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Magnetic and Thermodynamic Studies on Spin 1 Compounds

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MAGNETIC AND THERMODYNAMIC STUDIES ON SPIN 1 COMPOUNDS

By

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ABSTRACT

This dissertation presents EPR spectroscopic, \( dc \) magnetic susceptibility, and thermomagnetic studies of three spin \( S = 1 \) systems. This work is primarily focused on the complexes \([(\text{CH}_3\text{CN})_5\text{V}(\text{CH}_3\text{CN})_5][\text{BF}_4]_4\), \( \text{Cr}(\text{C}_4\text{H}_{13}\text{N}_3)(\text{O}_2)_2\cdot\text{H}_2\text{O} \) and \( \text{Cr}(\text{NH}_3)_3(\text{O}_2)_2 \). Chapter 2 discusses the experimental techniques used in this work.

Chapter 3 details the powder and single crystal magnetic susceptibility, magnetization and high field/frequency EPR characterization of \([(\text{CH}_3\text{CN})_5\text{V}(\text{CH}_3\text{CN})_5][\text{BF}_4]_4 \) complex. Analysis of the magnetic susceptibility and high frequency EPR data in the realm of Heisenberg exchange interactions and quantum mechanical spin interactions, reveal that the ferromagnetic spin state \( S_T = 2 \) is the ground state. The systematic study of this dinuclear \( \text{V}^{3+} \) complex provides a model system for understanding molecular magnetism.

Chapter 4 presents magnetic susceptibility and heat capacity experiments as a function of temperature over 1.8-300 K and magnetic field 0-9 T on the 3-dimensional antiferromagnet \( \text{Cr}(\text{NH}_3)_3(\text{O}_2)_2 \). The compound undergoes an antiferromagnetic phase transition at 8.46 K. The analysis of magnetic field vs transition temperature showed that the compound shows standard antiferromagnetic behavior.

The ligand is shown to play a key role in the ordering processes of such systems. Replacing \( \text{NH}_3 \) by \( \text{C}_4\text{H}_{13}\text{N}_3 \) gives the 2-d compound \( \text{Cr}(\text{C}_4\text{H}_{13}\text{N}_3)(\text{O}_2)_2\cdot\text{H}_2\text{O} \). Chapter 5 presents detailed study of magnetic susceptibility, torque magnetometry, heat capacity and magnetocaloric effect measurements on \( \text{Cr}(\text{C}_4\text{H}_{13}\text{N}_3)(\text{O}_2)_2\cdot\text{H}_2\text{O} \). Crystal structure analysis of \( \text{Cr}(\text{dien}) \) indicated the availability of low dimensional spin exchange pathways. Magnetic susceptibility and zero field heat capacity measurements showed that \( \text{Cr}(\text{dien}) \) undergoes an antiferromagnetic ordering transition at \( T_N = 2.55 \) K. The specific heat and magnetocaloric effect measurements have been performed for magnetic fields from 0-18 T and from temperatures of 0.2 K to 3 K to define previously undetermined phase boundary in the field-temperature phase space. Analysis of the magnetocaloric effect data revealed the compound undergoes a quantum phase transition at a zero temperature magnetic field value of 12.3 T. Therefore the
results presented here should provide a significant contribution to the understanding of quantum phase transitions in Cr(IV) compounds.
CHAPTER 1

INTRODUCTION AND OUTLINE

1.1 Introduction

The goal of the studies described in this dissertation was to obtain systematic information on the magnetic behavior of three new magnetic compounds, one of trivalent vanadium, V(III), and two of tetravalent chromium, Cr(IV), all containing two unpaired electrons, i.e., with a total spin $S = 1$. These compounds were selected for several reasons. First, compounds with oxidation states V(III) and Cr(IV) are rather rare, they are thus of interest from the viewpoint of discovering new magnetic materials. Second, the V(III) compound studied here, $[(\text{CH}_3\text{CN})_5\text{V-O-V(CH}_3\text{CN})_5][\text{BF}_4]_4$ (Figure 1.1) as reported recently [1], was considered to be a possible model system for V-O-V based single molecule magnets (SMMs), such as V-15 [2]. At the time of this undertaking, SMMs were thought of as highly promising compounds for information storage and related technology at the molecular dimensions. We recall that a SMM is a material that can display a magnetic hysteresis loop in principle at the single molecule level [3-5], as compared to the orders of magnitude larger number of atomic or molecular units needed in magnetic systems being used in current memory devices. Third, the magnetic lattices of $[(\text{CH}_3\text{CN})_5\text{V-O-V(CH}_3\text{CN})_5][\text{BF}_4]_4$, (in short V-O-V), as well as of the Cr(IV) compounds studied, Cr(C$_4$H$_{13}$N$_3$(O$_2$)$_2$H$_2$O and Cr(NH$_3$)$_3$(O$_2$)$_2$ complexes were thought to be of low-dimensional [1,6]. Low-dimensional materials are of current research interest as discussed next.
Figure 1.1: ORTEP view of the \[\{(\text{CH}_3\text{CN})_5\text{V-O-V(CH}_3\text{CN})_5\}_{4}^{4+}\] ion in crystals of \[\{(\text{CH}_3\text{CN})_5\text{V-O-V(CH}_3\text{CN})_5\}_{4}[[\text{BF}_4]_{4}.2\text{CH}_3\text{CN}\ [1].

In this dissertation, the term “magnetic dimensionality” is utilized in reference to the number of directions along which the dominant spin-correlations occur within a lattice. These spin correlations can occur along linear chains (1-d), layers (2-d) or between layers (3-d). Figure 1.2 illustrates such lattices [7].

Low-dimensional compounds are of high current interest since they can exhibit both classical and quantum magnetic behavior: they usually show classical magnetic properties at high temperatures but strong quantum correlations at liquid helium (4 K) and lower temperatures [8-17]. In particular, such compounds are thought to be good candidates for studying new phenomena such as a quantum phase transition (QPT) [18]. A QPT is defined as a phase transition that takes place at absolute zero of temperature \((T = 0)\) as we vary a physical parameter such as magnetic field \((H)\) or external pressure \((P)\). The point at which the quantum phase transition happens is called quantum critical point (QCP). At QCP – a zero temperature singularity in which a line of continuous phase transition terminates – quantum fluctuations diverge in space and time, leading to exotic phenomena that can be observed at non-zero temperatures. We have
indeed obtained fairly definitive evidence for a QPT in the Cr(C₄H₁₃N₃)(O₂)₂.H₂O lattice, as described in Chapter 5.

Figure 1.2: Magnetic lattices studied in this dissertation. The spheres represent magnetic ions and the solid lines denote exchange interactions \( (J) \) between them. (a) 1-d chains (b) 2-d planes such as those of Cr(C₄H₁₃N₃)(O₂)₂.H₂O. (c) System with 3-d spin correlations due to interlayer interactions as with Cr(NH₃)₃(O₂)₂ [7].

As mentioned above, our studies started with the investigation of the V-O-V compound, that was just synthesized by the Thomas Vaid group at Washington University. The simplest example of a vanadium-oxo cluster is a linear arrangement of antiferromagnetically interacting \( S = 1 \) centers. Initial solution phase magnetic susceptibility studies by the Vaid group indicated that the compound was strongly magnetic, perhaps because the two V(III) ions in the V-O-V chain were
ferromagnetically coupled. We were then contacted by Dr. Vaid for possible collaboration, with the idea that our group would carry out detailed magnetic characterization of the material in the solid phase, in both single crystalline and powder forms. X-ray structural analysis showed that the V(III)-O-V(III) units are linear chains of $S = 1$ systems, as can be seen from Figure 1.1. Further literature search showed that this bonding of V(III) is rather rare. We surmised that it could possibly serve as a model system for understanding the more complex magnetic lattices based on the V-O-V networks, such as the single molecule magnet V-15 [2]. A detailed study was thus undertaken, using magnetic susceptibility and high-field (101.6 GHz) EPR spectroscopy.

As discussed in detail in Chapter 3, we carried out ac and dc magnetic susceptibility measurements down to 1.8 K on the V-O-V complex. We established that the two V(III) ions are strongly coupled ferromagnetically with an exchange coupling of $\sim 70$ K, but no ferromagnetic or antiferromagnetic transition was seen. EPR measurements at 101.6 GHz showed that the compound does indeed have a ground state spin $S = 2$, well separated from the excited states of $S = 1$ and $S = 0$, fully supporting the magnetic susceptibility data. Some of the results were published recently [1], and full details are provided in Chapter 3.

The above system is a good example of a $S = 1$, $S = 1$ dimer, but lacked long-range correlations. We thus undertook a detailed study of two related $S = 1$ complexes, formed by bonding Cr(IV) with diperoxoamine ligands, which had been shown to be magnetically 2-dimensional or 3-dimensional, depending on the ligand [6]. Another reason for studying these complexes was that Cr(IV)-diperoxoamines are the only stable compounds of Cr in the tetravalent oxidation state [19]. For simplicity, we begin by discussing the complex with the lower dimensionality.

Specifically, the 2-dimensional case is Cr(C$_4$H$_{13}$N$_3$)(O$_2$)$_2$.H$_2$O. A 2-d lattice is an extension of the 1-d chains except that bisecting linear chains create layered systems as shown in Figure 1.2. This is appropriately deemed a quadratic layer lattice since each ion interacts with four nearest neighbors. Earlier reported X-ray and magnetic studies suggested that the $S = 1$ system, Cr(C$_4$H$_{13}$N$_3$)(O$_2$)$_2$.H$_2$O, can be described by this model [6]. The molecule is shown in Figure 1.3. Evidence for planar behavior is observed in the crystal structure. As Figure 1.4 shows, the antiferromagnetic interactions are
facilitated by Cr-O—O-Cr pathways in a 2-d array. The $J/k_B$ was estimated to be $\approx -2.8$ K within the layer [6]. Our study of the Cr(C$_4$H$_{13}$N$_3$)(O$_2$)$_2$.H$_2$O compound represents the first magnetic and thermodynamic studies of a 2-d Cr(IV) lattice studied at high fields and sub-helium temperatures.

Replacing the C$_4$H$_{13}$N$_3$ (diethylenetriamine) ligand by (NH$_3$)$_3$ results in the preparation of the 3-d antiferromagnet Cr(NH$_3$)$_3$(O$_2$)$_2$, implying significant magnetic interactions along all three Cartesian directions [6]. The molecular structure of Cr(NH$_3$)$_3$(O$_2$)$_2$ is shown in Figure 1.5. Figure 1.6 shows the crystalline unit cell of Cr(NH$_3$)$_3$(O$_2$)$_2$. 
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Figure 1.6: Projection down the 001 axis of the $\text{Cr(NH}_3\text{)(O}_2\text{)}_2$ crystal. The nearest neighbors are separated by 5-6 Å in each direction providing a 3-d antiferromagnet [6].
Previous work on the Cr(IV)-diperoxoamines has typically been limited to kinetic phenomena to help deduce Cr(IV)’s biological activity [20-23]. Little is known, however, about the magnetic or electronic structure of these or any other discrete Cr(IV) lattices. Two short reports on Cr(en)(O$_2$)$_2$(H$_2$O)$_2$.H$_2$O (en = ethylenediamine) [6] and Cr(NH$_3$)$_3$(O$_2$)$_2$ [24] suggest that these are canted and 3-d antiferromagnets, respectively. No g-values or exchange constants were provided, however. We therefore wished to fill the void in Cr(IV) behavior with a detailed study on Cr(C$_4$H$_{13}$N$_3$)(O$_2$)$_2$.H$_2$O at low temperature (in the milliKelvin range) and high magnetic fields.

Earlier reported magnetic susceptibility and heat capacity measurements on Cr(NH$_3$)$_3$(O$_2$)$_2$ showed it to be a classical three-dimensional antiferromagnet with sharp $\lambda$-type transitions at 8.80 and 8.46 K, respectively [6]. To determine the effect of magnetic field on this phase transition we determined the magnetic phase diagram of Cr(NH$_3$)$_3$(O$_2$)$_2$ in magnetic fields from 0 to 9 T and at temperatures from 1.8 to 12 K by means of specific heat measurements. Measurements on the shift in the position, $T_N(H)$, of the heat capacity peak under the influence of an externally applied magnetic field, to lower and lower temperature, agree with the fact that Cr(NH$_3$)$_3$(O$_2$)$_2$ shows standard antiferromagnetic behavior, as discussed in chapter 4. From the $(H, T)$ diagram the value of the critical field is found to be approximately 21 ± 1 T at $T = 0$ K. Systematic studies of this compound around 21 T and low temperatures would be of high interest in comparison with the results on Cr(C$_4$H$_{13}$N$_3$)(O$_2$)$_2$.H$_2$O which is discussed in chapter V.

Magnetic susceptibility measurements on Cr(C$_4$H$_{13}$N$_3$)(O$_2$)$_2$.H$_2$O showed that the spins order antiferromagnetically at $T_N = 2.55$ K in zero magnetic field [6]. We planned to carry out a systematic study of the effect of magnetic field on this phase transition. We therefore measured the magnetic phase diagram of Cr(C$_4$H$_{13}$N$_3$)(O$_2$)$_2$.H$_2$O in magnetic fields from 0 to 18 T and at temperatures from 0.2 K to 3 K by means of torque magnetometry, specific heat and magnetocaloric effect measurements. We observed that the application of magnetic field depresses the ordering temperature, pushing it to zero at about 12.3 T. The analysis of magnetocaloric effect data at low temperatures and high magnetic fields showed that this quasi-two-dimensional quantum magnet Cr(C$_4$H$_{13}$N$_3$)(O$_2$)$_2$.H$_2$O has a magnetic field tuned QCP at the field $H_c = 12.3$ T, where a highly polarized antiferromagnetic phase gives way to a field-induced
ferromagnetic phase. A detailed analysis was carried out to fit the measured phase transition temperature to $H - H_c = \text{constant} \cdot T^\alpha$. The value of $\alpha$ was determined as $2.01 \pm 0.02$. This is the first report on the detection of a QPT in a Cr(IV) material.

Another important study performed on this quantum antiferromagnet, near the QCP presents the calorimetric evidence that nuclear spins frozen in a high temperature nonequilibrium state by temperature quenching are annealed by quantum fluctuations near the QCP. This phenomena, with readily detectable heat release from the nuclear spins as they are annealed, serves as an excellent marker of quantum critical region around the QCP. Details are provided in chapter V.

1.2 Organization

This dissertation is organized as follows. Chapter 2 summarizes the experimental techniques used. Chapter 3 discusses the structural details, spectroscopic results, and thermomagnetic studies on the oxo-vanadium complex VOV. Chapter 4 contains the details of thermomagnetic studies on Cr(NH$_3$)$_3$(O$_2$)$_2$. Chapter 5 discusses detailed studies on the 2-d lattice Cr(C$_4$H$_{13}$N$_3$)(O$_2$)$_2$H$_2$O with the view of examining the details of a quantum phase transition at low temperatures and high magnetic field. Finally, chapter 6 summarizes the major results and conclusions of this undertaking.
CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1 Magnetic Measurements

DC Magnetic susceptibility ($\chi$) measurements were made on powder and aligned single crystals of \[(\text{CH}_3\text{CN})_5\text{VOV(CHR}_3\text{CN})_5][\text{BF}_4]_4\] using a Quantum Design SQUID magnetometer in the temperature range of 1.8 – 300 K at magnetic field of 1,000 Gauss (G) (10,000 G = 1 Tesla (T)).

2.2 High Frequency EPR Measurements

High frequency EPR measurements (101.6 GHz) were conducted on the powder and single crystal sample of \[(\text{CH}_3\text{CN})_5\text{VOV(CHR}_3\text{CN})_5][\text{BF}_4]_4\] in the Electron Magnetic Resonance Division of the National High Magnetic Field Laboratory on a custom-built spectrometer. The temperature was controlled with an Oxford continuous flow liquid He cryostat. The Zeeman field was applied using an Oxford Instruments Teslatron superconducting magnet sweepable between 0 and 17 T and a 92 – 97 (AB Millimeter #ESA1-95-5) gun diode provides tunable microwave energy for EPR experiments. The source is phase locked and the frequency is monitored with an EIP578B (EIP Microwave Inc.) frequency counter. Very high frequencies are achieved by fitting the microwave source with the appropriate harmonic filter (Radiometer Physics GmbH). Figure 2.1 shows a block diagram of the high frequency setup. Continuous wave radiation passes through a corrugated horn which causes the propagating \(\text{TE}_{01}\) wave to be transformed into a linearly polarized \(\text{HE}_{11}\) mode. This mode has low losses through an oversized circular corrugated waveguide which has a diameter of ~2 cm for 100 – 300 GHz. The 2m probe is constructed with two corrugated waveguides in parallel with a modulation coil at the bottom of one tube. The sample is placed within the tube here. As radiation passes through the sample, it is reflected by two 45° mirrors through the second waveguide to an InSb hot-electron Bolometer detector QF1/3BI (QMC Instruments Ltd.).
The bolometer has a wide useful detection frequency range of 50 – 1200 GHz, making it ideal for multi-frequency experiments. These systems have been described earlier [25,26].

![Block diagram of the High Frequency EPR Spectrometer at the National High Magnetic Field Laboratory. The microwave power is detected with the bolometer and “M” indicates mirrors [27].](image)

2.3 Specific Heat Measurements

Specific heat measurements between 1.8 and 10 K and 0-9 T were made using a Quantum Design Physical Properties Measurement System (QD PPMS) employing a time constant [28] method at Florida State University. The platform was calibrated by use of a copper standard [29]. The samples consisted of single crystals of \(\text{Cr(C}_4\text{H}_{13}\text{N}_3\text{)(O}_2\text{)}_2\text{H}_2\text{O}\) and multiple crystals of \(\text{Cr(NH}_3\text{)}_3\text{(O}_2\text{)}_2\). The typical sample mass was 2-3 mg. Specific heat measurements down to the temperature of 20 mK made on \(\text{Cr(C}_4\text{H}_{13}\text{N}_3\text{(O}_2\text{)}_2\text{H}_2\text{O}\) single crystal at National High Magnetic Field Laboratory, Tallahassee, FL, as described later.
Time Constant Method

Single crystals, generally, represent the purest form of a material and are necessary for the evaluation of the anisotropic properties relative to an applied magnetic field. The time constant, or thermal relaxation, method of measuring the specific heat does not require a large sample mass (1-3 mg), therefore single crystal may be easily employed [30]. The measurements herein were done with a commercial QD PPMS heat capacity option capable of specific heat measurements between 1.8 – 400 K and 0-9 T. Figure 2.2 presents a schematic of a typical sample mount. The platform is composed of alumina, the connecting wires are gold/palladium(35%), and the temperature is monitored with a cernox thermometer.

This technique, as published by Bachmann et. al. [31], and further reviewed by Stewart [27], involves heating the sample and platform a small temperature $\Delta T$ above the bath temperature $T_0$ (where $\Delta T/T_0$ was generally $\approx 2\%$), turning off the heat and observing the exponential decay. The equations of interest are [28]:

$$C = K \tau_1$$
where \( C \) is the specific heat of the sample plus platform, \( K \) is the thermal conductivity of the connecting wires, and \( \tau_1 \) is the time constant [32] of the decay such that:

\[
T = T_0 + \Delta T e^{-t/\tau_1}
\]

The software of the QD PPMS heat capacity option automatically fits the thermal pulse and decay, solving for the characteristic time constant \( \tau_1 \), and providing the user with the observed specific heat, \( C_p \). The contribution from the platform and silicon grease (addenda) are measured prior to the sample and subsequently subtracted out. The field dependence of the cernox thermometer at low temperatures was calibrated by use of a high purity vacuum annealed copper sample, whose heat capacity at 0 and 14 T over a range of \(~ 0.3-4 \) K is known [29].

2.4 Torque Magnetometry

2.4.1 Principle of Cantilever Magnetometry

The general principle behind the cantilever magnetometry is that a magnetic sample mounted on a flexible beam will respond to the application of a quasi-static magnetic field by experiencing a force and a torque which detects the flexible beam [33]. This technique was developed by Brooks et al. at MIT in the 1980s [34]. The magnitude of the force and torque is related to the magnetization of the sample by

\[
F = M \cdot \frac{dB}{dz}
\]

\[
\tau = M \times B
\]

The deflection of the flexible beam can be measured capacitively [35]. If the magnetic moment of a sample is anisotropic, the measurements of the torque are more sensitive than force measurements. The force on a sample in a field gradient of 0.1 T/cm is typically smaller than the torque. Hence, cantilever magnetometry is often called torque magnetometry. The sensitivity and resolution of cantilever magnetometers depend on the stiffness of the flexible beam material, the sensitivity of the cantilever to temperature fluctuations and mechanical vibration, the quality of the measurement instrumentation, and the magnitude of the applied field. The size of a cantilever is 5 mm long like that
used at the NHMFL for magnetometry measurements. The shape of the cantilever exhibits a diving board-like structure.

2.4.2 Design

In this section we discuss the design of capacitive cantilever magnetometer used at NHMFL [33]. A cantilever magnetometer consists of five parts: (1) the flexible beam, (2) the fixed plate, (3) the header, (4) the sensor mounting stage, (5) the grounding can. A simple drawing of a cantilever magnetometer is shown in Figure 2.3. A metal film of BeCu is used as the flexible beam. The header attaches to the sensor mounting stage. The purpose of the mounting stage is to provide a platform for placing thermometers and heaters near the sample. A hall probe can also be incorporated into the sensor mounting stage to assist in the determination of field center. The entire cantilever magnetometer is encased in a grounding can.

![Diagram of cantilever magnetometer](image)

Figure 2.3: Shown here are the basic parts of a cantilever magnetometer. The sample is attached to the flexible plate (typically with a small amount of Apiezon N grease). The thickness of the flexible plate varies depending on the magnetization of the sample. The fixed plate is made out of metal and is permanently attached to the header. Headers at the NHMFL are machined from G10 fiberglass. The fulcrum can either be a part of the flexible plate or part of the header [33].
2.4.3 Measurement Methods

Samples can be attached to the metal film cantilever with a spot of Apiezon N grease. Reason for using the Apiezon N grease is that it has a better thermal conductivity at low temperatures than other greases.

When a magnetic field is applied to the sample attached to the flexible plate, it experiences both torque and force. If the homogeneity of the magnet is good, the force term can be minimized by placing the sample in field center. This will result in a signal that is proportional to the torque on the sample.

Measurement of the capacitance of the cantilever magnetometer is made with a 1616 General Radio capacitance bridge. Any lock-in amplifier can be used to drive the bridge and detect the imbalance signal. A rule of thumb when making the measurements is to monitor the total capacitance change as the field is ramped up.

2.5 Specific Heat and Magnetocaloric Effect Measurements (18/20 T Superconducting Magnet, With Dilution Refrigerator (SCM1) at NHMFL)

2.5.1 Experimental Apparatus

Both specific heat and magnetocaloric effect measurements were performed using the relaxation calorimeter at millikelvin temperatures in high magnetic fields at the National High Magnetic Field Laboratory (NHMFL), Tallahassee, FL. We will describe these two complimentary measurement techniques in detail in the following sections.

First, we present the design of a relaxation calorimeter, used in our experiments, for a top-loading dilution refrigerator [36] on the 20 T superconducting magnet at the National High Magnetic Field Laboratory. The calorimeter works up to 3 K without disrupting a stable operation of the dilution refrigerator. The cool-down time from room temperature to the minimum temperature is just 5 hours.

Figure 2.4 shows the main components of the calorimeter that attaches to the bottom of the top-loading probe, which is directly inserted in the plastic tail of the mixing chamber. Figure 2.5 shows the physical picture of the relaxation calorimeter used in our experiment. An essential feature of the design is the 24.6 mm-diameter vacuum can that thermally isolates the calorimeter from the cold liquid helium in the mixing
chamber. The can is made of brass to protect the calorimeter from thermal radiation and eddy-current heating. A grease joint with a taper of \(7^\circ\) provides a superfluid-tight vacuum seal [37]. The can is evacuated at room temperature via a 1.3 mm-diameter CuNi tube, which runs along the length of the top-loading probe.

The vacuum feedthrough for the electrical leads consists of two rows of six gold-plated socket pins taken from a single in-line pin (SIP) socket [38] and epoxied with Stycast 2850FT [39] into individual holes drilled on the lid of the vacuum can. The original spacing of the pins of the SIP socket is maintained in the feedthrough, so that a pair of SIP sockets for the external leads and another pair for the internal leads directly plug to it from above and below, respectively.

In order to keep its time constant in the magnetic field reasonably short, the thermal reservoir is entirely made of silver, which has one of the smallest nuclear heat capacities. The reservoir consists of a 6.3 mm-thick silver block, which attaches to the lid of the vacuum can via a Vespel SP-22 [40] rod, and a split silver ring welded to the bottom of the block.

The thermal link between the silver reservoir and the cold helium outside the vacuum can is provided by twelve 79 \(\mu\text{m}\)-diameter silver leads that run from the silver block to the feedthrough. On the silver block, the end of each lead is tightly wrapped around a 0.64 mm diameter silver pin for heat sink and covered with EPO-TEK 417 silver epoxy [41].

A 220 \(\Omega\) Speer carbon resistor that has been ground to a 0.5 mm thickness is used as the reservoir thermometer. A Karma-alloy (Ni 74%, Cr 20%, Al 3%, and Fe 3%) wire of a 79 \(\mu\text{m}\) diameter and a 35 cm length is wound on the block as a heater.

The sample platform is a sapphire disk, 6.4 mm in diameter and 0.13 mm in thickness. A small slice of a 220 \(\Omega\) Speer resistor attached to the platform with EPO-TEK H31LV silver epoxy [41] is used as a thermometer. The platform heater is a thin evaporated layer of a 7% Ti-Cr alloy. The electrical leads for the thermometer and the heater are 76 \(\mu\text{m}\) diameter wire of Pt-10% Rh, which also serves as a mechanical support and a weak thermal link for the platform. Each lead is soft soldered to a heat sink.
made of a small piece of 0.1 mm-thick silver foil that has been glued with Stycast 2850FT to the ring.

Figure 2.4: Schematic cross section of the calorimeter cell [42].
Figure 2.5: Relaxation calorimeter used for the 18/20 T superconducting magnet at National High Magnetic Field laboratory (NHMFL), Tallahassee.
The crystal of Cr(dien)(O$_2$)$_2$.H$_2$O was oriented with the $b$ axis perpendicular to the flat surface. Azurite VL-10 silver paint [43] is used to coat the sample. The sample was glued to the platform with a thin layer of Wakefield 120 silicon compound [44]. Coating the sample with silver paint maximizes the thermal contact between the insulating sample and platform since the paint serves to thermally short the top and sides of the sapphire plate.

2.5.2 Experimental Methods

Using the experimental probe described in Sec 2.5.1, one may either measure the heat capacity at a given temperature and magnetic field or the magnetocaloric response as the applied field is changed [45]. The specific heat is an invaluable and unambiguous method for determining phase transitions with respect to, e.g., magnetic field and temperature. In addition to indicating possible phase transitions, the magnetocaloric effect has the additional benefit of quickly sweeping through large portions of the magnetic field-temperature phase space. This proves to be a useful guide in determining in which portion of phase space to concentrate on the more time consuming specific heat measurements. This section will devote itself to the derivation of the fundamentals of the two measurement methods. It will be divided into subsections, the first of which will be devoted to the method of relaxation time calorimetry and the second of which will concentrate on the magnetocaloric effect.

2.5.2.1 Relaxation Time Calorimetry

In the method of relaxation time calorimetry [31], the temperature of the sample is initially raised slightly above that of the block by applying a constant power $\dot{q}$ to the platform. Once a steady state has been established, the heating power is removed and, as will be shown, the sample platform temperature attains equilibrium with the block in an exponentially decaying manner with a time constant $\tau_1$ [45].

A temperature gradient is maintained between the sample platform and the block by a weak thermal contact between the two. The thermal response of the system
will be analyzed using a one dimensional heat flow model, as shown schematically in Figure 2.6a.

Figure 2.6: Thermal block diagram (a) for the case when the sample and platform are in good thermal equilibrium, (b) for the case when the sample to platform conductance is poor, and (c) for the case when both the sample conductance and the sample to platform conductance is poor [45].

Assuming that the thermal conductivity of the sample and platform is sufficiently larger than that of the weak link, the temperature of the sample plus platform remain in thermal equilibrium at temperature \( T(t) \), while that of the block is maintained at a constant temperature \( T_b \) by means of a heater. The thermal conductivity of the weak link, which depends on its temperature, varies between the two ends. With these assumptions, the heat flow equation may be written

\[
\dot{q}(t) = C(T) \frac{dT(t)}{dt} + \int_{T_b}^{T(t)} \kappa(T')dT'
\]  

(2.1)

where \( C(T) \) is the heat capacity of the sample plus platform, \( T(t) \) is the platform temperature, and \( \kappa(T) \) is the thermal conductivity of the weak link. In practice, the temperature difference, \( \Delta T(0) = T(0) - T_b \) is kept small enough so that both the weak link conductance and heat capacity are approximately constant. In this case,
\[
\int_{T_b}^{T(t)} \kappa(T')dT' = \kappa(T_{av}) \Delta T
\]

and \( C(T) = C(T_{av}) \), where \( T_{av} = \frac{1}{2} (T(0) + T_b) \). At \( t = 0 \), the platform heater is turned off, reducing Eq. (2.1) to

\[
\frac{d(\Delta T(t))}{dt} = -\frac{\kappa}{C_{|T=T_{av}}^{T_{av}}} \Delta T(t)
\]

Thus

\[
\Delta T(t) = \Delta T(0)e^{-\frac{t}{\tau_1}}
\]

where \( \Delta T(t) = T(t) - T_b \) and \( \tau_1 = C/\kappa|_{T=T_{av}} \). A typical relaxation curve for Cr(dien)(O\(_2\))\(_2\).H\(_2\)O at \( T = 2.4 \) K and \( H = 9 \) T is shown on a semi-log plot in Figure 2.7.

Figure 2.7: Typical relaxation curve showing single exponential decay. The black points are original data and the red is the result of fitting the data. \( V \) is the off balance voltage of the Wheatstone bridge, which is proportional to the temperature change in the narrow range covered in one measurement swing.
In many cases, particularly at the lowest temperatures, the thermal contact between the sample and platform becomes poor. In insulating samples, the conductance of the sample itself may become sufficiently small that a temperature gradient develops across the sample. In both cases, the temperature of the sample lags that of the platform, hence the measured platform temperature is not representative of the sample temperature. The assumptions on which the sample model shown in Figure 2.6a, leading to a single exponential decay, are not valid in either of these cases. However, in both cases, the sample heat capacity may still be derived based on a more thorough model.

The first case, in which the temperature is uniform throughout the sample but a gradient is developed across the interface between the sample and platform, is known as the lumped $\tau_2$ effect. This case may be modeled as shown in Figure 2.6b. The relaxation of the platform temperature is found to be [37]

$$\frac{\Delta T(t)}{\Delta T(0)} = a_1 e^{-\frac{t}{\tau_1}} + a_2 e^{-\frac{t}{\tau_2}}$$

(2.4)

where the four parameters have a detailed dependence on the individual heat capacities and conductances shown in Figure 2.6b. The heat capacity of the sample is then calculated from the time constant $\tau_1$ and the weight $a_1$ of the slow relaxation, which are obtained from the fit to the relaxation data, as

$$C_{sample}(T_{av}) = \kappa(T_{av}) \frac{a_1 \tau_1 \left(1 - \frac{C_{add}(T_{av})}{\kappa(T_{av}) \tau_1}\right)^2}{1 - a_1 \frac{C_{add}(T_{av})}{\kappa(T_{av}) \tau_1}}$$

(2.5)

Where $C_{add}$ is the addenda heat capacity due to the sample platform and $\kappa$ is the weak link thermal conductance.

In the case where, in addition to poor sample to platform conductance, the sample conductance is itself poor, a distributed $\tau_2$ effect occurs. When the heater is turned off at $t = 0$ a temperature gradient is produced within the sample as well as across the
sample to platform contact. The model for this situation is shown schematically in Figure 2.6c, where $\kappa_s$ is the sample conductance. In this model, the temperature profile, $T(z)$, of the sample is taken to be constant in planes parallel with the sample to platform boundary and varies only as a function of the distance, $z$, from that boundary. Though the heat flow equations may be solved analytically in terms of $C$, $\kappa_s$, and $\kappa'$, extraction of these parameters from the relaxation data is difficult [31, 46]. On the other hand, application of conservation of energy to the problem gives the heat capacity directly. The total energy which is removed from the sample plus platform must be equal to the heat which flows through the thermal link. This simple idea may be expressed as

$$C(T_{av})\Delta T(0) = \kappa \int_0^\infty \Delta T(t) dt \quad (2.6)$$

where $\kappa$ is the weak link thermal conductance. Due to the fundamental basis of this expression, it is applicable to all cases, without respect to the source of the poor conductance.

For all the circumstances considered, the conductance of the weak thermal link must be very well characterized in order to extract the heat capacity from the relaxation curve. A metallic alloy is chosen for the thermal link since the magnetic field dependence of the thermal conductance is small. This is because in an alloy the mean free path of the electrons is so foreshortened by the impurity scattering that the effect of the magnetic field becomes negligible. Calibration of the weak link thermal conductance as a function of temperature is obtained by measuring the heat capacity of some standard materials such as copper and/or platinum in addition to that of the platform alone. By using the well established heat capacities of the various materials, the sample analysis is conducted as detailed above, the only difference is that the unknown parameter is the conductance rather than the heat capacity. Another obvious method for measuring the weak link thermal conductance is to apply a steady heating power to the platform. Once a steady has been established, the heating power is related to the thermal conductance and temperature gradient between the platform and block by $\dot{q} = \kappa(T_{av})\Delta T$. When practical, the first method has been found to be more reliable. Once performed, the calibration is valid barring any physical changes to wires constituting the link.
2.5.2.2 Magnetocaloric Effect

The magnetocaloric effect refers to the response of the temperature or entropy of a magnetic system to a change in the applied magnetic field, $\Delta H$ [45]. It may either be expressed as the isothermal entropy change, $\Delta S (T_0)$, or the adiabatic temperature change, $\Delta T (S_0)$, where $T_0$ refers to the temperature in the former and $S_0$ refers to the entropy in the latter. All processes are adiabatically isobaric. The expressions for either the isothermal entropy change or the adiabatic temperature change may be derived starting with the Maxwell relation

$$\left( \frac{\partial S}{\partial H} \right)_T = \left( \frac{\partial M}{\partial T} \right)_H$$  \hspace{1cm} (2.7)

Where $S$ is the entropy, $H$ is the applied field, $M$ is the magnetization, and $T$ is the temperature. By integrating along an isotherm, one finds the isothermal entropy change as

$$\Delta S(T_0) = \int_{H_i}^{H_f} \left( \frac{\partial M}{\partial T} \right)_H dH$$  \hspace{1cm} (2.8)

where $H_i$ and $H_f$ are the initially applied fields, respectively. Thus, the magnetocaloric effect is stronger in regions of the phase diagram where the magnetization shows the largest dependence on temperature for a given magnetic field.

The total differential of the entropic equation of state $S = S(T, H)$ is

$$dS(T, H) = \left( \frac{\partial S}{\partial T} \right)_H dT + \left( \frac{\partial S}{\partial H} \right)_T dH$$  \hspace{1cm} (2.9)

If only adiabatic processes are considered, this quantity vanishes, i.e., $dS = 0$. Identifying the constant-field temperature derivative of the entropy with the constant field specific heat divided by the temperature, $(\partial S/\partial T)_H = C_H(T)/T$, and using the Maxwell relation (2.7) in conjunction with (2.9) where $dS = 0$, apparently
Thus, in an adiabatic process, the sample temperature changes in direct proportion to the change in the magnetic field. In many cases, e.g., a paramagnetic system, the magnetization is a monotonically decreasing function of temperature for a given magnetic field. In this case, since $(\partial M / \partial T)_H < 0$, the temperature rises (falls) as the magnetic field is increased (decreased). It is noteworthy to mention that this feature has been the basis of ultra-low temperature refrigeration for laboratory research for many years [47]. Hence, this effect may not only be used directly to probe the fundamental properties of materials, but also as a laboratory tool to study other physical phenomenon.

The magnitude of the magnetocaloric effect at a given temperature and for a given change in the applied field is governed by the coupling of the entropy to the external magnetic field, or equivalently the temperature dependence of the magnetization at that field. For a more complete analysis of the magnetocaloric effect, particularly in the neighborhood of first order phase transitions, see [48-50].

Thus, the magnetocaloric effect is a sensitive probe of the internal behavior of magnetic materials. Both first and second order magnetic phase transitions in the field-temperature phase space may be found and differentiated. Points at which $(\partial M / \partial T)_H = 0$ are easily identified. These points may either signify a second order phase transition or simply an extremum in the magnetization. Together with other measurements, e.g., specific heat, these unique points may be further characterized.

In the experimental arrangement described in Sec. 2.5.1, the sample is weak thermal contact to a thermal reservoir. The magnetocaloric measurement consists of measuring the sample temperature as a function of the applied magnetic field as it is swept nearly adiabatically at a constant rate. One may obtain the temperature deviation of the sample with respect to the reservoir, $\Delta T$, by considering the diagram of Figure 2.8. The left side of the diagram depicts the system at some initial time during the field sweep

\[
dT = -\frac{T}{C_H(T)} \left( \frac{\partial S}{\partial H} \right)_T dH \quad (2.10a)
\]

\[
dT = -\frac{T}{C_H(T)} \left( \frac{\partial M}{\partial T} \right)_H dH \quad (2.10b)
\]
when the field on the sample is $H$ and the temperature gradient across the weak thermal link is $\Delta T$. Assuming that the sample temperature is greater than that of the reservoir, heat flows from the sample, with heat capacity $C$, through the weak thermal link of conductance $\kappa$, into the reservoir at a rate $\dot{q}$.

Figure 2.8: Thermal schematic of the temperature deviation of a material in response to a change in the applied field. The applied magnetic field is swept at a constant rate, $dH/dt$, while the temperature difference between the sample and reservoir evolves as $\Delta T(t)$ as given in the text. The sample heat capacity, $C$, and the thermal conductance, $\kappa$, are assumed to be constant over the narrow temperature range considered. Additionally, the heat flow between the sample and reservoir is taken to be constant and equal to its average value [45].

The right side of the diagram portrays the same system at an infinitesimally small moment, $dt$, later, in which time the field has increased by an amount $dH$ and the sample temperature has changed by an amount $dT$ thus producing a change in the temperature gradient of $d(\Delta T)$ owing to its magnetocaloric response. Assuming that the reservoir temperature has not changed, $d(\Delta T) = dT$. Additionally, the heat capacity of the sample, the thermal conductance of the weak link, and the heat flow are constant during the process. Energy balance during the infinitesimal change dictates that the total energy change of the sample must equal the work done on the sample by the magnet minus the heat flow out of the sample through the weak thermal link to the reservoir. This may be expressed mathematically as

$$C \left( T_0 \right) d(\Delta T) = C \left( T_0 \right) dT_{MC} - \kappa(T_0)\Delta Tdt \quad (2.11)$$
where $T_0$ is the initial temperature of the sample, $C(T_0)$ and $k(T_0)$ are the initially sample heat capacity and weak link thermal conductance, respectively, $dT_{MC}$ is the temperature rise that the sample would have sustained in the absence of the thermal link. By rearranging the terms in the above equation and substituting in (2.10a), the evolution of the temperature derivation is obtained as

$$
\Delta T + \tau \frac{d(\Delta T)}{dt} = -\frac{T}{\kappa} \left( \frac{\partial S}{\partial H} \right)_{\tau} \frac{dH}{dt}
$$

(2.12a)

$$
= -\frac{T}{\kappa} \left( \frac{\partial M}{\partial T} \right)_{H} \frac{dH}{dt}
$$

(2.12b)

Where $\tau = C / \kappa$ is the thermal relaxation time of the platform. Equation (2.12b) is obtained straightforwardly from Eq. 2.12a by use of the Maxwell equation 2.7.

In practice, it is found that the sample and reservoir temperature depend upon both the magnitude and sweep rate of the applied field. Since the reservoir is metallic, eddy current heating is a significant source of heating even when the field is static. This is caused both by vibrations of the probe within the field and possible fluctuations in the field due to ripples in the magnet supply. The magnitude of this heating is proportional to $(\omega A H)^2$ where $\omega$ is the frequency of the probe vibration or the field ripple, $A$ is its amplitude at that frequency, and $H$ is the magnitude of the applied field. As the field is swept, an additional component of heating is observed which is proportional to the square of the sweep rate. To account for the heating effects, the field must be swept both up and down and the resulting temperature variations referenced to the average background temperature. Immediately after initiation of a field sweep, the platform temperature shows a sudden response due to the onset of the magnetocaloric effect. Also, a sudden increase in the platform temperature is invariably observed due to eddy current heating. This initial temperature rise levels off after the thermal relaxation time, $\tau$, and is followed, apart from the magnetocaloric response of the temperature, by a more gradual increase (decrease) with increasing (decreasing) field. Careful attention must be made to ensure that the reservoir temperature is stable, aside from its
reproducible field and sweep rate dependence, over the course of magnetocaloric measurement. Drifting of the refrigerator performance during the course of the measurement will affect the background temperature profile in an essentially nontrivial and non-reproducible way thus voiding any possible interpretation of the result. In order to verify that the performance of the fridge is stable, the platform temperature before sweeping the field up and after sweeping the field down must coincide. Likewise, its temperature after sweeping the field up and before sweeping the field down must also be equal.

2.5.3 Experimental Measurements

The platform thermometer is measured using a standard Wheatstone configuration. A PAR 124A lock-in amplifier is used as both the excitation and nullmeter. The excitation frequency is 2.63 kHz. At the lowest temperature for the given measurement, when the platform thermometer resistance will be the largest, the excitation amplitude is increased until just below the point at which sensor heating in order to maximize sensitivity. In relaxation time calorimetry, it is essential that the timing of the temperature measurement is made as accurately as possible. For this reason, the analog voltage output of the lock-in is fed directly to an ADC card installed to the data taking PC which has the capability of digitizing the voltage at a sufficiently constant rate [45].

As described earlier, there are two thermometers mounted to the block. The first is a Speer 220 Ω carbon resistive thermometer. Its resistance is measured using DC excitation current while monitoring the resulting voltage. The current is supplied by a Keithley 220 Programmable Current Source [51]. The resulting voltage, detected using a Keithley Model 2000 System DMM/Scanner [51], is averaged over several readings. The current is reversed and the voltage is again averaged. This method eliminates any zero offsets, e.g., thermal or contact EMFs. The benefit of using a carbon resistor as a thermometer is the reproducibility of the resistance over time and thermal cycles. However, these resistors are known to have non-negligible magnetoresistance which must be accounted for.

Due to its negligible magnetic field dependence, a glass dielectric capacitive thermometer mounted in parallel to the resistance thermometer on the silver
block serves to transfer the zero-field calibration of the resistance thermometer to high fields. The thermometer derives its temperature dependence from that of the field independent glass dielectric constant. The capacitance is measured using an AH 2500A 1 kHz automatic capacitance bridge [52]. However, it has been found that the capacitance is not sufficiently reproducible upon cycling between room temperature and low temperature. Additionally, the capacitance drifts monotonically during the course of the experimental run, typically several days, necessitating several zero-field calibrations against the resistive thermometer calibrations in the same time period in order to compensate for this effect.

Thermometry at low temperatures and in high magnetic fields is nontrivial. The method for creating reliable thermometry follows. A calibrated Ge resistance thermometer from Lake Shore Crytronics, Inc. [53], is used to calibrate the Speer 220 Ω block thermometer in zero applied magnetic field. This calibration, carried out separately from the experiment, has been repeated and it has been found that the block thermometer is reproducible over the experimental probe for use in other apparatus. During measurements in high magnetic fields the value of the capacitive thermometer, whose temperature dependent capacitance is taken to be the same as in zero field for which it has been calibrated, is recorded in parallel to the resistance value of the resistive thermometer. Thus, a calibration of the carbon resistor is obtained for each value of the magnetic field.
CHAPTER 3

MAGNETIC PROPERTIES OF A V$^{3+}$-O-V$^{3+}$ COMPLEX: A Spin 1 - Spin 1 Coupled System

This chapter summarizes our magnetic susceptibility and high frequency EPR spectroscopic investigations on the dinuclear vanadium(III) complex [(CH$_3$CN)$_5$V-O-V(CH$_3$CN)$_5$][BF$_4$]$_4$.2CH$_3$CN, to find if this compound could serve as a model single molecule magnet (SMM). As discussed below, this compound has a linear [V-O-V]$^{4+}$ dimer in its belt and we have examined the dimer’s spin environment. Magnetic susceptibility data establish a ferromagnetic spin exchange constant $J$ for the linear [V-O-V]$^{4+}$ moiety. Variable temperature, high frequency (101.6 GHz) EPR spectra reveal that the (V$^{3+})_2$ unit has $S_T = 2$ as the spin ground state. The $g$ tensor components and the zero-field parameters $D$ and $E$ were determined for this state. The sign of $D$ was shown to be positive, via variable temperature. Some of the results were published recently [1].
3.1 Introduction

There is substantial current interest in the chemical synthesis of novel magnetic materials, and vanadium(III) has played a significant role in recent research on that topic. The classes of materials of interest include molecular species (single-molecule magnets), two-dimensional layered materials, and three-dimensional materials. Investigations of single-molecule magnets began with the discovery of the manganese-oxo cluster \([\text{Mn}_{12}\text{O}_{12}(\text{O}_2\text{CCH}_3)_{16}(\text{H}_2\text{O})_4]\cdot 2\text{CH}_3\text{CO}_2\text{H} \cdot 4\text{H}_2\text{O}[54-56]\) and has continued with many variations on the \(\text{Mn}_{12}\text{O}_{12}\) structural motif [57] and expanded to include other metals, including vanadium(III). Although there is only one vanadium(III)-based single-molecule magnet [58], other multinuclear vanadium-oxo clusters are known [59-60], and V(III) has been proposed as a metal ion that should be worth exploring further for single-molecule magnets [57]. In two-dimensional materials, vanadium(III) has served as the magnetic center in layered, Kagomé-type lattices [61-63]. Finally, V(III) is a critical component of (three-dimensional) Prussian blue analogs that are magnetically ordered at room temperature [64] and even above 100 ºC [65]. The relevance of V(III) to magnetic materials has prompted recent fundamental investigations of the electronic structure of the \([\text{V(H}_2\text{O})]^3^+\) ion [66] and other, pseudoctahedral complexes of V(III) [67]. The vanadium(III) ion has a propensity to form the oxo-bridged \([\text{V-O-V}]^{4^+}\) ion in aqueous solution [68], which can be considered to be the first step toward the formation of vanadium-oxo clusters that are single-molecule magnets. The magnetic coupling between the vanadium centers of \([\text{V-O-V}]^{4^+}\), where the vanadium centers are bridged only by an oxygen atom, is often ferromagnetic [68]. A large number of complexes containing a \([\text{V-O-V}]^{4^+}\) core and a variety of ligands on the vanadium centers have been prepared [69-78].

The work presented in this chapter started as collaboration with the Thomas P. Vaid group at Washington University. They had synthesized the compound \([(\text{CH}_3\text{CN})_5\text{V-O-V(\text{CH}_3\text{CN})}_3][\text{BF}_4]_4\), henceforth referred to as \([\text{V-O-V}]^{4^+}\). Crystallographic data suggested that there should be strong magnetic coupling but the details were difficult to obtain without high field EPR measurements. We carried out a detailed SQUID and EPR study. Preliminary results were reported recently [1].
3.2 Synthesis and Experimental Details

3.2.1 Synthesis of [(CH$_3$CN)$_5$VOV(CH$_3$CN)$_5$][BF$_4$]$_4$

Vaid et al. synthesized the [(CH$_3$CN)$_5$VOV(CH$_3$CN)$_5$][BF$_4$]$_4$ according to the published procedure [1]. A 10.71 g (0.0308 mol) sample of V(acac)$_3$ was dissolved in 100 mL of CH$_3$CN to form a yellow-brown solution. Then under positive N$_2$ flow, 58mL (0.42mol) of HBF$_4$ as a solution in diethyl ether was added via syringe and the solution quickly turned deep red-purple. Stirring the solution for 24 h at 22 ºC led to a deep purple solution and dark purple microcrystals. The solution volume was reduced by half and the product was isolated by filtration, then left under vacuum for 1 h. This resulted in 12.48 g of crude product which was isolated and recrystallized from acetonitrile (yield 84%).

Single Crystals of [(CH$_3$CN)$_5$VOV(CH$_3$CN)$_5$][BF$_4$]$_4$·2CH$_3$CN were grown by slowly cooling a hot, saturated solution of [(CH$_3$CN)$_5$VOV(CH$_3$CN)$_5$][BF$_4$]$_4$ in CH$_3$CN to room temperature.

3.2.2 Crystal Structure

Crystals of VOV (0.45*0.25*0.15 mm$^3$) were mounted on a glass fibre for indexing and intensity data collection at 223 K on a Siemens SMART CCD single-crystal diffractometer. Siemens SAINT program was used to integrate data. Crystallographic data for VOV are summarized in table 3.1.

| Table 3.1. Crystal Structure Data for [(CH$_3$CN)$_5$VOV(CH$_3$CN)$_5$][BF$_4$]$_4$·2CH$_3$CN |
|------------------|------------------|------------------|------------------|
| emp formula       | C$_{24}$H$_{36}$N$_{12}$OB$_4$F$_{16}$V$_2$ | $\alpha$ (deg)   | 90.00            |
| Fw                | 957.77           | $\beta$ (deg)    | 109.6(1)         |
| crystal size (mm$^3$) | 0.45 × 0.25 × 0.15 | $\gamma$ (deg)   | 90.00            |
| space group       | $P2(1)/n$        | vol (Å$^3$)      | 2273.75(19)      |
| a (Å)             | 10.0610(5)       | $Z$              | 2                |
| b (Å)             | 22.2252(10)      | temp (K)         | 223              |
| c (Å)             | 10.7939(5)       |                  |                  |
3.2.3 Direct current (dc) Magnetic Susceptibility Measurements

Dc magnetic susceptibility and magnetization measurements were performed on a Quantum Design MPMS-XL SQUID magnetometer. The sample temperature was varied from 1.8 K to 300 K and the static field from 0 to 7 T. Static measuring fields of 0.1 T were employed for the temperature dependent measurements. A single crystal was oriented in a low susceptibility glass capillary for orientation dependent measurements. The data were then corrected for contributions from the sample holder and sample diamagnetism using Klemm constants [79].

3.2.4 EPR measurements

Initial Q band ($\nu \sim 34$ GHz) EPR measurements were made on a powder sample using Bruker Elexsys-500 spectrometer at 295 K. Additional measurements were conducted using a locally developed homodyne system at the National High Magnetic Field Laboratory, in Tallahassee, FL [25, 80]; the instrument details are given in section 2.2 of chapter 2. In all experiments the modulation amplitudes and microwave power were adjusted for optimal signal intensity and resolution and all EPR spectra were simulated using Andrew Ozarowski’s program [81].

3.3 Crystal Structure Analysis

The [$(\text{CH}_3\text{CN})_3\text{VOV}($CH$_3\text{CN})_5][\text{BF}_4]_4$\(\cdot\)2CH$_3$CN consists of two V$^{3+}$ ions bridged by an oxygen atom. The VOV bond angle is crystallographically required $180^0$. Both vanadium ions have five terminal acetonitrile molecules resulting in slightly distorted octahedron, with a small outward tilting of the CH$_3$CN ligands. The V-N(1) bond is longer than the other V-N bonds, presumably due to the stronger trans influence of the oxo ligand relative to the acetonitrile ligands. The separations of the two vanadium and five nitrogens along with bond angles are summarized in table 3.2.
Table 3.2 Selected bond lengths (Å) and angles (deg) around V atoms in [(CH$_3$CN)$_5$V-O-V(CH$_3$CN)$_5$]$^{4+}$.

<table>
<thead>
<tr>
<th>Bond Distances (Å)</th>
<th>Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V-O 1.7549(5)</td>
<td>O-V-N(1) 179.70(9)</td>
</tr>
<tr>
<td>V-N(1) 2.142(3)</td>
<td>O-V-N(2) 92.15(8)</td>
</tr>
<tr>
<td>V-N(2) 2.088(3)</td>
<td>O-V-N(3) 95.29(8)</td>
</tr>
<tr>
<td>V-N(3) 2.086(3)</td>
<td>O-V-N(4) 93.69(8)</td>
</tr>
<tr>
<td>V-N(4) 2.083(3)</td>
<td>O-V-N(5) 94.41(8)</td>
</tr>
<tr>
<td>V-N(5) 2.086(3)</td>
<td>V-O-V 180.00(2)</td>
</tr>
</tbody>
</table>
Figure 3.1: Ball and stick representation of \([(\text{CH}_3\text{CN})_5\text{VOV(\text{CH}_3\text{CN})_5}]^{4+}\). Hydrogen atoms have been omitted for clarity [1].
3.4 Solution-Phase magnetism

Initial measurements of the solution-phase magnetic susceptibility of [(CH$_3$CN)$_5$VOV(CH$_3$CN)$_5$][BF$_4$]$_4$ in CD$_3$CN by the Evans method [82,83] yielded a magnetic moment of 5.1 $\mu_B$ per [V-O-V]$^{4+}$ unit, slightly higher than the value of 4.9 $\mu_B$ expected for an $S = 2$ state if the vanadium ions are perfectly ferromagnetically coupled. This indicates that there is a strong ferromagnetic coupling between the two vanadium ions. If the two vanadium centers were neither ferromagnetically nor antiferromagnetically coupled, an apparent magnetic moment of 4.0 $\mu_B$ per dinuclear unit would have been observed. The strong ferromagnetic coupling of [(CH$_3$CN)$_5$VOV(CH$_3$CN)$_5$]$^{4+}$ was further investigated by solid-state magnetic susceptibility and EPR measurements.

3.5 Magnetic Susceptibility and EPR-Theoretical Analysis

The magnetic susceptibility and EPR data presented in this chapter have been analyzed using the electronic Hamiltonian given in Eq. (3.1).

$$H = H_{\text{exchange}} + H_{\text{spin}}$$  (3.1)

Where, $H_{\text{exchange}}$ accounts for spin-spin exchange interactions, $H_{\text{spin}}$ the quantum mechanical spin interactions. The Heisenberg, Dirac, and Van Vleck [84-86] (HDVV) spin Hamiltonian, given in Eq. (3.2), has been used to describe the spin-spin exchange interactions described in this work.

$$H_{\text{exchange}} = -2J \sum_{i,j} S_i \cdot S_j$$  (3.2)

Here, $J$ is the spin exchange constant between the $i^{th}$ and $j^{th}$ ions, $S_i$ and $S_j$ are the spins. The sign of $J$ differentiates antiferromagnets ($J < 0$) from ferromagnets ($J > 0$). In the presence of external magnetic fields, the eigenvalues of the Hamiltonian (3.2) will be split into $(2S_T + 1)$ levels, where $S_T$ is the total spin of the cluster. If we define the $z$-axis to be the direction of the applied magnetic field, the splitting effect can be accounted by
adding a term \( g\beta B M \) to the eigenvalues of the Hamiltonian (3.2). The complete eigenvalue equation can then be given as:

\[
E_i = E(S_T) + g\beta B M S_T
\]  

where, \( g \) is the Landé splitting factor, \( \beta \) the Bohr magneton, \( H \) the z-component of the applied field and \( M_{S_T} \) the eigenvalue of the z-component of total spin \( S_T \) of the cluster.

The magnetic susceptibility per mole of the cluster (\( \chi_m \)), as shown in Eq. (3.5) is then obtained by substituting Eq. (3.3) in the van Vleck formula [85,87] (cf. Eq. (3.4)).

\[
\chi = N \sum_n \left( \frac{(E_n^{(1)})^2}{kT} - 2E_n^{(2)} \right) \exp(-E_n^{(0)}/kT) \sum_n \exp(-E_n^{(0)}/kT)
\]  

(3.4)

Here, \( N \) is the Avogadro number; \( E_n^{(0)}, E_n^{(1)} \) and \( E_n^{(2)} \) are the nth level energies respectively, in zero field, first- and second-order Zeeman coefficients; \( k \) the Boltzmann constant and \( T \) the temperature in Kelvin.

\[
\chi_m = \frac{Ng^2\beta^2}{kT} \sum_{S_T} \sum_{M_{S_T}} M_{S_T}^2 e^{-E(S_T)/kT} \sum_{S_T} (2S_T + 1) e^{-E(S_T)/kT}
\]  

(3.5)

Here the summations are over all the allowed values of \( S_T \) and \( M_{S_T} \). Further simplification of Eq. (3.4) leads to the commonly used [84-86] HDVV equation (3.6)

\[
\chi_m = \frac{Ng^2\beta^2}{3kT} \sum_{S_T} \sum_{S_T} (S_T + 1)(2S_T + 1) e^{-E(S_T)/kT} \sum_{S_T} (2S_T + 1) e^{-E(S_T)/kT}
\]  

(3.6)

\( H_{\text{spin}} \), written in Eq. (3.7), is the standard EPR spin Hamiltonian [88-90] that describes the Zeeman splitting of spin levels within the system.

\[
H_{\text{spin}} = \beta_e \vec{H} \cdot g_e \cdot \vec{S} - \beta_n g_n \vec{H} \cdot I + I \cdot \vec{A} \cdot \vec{S} + D(\vec{S}^2 - \frac{S(S+1)}{3}) + E(\vec{S}_x^2 - S_x^2) + O^n
\]  

(3.7)

In Eq. (3.7) \( \beta_e \) and \( \beta_n \) are the Bohr and nuclear magnetons; \( \vec{H} \) is the applied field; \( g_e \) is the electronic \( g \)-tensor electron and \( g_n \) is the nuclear \( g \)-factor (usually isotropic); \( \vec{S} \) and \( \vec{I} \)
are the electron and nuclear spin operators; \( \tilde{A} \) is the hyperfine tensor; and \( D \) and \( E \) are the axial and rhombic zero field splitting parameters, respectively. The first and second terms yield the Zeeman splitting of the \( M_z \) and \( M_I \) levels. The third term represents the electron-nuclear hyperfine interaction. The \( D \) and \( E \) terms describe the axial and rhombic zero-field splitting while \( O^a \) accounts for higher order terms. The various terms in equations (3.2), (3.6) and (3.7) were adjusted to suit the spin system.

### 3.6 dc Magnetic Susceptibility Data Analysis

A plot of \( \chi_T \) vs \( T \) for the VOV compound is shown in Figure 3.2. Comparing the observed high temperature \( \chi_T \) value of \( \sim 3.3 \) emu-K/mol to the expected [84,85] value of 3 emu-K/mol for an \( S_{\text{total}} = 2 \) system with \( g = 2.0 \), it is clear that the \( \text{V}^{\text{III}} \) ions \( (S_a = S_b = 1) \) of \([\text{V-O-V}]^{4+}\) unit are strongly coupled via ferromagnetic exchange interaction and that the spin ground state is \( S_{\text{total}} = 2 \). The mechanism underlying the magnitude of \( \chi_T \sim 3.3 \) emu.K/mol, as compared to the expected spin-only value of 3 emu.K/mol, is not fully understood; but it can be attributed to a contribution from a small paramagnetic impurity and a term due to temperature-independent paramagnetism (TIP). Below 100 K the steady drop of \( \chi_T \) may be attributed to the zero-field splitting of the quintet state and/or intermolecular interactions or the changing population of \( J \) spin-orbit states. An estimate of the spin exchange interaction \( J \) can be obtained by analyzing the susceptibility data in the following manner.

The Hamiltonian for a dinuclear entity of interacting spins \( S_a \) and \( S_b \) can be written as [84]:

\[
H = -2JS_a \cdot S_b + \beta H g_{a} S_a + \beta H g_{b} S_b + S_a \cdot D_a S_a + S_b \cdot D_b S_b
\]  

(3.8)

Here, the first term represents the isotropic exchange interaction, while the 2\(^{\text{nd}}\) and 3\(^{\text{rd}}\) represent the Zeeman interaction of the electrons with external field. \( S_i \) is the spin operator of the \( i^{\text{th}} \) ion, \( g_i \) the \( g \)-tensor of \( i^{\text{th}} \) ion, \( H \) the external magnetic field and \( \beta \) the Bohr magneton. The last two terms represent the local or single-ion anisotropies of interacting ions \( S_a \) and \( S_b \). Based on the crystal structure, we approximate axial symmetry at each \( \text{V}^{\text{III}} \) center, with \( \text{V-O-V} \) axis as the symmetry axis. The Hamiltonian in eq (3.8) can then be re-written as [84]:

48
\[
H = -2JS_a S_b + \beta g_{au} H_u S_{au} + \beta g_{bu} H_u S_{bu} + D_u [S_{az}^2 - S_u (S_u + 1)/3] + \\
D_b [S_{bx}^2 - S_b (S_b + 1)/3]
\] (3.9)

where, index ‘\(u\)’ denotes the direction of the applied magnetic field, \(g_{iu}\) and \(S_{iu}\) are, respectively, the principal \(g\) value and spin operator of the \(i\)th ion along the direction ‘\(u\)’. \(D_i\) is the axial zero-field splitting parameter of \(i\)th ion. If the isotropic exchange interaction \(-2JS_a S_b\) is the leading term in eq 3.9, as is in our case, the total spin quantum number \(S_{total}\), characterizing the spin of dinuclear states, is a good quantum number. \(S_{total}\) varies from \(|S_a - S_b|\) to \(S_a + S_b\) with corresponding energies \(E_{(2)} = 0\), \(E_{(1)} = 4J\), \(E_{(0)} = 6J\). Furthermore, these dinuclear states are energetically well separated from each other and the zero-field splittings of the excited states do not contribute to the magnetic properties.

Considering the fact that the observed \(\chi T\) profile is mainly representative of an \(S_{total} = 2\) ground state, we formulate an effective Hamiltonian \(H_{ef\text{f}}\), shown in eq 3.10

\[
H_{ef\text{f}} = \beta g_{2, u} S_u H_u + D_2 [S_z^2 - 2]
\] (3.10)

g_2 and \(D_2\) are respectively related to \(g_a\), \(g_b\) and \(D_a\) and \(D_b\) as shown in Eqs. 3.11 and 3.12 [84].

\[
g_{2, u} = \frac{g_{a, u}}{2} + \frac{g_{b, u}}{2}
\] (3.11)

\[
D_2 = \frac{D_a}{6} + \frac{D_b}{6}
\] (3.12)

The principal magnetic susceptibilities \(\chi||\) and \(\chi\perp\), shown in Eqs. 3.13 and 3.14, can then be calculated by introducing the eigenvalues corresponding to Eq. 3.10 for \(H \parallel z\) and \(H \parallel x(y)\) along with the thermal population of the excited triplet and singlet states into van Vleck equation [84]. Table 3.3 lists the coefficients \(E^{(0)}_n\), \(E^{(1)}_n\) and \(E^{(2)}_n\) as they appear in the van Vleck equation.
Table 3.3. Eigenvalues of effective Hamiltonian $H_{\text{eff}}$ given in Eq. 3.10, collected as van Vleck coefficients $E_n^{(0)}$, $E_n^{(1)}$ and $E_n^{(2)}$.

<table>
<thead>
<tr>
<th></th>
<th>$H \parallel z$</th>
<th></th>
<th>$H \parallel x^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_n^{(0)}$</td>
<td>$E_n^{(1)}$</td>
<td>$E_n^{(2)}$</td>
<td>$E_n^{(0)}$</td>
</tr>
<tr>
<td>2D_2</td>
<td>-2g_{z\parallel} \beta</td>
<td>0</td>
<td>2D_2</td>
</tr>
<tr>
<td>-D_2</td>
<td>-g_{z\parallel} \beta</td>
<td>0</td>
<td>-D_2</td>
</tr>
<tr>
<td>-2D_2</td>
<td>0</td>
<td>0</td>
<td>-2D_2</td>
</tr>
<tr>
<td>-D_2</td>
<td>g_{z\parallel} \beta</td>
<td>0</td>
<td>-D_2</td>
</tr>
<tr>
<td>2D_2</td>
<td>2g_{z\parallel} \beta</td>
<td>0</td>
<td>2D_2</td>
</tr>
</tbody>
</table>

* $|D_2|$ is assumed to be larger than $g_{z\parallel} \beta H$

\[
\chi_\parallel = \left( \frac{2Ng_\parallel^2 \beta^2}{k_B T} \right) \left[ e^{(D_2/k_B T)} + 4e^{(-2D_2/k_B T)} + e^{(-4J/k_B T)} \right]
\]

(3.13)

\[
\chi_\perp = \left( \frac{2Ng_\perp^2 \beta^2}{k_B T} \right) \left[ \frac{(k_B T/3D_2)}{e^{(2D_2/k_B T)}} + 7e^{(-2D_2/k_B T)} - 2e^{(-2D_2/k_B T)} + e^{(-4J/k_B T)} \right]
\]

(3.14)

\[
\chi_{\text{dimer}} = (\chi_\parallel/3) + (2\chi_\perp/3)
\]

(3.15)

Reflecting that $[V-O-V]^{4+}$ unit is centrosymmetric, we can set $g_a = g_b = g$ and $D_a = D_b = D$, which implies that $g_2 = g$ and $D_2 = D/3$ (cf. eqs 3.11 & 3.12). Furthermore, for $S_a = S_b$ and $g_S = (g_a + g_b)/2$ for all values of total spin $S_{\text{total}}$ [84].

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To reproduce the powder experimental $\chi T$ profile shown in Figure 3.2, paramagnetic susceptibility from a mononuclear $S = 1$ impurity (denoted by $x$) had to be taken into account along with the dinuclear susceptibility given in Eq. 3.16.

\[
\chi = x*\chi_{\text{dinuclear}} + (1-x)*\left[\frac{Ng^2\beta^2s(s+1)}{3k(T-\theta)}\right] + \chi_{\text{TIP}} \tag{3.16}
\]

In order to reduce the number of fitting parameters, $g_\parallel$ was set equal to $g_\perp$. The theoretical fit to eqs 3.13 – 3.16, shown as solid red line in Figure 3.3, is considered satisfactory. The fitting parameters are: $g = 2.11 \pm 0.01$, $|D_2| = 2.34 \pm 0.08$ K, $J = 72 \pm 5$ K, $\theta = -10.0$ K (fixed) and $x = 0.90$ (fixed), and TIP = 0.0013 \pm 0.0001 emu/mol. The large uncertainties might be due to various approximations invoked in the theoretical derivations, in particular, the omission of the spin-orbit coupling effects. The overall magnitude of $g$, $D$ and $J$ are in agreement with other vanadium dinuclear compounds containing a [V-O-V]$^{4+}$ unit in which the vanadium ions are strongly ferromagnetically coupled [71,77].
3.7 Magnetization Data Analysis

Further affirmation of the ferromagnetic ground state of $[\text{V-O-V}]^{4+}$ unit was attained from the magnetization measurements performed on powder and single crystal samples $[(\text{CH}_3\text{CN})_5\text{VOV(Ch}_3\text{CN})_5][\text{BF}_4]_4$. Using the standard formula for paramagnetic saturation, $M_{\text{sat}}/N\beta = gS$, it is clear that for an $S_{\text{total}} = 2$ system, the saturation reduced magnetization, $M_{\text{sat}}/N\beta$, should approach 4.0 if $g = 2$. Indeed, the magnetization of the $[\text{V-O-V}]^{4+}$ powder sample, as shown in Figure 3.3(a), approaches the expected value of 4. Similar behavior was observed for the single crystal sample for $H \parallel 001$ axis (see Figure 3.4(b)).

The field dependence of the $M_{\parallel}$ can be derived by defining a partition function, as shown in Eq. (3.17).

$$Z = \sum_n \exp(-E_n/k_B T).$$  \hspace{1cm} (3.17)

where, the summation is over all the energy levels. Using the energies listed in Table 3.3 for $H \parallel z$, $Z$ can be expanded as:

$$Z_{\parallel} = \exp\left( \frac{-2g\beta H - 2D_z}{k_B T} \right) + \exp\left( \frac{2g\beta H - 2D_z}{k_B T} \right) + \exp\left( \frac{-g\beta H + D_z}{k_B T} \right) + \exp\left( \frac{g\beta H + D_z}{k_B T} \right) + \exp\left( -\frac{2D_z}{k_B T} \right).$$  \hspace{1cm} (3.18)

The magnetization is related to the partition function by Eq. (3.19).

$$M = N k T \left( \frac{\partial \ln Z}{\partial H} \right)$$  \hspace{1cm} (3.19)

Evaluating the differentials of $Z_{\parallel}$ and substituting them in Eq. (3.19) provides the orientation-dependent magnetization $(M_{\parallel})$ as:

$$M_{\parallel} = \frac{4g_e e^{(-2D_z/k_B T)} \sinh(2g_e \beta H/k_B T) + 2g_e e^{(-2D_z/k_B T)} \sinh(g_e \beta H/k_B T)}{2e^{(-2D_z/k_B T)} \cosh(2g_e \beta H/k_B T) + 2e^{(2D_z/k_B T)} \cosh(g_e \beta H/k_B T) + e^{(2D_z/k_B T)}}$$  \hspace{1cm} (3.20)

The single crystal data shown in Figure 3.3(b) were fit to $M_{\parallel}$ given in Eq. (3.20) with $|D_z| = 0.60 \pm 0.04$ K and $g_{\parallel} = 2.01 \pm 0.01$. The quality of fit is not very satisfactory. Again, this discrepancy might be pointing to the inadequacy of the isotropic Hamiltonian used.
herein. In addition, the sample orientation was fixed visually. Nevertheless, the data are consistent with our main conclusions from the powder measurements.

![Graph](image)

**Figure 3.3:** Reduced magnetization as a function of field of [(CH$_3$CN)$_5$VOV(CH$_3$CN)$_5$][BF$_4$]$_4$ (a) Powdered sample (b) single crystal ($H \parallel 001$ axis). The saturated magnetic moment of 4 BM, corresponds to $S = 2$. 
3.8 EPR Studies

Additional verification of the spin ground state and more precise Hamiltonian parameters, was obtained through EPR measurements as discussed below. EPR spectra of VOV were analyzed using the spin Hamiltonian shown in eq below.

\[
H_{\text{spin}} = \beta H \cdot g \cdot S_T + S_T \cdot D \cdot S_T
\]  (3.21)

Here, \(\beta\) is the electron Bohr magneton, \(H\) the external applied magnetic field, \(g\) the Landé \(g\)-factor, \(S_T\) the total spin operator and \(D\) the zero-field splitting parameter. However, the magnetic hyperfine interaction, \(I \cdot A \cdot S\), between the magnetic moment of the nucleus of spin \(I\) and an ion of spin \(S\) was neglected in the simulations because the hyperfine structure due to \(^{51}\)V \((I = 7/2)\) is not resolved in our EPR spectra, essentially because of the fast electron-electron exchange coupling between the vanadium centers. This conclusion is consistent with the fact that there seems to be only one example where \(^{51}\)V hyperfine structure has been resolved for an integral spin system [91]. In that system, the vanadium ions were doped at a low concentration in a diamagnetic host, so spin exchange was significantly reduced. Also, we do not consider \(J\) here because the variable frequency EPR analysis shows no other effects that could be related to the exchange interaction.

The middle panel of Figure 3.4 shows a typical EPR spectrum of powdered \([(\text{CH}_3\text{CN})_5\text{VOV(}\text{CH}_3\text{CN})_5][\text{BF}_4]_4\) at 101.6 GHz and 4 K. The four possible transitions of an \(S = 2\) system, shown as double-headed arrows in Figure 3.6, match the observed peaks very well, validating that the ground state is quintet \((S = 2)\). The peaks marked by ‘*’ arise from an \(S = 1\) impurity. The arrows marked by numbers denote the \(\Delta M_S = \pm 1\) Zeeman transitions.
Figure 3.4: EPR spectrum of a powdered sample of VOV at 101.6 GHz and 4 K along with the energy level diagram for an $S = 2$ system for field oriented parallel to the $z$-axis (top) and $x$-axis (bottom). The four double-headed arrows in the energy level diagram correspond to the four allowed transitions in the experimental spectrum (middle). The peak marked by ‘*’ is ascribed to a paramagnetic impurity, to be a triplet state, following the magnetic susceptibility data [1].
Figure 3.5 shows the result of all allowed transitions in the energy level diagram for $S = 2$ system for a magnetic field ($H$) oriented parallel to the $z$ axis at 101.6 GHz and 4 K.

Figure 3.5: Zeeman energies of VOV for $H \parallel z$-axis at 101.6 GHz and 4K. Arrows denote the allowed EPR transitions.
Figure 3.6 shows the result of all allowed transitions in the energy level diagram for $S = 2$ system for a magnetic field ($H$) oriented parallel to the $x$ axis at 101.6 GHz and 4 K.

Figure 3.6: Zeeman energies of VOV for $H \parallel x$-axis at 101.6 GHz and 4 K. Arrows marked by numbers are the allowed EPR transitions.
Temperature dependence of EPR spectra at 101.6 GHz is shown in Figure 3.7. As temperature increases, the intensity shifts into the high-field peak, establishing that the zero-field splitting parameter $D_2$ bears a positive sign.

Figure 3.7: Temperature dependence of powder EPR spectra of $[\text{[CH}_3\text{CN}]_5\text{VOV(CH}_3\text{CN})_3\text{]}\ [\text{BF}_4]_4$ at 101.6 GHz. Higher intensity of the high field perpendicular peak indicates that the zero-field splitting parameter $D$ is positive [1].
Figure 3.8 displays experimental and simulated EPR spectra of \([(\text{CH}_3\text{CN})_5\text{VOV(\text{CH}_3\text{CN})}_5]\text{[BF}_4\text{]}_4\) at 101.6 GHz and 10 K. The agreement between the simulated and the experimental spectra is considered fairly reasonable. The intensities of some of the peaks do not quite match the observed ones, most probably because of the powder nature of the sample. The simulated parameters for the quintet ground state are: \(g_\perp = 1.9725 \pm 0.0005\), \(g_\parallel = 1.9825 \pm 0.005\), \(D_2 = 0.57 \pm 0.03\) K. The Hamiltonian parameters for the triplet state of impurity are: \(g_\perp = 2.03 \pm 0.02\), \(g_\parallel = 1.83 \pm 0.02\), \(D = 0.50 \pm 0.03\) K.

Figure 3.8: Experimental and simulated powder EPR spectra of \([(\text{CH}_3\text{CN})_5\text{VOV(\text{CH}_3\text{CN})}_5]\text{[BF}_4\text{]}_4\) at 101.6 GHz and 10 K. The experimental spectrum was simulated using \(S = 2\) and a Lorentzian line shape and the parameters are listed in the text. The peak marked by ‘*’ is thought to be part of an impurity triplet state [1].
3.9 Conclusions

A new [V-O-V]^{4+} complex, [(CH$_3$CN)$_5$VOV(CH$_3$CN)$_5$][BF$_4$]$_4$, was synthesized by the reaction of V(acac)$_3$ and HBF$_4$ in CH$_3$CN. It was characterized by single crystal X-ray diffraction and magnetic measurements. DC magnetic susceptibility, magnetization, and EPR measurements show that the complex has a ground state spin $S = 2$, indicating that the two V(III) centers are ferromagnetically coupled with a $J \approx 50$ cm$^{-1}$. The low-temperature decrease in $\chi T$ is ascribed to the zero-field splitting term ($D \approx 0.57 \pm 0.03$K) and an intermolecular antiferromagnetic interaction. This easily accessible compound serves as a convenient precursor to other [V-O-V]$^{4+}$ complexes and possibly larger vanadium-oxo clusters.
CHAPTER 4

THERMOMAGNETIC STUDIES OF
Triamminodiperoxychromate, Cr(NH$_3$)$_3$(O$_2$)$_2$

This chapter presents single crystal growth, structural characterization and thermomagnetic measurements on the triamminodiperoxychromate, Cr(NH$_3$)$_3$(O$_2$)$_2$, with the view of understanding the effect of magnetic field on the magnetic ordering of a Cr(IV) $3d^3$, $S$ =1 lattice. For the investigated compound, a sharp $\lambda$-like transition was observed in $C_p$, with a maximum at 8.5 K; characteristic of three dimensional long range antiferromagnetic ordering. In an attempt to see the effect of magnetic field on this phase transition, we carried out detailed measurements of the magnetic phase diagram in magnetic fields from 0 to 9 T and at temperatures from 1.8 to 12 K by means of heat capacity measurements. From the analysis of the $H$ vs $T$ curve obtained we found that the Cr(NH$_3$)$_3$(O$_2$)$_2$ compound shows a standard antiferromagnetic behavior. The peak shifts to lower temperatures with increasing $H$. It is found that the peak broadens when $H$ increases and this ultimately restricts the accuracy of the determination of the position, $T_N(H)$, of the peak in $C_p$. The critical field for a possible quantum phase transition was estimated as about 21 $\pm$ 1 Tesla.
4.1 Introduction

The chemistry of Cr in its oxidation states other than +3 and +6 is rather limited [19]. Recently, however, there has been an increased interest in studies involving Cr\textsuperscript{IV} (3d\textsuperscript{2}) compounds, based in part on the highly successful utilization of CrO\textsubscript{2} in magnetic tapes [92,93]. In an effort to gain further understanding of the magnetic properties of Cr\textsuperscript{IV} compounds, especially involving the Cr\textsuperscript{IV}-O\textsubscript{2} bonds, we prepared single crystals of the compound triammino-diperoxychromate [94], Cr(NH\textsubscript{3})\textsubscript{3}(O\textsubscript{2})\textsubscript{2}, henceforth, Cr\textsuperscript{IV}-TADP. Earlier reported magnetic susceptibility,$\chi$ and specific heat, $C_p$, measurements demonstrated that Cr\textsuperscript{IV}-TADP undergoes a $\lambda$-type antiferromagnetic transition at 8.46 K ($C_p$) which is a characteristic of 3-d long range ordering [24]. But no further details were available regarding the interactions involved in the mechanism of this phase transition, and this provided the impetus for the studies described in this chapter.

In addition to being a model 3d\textsuperscript{2} lattice, Cr\textsuperscript{IV}-TADP might find utility as a precursor to CrO\textsubscript{2} and related materials. Since current synthetic methods [19,92,94-96] involve the hydrothermal reduction of CrO\textsubscript{3}, inexpensive and simpler precursors (devoid of unwanted by-products, i.e. Cr\textsubscript{2}O\textsubscript{3}) would be of industrial value.

Earlier work on Cr(IV) amine compounds was focused on their utility as precursors to Cr(III) amine complexes [97]. Some preliminary work has been reported on the magnetic susceptibility behavior of Cr(IV) tertiary alkoxides and triethylsilyloxide [98], but just down to temperatures of 98 K on powder samples. Fast electronic spin-relaxation due to a small energy difference between the ground and excited states allowed observation of EPR spectra only at 10 K on a frozen solution of Cr(O-t-Butyl)\textsubscript{4}, but it was not possible to isolate this compound for structural studies [98]. There has been no report of EPR spectra for the Cr(IV) diperoxo amine type complex [99], providing additional impetus for the present study of Cr\textsuperscript{IV}-TADP.
4.2 Synthesis and Experimental Details

![Molecular structure of Cr(NH3)3(O2)2.H2O](image)

Figure 4.1: The molecular structure of Cr(NH3)3(O2)2.H2O [6], CrIV-TADP.

4.2.1 Synthesis of Cr(NH3)3(O2)2

The synthesis [100] of CrIV-TADP was first reported in 1897, the crystal structure [101] determined in the mid-1960s. Figure 4.1 shows the molecular structure. The crystal is built up of molecules in which the coordination polyhedron around the central chromium atom can be considered in terms of a somewhat distorted pentagonal bi-pyramid, the four oxygen atoms and one nitrogen atom forming the base of the pyramid, while the two remaining nitrogen atoms occupy the apical positions [101,102]. Its molecular weight and density are, respectively, 139.07 g/mol and 1.65 g/cm³.

The CrIV-TADP used here was synthesized following the procedure of Weide [100,103]. 20.6 g CrO3 was added to 300 mL of NH4OH with stirring, cooled to 5°C in an ice bath, and the excess solid was filtered off, resulting in a
deep yellow liquid solution. Hydrogen Peroxide (30%) was added (slowly) drop-wise to the solution until bubbling occurred. The resulting brown-yellow solution was stored in the refrigerator for 2-3 days and yielded dark brown millimeter size needle shaped crystals, which can be recrystallized [103] from NH₄OH. The sample’s identity was confirmed by X-ray diffraction as discussed below.

4.2.2 Crystal Structure

X-ray diffraction measurements on single crystals of Cr⁴⁺-TADP were performed by Dr. Ronald C. Clark, using the departmental XRD facilities. The structure of the complex Cr⁴⁺-TADP has been reported previously [101]. Our results were essentially identical.

4.2.3 Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were performed on a single crystal sample of Cr⁴⁺-TADP, as reported earlier by Ramsey et al. [6]. A Quantum Design SQUID magnetometer was used for these measurements, covering the temperature range of 1.8-300 K. The measuring field employed was 3000 G. The higher field was necessitated by the smaller size of the available crystals. The data clearly indicated an antiferromagnetic phase transition around 8.80 K.

4.2.4 Heat Capacity Measurements

In order to support the magnetization data, heat capacity was measured. Heat capacity measurements were performed on a Quantum Design Physical Property Measurement System (PPMS) in our group employing a time constant method as described in section 2.3 of chapter 2. Measurement temperatures ranged between 1.8 and 12 K in applied fields of 0-9 T. The temperature/field dependence of the sample holder was measured beforehand and subtracted from the data. The sample consisted of multiple crystal of Cr⁴⁺-TADP. The typical sample mass was 2-3 mg.
### 4.3 Crystal Structure Analysis

**Table 4.1**: Atomic coordinates of Cr$^{IV}$-TADP (expressed in fractions of the cell edges) [101].

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr1</td>
<td>0.2015</td>
<td>0.0858</td>
<td>0.1331</td>
</tr>
<tr>
<td>Cr2</td>
<td>0.1090</td>
<td>0.25</td>
<td>0.6403</td>
</tr>
<tr>
<td>O1</td>
<td>0.2090</td>
<td>0.0027</td>
<td>0.1147</td>
</tr>
<tr>
<td>O2</td>
<td>0.3291</td>
<td>0.0268</td>
<td>0.01883</td>
</tr>
<tr>
<td>O3</td>
<td>0.1828</td>
<td>0.1669</td>
<td>0.1591</td>
</tr>
<tr>
<td>O4</td>
<td>0.3119</td>
<td>0.1463</td>
<td>0.2194</td>
</tr>
<tr>
<td>O5</td>
<td>0.1142</td>
<td>0.1657</td>
<td>0.6395</td>
</tr>
<tr>
<td>O6</td>
<td>0.9977</td>
<td>0.1904</td>
<td>0.7299</td>
</tr>
<tr>
<td>N1</td>
<td>0.0046</td>
<td>0.0867</td>
<td>0.0094</td>
</tr>
<tr>
<td>N2</td>
<td>0.1163</td>
<td>0.0747</td>
<td>0.3804</td>
</tr>
<tr>
<td>N3</td>
<td>0.2906</td>
<td>0.0971</td>
<td>0.8843</td>
</tr>
<tr>
<td>N4</td>
<td>0.2944</td>
<td>0.25</td>
<td>0.4881</td>
</tr>
<tr>
<td>N5</td>
<td>0.2239</td>
<td>0.25</td>
<td>0.8693</td>
</tr>
<tr>
<td>N6</td>
<td>0.0015</td>
<td>0.25</td>
<td>0.3965</td>
</tr>
</tbody>
</table>
The X-ray crystal structure was used to determine the authenticity of the sample. It appears that there are 12 molecules in the orthorhombic unit cell of Cr$^{IV}$-TADP, with lattice parameters being $a = 9.7726 \text{ Å}$, $b = 22.6521 \text{ Å}$, $c = 7.5889 \text{ Å}$, $\alpha = \beta = \gamma = 90^0$ [6]. The space group is $Pnma$. In the crystal, the molecules are held together by hydrogen bonds. The average oxygen-oxygen bond distance in the peroxo groups is $1.429 \pm 0.025$ Å, and the oxidation state of the central chromium atom is +4. Cr-Cr nearest neighbor distances suggested that Cr(IV) ion possesses nearest neighbors in a 3-d array based on distances < 6 Å. Figure 4.2 shows the Cr$^{IV}$-TADP lattice.

![Figure 4.2: Projection down the 001 axis of the Cr$^{IV}$-TADP crystal. The nearest neighbors are separated by 5-6 Å in each direction providing possible 3-d exchange pathways [6].](image)
4.4 Magnetic Susceptibility of An Antiferromagnet -Theoretical Analysis

The mean-field approximation (MFA) postulates that each spin “sees” the average field of all the other spins, and this result in each spin experiencing an additional field that is proportional to the magnetization. This additional field is called the exchange field, and this process may be written as:

\[ H_E = \lambda M \] (4.1)

In this equation, \( \lambda \) is referred to as the mean field constant. It is the mathematical formulation of the postulate that in the paramagnetic phase, an applied field causes a finite magnetization, \( M \), which in turn generates an exchange field, \( H_E \). The total field felt by that spin is now the sum of the applied field (\( H_a \)) and the exchange field:

\[ H = H_a + H_E \] (4.2)

This total field is now used to rewrite the paramagnetic susceptibility:

\[ \chi = \frac{M}{H} \]

\[ \chi = \frac{M}{H_a + H_E} \] (4.3)

If the paramagnetic susceptibility is given by the Curie law, and the exchange field is given by equation 4.1, the susceptibility may be written as:

\[ \frac{C}{T} = \frac{M}{H_a + \lambda M} \]

\[ CH_a + C\lambda M = MT \]

\[ C + C\lambda \frac{M}{H_a} = \frac{M}{H_a} - T \]

\[ C + C\lambda \chi = \chi T \]

\[ \chi = \frac{C}{T - C\lambda} \]

\[ \chi = \frac{C}{T - \theta} \] (4.4)
This is the so called Curie-Weiss Law, and $\theta = C\lambda$ is the Weiss temperature. Note that there is a discontinuity at $\theta = T$. At this temperature and below there exists a spontaneous magnetization since:

$$\frac{C}{T-\theta} = \frac{M}{H_a}$$

For $C/(T-\theta)$ equal to infinity (when $\theta = T$), there must be a magnetization, $M$, for zero applied field, $H_a$. This spontaneous magnetization corresponds to an infinite correlation length, when all the spins are aligned.

In an antiferromagnetic lattice the spins are ordered in an antiparallel arrangement, as diagrammed below. This results in the absence of a spontaneous moment below the critical temperature (called the Néel temperature, $T_N$), and the magnetic susceptibility approaches zero. The following approach is used to find the magnetic susceptibility of an antiferromagnet lattice:

Suppose in an antiferromagnetic lattice there are two sub-lattices. A and B, which are aligned anti-parallel to each other. For simplicity let all other interactions be zero except for the anti-parallel interaction between the two sites. In the mean field approximation, the exchange field experienced by each spin is:

$$H_A = -\mu M_B \quad \text{and} \quad H_A = -\mu M_B$$

Defining a separate Curie constant for each ion and using the exchange fields given above, the MFA gives:

$$\chi_A = \frac{M_A}{H_a - \mu M_B} \quad \text{and} \quad \chi_B = \frac{M_B}{H_a - \mu M_A}$$

$$\frac{C_A}{T} = \frac{M_A}{H_a - \mu M_B} \quad \text{and} \quad \frac{C_B}{T} = \frac{M_B}{H_a - \mu M_A}$$

$$M_A T = C_A H_a - C_A \mu M_B \quad \text{and} \quad M_B T = C_B H_a - C_B \mu M_A \quad (4.5)$$

In this set of equations, $H_a$ is the applied external field. Note that 4.5 forms a system of coupled equations. If the applied field is zero they may be written as:
\begin{align*}
M_A T &= -C_A \mu M_B \\
M_B T &= -C_B \mu M_A \quad (4.6)
\end{align*}

The system defined above has a non-zero solution for the magnetization in zero applied field if the determinant of the coefficients of \( M_A \) and \( M_B \) equals zero:

\[
\begin{vmatrix}
T & \mu C_A \\
\mu C_B & T
\end{vmatrix}
\]

\[T^2 - \mu^2 C_A C_B = 0\]

\[T_C = \mu \sqrt{C_A C_B} \quad (4.7)\]

The paramagnetic susceptibility of the entire lattice is given by the sum of the magnetizations of the sub-lattices divided by the applied field:

\[\chi = \frac{M_A + M_B}{H_a} \quad (4.8)\]

To determine the magnetization of each of the sub-lattices, substitute equation 4.5 (right) into 4.5 (left) and solve for \( M_A \). This gives:

\[M_A = \left( \frac{C_A H_a T}{T^2 - \mu^2 C_A C_B} - \frac{\mu C_B C_A H_a}{T^2 - \mu^2 C_A C_B} \right) \quad (4.9)\]

Similarly, putting 4.5 (left) into 4.5 (right) gives \( M_B \) as:

\[M_B = \left( \frac{C_B H_a T}{T^2 - \mu^2 C_B C_A} - \frac{\mu C_A C_B H_a}{T^2 - \mu^2 C_B C_A} \right) \quad (4.10)\]

Substituting 4.9 and 4.10 into 4.8 gives:

\[\chi = \frac{(C_A + C_B)T - 2\mu C_A C_B}{T^2 - \mu^2 C_A C_B} \quad (4.11)\]

In an antiferromagnetic lattice, \( C_A = C_B \)

This allows equation 4.11 to be written as:

\[\chi = \frac{2CT - 2\mu C^2}{T^2 - (\mu C)^2} \]

\[\chi = \frac{2C(T - \mu C)}{T^2 - (\mu C)^2} \quad (4.12)\]
Since $A^2 - B^2$ may be written as $(A+B)(A-B)$, the denominator may be rewritten to give:

$$
\chi = \frac{2C(T - \mu C)}{(T - \mu C)(T + \mu C)}
$$

$$
\chi = \frac{2C}{T + \mu C}
$$

$$
\chi = \frac{2C}{T + T_N}
$$

(4.13)

Where $T_N = \mu C$

In deriving equation 4.13, two sublattices were considered, hence the factor of 2 in the numerator. To consider only one mole of ions, multiply 4.13 by $\frac{1}{2}$. Equation 4.13 may now be written as:

$$
\chi = \frac{C}{T - \theta}
$$

In this equation, a negative $\theta$ is equivalent to $T_N$ and gives equation 4.13 for an AFM interaction. The critical temperature is usually referred to as $T_c$, regardless of the type of transition.

Above the critical temperatures, the susceptibilities are nearly isotropic, but a different situation is encountered below the critical temperature of antiferromagnets and the susceptibility depends on the orientation of the field (assumed to be much smaller than the exchange field) with respect to the spin axis. Below the Néel temperature, the AFM interaction tends to align the spins antiparallel. When a field is applied perpendicular to these spins it exerts a torque on them and sets up a competition between the AFM interaction and the tendency of the field to align them with itself. This competition gives rise to a roughly constant susceptibility below the Néel temperature. When the field is applied parallel to the spins, it can exert no net torque so the only force acting on the spins is the AFM interaction, and the susceptibility approaches zero. These cases are diagrammed below in Figure 4.3.
4.5 Earlier results on 3-d antiferromagnet Cr$^{IV}$-TADP

4.5.1 Magnetic Susceptibility

Figure 4.4 shows the temperature dependent magnetic susceptibility ($\chi(T)$) measurements on single crystal sample of Cr$^{IV}$-TADP with the field aligned along the orthogonal 001 and 010 axes [6]. As shown, the susceptibility of Cr$^{IV}$-TADP passes through a sharp cusp-like maximum at 8.80 K. This type of a sharp transition to antiferromagnetic ordering is a classic characteristic of a 3-d system. The $\chi(T)$ measurements for the field aligned parallel and perpendicular to the high symmetry 001 axis exhibit a significant amount of anisotropy in the system. For $H//001$, $\chi(T)$ decreases to near zero upon reducing the temperature to 1.8 K. On the other hand, the $H//010$ susceptibility becomes relatively constant below 7 K. Such behavior points toward the preferential spin alignment axis being the 001 direction. This is a reasonable assertion because the magnetic moment is effectively canceled by spin pairing in the $H//001$ case. In contrast, the effective cancellation of the neighboring magnetic moments cannot occur in the perpendicular susceptibility as the spins prefer aligning with the 001 axis, which in the $H//010$ data is perpendicular to the field.
4.5.2 Heat capacity

Figure 4.5 shows the result of heat capacity measurements on Cr\textsuperscript{IV}-TADP in zero field, performed by Chris Ramsey [6]. The lattice contribution was estimated by the standard $C_P = \alpha T^{-1} + \beta T^{-2}$ method [85], over the range of 13 to 20 K. The $\alpha$ and $\beta$ values are 0.00118 J/mol.K\textsuperscript{4} and 381 J.K/mol respectively. The presence of only a sharp $\lambda$-type anomaly is typical of long range antiferromagnetic ordering and, from this evidence; one should expect most of the magnetic entropy to be removed below $T_N$. 

Figure 4.4: The single crystal magnetic susceptibility of Cr\textsuperscript{IV}-TADP for two orthogonal crystal orientations. The sharp maximum is consistent with a 3-d antiferromagnet [6].
Figure 4.5: The heat capacity of Cr$^{IV}$-TADP. The data indicates the absence of short range interactions; rather, 3-d ordering seems to be the dominant dimensional process in this case [6].

Figure 4.6: The magnetic entropy of Cr$^{IV}$-TADP approaches the theoretical entropy entropy for an $S=1$ system. Note that most of the entropy is removed below $T_N$ [6].

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4.5.3 Magnetic Entropy

The antiferromagnetic ordering phenomena can be rationalized based upon the removal of entropy with decreasing temperature. Because $\Delta S$ should approach 0 as $T$ approaches 0 K, magnetic ordering provides a pathway for the entropy removal [6]. The magnetic entropy is determined by applying the typical thermodynamic relationship

$$\Delta S_{\text{mag}} = \int \frac{C_{\text{mag}}(T)}{T} dT$$

to the heat capacity data [85]. Theoretically, the total magnetic entropy is given by

$$\Delta S_{\text{mag}} = R \ln(2S + 1)$$

Where $R$ is the gas constant and $S$ the spin of the system. For $S = 1$, this predicts that the entropy acquired with increasing temperature should approach 9.13 J/mol.K. Figure 4.6 shows the magnetic entropy vs temperature plot for Cr$^{IV}$-TADP [6]. For Cr$^{IV}$-TADP, 62% of the entropy is removed below the onset of 3-d ordering at 8.46 K, as expected for a 3-d antiferromagnet [6].
4.6 New Results of Heat Capacity Measurements

Figure 4.7: Temperature dependence of the heat capacity of Cr$^{IV}$-TADP at magnetic fields from $H = 0$ to $H = 9$ T.
Figure 4.8: Magnetic field versus Néel temperature phase diagram for Cr$^{IV}$-TADP.

Figure 4.9: Magnetic field versus transition temperature phase diagram for Cr$^{IV}$-TADP. The red curve is an extrapolation of the transition temperature data points to $T = 0$ K, using origin.
4.6.1 Heat Capacity of Cr$^{IV}$-TADP: Discussion

The heat capacity data at magnetic field from 0 - 9 Tesla are presented in Figure 4.7. First, at $H = 0$ T, there is observed a sharp peak characteristic of a lambda type transition at 8.46 K, perhaps signaling the onset of long range antiferromagnetic ordering. The application of a magnetic field shifts the position of the maximum in the heat capacity to lower and lower temperatures and also makes the peak broader and suppressed. The suppression of the peak by increasing the magnetic field indicates that this peak is magnetic in origin. As seen in the plot with increase in magnetic field the transition temperature starts decreasing. This shows that Cr$^{IV}$-TADP having a 3-d ordering shows a standard antiferromagnetic behavior. The reason for the decrease in transition temperature with an increase in magnetic field is that the antiferroodmagnetic ordering is destroyed by the external magnetic field. So the system needs less thermal energy to undergo a phase transition from antiferromagnetic to paramagnetic state. For fields between 0 T and 4 T one single peak was observed. From 5 T onwards, an additional peak which indicates a second transition starts appearing. We explain this second peak as the reason given below:

The transition temperature of a sample usually depends on the orientation of the crystal with respect to the direction of the magnetic field. This leads to a distribution of transition temperatures if the sample is a polycrystal and is placed in a magnetic field. Because the orientations of crystallites within a polycrystal are usually random, one might expect naively that the distribution of transition temperatures will be also random and hence the peak in the specific heat will be rounded or smeared. But this expectation is incorrect. The specific heat will often acquire two peaks -- the so-called Peak doublet. Since our sample consisted of several single crystals, not a polycrystal, it is even more likely that the heat-capacity measurements picked up peaks from two dominant crystal orientations.

Another possibility is that your material does have two transitions at least for some crystal orientations in magnetic field. It would be useful to repeat these measurements with only one large crystal.
The magnetic phase diagram determined from the positions of the specific-heat peaks and shoulders in Figure 4.7 is given in Figure 4.8.

Since our heat capacity measurements showed that this compound shows standard antiferromagnetic behavior. And it is already 3-d. so we did not proceed for any further experiments. The extrapolation of the $H$ versus $T_N$ curve shown in Figure 4.9, shows that the value of the critical field when $T$ approaches zero is approximately 21.5 Tesla. Since this field was rather high, we looked for another Cr(IV), d$^2$ lattice. We were indeed able to show that the related compound Cr(C$_4$H$_{13}$N$_3$)(O$_2$)$_2$.H$_2$O exhibits a critical field of about 12.3 Tesla. Chapter 5 describes our detailed studies on the Cr(C$_4$H$_{13}$N$_3$)(O$_2$)$_2$.H$_2$O lattice.
CHAPTER 5

THERMOMAGNETIC STUDIES OF DiperoxodiethylenetriamineCr(IV) Monohydrate

[Cr(C₄H₁₃N₃)(O₂)₂.H₂O]: Evidence of a Quantum Phase Transition

This chapter presents large single crystal growth, structural characterization and thermomagnetic measurements on the diperoxodiethylenetriamineCr(IV) monohydrate complex, Cr(C₄H₁₃N₃)(O₂)₂.H₂O, with the view of understanding the magnetic ordering of a Cr(IV) 3d², S = 1 lattice, a rather rare case. Earlier reported X-ray structure shown in Figure 5.3 and magnetic susceptibility, χ(T), data suggested it to be a 2-d antiferromagnet. Fits to the single crystal χ(T) data using the Heisenberg model for S = 1 system yielded orientation dependent g-values and exchange constants. In the present study, we have carried out much more detailed measurements of the magnetic phase diagram of Cr(C₄H₁₃N₃)(O₂)₂.H₂O in magnetic fields from 0 to 18 T and at temperatures from 0.2 K to 3 K by means of torque magnetometry, specific heat and magnetocaloric effect measurements. From the analysis of magnetocaloric effect measurements, we determined that the high field phase closes at a zero temperature and a critical magnetic field value of 12.39 T with a critical exponent α ≈ 2.01 ± 0.02.
5.1 Introduction

While systems exhibiting 2-dimensional magnetic correlations are well known [104-114], no such study on a Cr(IV) complex has yet been reported. This is due to the fact that there are very few inorganic complexes which incorporate Cr(IV) ions [19]. One exception is the class of Cr(IV) diperoxoamines [115]. An example of the Cr(IV) diperoxoamines is diperoxodiethylenetriaminechromium(IV) Monohydrate, Cr(C_4H_13N_3)(O_2)_(2)_2.H_2O [116,117] which is the focus of this chapter. Figure 5.1 shows the molecular structure of Cr(C_4H_13N_3)(O_2)_(2)_2.H_2O, henceforth called Cr(dien).

There have been several reports of kinetic and mechanistic experiments on Cr(dien) [20-23], but these examples provided little information on the magnetic properties of this system especially at very low temperatures and high magnetic fields. Studies have suggested that Cr in the rare +4 oxidation state may contribute to Cr(VI) carcinogenesis through °OH radical generation [118,119]. Because of this reason, and due to its stability and water solubility [120] Cr(dien) has also been proposed as a model compound for Cr(IV) toxicity studies. The current work was thus motivated by the need to provide new magnetic data on Cr(dien) at low temperatures and high magnetic fields. Early heat capacity measurements from our laboratory [6] showed that as the magnetic field is increased the antiferromagnetic (AFM) transition temperature $T_N$ for 3-d antiferromagnetic ordering due to weak interplane exchange interactions first increased. The magnetic field was increased from 0 $\rightarrow$ 6 T, but the $T_N$ decreased as $H$ was increased above 6 T. Since Cr(IV) doped germaneucryptates may be a viable laser candidates [121], we wished to study the magnetic ordering phenomenon in Cr(dien). Additionally, the compound could also serve as precursor for the well known Cr (IV)-based magnetic memory agent CrO$_2$.

We therefore synthesized the Cr(dien) complex and grew large single crystals for heat capacity, magnetocaloric effect and torque magnetometry measurements as a function of temperature down to the millikelvin range and field up to 18 T. These thermomagnetic measurements showed that that the compound undergoes a quantum phase transition.

A Quantum Phase Transition is a transition that occurs at absolute zero temperature, as opposed to classical thermal phase transitions, if one has a transition
which is controlled by some variable (such as pressure or magnetic field) then at some critical value of this variable one can have a transition which can, in principle, occur at absolute zero. Such a zero temperature phase transition is called a quantum phase transition (QPT) and the point at which it occurs is a quantum critical point (QCP). Systems with quantum critical points are expected to show unusual dynamics which is controlled by quantum fluctuations. At a quantum critical point (QCP) – quantum fluctuations diverge in space and time, leading to exotic phenomena that can be observed at non-zero temperatures. We have tried to observe this phenomenon in Cr(dien).

### 5.2 Synthesis and Experimental Details

![Molecular Structure](image)

Figure 5.1: The molecular structure of Cr(C₄H₁₃N₃)(O₂)₂.H₂O, Cr(dien) [6].
5.2.1 Synthesis of Cr(dien)

Cr(dien) was synthesized via the method of House and Garner [116,117]. Typically, a solution of 5 g Na$_2$Cr$_2$O$_7$·3H$_2$O, 10mL deionized H$_2$O, and 6 mL of the diethylenetriamine (C$_4$H$_{13}$N$_3$) ligand were stirred and cooled in an ice bath. Once the solution was cool, 15mL of 30% H$_2$O$_2$ was added drop-wise. Vigorous bubbling occurred, resulting in an opaque brown-yellow solution, which appeared dark green after several hours. The solution was allowed to evaporate for approximately one week, upon which dark brown crystals of Cr(dien) had formed. The crystals were washed with cold deionized water and filtered. The crystals were of high quality and recrystallization was not necessary. The sample’s identity was confirmed by X-ray diffraction, vide infra.

5.2.2 Crystal Structure

X-ray diffraction measurements on Cr(dien) were performed by Dr. Ronald C. Clark. The data matched the X-ray diffraction data reported earlier [7]. The atomic coordinates and bond lengths are summarized in Tables 5.1 and 5.2.

5.2.3 Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were performed on a single crystal of Cr(dien), as reported earlier by Ramsey et al [6]. A Quantum Design MPMS XL7 (SQUID) magnetometer was used for these measurements, covering the temperature range of 1.8-300 K. Aligned single crystals (~5 mg) were used for angular variation studies. The measuring field employed was 1000 G. The data clearly indicated an AFM transition around 2.7 K at this a low field.

5.2.4 Heat Capacity Measurements

In order to support the magnetization data, heat capacity was measured. Initial measurements were performed on a Quantum Design Physical Property Measurement System (PPMS) employing a time constant method. Measurement temperatures ranged between 1.8 and 10 K and applied fields from 0-9 T. The temperature / field dependence of the sample holder was measured beforehand and subtracted from the data. The sample
consisted of a single crystal of Cr(dien). Typical sample mass was 2-3 mg. These magnetization and $C_p$ data were further augmented by use of additional magnetic fields and low temperatures. Measurements in the dilution fridge (SCM1, 18/20 T magnet, 20mK- 2 K) are carried in the Millikelvin facility, at National High Magnetic Field Laboratory (NHMFL), Tallahassee, FL, as described in chapter II.

5.2.5. Torque Magnetometry Measurements

Torque magnetometry was another technique we used to confirm the $C_p$ data. These measurements were performed on SCM2 (18/20 T magnet, 0.3 – 300 K) in the Millikelvin facility at NHMFL. Torque magnetometry enabled measurements close to the $T \rightarrow 0$ K, $H \sim 12.5$ T region. Details of torque magnetometry are given in chapter II.
5.3 Crystal Structure Analysis

Table 5.1: Atomic Coordinates (Å × 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for Cr(C_4H_13N_3)(O_2)_2.H_2O, Cr(dien) [7]

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>*U_{eq}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>2531(1)</td>
<td>4417(1)</td>
<td>8723(1)</td>
<td>17(1)</td>
</tr>
<tr>
<td>O1</td>
<td>3616(1)</td>
<td>5034(1)</td>
<td>8239(1)</td>
<td>23(1)</td>
</tr>
<tr>
<td>O3</td>
<td>2962(1)</td>
<td>5512(1)</td>
<td>8864(2)</td>
<td>26(1)</td>
</tr>
<tr>
<td>O4</td>
<td>1487(1)</td>
<td>3725(1)</td>
<td>9141(2)</td>
<td>26(1)</td>
</tr>
<tr>
<td>N1</td>
<td>1286(2)</td>
<td>4454(1)</td>
<td>6629(2)</td>
<td>22(1)</td>
</tr>
<tr>
<td>N2</td>
<td>3119(2)</td>
<td>3414(1)</td>
<td>8057(2)</td>
<td>23(1)</td>
</tr>
<tr>
<td>N3</td>
<td>3996(2)</td>
<td>4140(1)</td>
<td>10629(2)</td>
<td>23(1)</td>
</tr>
<tr>
<td>C1</td>
<td>1433(2)</td>
<td>3728(1)</td>
<td>5889(2)</td>
<td>29(1)</td>
</tr>
<tr>
<td>C2</td>
<td>2759(2)</td>
<td>3497(1)</td>
<td>6539(2)</td>
<td>29(1)</td>
</tr>
<tr>
<td>C3</td>
<td>4418(2)</td>
<td>3295(1)</td>
<td>9007(2)</td>
<td>31(1)</td>
</tr>
<tr>
<td>C4</td>
<td>4523(2)</td>
<td>3352(1)</td>
<td>10491(2)</td>
<td>29(1)</td>
</tr>
<tr>
<td>O5</td>
<td>2628(2)</td>
<td>1744(1)</td>
<td>8092(2)</td>
<td>44(1)</td>
</tr>
</tbody>
</table>

*U_{eq} is defined as one-third the trace of the isotropic U_{ij} tensor.

Table 5.2: Bond Lengths of Cr(C_4H_13N_3)(O_2)_2.H_2O (Å) [7]

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr-O3</td>
<td>1.8702(15)</td>
</tr>
<tr>
<td>Cr-O2</td>
<td>1.8753(15)</td>
</tr>
<tr>
<td>Cr-O4</td>
<td>1.9005(15)</td>
</tr>
<tr>
<td>Cr-O1</td>
<td>1.9084(14)</td>
</tr>
<tr>
<td>Cr-N2</td>
<td>2.04819(19)</td>
</tr>
<tr>
<td>Cr-N1</td>
<td>2.0705(17)</td>
</tr>
<tr>
<td>Cr-N3</td>
<td>2.0840(18)</td>
</tr>
<tr>
<td>O1-O2</td>
<td>1.465(2)</td>
</tr>
</tbody>
</table>
The X-ray crystal structure was used to determine the authenticity of the sample. Cr(dien) crystallizes in the monoclinic $C2/c$ space group with the unit cell dimensions $a = 12.216 \text{ Å}$, $b = 16.545 \text{ Å}$, $c = 10.525 \text{ Å}$, $\alpha = \gamma = 90^\circ$, $\beta = 115.531^\circ$ and $Z = 8$ [6]. The atomic coordinates and bond lengths are summarized in Tables 5.1 and 5.2. Figure 5.2 shows the shape of Cr(dien) crystal with the three assigned axes.

Figure 5.2: Structure of Cr(dien) crystal with the three axes assigned [6].
The projected view down the 010 axis of the crystal, shown in Figure 5.3 suggested the possibility of magnetic exchange interactions confined to the 100-001 plane. Within the plane, Cr-Cr nearest neighbors are spaced by less than 5.8 Å with the average distance being 5.64 Å. The individual layers are separated by about 6.90 Å, which should result in significantly weaker interlayer spin correlations.

![Cr(dien) crystal projection](image)

Figure 5.3: Projection down the 010 axis of the Cr(dien) crystal showing the 2-d exchange pathways. The blue arrows highlight Cr-Cr nearest neighbors of average distance 5.64 Å. The interlayer spacing is approximately 6.9 Å [6].

### 5.4 Summary of earlier results on 2-d antiferromagnet Cr(C_4H_13N_3)(O_2)H_2O, Cr(dien)

#### 5.4.1 Magnetic Susceptibility

Figure 5.4 shows temperature dependent magnetic susceptibility ($\chi(T)$) measurements on oriented samples of Cr(dien) single crystals [6] with the field aligned along the three crystal axes 100, 010, and 001. In each case, the susceptibility passes through a broad maximum suggestive of low-dimensional (1 or 2-d) antiferromagnetic correlations [85, 122] with the maxima being slightly anisotropic. The orientation dependent positions of $\chi_{max}$ and $T(\chi_{max})$ are summarized in Table 5.3. These differences will be discussed below.
On the basis of the X-ray evidence for planar exchange pathways and the observation of broad maxima in the susceptibility, these data were analyzed according to the Heisenberg model [122] for an antiferromagnet with four nearest neighbors, as in the case for Cr(dien). The Hamiltonian describing such a system is

$$H = -2J \sum_{i,j} S_i S_j - g \beta H \sum_i S_{i(z)}$$

(5.1)

where the first term in Eq. (5.1) accounts for the exchange interactions and the second term is the Zeeman interaction. Because no closed form solution to this model exists, Rushbrooke and Wood [104] developed a high temperature series expansion technique to describe these systems. Later, Lines [105] adapted their method to suit $S = 1$ lattices resulting in Eq. (5.2).
Table 5.3: Cr(dien) magnetic susceptibility parameters [6]

<table>
<thead>
<tr>
<th>Orientation</th>
<th>-2J/k_B (K)</th>
<th>g</th>
<th>T(χ_max) (K)</th>
<th>χ_max (emu/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H // 100</td>
<td>2.86 ± 0.0067</td>
<td>1.82 ± 0.0022</td>
<td>5.89</td>
<td>0.0448</td>
</tr>
<tr>
<td>H // 010</td>
<td>2.71 ± 0.0077</td>
<td>1.92 ± 0.0020</td>
<td>5.99</td>
<td>0.0518</td>
</tr>
<tr>
<td>H // 001</td>
<td>2.88 ± 0.0087</td>
<td>1.96 ± 0.0087</td>
<td>5.79</td>
<td>0.0525</td>
</tr>
</tbody>
</table>

\[
\frac{N g^2 \beta^2}{|J| \chi(T)} = 3\theta \left( 1 + \frac{8}{3\theta} + \frac{22}{9\theta^2} + \frac{1.19}{\theta^3} + \frac{1.19}{\theta^4} + \frac{1.41}{\theta^5} + \frac{0.40}{\theta^6} \right)
\]  

(5.2)

Here, \( \theta = k_B T/2|J| \), \( N \) is Avagadro’s number, \( g \) the electronic \( g \)-factor, and \( \beta \) the Bohr magneton. This procedure approximately describes the susceptibility for \( T > T(\chi_{\text{max}}) \) and fails in the lower \( T \) regime. Fits of Eq. (5.2) to the single crystal \( \chi(T) \) data are shown as red lines in Figure 5.4. The corresponding fitting parameters for the three orientations are \( g_{010} = 1.92, 2J_{010}/k_B = -2.71 \) K; \( g_{001} = 1.96, 2J_{001}/k_B = -2.86 \) K; and \( g_{100} = 1.82, 2J_{100}/k_B = -2.88 \) K. These are also given in Table 5.3. Further clarification for the appropriateness of this model was gained by comparison with the tabulated \( \chi_{\text{max}}T(\chi_{\text{max}})/C \) values of de Jongh and Miedema [122]. For the \( S = 1 \) Heisenberg model on a square lattice, they calculate \( \chi_{\text{max}}T(\chi_{\text{max}})/C = 0.344 \). With powder measurements the slope of \( 1/\chi \) versus \( T \) helped to determine \( C = 0.93 \) emu.K/mol, where \( C \) is the Curie constant.

The Curie law is given by:

\[
\chi_p = C/T
\]

where \( \chi_p \) is the paramagnetic susceptibility, \( C \) is the Curie constant and \( T \) is the temperature. Using the \( \chi_{\text{max}}T(\chi_{\text{max}}) \) values from the \( H // 010 \) data, an agreeable \( \chi_{\text{max}}T(\chi_{\text{max}})/C = 0.344 \) was obtained for Cr(dien), which supported the validity of proposed model. The orientation dependence of \( \chi_{\text{max}} \) and \( T(\chi_{\text{max}}) \) may be explained through \( g \)-value anisotropy as well as weak exchange interactions between layers. The position of \( \chi_{\text{max}} \) is primarily dependent on the magnitude of \( g \), with \( \chi_{\text{max}} \) increasing proportional to \( g \). Hence, the majority of the orientation dependence of \( \chi_{\text{max}} \) can be
attributed to $g$-anisotropy, expected to be present for Cr(IV) ions in a low symmetry environment. The $g$-values determined from fitting the susceptibilities to eq. (5.2) were in line with those of the other peroxochromate lattices [30,123-131]. A rough theoretical estimate for the in-plane anisotropy parameter $\alpha$ is given by Eq. (5.3) [122]

$$\alpha = 1 - \left( \frac{g_B}{g_C} \right)^2$$

(5.3)

which equals 0.04 for the Heisenberg systems. Employing the best-fit values $g_B = g_{010} = 1.92$ and $g_C = g_{001} = 1.96$, the value of $\alpha$ was obtained to be 0.04 for Cr(dien), further supporting the 2-d antiferromagnet assignment.

Notable in Figure 5.4 is the anomalous upturn in the $H//010$ susceptibility at 2.71 K. This orientation is that of Figure 5.3 with the field going into the page. Because the field is applied normal to the magnetic layers, this is also termed the perpendicular susceptibility. Such behavior in the perpendicular susceptibility has been predicted by spin-wave theory and has been observed in many 2-d antiferromagnets [122]. It arises through zero-point spin fluctuations facilitated by magnetic ion anisotropy. Thus, in the case of Cr(IV), zero field splitting may induce this upturn. The temperature at which the upturn occurs, 2.71 K, corresponds to the Néel temperature where 3-d ordering ensues.

### 5.4.2 Heat Capacity Measurements

In practice, one expects a magnetic phase transition to long range ordering when interlayer exchange interactions become significant. This transition temperature is the so-called Néel temperature ($T_N$) and should be evident by a singularity in the heat capacity. A preliminary estimate for $T_N$ can be obtained by a plot of $d\chi//T$ vs $dT$, the Fisher heat capacity [132]. The Fisher heat capacity for the $H//001$ data of Figure 5.4 is shown in Figure 5.5 and yields a sharp cusp at 2.55 K corresponding to $T_N$. 

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Figure 5.5: The Fisher heat capacity of Cr(dien). The sharp cusp provides an estimate of $T_N$ at 2.55 K [7].

The magnetic heat capacity data recorded by Chris Ramsey shown in Figure 5.6 indicated the general trend: as the field is increased; the magnitude of the broad component related to 2-d correlations is suppressed to lower values of $C_{mag}$. Also observed was the position of $T_N$ which is strongly field dependent and progresses through a maximum in temperature between 6 and 8 T. It is well known that $T_N$ generally decreases with increasing field [122]; therefore the behavior observed at 8 T seemed anomalous and needed further study. My dissertation work started from this observation. New heat capacity measurements on the freshly synthesized crystals were performed between 0-9 T on PPMS to check if the anomalous behavior observed at 8 T is real. Figure 5.7 presents the preliminary results obtained.
Figure 5.6: The magnetic heat capacity (lattice subtracted) of Cr(dien). The magnitude of the broad contribution is depressed with increasing field and the position of $T_N$ is strongly field dependent [7].
Figure 5.7: Heat capacity $C_p$ versus temperature $T$ of Cr(dien) single crystal for $H \parallel b$ in applied magnetic fields between 0-9T. The breaking line is meant to serve only as a guide to the eye.
5.5 New Results and Discussion

5.5.1 Torque magnetometry

Figure 5.8: Field dependence of the signal obtained for Cr(dien) single crystal in torque magnetometry. The crystal was oriented in way that $H \parallel b$ axis of the crystal.

Figure 5.8 shows an example of the raw data for field dependence of the signal obtained at a fixed temperature of 0.59 K. A step like behavior was observed for each temperature as the field was increased from 0 to 18 Tesla. The exact field at which the transition occurs for a fixed temperature is found by taking the derivative of this plot. Plotting transition temperature $T$ as a function of magnetic field $H$ yields the phase boundary shown in Figure 5.9.
For analysis of the results we rely on the specific heat measurements rather than the results obtained by torque magnetometry. Specific heat is better than any other tool for an accurate determination of a thermodynamic phase transition temperature. This is particularly so for second order transitions such as that of our sample. The reason is that in a first order transition, all relevant macroscopic quantities have a jump. One may measure any of those quantities and determine the transition temperature. In contrast, in a second order transition there is no such jump, making the determination of the transition temperature difficult. Specific heat is an exception. Since $C = T(dS/dT)_H$, it directly detects a change in the temperature dependence of the entropy. If we measure a magnetization $M$, we will have to find a change in the temperature dependence of $M$ at $T_C$ which is hard to do accurately. Magnetic torque is even worse, since it detects only an anisotropy in $M$, not the whole $M$. 

Figure 5.9: Magnetic Field $H$ – transition temperature $T$ phase diagram from torque magnetometry data obtained on single crystal of Cr(dien) for $H \parallel b$. 

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5.5.2 Specific Heat and Magnetocaloric Effect (18/20T Superconducting Magnet, with Dilution Refrigerator): Results and Analysis

The specific heat and magnetocaloric effect measurements have been performed for magnetic fields $H \parallel b$ from 0 to 18 T and from temperatures of 0.2 K to 3 K as described in chapter II. These measurements have served to define previously undetermined phase boundaries in the field-temperature phase space.

Analysis of the magnetocaloric effect data is straightforward. Figure 5.9 shows the results of magnetocaloric effect measurements. The curves for sweeping the field up and down are averaged, thus giving a baseline temperature as a function of the field. To determine the field at which the second order transition occurs, the maximum temperature deviation for either the upward or downward sweeping field is evaluated with respect to the baseline, providing an upper and lower limit on the transition field. The average of these two limits is taken as the transition temperature.
Figure 5.10: Typical magnetocaloric effect peaks from Cr(dien) single crystal at different temperatures. The arrows indicate the field scan direction. Red curves indicate increasing magnetic field and blue curves indicate decreasing magnetic field.
Any point at which the trace for the upward sweeping field and downward sweeping field cross indicates according to Eq. 2.10b that \((\partial M/\partial T)_H = 0\). This could indicate either a second order phase transition or simply an extremum in the magnetization. In these cases, complimentary measurements must be performed in order to confirm which is the case.

For each temperature a clear second order phase transition is seen in the field sweeps. As can be seen, the field at which the transition occurs increases with decreasing temperature. The positions of the transitions are plotted on the phase diagram of Figure 5.12.

The specific heat measurements from 0 to 12 T show peaks in the temperature range between 0.8 K to 3.0 K, as shown in Figure 5.11. The peak positions are plotted on the phase diagram of Figure 5.12. It is seen that as the field is increased from 5 T to 12 T, the specific heat decreases. This is expected since as the field increases, the Zeeman splitting of energy levels increases. As this transpires, the thermally activated population of the higher levels decreases resulting in a smaller heat capacity.

Together with the results of magnetocaloric measurements, it is seen that they lie along the same curve, which fits well to a power law dependence with a zero temperature intercept \(12.392 \pm 0.003\) T and exponent \(2.01 \pm 0.02\). The description of the power law used here is as below.

A key prediction of the behavior of system as \(T \to 0\) is obtained by fitting the magnetic field versus transition temperature data in the vicinity of the quantum critical point, to the power law, \(H - H_c \propto T^\alpha\), where \(H\) is the magnetic field, \(T\) is the transition temperature, \(H_c\) is the critical field and \(\alpha\) is the critical exponent. At a quantum critical point (QCP), quantum fluctuations diverge in space and time, leading to exotic phenomena that can be observed at non-zero temperatures. The value of \(\alpha\) is very sensitive to the value of \(H_c\) chosen for the fit, which is difficult to extrapolate from higher temperature data. In this present study, we obtain \(\alpha\) from magnetocaloric effect measurements to dilution refrigerator temperatures using an extrapolation method to zero temperature introduced by Sebastian et al [12].

As a first step, we fix \(\alpha\) and fit the \(H\) vs \(T\) data of Figure 5.12 to determine \(H_c\). This fit is performed between 0.20 K and \(T_{\text{max}}\) (as labeled in Figure 5.12) and repeated for different trial values of \(\alpha = 1.5, 1.75\) and 2.0. The resultant \(H_c\) values as
a function of $T$ for three values of $\alpha$ are shown in Figure 5.13. Linear extrapolations of the low-temperature behavior of $H_c$ for $\alpha = 1.5$, 1.75 and 2 yield three different values of $H_c$ at $T = 0$ as shown in Figure 5.14. Taking the weight average of these three different $H_c$ values produce final $H_c = 12.392 \pm 0.003$ T. In the expression $H - H_c \propto T^\alpha$, $H_c$ can now be fixed, and the phase diagram of Figure 5.12 is fit to determine $\alpha$ as a function of $T_{\text{max}}$ as shown. Linear extrapolation to $T = 0$ (Figure 5.15) show that $\alpha(T = 0)$ is $2.01 \pm 0.02$, which is consistent with the predicted value of $\alpha = 2$ for an Ising magnet.

To understand the magnetic behavior of solids, one can consider particular microscopic model of the magnetic interactions. A commonly studied model is the Ising model, in which the spins are only allowed to point up or down, i.e. we only consider the $z$ component of the spins, The Hamiltonian of this model is

$$H = -\sum_{<ij>} J S_i^z S_j^z$$

(5.4)

Here the dimensionality of the order parameter $D$ is equal to 1 (the spins are only allowed to point along $\pm z$).

Figure 5.16 shows the fitting of phase transition line to the magnetocaloric effect data using the power law $H - H_c = b T^\alpha$, where $H_c = 12.392 \pm 0.003$ T, $b = 0.692$ and $\alpha = 2.01 \pm 0.02$. The point at $T = 0$, where the phase transition line meets the y-axis at $H_c = 12.392 \pm 0.003$ T is our quantum critical point. At this quantum critical point, the system undergoes a quantum phase transition. A quantum phase transition is defined as the phase transition that occurs at the absolute zero of temperature, $T = 0$. It is important to study the quantum phase transitions because they leave characteristic fingerprints in the physical properties of materials at $T > 0$, and these fingerprints are often visible at room temperatures. A complete understanding of the physical properties of the materials emerges only upon understanding the relationship of their $T > 0$ K phases to the quantum phase transitions at $T = 0$.

Figure 5.17 shows the magnetic field versus transition temperature $T$ plot from different techniques: Magnetocaloric effect and heat capacity (18/20 magnet, with dilution fridge), heat capacity (PPMS). The solid green line represents a power-law curve for $H_c = 12.392 \pm 0.003$ T and $\alpha = 2.01 \pm 0.02$. The curve starts deviating towards
the high temperature, which shows that the power law universal behavior is valid only for $T \to 0$ [12]. Another important aspect observed in this plot was that in the low field heat capacity measurements, the transition temperature data point taken at 1 T did not fall on the same curve obtained for 0 – 4 T. A new set of heat capacity measurements were performed on a different Cr(dien) crystal between 0 T and 2 T which confirmed our result. The reason for this deflection in behavior at 1 T is not known yet.

Figure 5.11: Specific heat $C_p$ versus temperature $T$ of Cr(dien) single crystal for $H \parallel b$ in applied magnetic fields of 0-12 T. The breaking line is meant to serve only as a guide to the eye. Second order phase transitions are clearly observed between 0 t to 10 T. At higher fields, the transition becomes harder and harder to observe.
Figure 5.12: Magnetic field $H$ - transition temperature $T$ phase diagram from specific heat and magnetocaloric-effect data of Cr(dien) single crystal with $H \parallel b$. The solid purple curve shows that the specific heat data and the magnetocaloric effect data lie on the same curve. Magnetocaloric-effect data from 0.2 K to $T_{\text{max}}$ is used for further analysis.
Figure 5.13: Results from fit of data by the expression $H - H_c \propto T^\alpha$ up to a maximum fit temperature $T_{max}$ shown by vertical arrow in Figure 5.12. The values of $H_c$ are plotted against the transition temperature for various trial values of $\alpha$. The data points shown by solid circles were used for further analysis.
Figure 5.14: Straight line fit to the $H_c$ versus $T$ for different values of $\alpha$ to determine the final value of critical field $H_c$ as $T \to 0$. 
Figure 5.15: $\alpha$ versus $T$ plot obtained by fitting the power law $H = 12.392 + b \cdot T^\alpha$ from 0.26 K to $T_{\text{max}}$ shown in Figure 5.11. Weight average of the $\alpha$ values shown by solid circles was used to find the final value of $\alpha = 2.01 \pm 0.02$. The data shown by solid circles was used to perform weight averaging.
Figure 5.16: Magnetic field $H$ versus transition temperature $T$ plot from magnetocaloric- effect measurements. The solid green line represents a power-law curve for $H_c = 12.392 \pm 0.003$ T and $\alpha = 2.01$. 
Figure 5.17: Magnetic field versus transition temperature $T$ plot for Cr(dien) single crystal with $H \parallel b$ from different techniques: Magnetocaloric effect and specific heat (using 18/20 superconducting magnet (SCM1) at NHMFL and PPMS). The solid green line represents a power-law curve for $H_c = 12.392 \pm 0.003$ T and $\alpha = 2.01 \pm 0.02$. The curve starts deviating towards the high temperature, which shows that the power law universal behavior is valid only for $T \to 0$ [12]. The red points shown by open circles is another set of data obtained on a different Cr(dien) single crystal between 0 T and 2 T.
5.6 Conclusions:

Based on a detailed analysis of the magnetocaloric effect in the vicinity of quantum critical point, using the power law $H - H_c \propto T^\alpha$, we predict that Cr(dien) undergoes a quantum phase transition at the magnetic field $H_c = 12.392 \pm 0.003$ T, where a highly polarized antiferromagnetic phase gives way to a field-induced ferromagnetic phase. The value of critical exponent $\alpha$ obtained is $2.01 \pm 0.02$, which predicts that Cr(dien) behaves as a 3-d Ising magnet at low temperatures. In conclusion our magnetic susceptibility data indicates, and the absence of EPR suggests, that this material has strong single-ion anisotropy. It is very likely therefore that the 3-d Ising critical exponent arises from the easy axis due to the single-ion anisotropy lying somewhere on the ab plane. In our opinion, this result should stimulate new interest, both theoretical and experimental, in the studies of quantum phase transitions and 3-d Ising behavior of Cr(IV) compounds at low temperatures. It also opens a new angle for chemists to start the synthesis of new materials of this unusual oxidation state of Cr and related compounds.
5.7: A relaxation phenomenon near QCP: Quantum-fluctuations-driven heat release from hydrogen nuclear spins of Cr(dien)

In this section we report the finding of a relaxation phenomenon in Cr(dien) near the QCP [133]: Quantum-fluctuation-driven release of heat from nuclear spins. Cr(C_4H_13N_3)(O_2)H_2O (Cr(dien)) has been chosen to study the fluctuation-induced heat release from temperature-quenched nuclear spins near the quantum critical point, because of its large number of hydrogen nuclear spins [6,116]. As described earlier, this quasi-two-dimensional quantum magnet has a magnetic-field-tuned QCP at the field $H_c = 12.3$ T, where a highly polarized antiferromagnetic phase gives way to a field-induced ferromagnetic phase.

In the monoclinic crystal structure of Cr(dien), the $S = 1$ spins of Cr(IV) form a square lattice along the crystallographic $ac$ plane, with an exchange energy $J$ of 2.71-2.88 K. The spins order antiferromagnetically at $T_N = 2.55$ K in zero magnetic field [6]. Application of high magnetic field depresses the ordering temperature, pushing it to zero at the critical field $H_c$. The study reported here has been performed near this QCP [133].

The experiment is performed in a relaxation calorimeter described in chapter 2, section 2.5 [42,134]. A 1.02 mg single crystal of Cr(dien) is placed on the sample platform, weakly linked to the thermal reservoir through the leads for the thermometer and heater. This geometry allows the sample temperature to be raised with the heater with ease and to drop rapidly to the reservoir temperature when the heater is turned off. It also enables the detection of spontaneously released heat in the sample as an observable temperature difference between the sample and the reservoir.
Figure 5.18: Procedure of the experiment (see text). Broken line, terminating in a quantum critical point at $T = 0$, is the boundary between the highly polarized paramagnetic phase and the antiferromagnetic phase [133].

The procedure of the experiment is illustrated in Figure 5.18. First, the sample is heated from temperature $T_0$ (point $P_1$ or $P_1'$ in the figure) of the thermal reservoir to temperature $T_q$ (point $P_2$ or $P_2'$) ranging from 266 mK to 1.52 K, in magnetic field $H_q$ applied perpendicular to the $ac$ plane of the crystal. After 1.4 min at $T_q$, the sample is rapidly cooled back to $T_0$ in 1.8 s by turning off the heater. This temperature quenching leaves the hydrogen nuclear spins frozen in a nonequilibrium high-energy state corresponding to $T_q$. Subsequently, the magnetic field is swept at 0.2 T/min or 0.1 T/min through the critical field $H_c$. The field sweeps are made at four different $T_0$ ranging from 96 mK to 261 mK.

As the swept field approaches $H_c$, heat is released in the sample, manifesting itself as a pronounced peak in the temperature difference $\Delta T$ between the sample and the thermal reservoir, as shown in Figure 5.19(a) and 5.19(b). The heat release occurs only during the first field sweep after the temperature quenching of the sample from $T_q$, not during subsequent sweeps [135]. The amount of heat released $Q$ is obtained from the data via
\[ Q = \int k \Delta T dH / H \]  \hspace{1cm} (5.5)

Where \( k \) is the thermal conductance of the weak link between the sample and the thermal reservoir, and \( H \) the field-sweep rate. As shown in Figures 5.20(a) and 5.20(b), \( Q \) depends on \( T_q, H_q, \) and \( T_0 \). These dependences indicate unambiguously that the heat is indeed released from the hydrogen nuclear spins, as the following analysis reveals.

When hydrogen nuclear spins in magnetic field \( H_q \) are initially frozen in a nonequilibrium high-energy state determined by temperature \( T_q \)—while the lattice cools rapidly to temperature \( T_0 \)—and subsequently equilibrate with the lattice at another field \( H \), the amount of heat released by them is

\[ Q = n_H n R \left( \frac{\hbar \gamma}{k_B} \right)^2 \frac{I(I + 1)}{3} \left( \frac{H}{T_0} - \frac{H_q}{T_q} \right) H \]  \hspace{1cm} (5.6)

Where \( n_H \) is the number of hydrogen nuclear spins (per formula unit) that participate in heat release, \( n \) sample’s mole number, \( R \) the gas constant, \( \hbar \) the Planck constant, \( k_B \) the Boltzmann constant, and \( \gamma \) and \( I = \frac{1}{2} \) the gyromagnetic ratio and spin of the hydrogen nucleus.
Figure 5.19: Temperature difference $\Delta T$ between the sample and the thermal reservoir as a function of the magnetic field during field sweeps at 0.2 T/min. The thermal reservoir is held at 181 mK. Temperature $T_q$ from which the sample has been quenched ranges from 266 mK to 1.52 K. (b): Evolution of $\Delta T$ when the thermal reservoir is held at 96 mK, as the field is swept at 0.1 T/min. $T_q$ ranges from 300 mK to 797 mK. In (a) and (b), the peaks to the right are observed during downward field sweeps and those to the left during upward sweeps. The field indicated in the legends are $H_q$ [133].
The equation takes into account that the nuclear-spin temperature just before the heat release is $HT_q/H_q$ instead of $T_q$, as a result of the field sweep from $H_q$ to $H$ being adiabatic for the nuclear spins except very near $H$.

For $T_0 = 181$ mK, good agreement between experiment and Equation 5.6 is obtained with $n_H = 10$, as shown in Figure 5.20(a), except for a few points for which $H_q$ is 18 T or 16 T [136]. At $T_0 = 96$ mK, the peak that appears at 12.76 T in Figure 5.19(b) during downward field sweeps from 13.5 T is very sharp while $\Delta T > 36$ mK, i.e., while the sample temperature $T_0 + \Delta T$ is higher than 132 mK. This indicates that hydrogen nuclear spins whose relaxation times $\tau$ are very short when $T_0 > 132$ mK now participate in heat release. When $T_0 = 181$ mK, they have evidently reached thermal equilibrium with the lattice before each field sweep starts and therefore do not participate in heat release. As shown in Figure 5.20(b), good agreement between Equation 5.6 and the $T_0 = 96$ mK data for $H_q = 13.5$ T is obtained with $n_H = 15$, of which five whose $\tau$ are very short at $T_0 > 132$ mK are assumed to freeze at a nonequilibrium high-energy state at 132 mK instead of $T_q$. When quenched at $H_q = 10$ T, in the antiferromagnetic phase, $n_H = 10$ gives better agreement with the data, suggesting that those five hydrogen nuclear spins do not participate in heat release even at $T_0 = 96$ mK.

Cr(dien) contains 15 hydrogen atoms per formula unit, as shown in Figure 5.1. Among the 13 in the Cr(dien) molecule, the five bonded to nitrogens are closer to the Cr(IV) ion than eight that are bonded to carbons [137]. It is very likely that the five hydrogens with short nuclear-spin $\tau$ are those bonded to the nitrogens and thus experience stronger fluctuating dipolar field and transferred hyperfine field of the Cr(IV) ion, whereas the ten hydrogens with longer $\tau$ are those bonded to the carbons and the two in the water molecule.
Figure 5.20: Amount of heat released at (a) 181 mK and (b) 96 mK as a function of $T_q$, the temperature from which the sample has been rapidly quenched. In (a), the sample has been quenched at $H_q = 6$ T (O), 9 T (♦), 11.5 T (▼), 13.5 T (▲), 16 T (●), and 18 T (■). The lines represent Eq. (5.6) with $n_H = 10$: dash-dotted line for $H_q = 11.5$ T, dotted line 13.5 T, dashed line 16 T, and solid line 18 T. In (b), the sample has been quenched at 10 T (♦) and 13.5 T (■). The lines representing Eq. (5.6) are with $n_H = 10$ for $H_q = 10$ T (dashed line) and with $n_H = 15$, of which five are assumed to freeze only at 132 mK, for 13.5 T (solid line) [133].
Figure 5.21: Magnetic fields and temperatures of the peaks in the $\Delta T$ curves (squares), marking a quantum critical region delimited by two straight lines through the data points. Solid squares are for peaks at a sweep rate of 0.1 T/min, open squares at 0.2 T/min. Circles represent the phase boundary-detected by the magnetocloric effect-between the antiferromagnetic (AF) and highly polarized paramagnetic (P) phases, with the dashed line from a power-law fit of data points up to 0.84 K. At zero temperature, the P phase turns into a field-induced ferromagnetic phase [133].

The position of the heat-release peaks [138] are shown in Figure 5.21 along with the phase boundary between the highly polarized antiferromagnetic phase and similarly highly polarized paramagnetic phase, which turns into the field-induced ferromagnetic phase at zero temperature, of Cr(dien) near its QCP at $H_c$. This diagram suggests that, in the zero-temperature limit, the loci of the peaks converge on the QCP.
5.7.1 Conclusions

In conclusion, our results provide unambiguous evidence that temperature quenching of Cr(dien) leaves the hydrogen nuclear spins frozen in a nonequilibrium high-energy state and, as the magnetic field is then brought close to the QCP, quantum fluctuations of the Cr(IV) ionic spins quickly anneal them to reach thermal equilibrium with the lattice. These results also imply that the quantum-fluctuation-driven heat release from nuclear spins is a generic phenomenon to be found near a variety of QCPs. Because of the inextricable link between dynamic and static properties in quantum criticality, quantum critical systems are predicted to exhibit interesting, nontrivial relaxation phenomena during and after a sweep of a control parameter such as magnetic field and pressure through the QCP [139] and also after temperature quenching near the QCP [140]. Our results warn, however, that the response of nuclear spins—which is nearly ubiquitous to those changing parameters and to quantum fluctuations must be carefully taken into account in real solids.
This focus of this dissertation is to examine the magnetic and thermodynamic properties of three new Spin-1 compounds. We have mainly characterized three compounds using EPR, dc magnetic susceptibility and thermodynamic techniques. The compounds are \([(\text{CH}_3\text{CN})_5\text{VOV(\text{CH}_3\text{CN})}_5][\text{BF}_4]_4\), \(\text{Cr(NH}_3)_3(\text{O}_2)_2\) and \(\text{Cr(C}_4\text{H}_{13}\text{N}_3)(\text{O}_2)_2\cdot\text{H}_2\text{O}\). These studies were undertaken with several questions in mind: (i) what are the magnetic properties of \((\text{V}^{3+})_2\) containing molecules and can these be used as building blocks for single molecule magnets. (ii) What magnetic ordering phenomena are present in rare \(\text{Cr(IV)}\) lattices \(\text{Cr(NH}_3)_3(\text{O}_2)_2\) and \(\text{Cr(C}_4\text{H}_{13}\text{N}_3)(\text{O}_2)_2\cdot\text{H}_2\text{O}\) and what is the effect of magnetic field on the phase transition temperature of these compounds.

Chapter 3 details the magnetic and EPR studies of \([(\text{CH}_3\text{CN})_5\text{VOV(\text{CH}_3\text{CN})}_5][\text{BF}_4]_4\). Magnetic susceptibility (\(\chi\)) and magnetization studies suggested that the two \(\text{V}^{3+}\) centers are ferromagnetically coupled with \(J \approx 72\) K, yielding a ground state with a total spin \(S_{\text{total}} = 2\). High field EPR measurements show that the compound is axially symmetric with \(g_\parallel = 1.9825\), \(g_\perp = 1.9725\) and \(D = 0.57 \pm 0.03\) K. The \(D\) value is positive which implies that it cannot become a single-molecule magnet.

While 2-d magnetic lattices are well known [101-111], those containing \(\text{Cr(IV)}\) species are very uncommon. The work presented on \(\text{Cr(IV)}\)-diperoxoamines in this dissertation was motivated by the need to provide new magnetic data on solids in which the \(\text{Cr(IV)}\) is not a dopant or impurity. We wished to study magnetic ordering phenomena in these materials, which could lead to new \(\text{Cr(IV)}\) based magnets that might be superior to, or serve as precursors for, \(\text{CrO}_2\).

Chapter 4 contains X-ray diffraction and thermomagnetic measurements on a 3-d antiferromagnet \(\text{Cr(NH}_3)_3(\text{O}_2)_2\) (\(\text{Cr}^{IV}\)-TADP). Earlier reported magnetic susceptibility and \(C_p(T)\) measurements [6] suggested it to be a classical 3-d antiferromagnet which orders at \(T_N = 8.46\) K. Only 38% of the magnetic entropy was removed above \(T_N\) implying that nominal short range correlations occur, and the system is dominated by 3-d exchange interactions. In order to obtain supporting evidence that
Cr$^{IV}$-TADP is antiferromagnetic below the transition point, we tried to demonstrate the existence of a phase boundary between antiferromagnetic and paramagnetic regions. The experimental procedure utilized for this purpose was heat capacity measurements in magnetic fields. Measurements of the heat capacity of Cr$^{IV}$-TADP in external magnetic field showed that the position of the singularity shifts to lower temperatures with increasing $H$. It is found that the singularity broadens when $H$ increases and this ultimately restricts the accuracy of the determination of the position, $T_N$ of the singularity in $C_p$. The magnetic field versus transition temperature phase diagram showed that the compound behaves like a standard 3-d antiferromagnet. We thus searched for another $S = 1$ system with unusual properties.

In Chapter 5 X-ray diffraction and thermomagnetic measurements on Cr(C$_4$H$_{13}$N$_3$)(O$_2$)$_2$·H$_2$O (Cr(dien)). Earlier reported X-ray structure and $\chi(T)$ data suggested [6] it to be a 2-d antiferromagnet with dominant exchange interactions confined to the 001-100 plane. The analysis of single crystal $\chi(T)$ data yielded orientation dependent g-values and exchange constants which were $g_{010} = 1.92$, $J_{010}/k_B = -2.71$ K; $g_{001} = 1.96$, $J_{001}/k_B = -2.86$ K; and $g_{100} = 1.82$, $J_{100}/k_B = -2.88$ K. Here the indices coincide with the crystal’s alignment in the magnetic field. The heat capacity and entropy data supported this analysis and were consistent with the presence of short range correlations above the 3-d ordering temperature at 2.55 K. We wished to study the effect of magnetic field on this 3-d ordering temperature. Therefore we carried out torque magnetometry, heat capacity and magnetocaloric effect measurements at very high fields of 0 – 18 Tesla and temperatures in the millikelvin range. The analysis of the magnetocaloric effect data showed that this quasi-two-dimensional quantum antiferromagnet Cr(dien) has a magnetic-field-tuned quantum critical point (QCP) at 12.3 T, where a highly polarized antiferromagnetic phase turns into a field-induced ferromagnetic phase. The results provide the first report of the Quantum phase transition in Cr(IV)-diperoxoamine complexes and indicate ways that one may further design Cr(IV) systems with desireable magnetic properties.

Another important study performed near the QCP using this compound was to investigate the dynamics of quantum fluctuations that underlie the quantum criticality. Cr(dien) compound was chosen for this study because of its large number of
hydrogen nuclear spins. The study showed calorimetric evidence for quantum fluctuation-induced heat release from temperature quenched hydrogen nuclear spins near the QCP.

Overall, the work detailed in this dissertation should prove valuable in the future progression of molecular magnetism. We believe that our results should provide a basis for further theoretical and experimental investigations such as neutron scattering or very high frequency EPR measurements on the Cr(IV) complexes.
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32. The thermal charging can be described by \( T = T_0 + \Delta T(1-e^{-t/\tau}) \).


36. Model 400 TLM dilution refrigerator, Oxford Instruments plc, Witney, Oxfordshire OX29 4TL, UK.


38. Series X518 collet sockets with solder tail pins, Aries Electronics, Inc., Frenchtown, NJ 08825-0130, USA.

39. Emerson & Cuming, Inc., Canton, MA 02021, USA.

40. DuPont Engineering Polymers, Newark, DE 19714-6100, USA.

41. Epoxy Technology, Inc., Billerica, MA 01821, USA.


44. Wakefield Thermal Solution, Pelham, NH 03076, USA.


51. Keithley Instruments, Inc., 28775 Aurora Rd., Cleveland, OH 44139, USA.

52. Andeen-Hagerling, Inc., 31200 Bainbridge Rd., Cleveland, OH 44139-2231 USA.
53. Model GR-200A-50-0.1B, Serial 28739, Calibration 368717.


81. Ozarowski, A. Spin; National High Magnetic Field Laboratory: Tallahassee, FL.


134. The thermometers of the calorimeter have been self-calibrated in magnetic fields, by measuring the heat capacities of standard materials in situ. In the field range of the present experiment, calibration uncertainties are about 1.0% at 0.8 K and about 1.8% at 0.1 K.

135. \( \Delta T \) during the subsequent sweeps, exhibiting only the magnetocaloric effect of at most 1 mK and eddy-current heating by 8 mK (\( T_0 = 181 \) mK) and 3 mK (\( T_0 = 96 \) mK), have been subtracted from the data shown in Figures 5.18, 5.19 and 5.20.

136. For those points, 1.4 min of waiting is probably insufficient to thermalize the hydrogen nuclear spins.

137. The five hydrogens bonded to the nitrogens are located at 2.40-2.52 Å from the Cr(IV), whereas the eight hat are bonded to the carbons fall into two groups of four, each at 3.08-3.29 Å and 3.77-3.79 Å from the Cr(IV). The water
hydrogens are at 3.29 and 3.48 Å from the closest Cr(IV) ions, which are in Cr(dien) molecules shown in Figure 5.1.

138. The peak position depends slightly on the quenching conditions $T_q$ and $H_q$. For the data shown in Figure 5.21, in the highly polarized paramagnetic phase, $H_q = 13.5$ T and $T_q = 0.80$ K except for the 227 mK point for which $T_q = 1.04$ K. For those in the antiferromagnetically ordered phase, $H_q = 9-10.5$ T and $T_q = 0.76$ K except for the 226 mK point ($T_q = 1.00$ K) and the 201 mK point taken at 0.2 T/min ($T_q = 0.50$ K).


BIOGRAPHICAL SKETCH

EDUCATION

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PRESENTATIONS


10. **N. Kaur**, S. Nellutla and N. S. Dalal, Department of Chemistry and Biochemistry, Tallahassee, FL 32306-4390, Julie Cissell, T.M. Vaid, Washington University, St. Louis, Missouri, “Magnetic characterization of a newly synthesized [(CH3CN)3V-O-V(CH3CN)3][(BF4)2 2CH3CN, V-O-V compound” Florida Annual Meeting and Exposition of the American Chemical Society, Orlando, FL, May 11-13, 2006.

PUBLICATIONS


