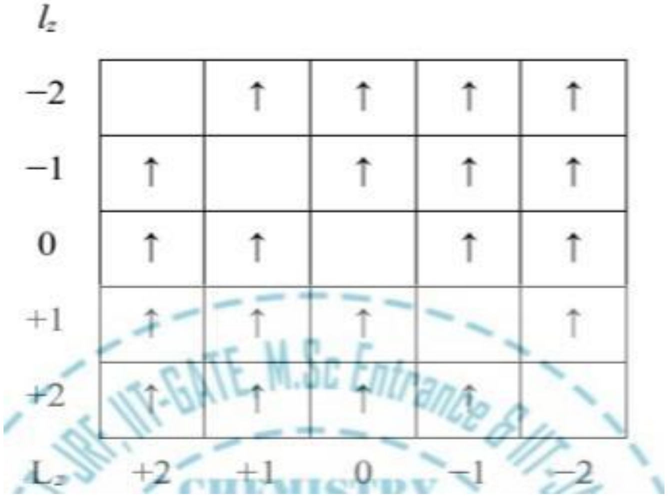
From S 1/2, the multiplicity is 2.

Thus, the overall term symbols are 2H, 2G, 2F, 2D, 2D and 2P.

Hence, all the 120 microstates for d^3 and d'-configurations are distributed in 4F, 4P, 2H, 2G, 2F, 2D, 2D and 2P term symbols.

10. d4 and d6-configuration:

For parallel arrangements,



l_z					
−2		↑	↑	↑	↑
−1	↑		↑	↑	↑
0	↑	↑		↑	↑
+1	↑	↑	↑		↑
+2	↑	↑	↑	↑	
L_z	+2	+1	0	−1	−2

Out of five values of L.. only one quantum-mechanically allowed series can be set up with L. = +2, +1, 0, -1, -2; giving resultant orbital angular momentum quantum number L=2

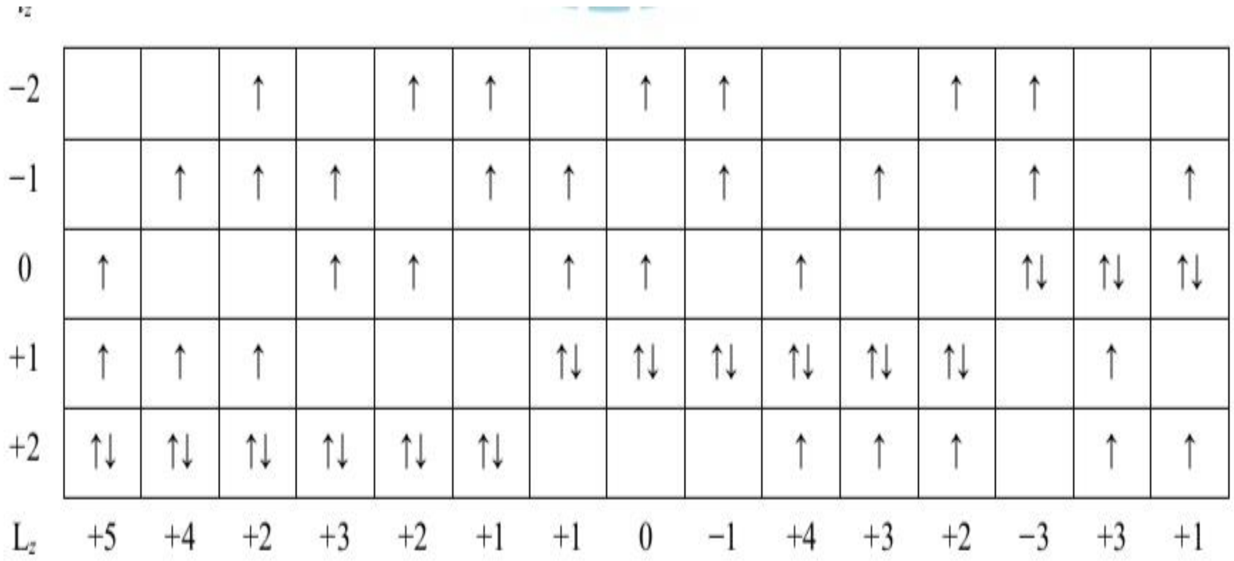
There are four unpaired electrons, therefore S=2

From L=2 the state is D

From S=2 the multiplicity is 5

Thus the overall term symbol is 5D

For two electrons Paired or opposite arrangement



−2			↑		↑	↑		↑	↑			↑	↑		
−1		↑	↑	↑		↑	↑		↑		↑		↑		↑
0	↑			↑	↑		↑	↑		↑			↑↓	↑↓	↑↓
+1	↑	↑	↑				↑↓	↑↓	↑↓	↑↓	↑↓	↑↓		↑	
+2	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓				↑	↑	↑		↑	↑
L_z	+5	+4	+2	+3	+2	+1	+1	0	−1	+4	+3	+2	−3	+3	+1

Out of forty-five values of L., seven quantum-mechanically allowed series can be setup as. First with L_2 = +5, +4, +3, +2, +1, 0, -1, -2, -3, -4, -5; giving resultant orbital angular momentum quantum number L = 5. Second series with L_2 =+4, +3, +2, +1, 0, -1, -2, -3, -4; giving resultant orbital angular momentum quantum number L = 4. The third and fourth series with L. = +3, +2, +1, 0, -1, -2, -3; giving resultant orbital angular momentum quantum number L = 3 and 3. fifth series with L. = +2, +1, 0, -1, -2; giving resultant orbital angular momentum quantum number L = 2. The sixth and seventh series is consisted of L. =+1, 0, -1; giving resultant orbital angular momentum quantum number L = 1 and 1, respectively.

There are two unpaired electrons, therefore S = 1.

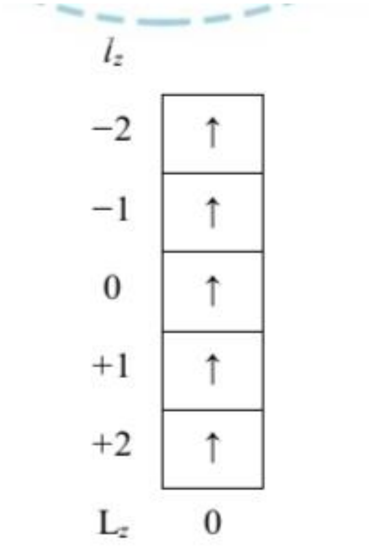
From L=5, 4, 3, 3, 2, 1 and 1; the states are H, G, F, F, D, P and P, respectively.

From S = 1, the multiplicity is 3.

Thus, the overall term symbols are 3H, 3G, 3F, 3F, 3D, 3P and ^3P.

11. d5-configuration:

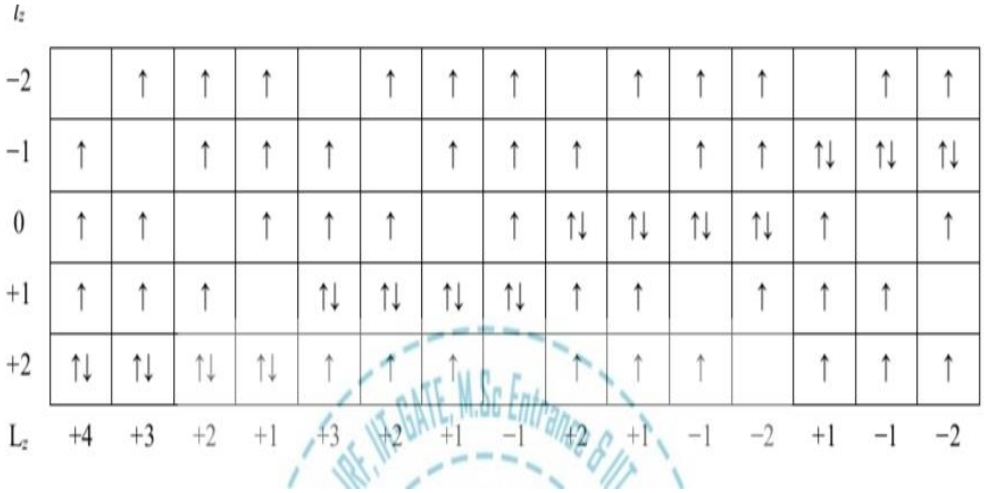
For parallel arrangement



l_z	
−2	↑
−1	↑
0	↑
+1	↑
+2	↑
L_z	0

As L = 0; the value of resultant orbital angular momentum quantum number L = 0. There are five unpaired electrons, therefore S = 5/2.

From L= 0, the state is S. From S = 5/2, the multiplicity is 6. Thus, the overall term symbol is "S. For two electrons paired or opposite arrangement,



l_z															
−2		↑	↑	↑		↑	↑	↑		↑	↑	↑		↑	↑
−1	↑		↑	↑	↑		↑	↑	↑		↑	↑	↑↓	↑↓	↑↓
0	↑	↑		↑	↑	↑		↑	↑↓	↑↓	↑↓	↑↓	↑		↑
+1	↑	↑	↑		↑↓	↑↓	↑↓	↑↓	↑	↑		↑	↑	↑	
+2	↑↓	↑↓	↑↓	↑↓	↑	↑	↑		↑	↑	↑		↑	↑	↑
L_z	+4	+3	+2	+1	+3	+2	+1	−1	+2	+1	−1	−2	+1	−1	−2

Out of twenty-four values of L., four quantum-mechanically allowed series can be setup as. First with L. = +4, +3, +2, +1, 0, -1, -2, -3, -4; giving resultant orbital angular momentum quantum number L = 4. Second series with L. +3, +2, +1, 0, -1, -2, -3; giving resultant orbital angular momentum quantum number L = 3. The third series with L = +2, +1, 0, -1, -2; giving resultant orbital angular momentum quantum number L = 3. The fourth series is consisted of L = +1, 0, -1; giving resultant orbital angular momentum quantum number L=1.

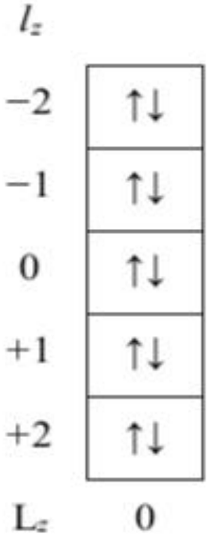
There are three unpaired electrons, therefore S = 3/2.

From L = 4, 3, 2 and 1; the states are G, F, D and P, respectively.

From S = 3/2, the multiplicity is 4.

Thus, the overall term symbols are "G, 4F, 4D and P.

12. d10-configuration:



-

As L. = 0; the value of resultant orbital angular momentum quantum number L = 0. There are no unpaired electrons, therefore S = 0.

From L 0, the state is S. From S 0, the multiplicity is 1. Thus, the only microstate of d-configuration. overall term symbol is. 'S contains only microstate of d10

It can clearly be seen that the number of microstates, as well as the term symbols for dn and d10-n configurations, are the same. This is due to the fact that the number of unpaired electrons is the same for both of the configurations. In other words, the possible arrangements for unpaired electrons in less than half-filled for holes in more than half-filled configurations are the same. The same analogy is true for s, p or f-subshell

Moreover, the number microstates distributed in any term symbol can be calculated using the

following relations:

1. Term symbols without J-value: (2L+1) (2S+1)

2. Term symbols without J-value: (2J+1)

Let us tally the number of microstates for p² electronic configuration with term symbols distribution.

(2L+1) × (2S+1)(2J+1)

Distribution 1S=(2x0+1) × (2×0+1) = 1So2x0+1=1

of 153P = (2×1+1) × (2×1+1) = 93P2=2×2+1=5

microstatesofp2 1D=(2x2+1)x(2x0+1) = 53P_1 =2×1+1=3

in 'S, 3p,1D3Po=2x0+1=1

term symbolsD2=2×2+1=5

D.N.R. COLLEGE(A), BHIMAVARAM

DEPARTMENT OF P.G. CHEMISTRY

INORGANIC CHEMISTRY –I

PRESENTED BY

N.Santhi

UNIT-IV

ELECTRONIC SPECTRA OF TRANSITION METAL COMPLEXES

6. Selectionrulesandtheirbreakdown

6.1 Selectionrules:

There are various selection rules that govern the feasibility of a transition for transition metal complexes. Some of the most important selection rules have been listed below.

(1) Laporte selection rule: This rule states that for a molecule having centre of symmetry, transitions within the same sub-shell are forbidden. As per this rule the p-p or d-d transitions are forbidden. Mathematically, the rule can be stated in the form of an equation.

For any transition to take place, change in the value of total orbital angular momentum between the final and initial stage should be Courses

$\Delta L=+-1(\Delta Lf=L-LA)$

Where ΔL is equal to Lr (total angular momentum of the initial state). momentum of the final state) subtracted by Li (total angular

The transitions occurring between the states of same parity are disallowed which means the d orbitals which are gerade in terms of parity or symmetric with respect to the centre of inversion cannot have transitions from one d orbital to the other. However, p orbitals are ungerade that are asymmetric with respect to the centre of inversion and thus, transition can take place between d and p orbitals. In very simple words d-d transitions as well as p-p transitions are not allowed, whereas d to p and p to d are allowed.

(2) In case of states with same spin multiplicity the transitions cannot occur. The spin multiplicity is given by the value (2S+1). Thus transitions between 'T, and 'A, are allowed in terms of spin multiplicity whereas between T_1 and A2 are not. The transitions which are feasible are called spin allowed whereas those are not allowed, are termed as spin forbidden. i.e.

$$\Delta S = 0$$

In case these rules are completely followed by the transition metal complexes, many of the transition must have not been observed. But, actually these transitions occur which suggest that we can have cases where these rules are broken down to actually display the forbidden transitions.

6.2 Breakdownoftheselectionrules:

There are various phenomena that lead to the breakdown of the solution rules mentioned above. These can be explained as follows.

(a) During the course of vibrations in a transition metal complex which is flexible in terms of movement about the bonds, the orbitals present can temporarily loose their center of symmetry. Since the parity is lost for the moment, it can be said that vibronic coupling results in the loss of their (orbitals) symmetric identity due to which the transitions from d to d orbitals are partially allowed. Although these transitions are observed but their molar extinction coefficient is extremely low, in the order of 10-50 L mol^{1} cm^{1}. These transitions are actually responsible for various colors of the transition metal complexes.

(b) Tetrahedral complexes have no centre of symmetry and thus they are not gerade in symmetric terms. Thus the d levels in them are e and t2 with no 'g' as subscript. In case of a metal-σ bonding, the hybridizations sp^3 as well as sd^3 both are sustainable and thus the p and d orbitals present are not pure but mixed. Because of this p-d mixing the Laporte selection rule is relaxed. Hence tetrahedral complexes are often more intensely colored as compared to their octahedral counterpart (figure 7). This is actually a consequence of laporte relaxation

(c) Spin-orbit coupling in case of certain complexes leads to relaxation of the spin selection rule. For metal ions, mostly 4d and 5d spin orbit coupling is quite strong and thus in these complexes the spin multiplicity rule is relaxed to a good extent that results in the occurrence of the forbidden transition.

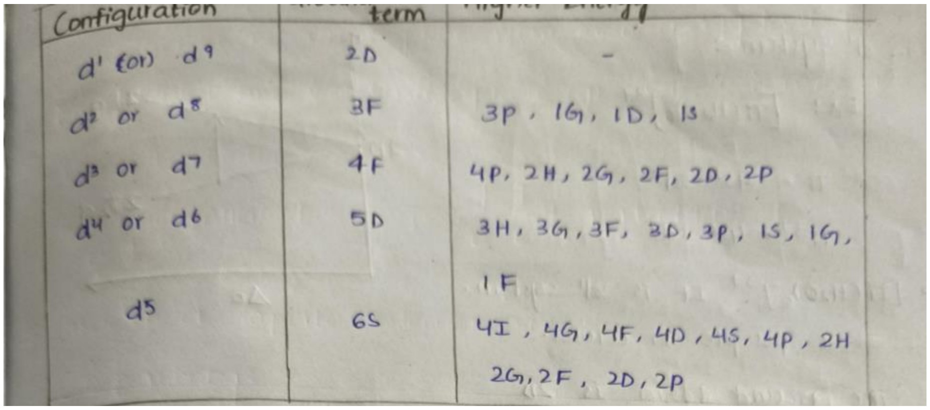
OrgelandTanabe-SuganoDiagramsforTransitionMetalComplexes (d^1 d9States) :

It is a well-known fact that electronic transitions are always accompanied by vibrational as well as rotational changes which results in a considerable broadening of the bands in the UV-visible spectra of transition metal complexes too. The nature of these transitions is quite complex to understand and requires some basic knowledge of quantum mechanics and chemical applications of group theory.

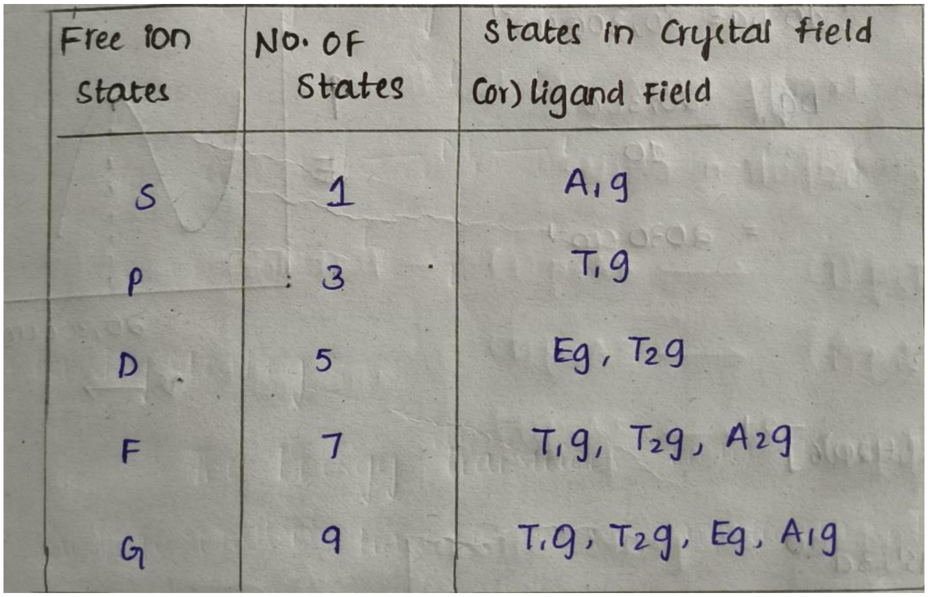
Thesplittingoffreeionterms:

It is pretty interesting to note that the degeneracy of free-ion terms like 2D or ^{3}F can be removed not only by L-S coupling alone but can also be removed by the perturbation produced by the ligands. Moreover, the wavefunctions for S, P, D, F or G states have the same symmetry as that s, p, d, f or g orbitals sets; which means that the splitting pattern of D and F states will same as d and f-subshell, respectively.

The s-orbital is spherically symmetric in nature and is not affected by any crystal field. Hence, S state also does not get split in any type of ligand field. The p-orbitals are directional in nature and are affected by different types of crystal field differently. Hence, P state may or may not get split in the presence of ligand field. For example, P state does not get split in octahedral or tetrahedral field but does get split in square planar crystal field. The d-orbitals are also directional in nature and are affected by different types of crystal field differently. Hence, D state does get split in the presence of the ligand field. For example, D state does get split in the octahedral or tetrahedral field with triply and doubly degenerate sets but the splitting pattern and degeneracy are totally different in pentagonal bipyramidal crystal field. The splitting profile of different electronic states in octahedral and tetrahedral crystal fields in the following tables, which will be used very frequently in the further text of this chapters



Configuration	term	
d^1 (or) d^9	2D	-
d^2 or d^8	3F	3P, 1G, 1D, 1S
d^3 or d^7	4F	4P, 2H, 2G, 2F, 2D, 2P
d^4 or d^6	5D	3H, 3G, 3F, 3D, 3P, 1S, 1G, 1F
d^5	6S	4I, 4G, 4F, 4D, 4S, 4P, 2H 2G, 2F, 2D, 2P



Free ion states	No. of States	States in Crystal field (or) ligand Field
S	1	A_1g
P	3	T_1g
D	5	Eg, T_2g
F	7	T_1g, T_2g, A_2g
G	9	T_1g, T_2g, Eg, A_1g

Terms correlation in the tetrahedral and octahedral field:

The qualitative description of different energy term for d" and do configuration, from free ion to strong crystal field configurations ignoring inter-electronic repulsions, can be given as:

1. The total number of energy levels remain the same under the influence of weak and strong crystal fields.

2. The one to one correspondence of different energy levels in a strong crystal field may get stabilized or destabilized in comparison to the weak field case.

3. Energy levels of the same symmetry never cross each other and each level has a contribution in its energy from all other energy states of the same symmetry.

4. Term correlation for d', d', d, d configuration are shown completely while for d, d, ď, d, d' are shown partially by taking only lower energy levels.

5. According to hole formalism, the number of microstates and hence all free ion terms for d" and 10- configuration are same. Now, as the magnitude of the crystal field experienced positive electrons is the same as what experienced by the negative electrons, but and d^1 configurations are opposite of each other. is. of of sign. Therefore, the splitting pattern for dn and dn-1 are opposite to each other

6. Owing to the hole formalismin quantum mechanics, strong field configuration 4 5 of 12g, 12g, eg give rise to the same terms as given by the strong field configuration of fa fa e. However, weaker inter-electronic repulsion is considered as the e perturbation over stronger

7. The splitting pattern of d tetrahedral is just the opposite of what is for 1-0002025820) are used in the tetrahedral case because there is no center of symmetry in of symmetry in a tetrahedral geometry.

It has already been discussed that the total number of microstates for electronic configuration without inter-electronic repulsion or with inter-electronie repulsion (free ion terms) remains the same. Furthermore, the number of microstates also remains same even in the presence of weak or strong crystal field; and when the inter-electronic repulsion is completed neglected ected in in comparison to to the t ligand field strength, the calculation of microstates is carried out individually för tag and eg set and multiplied afterward to give the total.

Furthermore, the strength of the crystal field does not alter the ground state Mulliken symbol in thecase of d', d-octahedral or tetrahedral complexes. However, in the case of d-d electronic configurations, the splitting pattern of free ion term at weak and strong crystal fields is quite different. Generally, the energy ofsome irreducible component of low multiplicity free ion term decreases so rapidly with the increase in thestrength of the crystal field that it becomes the ground state symbol. In other words, the ground state termsymbol of metal complexes with d-d electronic configurations is different in weak and strong crystal fields.For example, the ground state term symbol for d-configuration with small ligand field is 'A1g (from 'S) but asthe magnitude of crystal field increases, the T2g Mulliken state (from I) becomes highly stable and also makeup the ground electronic state.

The correlation diagrams (with the corresponding microstates shown below each level) for different electronic configurations in transition metal complexes with four-coordinated tetrahedral and six-coordinated octahedral symmetry are given below.

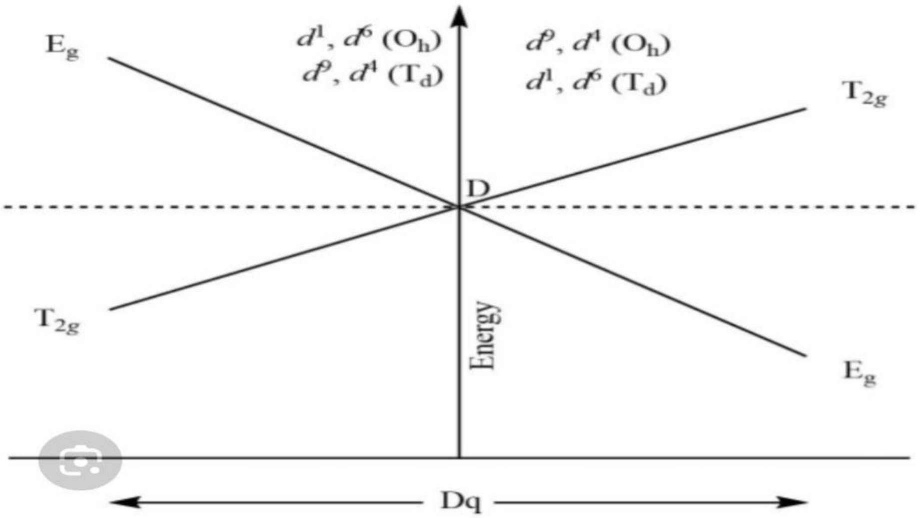
➤**OrgelDiagrams:-**

Orgel diagrams are the oversimplified version of correlation diagrams that show the relative energies of electronic terms in transition metal complexes. They are named after their inventor, Leslie Orgel. These diagrams are restricted only to show weak field cases and offer no information about strong field cases. Because Orgel diagrams are qualitative, no energy calculations can be performed from these diagrams. Moreover, Orgel diagrams only show the symmetry states of the highest spin multiplicity instead of all possible terms, unlike a general correlation diagram. Thus, Orgel diagrams include only those transitions which are spin-allowed in nature, along with corresponding symmetry designations.

In an Orgel diagram, the parent term (P, D, or F) in the presence of no ligand field is located in the center of the diagram; and the Mulliken terms arising from different electronic configurations in a ligand field are represented at each side. There are two Orgel diagrams, one for d^1, d, d, and d configurations and the other with d^2, d, d', and d configurations. An Orgel diagram for d has also been very popular which includes spin-forbidden transitions too. In the Orgel diagram, lines with the same Russell-Saunders terms will diverge due to the non-crossing rule, but all other lines will diverage due to the non crossing rule but all the line will be linear

1. d', d9, d4, d6 s ystems:

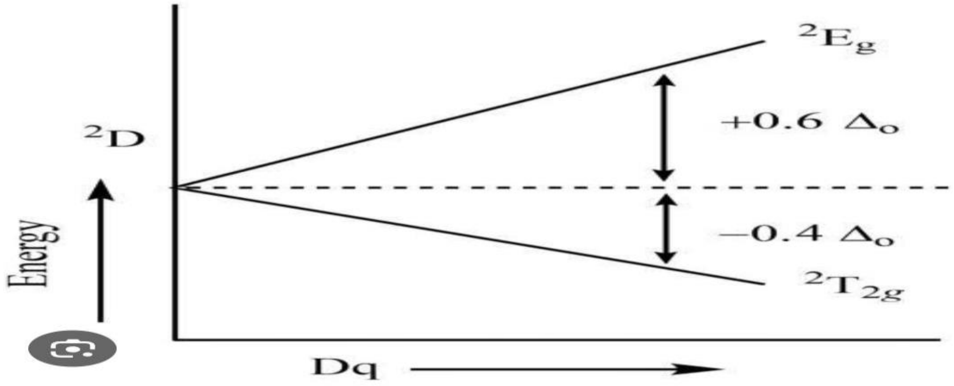
For the "D" Orgel diagram, the left side contains d' and doetahedral, and d' and d^o tetrahedral complexes. The right side contains d' and d' octahedral, and d' and do tetrahedral complexes. The lowest energy absorption band on the left side of the spectrum is T2g Eg while on the right side of the spectrum is T2g-Eg while on the right



side of the spectrum iEg – T2g transition.

i) Spectra of d' and d9 octahedral complexes:

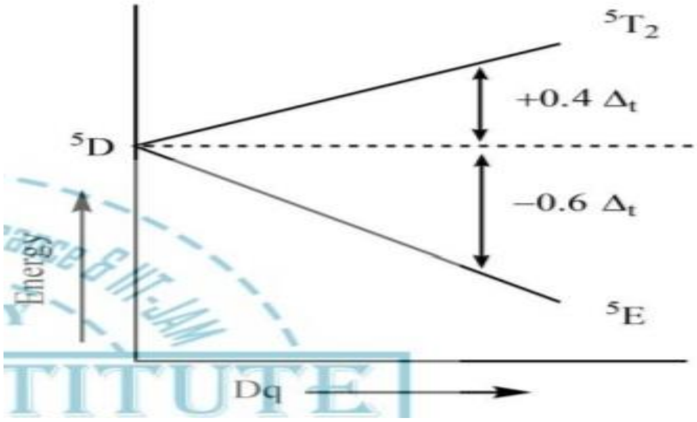
The ground state term symbol for d^1 and d complexes is 2D; but the splitting pattern of their 'D states is just the opposite of each other, which can be attributed to the electron-hole inverse relationship or simply the hole-formalism. In other words, a d^o metal has an electron vacancy or "hole" in its d-subshell and thus can be considered as the inverse of the d' arrangement. Therefore, despite having identical ground state term symbol 2D (split into 2T2g and Eg in the octahedral field), the energy order of Mulliken states in d-configuration complexes will be just the inverse of what is in d^1 system.



iii) Spectra of d4and d6 octahedral complexes:

The ground state term symbol for d^a and d complexes is 'D; but the splitting pattern of their 'D states is just the opposite of each other, which can be attributed to the electron-hole inverse relationship or simply the hole formalism. In other words, a do metal has an electron vacancy or "hole" in its d-subshell and thus can be considered as the inverse of the d arrangement. Therefore, despite having identical ground state term symbol 'D (split into 'T2g and Eg in the octahedral field), the energy order of Mulliken states in d configuration will be just the inverse of what is in d system.

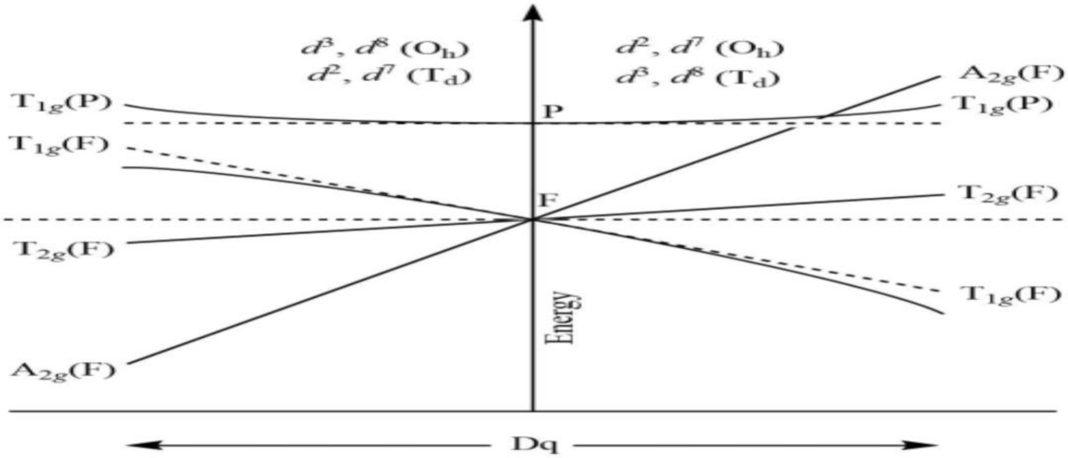
Diagram



2. d^2, d8,d3, d7systems:

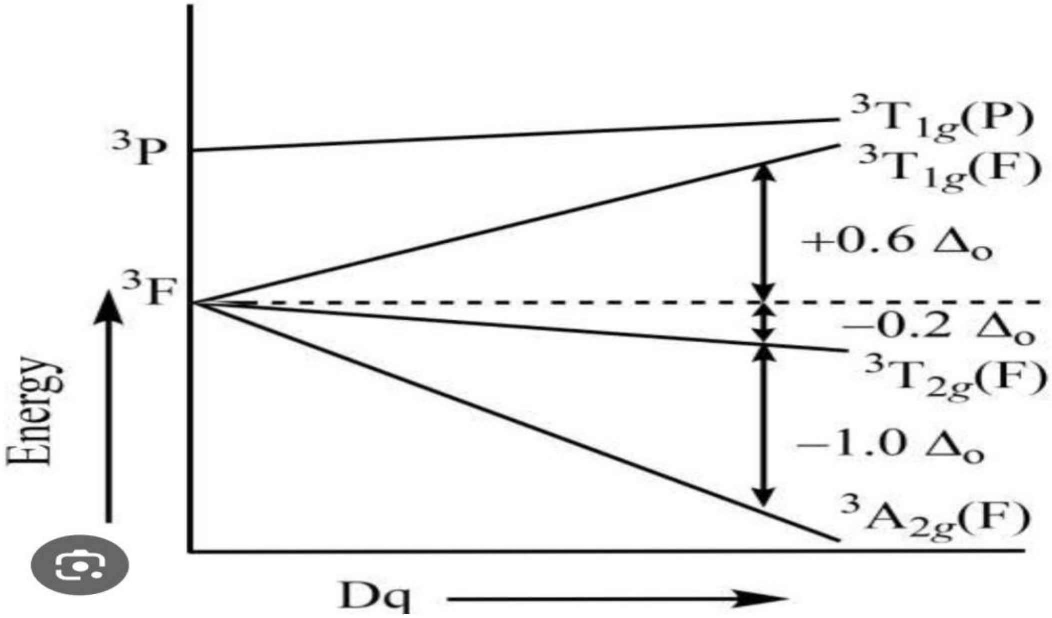
For the "F" Orgel diagram, the left side contains d^2 and d' tetrahedral and d and de octahedral complexes. The right side contains d^3 and de tetrahedral and d^2 and high spin d' octahedral complexes. The lowest energy absorption band on the left side of the spectrum is A2g(F)→ T2g(F) while on the right side of the spectrum it is Tig(F) T2g(F) transition. The difference in energy between these two states is solely attributable to electron-electron repulsions. The two free ion electronic states are separated by an energy difference 15B, where B is the Racah parameter that acts as a measure of electron-electron repulsions. The value of B can be calculated experimentally in a very similar manner as the value of ligand-field splitting A is obtained.

For instance, in an octahedral de complex, there are three ways of arranging the two d electrons. One is 12g^2, second is 12g eg and the last is eg^2. These are the three electronic states under consideration and are one should use the right-hand side of the diagram. Moreover, the energy gap between each state is equal to A since it requires the promotion of one electron from 12g to eg. It is clear from the Orgel diagram that there are four states: two Tig states, one T2g state, and one A state. The spin multiplicities are omitted in the diagram that allows it to be generalized for d complexes. The subscript g and a should be omitted if the same diagram is to be used to generalize the spectra oftetrahedral counterparts. It is also worthy to note that the ordering of the second and third transition on the right-hand side is reversed after the crossover point



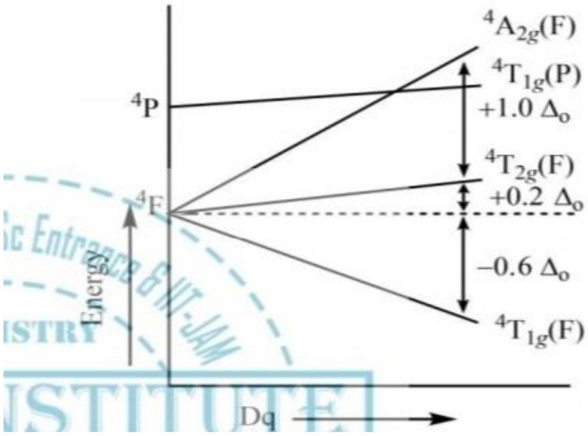
i) Spectra of d2 and d8 octahedral complexes:

The ground state term symbol for d^2 and de complexes is ^{3}F; but the splitting pattern of their ^{3}F states is just the opposite of each other, which can be attributed to the electron-hole inverse relationship or simply the hole-formalism. In other words, a d metal has two electron vacancies or "holes" in its d-subshell and thus can be considered as the inverse of the d^2 arrangement. Therefore, despite having identical ground state term symbol F (split into 3A2g, 3T2g and Tig in the octahedral field), the energy order of Mulliken states in d^3- configuration complexes will be just the inverse of what is in d2 system.



iii) Spectra of d3 and d7octahedral complexes:

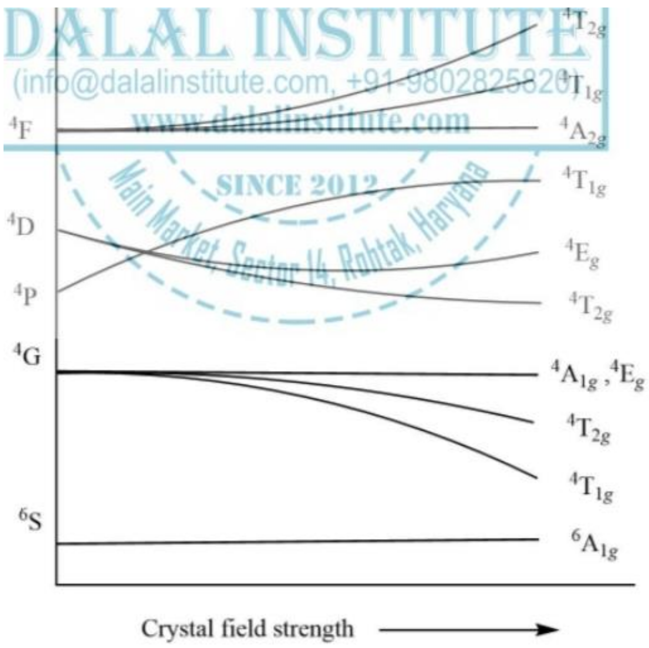
The ground state term symbol for d^3 and d' complexes is 4F; but the splitting pattern of their 'F states is just the opposite of each other, which can be attributed to the electron-hole inverse relationship or simply the hole formalism. In other words, a d' metal has an electron vacancy or "hole" in its d-subshell and thus can be considered as the inverse of the d^3 arrangement. Therefore, despite having identical ground state term symbol 4F (split into 4A2g, 4T2g and Tig in the octahedral field), the energy order of Mulliken states in d configuration will be just the inverse of what is in d^3 system.



3. **d5systems**:

Orgel diagrams we have studied so far include only spin allowed transitions. However, in the case of d-configuration, this is not possible as there is only one electronic state with a multiplicity of six, Alg. Therefore, all the transitions must occur with a change in the spin multiplicity and are spin forbidden for octahedral as well as tetrahedral complexes. The lowest energy absorption band of the spectrum is 'A1g(S)→ 4T1g(G) in octahedral; while in the tetrahedral complex, it is A_1 (S)→ 4T_1 (G) transition. The difference in energy between these two states is also attributable to electron-electron repulsions and B, the Racah parameter that acts as a measure of electron-electron repulsions.

The electronic configuration for ground state term symbol is t2g^3 eg with five unpaired electrons having parallel spins and any promotion or rearrangement of the electrons would lead to a lower multiplicity state. Moreover, if we combine this fact perfect octahedral complexes like [Mn(H2O)6]2+, the absorption intensities become very weak due to the additional selection rule of Laporte forbiddance. This makes [Mn(H2O)6]2+ pale pink in color but the tetrahedral complexes of Mn2+ are quite instance due to the absence of the centre of symmetry. The subscript g and should be omitted if the same diagram is to be used to generalize the spectra of tetrahedral counterparts. It is also worthy to note that the electronic states with symmetry never cross each other but repel each other due to their quantum mechanical mixing.



Tanabe-SuganoDiagrams:-

i) d^1-configuration:-

Metal complexes with d-configuration do not have any inter electronic repulsion and the single electron resides in the 12g orbital ground state. When 12g orbital set holds the single electron, six microstates will have 2T2g state energy of -4 Dq; and when the electron is promoted to the eg orbital, the four microstates will have Eg state energy of +6 Dq. This is in accordance with the single absorption band in a UV-vis experiment; and thus, the transition from 2T2g to Eg does not require a Tanabe-Sugano diagram.

Consider the example of [Ti(H2O)6]3+

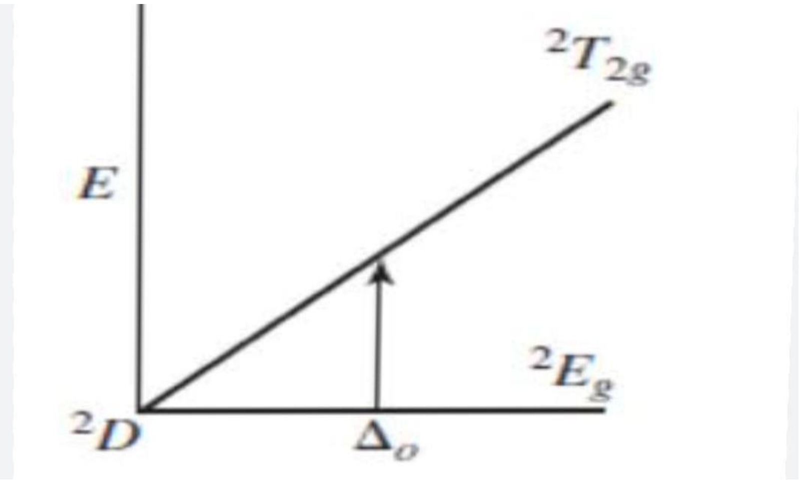
1. Calculation of B: No need to calculate the Racah parameter.

2. Calculation of A.: The purple color of the complex ion [Ti(H2O)6]3+ is due to a broad absorption band at 20300 cm^1 arising from 2T2g→ 2Eg transition. Hence, 10 Dq for this complex is 20300 cm-^{1}.

3. Calculation of ß: No need to calculate the nephelauxetic ratio.

ii) d9-configuration:-

In d' octahedral metal complexes, the ground state filling of electrons (12g eg^3) has only four microstates that have Eg energy state with -6 Dq. When the electron from 12g is promoted to the ez orbital set; the new configuration will have six microstates that have Tag energy state with +4 Dq. This could also be described as a positive "hole" that moves from the the e e to to the 12 orbital set. The sign of Dq is opposite that for d^1, with a 2Eg ground state and a 2T2g excited state. Like the d' case, d' octahedral complexes do not require the Tanabe-Sugano diagram to predict their absorption spectra.



Consider the example of [Cu(H2O)6]2+.

1. Calculation of B: No need to calculate the Racah parameter.

2. Calculation of Ao: In the UV-visible spectra of [Cu(H2O)6]2+, the broad band at 12000 cm^1 is due to spin- allowed Eg→ 2T2g transition; and hence, 10 Dq for this complex is 12000 cm^{-1}.

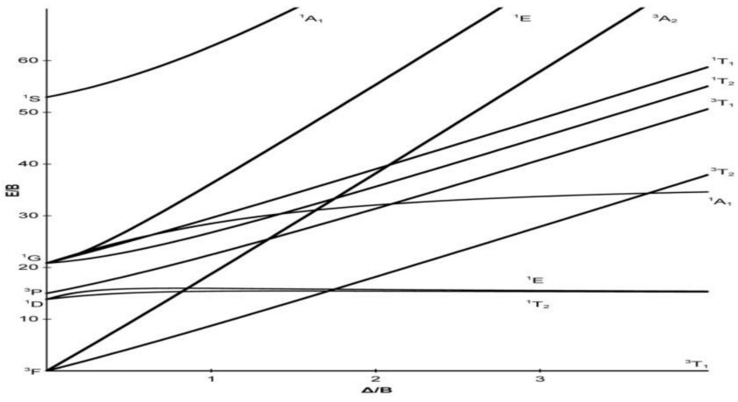
3. Calculation of ẞ: No need to calculate the nephelauxetic ratio.

2. **d2 systems**:

Metal complexes with d^2-configuration have 'F ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes T1g and remains as such in the weak field as well as strong ligand field.

Consider the example of [V(H2O)6]3+.

1. Calculation of B: From the Orgel diagram, it can be clearly seen that the ground state for d^2-octahedral complexes is T1g and there are three main transitions before the crossover point. Moreover, it is worthy to note down that the order of second and third



transitions is reversed after the crossover point and only two bands will be observed at or near the crossover point. As the magnitude of the crystal field splitting energy increases, the T1g(F) and T1g(P) states repel each other more and more with a magnitude of x energy value.

V1=3T1g→3T2g

V2 = 3T1g→3A2g

V3=3T1g3T1g(P)

Now slide a ruler across the printed diagram (perpendicular to the abscissa) until the ratio of E2/B to E1/B between lines becomes equivalent to 1.49. In this particular example, this ratio becomes 1.49 when A/B 31. Stop the ruler movement and find out the values of E2/B and E_1 /B

E2/ B = 43;   E1/B = 27

Thus, on the T-S diagram, where A/B = 31; the value of Tig→ 3T2g and Tig→ T1g(P) i.e. E/B and E2/B, are 27 and 43, respectively. The Racah parameter can be found by calculating B from both v2 and v1.

26000 /B =43 , 17500 /B = 27

26000 /43 = 604 cm-1; 17500/27   = 648 cm-1

Average value of Racah parameter (B) = 604+648/ 2 = 626 cm-1

2. Calculation of A: Being a weak-complex, the theoretical value of lowest-energy absorption band given by the Orgel diagram is 8 Dq (T T); and the experimental the experimental value for lowest-energy absorption band is 17500 cm^{1}. Hence, the value of 10 Dq or Δ can be calculated as

8Dq = 0.8 Δ°=17500

Δ°=17500/0.8

Δ°=10 Dq=21875cm-1

However, this is just the approximation and a more precise and refined calculation should be carried out using the Tanabe-Sugano diagram. From the average value of the Racah parameter, the ligand field splitting parameter can be found as follows.

Δ°\B = 31;Δo/ 626 cm-1 = 31,Δ°=19406 cm-1

3. Calculation of ß: In order to calculate the nephelauxetic ratio, we must have the value of Racah parameter for a free metal ion in its gaseous state. For free d ion like V^{3}+, it

has been observed that P state lies 12925 cm above to the 'F state. Hence, 15B 12925 cm^1 or B = 862 cm^1. Now, the value of nephelauxetic ratio can be calculated as

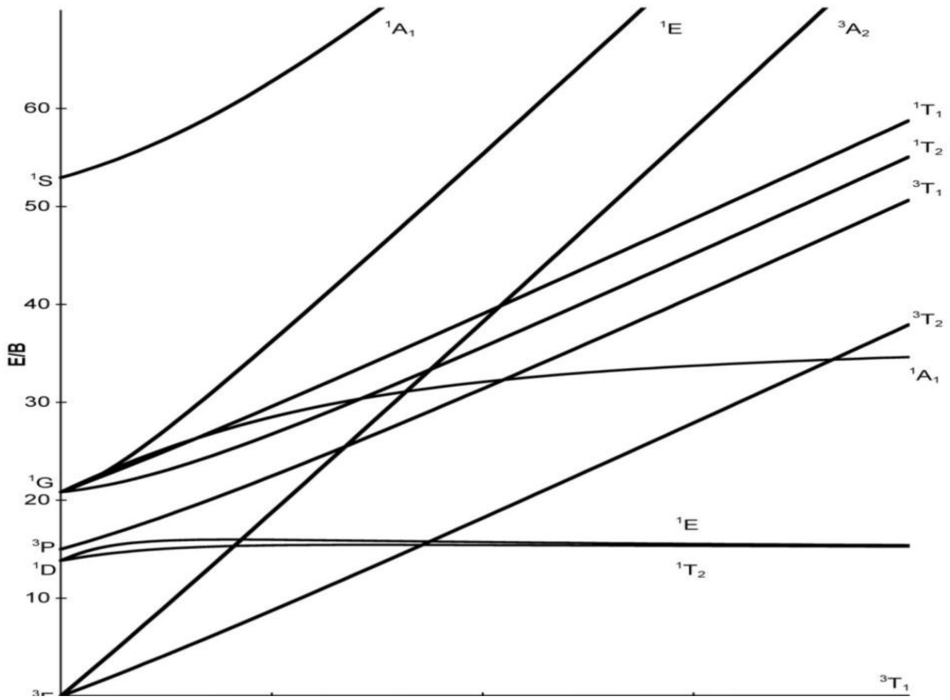
Nephelauxetic ratio =

ß = Bcomplex/ Bfree ion 626 cm-1 /862 cm -1 = 0.726

Hence, inter-electronic repulsion has been decreased during the process of complexation.

➤d8 complexes

Metal complexes with d-configuration have ^{3}F ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes 3A2g and remains as such in weak as well as in strong ligand fields. The Orgel and Tanabe-Sugano diagram for d-configuration can be used to estimate the value of crystal field splitting energy for these transition metal complexes.



Consider the example of [Ni(H2O)6]2+.

1. Calculation of B: From the Orgel diagram, it can be clearly seen that the ground state for d-octahedral complexes is 3A2g and there are three main transitions. As the

magnitude of the crystal field splitting energy increases, the T1g(F) and 3T1g(P) states repel each other more and more with a magnitude of x energy value owing to the non-crossing rule of the same symmetry states. V1=3A2g→3T2g

V2=3A2g→3T1g

V33A2g3T1g(P)

Which gives

V1 = 10 Dq. ………. (1)

V2=18 Dq+x. …………….(2)

V3=15 B+12 Dq + x………(3)

Putting value of x from equation (2) in (3), we get

V315 B+12 Dq + 18 Dq-V2

V315 B+30 Dq –V2………..(4)

Multiplying equation (1) by 3 and putting the value of 30 Dq from equation (1) in (4), we get

V3=15 B+3v1-v2

15B=V3+V2-3V1

B= V3+V2-3V1/15…….(5)

However, this method is applicable only when three transitions are observed. Moreover, this method is difficult to apply in a precise manner and only gives approximations.

From the Tanabe-Sugand diagram in the UV-visible spectra of Ni(HO)]2+, three bands are observed with maxima at around 8500, 14500 and 25300 cm. There are three possible transitions expected, A2g which include: Vi=3A2g→ T2g, v2 al energies of v3 to v2 is: →Tig, and v3 SINCE A28 (P). The ratio of experimental band of energies V3 and v2 is

V3/V2=E3/E2= E3/B/E2/B=25300/14500= 1.74

Now slide a ruler across the printed diagram (perpendicular to the abscissa) until the ratio of E2/B to E1/B between lines becomes equivalent to 1.74. In this particular example, this ratio becomes 1.74 when A/B = 10. Stop the ruler movement and find out the values of E3/B and E2/B as: B

E3 /B= 28;E2/B= 16

Thus, on the T-S diagram, where A/B = 10; the value of 3A2g 3T1g and 3A2g 3T1g(P) i.e. E2/B and E3/B, are 28 and 16, respectively. The Racah parameter can be found by calculating B from second and third i.e. from v3 and v2 transitions.

From v3, we get

25300 / B = 28

B=25300/ 28 = 904 cm-1

Similarly

14500/B= 16

B=14500 /16 = 906 cm-1

Therefore,

Average value of Racah parameter (B) = 904+906/ 2 = 905 cm-1

2. Calculation of Ao: Being a weak-complex, the theoretical value of lowest-energy absorption band given by the Orgel diagram is 10 Dq Ag T2); and the experimental value for lowest-energy absorption band is 8500 cm. Hence, the value of 10 Dq or A. can be calculated as

10Dq=8500cm-1

∆°=8500cm-1

However, this is just the approximation and a more precise and refined calculation should be carried out using the Tanabe-Sugano diagram. From the average value of the Racah parameter, the ligand field splitting parameter can be found as follows.

∆°\B=10

Δo /905 cm-1 = 10

Δo= 9050 cm-1

3. Calculation of ß: In order to calculate the nephelauxetic ratio, we must have the value of the Racah parameter for a free metal ion in its gaseous state. For free d^a ion like Ni2+, it has been observed that 'P state lies 16200 cm above to the 'F state. Hence, 15B 16200 cm^1 or B 1080 cm^1. Now, the value of nephelauxetic ratio can be calculated as

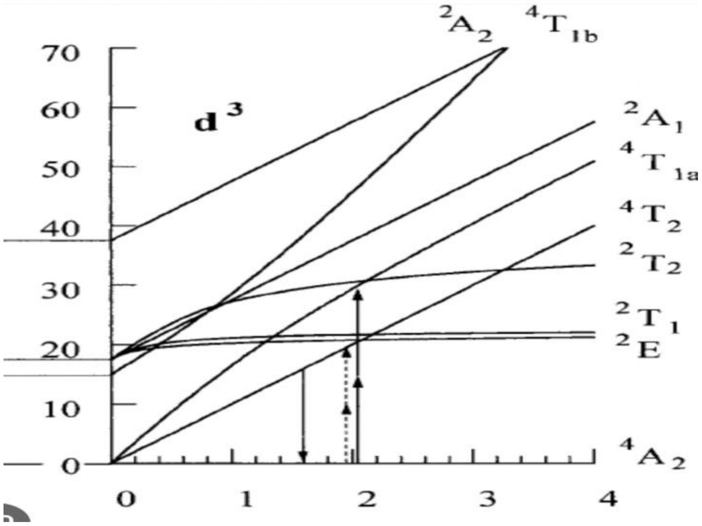
Nephelauxetic ratio =

ß = Bcomplex / Bfree ion=905 cm-1/ 1080 cm-1 =0.838

Hence, inter-electronic repulsion has been decreased during the process of complexation.

➤d3Complexes

Metal complexes with d^3-configuration have 'F ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes 4A2g and remains as such in weak as well as in strong ligand fields. The Orgel and Tanabe-Sugano diagram for d-configuration can be used to estimate the value of crystal field splitting energy for these transition metal complexes.



Consider the example of [Cr(H2O)6]3+.

1. Calculation of B: From the Orgel diagram, it can be clearly seen that the ground state for d^3-octahedral complexes is 4A2g and there are three main transitions. As the magnitude of the crystal field splitting energy increases, the Tig(F) and T1g(P) states repel each other more and more with a magnitude of x energy value owing to the non-crossing rule of the same symmetry states.

V1 =4A2g4T2g

V2=4A2g→4Tig

V34A2g4T1g(P)

Which gives

V1 = 10 Dq…….(1)

V2 = 18 Dq-x……(2)

V3 = 15 B+ 12 Dq + x…..(3)

Putting the value of x from equation (2) in (3), we get

$V3=15 B + 12 Dq + 18 Dq-v2$

$V3 = 15 B+30 Dq –V2$……..(4)

Multiplying equation (1) by 3 and putting the value of 30 Dq from equation (1) in (4), we get

$V3=15 B+3V1-V2$

$15B= V3+V2-3V1$

$B= V3+V2-3V1/15$…..(5)

However, this method is applicable only when three transitions are observed. Moreover, this method is difficult to apply in a precise manner and only gives approximations.

From the Tanabe Sugandalagrant in the UV-visible spectra offer(H_2 O)]+, three bands are observed with maxima at around 17000, 24000 and 37000 cm. There are three possible transitions expected, which include: vi =4A2→ energies of v2 to v_1 is: 4T2g, V2 →4T1g, and v3 ratio of experimental band of energies V3 and v1 is

$V2/V1=E2/E1=E2/B/E1/B=24000/17000=1.41$

Now slide a ruler across the printed diagram (perpendicular to the abscissa) until the ratio of E2/B to E1/B between lines becomes equivalent to 1.41. In this particular example, this ratio becomes 1.41 when A/B = 24. Stop the ruler movement and find out the values of E2/B and E1/B as:

$E2/ B = 33.90$; $E1 /B = 24$

Thus, on the T-S diagram, where A/B = 24; the value of 4A2g 4T1g and 4A2g4T1g(P) i.e. E2/B and E3/B, are 33.90 and 24, respectively. The Racah parameter can be found by calculating B from first and second i.e. from v2 and v_1 transitions. From v2, we get

$24000 /B =33.90$

$24000 /33.90= B = 708$ cm-1

Similarly

17000 \B = 24

$17000/ 24= B = 708$ cm-1

Therefore,

Average value of Racah parameter (B) = 708+708 /2 = 708 cm-1

2. Calculation of A.: Being a weak-complex, the theoretical value of lowest-energy absorption band given by the Orgel diagram is 10 Dq (A2g T2g); and the experimental

value for lowest-energy absorption band is 17000 cm^{21}. Hence, the value of 10 Dq or A. can be calculated as

10Dq=17000cm-1

Δ°=17000cm-1

However, this is just the approximation and a more precise and refined calculation should be carried out using the Tanabe-Sugano diagram. the average value of parameter, parameter can be found as follows. Racah the ligand field splitting can be found as follows

Δ°/B=24

Δ°/708=24

Δ°=16992cm-1

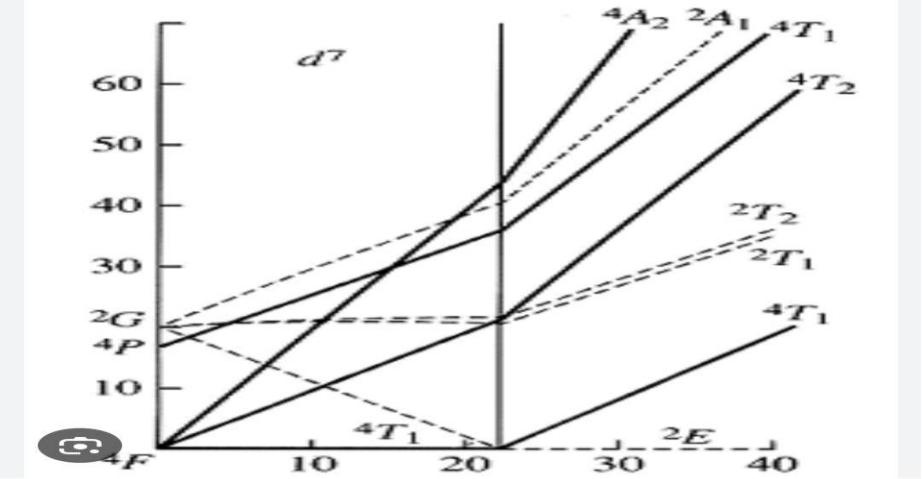
3. Calculation of ß: In order to calculate the nephelauxetic ratio, we must have the value of the Racah parameter for a free metal ion in its gaseous state. For free d ion like Cr^{3}+, it has been observed that 3P state lies 15450 cm above to the 'F state. Hence, 15B 15450 cm^{1} or B 1030 cm^{1}. Now, the value of nephelauxetic ratio can be calculated as:

Nephelauxetic ratio = β = Bcomplex /Bfree ion 708 cm-1/1030 cm-1 = 0.687

Hence, inter-electronic repulsion has been decreased during the process of complexation.

d7Complexes

Metal complexes with d'-configuration have 4F ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes 4T1g in the weak field; and becomes Eg when the ligand field becomes sufficiently strong. The Orgel and Tanabe-Sugano diagram for d-configuration can be used to estimate the value of crystal field splitting energy for these complexes.



Consider the example of [Co(H2O)6]2+

1. Calculation of B: From the Orgel diagram, it can be clearly seen that the ground state for d'-octahedral complexes is Tig and there are three main transitions before the crossover point. Moreover, it is worthy to note down that the order of second and third transitions is reversed after the crossover point and only two bands will be observed at or near the crossover point. As the magnitude of the crystal field splitting energy increases, the Tig(F) and 4T1g(P) states repel each other more and more with a magnitude of x energy value.
   $V1=4Tig\rightarrow 4T2g$
   $V2=4T1g\rightarrow 4A2g$
   $V3=4T1g4T1g(P)$
   Which gives
   $V1 = 8\ Dq + x$……..(1)
   $V2 = 18\ Dq + x$……..(2)
   $V3=15\ B+ 6\ Dq + 2x$……(3)
   Adding equation (1) and (2), we get
   $V2 + V1=18\ Dq + x + 8\ Dq + x$
   $V2 + V1=26\ Dq + 2x$………(4)
   Subtracting equation (1) and (2), we get
   $V2-V1 = 18Dq+x-8Dq-x$
   $V2-V1= 10Dq$…………(5)
   Putting the value of 2x from equation (4) in equation (3), we get
   $V3=15\ B+ 6\ Dq+v2+vi-26\ Dq$

$V3=15\ B+V2+V1-20\ Dq$

Multiplying equation (5) by 2 and putting the value of 20 Dq from equation (5) in equation (6), we get
V3=15 B+V2+V1-20Dq
V3= 15B+V2+V1-2V2+2V1

15B= V3+V2-3V1

B = V3+V2-3V1 15…..(7)

However, only two transitions are observed, this method is difficult to apply in a precise manner and only gives approximations.

From the Tanabe-Sugano diagram, in the UV-visible spectra of [Co(H2O)6]2+, two bands are observed with maxima at around 8000, 19600 and 21600 cm^{1}. There are three possible transitions expected, which include: v_1 =4T1g4T2g, V2=4T1g→4A2g and V3 = 4T1g4T1g(P). The ratio of experimental band energies is:

V3/V1=E3/EE1E3/B/E1/B=21600/ 8000 = 2.70

Now slide a ruler across the printed diagram (perpendicular to the abscissa) until the ratio of E3/B to E_1 /B between lines becomes equivalent to 2.70. In this particular example, this ratio becomes 2.70 when A/B = 9.5. Stop the ruler movement and find out the values of F2/B and E1/B as:

E3/B = 22; E1/ B = 8.2

Thus, on the T-S diagram, where A/B = 31; the value of Tig→ 3T2g and Tig→ T1g(P) i.e. E_1 /B and E3/B, are 8.2 and 22, respectively. The Racah parameter can be found by calculating B from both v2 and V1. 21600 /B =228000 /B = 8.2

B = 21600/22= 982 cm-1; B = 8000/ 8.2 = 976 cm-1

Average value of Racah parameter (B) = 982+976 /2 = 979 cm-1

2. Calculation of A.: Being a weak-complex, the theoretical value of lowest-energy absorption band given by the Orgel diagram is 8 Dq (Tig T3); and the experimental value for lowest-energy absorption band is 8000 cm^{1}. Hence, the value of 10 Dq or A, can be calculated:

8Dq=0.8∆°=8000cm-1

∆°=8000/0.8

∆°= 10 Dq = 10000 cm-1

However, this is just the approximation and a mo a more precise and refined calculation should be carried out using the Tanabe-Sugano diagram. From the average value of the Racah parameter, the ligand field splitting parameter can be found as follows.

∆°/B = 9.5,∆o/979 cm-1 = 9.5;∆o= 9300 cm-

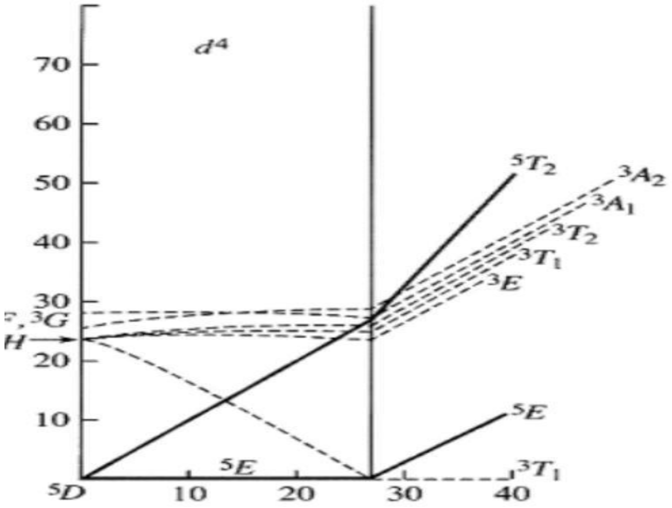
3. Calculation of ß: In order to calculate the nephelauxetic ratio, we must have the value of the Racah parameter for a free metal ion in its gaseous state. For free d' ion like Co2+, it has been observed that ^{3}P state lies 16755 cm above to the 'F state. Hence, 15B 16755 cm^1 or B 1117 cm^1. Now, the value of nephelauxetic ratio can be calculated as:

Nephelauxetic ratio = ß = Bcomplex /Bfree ion =979 cm-1/ 1117 cm-1 = 0.876

Hence, inter-electronic repulsion has been decreased during the process of complexation.

➤d4 complexes:-

Metal complexes with d-configuration have 'D ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes Eg in the weak field; and becomes Tig when the ligand field becomes sufficiently strong. The Orgel and Tanabe-Sugano diagram for d-configuration can be used to estimate the value of crystal field splitting energy for these complexes.



Consider the example of [Mn(CN)6]3-

1. Calculation of B: From the Tanabe-Sugano diagram, it can clearly be seen that the spin-allowed d-d transitions in low-spin d metal complexes are Tig→ Eg, Tig→ T2g, Tig→ Aig and Tig→ 3A2g. In the UV-visible absorption spectra of [Mn(CN)6]3, three

bands are observed; one strong band with maxima at around 27000 and other two bands at 29000 and 34000 cm^{-1}. Moreover, the bands at 21800 and 43500 cm-^{1} can be ignored as they correspond to charge transfer transitions. Thus, the ratio of experimental energies is

V2/V1= E2/E1=E1/B/E2/B =29000 cm-1 / 27000 cm-1 = 1.07

Now slide a ruler across the printed diagram (perpendicular to the abscissa) until the ratio of E2/B to E_1 /B i.e. the ratio between the lines corresponding to the first two spin-allowed transitions becomes equivalent

to 1.07. In this particular example, this ratio becomes 1.07 when A/B = 40. Stop the ruler movement and find out the values of E2/B and E1/B.

E2/ B = 38;E1/B = 35 B

Thus, on the T-S diagram, where A/B = 40; the value of Tig→3T2g and Tig→ Eg i.e. E2/B and E_1 /B, are 38 and 35, respectively. The Racah parameter can be found by calculating B from both v2 and v1.

29000 cm-1 /B = 38;27000 cm-1/ B = 35

29000/38 =763 cm-1; =27000 cm-1 /35 = 771 cm-1

Average value of Racah parameter (B) = - 763 cm-1+771 cm-1 /2 = 767 cm-1

2. Calculation of A.: The only parameter that is needed to be sought for the calculation of the magnitude of crystal field splitting energy (10 Dq) in weak field complexes is the single absorption band in a UV-vis experiment. Hence, the energy of the transition ETS Eg T2g should give the value of A directly. In other words, the lowest energy absorption band in d high-spin complexes is equal to the crystal field splitting energy. However, the magnitude of crystal field splitting energy for high-spin d complexes cannot be obtained accurately from the Orgel diagram as the Jahn-Teller, distortion reduces the symmetry from perfectly octahedral to a tetragonal geometry. The effect of Jahn-Teller distortion will be discussed later in this chapter. Furthermore, the practical applicability of the Tanabe-Sugano diagram int the high-spin region (before A/B = 27) is strongly doubted because only one spin allowed transition spin-allowed transitions are required for the ratio calculation. present. and it is a fact that two minimum spin allowed transition are required for the ratio calculation .

Being a strong-field complex, the theoretical Va crystal field splitting energy in [Mn(CN)6]3- cannot be given by the Orgel diagram; hence, we are bound to use Tanabe-Sugano diagram. From the average value of the Racah parameter, what we have deduced earlier, the ligand field splitting parameter can be found as follows.

Δo/B=40 ;Δo/767= 40 ;Δo= 30680cm-1

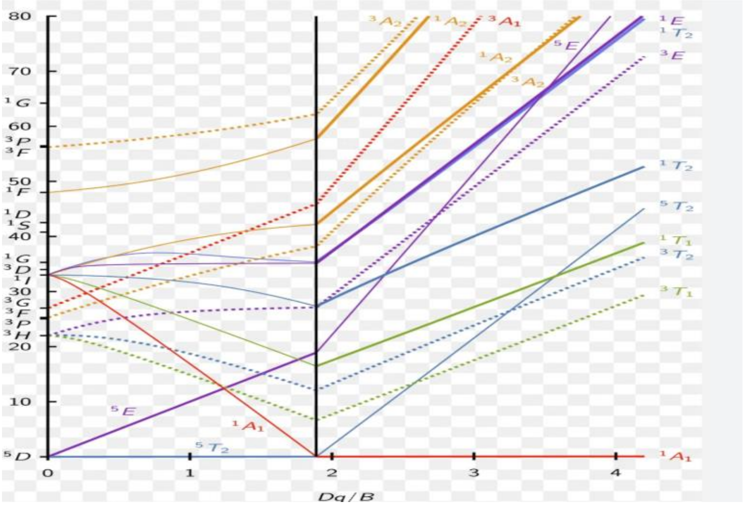
3. Calculation of ß: In order to calculate the nephelauxetic ratio, we must have the value of the Racah parameter for a free metal ion in its gaseous state. For free dt ion like Mn^{3}t, the value of B is found to be 1140 cm^{1}. Now, the value of nephelauxetic ratio can be calculated as

Nephelauxetic ratio = ß = Bcomplex/ Bfree ion 767 cm-1 /1140 cm-1 = = 0.673

Hence, inter-electronic repulsion has been decreased during the process of complexation.

➤d6Complexes

Metal complexes with d-configuration have 'D ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes T2g in the weak field; and becomes 'A1g when the ligand field becomes sufficiently strong. The Orgel and Tanabe-Sugano diagram for de-configuration can be used to estimate the value of crystal field splitting energy for these complexes.



Consider the example of [Co(en)3]3+

1. Calculation of B: From the Tanabe-Sugano diagram, it can clearly be seen that the spin-allowed d-d transitions in low-spin d metal complexes are 'Aig→ Tig and 'A1g→ T2g. In the UV-visible absorption spectra of [Co(en)3]3+, two bands are observed; one strong band with maxima at around 21450 and the other band at 29450 cm^{1}. Therefore, the ratio of experimental band energies is

V2/V1= E2/E1=E2/B/E1/B= 29450 cm-1/ 21450 cm-1 = 1.37

Now slide a ruler across the printed diagram (perpendicular to the abscissa) until the ratio of E2/B to E1/B i.e. the ratio between the lines corresponding to the first two spin-allowed transitions becomes equivalentto 1.37. In this particular example, this ratio becomes 1.37 when A/B = 40. Stop the ruler movement and find out the values of E2/B and E1/B.

E2/ B = 52;E1/B=38

Thus, on the T-S diagram, where A/B = 40; the value of 'A1g→ T2g and 'Aig→ Tig i.e. E2/B and E_1 /B, are 52 and 38, respectively. The Racah parameter can be found by calculating B from both v2 and vi.

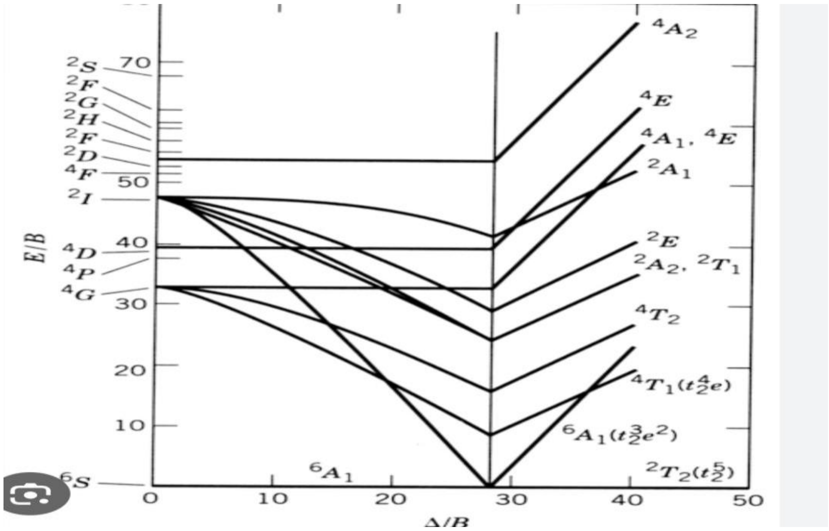
29450 cm-1/ B = 52;21450 cm-1/ B = 38

B=29450 cm-1 /52 = 566 cm-1; B = 21450 cm-1 38 = 564 cm-1

Average value of Racah parameter (B) = 566 cm-1+564 cm-1 /2 = 565 cm-1

➤d5Complexes:-

Metal complexes with d-configuration have 'S ground state term symbol in the absence of any crystal field. However, when six ligands approach in octahedral coordination, the ground state term symbol becomes A1g in the weak field; and becomes 2T2g when the ligand field becomes sufficiently strong. The Tanabe-Sugano diagram for d-configuration can be used to estimate the value of crystal field splitting energy for these complexes.



Consider the example of [Mn(H2O)6]2+

1. Calculation of B: From the Tanabe-Sugano diagram, it can clearly be seen that there is no spin-allowed d- d transitions in high-spin d metal complexes. However, main spin-forbidden transitions are A1g → Tig(G), 6A1g4T2g(G), Aig→ 4A1g(G), A1g 4Eg(G), 'Aig→ T2g(D) and 'Aig→ E(D). In the UV-visible absorption spectra of [Mn(H2O)6]2+, the first two bands are observed at around 18600 and the other band at 22900 cm^{1}. Therefore, the ratio of experimental band energies is

V2/V1=E2/E1=E2/B /E1/B= 22900 / 18600 = 1.23

Now slide a ruler across the printed diagram (perpendicular to the abscissa) until the ratio of E2/B to E1/B i.e. the ratio between the lines corresponding to the first two spin-allowed transitions becomes equivalentto 1.23. In this particular example, this ratio becomes 1.23 when A/B = 11. Stop the ruler movement and find out the values of E2/B and E1/B.

E2 /B = 29

E1/ B = 24

Thus, on the Tanabe-Sugano diagram, where A/B = 11; the value of A1g 4T2g(G) and A1g→ 4T1g(G) i.e. E2/B and E_1 /B, are 29 and 24, respectively. The Racah parameter can be found by calculating B from both v2 and v1.

22900 cm-1/B= 2918600cm-1/B=24

B= 22900/29=789 cm-. B= 18600/24=776cm-1

Average value of Racah parameter(B)= 789+776/2=782cm-1

2. Calculation of A: The magnitude of crystal field splitting energy for high-spin d complexes cannot be w.uata Institute.com obtained accurately from the Orgel diagram as the degeneracy of the ground state term is only one and does not split at all in the octahedral field. Therefore, we are bound to use the Tanabe-Sugano diagram. From the average value of the Racah parameter, , twe have deduced earlier, the ligand field splitting parameter can be found as follows.

∆o/B=11

Δo /782 cm-1 = 11

∆o=8602 cm-1

3. Calculation of ß: In order to calculate the nephelauxetic ratio, we must have the value of Racah parameter for a free metal ion in its gaseous state. For free d ion like Mn2+, the value of B is found to be 960 cm^{-1}. Now, the value of nephelauxetic ratio can be calculated as

Nephelauxetic ratio = ß = Bcomplex /Bfree ion 782 cm-1 /960 cm-1 = 0.814

Hence, the inter-electronic repulsion has been decreased during the process of complexation.

ChargeTransferSpectra:

A charge transfer band may be defined as the peak arising from the transition in which an electron is transferred from one atom or group in the molecule to another one.

In other words, the transition occurs between molecular orbitals that are essentially centered on different atoms or groups. These transitions are neither Laporte nor spin-forbidden in nature; and therefore, show very intense absorption. Charge transfer transitions are primarily classified in four types as:

LigandtoMetalChargeTransfer:-

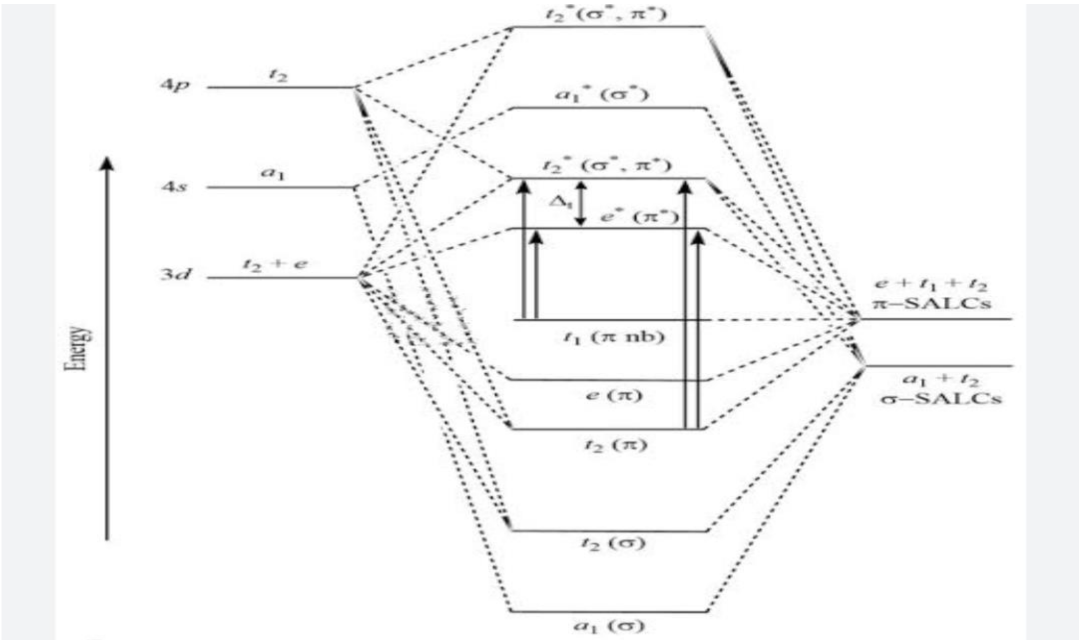
The ligand to metal charge transfer (LMCT) in metal complexes arises when the electrons are transferred from a molecular orbital with a ligand-like character to those with metal-like character. This type of transfer is predominant if the following conditions are fulfilled:

1) The ligands should have tone pair of electrons with relatively high-energy such as O2, Cl, Br, S^2 or Se.

II) The metal should be in a high oxidation state and must have low-lying empty orbitals.

These conditions imply that the acceptor level is available and low in energy. Moreover, the charge transfer transitions for octahedral and tetrahedral complexes are different; therefore, these two types of ligand to metal charge transfer are quite important and must be discussed in detail.

1. LMCT in octahedral complexes: Before we discuss the ligand to metal charge transfer in octahedral complexes, the molecular orbital diagram for o and-bonding in ML6 geometry should be recalled. The electrons can be excited, not only from the 12g to eg but also from the bonding molecular orbitals of o and in nature that are predominantly associated with the ligands. The latter two types of excitation modes result inthe charge transfer spectra, labeled as the ligand to metal charge transfer. This type of transition results in a formal reduction of the metal.



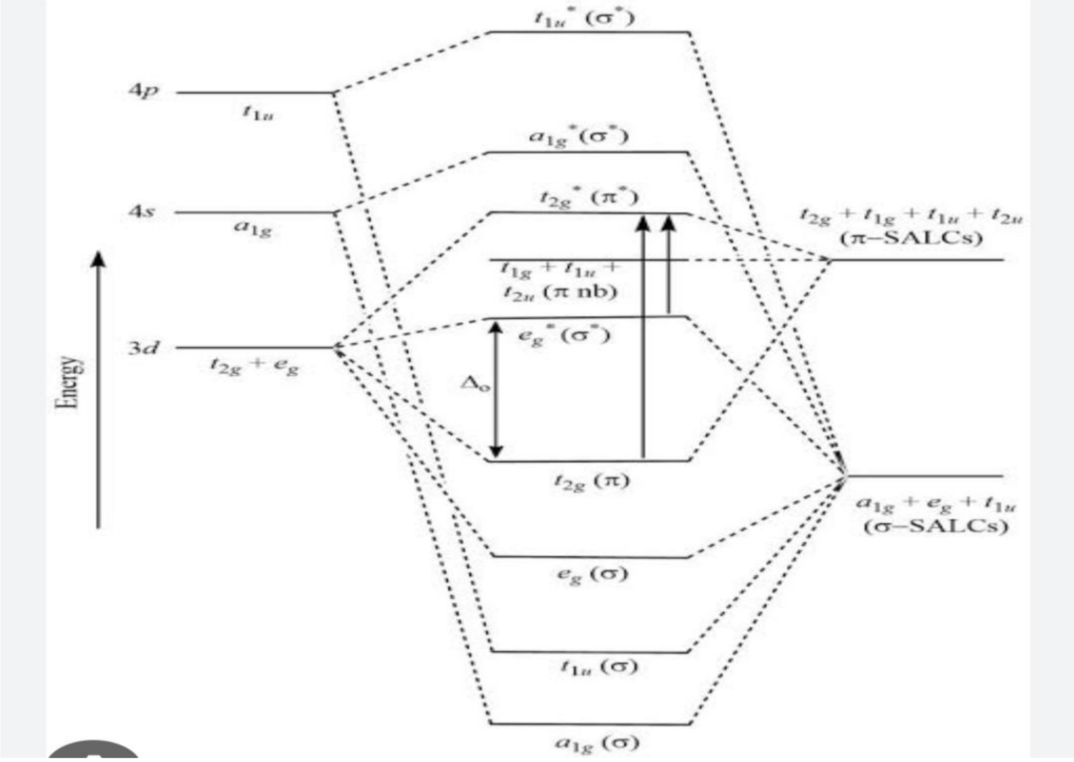
Consider a do octahedral complex, such as [Co(NH3)5(X)]2+ (X = F, Cl, Br or I), whose tag levels are filled. As a consequence, an intense absorption band in [Co(NH3)5F]2+ is observed above 40000 cm; and that is corresponding to a transition from ligand o- bonding molecular orbital to the empty es molecular orbital. However, in [Co(NH3)5C1]2+ this intense band with two components is observed above 30000 cm-1.

The charge-transfer bands appear at lower energy for [Co(NH3)sBr] and at still lowerenergy for [Co(NH3)51]2+, overlapping with ligand-field bands and masking their higherenergy peaks. It must be noted that the ligand-field peaks shift slightly according to theincreasing strength of the crystal field of X, but the charge-transfer bands show verylarge shifts. The shifts in the energies of the LMCT transitions in [Co(NH3)5(X)]2+correspond to the changes in ease of removal of the electron (oxidation) from X. Thoughthe transition corresponds to the transfer of an electron from X to Co^{3}+; and therefore, nonet oxidation-reduction occurs because of the very short lifetime of the excited

state.Nonetheless, this process, provide a mechanism for photochemical decomposition thatoccurs for many complexes stored in strong light. A similar pattern has been observed in the case of [Cr(NH3)5(X)]2+ (X = F, Cl, Br or I)

2. LMCT in tetrahedral complexes: Before we discuss the ligand to metal charge transfer in ttetrahedracomplexes, the molecular orbital diagram for o and t-bonding in ML4 geometry should be recalled. The electrons can be excited, not only from the e to t2", but also from the-bonding molecular orbitals of t2 symmetry and nonbonding π-SALCs of t,-symmetry; both of which are predominantly associated with the ligands. The

latter two types of excitation modes result in the charge transfer spectra, labeled as the ligand to metal charge transfer. This type of transition results in a formal reduction of the metal.



Consider a d tetrahedral complex, such as MnO4, whose e and t2 levels are totally empty. As a consequence, very intense absorption spectra in permanganate is obtained and all of the four ligand-to-metal-charge-transfer (LMCT) transitions are observed. However, it must be noted that three out of four peaks happen to arise in the ultra-violet region and only te transition belongs to the visible range. Moreover, this particular transition is also responsible for the deep purple color of permanganate ion.

➤MetaltoLigandChargeTransfer

The metal to ligand charge transfer (MLCT) in metal complexes arises when the electrons are transferred from a molecular orbital with a metal-like character to those with a ligand-like character. This type of transfer is predominant if the following conditions are fulfilled:

i) The ligands should have high-energy empty π" orbitals such as CO, CN, SCN or NO.

ii) The metal should be in a low oxidation state and must have high-lying filled orbitals.

These conditions imply that the empty π" orbitals on the ligands become the acceptor orbitals on the absorption of light. The available acceptor level is relatively high in energy. However, before we discuss the ligand to metal charge transfer in transition metal complexes, the molecular orbital diagram for 6 and π- bonding in ML6 geometry should be recalled.

The electrons can be excited, not only from the 12g to eg, but also from the bonding molecular orbitals of t and antibonding molecular orbitals of o nature (predominantly associated with the ligands) to antibonding π". The latter two types of excitation modes result in the charge transfer spectra, labeled as the metal to ligand charge transfer. This type of transition results in formal reduction of the metal. The common type of ligands taking part in MLCT include 2,2'- bipyridine (bipy), 1,10-phenanthroline (phen), CO, CN- and SCN-. Examples of these complexes include: Tris (2,2'-bipyridyl) ruthenium(II), W(CO)4(phen), K4[Fe(CN)6], K3[Fe(CN)6], [Fe(phen)3], [Fe(acac)3] and Fe(CO)3(bipyo

An orange-colored complex of bivalent ruthenium, [Ru(bpy)3], is being analyzed because the excited electronic state that results from this charge transfer has an average life-time around microseconds and the complex can act as an adaptable photochemical reagent. The photo-reactivity of these complexes arises from the nature of the reduced ligand and oxidized metal center. Now although the states of MLCT complexes such as [Ru(bipy)3]^{2}+ and Re(bipy) (CO)3Cl were intrinsically not that much reactive, there are many MLCT complexes which are characterized by reactive MLCT states. Vogler and Kunkely proposed that a MLCT complex can be considered as an isomer of the ground state, that possesses a reduced ligand and oxidized metal. Hence, many reactions like electrophilie attack, oxidative addition at the metal ion due to the reduced ligand, the radical reactions on the reduced ligand, or the outer-sphere charge-transfer reactions can be attributed to states arising from metal-to-ligand-charge-transfer transitions. The reactivity of MLCT states usually depends on the oxidation of the metal center. The succeeding processes include exciplex formation, cleavage of metal-metal bonds, associative ligand substitution.

Metal - **Metalchargetransfer**:

The metal to charge transfer may simply be defined as the excitationand subsequent transfer of an electron from a low oxidation state caution oxidation state. neighboring cation of a higher certain Thetransfer is usually excited by a visible the light of and produces acharacteristic color. The electron then drops back down, giving off the extra energy as a small amount of heat. An example is corundum with the coupled substitution. The simplified chemical equation representing various oxidation states can be given as:

$$Fe2++ Ti+ Fe3+ + Ti^{3}+$$

This reaction absorbs red photons and gives sapphire its characteristic blue color. In hematite, the process absorbs all visible photons. Materials that exhibit this property retain their dark color regardless of how finely they are ground. Materials exhibiting metal to metal charge transfer (MMCT) are also conductors. MMCT generally shows a strong sloping spectral signature in the range 500-1000 nm. Edge-shared octahedral geometries generally exhibit MMCT in the range 700-800 nm, while face-shared octahedral complexes exhibit it is in the range of 800-900 nm. In order for metal-to-metal-charge-transfer (MMCT) to occur, orbital must overlap so electrons can flight back and forth. Examples of the systems displaying metal to metal charge transfer are:

The most popular example of inter-valence charge transfer is "Prussian blue". This compound has the formula KFe[Fe(CN)6] and shows a very intense blue color owing to the transfer of an electron from Fe2+ to $Fe^{3}t$. In the crystal structure of Prussian blue, the Fe2+ ions are bonded with N atom while the Fe3+ ions are bonded with C atom of through the cyanide bridge. Therefore, the charge transfer takes place

4.**LigandtoLigandChargeTransfer:-**

The ligand to ligand or inter-ligand charge transfer may be defined as the excitation and subsequent transfer of an electron from a one ligand orbitals to a neighboring ligand orbital.

The ligand to ligand charge transfer (LLCTy or inter-ligand charge transfer transitions are quite uncommonand rarely observed. In comparison to the enormousliterature on metal-to-ligand and ligand-to-metalcharge transfer, very little has been published on LLCT.In most of the cases, LLCT peaks are difficult to detect in UV-visible absorption spectra; which can be attributed to the fact that these peaks may beobscured or hidden under absorption bands of different origins, or they may occur at a position very distinctfrom those ordinarily analyzed. The LLCT bands are oflow intensity due to the poor overlap between theparticipating orbitals. Molecular orbitals with dominantligand characters may have some amount of metal character also, and a transition that is labelled asligand to ligand may in fact also involve the metal tosome point. However, if the LLCT is pure, it would have transition energy that does not change considerablywhen the metal is changed. A more specific form ofLed-M-Lox complexes is mixed-valence compounds (ligand-based), which possesses the same ligand in twodifferent redox states. In this case, the interactionbetween ligands may yield a partial or completeelectron delocalization between the oxidized andreduced form of the ligands. Therefore, the LLCT losesits charge-transfer character because now it isoccurring between delocalized orbitals.

One of the recent examples of metal complexes involving ligand to ligand charge transfer is (CuTpAsPh3). The emission and UV-visible absorption spectra of (CuTpAsPh3), contain low-energy bands (with a band maximum at 16 500 cm in emission and a weak shoulder at about 25000 cm in absorption) that are not present in the corresponding spectra of the phosphine or amine complexes. The peaks are assigned to the ligand to ligand charge transfer (LLCT) may have some contribution from the metal.

5.4 MAGNETIC PROPERTIES OF COMPLEXES

Magnetic properties are useful in deciding the oxidation state, electronic configuration and coordination number of the central metal atom or ion.

In 1845 Faraday classified the substances as diamagnetic and paramagnetic. Later on these terms were related with electronic structure. The substances, which have paired electrons, are known as diamagnetic and which have one or more unpaired electron(s) are known as paramagnetic. The paramagnetic effect is observed only in the presence of an external field. When the field is removed, the substance has no overall moment.

When any substance is placed in a magnetic field, the field developed within the substance will either be greater than or less than the applied magnetic field, which depends upon the nature (paramagnetic or diamagnetic) of the substance. The difference between the two (AH) may be given as follows

$\Delta H - B - HO$ ……..(1)

Where

B = Induced Field Inside the Sample

H = Free Field Value

Evidently for Paramagnetic $B > H$ and for Diamagnetism $B < H$

Generally AH is expressed as Intensity of Magnetization (I) which is Magnetic Moment Per Unit Volume, therefore,

$4\pi I = B - H$

Or$4\pi I/Ho = B/Ho - 1$. ………..(2)

Where I/H, is known as Magnetic Susceptibility Per Unit Volume (k).

Therefore $4pk = B/Ho$

But, experimentally we determined the Specific (or Mass) Susceptibility (x)

Therefore, $x = k/d$ …….(4)

Where d is Density of the substance.

When x is multiplied by molecular weight of the substance then it is called Molar Susceptibility, represented as x...

Or

$$Xm = X. \text{ Molecular Weight}$$

There are many methods for the measurement of magnetic susceptibility, such as the Gouy, Faraday or NMR methods. But Gouy's method is generally used. In this method we determine the molar susceptibility (x) of the substance, i.e., the molar susceptibility of the substance is calculated. It is related with Magnetic Moment (u) of the substance as follows:

$\mu = 284\surd/Xm\text{-}T$ BM……(6)

Where Tis the temperature in Kelvin, BM is Bohr Magnetrons.

$1\ BM = eh/4n\ me = 9.273 \times 10\text{-}24\ JT\text{-}1$.

In place of magnetic moment generally Effective Magnetic Moment (μ) term is used which is obtained as follows:

$\mu\ eff = 284\surd XmT$ BM……..(7)

$$Xm = Xm - Xdia$$

The value of Xdia for different atoms, ions and bonds are known which can be taken from the literature.

Since, the paramagnetic originates in the spins and orbital motions of the unpaired electrons in the substance, hence following three types of couplings are possible:

Spin-Spin

Orbital-Orbital

Spin-Orbital

These types of couplings are common especially in Lanthanides which are given in Table

$\mu = g\ [J\ (J+1)]1/2$……(8)

Where J= Total Spin Angular Momentum Quantum Number

g = Lande's Splitting Factor which may be given as,

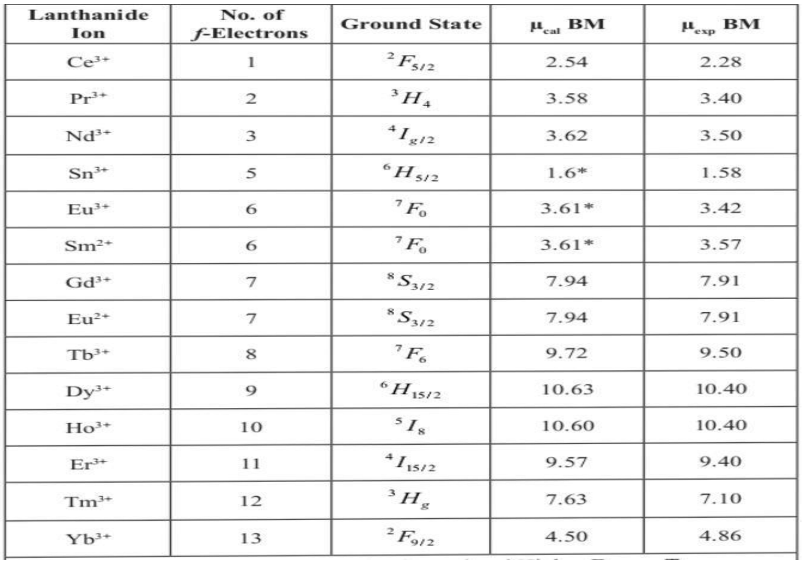
$g = 1 + J(J+1)+S(S+1) – L(L+1) /2J(J+1)$…..(9)

S = Total Spin Angular Momentum Quantum Number

L = Total Orbital Angular Momentum Quantum Number

For the complexes where spin and orbital contributions are significant and Spin-Orbital Coupling is negligible, the expression for u may be given as follows:

$\mu = [4(S)(S+1) + Z(L+1)]1/2$……(10)



Lanthanide Ion	No. of *f*-Electrons	Ground State	μ_{cal} BM	μ_{exp} BM
Ce^{3+}	1	$^2F_{5/2}$	2.54	2.28
Pr^{3+}	2	$^3H_4$	3.58	3.40
Nd^{3+}	3	$^4I_{g/2}$	3.62	3.50
Sn^{3+}	5	$^6H_{5/2}$	1.6*	1.58
Eu^{3+}	6	$^7F_0$	3.61*	3.42
Sm^{2+}	6	$^7F_0$	3.61*	3.57
Gd^{3+}	7	$^8S_{3/2}$	7.94	7.91
Eu^{2+}	7	$^8S_{3/2}$	7.94	7.91
Tb^{3+}	8	$^7F_6$	9.72	9.50
Dy^{3+}	9	$^6H_{15/2}$	10.63	10.40
Ho^{3+}	10	$^5I_8$	10.60	10.40
Er^{3+}	11	$^4I_{15/2}$	9.57	9.40
Tm^{3+}	12	^3H_g	7.63	7.10
Yb^{3+}	13	$^2F_{9/2}$	4.50	4.86

It is observed that Equation (10) is never satisfied in complexe because actual orbital contribution is always somewhat less than the idea value. Because it is reduced in the presence of ligands. When the value o 'L' reduces to zero, the magnetic moment is said to be quenched. This is fo the complexes having 'A or E Ground State' and 'Complexes of 3d-Serie Transition Metals'. For such complexes L = 0, therefore the Equation (10) reduces to the form

, $\mu = [4S (S +1)]1/2 = 2 [S (S+1)]1/2$ ...(11)

Equation (11) is known as Spin-Only formula for magnetic moment Since S is related with unpaired electrons and S = n/2, therefore Equation may be written as

$M=[n(n+2)]1/2$

The value of M can be calculated as different number of unpaired electrons