

Spin fluctuations and orbital ordering in quasi-one-dimensional α -Cu(dca)₂(pyz) {dca = dicyanamide = N(CN)₂⁻; pyz = pyrazine}, a molecular analogue of KCuF₃

Jamie L. Manson^{a,*}, Tom Lancaster^b, Stephen J. Blundell^b, Yiming Qiu^{c,d}, John Singleton^e, Pinaki Sengupta^{e,f}, Francis L. Pratt^g, Jinhee Kang^h, Changhoon Lee^h, Myung-Hwan Whangbo^h

^a Department of Chemistry and Biochemistry, Eastern Washington University, Cheney, WA 99004, USA

^b Clarendon Laboratory, Department of Physics, Oxford University, Oxford, OX1 3PU, UK

^c NIST Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

^d Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742, USA

^e National High Magnetic Field Laboratory, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

^f Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

^g ISIS Pulsed Muon Facility, Rutherford Appleton Laboratory, Chilton, Oxfordshire, OX11 0QX, UK

^h Department of Chemistry, North Carolina State University, Raleigh, NC 27695, USA

ARTICLE INFO

Article history:

Available online 1 July 2009

Keywords:

Low-dimensional
Copper
Dicyanamide
Pyrazine
Molecular magnet

ABSTRACT

The magnetic properties of α -Cu(dca)₂(pyz) were examined by magnetic susceptibility, magnetization, inelastic neutron scattering (INS), muon-spin relaxation (μ SR) measurements and by first-principles density functional theoretical (DFT) calculations and quantum Monte Carlo (QMC) simulations. The χ versus T curve shows a broad maximum at 3.5 K, and the data between 2 and 300 K is well described by an $S = 1/2$ Heisenberg uniform chain model with $g = 2.152(1)$ and $J/k_B = -5.4(1)$ K. μ SR measurements, conducted down to 0.02 K and as a function of longitudinal magnetic field, show no oscillations in the muon asymmetry function $A(t)$. This evidence, together with the lack of spin wave formation as gleaned from INS data, suggests that no long-range magnetic order takes place in α -Cu(dca)₂(pyz) down to the lowest measured temperatures. Electronic structure calculations further show that the spin exchange is significant only along the Cu–pyz–Cu chains, such that α -Cu(dca)₂(pyz) can be described by a Heisenberg antiferromagnetic chain model. Further support for this comes from the M versus B curve, which is strongly concave owing to the reduced spin dimensionality. α -Cu(dca)₂(pyz) is a molecular analogue of KCuF₃ owing to $d_{x^2-y^2}$ orbital ordering where nearest-neighbor magnetic orbital planes of the Cu²⁺ sites are orthogonal in the planes perpendicular to the Cu–pyz–Cu chains.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

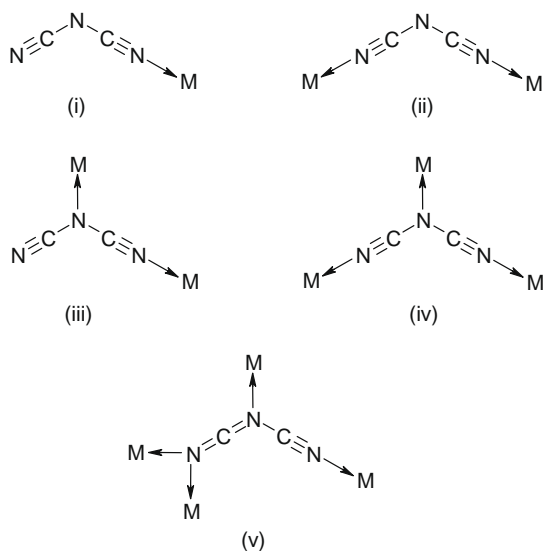
Over the past several years, we and others have been interested in the magnetic properties of dicyanamide (dca) containing coordination polymers. Much of the interest in these materials can be attributed to the coordinative versatility of the dca ligand and its subsequent role as a superexchange mediator [1]. To date, several modes have been identified (Scheme 1) although the vast majority of the reported polymeric coordination compounds consist of $\mu_{1,5}$ -dca bridges [2]. Three-coordinate M -dca complexes are exemplified by rutile-like α - M (dca)₂ ($M = V, Cr, Mn, Fe, Co$ and Ni) in which the M ion is divalent [1]. Combining dca bridges with auxiliary organic ligands of varying denticity can lead to zero-, one-,

two- and three-dimensional (0D, 1D, 2D and 3D, respectively) spin dimensionality.

The 3D polymeric structures exhibited by α - M (dca)₂(pyz) ($M = Mn$ [3,4], Fe [4], Co [4], Ni [4], Cu [5], and Zn [4]; pyz = pyrazine) are particularly interesting in that they possess 2-fold interpenetrating networks. Two-dimensional (2D) M (dca)₂ layers are linked via M -dca- M bridges that are further connected by μ -pyrazine ligands to yield a rigid 3D lattice. In essence the general structure of the α -phase can be viewed as 1D M -pyz- M chains that are joined to form a 3D framework via $\mu_{1,5}$ -dca ligands. It should be noted that β -phases of the same chemical composition can be produced for $M = Co, Ni, Cu$, and Zn although this structure type consists of 2D sheets of 1D bi-bridged M -(dca)₂- M ribbons that are linked via μ -pyz ligands [4,5].

Of particular interest to us is α -Cu(dca)₂(pyz) because it can be described as a molecular analogue of KCuF₃. While a low-temperature crystal structure and variable-temperature magnetic

* Corresponding author. Tel.: +1 (509)359 2878; fax: +1 (509)359 6973.
E-mail address: jmanson@ewu.edu (J.L. Manson).



Scheme 1.

susceptibility study of fully protonated α -Cu(dca)₂(pyz) were previously reported [5], a 2D theoretical model to describe its magnetic behavior was proposed in that work which we deemed inadequate. Herein, we find α -Cu(dca)₂(pyz) to be an excellent experimental realization of the spin-1/2 Heisenberg uniform chain model on the basis of magnetic susceptibility, pulsed-field magnetization, inelastic neutron scattering, and μ SR measurements as well as spin dimer analysis of its spin exchange interactions and QMC simulation of the magnetization. The results of these studies will be described in the present work.

2. Experimental procedures

2.1. Sample preparation

Pure, polycrystalline samples of α -Cu(dca)₂(pyz-*h*₄) and α -Cu(dca)₂(pyz-*d*₄) were prepared by the rapid precipitation of aqueous solutions of Cu(NO₃)₂, Nadca, and either pyz-*h*₄ or pyz-*d*₄, respectively. In a typical synthesis of α -Cu(dca)₂(pyz-*h*₄), 0.600 g (2.58 mmol) of Cu(NO₃)₂·2.5H₂O was dissolved in 5 mL of H₂O and quickly added, while stirring, to a 5-mL aqueous solution that contained Nadca (0.482 g, 5.41 mmol) and pyz (0.207 g, 2.58 mmol). The result was immediate precipitation of the desired blue–green product which was collected via suction filtration, washed with ethanol, and dried *in vacuo* for 4 h. The α -phase was obtained in 87% yield. Slow solvent evaporation of the filtrate overnight yielded turquoise crystals of β -Cu(dca)₂(pyz-*h*₄) which has a 2D layered structure. A similar, although scaled up, chemical reaction was used to prepare a 5.5 g sample of α -Cu(dca)₂(pyz-*d*₄) as required for the inelastic neutron scattering measurements. Infrared spectroscopy and X-ray powder diffraction were used to confirm the isostructural nature of the hydrogenated and deuterated materials.

2.2. Bulk magnetic measurements

Isofield temperature-dependent measurements, $M(T)$, were carried out using a Quantum Design MPMS-5XL ac/dc SQUID magnetometer equipped with a 5-T superconducting magnet, a continuous low-temperature option and RSO transport. Powdered samples of hydrogenated α -Cu(dca)₂(pyz-*h*₄) and deuterated α -Cu(dca)₂(pyz-*d*₄) were loaded into gelatin capsules and affixed to the end of a carbon fiber rod. Each sample was cooled in zero-

field to a base temperature of 2 K, the magnet was charged to 0.1 T and magnetization data were collected upon warming to room temperature. Careful comparison of these data for the hydrogenated and deuterated samples revealed no discernable differences. All data were corrected for core diamagnetism and temperature-independent paramagnetism ($\chi^{\text{TP}} = 60 \times 10^{-6}$ emu/mol).

Isothermal magnetization measurements, $M(B)$, were conducted at the National High Magnetic Field Laboratory, Los Alamos, NM, using a 65-T pulsed magnet. Small samples (~1–2 mg) were loaded into conical-shaped ampoules and affixed to the end of a probe. The probe was placed in a ³He cryostat where temperatures as low as 0.5 K could be reached. The sample's magnetization was measured *in situ* by insertion into and extraction out of a compensated coil. The magnet pulsed width was ~100 ms, giving a magnet rise time of ~650 T/s.

2.3. Muon-spin relaxation

Zero-field and longitudinal-field μ SR measurements were performed on a polycrystalline sample of α -Cu(dca)₂(pyz) using the LTF and GPS instruments at the Swiss Muon Source, Paul Scherrer Institute, Villigen, Switzerland. The measurements were made in the time range $0 \leq t \leq 9.5 \mu\text{s}$.

In a μ^+ SR experiment spin-polarized positive muons are stopped in a target sample, where the muon usually occupies an interstitial position in the crystal [6]. The observed property in the experiment is the time evolution of the muon spin polarization, the behavior of which depends on the local magnetic field B at the muon site. Each muon decays, with a lifetime of 2.2 μs , into two neutrinos and a positron, the latter particle being emitted preferentially along the instantaneous direction of the muon spin. Recording the time dependence of the positron emission directions therefore allows the determination of the spin polarization of the ensemble of muons. In our experiments positrons are detected by detectors placed forward and backward of the initial muon polarization direction. The histograms $N_F(t)$ and $N_B(t)$ record the number of positrons detected in the “forward” and “backward” detectors as a function of time t following the muon implantation. The quantity of interest is the decay positron asymmetry function, defined as:

$$A(t) = \frac{N_F(t) - \alpha N_B(t)}{N_F(t) + \alpha N_B(t)} \quad (1)$$

where α is an experimental calibration constant. $A(t)$ is proportional to the spin polarization of the muon ensemble.

2.4. Inelastic neutron scattering

Measurements were made on a polycrystalline sample of α -Cu(dca)₂(pyz-*d*₄) using the cold-neutron disk-chopper spectrometer (DCS) with a wavelength of 4.8 Å at the NIST Center for Neutron Research, Gaithersburg, MD [7]. For INS measurements it is important to substitute H-atoms for deuterium in order to remove the otherwise large incoherent scattering background imposed by H-atoms. The deuterated sample, which had a mass of 5.5 g, was loaded into a cylindrical vanadium can (0.9 cm width) and sealed under a helium exchange gas. The can was mounted on a stick and inserted into a dilution refrigerator equipped with a 12-T superconducting magnet. Sample temperatures to as low as 0.1 K were achieved and several data sets acquired at that temperature for $B = 0$ and 4 T.

2.5. Quantum Monte Carlo simulations

The stochastic series expansion (SSE) method [8,9] is a finite-temperature QMC technique based on importance sampling of

Download English Version:

<https://daneshyari.com/en/article/1339540>

Download Persian Version:

<https://daneshyari.com/article/1339540>

[Daneshyari.com](https://daneshyari.com)