8.3.3: 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:

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

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.

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

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

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)	√15 = 3.88	4.3-5.2
Co(II)	d^7 low spin (t_{2g}^6 e_g^1)	√3 = 1.73	1.8
Ni(II)	d^8 (t_{2g}^6 e_g^2)	√8 = 2.83	2.9-3.3
Cu(II)	d^9 (t_{2g}^6 e_g^3)	√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)	√3 = 1.73	1.7-1.8
Cr(IV) / Mn(V)	d_2 (e^2)	√8 = 2.83	2.6 - 2.8
Fe(V)	d^3 (e^2 t_2^1)	√15 = 3.88	3.6-3.7
-	d^4 (e^2 t_2^2)	√24 = 4.90	-
Mn(II)	d^5 (e^2 t_2^3)	√35 = 5.92	5.9-6.2
Fe(II)	d^6 (e^3 t_2^3)	√24 = 4.90	5.3-5.5
Co(II)	d^7 (e^4 t_2^3)	√15 = 3.88	4.2-4.8
Ni(II)	d^8 (e^4 t_2^4)	√8 = 2.83	3.7-4.0
Cu(II)	d^9 (e^4 t_2^5)	√3 = 1.73	-

Contributors and Attributions

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