E. MAGNETIC PROPERTIES OF COORDINATION COMPOUNDS

Introduction:

Electrons have a magnetic moment that can be aligned either with/or in opposition to an applied magnetic field, depending on whether the spin magnetic quantum number, $\boldsymbol{m_s}$, is +1/2 or –1⁄2. For an atom or ion with only paired electrons, the individual electron contributions to the overall spin magnetic quantum number, $\boldsymbol{M_s}$, cancel one another, giving a zero net value of the overall spin quantum number; i.e., $S = 0$. Such a species is said to be *diamagnetic*. If a diamagnetic material is placed between the poles of a strong magnet it will experience a repulsion for the applied field. The repulsion arises from circulation of the electrons caused by the applied field, resulting in an induced magnetic field in opposition. Suppose the sample is suspended between the poles of the magnet and is connected to the pan of an analytical balance. This is the experimental arrangement of a *Gouy balance*. As a result of the induced diamagnetic repulsion, the sample will appear to weigh less in the magnetic field, compared to its true weight outside the field. When removed from the applied field, the sample has no residual magnetic moment, and its apparent weight will be its true weight.

If the sample contains one or more unpaired electrons, the overall spin quantum number will be greater than zero; i.e., $S > 0$. Such a species is said to be *paramagnetic*. If a paramagnetic species is placed between the poles of a strong magnet it will experience an attraction for the field, due to the alignment of the permanent paramagnetic moment with the applied field. If the sample is weighed with a Gouy balance, it will appear to be heavier in the magnetic field, compared to its true weight outside the field. With the exception of monatomic hydrogen, all atoms or ions with unpaired electrons also have paired electrons. In an applied field, these paired electrons and their associated induced diamagnetic moment slightly mitigate the paramagnetic attraction for the applied field. Nonetheless, the paramagnetic moment is always stronger than the opposing diamagnetic moment, so the net effect is an attraction for the field. However, whenever we refer to a substance as paramagnetic, owing to an electronic configuration having unpaired electrons, we must realize that there is also a subtractive diamagnetic contribution to the overall magnetic moment of the sample.

Transition metals, by definition, have at least one oxidation state with an incompletely filled d or f subshell and are consequently paramagnetic. The magnetic moment, μ, results from both the spin and orbital contributions of these unpaired electrons. The presence of coordinated ligands around the metal ion quenches the orbital contribution to greater or lesser degree, making the spin contribution most important. As an approximation, the expected magnetic moment for an ion with a certain number of unpaired electrons can be estimated from the spin-only magnetic moment, μs, which disregards orbital contributions:

$$\mu_s = g\sqrt{[S(S+1)]} \qquad \textbf{(1)}$$

In equation (1), g is the gyromagnetic ratio (g = 2.00023) and $S = n$ (1⁄2), where n is the number of unpaired electrons in the configuration. Substituting $g = 2$ and $S = n$ (1⁄2) into equation (1), we can calculate the spin-only moment in terms of the number of unpaired electrons from the expression:

$$\mu_s = \sqrt{[n(n+2)]} \qquad \textbf{(2)}$$

Thus, for a d^1configuration, such as Ti^{3+}, we obtain μs = √[1(1 + 2)] = √3 = 1.73. The units of the magnetic moment are Bohr magnetons (BM). Actual magnetic moments tend to be somewhat larger than the spin-only values obtained from either equation (1) or (2), owing to incomplete quenching of the orbital contribution. Nonetheless, the experimentally obtained value of the *effective magnetic moment*, μ_{eff}, taken as approximately the spin-only value, often serves as a practical means of determining the number of unpaired electrons on the transition metal in a complex. This, in turn, gives information about the spin state of the metal and can suggest its oxidation state or mode of bonding.

Magnetic moments are not measured directly. Instead, they are calculated from the measured *magnetic* *susceptibility*, χ. Over the years there have been a number of techniques used to determine magnetic susceptibilities of transition metal complexes. These include the Gouy method, the Faraday method, and the NMR method. Of these, only the Faraday and NMR techniques are suitable for microscale samples of 50 mg or less. In 1974, D. F. Evans2 of Imperial College, London, developed a new type of magnetic susceptibility balance suitable for semi-microscale samples, which is commercially available from Johnson Matthey. The Evans balance employs the Gouy method in a device that is compact, lightweight, and self-contained. It does not require a separate magnet or power supply, and is therefore portable. The instrument has a digital readout that provides quick and accurate readings, with sensitivity matching traditional apparatus. It can be used with solids, liquids, and solutions. As such, the Evans balance is ideal for our purposes.

In the Gouy method, as previously noted, the balance measures the apparent change in the weight of the sample created by the sum of the diamagnetic repulsion and paramagnetic attraction for the applied field. The Evans balance uses the same principle, but instead of measuring the force that the magnet exerts on the sample, it measures the equal and opposite force the sample exerts on a suspended permanent magnet. The Evans balance determines this force by measuring the change in current required to keep a set of suspended permanent magnets in balance when their fields interact with the sample. The magnets are on one end of a balance beam, and when interacting with the sample change the position of the beam. This change is registered by a pair of photodiodes set on opposite sides of the balance beam's equilibrium position. The diodes send signals to an amplifier that in turn supplies current to a coil that will exactly cancel the interaction force. A digital voltmeter, connected across a precision resistor in series with the coil, measures the current directly. This current is displayed on the digital readout.

The sample's magnetic susceptibility per gram is called the *mass magnetic susceptibility*, χ_g. For the Evans balance, the general expression for the mass magnetic susceptibility is

$$\chi_g = L/m\ [C(R-R_o) + \chi_v' A] \qquad \textbf{(3)}$$

where

χ_g : mass (gram) magnetic susceptibility
L : sample length in centimeters
m : sample mass in grams
C : balance calibration constant of the instrument
R : reading from the digital display when the sample (in the sample tube) is in place in the balance
R_o : reading from the digital display when the empty sample tube is in place in the balance
χ_v' : volume susceptibility of air (0.029×10^{-6} erg . G^{-2} . cm^{-3})
A : cross-sectional area of the sample

The volume susceptibility of air is usually ignored with solid samples, so equation (3) can be rewritten as:

$$\chi_g = \frac{C.L.(R - R_o)}{m\ .\ 10^9} \qquad \textbf{(4)}$$

Equation (4) gives the mass magnetic susceptibility in the cgs-units of erg . G^{-2} . cm^{-3} (where G is Gauss). The calibration standards usually employed in magnetic susceptibility measurements are $Hg[Co(SCN)_4]$ or $[Ni(en)_3]S_2O_3$, which have χ_g values of 1.644×10^{-5} and 1.104×10^{-5} erg . G^{-2} . cm^{-3}, respectively. A preferred method to evaluate C in equation (4) is to perform the experiment with one of these calibration standards employing the appropriate value of χg. In order to avoid the use of a mercury compound we will use the $[Ni(en)_3]S_2O_3$.

The *molar magnetic susceptibility*, χ_M , is obtained from the mass magnetic susceptibility by multiplying by the molecular weight of the sample in units of g/mol; i.e.,

$$\chi_M = M\chi_g \qquad \textbf{(5)}$$

The units of χ_M are erg . G^{-2}. This experimentally obtained value of χM includes both paramagnetic and diamagnetic contributions, which we may identify as χA and $\chi\alpha$, respectively. All sources of paired electrons (e.g., ligands, counter ions, core electrons on the paramagnetic species) contribute to the diamagnetic portion of the overall susceptibility. In 1910, Pascal observed that these contributions were approximately additive and consistent from sample to sample. Consequently, the diamagnetic contribution to the observed molar susceptibility can be estimated as the sum of constants (called Pascal's constants) for each diamagnetic species in the sample. We are interested in the paramagnetic molar susceptibility, which can be obtained by removing the diamagnetic contributions from χ_M. Thus we may write

$$\chi_M^{corr} = \chi_M - \Sigma\, \chi_\alpha \qquad \textbf{(6)}$$

Values of χ_M^{corr}, called the corrected magnetic susceptibility, are inherently positive, while those of χ_α are inherently negative. Thus, for a paramagnetic substance, it must be that $\chi_M^{corr} > \chi_M$

$$\mu_{eff} = \sqrt{[3kT\chi_M^{corr} / N\beta]} \qquad \textbf{(7)}$$

The value of the effective magnetic moment, μ_{eff}, can be determined from χ_M^{corr} by the *Curie Law* equation where k is the Boltzmann constant, T is the absolute temperature (K), N is Avogadro's number, and β is the Bohr magneton. If the appropriate constants are substituted, equation (7) becomes

$$\mu_{eff} = 2.828 \sqrt{[\chi_M^{corr} . T]} = \sqrt{[n.(n+2)]} \qquad \textbf{(8)}$$

where n is the numper of unpaired electrons on metal.

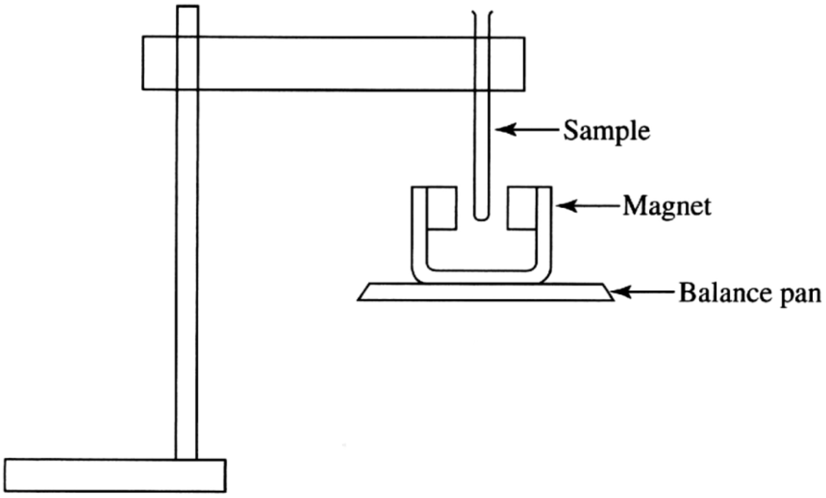
From $\mu_{eff} = \sqrt{[n.(n + 2)]}$ Bohr Magneton (BM) the expected values of μ_{eff} for transition-metal complexes with n = 1–5 unpaired electrons are as follows.

n	***S***	**μ_{eff} (BM)**
1	1/2	1.73
2	1	2.83
3	3/2	3.87
4	2	4.90
5	5/2	5.92

Experiment 8.

Experimental Procedure:

This experiment uses a modified form of the Guoy balance method, using a microscale apparatus devised by D. F. Evans and manufactured by Johnson-Matthey.



A moveable magnet attached to a torsion balance detects the force created by diamagnetic and paramagnetic moments in the sample. Diamagnetic moment makes the magnet move down. Paramagnetic moment makes the magnet move up.

The first measurement have been made with the calibration standard $[Ni(en)_3]S_2O_3$ in order to obtain a value of instrument constant, ***C***, and the instrument constant in equation (4) has been calculated as **1.30**. The following procedure will be completed for ***i)*** **$[Co(NH_3)_6]Cl_2$**, (product material of experiment #5 part-I), ***ii)*** **$[Co(NH_3)_5NO_2]SO_4$** (product material of experiment #5 part-II), ***iii)*** **$[Ni(NH_3)_6]Cl_2$** (product material of experiment #2 part-I), ***iv)*** **$FeCl_3.6H_2O$**, ***iv)*** **$VO(acac)_2$** (product material of experiment #7), and ***vi)*** **$K[Cr(ox)_2(H_2O)_2].2H_2O$**, (product material of experiment #5), the compounds you have already produced and stored in previous experiments.

1. Turn the RANGE knob on the balance to ×1 and allow the balance to warm up for 30 min.

2. Adjust the ZERO knob until the display reads 000. The zero should be readjusted if the range is changed.

Note: The zero knob on the balance has a range of 10 turns. It is best to operate the balance in the middle of this range. This can be accomplished by turning the knob 5 turns from one end and then, ignoring the bubble level, adjusting the back legs of the balance until the digital display reads about zero. Once this is done at the beginning of the laboratory, all further adjustments can be made with the knob on the front of the instrument.

3. Place an empty tube of known weight (analytical balance) into the tube guide on top of the instrument and take the reading $\mathbf{R_o}$.

Note: The instrument can drift over short periods of time and should be rezeroed before each measurement. On the ×1 setting the digital display should fluctuate by no more than ±1. However, when you record R or Ro take a "visual average" of this fluctuation and use this as your reading.

4. Carefully fill the sample tube with the solid so that the height will be at least 2 cm after packing. A lesser amount will not give a stable reading of **R**. Gently tap the bottom of the tube on a hard surface (not the table the balance is on) to pack the sample. When it is well packed, measure the sample length in centimeters to obtain the value of L. Then, obtain the mass of the sample in grams.

Note: If necessary, use a mortar and pestle to grind the sample into a fine powder before attempting to fill the sample tube.

5. Rezero the instrument, place the packed sample tube into the tube guide, and take the reading **R**. A negative reading indicates a diamagnetic sample. If the reading is off-scale, change the RANGE knob to ×10, rezero, and multiply the reading by 10.

Note: A critical part of the technique is correctly packing the well-powdered solid in the sample tube. To be sure you have the true value of R after the first reading, repeatedly tap the bottom of the tube firmly but gently on a hard surface for about 30 - 60 seconds. Then, take another reading of ***R****. Continue this until you have three values that agree within ±1. Also, during the tapping process ensure that the solid forms an even surface in the tube and is not sloped to one side.*

6. Using a thermometer placed or suspended near the instrument, determine the temperature in ^{o}C.

7. Remove the sample from the tube by inverting it and gently tapping it on a piece of weighing paper on a hard surface. Do not tap too hard, since the glass lip can be easily broken. After the tube is empty, rinse with an appropriate solvent from a disposable pipette with a fine tip (Pasteur pipette).

Calculating Magnetic Moment:

1. Using equation (4), calculate the gram susceptibility, X_g by using the mass susceptibility (sample) from your recorded values of L, R_o, R, m, and C. You will need the value of T for the calculation of μ from the Curie Law, equation (8).

2. The molar magnetic susceptibility, X_M, is obtained from X_g by multiplying by the molecular weight of the sample in units of g/mol.
$X_M = M.X_g$
Units of X_M are erg.G^{-2}.

3. Diamagnetic corrections need to be applied to this measured molar magnetic susceptibility. The diamagnetic contributions arise from core paired electrons, ligand electron pairs, and counter ion electron pairs. Therefore,

$X_M^{corr} = X_M - \{ X_M \text{(core)} + X_M \text{(ligand)} + X_M \text{(ion)}\}$

Each ligand or ion correction factors should be multiplied by stoichiometric number in the chemical formula. The diamagnetic correction factors are tabulated values, called Pascal's constants (values from *G. A. Bain and J. F. Berry, J. Chem. Educ., 2008, 85, 532*).

4. Apply Curie Law, equation (8) in order to find the number of unpaired electrons, n,

$\mu_{eff} = 2.828 \sqrt{[\chi_M^{corr} . T]} = \sqrt{[n.(n + 2)]}$

Do not forget to take the temperature (in Kelvin) at the time of the measurements to use in this calculation.

DATA SHEET

Sample	Mass (g)	Height (cm)	R_o	R	MW	*n*
i) **$[Co(NH_3)_6]Cl_2$**						
ii) **$[Co(NH_3)_5NO_2]SO_4$**						
iii) **$[Ni(NH_3)_6]Cl_2$**						
iv) **$FeCl_3.6H_2O$**						
iv) **$VO(acac)_2$**						
vi) **$K[Cr(ox)_2(H_2O)_2].2H_2O$**						

T=__________ ^oC= _______ K

Appendix
Diamagnetic Correction Constants (Pascal's Constants)*

Cations	$-10^6\chi_\alpha$	Anions	$-10^6\chi_\alpha$	Molecules	$-10^6\chi_\alpha$
Li^+	1	F^-	9	H_2O	13
Na^+	7	Cl^-	23	NH_3	16
K^+	15	Br^-	34	en	47
Rb^+	22	I^-	50	py	49
Cs^+	33	$CH_3CO_2^-$	29	PPh_3	167
NH_4^+	13	$C_6H_5CO_2^-$	71		
Mg^{2+}	4	CN^-	13		
Ca^{2+}	9	CNO^-	23		
Sr^{2+}	16	CNS^-	34		
Ba^{2+}	26	ClO_4^-	32		
Cu^+	15	CO_3^{2-}	28		
Ag^+	27	$C_2O_4^{2-}$	28		
Zn^{2+}	13	HCO_2^-	17		
Cd^{2+}	20	NO_3^-	19		
Hg^{2+}	36	O^{2-}	6		
Tl^+	36	OH^-	11		
Pb^{2+}	32	S^{2-}	28		
core**	13	SO_4^{2-}	38		
		$S_2O_3^{2-}$	46		
		$acac^-$	55		

*All values are $-10^6\chi_\alpha$ in cgs units. Example: for Li^+, $\chi_\alpha = -1 \times 10^{-6}$ erg·G^{-2} mol^{-1}. Abbreviations: $acac^-$ = acetylacetonate; en = ethylenediamine; PPh_3 = triphenylphoshpine; py = pyridine. Values of Bain and Berry (cf. ref. 3) may be used instead of these values.

**Core electrons of first-row transition metal ions.