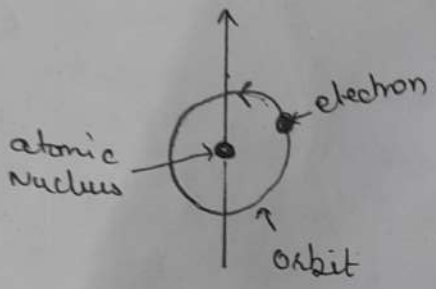
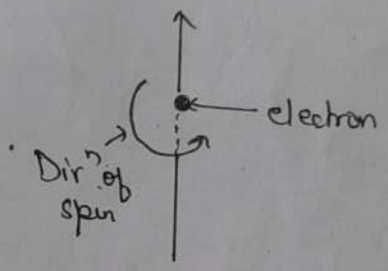
Magnetic Properties

Transition metals complexes show magnetic properties which are studied in terms of their magnetic moments.

→ Magnetic properties arises dues to — orbital motion of electrons / spining motion



orbital Magnetic moment



Spin magnetic moment

As electron is a charged particle, its orbital motion produces a small magnetic field along the axis of rot" and its spining motion produces a magnetic field along the spin axis

↓

∴ each electron considered as a small magnet.

As Mag. moment is vector quarility, the net Mag. moment of an electron may be represented by an arrow.

Thus a material may be considered to contain a no. of magnetic dipoles. Based on the behaviour of mag. substance in the external mag. field, the magnetism of Trans. metal complexes are:

1) Paramagnetism
2) Diamagnetism
3) Ferromagnetism
4) Antiferromagnetism

Magnetic moment expressed in terms of Bohr Magenton (B.M.)

→ represented by β or μ_B

⇒ $$1BM = \frac{eh}{4\pi mc}$$

e = electric charge
h = Plank's constant
m = mass of electron
c = vel. of light

$1BM = 0.927 \times 10^{-23}$ Am^2/molecule
or 0.927×10^{-20} erg/gauss

{ 1 erg = 10^{-7} Joule
{ 1 gauss = 10^{-4} tesla

PARAMAGNETISM:

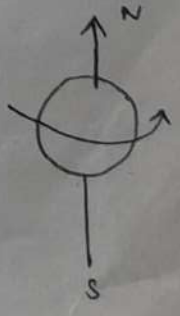
Substances that are freely magnetised in the direction of the magnetic field in which they are placed are Paramagnetic substances. This property of the substance is known as Paramagnetism

Characteristics:

1) When a P.S placed in a magnetic field, the magnetic lines of force prefer to pass thru the substance rather than thru the air.

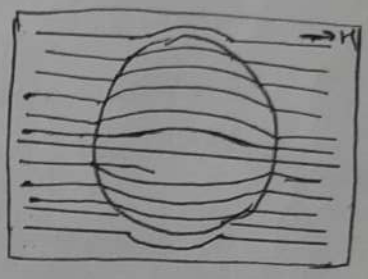
2) Substance $\bar{c}$ one or more unpaired electrons show paramagnetic character. A single e^- (unpaired) spining on its axis generates a magnetic field & behaves like magnet.

∴ When a substance whose orbital contains unpaired e^- is placed in an electromagnet, it is attracted towards the pole of electromagnet. ∴ An atom, ion or molecule containing one or more unpaired electrons will be paramagnetic.



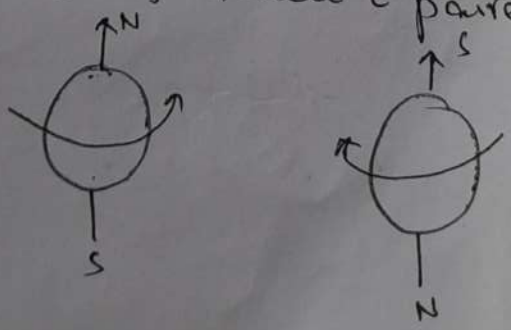
Diamagnetism:

1) Substances which are repelled by the mag. field are diamagnetic.
∴ When a diamagnetic field is placed in mag. field, the no. of lines of forces passing thru sub. would be less than that would pass thru air.



2) ~~Diag~~ Diamagnetic behaviour of a substance is due to the fact that when a dia. sub. is placed in mag. field, small mag. moments are induced in the substances, which are in opposition to the induced field. This results in the repulsion of substance in mag. field.

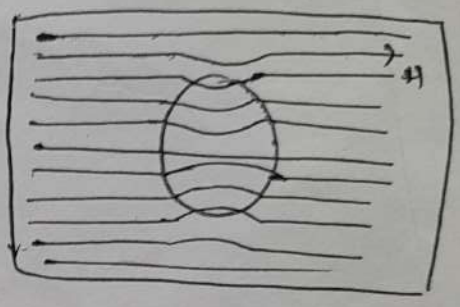
3) Substances with all e^-s in paired state ($n=0$) shows diamagnetic character. When an orbital $\bar{c}$ 2 e^-s with opposite spin ($\uparrow\downarrow$), the mag. moment generated by one e^- is cancelled by that generated by other electron. As mag. moments of 2 electrons in an orbital are same and opposite.
∴ An atom, ion, molecule $\bar{c}$ paired e^-s → diamagnetic.



4) Magnetic moment (μ_{eff}) of diamag. substance = Zero.

3) When a paramagnetic substance is placed in an external magnetic field, the individual atoms or molecules of the substances behave as permanent magnet and align themselves in same dir^{n} as that of permanent magnetic field.

∴ Paramagnetic substances are attracted towards magnet.



As a result P.s when placed in mag. field, the no. of lines of force passing thru P.s would be more as compared to lines of force passing thru the air.

4) Paramagnetic nature can be found by weighing the substance; first in air & then after suspending it b/w the poles of mag. field. If,

weight of substance in magnetic field > weight of substance in air

↓

Paramagnetic.

5. Diamagnetic nature of substance can be found by weighing substance in air & b/w the poles of mag. field. If

weight of substance b/w the mag. field < weight of substance in air

↓ repelled by mag. field

Diamagnetic

6. Ions of 2d & 3d transitional metal series are diamagnetic, if ions have even no. of electrons.

Ferromagnetism: Substance which show permanent magnetism even in the absence of mag. field are c/d Ferromagnetic substances. This type of magnetism arises due to spontaneous alignment of mag. moments due to unpaired electrons, in the same direction. This is a case of large amt ↑ ↑ ↑ ↑ ↑ ↑ of paramagnetism.

→ Ferromagnetism is shown by the substances which contain atoms or ions ē incompleted or f^{sub}_{n} shell; like
→ Example Fe, Co, Ni, Gd, Dy etc.

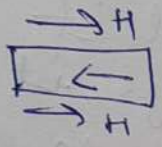
Anti-ferromagnetism: substances which are expected to possess paramagnetism or ferromagnetism on the basis of unpaired ē's but actually they possess zero net mag. moment are c/d Antiferromagnetic substances.

Antiferromagnetism is due to true of an equal no. of magnetic moments in opposite directions. ↑↓↑↓↑↓

Dia

feebly repelled by magnet

→ when placed in a mag field, it acquires feeble magnetism opp. to the dir^n of mag field

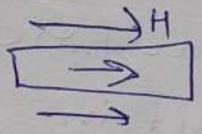


Param.

→ feebly attracted by a magnet (weekly attracting)

→

it aquires feeble magnetic in the dir^n of mag field

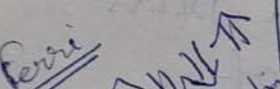


Ferro

strongly attracted by a magnet

Same as paramagnetic but strongly.

Ferri



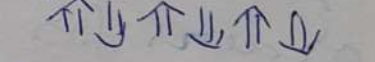
uneven distribution

even → diamagnetic

odd → paramagnetic

10, 16] - Para (exceptional)

Anti ferro



Half domain works in dir^n of magnetic field & Half domain works in opposite

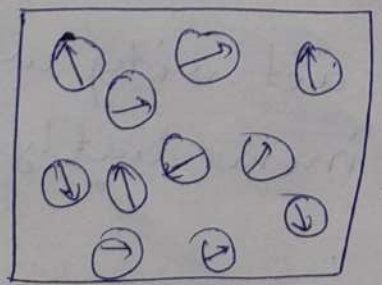
Lesser closed

ferro, Anti ferri → unpaired e^- ↑↑

Ferromag → Enhanced Paramagnetism

Antiferromag → unpaired e^- is ↑↑ but material behave like diamagnetic material

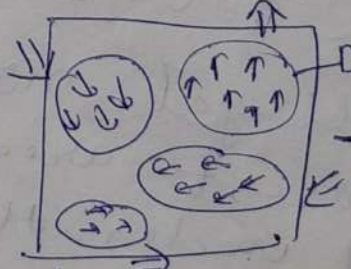
fe



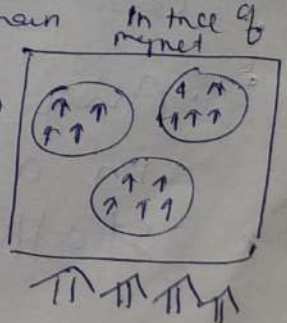
atoms behave as small magnet

→ All atoms ↑↑ in gas

Ferrimagnetic → ~~Decay~~ Supressed Paramagnetism



In a domain small magnets work in one dir^n



Magnetic properties

Diamagnetic

↓

no unpaired e^-

↓

in presence of mag field, shows repulsion

$[Fe(CN)_6]^{4-}$

O_2

$[Ni(CN)_4]^{2-}$

$[Co(CN)_6]^{3-}$

Paramagnetic

↓

In presence of mag field, shows attraction

↓

atleast 1 paired e^-

$[Fe(CN)_6]^{3-}$

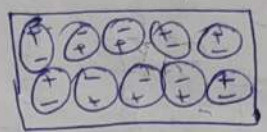
O_2

$[Cu(CN)_4]^{2-}$

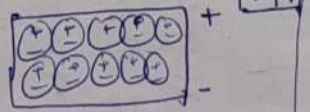
$[Cr(CN)_6]^{3-}$

Ferromagnetic

↓ Fe, Co, Ni, alloys.



Metals are made up of small dipoles / small grains, where the dir^n of these grains are random, but when any external field is applied these grains are arranged in one dir^n ie all +ve on one side & -ve another



Fe, Ni, CrO_2

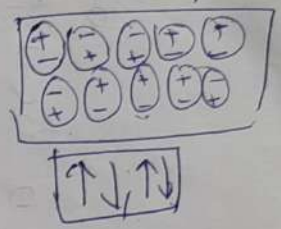
itself behave like a magnet even after removal of mag field

→ strong attraction

μ_{eff} = maximum

Antiferromagnetic

↓ F



But when these grains are opposing ie cancels each others dipole.

→ Not behave as magnet

→ strong repulsion

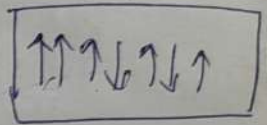
Fe_2O_3, MnO, FeMn

MnO_2, Mn_2O, NiO

Cr

dipole moment = 0

Ferrimagnetic



$\mu_{eff} \neq 0$

$\mu_{net} \leq \mu_{net}$ ferro ferri

uneven dipole

Fe_3O_4

anisotropy

Metal → electron donor $M \rightarrow M^{n+} + ne^-$

Metals have small dipole  grains / small dipole

Mag moment $\mu = \sqrt{n(n+2)}$

Calculation of Magnetic Moment :

$\mu = \sqrt{n(n+1)}$ n = no. of unpaired electrons

Before calculation, two data must be known
1. Electronic conf. of d-transition metals
2. Secondary oxidn state value of metal ion

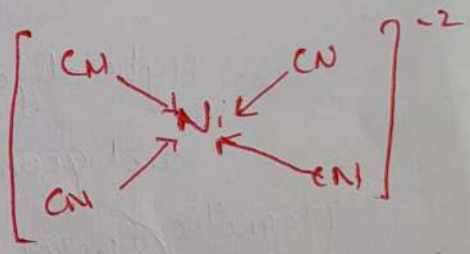
Tip
1) Oxidn state
2) Nature of ligand
   - W.F → e⁻ pairing ✗
   - S.F → e⁻ pairing ✓

1) $[Ni(CN)_4]^{2-}$ { As we know CN^- is strong ligand so e⁻ pairing takes place.

$A = Z - nZ_e$

$= (-2) - 4(+1) = 2$

∴ Tetra cyano nickelate (II) ion



Geometry :

Ni (28) → [Ar] $3d^8\ 4s^2$

Ni^{+2} (26) → [Ar] $3d^8\ 4s^0$

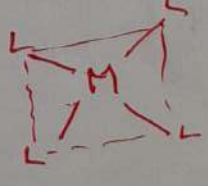
	3d	4s	4p
Ni (28) →	↿⇂ ↿⇂ ↿⇂ 1 1	↿⇂	— — —
Ni^{+2} →	↿⇂ ↿⇂ ↿⇂ 1 1	—	— — —

As CN^- is strong ligand, so e⁻ pairing takes place

$[Ni(CN_4)]^{2-}$ → ↿⇂ ↿⇂ ↿⇂ ↿⇂ ✗✗ ✗✗ ✗✗ ✗✗ —

Hybridization = dsp^2 (d, s, p^2)

So, the geometry of dsp^2 - Square planner



Mangenetic Moment :

Magnetic moment $\mu = 0$

As there is no unpaired electron

∴ μ = zero.

2) $[NiCl_4]^{2-}$ tetrachloro Nickelate (II) ion

Cl^- is weak ligand so, no e^- pairing

A = 2

Ni (28) → [Ar] ↑↓ ↑↓ ↑↓ ↑ ↑ ↑↓ — — —

3d 4s 4p

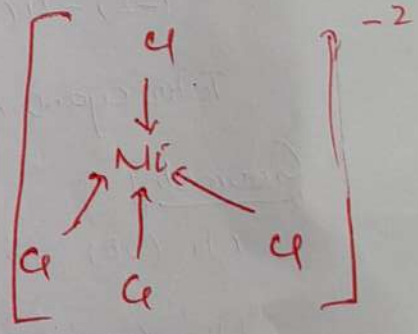
Ni^{2+} (26) → [Ar] ↑↓ ↑↓ ↑↓ ↑ ↑ — — — —

$[NiCl_4]^{2-}$ → [Ar] ↑↓ ↑↓ ↑↓ ↑ ↑ xx xx xx xx

sp^3

∴ Hybridization of $[NiCl_4]^{2-}$ = sp^3

and geometry = tetrahedral



Magnetic moment = $\mu = \sqrt{n(n+2)}$

$= \sqrt{2(2+2)} = \sqrt{8}$

3) $[Fe(CN)_6]^{3-}$

$A = (-3) - 6(-1)$

$A = 3$

CN^- = strong ligand

VI

Hexacyano ferrate (III) ion

Fe (26) → $[Ar]\ 3d^6 4s^2$

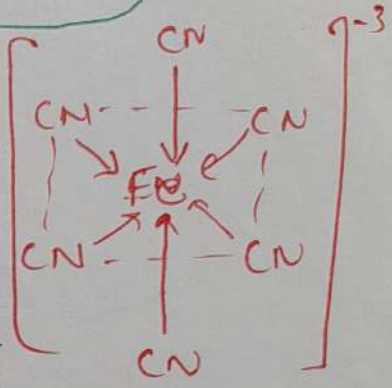
→ [Ar] ↑↓ ↑ ↑ ↑ ↑ ↑↓ — — —

Fe^{3+} (23) → $[Ar]\ 3d^5 4s^0$

→ [Ar] ↑ ↑ ↑ ↑ ↑ ↑ — — —

$[Fe(CN)_6]^{3-}$ → [Ar] ↑↓ ↑↓ ↑ xx xx xx xx xx

d^2sp^3



Hybridization = d^2sp^3

∴ Geometry = octahedral

Magnetic moment $\mu = \sqrt{n(n+2)}$

$= \sqrt{1(1+2)} = \sqrt{3} = 1.83$

∴ $\mu = 1.83$

⇒ Inner orbital complex

⇒ low spin complex

4) $[FeF_6]^{3-}$

$A = (-3) - 6(-1)$

$A = 3$

∴ Hexafluoro Ferrate(III) ion ∵ F_6 → week ligand

Fe (26) → [Ar] ↑↓ ↑ ↑ ↑ ↑ ↑↓ — — —

Fe^{+3} (23) → [Ar] ↑ ↑ ↑ ↑ ↑ — — — —

$[FeF_6]^{+3}$ → [Ar] ↑ ↑ ↑ ↑ ↑ xx xx xx xx xx xx — — —

3d 4s 4p 4d

sp^3d^2

Hybridization = sp^3d^2

Geometry = octahedral

Magnetic moment ∴ $\mu = \sqrt{n(n+2)}$

$= \sqrt{5(5+2)} = \sqrt{35}$

$= 5.83$

outer d-orbital complex, High spin complex.

Magnetic Moments of Transition Metals

Magnetic moments are often used in conjunction with electronic spectra to gain information about the oxidation number and stereochemistry of the central metal ion in coordination complexes. A common laboratory procedure for the determination of the magnetic moment for a complex is the Gouy method which involves weighing a sample of the complex in the presence and absence of a magnetic field and observing the difference in weight. A template is provided for the calculations involved.

For first row transition metal ions in the free ion state, i.e. isolated ions in a vacuum, all 5 of the 3d orbitals are degenerate.

A simple crystal field theory approach to the bonding in these ions assumes that when they form octahedral complexes, the energy of the d orbitals are no longer degenerate but are split such that two orbitals, the d_{x2-y2} and the d_{z2} (e_g subset) are at higher energy than the d_{xy}, d_{xz}, d_{yz} orbitals (the t_{2g} subset).

For octahedral ions with between 4 and 7 d electrons, this gives rise to 2 possible arrangements called either high spin/weak field or low spin/strong field respectively. The energy gap is dependent on the position of the coordinated ligands in the SPECTROCHEMICAL SERIES.

Note

A good starting point is to assume that all Co(III), d^6 complexes are octahedral and LOW spin, i.e. t_{2g}^6.

In tetrahedral complexes, the energy levels of the orbitals are again split, such that the energy of two orbitals, the $d_{x^2-y^2}$ and the d_{z^2} (e subset) are now at lower energy (more favored) than the remaining three d_{xy}, d_{xz}, d_{yz} (the t_2 subset) which are destabilized.

> *Tetrahedral complexes are ALL high spin since the difference between the 2 subsets of energies of the orbitals is much smaller than is found in octahedral complexes.*

The usual relationship quoted between them is:

$$\Delta_{tet} \approx \frac{4}{9}\Delta_{oct} \tag{1}$$

Square planar complexes are less common than tetrahedral and d^8 e.g. Ni(II), Pd(II), Pt(II), etc, have a strong propensity to form square planar complexes. As with octahedral complexes, the energy gap between the d_{xy} and $d_{x^2-y^2}$ is Δ_{oct} and these are considered strong field / low spin hence they are all diamagnetic, μ=0 Bohr Magneton (B.M.)

The formula used to calculate the spin-only magnetic moment can be written in two forms; the first based on the number of unpaired electrons, n, and the second based on the electron spin quantum number, S. Since for each unpaired electron, $n = 1$ and $S = 1/2$ then the two formulae are clearly related and the answer obtained must be identical.

$$\mu_{so} = \sqrt{n(n+2)} \tag{2}$$

$$\mu_{so} = \sqrt{4S(S+1)} \tag{3}$$

Comparison of calculated spin-only magnetic moments with experimental data for some octahedral complexes

Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Ti(III)	d^1 (t_{2g}^1)	√3 = 1.73	1.6-1.7
V(III)	d^2 (t_{2g}^2)	√8 = 2.83	2.7-2.9
Cr(III)	d^3 (t_{2g}^3)	√15 = 3.88	3.7-3.9
Cr(II)	d^4 high spin ($t_{2g}^3 e_g^1$)	√24 = 4.90	4.7-4.9
Cr(II)	d^4 low spin (t_{2g}^4)	√8 = 2.83	3.2-3.3
Mn(II)/ Fe(III)	d^5 high spin ($t_{2g}^3 e_g^2$)	√35 = 5.92	5.6-6.1
Mn(II)/ Fe(III)	d^5 low spin (t_{2g}^5)	√3 = 1.73	1.8-2.1
Fe(II)	d^6 high spin ($t_{2g}^4 e_g^2$)	√24 = 4.90	5.1-5.7

Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Co(III)	d^6 low spin (t_{2g}^6)	0	0
Co(II)	d^7 high spin ($t_{2g}^5 e_g^2$)	$\sqrt{15} = 3.88$	4.3-5.2
Co(II)	d^7 low spin ($t_{2g}^6 e_g^1$)	$\sqrt{3} = 1.73$	1.8
Ni(II)	d^8 ($t_{2g}^6 e_g^2$)	$\sqrt{8} = 2.83$	2.9-3.3
Cu(II)	d^9 ($t_{2g}^6 e_g^3$)	$\sqrt{3} = 1.73$	1.7-2.2

Comparison of calculated spin-only magnetic moments with experimental data for some tetahedral complexes

Ion	Config	μ_{so} / B.M.	μ_{obs} / B.M.
Cr(V)	d^1 (e^1)	$\sqrt{3} = 1.73$	1.7-1.8
Cr(IV) / Mn(V)	d_2 (e^2)	$\sqrt{8} = 2.83$	2.6 - 2.8
Fe(V)	d^3 ($e^2 t_2^1$)	$\sqrt{15} = 3.88$	3.6-3.7
-	d^4 ($e^2 t_2^2$)	$\sqrt{24} = 4.90$	-
Mn(II)	d^5 ($e^2 t_2^3$)	$\sqrt{35} = 5.92$	5.9-6.2
Fe(II)	d^6 ($e^3 t_2^3$)	$\sqrt{24} = 4.90$	5.3-5.5
Co(II)	d^7 ($e^4 t_2^3$)	$\sqrt{15} = 3.88$	4.2-4.8
Ni(II)	d^8 ($e^4 t_2^4$)	$\sqrt{8} = 2.83$	3.7-4.0
Cu(II)	d^9 ($e^4 t_2^5$)	$\sqrt{3} = 1.73$	-

Contributors and Attributions

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