

Magnetic Properties of Transition Metals.

To understand the mag. properties of transition metals, we should consider the parameters related with magnetic properties.

1) **Diagnagnetism** - The compd. is repelled in the mag. field. Such a phenomenon is shown when the compd. has no unpaired e⁻s.

2) **Paramagnetism**: The compd. is attracted in the magnetic field due to the presence of unpaired e⁻s.

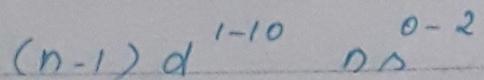
3) **Ferromagnetism**: Seen in Fe, Co & Ni)

They are strongly attracted in the magnetic field, and they also possess unpaired e⁻s. But, here, when the compd. is placed in a magnetic field, the spin of all metal ions get aligned in the same direction.

4) **Anti ferromagnetism**:

They are strongly repelled in the magnetic field. But it also possess unpaired e⁻s. But in the magnetic field, the spin of all metal ions alligned in such a way that, they get pair up.

For Transition Metals the E.C is



In transition metals, the e^- 's are filled in the d orbitals. Hence, those are the e^- 's that decide the magnetic property of the transition metals. In case of transition metals, the magnetic property greatly differs when it is present in the free state as in the ionic state. or when it gets complexed with the ligands.

Let us consider, the following 1st transition series

1	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
II				III		IV		V		VI

Most of the transition metals show paramagnetism due to the presence of unpaired e^- .
Mn - Highest para magnetism.

Zn - does not show paramagnetism (diamagnetic)
 Zn^{+2} , Cd^{2+} , Hg^{0+} - diamagnetic.

Greater the no. of unpaired e^- 's, greater will be paramagnetism & magnetic moment.

For free metal ion, the magnetic moment is given by the contribution of spin angular momentum & orbital angular momentum. Because there is spin orbital coupling.

Hence, the total magnetic moment is given by

$$M_{SL} = \sqrt{4S(S+1) + L(L+1)} \text{ B.M. (or)}$$

S. Spin quantum no. $\sqrt{n(n+2) + L(L+1)}$

L. Orbital " "

But for the metal complex, the orbital contribution is usually quenched (i.e. it is equal to 0) due to non-spherical environment. In such cases, the magnetic moment is given by the spin only formula.

$$\text{i.e } M_S = \sqrt{4S(S+1)} \text{ or } \sqrt{n(n+2)}$$

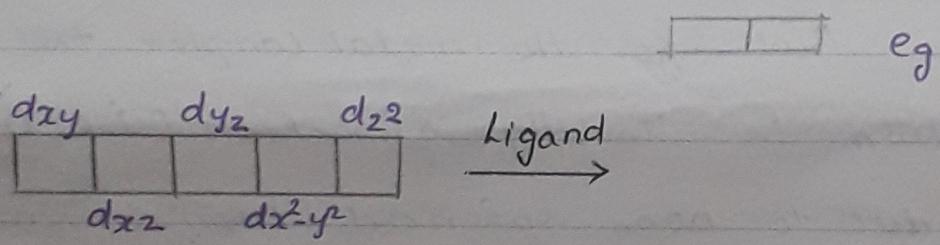
n - no. of unpaired e⁻s. (The value of

8- Spin quantum no..

$$BM = 9.2 \times 10^{-24} J T^{-1} m^2$$

The change in the behaviour of transition metals when it gets complexed with the ^{ligands} metals is explained on the basis of CFT.)

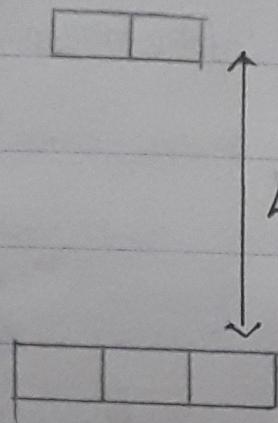
Acc. to CFT, when the metals is in the free state (not combined with the ligand) all the d orbitals are in the same energy. So, all the e's got paired and hence, the rotation around the nucleus forms an ~~an~~ orbital angular momentum. Hence, the magnetic moment will be the sum of spin & orbital angular momentum.



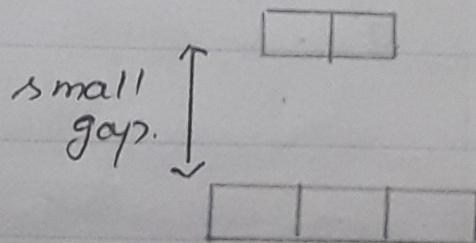
But, when the ligand comes near to the metal, the degeneracy of the five d orbitals is removed. So, the three orbitals d_{xy} , d_{xz} & d_{yz} gets lowered in energy. These are called three t_{2g} orbitals whereas $d_{x^2-y^2}$ & d_{z^2} orbitals gets higher in energy. Then this forms the e_g set of the orbitals. These t_{2g} & e_g orbitals differ in energy.

Now, two things can happen. When the ligand is a strong field ligand and when it is a weak field ligand.

Strong field ligand



Weak field ligand



Ex: CN^- , CO

Cause high splitting
of d orbitals.

i.e On complexes.

Hence, the energy required
for an e^- to jump to t_{g}
level is very much high,

than to pair up in t_{g} level.

Hence, the e^- 's wants to pair

up. Hence, the complex we
will get a low spin complex.

i.e the max. e^- 's gets paired

and we will get a diamagnetic
complex.

Ex: Cl^-

In such cases the splitting
is very low. i.e the gap is
very small. Hence, the e^- 's

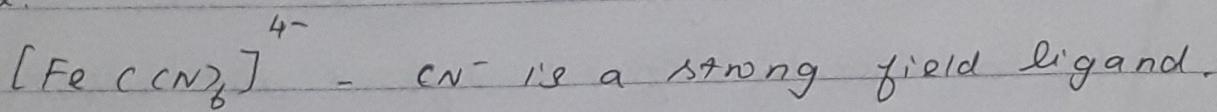
can jump easily to t_{g} level.

In this case, they will
give rise to high spin

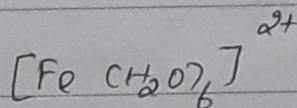
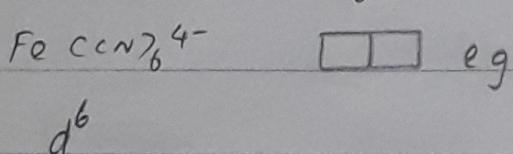
complexes and they will

be paramagnetic.

Ex:



Hence, there energy gap between t_{2g} & e_g level will be large.



$\boxed{1/1}$

$\boxed{1/1 \quad 1/1}$

$\boxed{1/1 \quad 1/1 \quad 1/1} \quad t_{2g}$

$$M_B = \sqrt{n(n+2)}$$

= 0 B.M.

$$M_S = \sqrt{4(4+2)} = \sqrt{24}$$

= 4.90 B.M. (or) 5.48 B.M.

In $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ H_2O is a weak field ligand.

So, the splitting of t_{2g} & e_g level will be small.

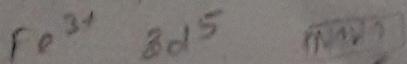
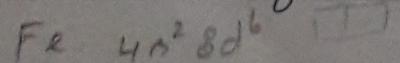
Hence, all the e's will be filled up first in each orbital and then they will pair up. Hence,

H will now have 4 unpaired e's and is paramagnetic.

In 4d & 5d series, the magnetic moment is given by spin & orbital contribution.

But in the 1st transition series, the magnetic moment is given by the spin only formula.

In the first transition series, for low spin Fe^{3+} ,



Fe^{+2} 4s²
 Co^{+2} 4s² 3d⁷

High
Low
Mossbauer

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high spin Fe^{+2} , so Co^{+2} $M_{\text{eff}} > M_s$. (i.e the mag. moment value is $>$ than the spin only value)

If we look at the transition series carefully, we can find that for d¹, d², low spin d⁵, high spin d₆ & d₇ complexes, $M_{\text{eff}} > M_s$. i.e their magnetic moment is given by spin & orbital contribution.

Why in some cases we are getting the mag. moment by spin only formula & in some cases by spin & orbital angular momentum formula?

Explanation:

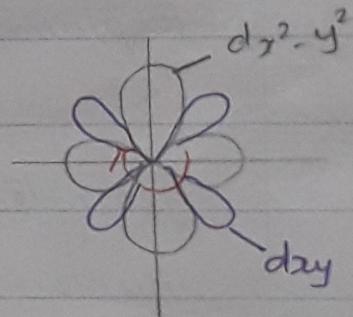
The orbital angular momentum is generated due to the rotation of e⁻s around the nucleus (via orbital). i.e the e⁻s rotates first inside the orbital (1) and then it rotates around the nucleus, and then only the orbital angular momentum generates. If there is no part for the e⁻ to rotate, then it can not produce the orbital angular momentum.

In most of the metals, this momentum is quenched (i.e 0) due to the restricted rotation

(i.e the σ^- will not get a place to rotate) and the outer environment. (effect of the ligand)

For orbital angular momentum to contribute, there must be one or more empty or half filled orbitals similar in energy to that of the orbitals occupied by unpaired σ^+ s; and this orbital should be of appropriate energy. This orbital should not possess the e^- of same spin as that of the rotating e^- . So, the σ^- can use this nearby orbital to circulate around the nucleus and generate orbital momentum.

In the diagram, for $d_{z^2} e^-$
if d_{xy} lobe is free, that e^-
can rotate freely & will generate

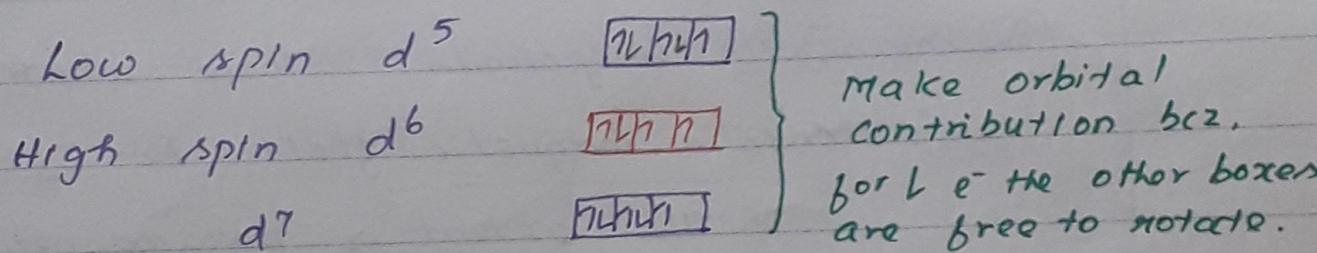


orbital angular momentum. Otherwise the rotation will be restricted.

t_{2g} orbitals:

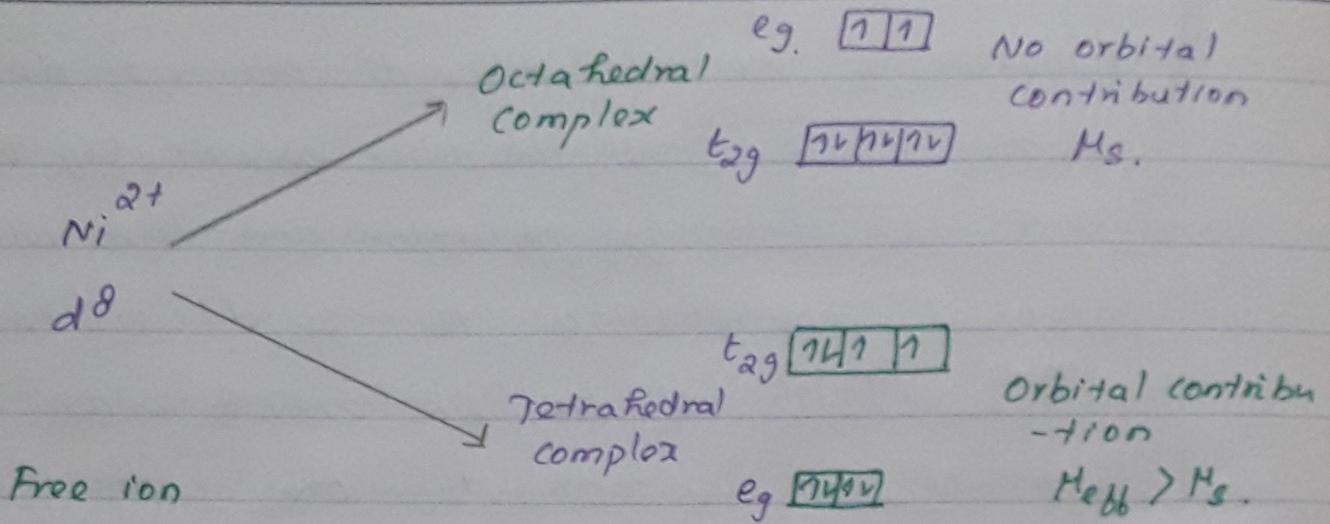
All t_{2g} orbitals are degenerate (d_{xy} , d_{xz} & d_{yz}) and have same energy, shape and symmetry. They can be transformed into one another via rotation around 90° .

Hence, if we see d^1 & d^2 orbitals, the e^- s can
 d^1 $\boxed{\uparrow \downarrow}$ use the other vacant t_{2g} orbital
 d^2 $\boxed{\uparrow \uparrow \uparrow}$ for rotation and there will be
orbital contribution. But for d^3 orbital,
 d^3 $\boxed{\uparrow \uparrow \uparrow \uparrow}$ all the e^- s are of same spin and
there is no vacant t_{2g} orbital and hence there
is no path & no orbital contribution, and
in this the mag. moment will be given by only
spin only formula.



Hence, in these cases $M_{BGB} > M_{\text{spin only}}$ formula.
But, when all t_{2g} orbitals are singly or doubly occupied ($\boxed{\uparrow \uparrow \uparrow}$ - same spin do not have empty space to rotate; $\boxed{\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow}$ - no place for rotation), they will not make orbital contribution. i.e. $M_{BGB} = M_s$.

Hence, H is also affected by the geometry of the complex.



$$\mu_{L+S} = 4.47$$

Magnetic Properties of coordination complexes:

Diamagnetic Compounds: Those which tend to move out of a magnetic field. Ex: N_2

Paramagnetic Compounds: Those which tend to move into a magnetic field. Ex: O_2 .

(The extent of paramagnetism is measured in terms of magnetic moment μ . The larger the magnitude of μ , the greater the paramagnetism of the compound.)

Magnetic moment has contributions from spin and orbital angular momentum. A non-spherical environment may lead to quenching of the contribution from orbital angular momentum. (i.e $L=0$)

However, the spin-only magnetic moment survived

in all cases and is related to the total no. of unpaired e⁻s

$$\therefore M_{\text{eff}} = M_{\text{g.o.}} = 2 \sqrt{s(s+1)} = \sqrt{n(n+2)} \text{ BM.}$$

Ion	No. of unpaired e ⁻ s (n)	s
Ti ³⁺	1	1/2
V ³⁺	2	1
Cr ³⁺	3	3/2
Hn ³⁺	4	2
Fe ³⁺	5	5/2.

If there is a possibility for contribution from the orbital angular momentum

$$\mu = \sqrt{l(l+1) + 4s(s+1)}$$

For a given value of orbital angular quantum no. l, the mag. quantum no. m, can have any values from -l to +l. & l = sum of

$$1 \quad 1 \quad 1 \quad 1 \quad 1$$

$$\text{For d orbital } e^- \quad m = 2, 1, 0, -1, -2$$

If there is only one e⁻ in the d orbital, l =

0.

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Configuration d^n , $n =$	No. of Unpaired $e^-s.$	$M_{S+0} =$ $\sqrt{L(L+1) + 4S(S+1)}$	M_S $= \sqrt{4S(S+1)} \text{ (or)}$ $\sqrt{n(n+2)}$
1	1	3.00	1.73
2	2	4.47	2.83
3	3	5.20	3.87
4	4	5.48	4.90
5	5	5.92	5.92
6	4	5.48	4.90
7	3	5.20	3.87
8	2	4.47	2.83
9	1	3.00	1.73
10	0	0	0

$K_3[Fe(CCN)_6]$ has a magnetic moment of 1.73 BM ,
 which is a d^5 low spin complex with one unpaired e.
 Low spin - Strong field ligand

Energy diff. between e_g & t_{2g} will more.
Hence, first e^- will pair.

$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ions are high spin with 5 unpaired. It has a magnetic moment of 6 BM ($\sqrt{n(n+2)}$)

Consider a $\text{Ni}(\text{II})$ complex, E.C is d^8 .

For a free metal ion

d^8

$\frac{1L}{2}, \frac{1L}{1}, \frac{1L}{0}, \frac{1}{-1}, \frac{1}{-2}$

$$S = \frac{1}{2} + \frac{1}{2} = 1; L = 2+1 = 3.$$

$$\text{and } M = \sqrt{L(L+1) + 4S(S+1)} = 4.47 \text{ BM}.$$

For an octahedral complex.

d^8

$\frac{1}{1}$ (no space Orbital contribution is zero)

for rotation in one orbital (same spin)

and magnetic moment is close

$\frac{1L}{1}, \frac{1L}{1}, \frac{1L}{1}$ to the spin only value.

For a tetrahedral complex

d^8

$\frac{1L}{1}, \frac{1}{1}, \frac{1}{1}$ Magnetic moment is higher than the spin only

$\frac{1L}{1}, \frac{1L}{1}$

value because there is a positive orbital contribution