Abstract

The magnetic properties of inorganic materials compounded with transition metals such as manganese, iron, copper, and cobalt have been the subject of experimental study this summer. Determining the magnetic susceptibility as a function of temperature and discovering whether these samples are liquid crystals have heightened interest on how these materials behave at temperatures greater than or equal to 2 K. The aim of the present work is to investigate the magnetic spin interactions in the specimen, thereby determining whether they experience long-range ordering by measuring the magnetism as a function of temperature and magnetic field.

Introduction

An electron in a magnetic field with an electron orbital may be characterized by two parameters, a spin value and a g value. The spin value denotes the direction of the electron spin and describes the angular momentum of an electron. The g value describes the combination of the total momentum, the angular momentum, and the orbital momentum and its effect on the net magnetic moment [1]. Three spin dimensions for the effective magnetic moment: the Ising, the XY or planar, and the Heisenberg. The Ising dimension denotes that an electron can only point in one direction, up or down, whereas the XY dimension indicates that an electron’s movement is confined to the XY plane. The Heisenberg dimension signifies that an electron can move in three-dimensional coordinates. The sign of the spin interaction strength J determines whether the material is ferromagnetic or antiferromagnetic [1].

Liquid crystals are a phase matter whose order is intermediate between that of a liquid and that of a crystal. A liquid crystal is fluid-like but is anisotropic in its optical and electro-
magnetic characteristics like a solid [2]. In the crystalline solid state there exists a rigid arrangement of molecules that stay in a fixed position and orientation with a small amount of variation from molecular vibration. To maintain this arrangement, large forces hold the molecules in place, and, therefore, a solid is difficult to deform. In the liquid phase, the molecules have no fixed position or orientation and are free to move in a random fashion; the liquid state has less order than the solid state. The random motions of the molecules mean that the intermolecular attractive forces that kept a solid together are now only strong enough to keep the liquid molecules fairly close together. A liquid can therefore easily be deformed. The differences between the states can be attributed to the temperature of the substance [3]. Temperature is a measure of the randomness of the molecules, and therefore less order exists at higher temperatures. When the liquid crystal is formed from the isotropic state, some amount of the positional or orientational order is gained. It is this order that accounts for the anisotropies of the substance. Some examples of liquid crystals are the LCD displays on the faces of watches and calculators [4]. The purpose of this work, is to investigate the magnetic properties of the Mn(bipyridine)Cl$_2$, Mn(bipyridine)Br$_2$, and their liquid crystal derivatives.

**Materials and Crystal Structures**

The samples of Manganese (Mn) provided by Williams College consist of two parent materials and four derivatives of the parent. The crystal structure of the parent specimen is shown in Fig. 1, where M is the transition metal, Mn, X is the Bromine (Br) or Chlorine (Cl), and the complex attached by Nitrogen (N) is Bipyridine (bipy) [5].
The derivatives are similar to the parent in crystal structure except it has a Carbon-14 (C-14) polymer attached as seen in Fig. 2., where M is the metal Mn, 5-5’ is the position of the polymer hanging from the parent, and X is the Br or Cl [5].

These samples came prepared in powder form for testing. Details of the molecular weight and appearance were also provided along with nicknames for each sample with indication of the parent materials as seen in Table I [5].
TABLE I: Sample names, labels, molecular weights, and appearances.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>LABEL</th>
<th>MOLECULAR WEIGHT</th>
<th>APPEARANCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(bipy)Br₂</td>
<td>EAM1-16 (Parent)</td>
<td>371.06 g/mol</td>
<td>yellow –green powder</td>
</tr>
<tr>
<td>Mn(4-4’-C₁₄ bipy)Br₂</td>
<td>EAM1-24</td>
<td>1823.13 g/mol</td>
<td>pale gold powder</td>
</tr>
<tr>
<td>Mn(5-5’-C₁₄ bipy)Br₂</td>
<td>EAM1-26</td>
<td>1823.13 g/mol</td>
<td>beige powder</td>
</tr>
<tr>
<td>Mn(bipy)Cl₂</td>
<td>STS1-8 (Parent)</td>
<td>282.154 g/mol</td>
<td>beige powder</td>
</tr>
<tr>
<td>Mn(4-4’-C₁₄ bipy)Cl₂</td>
<td>STS1-14</td>
<td>1734.22 g/mol</td>
<td>beige powder</td>
</tr>
<tr>
<td>Mn(5-5’-C₁₄ bipy)Cl₂</td>
<td>STS1-15</td>
<td>1734.22 g/mol</td>
<td>beige powder</td>
</tr>
</tbody>
</table>

Experimental Measurements

All materials were measured using a device known as a Superconducting Quantum Interference Device (SQUID). This measurement system is a complex analytical apparatus made specifically to study the magnetic properties of small experimental samples over a broad range of temperatures starting at 2 K and magnetic fields from 0 to 7 T. Automatic control and data collection are provided by a computer and two independent subsystem controllers. Within the dewar, a cryogenic probe integrates a superconducting magnet with a SQUID detection system.
and a high performance temperature control system. The SQUID provides prompt measurements over a temperature range of 2 to 300 K, and has an inside coil of 3 cm, a sensing loop, a superconducting transformer, a SQUID sensor, and control electronics. The coils are designed to be insensitive to any changes of the uniform field from the superconducting magnet to a precision of approximately 0.1%, making the SQUID detector relatively insensitive to drifts in the magnet, even following very large field changes [6].

**Procedure**

A small gelcap and plastic straw were used as the sample holder during the measurements. The samples were weighed and packed in the gelcap, which was then placed inside the straw so that measurements could be taken. Magnetizations versus temperature measurements were taken from 2 to 300 K. The sample was then zero-field cooled to 2 K before a measuring field of 0.01 T (100 G) was applied. Data were then recorded while the sample was warmed from the lowest temperature. The sample was then cooled again to 2 K, but in the presence of a 0.01 T field, and additional field-cooled (FC) data were acquired. Any difference between the FC and ZFC magnetizations is must arise from long-range ordering. The specimen was then ZFC to 5 K where a magnetic field was then applied between 0-7 T and the temperature was fixed at 5 K. The diamagnetic contribution of each sample was estimated from Pascal constants [7].
Results and Discussion

The salient features of the results of the magnetic susceptibility studies are presented in Fig. 3, which indicates that all three Mn(Br₂) specimens are paramagnetic in nature between 2 and 300K. Fitting the parent data to the Curie-Weiss Law

\[ \chi = \frac{C}{T - \theta} \]  \hspace{1cm} (1)

where \( \chi \) is the magnetic susceptibility, \( C \) is the Curie constant, \( T \) is the absolute temperature, and \( \theta \) is the Weiss temperature in units of temperature suggests that there are no magnetic spin interactions in the parent material [8]. Fits were also acquired for the derivatives and are typical to the fit in the parent material; therefore, these fits were not shown. Parameters were extracted indicating the g value, \( \theta \), spin, mass of material, and the mass of the gelcap for each sample as shown in Table II.
The values presented are resulting values after the gelcap background and the core diamagnetism have been subtracted. The gelcap background and core diamagnetism have a minuscule effect on the results. It has been proven that the derivatives possess a liquid crystal nature at room temperature and above, whereas the parent material possesses no signs of the liquid crystal state at any temperature [9]. The Curie constant can be calculated by Eq. (2) [8].

\[
C = N g^2 \mu_B^2 S(S+1)/3k_B
\]  

The graph of \(\chi_T\) vs \(T\) gives visual insight to what the Curie constant is at high temperatures, and whether long-range ordering is starting to set in. Possibilities of anti-ferromagnetic ordering and the tendency of different Curie constants can be seen in Fig. 4.
FIG. 4: Magnetic data for the three Mn(Br₂) substances, presented as molar paramagnetic susceptibility times temperature versus temperature.
As has been similarly observed in the Mn(Br$_2$) specimen, paramagnetic behavior is also present in Mn(Cl$_2$) sample as shown in Fig. 5. Some indication of magnetic spin interaction is seen from temperatures 100K and below because these three samples do not fit the Curie-Weiss Law at these temperatures. Parameters were extracted indicating the $g$ vale, spin value, $\theta$, material mass, and gelcap mass as shown in Table III.
The values presented are resulting values after the gelcap background and the core diamagnetism have been subtracted. The gelcap background and core diamagnetism have a minuscule effect on the results as seen in the Mn(Cl₂). Similarly, the derivatives possess a liquid crystal nature at room temperature and above, whereas the parent material possesses no signs of the liquid crystal state at any temperature [9]. The Curie constant can again be calculated by Eq. (2) [8]. For this sample, C was calculated to be 4.3 emu K / mol. \( \chi_T \) vs T gives a visual approximation of the Curie constant and how it remains a constant at high temperatures as seen in Fig.6. C is approximately equal to 4 emu K / mol at high temperatures also seen in Fig. 6.
FIG. 6: Magnetic data for the three Mn(Cl₂) substances, presented paramagnetic susceptibility times temperature versus temperature.

FIG. 7: Magnetization versus magnetic field.

As the applied field increases the magnetic moment increases as shown in Fig. 7. This M vs B plot is typical of all Mn samples tested, therefore those graphs are not shown. A Brillouin fit was done.
to determine the g-value of the materials. The spin value, S, was fixed at 5/2 and the temperature was fixed at 5 K. The experimental g–value is 2 with an error of ±0.02.

**Conclusion**

These results are typical and expected of Mn$^{2+}$ because the spin value is usually 5/2 which produces a strong magnetic signal even at temperatures greater than or equal to 2 K. The Mn produces standard paramagnetic behavior with some possibilities of magnetic spin interactions and long range ordering. All samples proved to be antiferromagnetic with the exception of the Mn(bipy)Cl$_2$. This material proved to be ferromagnetic, a result that is consistent in the literature (10). More accurate results of the low temperature behavior of these samples can be obtained by testing a sample of the C-14 polymer alone between 2 and 300 K.

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References


