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Magnetic Properties of Dinuclear and Trinuclear Copper (II) Complexes

Hrachya Babujyan

CANDLE Synchrotron Research Institute, Condensed Matter and Polymers, Yerevan, 0022, Armenia

E-mail: babujyan.hrach@gmail.com

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Abstract. In this work, I present the synthesis, structural characterization, and magnetic properties of trinuclear and dinuclear antiferromagnetic copper (II) complexes. Different bridging ligands were employed to investigate the impact of exchange interactions on the magnetization behavior. Utilizing both experimental data and theoretical antiferromagnetic models, I analyze magnetization plateaus, magnetic susceptibility, and entanglement entropy. Notably, the results reveal distinct magnetization plateaus and saturation points, which correlate with variations in exchange interactions and ligand frameworks. Furthermore, I calculate the thermal logarithmic negativity of the complexes, highlighting quantum entanglement behavior at low temperatures. My findings emphasize the role of ligand design in tuning magnetic and quantum properties, paving the way for future studies on related antiferromagnetic systems. Additionally, I explore connections between the quantum magnetic properties of these copper complexes and radiation field calculations in waveguide systems, drawing parallels in mathematical modeling techniques and spectral analysis.

Keywords: Quantum magnetism, quantum thermal entanglement, antiferromagnetic interactions, magnetization, magnetic susceptibility, copper (II) complexes, spin-1/2 systems, low-temperature quantum correlations

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1. Introduction

Strongly interacting quantum magnetic systems provide a rich platform for exploring correlated materials and intricate physical phenomena [1,2]. Quantum thermal entanglement serves as a powerful tool in analyzing phase transitions within many-body systems, offering insights into the influence of quantum fluctuations, competing interactions, and critical points. These elements contribute to emergent behaviors that exhibit strong correlations, leading to intriguing quantum effects [5, 6, 7].

In particular, thermal quantum correlations, including entanglement, play a significant role in antiferromagnetic systems, where distinct features such as magnetization plateaus, peaks in magnetic susceptibility, and variations in specific heat arise at low temperatures. The study of these properties allows for a deeper understanding of the fundamental interactions governing these quantum materials [8-19].

Our study focuses on copper (II) complexes with spin-1/2, specifically examining a dinuclear complex $[Cu_2(\mu_{1.1}-N_3)_2(Him_2-py)_2(N_3)_2]$ and a trinuclear complex $[Cu_3(C_5H_9PO_3)_2(bpy)_3(MeOH)(H_2O)](ClO_4)_2$. A key aspect of this research is the interplay between experimental data and exact theoretical calculations of magnetic susceptibility across temperature variations. The results demonstrate a strong correlation between magnetization anomalies, susceptibility peaks, and thermal quantum correlations, reinforcing the crucial role of entanglement in such systems. Furthermore, this study explores how external magnetic fields impact the observed quantum magnetic properties, shedding light on the intricate behavior of these metal-containing compounds at low temperatures.

2. Analysis of Dinuclear and Trinuclear Copper(II) Complexes

This comprehensive analysis delves into the intricate two-dimensional network formed by dinuclear and trinuclear copper(II) complexes. We will examine the Hamiltonian governing these structures, their specific structural arrangement, and the critical role of exchange interactions. By scrutinizing these factors, we aim to elucidate how variations in bonding, ligand coordination, and metal-metal interactions influence the overall magnetic properties of these complexes. These properties include susceptibility, magnetization plateaus, and, importantly, thermal quantum correlations.

To gain a deeper understanding of the thermodynamic and magnetic behaviors inherent to these systems, we leverage the Heisenberg XXX model. This theoretical model is particularly well-suited for describing the magnetic behavior observed in copper (II) complexes that exhibit antiferromagnetic interactions. The Heisenberg XXX model effectively captures the intricate spin-exchange dynamics that occur within these systems. This makes it a valuable tool for accurately characterizing their quantum magnetic properties, providing insights into the fundamental quantum behavior of these complexes.

2.1. Dinuclear complex

The crystal structure in our study consists of binuclear units $[Cu_2(\mu_{1.1}-N_3)_2(Him_2-py)_2(N_3)_2]$ complex 1 (Table 1) in which the copper (II) ions are bridged by two asymmetric azido ions in end-on fashion [26].

The Hamiltonian of this dinuclear copper (II) complex 1 (Table 1) can be expressed as:

$$\hat{H} = -\sum_{i\neq j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j - \mu_B h \sum g_i S_i^z \quad (1)$$

In the Hamiltonian (Eq.1) h is the applied homogeneous magnetic field in the z-axis, g is the Landé g-factor and μ_B is the Bohr magneton. The corresponding constant values are shown in Table 1.

The number of spin-½ particles is 2 and the particle's space states are inter-combined, therefore the Hilbert space will be of 2^2 dimensionality, which equals in total to 4. In the Hamiltonian equation the two parts are:

$$(\mathbf{S}_i \cdot \mathbf{S}_j)_J = J(S_i^x S_j^x + S_i^y S_j^y + S_i^z S_j^z) \quad (2)$$

The Heisenbergian couplings between spins that are interacting with each other, which can be paraphrased to, and the sign and magnitude of J determine the nature and strength of the exchange coupling, with negative J values indicating antiferromagnetic interactions. Each S_α in the equation, where $\alpha \in \{x, y, z\}$, are spin-1/2 operators, corresponding to

$$S^x = \frac{\hbar}{2}\sigma_x, \quad S^y = \frac{\hbar}{2}\sigma_y, \quad S^z = \frac{\hbar}{2}\sigma_z \quad (3)$$

where $\hbar$ is 1 and $\sigma_\alpha{}'s$ are the Pauli matrices which for spin ½ case have the following representation:

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \quad (4)$$

2.2. Trinuclear complex

The crystal structure in our study consists of trinuclear units $[Cu_3(C_5H_9PO_3)_2(b\ py)_3(MeOH)(H_2O)](ClO_4)_2$. The Hamiltonian of the dinuclear copper (II) complex 2 (Table 1) [27] can be expressed as:

$$\hat{H} = -\sum_{i\neq j} J_{ij}\mathbf{S}_i \cdot \mathbf{S}_j - \mu_B h \sum g_i S_i^z \tag{5}$$

assuming periodic boundary conditions $S_4^\alpha = S_1^\alpha$.

Table 1: Landé g-factors, Coupling Constants, Chemical Formulas, and External Magnetic Fields

N	Reference	J (cm⁻¹)	g	Compound	Exp h(T)
1	26	-0.3	2.15	$Cu_2(\mu_{1,1} - N_3)_2(Him_2 - py)_2(N_3)_2$	0.2
2	27	-8.8	2.12	$[Cu_3(C_5H_9PO_3)_2(b\ py)_3(MeOH)(H_2O)](ClO_4)_2$	0.2

3. Theoretical Study of Copper (II) Complexes

The partition function of the model is given by $Z = Tr[\exp(-\beta H)]$, where $\beta = 1/k_\mathrm{B}T$, k_B is the Boltzmann's constant and T is the temperature. The Gibbs free energy was derived from the system's partition function as $F = -k_\mathrm{B}Tln(Z)$. Additionally, specific quantities like magnetization and magnetic susceptibility can be calculated using the provided equation [28]:

$$M = -\left(\frac{\partial F}{\partial B}\right)_T, \quad \chi = \left(\frac{\partial M}{\partial B}\right)_T \tag{6}$$

Our research utilizes analytical (exact) calculations, which are derived directly from the diagonalization of the density matrix on finite clusters. A key tool in this computational process is Eq.5, which allows for the analytical calculation of both magnetization and magnetic susceptibility – two crucial properties in the investigation of materials containing metals, such as the copper (II) complexes central to this study. By applying Eq. 5, we can generate precise theoretical predictions for these quantities, thereby providing a deeper understanding of the magnetic behavior exhibited by these complexes.

Furthermore, the analytical results obtained through these calculations are then compared with experimental measurements. Specifically, the theoretical values for dinuclear copper(II) complexes are juxtaposed with empirical data from, while those for trinuclear copper(II) complexes are compared to experimental results from. This comparative analysis serves as a critical validation step, assessing the accuracy and applicability of our theoretical model by examining how well its predictions align with real-world observations.

4. Results

The research delved into the intricate magnetic behavior displayed by copper (II) complexes, with a particular emphasis on comprehending the influence of temperature variations on their magnetic susceptibility and magnetization. To achieve this, theoretical calculations were meticulously executed across a wide temperature range, starting from the extremely low temperature of 1 Kelvin and extending up to room temperature, which is 300 Kelvin. These calculations were consistently performed under a constant external magnetic field of 0.2 Tesla.

The investigation also encompassed an analysis of how these magnetic properties reacted to changes in external magnetic fields, especially under low-temperature conditions. This comprehensive approach was designed to gain a more profound understanding of the magnetic characteristics of copper (II) complexes. This knowledge could potentially unlock their applications in various technological and scientific fields, such as quantum computing, data storage, and magnetic resonance imaging.

Additionally, the findings of this research could contribute to the development of novel materials with tailored magnetic properties. These materials could find use in a wide range of applications, including magnetic sensors, switches, and actuators. Furthermore, the insights gained from this study could potentially advance our understanding of fundamental magnetic phenomena and pave the way for new discoveries in the field of magnetism.

4.1. Dinuclear complex

The results obtained for the dinuclear complex 1, as outlined in Table 1, are visually represented in Fig.1. This figure provides a comprehensive depiction of both the magnetization and susceptibility curves specifically for the copper (II) dinuclear complexes under investigation. These curves offer valuable insights into the magnetic behavior of the complex, allowing for a deeper understanding of its properties and potential applications.

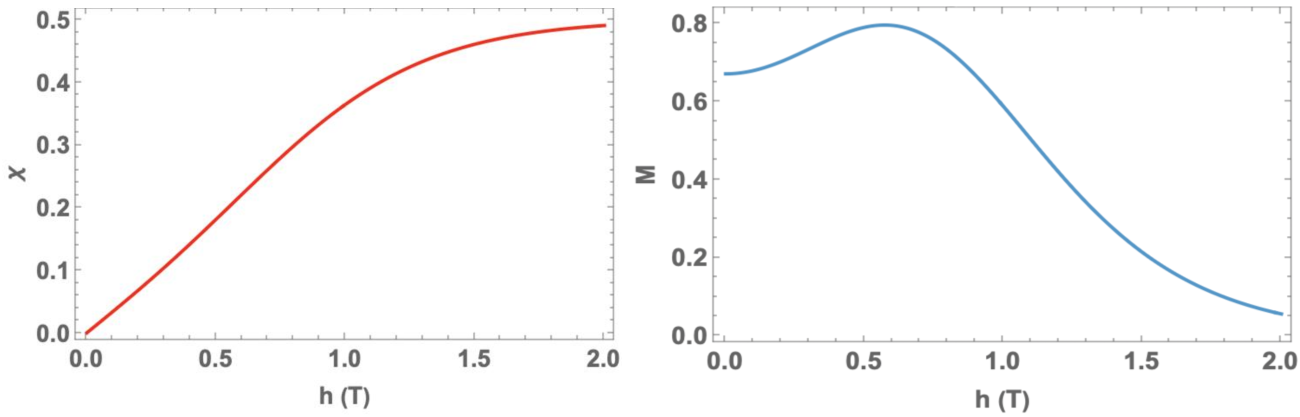

Fig. 1. Magnetization and susceptibility curves for dinuclear complexes of copper (II).

4.2. Trinuclear complex

Fig.2 displays the magnetization and susceptibility data obtained for the copper (II) trinuclear complex 2, the structure of which is detailed in Table 1. The results derived from these measurements demonstrate a significant correlation with the empirical data obtained through experimental procedures.

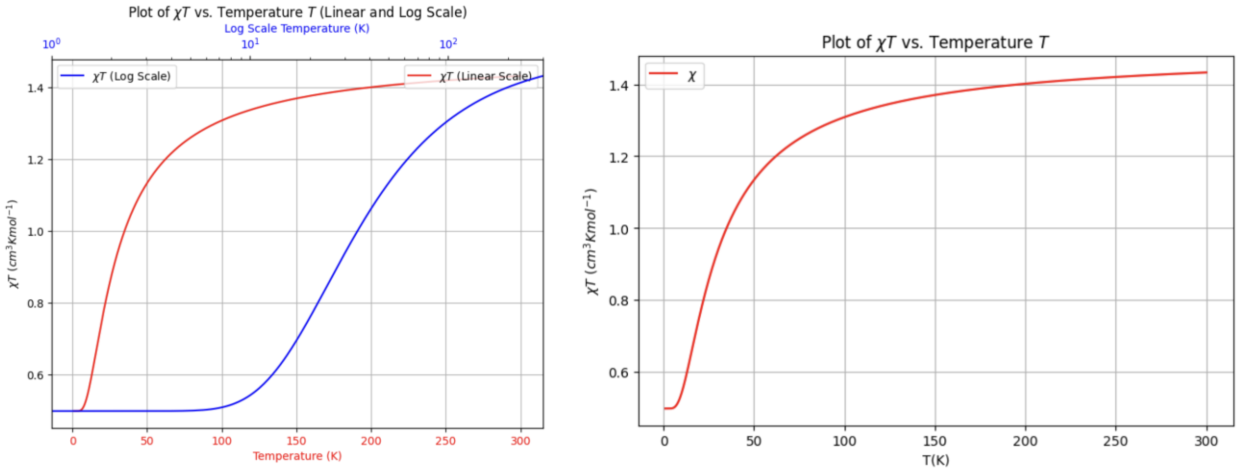

Fig. 2. Magnetization and susceptibility for trinuclear complexes of copper (II).

This correlation suggests that the theoretical model used to predict the magnetic behavior of the complex accurately reflects the actual behavior observed in the laboratory setting. The close agreement between the theoretical and experimental data provides strong evidence for the validity of the model and supports its use in understanding the magnetic properties of similar copper (II) trinuclear complexes. Furthermore, this correlation can be used to refine the model and improve its predictive capabilities, leading to a deeper understanding of the underlying physics governing the magnetic behavior of these complexes.

6. Conclusions

Thus, in this study, we conducted a comprehensive investigation of the quantum magnetic properties and entanglement in dinuclear and trinuclear copper (II) complexes. Our findings reveal a delicate balance between antiferromagnetic interactions in these systems, which is reflected in the observed magnetic susceptibility behavior, magnetization plateaus, and thermal quantum correlations. The theoretical models employed in this work show strong agreement with experimental results, reinforcing the validity of the applied Heisenberg spin-1221 framework and the methodologies used. Notably, we identify a clear correlation between magnetization anomalies, susceptibility peaks, and thermal entanglement as a function of the external magnetic field. This interplay not only provides deeper insights into the quantum behavior of spin-1221 copper complexes at low temperatures but also underscores the necessity of further experimental studies in this area. Given the complexity of these quantum magnetic interactions, we emphasize the importance of additional experimental measurements to refine our understanding and uncover potential novel quantum correlations and behaviors in similar transition metal-based systems.

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