Coordination Chemistry-II

Magnetochemistry:

Dr. Tapan Kumar Si

1) **Dia-, para-, ferro- and anti-ferro magnetic properties**
2) **Orbital and Spin magnetic moment**
3) **Spin only moments of d^n ions**
4) **Superexchange and antiferromagnetic ineractions**

B. C. College/VI Semester (H)/ Inorg. Chem./ Lecture-3/TKS/ March-2020

Dia-, para-, ferro and anti-ferromagnetic properties of Coordination compounds

In terms of magnetism, there are two classes of compounds distinguished by their behaviour in a magnetic field:

a) ***Diamagnetic*** –compounds that are *repelled from* the strong part of an external magnetic field;

b) ***Paramagnetic*** –compounds that are *attracted into* the strong part of a magnetic field and unpaired electron/s must present.

c) ***Ferromagnetism :*** It is a special case of paramagnetism. In this case the overall magnetic susceptibility of compound increases by interacting their individual paramagnetic center depending on temperature. This type of substance are termed as *ferromagnetic substances* (*metallic phases such as Fe, Co, Ni, Tb, Dy, and certain oxides such as* CrO_2*.)*

d) ***Anti -ferromagnetism :*** It is also a special case of paramagnetism. In this case the overall magnetic susceptibility of compound decreases through coupling of neighboring paramagnetic center depending on temperature. This type of substance are termed as *anti-ferromagnetic substances such as MnO, CoO, NiO,* FeF_2*, and* MnF_2

Relation of Temperature with Magnetic Susceptibility

***According to Curie-Wiess law** the*

magnetic susceptibility (χ) of

*compound is inversely proportional with temperature like **curve A (**Fig.1)*

*But for **ferromagnetic** substances, the magnetic susceptibility sharply **increases** after certain temperature **(Curve B**) .*
*This particular temperature is known as Curie point or **Curie Temperature,(T_c).***

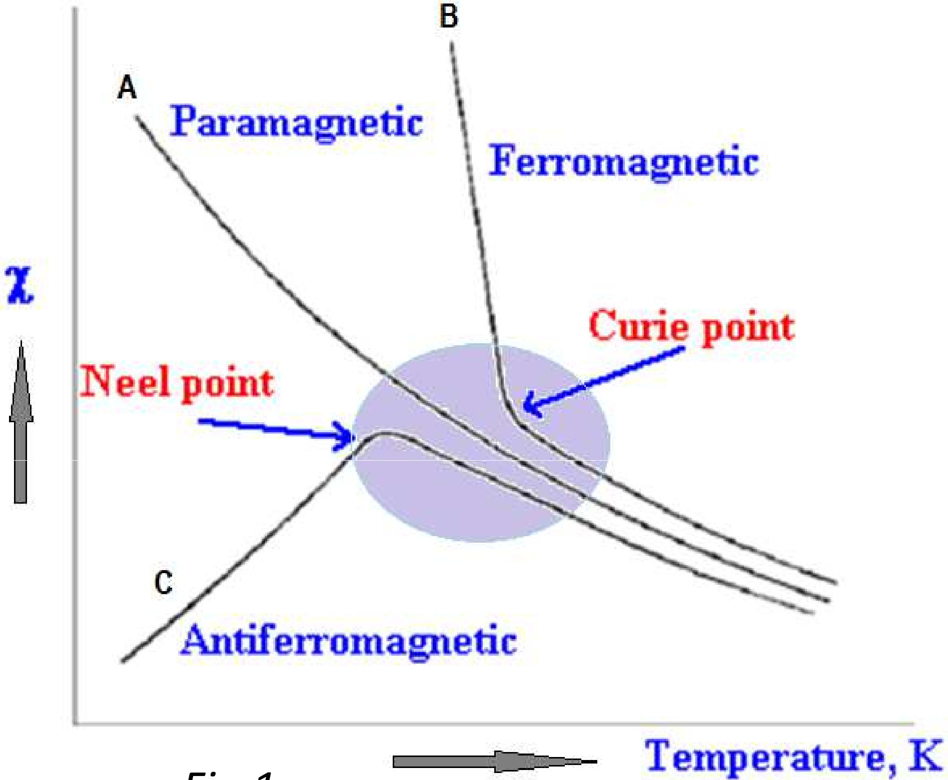

Fig.1

***O**n the other hand, for **anti-ferromagnetic substances,** magnetic susceptibility sharply decreases after certain temperature **(Curve C)** and this particular temperature is known as **Neel Temperature (T_n)**.*

Orbital and spin magnetic moment, spin only moments of d^n ions

Paramagnetism arises whenever an atom, ion or molecule possesses *one or more unpaired electrons*. It is not restricted to transition metal ions, and even non-metallic compounds can be paramagnetic; dioxygen is a simple.

The electrons in orbitals, have both orbital motion and spin motion; both contribute to the (para) magnetic moment. Quantum theory associates quantum numbers with both these motions. The spin and orbital motion of an electron in an orbital involve quantum numbers for both ***spin momentum*** **(*S*),** which is actually related to the number of unpaired electrons (n) as $S = n/2$, and the ***orbital angular momentum*** **(*L*).**

The **magnetic moment (μ)** which is expressed in units of Bohr magnetons, *B* is a measure of the magnetism, and is defined by an expression involving both quantum numbers.

$$\mu=[4S(S+1)+L(L+1)]^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Spin only moments of d^n ions

Firstly, for *first-row* transition metal ions, ***the effect of L on (μ) is small***, so a fairly valid approximation can be reached by neglecting the *L* component, and then our expression reduces to the ***so-called 'spin-only'(μ_s)*** where the only quantum number remaining is *S.*

$$\mu_s = [4S(S + 1)]^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Now, we may readily replace this quantum number by using the ***S = n/2*** *relationship, the substitution then leading to the 'spin-only'* formula for the magnetic moment (2).

$$\mu_s = [n(n + 2)]^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Using this 'spin-only' Equation (3), the value of μ_s *can be readily calculated and predictions compared with actual experimental values (Table 1).*

Comparisons of predicted and actual experimental magnetic moments (in units of *B)* for octahedral transition metal complexes

Table-1

Sl.No.	Number of unpaired electrons (n)	Calculated Spin Only magnetic moment (μ_s)	Experimental magnetic Moment(μ)	Typical metal ions with d^n electrons
1	0	0	0	Co^{3+} low spin
2	1	1.73	1.70	Ti^{3+}, Cu^{2+}
3	2	2.83	2.75-2.85	V^{3+}, Ni^{2+}
4	3	3.88	3.80–3.90	V^{2+}, Cr^{3+}, Mn^{4+}
5	4	4.90	4.75–5.00	high-spin Cr^{2+} & Co^{3+}
6	5	5.92	5.65–6.10	high-spin Mn^{2+}

The techniques that effectively distinguish between high and low spin complexes

- For example, Co(II) is a d^7 system, which will have **three unpaired electrons** (t_{2g}^5 e_g^2) if high spin and **one unpaired electron** if low spin (t_{2g}^6, e_g^1) with calculated magnetic moments of **3.88** and **1.73** ***B*** *respectively.*

  If a particular complex has as experimental magnetic moment of **3.83** ***B****,* *then it must, by comparison* with the two options, be **high spin**.

- The technique can very effectively distinguish between high and low spin states. **For Co(III) (d^6),** for example, $[Co(NH_3)_6]^{3+}$ **(low spin, *n = 0*)** has an experimental magnetic moment close to **zero**, whereas $[CoF_6]^{3-}$ **(high spin, *n* = 4*)*** has an experimental magnetic moment of **nearly 5** ***B****, readily differentiated. The simple*

Anti-ferromagnetic coupling

A simple qualitative model can explain anti-ferromagnetic and ferromagnetic superexchange between two spin centers that involves the valence orbitals of bridging ligands.

Key to this model is the assumption of a partial spin pairing between the unpaired electron of a "magnetic orbital," usually a d-orbital of a magnetic transition metal ion, and the electrons of the fully occupied ligand orbital that overlaps with the metal d-orbital.

For example, If the ligand orbital is a p-orbital, then it overlaps with symmetry-equivalent d-orbitals of both metal sites, this partial spin pairing will result in an anti-ferromagnetic orientation of the two unpaired electrons localized on the two metal ions. Here, both s and p binding modes can cause the same result.

Ferromagnetic coupling

- *Ferromagnetic coupling, on the other hand, requires that no overlap exists between the involved magnetic orbitals of the M and M′ sites. This then leads to a parallel spin orientation of the two unpaired electrons according to Hund's rule.*

- *To this end, the magnetic orbitals of the metal centers need to be orthogonal, or the coupling involves two orthogonal orbitals on the same ligand donor position, for example, a p_x- and a p_y orbital (Fig. 2).*

If several exchange pathways exist in polynuclear coordination complexes, ferromagnetic and antiferromagnetic pathways can compete for a given spin dimer, usually resulting in a dominant antiferromagnetic exchange.

Coupling of paramagnetic metal centers with single-occupied d-orbitals bridged by a monoatomic ligand

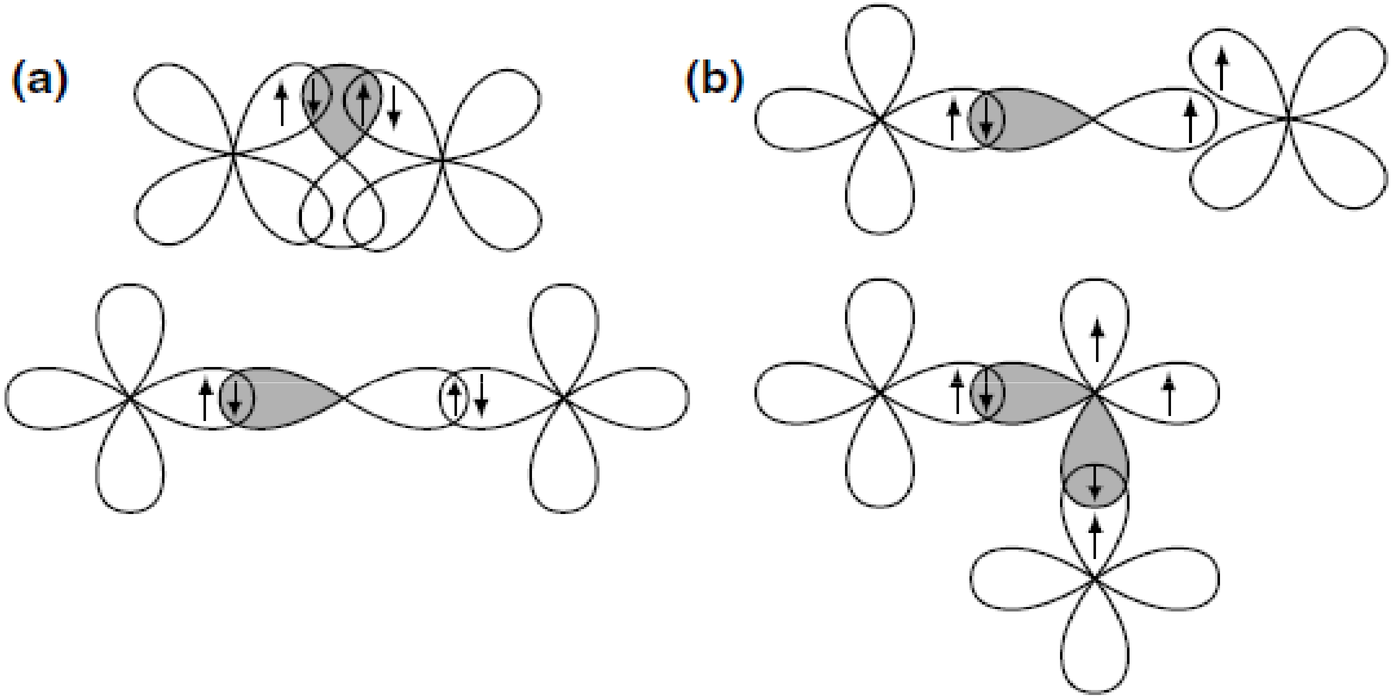

Fig.2 (a)Overlap scenarios leading to antiferromagnetic exchange; (b)Overlap scenarios resulting in orthogonal singly occupied dorbitals, that is, ferromagnetic coupling