Design and synthesis of magnetic ladders: structure and magnetic properties of Cu(2,3-dimethylpyrazine)Br$_2$

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Abstract

The compound copper(2,3-dimethylpyrazine)dibromide has been prepared and its structure solved by single crystal X-ray diffraction. The compound occurs as a coordination polymer with chains of Cu-2,3-dimethylpyrazine groups cross-linked into a ladder structure by the bromide ions. Magnetic susceptibility and magnetization data support a ladder model.
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1. Introduction

Copper oxides and mixed copper/metal oxides are used as catalysts for a wide variety of reactions. Recent reports have shown that these compounds are applicable to a wide range of redox reactions including reduction of NO [1], oxidation of CO [2], and the preparation of methanol from CO$_2$ [3]. A sub-group of these mixed metal oxides includes the copper oxide based superconductors. Although the focus on this group of copper oxide compounds has been on their superconducting properties, their application as catalysts has also been demonstrated especially for the Sr/Cu/O system where recent applications have included uses in fuel cells [4], oxidation of ethane [5] and cyclohexanol [6], peroxide deomposition [7], and the decomposition of nitric oxide [8]. The reactivity of these compounds has been tied to their low-dimensional structure.

We are interested in the magnetic properties of these materials and the possible interactions between their magnetic and electronic properties. The potential for quantum ($S = 1/2$) antiferromagnetic spin ladders to become superconducting when doped with charge carriers was predicted by Dagotto and Rice [9] and subsequently demonstrated experimentally on Sr/Cu/O systems [10]. These reports sparked renewed interest in the preparation and study of spin ladders as sources of both novel properties and a means to test fundamental magnetic theories. A magnetic ladder is a system wherein two chains of magnetic moments are connected to each other, but isolated from further magnetic exchange within the crystal lattice (see Fig. 1). The linkages between the magnetic moments, which provide the exchange pathway, may result from direct chemical bridging of the sources of magnetic moment [11] (metal ions, organic radicals), or via through-space interactions [12]. However, the magnetic exchange interactions in the Sr/Cu/O based ladders are so strong that many experiments are prohibited and hence model compounds with more moderate magnetic exchange are required.

We have long been interested in the use of pyrazine and pyrazine derivatives for the preparation of low-dimensional magnetic systems and have prepared and studied a number of linear chain [13] and square systems [14]. More recently we have begun studies on the synthesis and properties of magnetic ladders, which employ pyrazine derivatives as bridging ligands. The report by Lindroos and Lumme of the struc-

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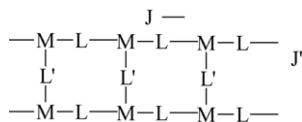*E-mail address:* mturnbull@clarku.edu (M.M. Turnbull).

Fig. 1. Pictorial representation of a magnetic spin ladder. M is a magnetic moment and L and L' represent groups providing for magnetic superexchange between the individual moments. The exchange energy along the ladder rails, J, and the ladder rungs, J', may or may not be the same.

ture of Cu(quinoxaline)Cl$_2$ clearly demonstrated that such compounds were possible [15]. The compound crystallizes as isolated ladders with the rungs provided by bridging chloride ions and the rails constructed by bridging quinoxaline molecules. We subsequently reported the synthesis of the isomorphous bromide analog and a preliminary examination of the magnetic properties of both compounds, which are well described by a ladder model [16].

The structures of these compounds as ladders are somewhat surprising in light of the structure of the parent compound Cu(pyrazine)Br$_2$ [17]. In this compound the bridging halides do not simply link adjacent Cu(II) ions into dimeric units, but rather into extended chains which are then linked by the pyrazine molecules into extended layers. Comparison of the pyrazine and quinoxaline structures reveals that the steric bulk of quinoxaline, relative to pyrazine, provides a blockade, preventing the halides ions from extended bridging. With this knowledge in hand, we postulated that other pyrazine derivatives, which possessed similar steric properties, would produce similar ladder complexes. We report here the synthesis, structure and powder magnetic susceptibility of Cu(2,3-dmpz)Br$_2$ and the copper(I) complex Cu$_3$(2,3-dmpz)$_2$Br$_3$ [2,3-dmpz = 2,3-dimethylpyrazine].

2. Experimental

2,3-Dimethylpyrazine was purchased from Aldrich and used as received. Copper(II) bromide was purchased from Aesar and used as received. IR spectra were recorded on a PE-1600, or PE Paragon 500 spectrophotometer and referenced to polystyrene.

2.1. Dibromo-2,3-dimethylpyrazinocopper(II) (1)

Compound **1** was synthesized by slow diffusion of 0.50 M solutions of CuBr$_2$ and 2,3-dimethylpyrazine in methanol. The prepared solutions were added to individual beakers which were then placed approximately 5 cm apart in a larger container. Additional methanol ($\sim$600 ml) was then slowly added (to avoid mixing) to the larger vessel to allow the reagents to diffuse together. The container was then closed and left in the dark. After approximately one month, the resulting crystals were harvested by vacuum filtration and washed with methanol to yield brown acicular crystals. IR (KBr): 3084m, 1437s, 1402s, 1372m, 1256m, 1187s, 1164s, 1104m, 970m, 847m cm^{-1}.

2.2. Tribromo-bis(2,3-dimethylpyrazino)tricopper(I) (2)

Crystals of **2** were isolated as a by-product of the synthesis of **1**. Careful examination of the product revealed a minute quantity (<1%) of crystals of **2** which were removed under a microscope for X-ray analysis.

2.3. Magnetic data collection

Data were collected using a Quantum Design MPMS-XL SQUID magnetometer. Crystals of **1** were powdered and packed into a #3 gelatin capsule. The magnetization of the sample as a function of applied field was collected from 0 to 5 T; no hysteresis was observed. Susceptibility data were taken over the temperature range from 1.8 to 330 K in an applied field of 1000 Oe. High field data were collected between zero and 33 T at 1.95 K.

2.4. X-ray data collection

Suitable crystals of **1** and **2** were selected from each sample and attached to glass fibers. Data were collected at 295(2) K for **1** and 292(2) K for **2** using a Bruker/Siemens SMART APEX instrument (Mo Kα radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low temperature device. Data were measured using omega scans of 0.3° per frame for 5 s, and a full sphere of data was collected. A total of 2132 frames were collected with a final resolution of 0.77 Å for both **1** and **2**. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART [18] software and refined using SAINTPlus [19] on all observed reflections. Data reduction and correction for Lp and decay were performed using the SAINTPlus software. Absorption corrections were applied using SADABS [20]. The structure was solved by direct methods and refined by least squares method on F^2 using the SHELXTL program package [21]. The structures were solved in the space group $C2/m$ and P-1 respectively, by analysis of systematic absences. All atoms were refined anisotropically. No decomposition was observed during data collection. There are high residuals in both structures; in **1** the residual 1.78 eÅ^{-3} is 0.86 Å from Br1 and in **2** the remaining density of 1.58 eÅ^{-3} is only 0.85 Å from Cu3. These are due to absorption effects and could not be modeled or eliminated. Details of the data collections and refinements are given in Table 1.

3. Results

3.1. Synthesis and structure

Reaction of CuBr$_2$ with 2,3-dimethylpyrazine in methanol solution under slow diffusion conditions resulted in the formation of brown crystals of Cu(2,3-dmpz)Br$_2$ (**1**) (Scheme 1)

Table 1
Crystal data and structure refinement for compounds **1** and **2**

	1	**2**
Empirical formula	$C_6H_8Br_2CuN_2$	$C_{12}H_{16}Br_3Cu_3N_4$
Formula weight	331.50	646.64
Temperature	295(2) K	292(2) K
Crystal system	Monoclinic	Triclinic
Space group	*C2/m*	*P*-1
Unit cell dimensions	$a = 13.1663(15)$ Å	$a = 7.2257(14)$ Å
	$b = 6.8831(8)$ Å	$b = 9.830(2)$ Å
	$c = 10.2366(12)$ Å	$b = 9.830(2)$ Å
	$\alpha = 90°$	$\alpha = 82.84(3)°$
	$\beta = 108.112(2)°$	$\beta = 85.61(3)°$
	$\gamma = 90°$	$\gamma = 80.93(3)°$
Volume	881.72(18) Å^3	906.0(3) Å^3
Z	4	2
Density (calculated)	2.497 mg/m^3	2.370 mg/m^3
Absorption coefficient	11.474 mm^{-1}	10.103 mm^{-1}
F(0 0 0)	628	616
Crystal size (mm^3)	$0.47 \times 0.10 \times 0.07$	$0.81 \times 0.12 \times 0.02$
Crystal color and habit	Brown needle	Gold needle
Theta range for data collection	2.09–27.48°	2.11–27.50°
Index ranges	$-16 \leq h \leq 16$	$-9 \leq h \leq 9$
	$-8 \leq k \leq 8$	$-12 \leq k \leq 12$
	$-13 \leq l \leq 13$	$-16 \leq l \leq 16$
Reflections collected	5637	11901
Independent reflections	1091 [R(int) = 0.0344]	4146 [R(int) = 0.0419]
Completeness to theta = 27.48°	99.8%	99.7%
Absorption correction	Semi-empirical from equivalents	
Maximum and minimum transmission	0.5006 and 0.0747	0.8235 and 0.0449
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	1091/0/56	4146/0/203
Goodness-of-fit on F^2	1.079	1.042
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0384$, $wR2 = 0.1080$	$R1 = 0.0460$, $wR2 = 0.1110$
R indices (all data)	$R1 = 0.0422$, $wR2 = 0.1103$	$R1 = 0.0652$, $wR2 = 0.1225$
Largest diff. peak and hole	1.784 and -0.892 e.Å^{-3}	1.579 and -1.454 eÅ^{-3}

along with traces amounts of the copper(I) compound $Cu_3(2,3\text{-dmpz})_2Br_3$ (**2**).

Crystals of **2** were so few in number that **1** could be rendered analytically pure by careful removal of **2** under a stereomicroscope. The initial reaction produced crystals of suitable quality for single crystal X-ray diffraction. Compound **1** crystallizes in the monoclinic space group *C2/m* as brown needles. The molecular unit is shown in Fig. 2. Selected bond lengths and angles are given in Table 2.

Compound **1** occurs as covalently bonded ladders with the rungs of the ladder formed by bridging bromide ions (Br1) while the rails are formed by bridging 2,3-dmpz molecules (see Fig. 3a). The coordination sphere of the Cu(II) ion is roughly square pyramidal with two Br ions and two N atoms lying in the basal plane and a semi-coordinate Cu−Br bond in the axial position.
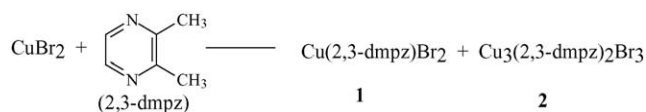
Scheme 1.

The Cu1−Br1 bond lengths are asymmetric with one short bond (2.442(1) Å) and one long bond (2.901(1) Å). Such asymmetric bonding is well known in five-coordinate systems [22], but more symmetric bonding is observed in Cu_nBr_{2n+2}
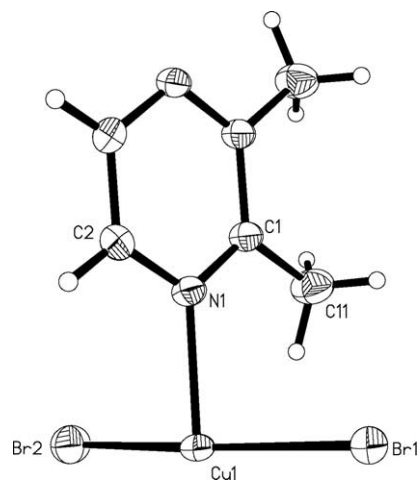
Fig. 2. The molecular unit of **1** showing 50% thermal ellipsoids. Only the asymmetric unit has been labeled.

Table 2
Selected bond lengths (Å) and angles (°) for **1** and **2**

	1		**2**	
Cu1—Br1#1	2.9011(12)	Br(1)—Cu(2)		2.5580(14)
Cu1—Br2	2.3833(10)	Br(2)—Cu(2)		2.3989(15)
Cu1—N1	2.057(4)	Br(2)—Cu(3)		2.3929(13)
N1—C1	1.341(6)	Br(3)—Cu(1)		2.6282(13)
N1—C2	1.341(6)	Br(3)—Cu(2)		2.8262(17)
C1—C1#3	1.417(9)	Br(3)—Cu(3)		2.5201(15)
C2—C2#3	1.373(9)	Cu(1)—N(1)		2.024(5)
C1—C11	1.484(7)	Cu(1)—N(7)		2.018(4)
		Cu(3)—N(10)#5		1.974(4)
		Cu(2)—N(4)#4		1.976(5)
		Cu(2)—Cu(3)		2.5155(13)
Cu(1)—Br(1)—Cu(1)#1	92.02(3)	Cu(1)—Br(1)—Cu(2)		82.50(4)
N(1)#2—Cu(1)—N(1)	173.2(2)	Cu(3)—Br(2)—Cu(2)		63.33(4)
N(1)—Cu(1)—Br(2)	88.73(10)	Cu(3)—Br(3)—Cu(1)		84.25(4)
N(1)—Cu(1)—Br(1)	90.56(10)	Cu(3)—Br(3)—Cu(2)		55.78(4)
Br(2)—Cu(1)—Br(1)	167.56(5)	Cu(1)—Br(3)—Cu(2)		75.33(4)
N(1)—Cu(1)—Br(1)#1	93.38(11)	N(7)—Cu(1)—N(1)		132.2(2)
Br(2)—Cu(1)—Br(1)#1	104.46(4)	N(7)—Cu(1)—Br(1)		105.03(13)
Br(1)—Cu(1)—Br(1)#1	87.98(3)	N(1)—Cu(1)—Br(1)		108.98(13)
N(1)—C(2)—C(2)#3	121.6(3)	N(7)—Cu(1)—Br(3)		103.71(13)
C(2)—N(1)—C(1)	117.9(4)	N(4)#4—Cu(2)—Br(2)		128.24(16)
C(2)—N(1)—Cu(1)	118.6(3)	N(4)#4—Cu(2)—Cu(3)		165.82(16)
C(1)—N(1)—Cu(1)	123.5(3)	Br(2)—Cu(2)—Cu(3)		58.22(4)
N(1)—C(1)—C(1)#3	120.5(3)	Cu(3)—Cu(2)—Br(1)		73.69(5)
N(1)—C(1)—C(11)	118.4(4)	Br(2)—Cu(3)—Br(3)		112.12(5)
C(1)#3—C(1)—C(11)	121.2(3)	N(10)#5—Cu(3)—Br(2)		131.45(15)

Symmetry transformations used to generate equivalent atoms: (#1) $-x+2,\ -y+1, -z+2$; (#2) $x, -y+1, z$ (#3) $x, -y, z$; (#4) $-x+1, -y+1, -z+1$; (#5) $-x, -y+1, -z$.
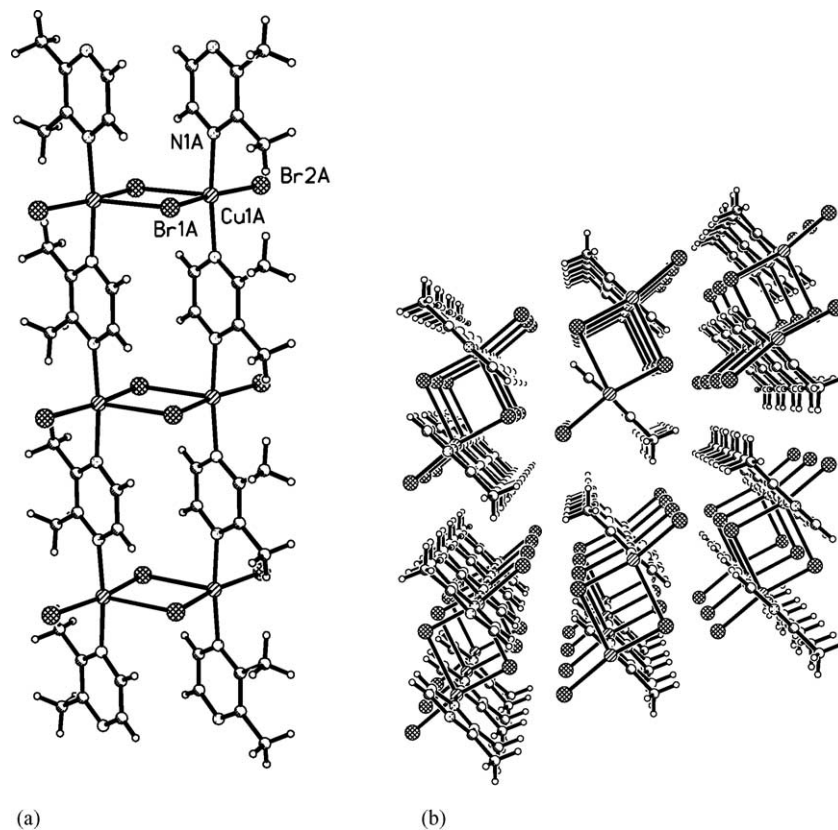

Fig. 3. (a) Ladder structure of **1**. (b) Packing diagram of **1** viewed parallel to the ladder axis.
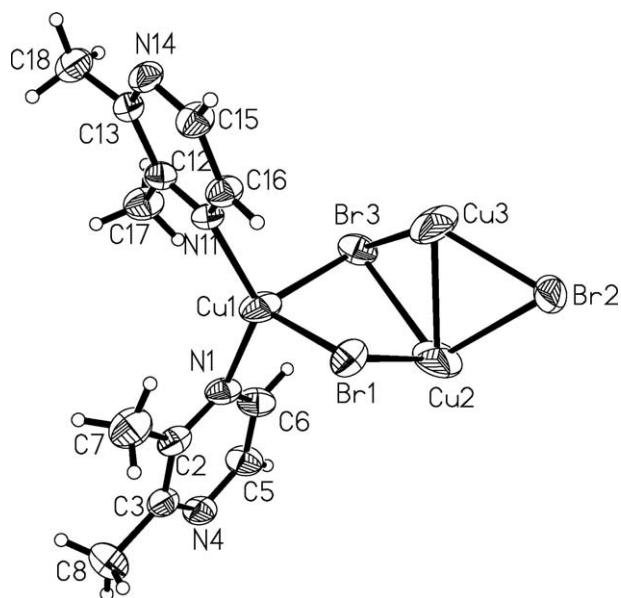
Fig. 4. A plot of the asymmetric unit of **2** showing 50% probability ellipsoids.

oligomers where all Cu−Br bonds lie in the equatorial plane [23]. Both asymmetric [24] and symmetric [25] bridging has been observed when the geometry at the Cu ion is pseudo-tetrahedral. The terminal Cu−Br bond is slightly shorter than the bonds to bridging bromines as is observed in all cases.

The ladders pack parallel to the *b*-axis and are separated from each other by the steric bulk of the methyl substituents attached to the pyrazine rings (Fig. 3b). The closest Br···Br contacts between ladders are 4.172(1) Å parallel to the *a*-axis.

Crystals of **2** suitable for single crystal X-ray analysis were also isolated from the reaction mixture. Compound **2** is a copper(I) complex which crystallizes in the triclinic space group *P*-1 with three unique copper ions in the asymmetric unit (see Fig. 4). Selected bond lengths and angles are given in Table 2.

Br1 and Br2 both bridge two copper ions while Br3 bridges all three unique copper ions. Cu1 is further bonded to nitrogen atoms from two independent 2,3-dmpz rings to make it four-coordinate while Cu2 and Cu3 are each bonded to a single N-atom. The copper–bromine bond lengths vary greatly with those to Br2 being the shortest ($\sim$2.395(5) Å) and those

to Br1 and Br3 ranging from $\sim$2.502 to $\sim$2.856 Å. The short Cu2–Cu3 distance (2.5155(13) Å) is the smallest separation reported for Cu ions bridged by bromides and is less than that observed in copper acetate dihydrate [26] and many of its derivatives, although shorter separations are known for some carboxylate bridged systems [27] and are common for alkylidene bridged systems [28] and some polyaza systems [29]. Neglecting the Cu−Cu bond, the geometry about Cu2 is distorted tetrahedral while Cu3 is distorted trigonal (the sum of the non Cu–Cu bonds about Cu3 $\sim$ 354°). Bond lengths and angles within the pyrazine moiety are comparable to those seen in **1**.

The combination of bridging bromide ions and 2,3-dmpz molecules generates a ladder like structure parallel to the *ac*-face diagonal (Fig. 5). The rails of the ladder are formed by alternating Cu1 ions and Cu2–Cu3 pairs linked by the 2,3-dmpz molecules. The rungs are formed by the bridging Br1 and Br3 ions.

3.2. Magnetic data

Susceptibility and magnetization data were collected for **1**. The susceptibility (Fig. 6) shows a rounded maximum near 20 K and then drops rapidly at lower temperatures, approaching zero as expected for a material with antiferromagnetic exchange and a singlet ground state. The slight upturn in susceptibility at the lowest temperatures is indicative of a trace paramagnetic impurity. Extrapolation of the high temperature portion of the Curie–Weiss plot of the data (χ^{-1} versus temperature, Fig. 6) gives a value of approximately −10 K for the Weiss constant θ.

The plot of magnetization as a function of applied field (Fig. 7) shows a lower critical field near 14 T. Saturation of the magnetization is not observed below 33 T (the maximum field available in the experiment).

4. Discussion

As anticipated based on the previous prepared CuX_2 (quinoxaline) complexes, compound **1** crystallizes as ladders and is isostructural with the quinoxaline complexes. The steric bulk of the methyl substituents on the pyrazine ring,
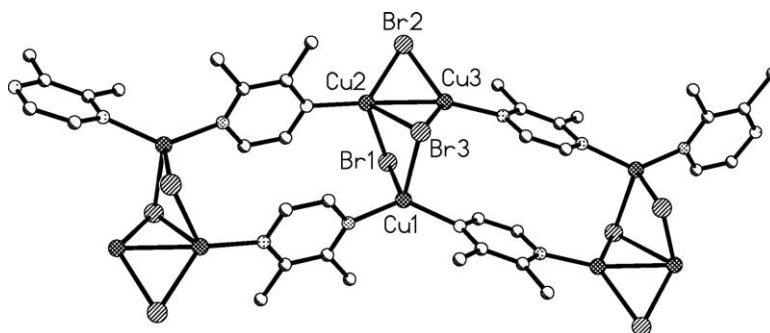

Fig. 5. Packing diagram of **2** showing the ladder-like structure.
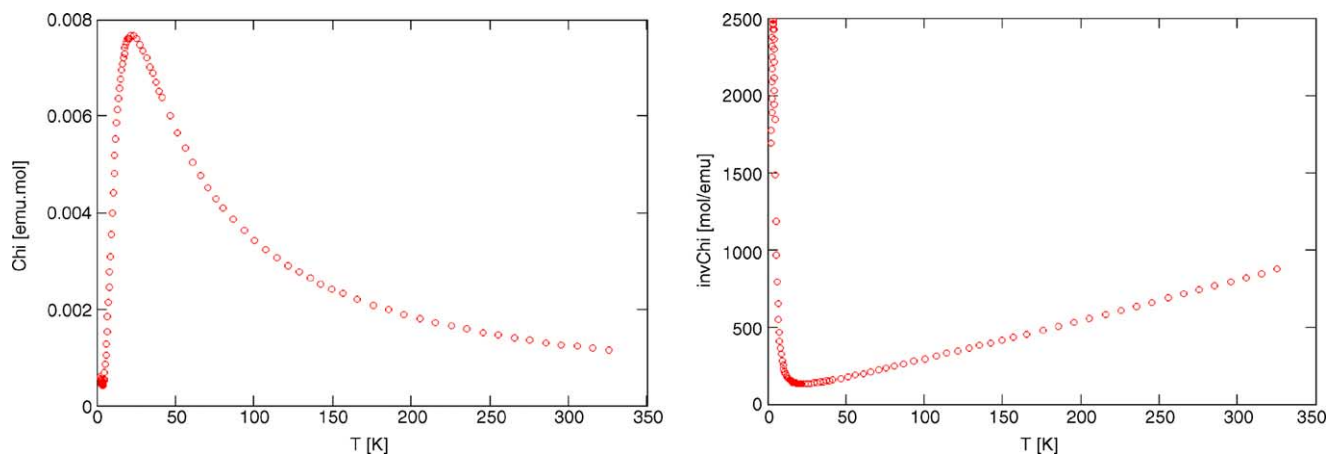
Fig. 6. Magnetic susceptibility vs. temperature (left) and χ^{-1} vs. temperature for **1**.

while not as great as the benzene ring which occupies that position in the quinoxaline compounds, is sufficient to prevent continuation of the bihalide bridges beyond formation of the ladder rung. However, the separation of the ladders themselves is not as great as is observed in the quinoxaline compounds so there is the possibility of stronger inter-ladder interactions.

The susceptibility data is in complete agreement with that expected for a magnetic ladder, dropping rapidly toward zero below the rounded maximum that is characteristic of low-dimensional magnetic materials. However, magnetic ladders cannot be distinguished from magnetic chains with alternating exchange by susceptibility data alone. The magnetization data does appear to support the ladder model with the lower critical field easily visible at ~14 T. It is interesting to note that this is the same lower critical field observed for Cu(quinoxaline)Br$_2$[16] which has the same bibromide bridged rung motif. The upper critical field could not be observed up to 33 T, and there is not even a hint of the magnetization saturating at that field, implying that the upper critical field must be much greater than 33 T. The presence of trace quan-

tities of the diamagnetic Cu(I) compound **2** in the product is not surprising; solutions of Cu(II) and 2,3-dimethylpyrazine have been observed to undergo spontaneous reduction of the metal previously [30].

Studies are in progress to fit the magnetic data to the ladder model [31] in order to extract the respective rung and rail exchange values. Higher field magnetization studies, to 65 T, at Los Alamos National Laboratory are also planned. Finally, the corresponding chloride complex, Cu(2,3-dmpz)Cl$_2$ has been recently isolated and preliminary magnetic data are similar to those observed for the bromide complex [32].

Acknowledgments

References

[1] R. Nickolov, N. Stankova, M. Khristova, D. Mehandjiev, J. Coll. Int. Sci 265 (2003) 121;
S. Bennici, A. Gervasini, V. Ragaini, Vittorio, Ultrason. Sonochem. 10 (2003) 61.
[2] T.-J. Huang, Y.-C. Kung, Catal. Lett. 85 (2003) 49.
[3] J.B. Wang, H.-K. Lee, T.-J. Huang, Catal. Lett. 83 (2002) 79.
[4] A.-L. Sauvet, J. Fouletier, J. Power Sources 101 (2001) 259.
[5] H.X. Dai, C.F. Ng, C.T. Au, J. Catal. 197 (2001) 251;
H.X. Dai, H. He, C.F. Ng, C.T. Au, J. Mol. Cat. A: Chem. 171 (2001) 217.
[6] T. Sivakumar, T.R.C. Nayar, K. Shanthi, B. Sivasankar, Ind. J. Chem. Tech. 5 (1998) 293.
[7] J. Hollingworth, W.R. Flavell, A.G. Thomas, S.C. Grice, C.E.J. Mitchell, P.M. Dunwoody, S. Warren, S.J. Squire, P.G.D. Marr, S.W.
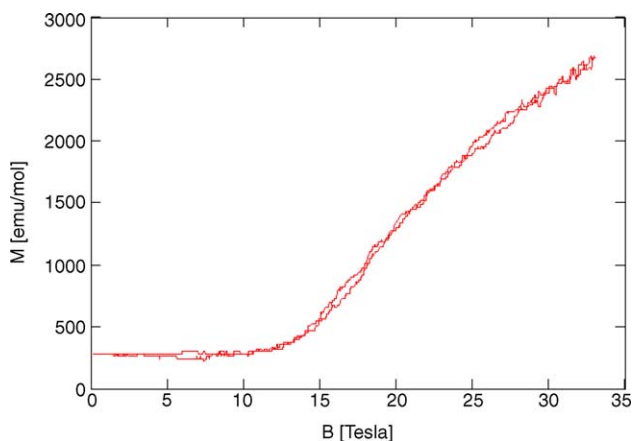

Fig. 7. Magnetization of **1** as a function of applied field at 1.95 K.

Downes, F.E. Hancock, J. Electron. Spectrom. Rel. Phen. 101–103 (1999) 765.

[8] L. Forni, C. Oliva, F.P. Vatti, N.A. Sinitsina, S.V. Sorochkin, A.V. Moev, A.V. Vishnyakov, J. Chem. Soc., Faraday Trans. 88 (1992) 1041.

[9] E. Dagotto, T.M. Rice, Science 271 (1996) 618;
E. Dagotto, Rep. Prof. Phys. 62 (1999) 1525.

[10] T. Nagata, M. Uehara, J. Goto, J. Akimitsu, N. Motoyama, H. Eisake, S. Uchida, H. Takahashi, T. Nakanishi, N. Mori, Phys. Rev. Lett. 81 (1988) 1090;
H. Mayaffre, P. Auban-Senzier, M. Nardone, D. Jerome, D. Poilblanc, C. Bourbonnais, U. Ammerahl, G. Dhalenne, A. Revcolevschi, Science 279 (1998) 345.

[11] D.N. Hendrickson, in: R.D. Willett, D. Gatteschi, O. Kahn (Eds.), Magneto-structural Correlations in Exchange Coupled Systems, Reidel, Dordrecht, 1985, pp. 555–602.

[12] M. Deumal, C.P. Landee, J.J. Novoa, M.A. Robb, M.M. Turnbull, Polyhedron 22 (2003) 2235.

[13] P.R. Hammar, M.B. Stone, D.H. Reich, C. Broholm, P.J. Gibson, M.M. Turnbull, C.P. Landee, M. Oshikawa, Phys. Rev. B 59 (1999) 1008;
C.P. Landee, M.M. Turnbull, Mol. Cryst. Liq. Cryst. 335 (1999) 193;
S. Amaral, W.E. Jensen, C.P. Landee, M.M. Turnbull, F.M. Woodward, F. M. Polyhedron 20 (2001) 1317.

[14] A.S. Albrecht, C.P. Landee, Z. Slanic, M.M. Turnbull, Mol. Cryst. Liq. Cryst. 305 (1997) 333;
M.M. Turnbull, A.S. Albrecht, G.B. Jameson, C.P. Landee, Mol. Cryst. Liq. Cryst. 335 (1999) 245.

[15] S. Lindroos, P. Lumme, Acta Crystallogr., Sect. C 46 (1990) 2039.

[16] C.P. Landee, A. Delcheva, C. Galeriu, G. Peña, M.M. Turnbull, R.D. Willett, Polyhedron 22 (2003) 2325.

[17] Th. Fetzer, A. Lentz, T. Debaerdemaeker, Z. Natursfursch, Z Natursfursch Teil B 22 (1989) 553.

[18] SMART: v.5.626, Bruker Molecular Analysis Research Tool, Bruker AXS, Madison, WI, 2002.

[19] SAINTPlus: v. 6.36a, Data Reduction and Correction Program, Bruker AXS, Madison, WI, 2001.

[20] SADABS: v. 2.01, an empirical absorption correction program, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, 2002.

[21] SHELXTL: v. 6.10, Structure Determination Software Suite, Sheldrick, G.M., Bruker AXS Inc., Madison, WI, 2001.

[22] M.R. Bond, H. Place, Z. Wang, R.D. Willett, Y. Liu, T.E. Grigereit, J.E. Drumheller, G.F. Tuthill, Inorg. Chem. 34 (1995) 3134;
I. Diaz, V. Fernandez, J.L. Martinez, L. Beyer, A. Pilz, U. Muller, Z. Naturforsch.; Teil B 53 (1998) 933;
J.T. Blanchette, R.D. Willett, Inorg. Chem. 27 (1988) 843.

[23] U. Geiser, R.D. Willett, M. Lindbeck, K. Emerson, J. Am. Chem. Soc. 108 (1986) 1173;
M. Honda, C. Katayama, J. Tanaka, M. Tanaka, Acta Crystallogr. Sect. C 41 (1985) 688;
A. Tosik, M. Bukowska-Stryzewska, J. Mrozinski, J. Coord. Chem. 21 (1990) 253.

[24] S. Haddad, R.D. Willett, Inorg. Chem. 40 (2001) 809;
R.D. Willett, K. Halvorson, Acta Crystallogr., Sect. C 44 (1988) 2068.

[25] R.D. Willett, Inorg. Chem. 40 (2001) 966;
C. Hasselbren, S. Jagner, I. Dance, Chem. Eur. J. 8 (2002) 1269.

[26] P. de Meester, S.R. Gletcher, A.C. Skapski, J. Chem. Sol. Dalton Trans. (1973) 2575.

[27] B. Chen, M. Eddaoudi, T.M. Teineke, J.W. Kampf, M. O'Keeffe, O.M. Yaghi, J. Am. Chem. Soc. 122 (2000) 11559;
S.M.-F. Lo, S.S.-Y. Chui, L.-Y. Shek, Z.-Y. Lin, X.-X. Zhang, G.-H. Wen, I.D. Williams, J. Am. Chem. Soc. 122 (2000) 6293.

[28] M. Hakansson, H. Eriksson, A.B. Ahman, S. Jagner, J. Organomet. Chem. 595 (2000) 102;
D.M. Knotter, W.J.J. Smeets, A.L. Spek, G. van Koten, J. Am. Chem. Soc. 112 (1990) 5895.

[29] C. Mealli, C.S. Arcus, J.L. Wilkinson, T.J. Marks, J.A. Ibers, J. Am. Chem. Soc. 98 (1976) 711;
M. Corbett, B.F. Hoskins, N.J. McLeod, B.P. O'Day, Aust. J. Chem. 28 (1975) 2377;
J.A. Farrar, V. McKee, A.H.R. Al-Obaidi, J.J. McGarvey, J. Nelson, A.J. Thomson, Inorg. Chem. 34 (1995) 1302.

[30] M.M. Turnbull, G. Pon, R.D. Willett, Polyhedron 10 (1991) 1835;
C. Navas, M.M. Turnbull, C. Giogas, C.P. Landee, W. Zhang, G. Pon, R.D. Willett, Polyhedron 12 (1993) 1019.

[31] D.C. Johnston, M. Troyer, S. Miyahara, D. Lidsky, K. Ueda, M. Azuma, Z. Hiroi, M. Takano, M. Isobe, Y. Ueda, M.A. Korotin, V.I. Anisimov, A.V. Mahajan, J.L. Miller, arXiv:cond-mat/0001147 (2000).

[32] B. Wells, C.P. Landee, M.M. Turnbull, unpublished results.