Magnetic Moments

Lecture 4. CHEM1902 (C 10K) Coordination Chemistry

Magnetic moments are often used in conjunction with electronic spectra to gain information about the oxidation state 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 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 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. See an interactive JAVA applet for examples.

Note: For CHEM1902 (C10K), we 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 two orbitals, the d_{x2-y2} and the d_{z2} (e subset) are now at lower energy (more favoured) than the remaining three d_{xy}, d_{xz}, d_{yz} (the t2 subset) which are destabilised.

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

The usual relationship quoted between them is: Δtet= 4/9 Δoct.

Square planar complexes are less commmon than tetrahedral and **for CHEM1902 (C10K) we will assume that the only ions forming square planar complexes are d^8 e.g. Ni(II), Pd(II) and Pt(II).** As with octahedral complexes, the energy gap between the dxy and dx2-y2 is Δoct 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.

$\mu = \sqrt{n(n+2)}$ B.M.

$\mu = \sqrt{4S(S+1)}$ B.M.

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)	d1 ($t_{2g}1$)	$\sqrt{3}$ = 1.73	1.6-1.7
V(III)	d2 ($t_{2g}2$)	$\sqrt{8}$ = 2.83	2.7-2.9
Cr(III)	d3 ($t_{2g}3$)	$\sqrt{15}$ = 3.88	3.7-3.9
Cr(II)	d4 high spin ($t_{2g}3$ e_g1)	$\sqrt{24}$ = 4.90	4.7-4.9
Cr(II)	d4 low spin ($t_{2g}4$)	$\sqrt{8}$ = 2.83	3.2-3.3
Mn(II)/ Fe(III)	d5 high spin ($t_{2g}3$ e_g2)	$\sqrt{35}$ = 5.92	5.6-6.1
Mn(II)/ Fe(III)	d5 low spin ($t_{2g}5$)	$\sqrt{3}$ = 1.73	1.8-2.1
Fe(II)	d6 high spin ($t_{2g}4$ e_g2)	$\sqrt{24}$ = 4.90	5.1-5.7
Co(III)	d6 low spin ($t_{2g}6$)	0	0
Co(II)	d7 high spin ($t_{2g}5$ e_g2)	$\sqrt{15}$ = 3.88	4.3-5.2
Co(II)	d7 low spin ($t_{2g}6$ e_g1)	$\sqrt{3}$ = 1.73	1.8
Ni(II)	d8 ($t_{2g}6$ e_g2)	$\sqrt{8}$ = 2.83	2.9-3.3
Cu(II)	d9 ($t_{2g}6$ e_g3)	$\sqrt{3}$ = 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)	d1 (e^1)	$\sqrt{3}$ = 1.73	1.7-1.8
Cr(IV) / Mn(V)	d2 (e^2)	$\sqrt{8}$ = 2.83	2.6 - 2.8
Fe(V)	d3 (e^2 t_2^1)	$\sqrt{15}$ = 3.88	3.6-3.7
-	d4 (e^2 t_2^2)	$\sqrt{24}$ = 4.90	-
Mn(II)	d5 (e^2 t_2^3)	$\sqrt{35}$ = 5.92	5.9-6.2
Fe(II)	d6 (e^3 t_2^3)	$\sqrt{24}$ = 4.90	5.3-5.5
Co(II)	d7 (e^4 t_2^3)	$\sqrt{15}$ = 3.88	4.2-4.8
Ni(II)	d8 (e^4 t_2^4)	$\sqrt{8}$ = 2.83	3.7-4.0

Cu(II)	d9 (e^4 t_2^5)	$\sqrt{3} = 1.73$	-

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Created Dec 1995. Links checked and/or last modified 15th January 2013.
URL http://wwwchem.uwimona.edu.jm/spectra/MagMom.html