EXPERIMENT

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Magnetic Susceptibility of Coordination Compounds

REFERENCES

(1) Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

(2) Szafran, Z.; Pike R. M.; Singh M. M., *Microscale Inorganic Chemistry: A Comprehensive Laboratory Experience, 1st Ed., John Wiley & Sons, Inc. 1991.*

(3) McMills L.; Nyasulu F.; Barlag R., *Journal of Laboratory Chemical Education* **2014,** *2*, 11.

(4) Cornell University Library. *The Stern Gerlach Experiment.* http://arxiv.org/abs/1007.2435v1 (accessed 05APR2016).

SAFETY RECOMMENDATIONS

CAUTION: Avoid physical contact with chemicals, use proper lab technique and when handling all chemicals during this lab.

INTRODUCTION

The definition of a transition metal is that it is an element that has an incomplete d subshell in either the neutral atom or its ions. While keeping this definition in mind, inorganic compounds can broadly be classified into two sets; paramagnetic if they are attracted by a magnetic field, or diamagnetic if they are repelled by it. Electron “spin” is the manifestation of angular momentum that arises from the quantum mechanical treatment of particles. The evidence for it was provided by Gerlach and Stern in 1921 when they observed that a molecular beam of silver atoms was split into two beams when passed through a magnetic field. After carefully repeating their results, which allowed them to calculate the magnetic susceptibility of the Ag atom to within 10% accuracy, the published their findings in 1922. This was before the concept of electron spin was proposed! In 1933, Stern was force to leave Germany for the U.S. due to racial laws imposed by the Nazi regime. Stern remained in Germany. Gerlach was awarded the Nobel Prize in 1944 for “his contribution of the molecular ray method and his discovery of the magnetic moment of the proton.” Neither Gerlach nor their joint experiment was mentioned. (http://arxiv.org/abs/1007.2435v1)

The magnetic properties of molecules and materials provide information about their electronic structure and have wide-ranging applications the range from data storage in electronic devices and cell phones to refrigeration. Most organic compounds have all of their electrons paired. Such molecules are diamagnetic and have very small magnetic moments. However, transition metal compounds can have one or more unpaired electrons and, if so, are termed paramagnetic. The number of unpaired electrons on a given metal ion determines the magnetic moment, ***μ***. The magnetic moment is the result of both spin and orbital contributions of unpaired electron density. The spin contribution is an important part, and the spin-only moment of a complex can be estimated using the following equation:

$$\mu_S = \mathrm{g}\sqrt{S(S+1)} \tag{1}$$

g is the gyromagnetic ratio for an electron (g = 2.0023) and **S** is the total spin of the unpaired electrons (each are ½). Typicallly, g ~ 2, and eq 1 can be rewritten with as:

$$\mu_S = \sqrt{n(n+2)} \tag{2}$$

Using eq 2, the theoretical spin-only moment, μ_s, can be calculated from the number of unpaired electrons.

Example: For one unpaired electron, such as Ti^{3+}*:*

$$\mu_S = \sqrt{1(1+2)} = 1.732 \tag{3}$$

The units of the magnetic moment are Bohr magnetons (or BM) and the actual magnetic moments, determined experimentally, are often larger than the spin-only moment value because of the orbital contribution. So finally, how can we estimate the magnetic moment? Experimentally, this is done by determining the *magnetic susceptibility* of a substance.

Magnetic susceptibility, χ, of a material is a dimensionless constant that relates the magnetization, **M**, of a substance in response to the magnetic field, **H** (eq 4).

$$\mathbf{M} = \chi \mathbf{H} \tag{4}$$

This lab will feature two techniques to determine magnetic susceptibility: 1) The Evan's Method and 2) The Evan's Balance.

1) The Evan's Method

Dr. Dennis F. Evans, a British inorganic chemist, invented a method for determining the magnetic susceptibility of compounds in solution by NMR. His discovery was published in 1959 and since then this technique has been properly named "Evans Method." Dr. Evan observed and correlated the difference in chemical shift from an inert reference compound in the absence and in the presence of paramagnetic complexes using Equation 5.

$$\chi_g = \chi_0 \frac{3000\Delta v}{4\pi v_0 cM} + \frac{\chi_0(\rho_0 - \rho_s)}{c} \tag{5}$$

Where: χ_g = mass susceptibility of the solute

Δv = observed frequency shift of reference resonance (Hz)

v_0 = spectrometer frequency (Hz)

χ_0 = mass susceptibility of solvent

c = concentration of substance in mol/L

ρ_0 = density of the pure solvent

ρ_s = density of the solution

M = molecular weight

Assuming ρ_0- ρ_s is zero and then multiplying by M simplifies to give Equation 6:

$$\chi_M = \frac{3000\Delta v}{4\pi v_0 c} \tag{6}$$

Where: χ_M = is the molar susceptibility of the solute (cm^3 mol^{-1}).

2) The Evan's Balance

An alternative technique to determine the magnetic susceptibility uses the Evan's Balance. The Evan's balance measures the change in current required to keep a set of suspended permanent magnets in balance after their magnetic fields interact with the sample. The magnets are located on one end of the balance beam and after interacting with the sample, change the position of the beam. This change is registered by a pair of photodiodes set on the opposite side of the balance beam's equilibrium position. These diodes send signals to an amplifier that 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 and is displayed on the digital readout. Use eq. 7 to determine the magnetic susceptibility from the Evan's balance.

$$X_g = \frac{C_{bal} \times l \; x \; (R - R_o)}{m \times 10^9} \tag{7}$$

Where: C_{bal}= balance calibration constant
l = sample height (in cm)
R = Sample reading
R_o = empty tube reading
m = sample mass (in g)

After the mass susceptibility of the sample has been determined, the effective magnetic moment can be calculated from the molar susceptibility. The molar susceptibility, χ_M, is calculated using eq 8.

$$\chi_M = M\chi_g \tag{8}$$

χ_M includes both paramagnetic (χ_p) and diamagnetic (χ_d) contributions eq 9.

$$\chi_p = \chi_M - \chi_d \tag{9}$$

χ_p, the paramagnetic contributions, is what gives the information on the electronic structure of the sample. However, the diamagnetic contributions, χ_d, (from the ligands, ions, inner-core electrons, etc.) need to be factored in to solve for this. The molar susceptibility can be corrected for the diamagnetic contributions **(see attachment for values).**

Now that χ_p has been solved, the effective magnetic moment can be calculated using the Curie-Weiss law, shown in eq 10.

$$\mu_{eff} = \frac{3kT\chi_p}{N\mu_B{}^2} \tag{10}$$

Where: k = Boltzmann constant

T = Temperature in Kelvin

N = Avogadro's Number (6.023 X 10^{23} mol^{-1})

μ_B= is the Bohr magneton

After the addition of the constants the equations becomes eq 11. Thus, solving for the effective magnetic moment of the sample (in BM).

$$\mu_{eff} = 2.828\sqrt{\chi_p T} \tag{11}$$

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PROCEDURE

$VO(CH_3COCHCOCH_3)_2$

Place 1.5 mL distilled water in a 25 mL round bottom flask and slowly add an equal volume of H_2SO_4 to the round bottom. Then add 4 mL of ethanol followed by 0.75 g vanadium(V) oxide, V_2O_5. Attach a water-cooled condenser and reflux this mixture for 1.5 hours using a heating mantle. The solution will turn a dark blue-green color.

Cool the mixture and filter using a small plug of glass wool, discarding any solid residue. Add 2 mL of acetylacetone dropwise to the filtrate while stirring. Neutralize the mixture by adding it carefully to a solution of 6 g of anhydrous Na_2CO_3 in 45 mL of distilled water, contained in a 150 mL beaker, while stirring the mixture using magnetic stirrer. The resulting mixture should then be cooled in ice water for 15 minutes before vacuum filtering. Wash the dark green product with cold distilled water (2 x 5 mL). Dry under vacuum for 15 minutes, then dry in a vacuum dessicator over $CaCl_2$, until the next class period. Weigh the dried product and calculate the percent yield (eqs 12 and 13).

$$V_2O_5 + 2H_2SO_4 \rightarrow 2(VOSO_4)^{2+} + 3H_2O + CH_3CHO \qquad (12)$$

$$(VOSO_4)^{2+} + 2CH_3COCH_2COCH_3 \rightarrow H_2SO_4 + VO(CH_3COCHCOCH_3)_2 \qquad (13)$$

Determine the melting or decomposition point

$Cr(CH_3COCH_2COH_3)_3$

Weigh directly into 100-mL Erlenmeyer flask 0.7 g chromium(III) chloride hexahydrate ($CrCl_3•6H_2O$) and dissolve it in 25 mL distilled water. Weigh out 3 or 4 portions to the deep green chromium solution, stirring well after each addition. Then add 1.75 mL of acetylacetone drop-wise, using a pipette. Clamp the flask in a boiling water bath and heat the mixture while stirring for approximately one hour. The solution should initially be very dark, almost black in appearance, but as the reaction proceeds, deep maroon plate-like crystals form a crust on the surface of the reaction mixture.

Cool the reaction mixture and vacuum-filter the product. **Do not** wash the product with water. Dry it in air. Weigh the dried product and calculate the percent yield (eqs 14 and 15).

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2 \qquad (14)$$

$$Cr^{3+} + 3CH_3COCH_2COH_3 + 3NH_3 \rightarrow 3NH_4^+ + Cr(CH_3COCH_2COH_3)_3 \qquad (15)$$

The urea undergoes slow hydrolysis, liberating ammonia, which then controls the pH of the reaction mixture.

Determine the melting or decomposition point.

$\boldsymbol{Mn(CH_3COCH_2COH_3)_3}$

Dissolve 0.52 g of manganese(II) chloride tetrahydrate ($MnCl_2 \bullet 4H_2O$) and 1.4 g of sodium acetate in 20 mL of distilled water in a 100 mL beaker. Stir the mixture using a stir bar and magnetic stirring hot plate. When dissolution is complete, add 2 mL of acetylacetone. Prepare a solution of 0.11 g of potassium permanganate in 6 mL of distilled water. Stir well and thoroughly as $KMnO_4$ solution dropwise over a 10-15 minute period to the reaction mixture. Stir for an additional 10 minutes and then add dropwise a solution of 1.4 g of sodium acetate in 5 mL of distilled water. While continuing to stir, heat the resulting dark mixture in a water bath to between 60-70 °C for 15 minutes. Monitor the temperature carefully using a thermometer, then cool to room temperature.

Filter off the very dark, almost black product and wash it with ~10 mL of cold distilled water. Vacuum dry for 15 minutes and dry it in a vacuum desiccator over anhydrous $CaCl_2$, until the next class period. Weigh the dry product and record the yield. Calculate the percent yield.

Note The stoichiometry of this preparation is complicated. First the Mn(II) complex is formed according to eq 16. The manganese(II) then reacts with the manganese(VII) of the permanganate to give manganese(III) eq 17 and, in outline, the overall stoichiometry is in eq 18. In this preparation, the potassium permanganate is the limiting component on which the percent yield should be based, *i.e.* 1 mol $KMnO_4$ give 5 mol product.

$$Mn^{2+} + 2CH_3COCH_2COH_3 \rightarrow 2H^+ + Mn(CH_3COCH_2COH_3)_2 \qquad (16)$$

$$Mn(VII) + 4Mn(II) \rightarrow 5Mn(III) \qquad (17)$$

$$5Mn^{2+} + MnO_4^- + 15CH_3COCH_2COH_3 \; 4H_2O + 7H^+ + 5Mn(CH_3COCH_2COH_3)_3 \qquad (18)$$

The purpose of the sodium acetate is to neutralize the acid released, since acetic acid is a weak acid eq 19.

$$7H^+ + 7CH_3COO^- \rightarrow 7CH_3COOH \qquad (19)$$

Determine the melting or decomposition point.

$\boldsymbol{Fe(CH_3COCHCOCH_3)_3}$

Dissolve 0.7 g of finely-ground iron(III) chloride hexahydrate ($FeCl_3 \bullet 6H_2O$) in 5 mL of distilled water in a 50-mL beaker. Add, over a period of 15 minutes, add a solution of 0.8 mL of acetylacetone in 5 mL of methanol. Stir throughout the addition using a large magnetic stirrer. Add to the resulting blood red mixture, over a period of 5 minutes, a solution of 1.1 g of sodium acetate in 3 mL of distilled water, maintaining the stirring throughout. At this point, a red crystalline solid should precipitate. Heat the whole mixture rapidly to about 80 °C in a hot water bath. Monitor the temperature carefully with a thermometer and maintain this temperature for 15 minutes while rapidly stirring. Cool to room temperature with a water bath and then cool further in an ice bath. Vacuum-filter the product and wash with 10 mL of cold distilled water. Vacuum dry for 15 minutes. Then dry in a vacuum desiccator over anhydrous

$CaCl_2$, until the next class period. Weigh the dry product and calculate the percent yield (eq 20).

$$Fe3 + + CH3COCH2COCH3 \rightarrow 3H + + Fe(CH_3COCHCOCH_3)_3 \tag{20}$$

The sodium acetate is added to neutralize the acid released: acetic acid is a *weak* acid (eq 21).

$$3H^+ + 3CH_3COO^- \rightarrow 3CH_3COOH \tag{21}$$

Determine the melting or decomposition point.

$Co(CH_3COCHCOCH_3)_2$

Weigh into a 30 mL beaker 0.38 g of cobalt(II) carbonate and add 3 mL of acetylacetone. Heat the mixture to about 90 °C using a hot water bath with continuous stirring. Monitor the temperature carefully with a thermometer. While maintaining the temperature around 90 °C, add drop-wise 4.5 mL of a 10% hydrogen peroxide solution using a dropping pipette. Cover the flask with a watch glass between H_2O_2 additions. The whole addition of the H_2O_2 solution should occur over about 15 minutes or when effervescence ceases. Stirring should be maintained throughout the addition and then for a further 15 minutes. Cool in an ice-water bath for 30 minutes. Vacuum-filter the dark green product. Wash with ~5-10 mL of cold ethanol. Vacuum dry for 15 minutes and then dry in an oven at 110 °C for 30 minutes. Weigh the dry product and record the percent yield (Eqns. 22, 23 and 24).

In this preparation, the Co(II) complex is formed first according to eq 22. This Co(II) complex is then oxidized by the hydrogen peroxide (eq 23) and the overall stoichiometry may be written as in eq 24.

$$CoCO_3 + 2CH_3COCH_2COCH_3 \rightarrow CO_2 + H_2O + Co(CH_3COCHCOCH_3)_2 \tag{22}$$

$$2Co^{2+} + H_2O_2 \rightarrow 2Co^{3+} + 2OH^- \tag{23}$$

$$2CoCO_3 + 6CH_3COCH_2COCH_3 + H_2O_2 \rightarrow 2Co(CH_3COCHCOCH_3)_3 + 2CO_2 + 4H_2O \tag{24}$$

Determine the melting or decomposition point.

Cu^{2+} Complex

To a solution of 0.6 g copper(II) chloride dihydrate ($CuCl_2 \bullet 2H_2O$) in 4 mL of distilled water in a 50 mL beaker, add dropwise over a period of 20 minutes a solution of 0.75 mL of acetylacetone in 3 mL of methanol, while maintaining constant stirring. Add to the resulting mixture 1.0 g of sodium acetate in 3 mL of distilled water over a period of 5 minutes. Heat the mixture to *ca.* 80 °C in a hot water bath for 15 minutes, still maintaining rapid stirring. Monitor the temperature carefully with a thermometer. Cool to room temperature and then place in an ice water bath. Filter off the blue-gray product and wash with ~8 mL of cold distilled water and vacuum dry for 15 minutes before drying in an oven at 110 °C for 30 minutes. Weigh the dry product and record the percent yield (eq 25).

$$Cu^{2+} + 2CH_3COCH_2COCH_3 \rightarrow 2H^+ + Cu(CH_3COCHCOCH_3)_2 \qquad (25)$$

The sodium acetate is added to neutralize the H^+ liberated: acetic acid is a *weak* acid (eq 26).

$$H^+ \; CH_3COO^- \rightarrow CH_3COOH \qquad (26)$$

Determine the melting or decomposition point.

Unknown Sample Determination

Each student will be given an unknown sample. Using an Evans-Johnson balance students will determine the magnetic susceptibility. From this the number of unpaired electrons for each sample can be solved.

In your report, address the following points:

Acac Complex

1. Determine how many unpaired electrons for your assigned acac complex. Show all calculations!
2. Determine the oxidation state and d-electron count.
3. Determine the electronic structure of your assigned acac complex.
4. Using Chemdraw, show your assigned acac complex in the proper geometry.
5. Assign your IR spectra, determine melting point.
6. Provide literature references/data that support your assigned acac complex. (i.e. literature IR peaks are: X,Y,Z. Observed are: X', Y', Z')

Unknown Complex

1. Determine how many unpaired electrons for your unknown has. **Show all calculations**!

2. Determine the oxidation state, d-electron count, coordination number and geometry.
3. Deduce the proper energy level diagram. Explain your reasoning.
4. Determine the electronic structure of the unknown compound. Is the compound high spin or low spin?

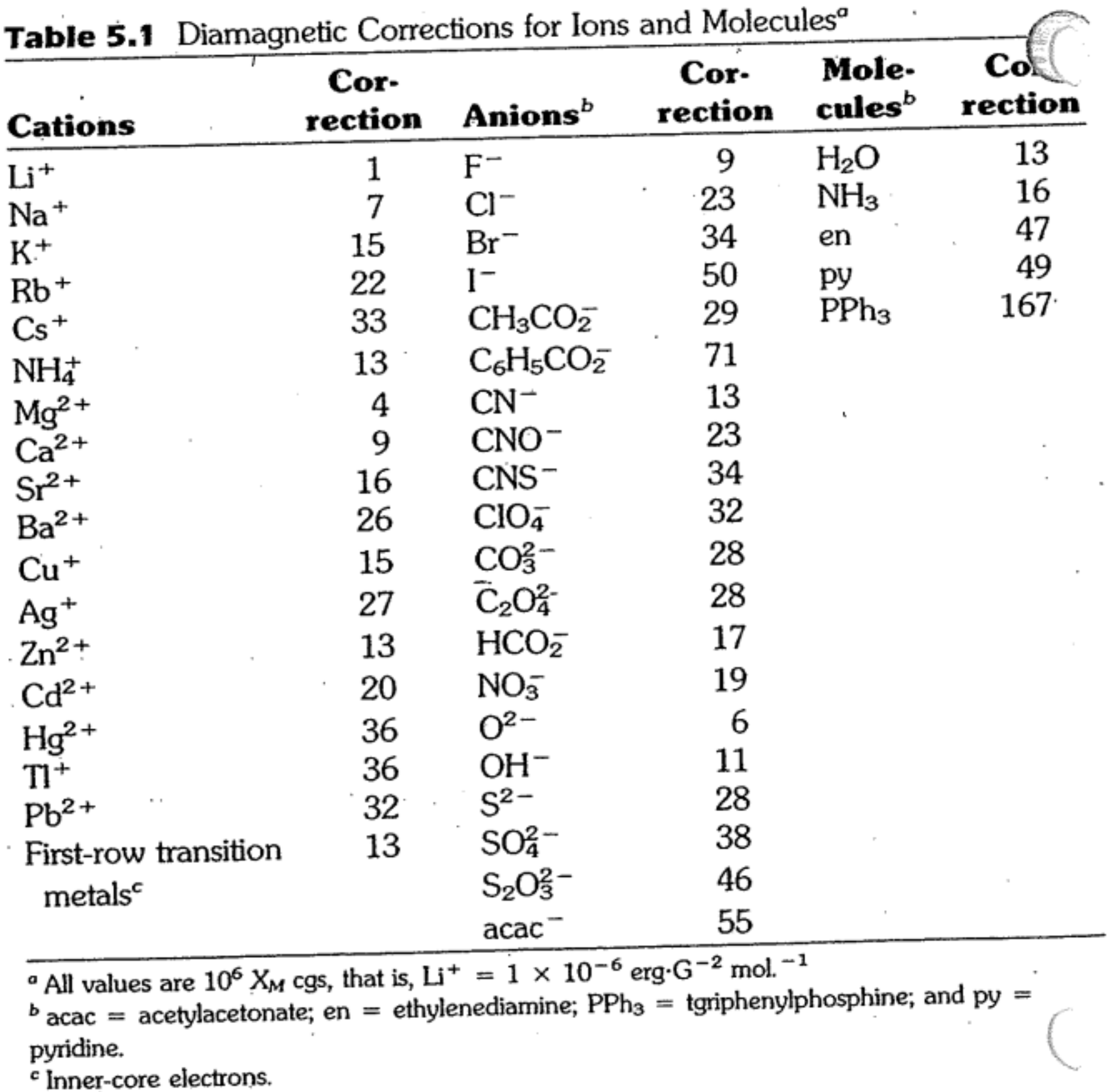

Table 5.1 Diamagnetic Corrections for Ions and Molecules[a]

Cations	Correction	Anions[b]	Correction	Molecules[b]	Co[illegible]rection
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		
First-row transition metals[c]	13	SO_4^{2-}	38		
		$S_2O_3^{2-}$	46		
		$acac^-$	55		

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[a] All values are $10^6 X_M$ cgs, that is, $Li^+ = 1 \times 10^{-6}$ erg·G^{-2} mol.$^{-1}$

[b] acac = acetylacetonate; en = ethylenediamine; PPh_3 = tgriphenylphosphine; and py = pyridine.

[c] Inner-core electrons.