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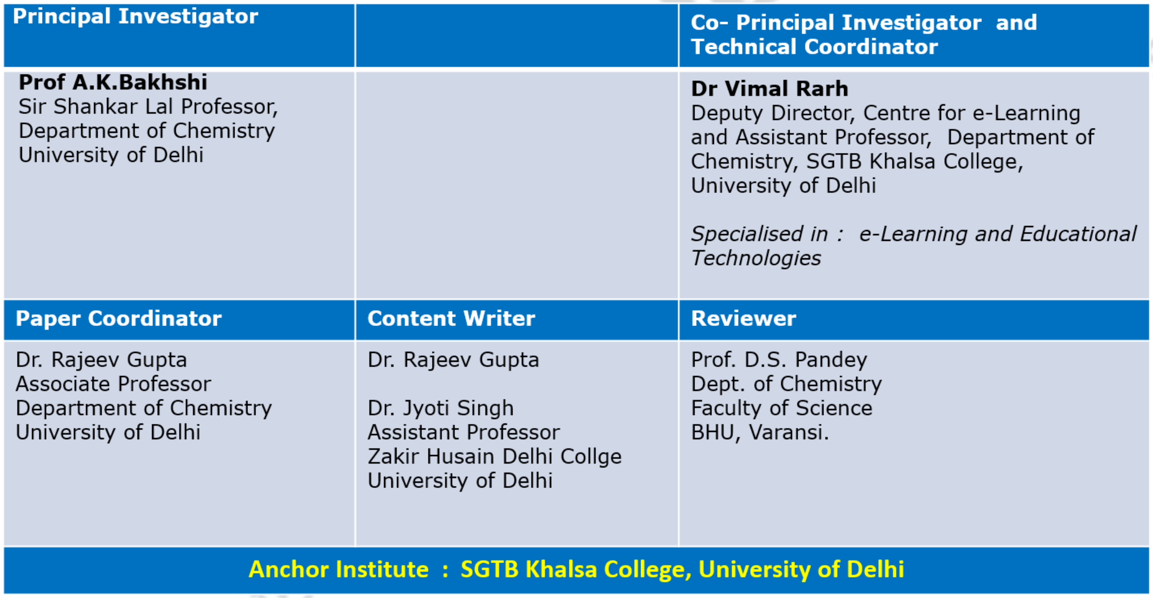

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## 1. Learning Outcomes

After studying this module, you shall be able to

- Know about magnetic properties of the transition metal ions.
- Know the magnetic properties of coordination complexes on the basis of crystal field theory
- Learn that the magnetic moment of most of the transition metal ions are very close to spin only magnetic moment $\mu_S$.
- Identify the transition metal ions having the magnetic moment higher than spin only magnetic moment $\mu_S$.
- Evaluate the reasons for having the higher magnetic moment.

## 2. Magnetic Properties of Transition Metal Ions

The first transition group elements possess an incomplete inner 3d shell. But for these elements the incomplete shell is not effectively shielded from external influence. These 3d orbitals are greatly affected by the ligands such that the rotations of electrons about the nucleus, which are essential for generating the orbital magnetic moment, get significantly restricted (i.e. L becomes zero). This leads to great difficulty in estimating the degree of quenching of the orbital contribution to the magnetic moment, but in some cases the results are actually easier to interpret than are those for the rare earths.

The ions of the first transition series starting from scandium, $Sc^{3+}$, ion and ending with zinc, $Zn^{2+}$, ion have progressively 0 to 10 electrons in the 3d shell. The first and last members are diamagnetic but all the others with intermediate number of electrons are paramagnetic. It might be supposed that these ions would be alternately paramagnetic and diamagnetic depending on whether they have an odd or an even number of electrons. But, as for the rare earths are concerned, the ions are all paramagnetic because the electrons in the incomplete shell tend not to pair off until these are forced to do so. For instance, in the 3d shell there are 5 orbitals which can accommodate 10 electrons. If 6 electrons are present they will take 1 paired and 4 unpaired place instead of 3 pairs. The 4 unpaired electrons will contribute to the paramagnetism. It is therefore an easy matter to compute the number of unpaired electron spins in any given ion. The difficulty that arises is in connection with the orbital contribution.

The orbital moments of these ions are not free to move as they are for the rare earths, and yet, on the other hand, they may not be entirely quenched. But the best agreement with the experiment is obtained by completely neglecting the orbital motion. For all the transition metal ions the magnetic moments are calculated by using following equations

$$\mu_J = \sqrt{J(J+1)}\, g\beta \ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

$$\mu_{L+S} = \sqrt{4S(S+1) + L(L+1)}\, \beta \ldots\ldots\ldots\ldots..(2)$$

For spin only magnetic moment, L= 0, so that J = S and hence g=2. Therefore,

$$\mu_S = \sqrt{4S(S+1)}\, \beta \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3)$$

$$\mu_S = \sqrt{n(n+2)}\, \beta \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(4)$$

(Where n = number of unpaired electrons)

Let us calculate $\mu_J$, $\mu_{L+S}$ and $\mu_S$ for one transition metal ion using equation (1), (2) and (3). For example, $Cr^{3+}$ has $d^3$ configuration, thus,

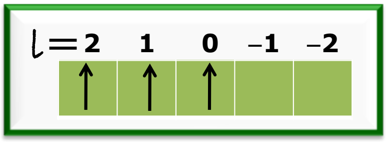

**Figure 1**

Total spin quantum number (S) = 1/2 + 1/2+ 1/2 = 3/2
Spin multiplicity (2S+1) = 4
Total angular momentum number (L) = (2×1) + (1×1) + (0×1) = 3
J = L+S, L+S-1,……L-S. i.e.J = 9/2 to 3/2. According to Hund’s rule J =3/2 is chosen for the calculation of g,

$$g = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)}$$

$$g = \frac{3}{2} + \frac{3/2(3/2+1) - 3(3+1)}{2 \times 3/2(3/2+1)}$$

$$g = \frac{3}{2} + \frac{15 - \ 48}{30} = 0.4$$

Calculation of $\mu_J$,

$$\mu_J = \sqrt{J(J+1)}\, g \ B.M.$$

$$\mu_J = 0.4\sqrt{3/2(3/2+1)}\ B.M.$$
$$\mu_J = 0.8\sqrt{15/4}\ B.M$$
$$\mu_J = 0.77\ B.M$$

Calculation of $\mu_{L+S}$,

$$\mu_{L+S} = \sqrt{4S(S+1) + L(L+1)}\ B.M.$$
$$\mu_{L+S} = \sqrt{4 \times \frac{3}{2}\left(\frac{3}{2} + 1\right) + 3(3+1)}\ B.M.$$
$$\mu_{L+S} = \sqrt{\left(4 \times \frac{3}{2} \times \frac{5}{2}\right) + (3 \times 4)}\ B.M$$
$$\mu_{L+S} = \sqrt{27}\ B.M = 5.20\ B.M.$$

Calculation of $\mu_S$,

$$\mu_S = \sqrt{n(n+2)}\ B.M.$$
$$\mu_S = \sqrt{3(3+2)}\ B.M. = 3.87\ B.M.$$
$$\mu_S = 3.87\ B.M.$$

Observed $\mu_{eff}$ for the $Cr^{3+}$ is 3.68 – 3.86 B.M., very close to spin only magnetic moment $\mu_S$. Similarly, $\mu_J$, $\mu_{L+S}$ and $\mu_S$ can be calculated for the other transition metal ions. The calculated and experimental magnetic moments are given in the table 1,

**Table 1**

| No of d electrons | Ion | L | S | Ground State Term | Calculated $\mu_J$ (B.M) | Calculated $\mu_{L+S}$ (B.M) | Calculated $\mu_S$ (B.M) | Observed $\mu_{eff}$ (B.M) |
|---|---|---|---|---|---|---|---|---|
| **0** | $Sc^{3+}$<br>$Ti^{4+}$<br>$V^{5+}$ | 0 | 0 | $^1S_0$ | 0 | 0 | 0 | 0 |
| **1** | $Ti^{3+}$<br>$V^{4+}$ | 2 | 1/2 | $^2D_{3/2}$ | 1.55 | 3.00 | 1.73 | 1.7 – 1.8 |
| **2** | $Ti^{2+}$<br>$V^{3+}$ | 3 | 1 | $^3F_2$ | 1.63 | 4.47 | 2.83 | 2.7 – 2.9 |
| **3** | $V^{2+}$<br>$Cr^{3+}$<br>$Mn^{4+}$ | 3 | 3/2 | $^4F_{3/2}$ | 0.77 | 5.20 | 3.87 | 3.81 – 3.86<br>3.68 – 3.86<br>4.00 |
| **4** | $Cr^{2+}$<br>$Mn^{3+}$ | 2 | 2 | $^5D_0$ | 0 | 5.48 | 4.90 | 4.80<br>5.00 |
| **5** | $Mn^{2+}$<br>$Fe^{3+}$ | 0 | 5/2 | $^6S_{5/2}$ | 5.92 | 5.92 | 5.92 | 5.2 – 5.96<br>5.4 – 6.0 |
| **6** | $Fe^{2+}$<br>$Co^{3+}$ | 2 | 2 | $^5D_4$ | 6.70 | 5.48 | 4.90 | 5.0 – 5.5<br>2.5 |
| **7** | $Co^{2+}$ | 3 | 3/2 | $^4F_{9/2}$ | 6.64 | 5.20 | 3.87 | 4.3 – 5.2 |
| **8** | $Ni^{2+}$ | 3 | 1 | $^3F_4$ | 5.59 | 4.47 | 2.83 | 2.8 – 4.0 |
| **9** | $Cu^{2+}$ | 2 | 1/2 | $^2D_{5/2}$ | 3.55 | 3.0 | 1.73 | 1.7 – 2.2 |
| **10** | $Cu^{1+}$<br>$Zn^{2+}$ | 0 | 0 | $^1S_0$ | 0 | 0 | 0 | 0 |

We observed that the magnetic moments obtained by using $\mu_J$ equation are different from those worked out by applying $\mu_s$ equation. Further, the magnetic moments obtained by using $\mu_{L+S}$ equation are different from those worked out by using $\mu_s$ equation. We also know that if L= 0 then $\mu_{L+S}$ equation reduces to $\mu_s$ equation. Thus, magnetic moments of most of the first transition series metal ions are given by the $\mu_s$ equation. However, the experimental magnetic moments of $Co^{2+}$ and $Ni^{2+}$ are found to be very higher than the calculated from the $\mu_s$ equation.

## 3. Magnetic Properties of Coordination Complexes: Crystal Field Theory

The magnetic behavior of coordination complexes can be easily explained using crystal field theory. In general, the ligands having very high splitting energy leads to the formation of low spin complexes, since the gap between $t_{2g}$ and $e_g$ level is much higher. However, for low field ligands splitting are less and thus they lead to the formation of high spin complexes.

Consider the complex $[Fe(CN)_6]^{4-}$and $[Fe(H_2O)_6]^{2+}$, in both the cases (figure 6), Fe is in the (+2) oxidation state and has octahedral geometry but the complex with $CN^-$ as ligand forms a low spin diamagnetic complex (where all the electrons are paired up) whereas the complex with $H_2O$ as the ligand form high spin complex. This can be explained on the basis of different ligand coordination taking place with the same metal ion that is $CN^-$ and $H_2O$ in this particular case. $CN^-$ is a strong field ligand that leads to high amount of crystal field splitting and thus forms low spin complexes whereas $H_2O$ is a weak field ligand which give rise to lower splitting and thus forms high spin paramagnetic complexes. This difference is explained with the help of following figure.

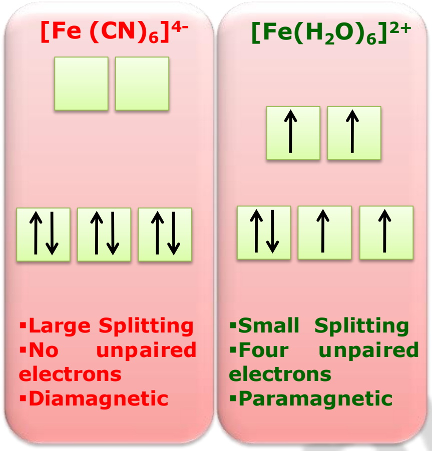

**Figure 2**

Hence, the ligands lying at the end of the spectrochemical series are high field strong ligands which form low spin complexes. Examples include ethylenediamine (en), $NO^{2-}$, $CN^-$, CO etc. As we have already discussed that the magnetic moment, μ, for the complexes of 3d metal ions, can be deduced from spin only formula (Equation 4). This formula works reasonably well with the metal ion of the first transition series. In case of the metals of second and third transition series, equation 4 is not applicable. For 4d and 5d metal ion the angular orbital moment along with the spin motion makes a large contribution. Since the complex $[Fe(CN)_6]^{4-}$ is diamagnetic in nature thus, its magnetic moment is zero, but for the complex$[Fe(H_2O)_6]^{2+}$ it can be calculated as follows;

For, $[Fe(H_2O)_6]^{2+}$, n = 4
$\mu_s = [\ 4(4+2)\ ]^{1/2}$
$= 4.90$ BM

Observed $\mu_{eff}$ for the high spin complexes of $Fe^{2+}$ is 5.10 – 5.70 B.M., very close to spin only magnetic moment $\mu_S$.The calculated and experimental magnetic moments for complexes of 3d transition metal ions are given in table 2.

**Table 2**

| **No of d electrons** | **Ion** | **High Spin Complexes** | | | **Low Spin Complexes** | | |
|---|---|---|---|---|---|---|---|
| | | No of unpaired electrons | Observed $\mu_{eff}$ (B.M) | Calculated $\mu_S$ (B.M) | No of unpaired electrons | Observed $\mu_{eff}$ (B.M) | Calculated $\mu_S$ (B.M) |
| **1** | $Ti^{3+}$ | 1 | 1.73 | 1.73 | – | – | – |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| **2** | $V^{3+}$ | 2 | 2.7 – 2.9 | 2.83 | – | – | – |
| **3** | $Cr^{3+}$ | 3 | 3.70 – 3.90 | 3.87 | – | – | – |
| **4** | $Cr^{2+}$ | 4 | 4.75 – 4.90 | 4.90 | 2 | 3.20 – 3.30 | 2.83 |
| **5** | $Mn^{2+}$ | 5 | 5.65 – 6.10 | 5.92 | 1 | 1.80 – 2.10 | 1.73 |
| | $Fe^{3+}$ | 5 | 5.70 – 6.00 | 5.92 | 1 | 2.00 – 2.50 | 1.73 |
| **6** | $Fe^{2+}$ | 4 | 5.10 – 5.70 | 4.90 | 0 | – | – |
| **7** | $Co^{2+}$ | 3 | 4.30 – 5.20 | 3.88 | 1 | 1.8 | 1.73 |
| **8** | $Ni^{2+}$ | 2 | 2.80 – 3.50 | 2.83 | – | – | – |
| **9** | $Cu^{2+}$ | 1 | 1.70 – 2.20 | 1.73 | – | – | – |

### 3.1 Spin-Orbit Coupling

As already pointed out that some of the first transition series metal complexes (e.g., low spin $Fe^{3+}$, high spin $Fe^{2+}$, and $Co^{2+}$) give magnetic moment much higher than calculated from the $\mu_s$ equation. So every metal ion except for $d^1$, $d^2$, low spin $d^5$ and high spin $d^6$ and $d^7$ follow spin only formula. The valance bond theory does not offer any explanation for this higher magnetic moment, but the crystal field theory does.

As we know that classical model of orbital magnetic moment assumes that the electrons have to go around the nucleus so that Amperes theorem is applicable. In most of the transition metal complexes the motion of electrons is very much restricted, so that effectively orbital magnetic moments quenched.

The unpaired electrons in a first transition series metal ion are located in the 3d orbitals. A transition metal ion has five degenerate 3d orbitals. In order for these electrons to the orbital magnetic moment, the electrons should go around the nucleus via these orbitals. In such a case spin-orbit coupling takes place and contributes to the overall moment (i.e. $\mu_{eff} > \mu_s$). Spin-orbit coupling is the interaction of an electrons orbital angular momentum and its spin angular momentum leading to a magnetic moment. For spin-orbit coupling to occur, the following three conditions must be satisfied:

1. There must be a half-filled or empty orbital similar in energy to the orbital holding the unpaired electron(s).
2. There must be a half-filled or empty orbital similar in shape and symmetry, i.e., they should be transformable into one another by rotation about same axis.
3. The nearby symmetry related orbital must not contain an electron with the same spin as the first one (Hund`s rule).

Electron in this orbital can make use of this nearby orbital vacancy (by moving into it) to circulate around the centre of the complex and generate orbital momentum ($\mu_L$). This leads to additional magnetic moment. As we know that spin-orbit coupling means that S and L do not operate independently and J states need to be defined. But spin-orbit coupling is usually small for lighter transition metals; we can treat S and L independently (as was done inthe earlier equation for $\mu_{L+S}$). This isn't true for heavy metals and their magnetism is much more complicated to predict.

## 4.Orbital Contribution to the Magnetic Moment in Transition Metal Ions

### 4.1 Orbital Contribution from $e_g$ Orbital Set

For orbital angular momentum to contribute, and hence for the paramagnetism to differ significantly from the spin-only value, the orbital in which electron resides must be able to transform the orbital it occupies into an equivalent and degenerate orbital by a simple rotation (it is the rotation of the electrons whichinduces the orbital contribution). In a free ion, the five d-orbitals are degenerate and some orbitals can be transformed into others by rotations. The figure 3 illustrates that a 90° or 45° rotation about z-axis transform $d_{xz}\leftrightarrow d_{yz}$, $d_{xy}\leftrightarrow d_{yz}$, $d_{xy}\leftrightarrow d_{xz}$ and $d_{xy}\leftrightarrow d_{x^2-y^2}$ orbitals, respectively. In an octahedral complex, due to crystal field splitting, the five d orbitals split into two sets of orbitals of different energy ($t_{2g}$: $d_{xy}$, $d_{xz}$, $d_{yz}$and $e_g$: $d_{x^2-y^2}$, $d_{z^2}$). The energy barrier between these two sets restricts the orbital magnetic moment of the electrons. The degeneracy between the $d_{xy}$ and $d_{x^2-y^2}$ orbitals is also removed, the transformation $d_{xy}\leftrightarrow d_{x^2-y^2}$ is now restricted. In an octahedral field, $d_{x^2-y^2}$ and $d_{z^2}$ orbitals are degenerate, but the shapes of these orbitals are such that one is not transformable into the other by rotation. Thus, due to the condition 2 discussed in previous section the $e_g$ orbital set in octahedral geometry (e orbital set in tetrahedral geometry) cannot generate any orbital magnetic moment. Hence, the, $d_{x^2-y^2}$ and $d_{z^2}$ orbitals ($e_g$ orbital set) are known as nonmagnetic doublet. These orbitals are nonmagnetic in the sense of orbital magnetic moment; however, spin magnetic moment is still generated by these orbitals.

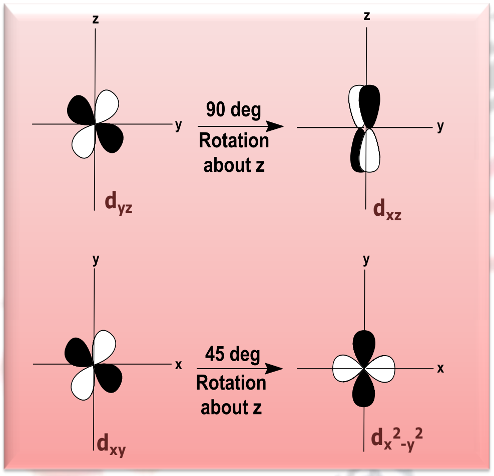

**Figure 3**

### 4.2 Orbital Contribution from $t_{2g}$ Orbital Set

The $t_{2g}$ set of orbitals $d_{xy}$, $d_{xz}$ and $d_{yz}$ are similar in energy, shape and symmetry. For example, the $d_{xy}$ and $d_{yz}$ orbitals are degenerate; moreover, the $d_{xy}$ orbital can transformed into $d_{yz}$ orbital by rotating it through 90° about the z-axis. There is a further factor that needs to be taken into consideration: if all the $t_{2g}$ orbitals are singly occupied, an electron in, say, $d_{xy}$ orbital cannot be transferred into $d_{yz}$ orbital because it already contains an electron having the same spin quantum number as the incoming electron; if all the$t_{2g}$ orbitals are doubly occupied the transfer is not possible. Thus only configurations which have $t_{2g}$ electron other than three or six electrons make orbital contributions to the magnetic moments for octahedral complexes. Thus, octahedral complexes with $d^1$ and $d^2$ configurations will have orbital magnetic moment but the octahedral complexes with $d^3$ configuration will The expected orbital contribution in high-spin octahedral or tetrahedral complex with any of the $d^1$– $d^{10}$ complexes is shown in table 3

This table also lists the ground state terms corresponding to the $d^n$ configurations. When an electron distribution can take up only one arrangement, the corresponding ground state term is singlet (A); when two arrangements are possible, ground state term is doublet (E) and for three arrangements, ground state term is triplet (T). In a term symbol, the left hand superscript denotes the spin multiplicity and the right hand subscript g indicates gerade (a tetrahedron has no inversion centre and hence the subscript g is not used for tetrahedral complexes). Looking at the table it is clear that metal ions having A and E ground state terms don’t show orbital contributions, however, those having T ground state terms are expected to show orbital contributions to the effective magnetic moment. This explains why the effective magnetic moment for tetrahedral $Ni^{2+}$, octahedral $Co^{2+}$, and octahedral $Fe^{2+}$ complexes is higher than the spin–only value.

An example helps to understand the quenching of orbital moment in different metal complexes. Let us consider $Ni^{2+}(d^8)$ complex. As a free ion, the total magnetic moment $\mu_{L+S}$ is calculated to be 4.47. In octahedral $d^8$ complex, the orbital contribution is zero. On the contrary, $d^8$ tetrahedral complex will have contributions from the orbital magnetic moment. Hence, although both the complexes have two unpaired electrons, the $[Ni(H_2O)_6]^{2+}$has magnetic moment close to the spin-only value, but the magnetic moment in $[NiCl_4]^{2-}$ is higher than the spin-only value.

| Metal Ion | High Spin Octahedral Complex | | | High Spin Tetrahedral Complex | | |
|---|---|---|---|---|---|---|
| | Configuration | Ground State Term | Orbital Contribution | Configuration | Ground State Term | Orbital Contribution |
| $d^1$ ($Ti^{3+}$) | $t_{2g}^1\ e_g^0$ | $^2T_{2g}$ | Yes | $e^1\ t_2^0$ | $^2E$ | No |
| $d^2$ ($Ti^{2+}$ ,$V^{3+}$) | $t_{2g}^2\ e_g^0$ | $^3T_{1g}$ | Yes | $e^2\ t_2^0$ | $^3A_2$ | No |
| $d^3$ ($V^{2+}$ ,$Cr^{3+}$) | $t_{2g}^3\ e_g^0$ | $^4A_{2g}$ | No | $e^2\ t_2^1$ | $^4T_1$ | Yes |
| $d^4$ ($Cr^{2+}$ ,$Mn^{3+}$) | $t_{2g}^3\ e_g^1$ | $^5E_g$ | No | $e^2\ t_2^2$ | $^5T_2$ | Yes |
| $d^5$ ($Mn^{2+}$ ,$Fe^{3+}$) | $t_{2g}^3\ e_g^2$ | $^6A_{1g}$ | No | $e^2\ t_2^3$ | $^6A_1$ | No |
| $d^6$ ($Fe^{2+}$ ,$Co^{3+}$) | $t_{2g}^4\ e_g^2$ | $^5T_{2g}$ | Yes | $e^3\ t_2^3$ | $^5E$ | No |
| $d^7$ ($Co^{2+}$) | $t_{2g}^5\ e_g^2$ | $^4T_{1g}$ | Yes | $e^4\ t_2^3$ | $^4A_2$ | No |
| $d^8$ ($Ni^{2+}$) | $t_{2g}^6\ e_g^2$ | $^3A_{2g}$ | No | $e^4\ t_2^4$ | $^3T_1$ | Yes |
| $d^9$ ($Cu^{2+}$) | $t_{2g}^6\ e_g^3$ | $^2E_g$ | No | $e^4\ t_2^5$ | $^2T_2$ | Yes |
| $d^{10}$ ($Cu^+$ ,$Zn^{2+}$) | $t_{2g}^6\ e_g^4$ | $^1A_{1g}$ | No | $e^4\ t_2^6$ | $^1A_1$ | No |

Table 3

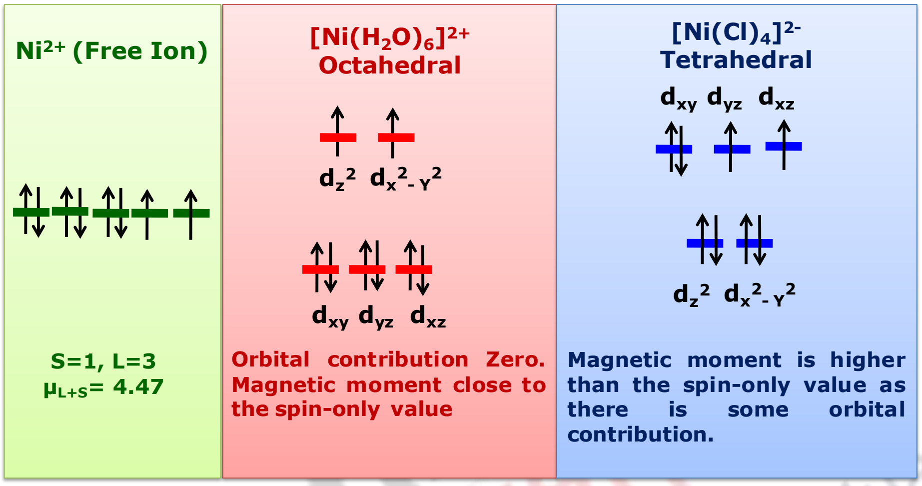

Figure 4

### 4.3 Orbital Contribution from Excited States

From above discussion the octahedral $Ni^{2+}$ or tetrahedral $Co^{2+}$ are expected to have no orbital magnetic moment, but only spin magnetic moment. However, such a complex in reality exhibits a magnetic moment significantly higher than $\mu_S$. This is because the excited states of octahedral $Ni^{2+}$ ($t_{2g}^5$ $e_g^3$, $^3T_{2g}$) and tetrahedral $Co^{2+}$ ($e^3$ $t_2^4$,$^4T_2$) carry the orbital magnetic moment. In a system having such an excited state, the spin-orbit coupling brings about some mixing of the ground state with the excited state, thus forcing some orbital contribution. The quantitative relation between $\mu_{eff}$ and $\mu_S$ is

$$\mu_{eff} = \mu_s\left[1-\frac{\alpha\lambda}{\Delta}\right]+\frac{2\alpha N\beta^2}{\Delta} \quad \dots\dots\dots\dots\dots\dots (5)$$

Where $\alpha$ is a constant which depends upon the ground state and the number of d electrons. The value of $\alpha$ is 2 for $E_g$ ground state term and 4 for an $A_{2g}$ . $\Delta$ is the separation between ground and the excited state and can be obtained from the electronic spectra. $\lambda$ is the spin-orbit coupling constant and it is positive for $d^1$, $d^2$, $d^3$ and $d^4$ ions and negative for $d^6$, $d^7$, $d^8$ and $d^9$ ions. The first term $\alpha\beta^2/\Delta$ arises from the mixing in of an excited state via spin-orbit coupling and the second term $2\alpha N\beta^2/\Delta$ is the temperature independent paramagnetism which is field induced. Now it is clear from the above relation that the greater the 10Dq value, the smaller the mixing effect, therefore, the lesser orbital contribution. i.e., a strong donor ligand is likely to reduce the orbital contribution. Further, depending upon the sign of $\lambda$, $\mu_{eff}$ will be higher or lower than $\mu_S$. For example, the sign of $\lambda$ is negative for $Ni^{2+}$ ($d^8$) and positive for $Cr^3$ ($d^3$).

The high spin octahedral complex of $Mn^{2+}$ ($d^5$), $[Mn(H_2O)_6]^{2+}$ with the ground state $^6A_{1g}$, has no excited state of same spin multiplicity as that of the ground state. Therefore, mixing of the ground state with any of the excited states due to spin-orbit coupling is not possible. Thus, there is no orbital contribution to $\mu_{eff}$ due to spin-orbit coupling. Therefore, $\mu_{eff}$ is same as $\mu_S$. In high spin octahedral complexes of $Co^{2+}$ ($d^7$), the ground state is $^4T_{1g}$ and a large orbital contribution to the magnetic moment is expected. Mixing of excited state lowers the moment somewhat, but a value of $\mu_{eff}$ (4.30 –5.20) is still larger than the $\mu_S$ (3.88) in excess of 5 B.M. is usually found. The ground state for the tetrahedral complexes of $Co^{2+}$ ($d^7$), is $^4A_2$ and a low magnetic moment approaching to spin only value might be expected. However, an excited magnetic state is comparatively low in energy in the tetrahedral complexes and can be mixed with the ground state. So the magnetic moments in the range from 4 to5 B.M. have been predicted and are found experimentally. An inverse relationship exists for tetrahedral complexes between the magnitude of the moment of the complex and the value of $\Delta$ as predicted by equation (5).

In general, using three conditions discussed in the previous section, it is also possible to make out whether a low spin octahedral configuration will have orbital contribution or not. For example, in a low spin complex of $Mn^{2+}$ ($d^5$), the ground state is $^2T_{2g}$ and therefore fulfills all the three conditions. So the complex will have orbital contribution. The ground state for low spin complex of $Fe^{2+}$ ($d^6$) ion is $A_{1g}$ but all the electrons are paired and hence the complex is diamagnetic. Moreover, the ground state for low spin complex of $Co^{2+}$($d^6$) ion is $^2E_g$ and hence it has no orbital contribution.

For the 4d and 5d ions, diamagnetism results for even numbered electrons, and paramagnetism to the extent of one unpaired electron only is observed for the odd numbered electrons, indicating that spin pairing takes place for these ions as far as possible. This may be due to (i) reduced interelectronic repulsions in large sized ions reducing the electron pairing energies, (ii) higher ligand field splitting. The $\mu$ at room temperature is generally lower than $\mu_s$ and cannot be used to determine the unpaired electrons due to (iii) high spin-orbit coupling constants which align L and S vectors in opposite directions destroying the paramagnetism.

Further, (iv) the Curie or Curie-Weiss law does not hold, the variation of $\mu$ with L is complex and depends upon the number of the electrons present.

Some ions like $MnO_4^-$, $CrO_4^{2-}$ and low spin $Co^{3+}$ complexes show temperature-independent paramagnetism (TIP) even though they do not have any unpaired electron. This is due to the spin-orbit coupling of the ground state to a paramagnetic excited state under the influence of the magnetic field. The degree of mixing is independent of temperature, but depends on the applied magnetic field, as the excited state is well separated from the ground state, whose population does not change with temperature.

## 5.Quenching of Orbital Magnetic Moment due to Loss of Orbital Degeneracy

The loss of degeneracy of the d orbitals affects the unrestricted motion of electrons about the nucleus. The degeneracy of d orbitals is lost (Figure 5) to a greater extent in case of tetragonally distorted octahedral complex, trigonal bipyramidal complex and square pyramidal complex. In such a complex, the magnetic moment $\mu_{eff}$ is close to $\mu_S$.

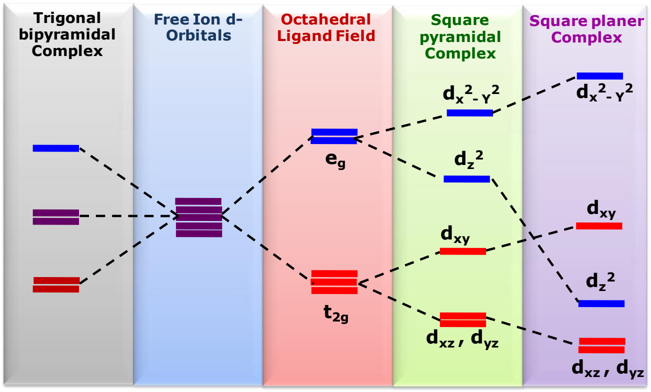

**Figure 4**

## 7. Summary

In this module, we discussed that,

- The magnetic moment of the most of transition metal ions are very close to spin only magnetic moment $\mu_S$ means completely neglecting the orbital motions.
- The magnetic behavior of the coordination complexes can be easily explained based on the crystal field theory. Strong field ligands having very high splitting energy lead to the formation of the low spin complexes, however, weak field ligands having low splitting energy lead to the formation of the high spin complexes.
- In some transition metal ions spin-orbit coupling takes place and contributes to the overall moment. For spin-orbit coupling to occur, following three conditions must be satisfied:

  (1.) There must be a half-filled or empty orbital similar in energy, (2.) There must be a half-filled or empty orbital similar in shape and symmetry, (3.) The nearby symmetry related orbital must not contain an electron with the same spin as the first electron.

- The loss of degeneracy of the d orbitals affects the unrestricted motion of electrons about the nucleus. The degeneracy of the d orbitals is lost to a greater extent. In such a complex, the magnetic moment $\mu_{eff}$ is close to $\mu_S$.