Molecular-based quantum magnets: the isotropic spin ladder Cu(quinoxaline)Br$_2$

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Abstract

The structure, susceptibility, and high-field magnetization of μ-quinoxalinecopper(II) dibromide are reported. The compound crystallizes in the space group $C2/c$ as a coordination polymer of neutral Cu$_2$Br$_4$ dimers bridged into chains by quinoxaline molecules forming a ladder structure. The susceptibility data are well described by a spin-ladder model with two antiferromagnetic exchange strengths $2J_\perp = 35.0$ K within the dimers, and $2J = 30.3$ K through the quinoxaline groups. The ratio of exchange strengths, $R \equiv J_\perp/J = 1.16$, is the closest to unity yet found for a spin ladder. The magnetization study shows the compound at low temperatures to be in a non-magnetic singlet state for low fields, but that a phase transition to a magnetized state occurs near 14 T, indicating the presence of an energy gap $\Delta \approx 20$ K.
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1. Introduction

The use of diazines, such as pyrazine, pyrimidine, quinoxaline, and phenazine, has a long history in magnetochemistry. In a seminal review article a quarter century ago [1] the use of nitrogen-heterocyclic ligands for bridging metal complexes was discussed. The general subject of magnetic exchange interactions propagated by multiatom bridges (including diazines) was also reviewed at one of the founding conferences of the Molecular Magnetism community [2]. In our own recent work examining the quantum behavior of low-dimensional $S = 1/2$ antiferromagnets, we have frequently made use of pyrazine and it's substituted analogs [3]. The use of quinoxaline and phenazine [1,4] as exchange mediators has also been reported, but less frequently than the use of pyrazine.

A quantum ($S = 1/2$) antiferromagnet of current interest is the spin ladder [5] which can become a superconductor when doped with charge carriers [6]. Spin ladders consists of two coupled linear chains, each spin interacting with it's nearest intrachain (rail) neighbors with an exchange strength J and it's interchain (rung) neighbor with $J_\perp$. The ground state is a non-magnetic singlet separated from the closest magnetic state by an energy gap Δ for any value of $J_\perp$. In general, properties of the ladder depend strongly on the ratio of exchange strengths $R \equiv J_\perp/J$, The most interesting case occurs for isotropic exchange, $J_\perp = J$ for which $R = 1$. Only a few transition metal compounds have been found [7] which are physical realizations of a spin ladder; without exception they belong to the strongly coupled class in which the exchange within the dimeric units is considerably greater than the intrachain exchange, $R > 3$. An organic spin ladder, (DT-TTF)$_2$-Au(mnt)$_2$ has been reported [8] with $R \approx 1.7$, albeit with strong exchange constants ($2J = 142$ K, $2J_\perp = 83$ K) and a larger gap ($\Delta \approx 78$ K). In order to explore the full potential of spin ladders, we have been engaged in the search for, and study of, more isotropic spin ladders,

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$R \approx 1$, with particular emphasis on systems with gaps small enough to be closed by available magnetic fields. We report here on the synthesis, structure and magnetic properties of Cu(quinoxaline)Br$_2$, CuQBr.

2. Experimental

2.1. Synthesis

Direct combination of 0.1 M aqueous solutions of copper(II) dibromide and quinoxaline resulted in an immediate precipitation of polycrystalline μ-quinoxaline copper(II) dibromide in near quantitative yield. Crystals of the materials studied were obtained by a slow diffusion technique. Two 50 ml beakers containing, respectively, 0.1 molar aqueous solutions of the appropriate copper halide and quinoxaline, were filled and placed inside a 1-l beaker. Distilled water was added slowly to the larger beaker until the water level was several centimeters above the height of the smaller beakers. The larger beaker was then covered and set in a dark room. Small yellow flat crystals were obtained after several days.

2.2. Magnetic studies

The magnetic susceptibility of polycrystalline samples of CuQBr was determined in a field of 1 T using a Quantum Design MPMS SQUID Magnetometer and a Lake Shore Model 730 vibrating sample magnetometer. Corrections were make for the diamagnetic contributions calculated from Pascal's constants and for the temperature-independent paramagnetism of the Cu(II) ion ($\chi_{TIP} = 60 \times 10^{-6}$ emu/mol). High-field magnetization studies in fields up to 30 T were made using a Lake Shore Model 7600 vibrating sample magnetometer, a helium cryostat and a 30 T Bitter magnet at the National High Magnetic Field Laboratory in Tallahassee, FL. Temperatures were determined by calibrated Cernox resistors and the vapor pressure of the helium baths.

3. Results and discussion

3.1. Structure of CuQBr

CuQBr crystallizes in the monoclinic system, space group $C2/m$, with unit cell parameters $a = 13.1745(15)$, $b = 6.9293(8)$, $c = 10.3564(12)$ Å, and $\beta = 107.699(2)°$. The structure of CuQBr is isomorphous to that of CuQCl, reported previously [9]. It consists of neutral Cu$_2$Br$_4$ dibromo-bridged dimers that are linked to adjacent dimers by bridging quinoxaline molecules along the b-axis. The two halves of the dimer are related

by an inversion center. Each copper is coordinated to three bromide ions and two quinoxaline molecules in a 4+1 geometry. The copper center forms both a short (Cu–Br2 = 2.4285(6) Å) and a long (Cu–Br2′ = 2.9162(6) Å) bond to the bridging bromides as well as a short bond to its terminal bromide (Cu–Br1 = 2.3702(6) Å). The two Cu–N bonds are related by a mirror plane containing the dimeric unit and are each 2.0610(19) Å. Given this coordination, it is expected that the unpaired electron resides in the d$x^2–y^2$ orbital, which has lobes pointing along the Cu–N bonds and the two short Cu–Br bonds.

The structures of Cu(quinoxaline)X$_2$ present interesting contrasts to those of Cu(pyridine)$_2$X$_2$ and Cu(pyrazine)X$_2$. Each structure contains bibridged CuX$_2$ units, with the organic molecules coordinated to the copper ions through the ring nitrogens orthogonal to the CuX$_2$ axis. Cu(pyridine)$_2$X$_2$ consists of extended CuX$_2$ linear chains with each copper bonded to two local halide ions and two more distant halide ions from neighboring sites in the chain [10]. The pyridine molecules coordinate in a *trans* configuration, completing the 4+2 coordination about the copper site. Magnetically, Cu(py)$_2$X$_2$ corresponds to very well isolated $S = 1/2$ antiferromagnetic chains [11]. In a similar manner, Cu(pyrazine)X$_2$ contains very similar CuX$_2$ bihalide bridged chains with pyrazine molecules in *trans* configuration. However, the bridging bidentate character of the pyrazines links the chains together into a two-dimensional extended network, with Cu–pz–Cu–pz–interactions occurring perpendicular to the Cu–X$_2$–Cu–X$_2$–Cu-pathway [12]. Magnetically, Cu(pz)X$_2$ corresponds to a *rectangular* 2D lattice with inequivalent exchange interactions occurring along both axes of the rectangular lattice [13].

The bridging bidentate nature of quinoxaline also gives it the ability to provide a superexchange path between copper ions but the structure of the copper quinoxaline dihalides is very different from a rectangle. The one-dimensional Cu–diazine–Cu–diazine–Cu–network is again present, similar to the Cu–pz axis in the Cu(pz)X$_2$ structures, but the copper dihalide network is truncated after only two CuX$_2$ units, Fig. 1. The reason for this interruption is the additional bulk of the quinoxaline molecule. The second ring in quinoxaline projects into the coordination sphere of the copper ion, interfering with the ability of the copper to form a semi-coordinate bond to the halide of the adjacent copper ion. Each copper ion can form semi-coordinate bonds in one direction but not in the other so Cu$_2$X$_4$ dimers are formed instead of polymeric (CuX$_2$)$_n$ structures. Hence, the ladder structure is created.

3.2. Magnetic susceptibility results

Susceptibility studies were first carried out on the initial precipitates of the synthesis. These precipitates
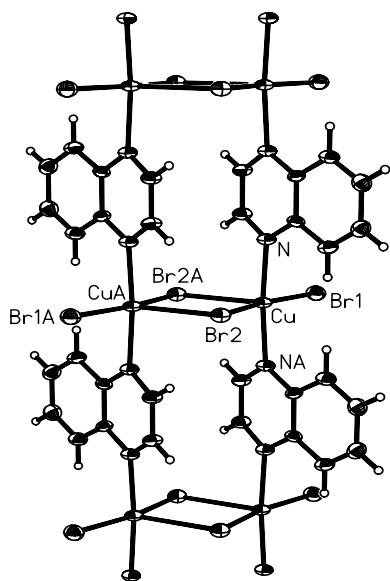
Fig. 1. Ladder structure of copper quinoxaline dibromide, CuQBr. The ladder extends along the crystallographic *b*-axis.

were found to contain between 1 and 2% paramagnetic impurity. Purer samples and single crystals appropriate for X-ray diffraction studies were grown by slow diffusion over several days

The magnetic susceptibility of a crushed single crystals sample of CuQBr between 2 and 100 K is shown in Fig. 2. The data are characterized by a broad rounded maximum near 22 K and a rapid decrease of susceptibility towards zero at lower temperatures. Below
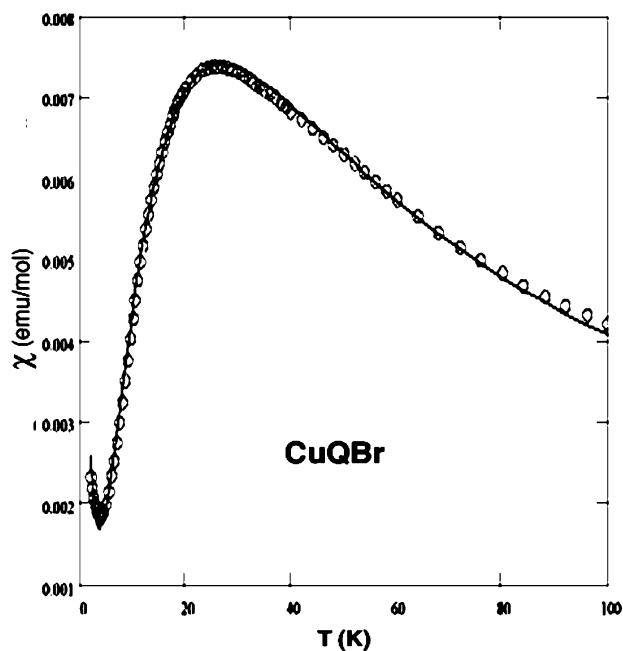

Fig. 2. Molar susceptibility of copper quinoxaline dibromide, CuQBr. The solid line corresponds to the fit to a spin ladder model with parameters $J_{rung} = 35.0$ K, $J_{rail} = 30.3$ K, $C = 0.42$ emu K/mol, and an impurity fraction of 0.7%.

4 K, the susceptibility begins to rise again in a paramagnetic T^{-1} manner. The rounded maximum is characteristic of a low-dimensional antiferromagnet, while the rapid decrease at lower temperatures indicates the presence of a singlet ground state, separated from excited, moment-bearing states by an energy gap.

The data have been fit to a polynomial expression [14] for the susceptibility of an antiferromagnetic ladder with three independent variables: $J_\perp$, J, and the Curie constant C. The Hamiltonian used is the $+2J$ form, $H = 2J\Sigma\, S_i \cdot S_j$, in which a positive value for J corresponds to antiferromagnetic exchange. An additional term was added to account for the paramagnetic tail seen below 4 K. The four parameters were allowed to vary independently and convergence was found for $2J_\perp = 35.0$ K, $2J = 30.3$ K, $C = 0.42$ emu K/mol, and an impurity fraction of 0.7%. The ratio of exchange strengths, $R \equiv J_\perp/J = 1.16$, corresponding to an excellent degree of isotropic exchange. The susceptibility data for the chloride analog, CuQCl, are qualitatively similar and are well described with exchange parameters $2J_\perp = 33.2$ K, $2J = 21.1$ K, $R = 1.50$.

It is surprising that the substitution of chloride for bromide ions does not significantly affect the exchange within the dimers, but does reduce the exchange through the quinoxaline groups by 30%. Given the well-known ability of bromide ions to connect copper ions with stronger magnetic exchange [15], we anticipated the dimeric exchange $J_\perp$ to be primarily affected by the halide substitution. However, the origin of the effect may lie in the insensitive nature of the spin-ladder susceptibility to different ratios $J_\perp/J$ in the isotropic regime [14]. Statistically, the best fit to the experimental data is found with the set of exchange parameters given but a nearly equivalent fit is also found with similar values but with the exchange through the quinoxaline groups larger than through the halides. Further examination will be required to definitively decide on the exchange values.

There are many known examples of Cu_2X_4 antiferromagnetic dimers [16]. The exchange strengths can be either ferromagnetic or antiferromagnetic, with values depending on copper halide bond lengths and angles, as well as the degree of nonplanarity within the copper basal plane. An exchange constant as large as $2J_{dimer} = 48$ K has been found [17] for $[Cu(TMSO)_2Br_2]_2$ so the values determined for the CuQBr and CuQCl are not surprising.

The literature is much less rich in examples of copper(II) bridged by quinoxaline molecules. One known example is $Cu(quinoxaline)(NO_3)_2$ for which an exchange strength of $2J = 13$ has been reported [4a], a value within a factor of two of those found in CuQBr and CuQCl.

3.3. High-field magnetization results

The high-field magnetization data at 0.7 K for a precipitated powder sample of CuQBr in fields out to 30 T is presented in Fig. 3. The data is marked by a small initial rise that saturates near 100 emu/mol, followed by a slow decrease of moment that continues until about 14 T. At that field, the moment shows strong upward curvature, followed by a region of linear behavior between 19 and 30 T. The slope of the linear region (in strikingly non-SI units) is about 115 emu mol^{-1} T^{-1}. At this rate, the moment will reach its saturation value of 6000 emu mol^{-1} at a field near 65 T.

The rapid onset of the moment near 14 T is due to field-induced change of ground state as the energy gap Δ is closed. The $m_s = 1$ state of the lowest lying excited triplet state is reduced in energy by the Zeeman contribution, and crosses the singlet ground state at the critical field, H_{C1}. Equating the Zeeman energy $g\mu_\beta m_s H_{C1}$ to the energy gap yields a value $\Delta = 20$ K. This value is consistent with the temperature at which the susceptibility begins its rapid decrease.

The initial onset of moment that saturates near 80 emu/mol by 3 T can be caused by about a 1.5% paramagnetic impurity. Since this data was collected on a sample of rapidly precipitated material, such a level of impurity is not unexpected. Preliminary susceptibility studies of the same batch of CuQBr also revealed the same amount of paramagnetic phase.
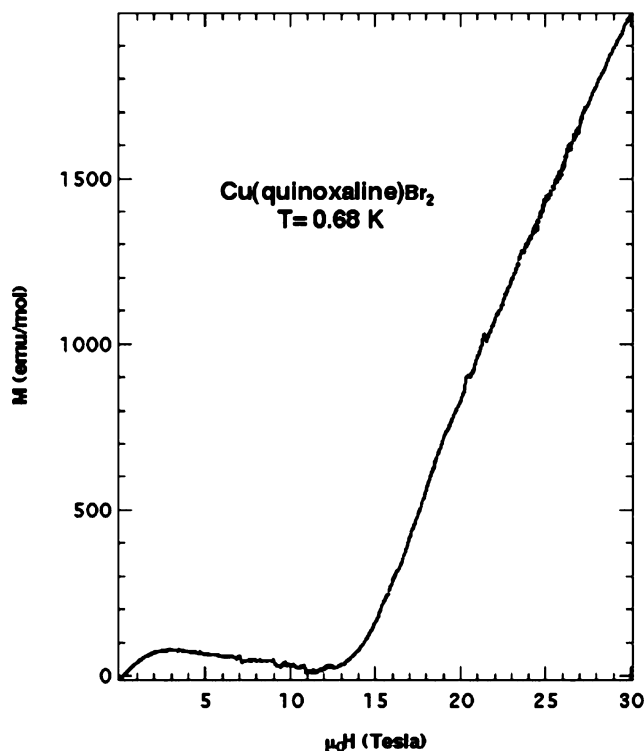
The decrease in the moment from 80 emu/mol at 3 T to 45 emu/mol at 13 T is due to the diamagnetic response of the sample to the large external field. This decrease is only observed in the lowest temperature magnetization data, in which the system is in the non-magnetic singlet ground state. Data collected at 1.5 and 4.6 K showed steadily increasing moments for all fields, due to thermal population of the excited magnetic states.

4. Conclusions

Copper quinoxaline dibromide has been shown to behave magnetically as a spin ladder, with a singlet ground state and an energy gap $\Delta \approx 20$ K and a critical field near 14 T. While there still remains some uncertainty as to the exact values of the two exchange strengths, it is clear that their ratio is close to one, confirming CuQBr as an isotropic spin ladder. The additional bulk of the quinoxaline group prevents the formation of the common CuBr$_2$ chain motif found in many other copper halide/azine or diazine compounds and leads to the unique ladder structure.

Fig. 3. The molar magnetization of copper quinoxaline dibromide, CuQBr at $T = 0.7$ K.

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