B.Sc. Semester-IV
Core Course-VIII (CC-VIII)
Inorganic Chemistry

I. Coordination Chemistry

6. Magnetic Properties of 3d-Compounds

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Coordination Chemistry: 20 Lectures

Werner's theory, valence bond theory (inner and outer orbital complexes), electroneutrality principle and back bonding. Crystal field theory, measurement of 10 Dq (Δo), CFSE in weak and strong fields, pairing energies, factors affecting the magnitude of 10 Dq (Δo, Δt). Octahedral vs. tetrahedral coordination, tetragonal distortions from octahedral geometry Jahn-Teller theorem, square planar geometry. Qualitative aspect of Ligand field and MO Theory.

IUPAC nomenclature of coordination compounds, isomerism in coordination compounds. Stereochemistry of complexes with 4 and 6 coordination numbers. Chelate effect, polynuclear complexes, Labile and inert complexes.

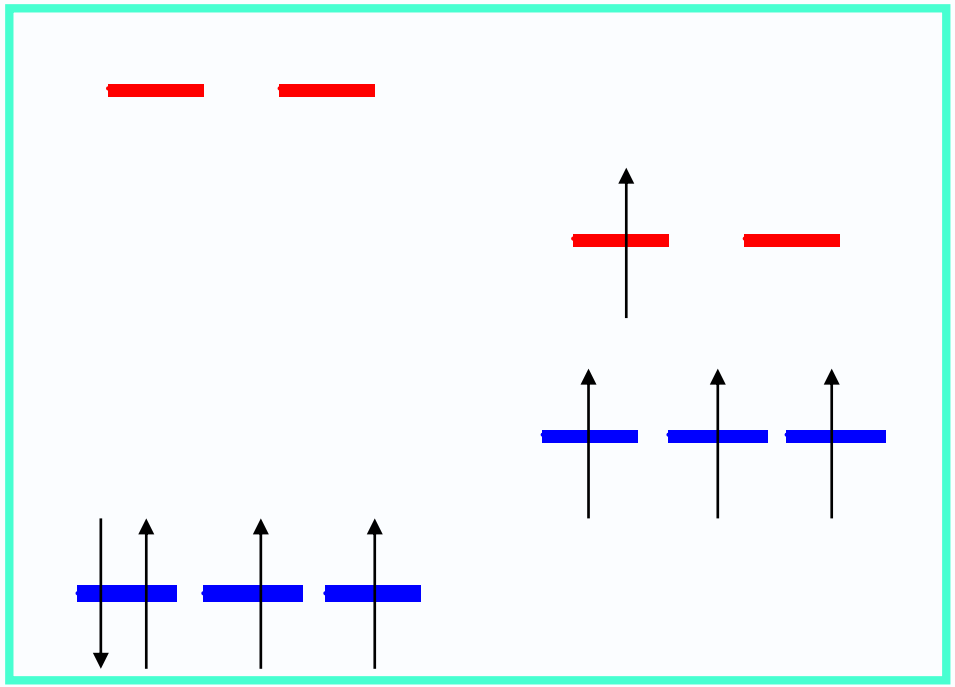
Coverage:

1. Magnetic Properties of 3*d*-Compounds

Ground-state Electronic Configuration and Magnetic Properties of 3*d*-Compounds

An Example - d^4 :

Strong field = Low spin (2 unpaired)



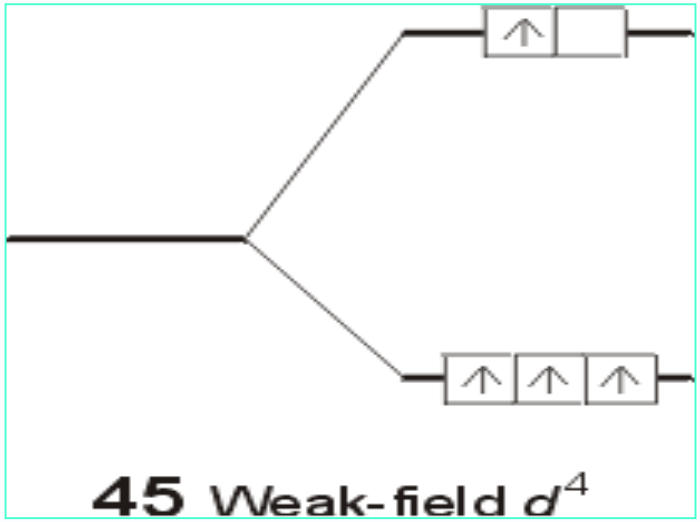
Weak field = High spin (4 unpaired)

$\mathbf{P < \Delta_o}$ $\mathbf{P > \Delta_o}$

Coulombic repulsion energy and exchange energy

When the 4th electron is assigned it will either go into the higher energy e_g orbital at an energy cost of D_o or be paired at an energy cost of P, the pairing energy.

Ground-state Electronic Configuration and Magnetic Properties

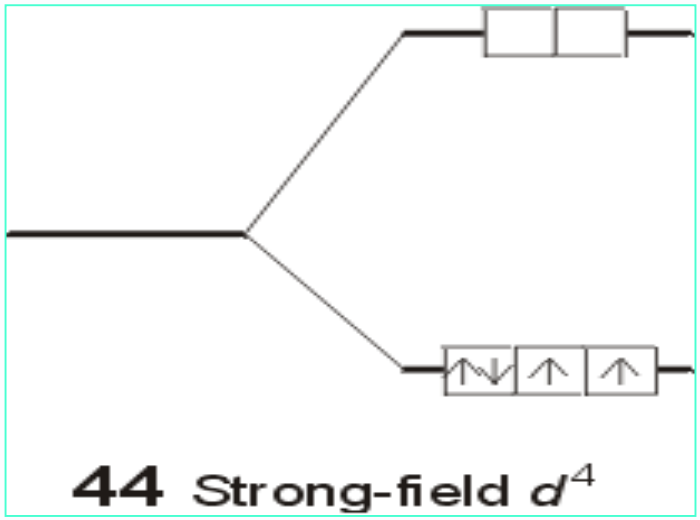


$[Mn(H_2O)_6]^{3+}$

Weak Field Complex

the total unpaired spin is $4 \times ½ = 2$

High Spin Complex



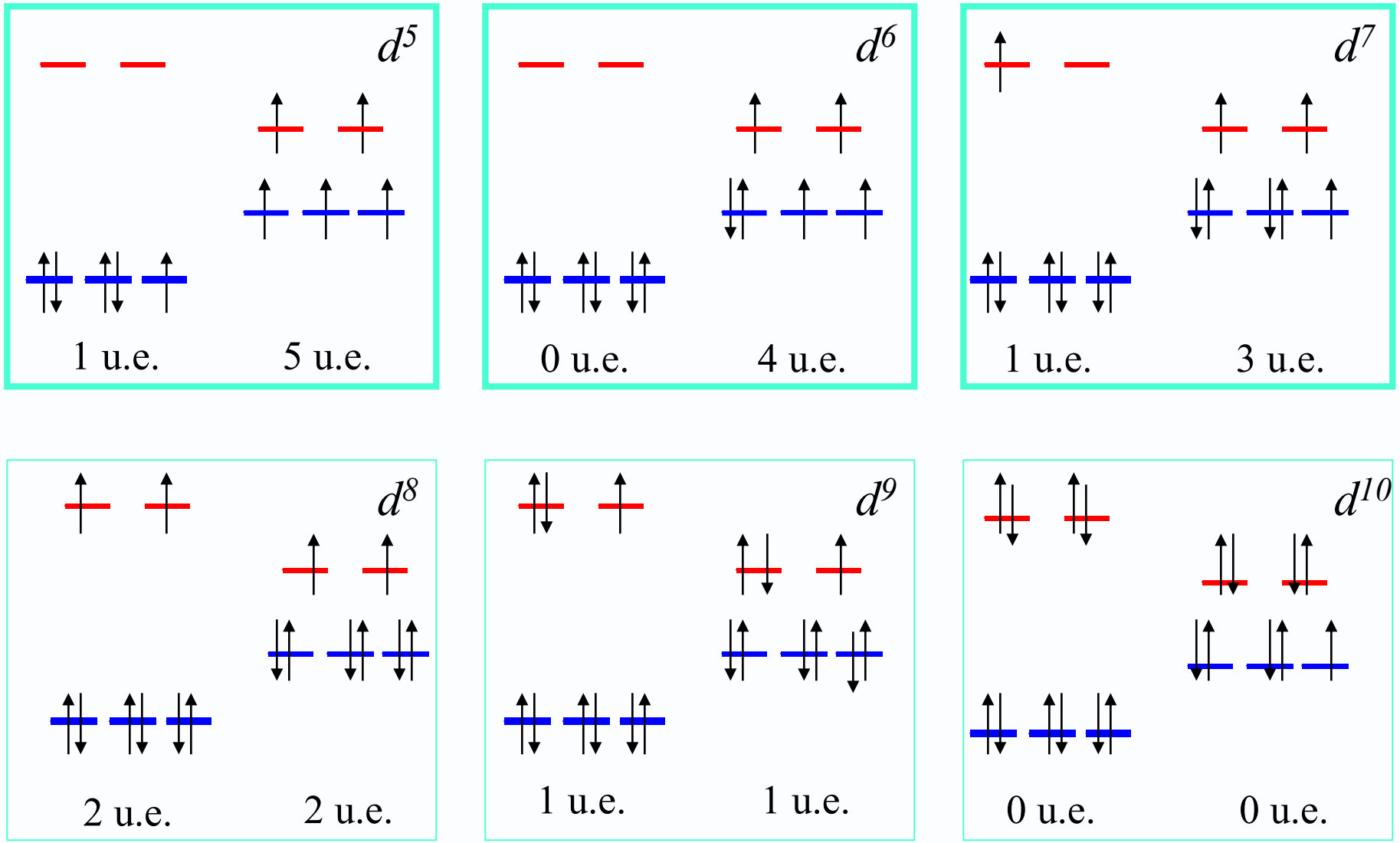
$[Mn(CN)_6]^{3-}$

Strong field Complex

total unpaired spin is $2 \times ½ = 1$

Low Spin Complex

Placing Electrons in *d*-Orbitals

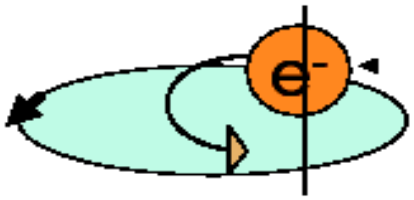


Magnetic Properties of 3*d*-Compounds

Each electron has a magnetic moment owing to its:

spin angular momentum

orbital angular momentum



Orbital motion of e generates current and magnetic field

Spin motion of e about its own Axis also generates a magnetic field

- The magnetic moment μ of a complex with total spin quantum number S is:
- $\mu = 2\{S(S+1)\}^{1/2}\ \mu_B$ (μ_B is the Bohr magneton)
- $\mu_B = eh/4\pi m_e = 9.274 \times 10^{-24}\ J\ T^{-1}$
- Since each unpaired electron has a spin ½,
- S = (½)n, where n = no. of unpaired electrons
- $\mu = \{n(n+2)\}^{1/2}\ \mu_B$
- In d^4, d^5, d^6, and d^7 octahedral complexes, magnetic measurements can very easily predict weak versus strong field.
- Tetrahedral complexes - only high spin complexes result, for $\Delta_t << \Delta_O$.

Magnetic Properties of 3*d*-Compounds

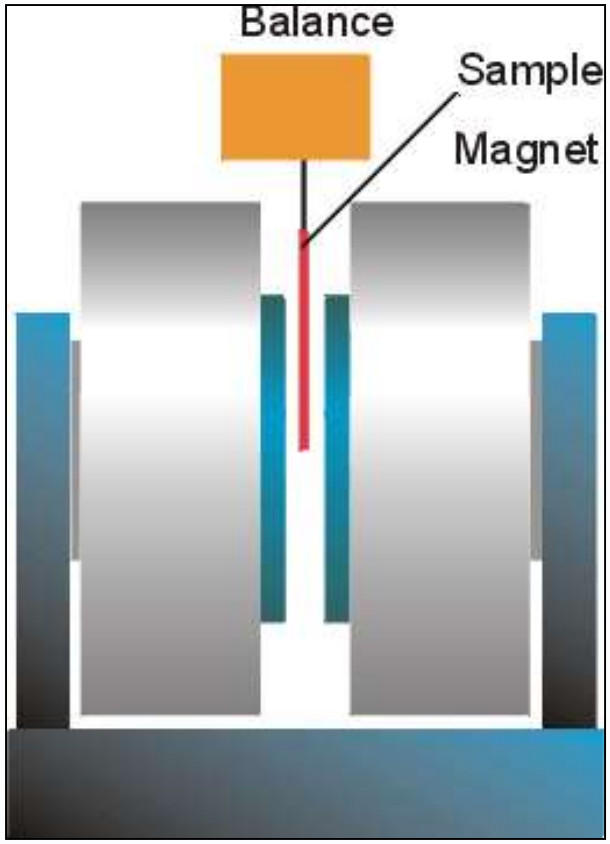
n = no. of unpaired electrons

$$\mu = \{n(n+2)\}^{1/2}\ \mu_B$$

Ion	n	S	μ/μ_B Calculated	Experimental
Ti^{3+}	1	1/2	1.73	1.7 – 1.8
V^{3+}	2	1	2.83	2.7 – 2.9
Cr^{3+}	3	3/2	3.87	3.8
Mn^{3+}	4	2	4.90	4.8 – 4.9
Fe^{3+}	5	5/2	5.92	5.3

Similar Calculation can be done for Low-spin Complex

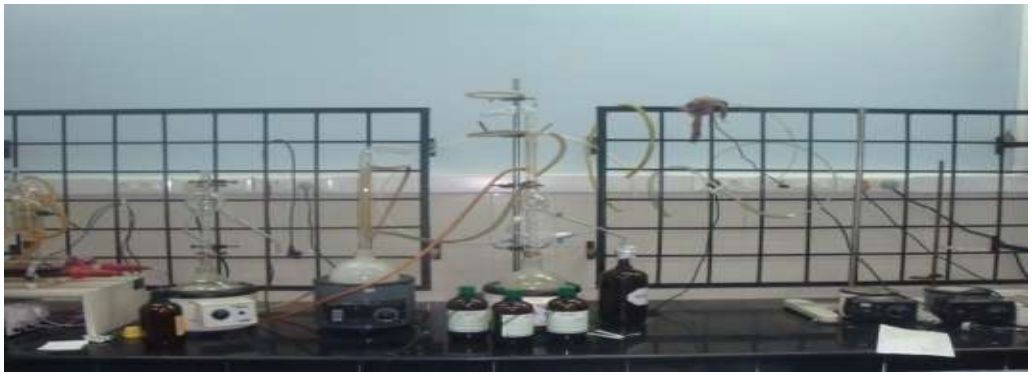
Magnetic Properties of 3*d*-Compounds



Gouy balance to measure the magnetic susceptibilities

- We can measure the magnetic properties of a sample by hanging a vial of material from a balance so that it sits partly in a magnetic field
  - The sample will be pulled down into the magnet if it contains unpaired electrons (said to be paramagnetic)
  - It will tend to be pushed out of the field if it contains no unpaired electrons (diamagnetic)
- The amount of material in the vial along with the extent to which the sample is pulled into the magnet allows us to calculate the magnetic susceptibility of the sample
  - Sample with a high magnetic susceptibility is strongly pulled into the magnetic field

Thank You



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