

Magnetic Susceptibility

The magnetic properties of complexes in terms of unpaired electrons and their magnetic or spin properties are useful in determining structural features in transition metal compounds. Complexes that contain unpaired electrons are paramagnetic and are attracted into magnetic fields. Diamagnetic compounds are those with no unpaired electrons are repelled by a magnetic field. All compounds, including transition metal complexes, possess some diamagnetic component which results from paired electrons moving in such a way that they generate a magnetic field that opposes an applied field. A compound can still have a net paramagnetic character because of the large paramagnetic susceptibility of the unpaired electrons. The number of unpaired electrons can be determined by the magnitude of the interaction of the metal compound with a magnetic field. This is directly the case for 3d transition metals but not always for 4d or 5d transition metals, whose observed magnetic properties may arise not only from the spin properties of the electrons, but also from the orbital motion of the electrons.

The Johnson-Matthey magnetic susceptibility balance is very similar to the traditional Gouy balance but, instead of measuring the force that a magnet exerts on a sample, the opposite force that the sample exerts on a suspended permanent magnet is observed.

The mass susceptibility, χ_g , is calculated using:

$$\chi_g = \frac{C_{bal} l (R - R_o)}{10^9 m}$$

where: l = sample length (cm)
 m = sample mass (g)
 R = reading for tube plus sample
 R_o = empty tube reading
 C_{bal} = balance calibration constant

The molar susceptibility, χ_m , is then calculated by multiplying χ_g by the molecular mass of the substance. The molar susceptibility is positive if the substance is paramagnetic and negative if the substance is diamagnetic. The molar susceptibility measured is a sum of the paramagnetic contribution from the unpaired electrons in the metal ion and the

diamagnetic contributions from the ligands and the counter ions. This can be expressed by:

$$\chi_{\text{total}} = \chi_{\text{para}} + \chi_{\text{dia. (L+ ions)}}$$

Therefore

$$\chi_{\text{para}} = \chi_{\text{corr.}} = \chi_{\text{total}} - \chi_{\text{dia.}}$$

Note: $\chi_{\text{dia.}}$ is negative

The diamagnetism factors for common ligands and ions as well as the Pascal constants used to calculate the diamagnetic corrections for complex ligands can be found at the end of the lab write up. Once the $\chi_{\text{corr.}}$ is determined μ_{eff} can be calculated using:

$$\mu_{\text{eff}} = \sqrt{8\chi_{\text{corr}} T}$$

And it follows that in the absence of spin-orbit coupling the number of unpaired electrons can be determined by:

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

Pascal's Constants

TABLE I. Molar susceptibilities (χ_d) of common ligands and ions
All values $\times 10^{-6}$ /mole

Cations		Anions	
Li ⁺	-1.0	F ⁻	-9.1
Na ⁺	-6.8	Cl ⁻	-23.4
K ⁺	-14.9	Br ⁻	-34.6
Rb ⁺	-22.5	I ⁻	-50.6
Cs ⁺	-35.0	CN ⁻	-13.0
NH ₄ ⁺	-13.3	CNS ⁻	-31.0
Mg ²⁺	-5.0	CO ₃ ²⁻	-28.0
Ca ²⁺	-10.4	ClO ₄ ⁻	-32.0
Zn ²⁺	-15.0	NO ₂ ⁻	-10.0
Hg ²⁺	-40.0	NO ₃ ⁻	-18.9
		OH ⁻	-12.0
		O ²⁻	-7.0
		PtCl ₆ ²⁻	-148
		SO ₄ ²⁻	-40.1
		SO ₄ H ⁻	-35.0
Common ligands			
H ₂ O	water	-13	C ₂ O ₄ ²⁻ oxalate -25
NH ₃	ammonia	-18	C ₃ H ₂ O ₄ ²⁻ malonate -45
N ₂ H ₄	hydrazine	-20	C ₄ H ₇ O ₂ ⁻ acac -52
CO	carbonyl	-10	C ₅ H ₅ ⁻ cyclopenta-
CHO ₂ ⁻	formate	-17	dienyl -65
CH ₄ N ₂ O	urea	-34	C ₅ H ₅ N py -49
CH ₄ N ₂ S	thiourea	-42	C ₆ H ₅ NO ⁻ oxinate -86
C ₂ H ₄	ethylene	-15	C ₁₀ H ₈ N ₂ bipy -105
C ₃ H ₃ O ₂ ⁻	acetate	-30	C ₁₂ H ₈ N ₂ phen -128
C ₂ H ₄ NO ₂ ⁻	glycinate	-37	C ₁₀ H ₁₄ N ₂ O ₂ ²⁻ salen -182
C ₂ H ₈ N ₂	en	-46	C ₁₀ H ₁₆ As ₂ diarsine -194
			C ₃₂ H ₁₆ N ₄ ²⁻ phthalocyanine -422

The effective magnetic moment is a combination of spin (moment due to unpaired electrons) and the orbit (moment due to orbital angular momentum) terms. Spin-orbit coupling arises in equivalent, degenerate orbitals which, in the presence of a magnetic field allow electrons to revolve about an axis (e.g. $d_{x^2-y^2}$ and d_{xy} lie in the xy plane and would allow circulation about the z-axis, hence creating a moment along the z axis). This effect is quenched when the orbital degeneracy is removed, as in a ligand field, and does not exist in half-filled or filled shells because the ground state is S. Calculate the spin-only value for the magnetic moment from the following :

$$\mu_s = g\sqrt{S(S+1)}$$

$g = 2.00$ for electron

$S =$ total atom spin

Calculate the moment due to spin + orbital momentum, μ_{S+L}

$$\mu_{S+L} = \sqrt{g^2 S(S+1) + L(L+1)} \quad \text{B.M.}$$

$L =$ Total angular momentum (for first row transition metals this works out to be $L = 3$ and will be discussed later in the semester).

Question:

If the value of μ_{eff} that you measure is between the μ_s and the μ_{S+L} , what does this suggest about L ?