



Quantum linear magnetic chains: structure and magnetic behavior of (2-methylpyrazine)copper(II) nitrate

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Dedicated to the memory of Prof. Olivier Kahn who challenged, encouraged and supported so many of us

Abstract

The X-ray structure, susceptibility and magnetization of (2-methylpyrazine)copper(II) nitrate are reported. The compound crystallizes in the space group *Pmna* as a coordination polymer of Cu(II) ions bridged by 2-methylpyrazine. The resulting chains are magnetically well isolated and the susceptibility of the compound is well modeled as a one-dimensional Heisenberg antiferromagnet with $2J = 9.5(1)$ K. High-field magnetization studies to 30 T confirm the value of the exchange constant. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

One-dimensional antiferromagnetic systems linked by pyrazines (pz) have been studied for some time [1]. The linear chain coordination polymer Cu(pz)(NO₃)₂ was originally reported by Santoro et al. [2] and its magnetism studied by Hatfield and co-workers [3] who reported moderate Heisenberg-type exchange ($2J = 10.6$ K). Others have shown that the one-dimensional isolation of the chains is excellent, with no ordering observed down to 0.07 K [4]. Additional work by Richardson and Hatfield [5] on substituted-pyrazine/Cu(NO₃)₂ complexes showed similar magnetic behavior and thus suggested that these complexes also existed as linear chain coordination polymers, but they were hampered by the lack of suitable crystals for these substituted complexes.

We are interested in magneto-structural relationships and the use of the techniques of *molecular magnetism* [6] to study the effects of changes in packing, bond

lengths and angles, and electron density distribution in bridging species on magnetic exchange in low-dimensional systems, including linear chains. As such, we have been studying the magnetic properties of pyrazine and substituted pyrazine bridged one- and two-dimensional systems [7]. Here we report the crystal structure, temperature dependent magnetic susceptibility and magnetization for Cu(2-mepz)(NO₃)₂ [2-mepz = 2-methylpyrazine].

2. Experimental

2.1. Synthesis

Copper(2-methylpyrazine) nitrate, 1-Cu(NO₃)₂·3H₂O (2.42 g, 10 mmol) was dissolved in 5 ml of H₂O and added dropwise to a stirred solution of 2-methylpyrazine (0.944 g, 10 mmol) in 5 ml of H₂O. The resulting dark blue solution was covered with a piece of filter paper and allowed to evaporate slowly at room temperature. After nearly one month, blue-lavender crystals were isolated by filtration, washed quickly with cold water, and dried under vacuum to give 0.662 g IR

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(KCl, cm^{-1}): ν 3104 w, 3057 w, 1506 s, 1486 s, 1377 vs-br, 1288 m, 1162 m, 1008 m, 521 m.

2.2. X-ray data collection and refinement for $\text{I-C}_5\text{H}_6\text{CuN}_4\text{O}_6$

Mo $\text{K}\alpha = 0.71073 \text{ \AA}$; Crystal system, orthorhombic; space group, $Pmna$; $Z = 4$; unit cell dimensions: $a = 6.713(3)$, $b = 11.872(5)$, $c = 11.578(5) \text{ \AA}$; Temperature = $168(2) \text{ K}$; $\mu = 2.391 \text{ mm}^{-1}$; θ range = $2.46\text{--}26.38^\circ$; Total reflections collected (via ϕ and ω scans) = 6117 [1006 independent; $R_{\text{int}} = 0.0293$]; completeness to $\theta = 26.38^\circ$, 96.7%. A blue needle-shaped crystal, $0.02 \text{ mm} \times 0.05 \text{ mm} \times 0.80 \text{ mm}$, was mounted on a Bruker SMART system for data collection, cell refinement and data reduction [8]. The structure was solved via direct methods [9] and refined [10] via full-matrix least-squares. Absorption corrections were made via SADABS [11]. Hydrogen atoms were placed in calculated positions and refined as a riding model with fixed isotropic U . Neutral scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from Ibers and Hamilton [12]. Full-matrix least-squares refinement on F^2 for 1006 data and 87 parameters gave final R indices of $R_1 = 0.0338$, $wR_2 = 0.0848$ [$I > 2\sigma(I)$] and $R_1 = 0.0477$, $wR_2 = 0.0893$ (all data).

Selected bond distances and angles are given in Table 1.

Table 1
Bond lengths (\AA) and angles ($^\circ$) for (2-methylpyrazine)copper(II)

Bond lengths			
Cu–N(1)	1.985(3)	Cu–O(1)	2.014(3)
Cu–O(2)	1.978(3)	Cu–O(3)	2.479(3)
Cu–O(4)	2.446(4)	N(3)–O(1)	1.289(4)
N(3)–O(3)	1.247(5)	N(3)–O(5)	1.216(4)
N(1)–C(2)	1.329(4)	N(1)–C(1)	1.333(4)
C(1)–C(1) ^a	1.382(5)	C(2)–C(2) ^a	1.381(6)
C(2)–C(3)	1.495(7)		
Bond angles			
O(2)–Cu–N(1)	89.98(7)	N(1) ^b –Cu–N(1)	178.51(14)
O(2)–Cu–O(1)	177.81(12)	N(1)–Cu–O(1)	90.00(7)
O(2)–Cu–O(4)	57.43(11)	N(1)–Cu–O(4)	89.36(7)
O(1)–Cu–O(4)	120.38(11)	O(2)–Cu–O(3)	125.76(11)
N(1)–Cu–O(3)	90.62(7)	O(1)–Cu–O(3)	56.43(11)
O(4)–Cu–O(3)	176.81(10)	O(5)–N(3)–O(3)	124.0(4)
O(5)–N(3)–O(1)	118.9(4)	O(3)–N(3)–O(1)	117.1(3)
N(3)–O(1)–Cu	103.6(2)	N(3)–O(3)–Cu	82.9(2)
N(2)–O(2)–Cu	102.9(2)	N(2)–O(4)–Cu	82.3(2)
C(2)–N(1)–C(1)	118.4(3)	C(2)–N(1)–Cu	121.5(2)
C(1)–N(1)–Cu	120.1(2)	N(1)–C(1)–C(1) ^b	120.7(2)
N(1)–C(2)–C(2) ^b	120.8(2)	N(1)–C(2)–C(3)	124.9(4)

^a Symmetry transformations used to generate equivalent atoms: $-x - 1, y, z$.

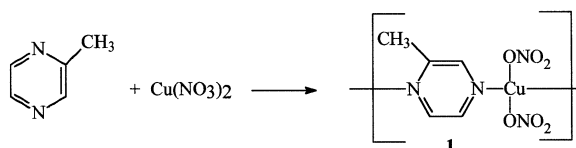
^b Symmetry transformations used to generate equivalent atoms: $-x, y, z$.

2.3. Magnetic studies

The magnetic susceptibility of a polycrystalline sample of $\text{Cu}(2\text{-mepz})(\text{NO}_3)_2$ was studied in a field of 1 T using a Quantum Design MPMS SQUID Magnetometer. Corrections were made for the temperature-independent magnetism of the Cu(II) ion ($\chi_{\text{TIP}} = 60 \times 10^{-6} \text{ emu mol}^{-1}$) and for the diamagnetic contributions calculated from Pascal's constants. The high-field magnetization studies were made using a vibrating sample magnetometer (Lake Shore Model 7600 VSM), a helium cryostat, and the 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 bath.

3. Results and discussion

Reaction of copper(II) nitrate with 2-methylpyrazine in aqueous solution gave (2-mepz)copper(II) nitrate, **1**.



Single crystals suitable for X-ray diffraction were grown after multiple attempts by slow evaporation of the solution over a period of several weeks. Relevant bond lengths and angles are given in Table 1. A portion of one chain is shown in Fig. 1.

The structure of **1** consists of alternating copper(II) ions and 2-methylpyrazine ligands forming chains parallel to the a -axis. The two crystallographically independent nitrate ions sit on a mirror plane and are coordinated to the coppers through one short Cu–O bond ($\sim 2.0 \text{ \AA}$) and one semi-coordinate bond ($\sim 2.45 \text{ \AA}$). Bond lengths and angles within the two nitrate moieties are identical within experimental error.

Compound **1** crystallized in the orthorhombic space group $Pmna$, the same space group as observed for the parent compound $\text{Cu}(\text{pyrazine})(\text{NO}_3)_2$ [13]. This was unexpected due to the much lower symmetry of the 2-methylpyrazine ligand compared to pyrazine itself.

The copper atom is located at $0, y, z$ and sits upon the same crystallographic mirror as the nitrate groups. As such, it is distinct from the pyrazine complex where the copper is located at the origin. The lowered symmetry of the 2-methylpyrazine ring, relative to pyrazine, is accommodated in the structure by a disorder in the position of the methyl group between the 2- and 3-positions relative to any given copper atom. This type of disorder has not been reported previously, although Teichert and Sheldrick [14] have reported a disorder of

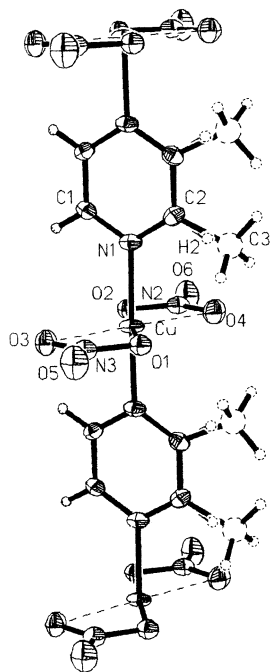


Fig. 1. ORTEP drawing of the chain structure of **1** showing 50% probability ellipsoids. Only those atoms in the asymmetric unit are labeled. The disordered methyl group (C3) and hydrogen (H2) bonded to C2 shown dotted.

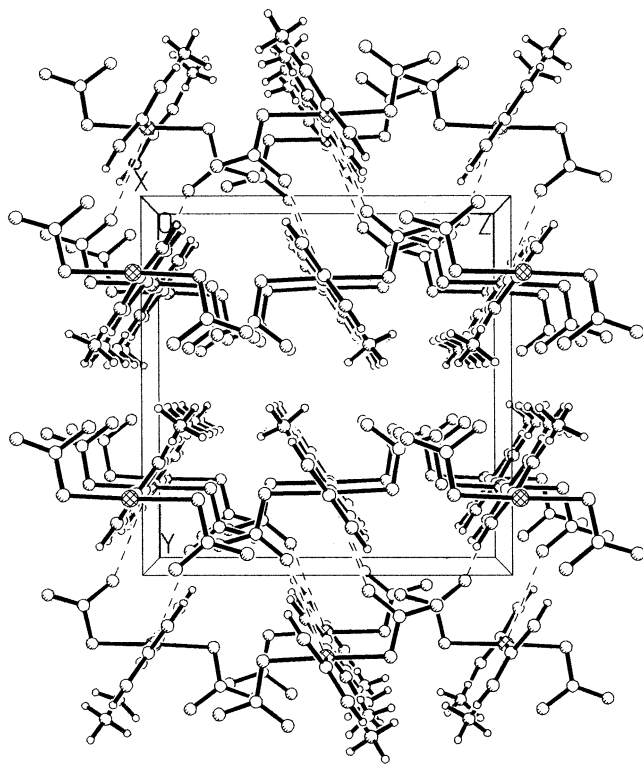


Fig. 2. Packing diagram of **1** viewed parallel to the *a*-axis showing the orientation of the methyl groups into layers parallel to the B-face and weak inter-chain interactions between nitrate oxygens and copper(II) ions in adjacent chains (dotted lines).

the methyl group between the 2- and 5-positions in two copper(I) coordination polymers of 2-methylpyrazine. There is no evidence of disorder of the methyl substituent to the 5-, or 6-positions in the present compound nor of any disorder in the nitrates. The Cu–N1 bond length of 1.985(3) Å is surprisingly short. In two Cu(I) complexes where disorder results in a single Cu–N bond, lengths vary from 2.07 to 2.12 Å, while in a similar non-disordered Cu(I) complex the Cu–N bonds are 2.162 and 2.170 Å to the nitrogen distal to the methyl substituent and 2.216 and 2.224 Å to the nitrogen proximal to the methyl substituent [14]. In Cu(II) complexes, only coordination to the distal nitrogen is observed with bond lengths of 2.03 ± 0.01 Å [15]. One report of a bridging 2-methylpyrazine–Cu(II) structure has been made [16], but the proximal nitrogen in the ring is only semi-coordinated resulting in distances of 2.07 and 2.73 Å to the distal and proximal nitrogens, respectively.

The packing of the chains in the lattice produces an interesting alternating sheet motif, with the sheets parallel to the crystallographic B-face. As can be seen in Fig. 2, the methyl substituents on the pyrazine rings are oriented in double layers such that the methyl groups of adjacent sheets face toward each other, with the hydrogens attached to C5 and C6 left facing each other in the alternate layers. As a result, the distance between Cu atoms parallel to the *b*-axis alternates between 6.73 and 5.15 Å. A similar packing is observed in the structure of Cu(2,3-dimethylpyrazine)(NO₃)₂ [17].

Short contacts are observed between copper atoms and nitrate oxygen O3 of the adjacent chain across the short sheet spacing ($\text{Cu–O3}_{(x, -y, 1-z)} = 3.29$ Å), but similar contacts were observed in the structure of the parent complex and do not lead to detectable inter-chain exchange [13]. Adjacent chains along the *c*-axis are related by the *a*-glide and offset by 1/2 unit cell so that the distance between the Cu atoms is 6.59 Å, slightly shorter than the inter-copper distance with the pyrazine-bridged chains (6.71 Å).

The lack of disorder in the nitrate groups and the excellent correlation of the magnetic properties of **1** with a uniform magnetic chain raises a question regarding the nature of the disorder of the methyl substituent. If the methyl group were truly randomly placed between the 2- and 3-positions within a chain, three types of Cu centers would result: those coordinated to two distal nitrogens, those coordinated to two proximal nitrogens and those coordinated to one of each. These three different coordination environments about the copper atom would lead to three slightly different magnetic environments within a chain.

An alternative interpretation of the disorder is that within any given chain, the orientation of the methyl groups is all the same, such that each copper is coordinated to one proximal and one distal nitrogen, but that

half of the chains run in each direction and that the relative direction of adjacent chains within the structure is random. This type of disorder has been characterized previously in the complexes $[\text{Ni}(\text{en})_2(\text{NO}_2)]\text{BF}_4$ [18] and $[\text{Ni}(\text{en})_2(\text{NO}_2)]\text{ClO}_4$ [19]. While the actual space group in these cases is $Pn2_1a$, the structure must be solved in the space group $Pnma$. The apparent mirror symmetry results from uni-directional chains that are randomly placed in the lattice, as we favor for the current complex.

3.1. Magnetic susceptibility results

We use $2J$ for of the Heisenberg Hamiltonian

$$H = 2J \sum S_i \cdot S_{i+1}$$

where a positive value of J corresponds to antiferromagnetic interactions. The magnetic susceptibility of **1** is plotted as the top data set in Fig. 3(a). The data set is characterized by a broad rounded maximum at 6.2 K with a value of $\chi_{\text{max}} = 0.0257 \text{ emu mol}^{-1}$. The susceptibility data have been fit to an expression for the molar susceptibility χ_{mol} of the $S = 1/2$ Heisenberg antiferromagnetic linear chain [20], as has been found appropriate for other copper linear chain compounds, with the parameters J and g allowed to vary freely.

The exchange constant for **1** was found to be $2J = 9.5(1) \text{ K}$, and $g = 2.11(1)$. For comparison, the exchange constant for $\text{Cu}(\text{pz})(\text{NO}_3)_2$ is $2J = 10.4(2) \text{ K}$. The molar susceptibility of $\text{Cu}(\text{pz})(\text{NO}_3)_2$ is also plotted in Fig. 3(a) for comparison, where it is observed that the maximum susceptibility occurs at a higher temperature and reaches a lower value than is the case of the 2-methylpyrazine analog, consistent with a larger exchange strength for $\text{Cu}(\text{pz})(\text{NO}_3)_2$. Fitting the latter

data set to the same model yields an exchange constant of $2J = 10.5(2) \text{ K}$ and a g -factor of $2.11(1)$. The solid curves in Fig. 3(a) correspond to the theoretical expressions for χ_{mol} using the parameters above. The agreement is excellent.

The universality of the magnetic behavior of different compounds can be examined by plotting the dimensionless susceptibility $\chi^* = \chi_{\text{mol}} J / C$ as a function of the dimensionless temperature $T^* = kT / J$ (where C is the Curie constant). If the compounds are all described by the same magnetic model, the reduced data will fall in one universal curve, independent of their different exchange strengths or Curie constants. Fig. 3(b) is a plot of χ^* versus T^* for $\text{Cu}(\text{2-mepz})(\text{NO}_3)_2$, **1**, and $\text{Cu}(\text{pz})(\text{NO}_3)_2$. The two data sets superimpose within experimental error, demonstrating both of them to be excellent realizations of the one-dimensional $S = 1/2$ Heisenberg antiferromagnetic model. As will be reported later [21], all four members of the $\text{Cu}(\text{subpz})(\text{NO}_3)_2$ family with either one or two methyl groups correspond very closely to this same magnetic model.

3.2. High-field magnetization results

The high-field, low-temperature (2.0 and 4.2 K) relative magnetization curves $M(H)/M_{\text{sat}}$ of $\text{Cu}(\text{2-mepz})(\text{NO}_3)_2$ are plotted as a function of applied field in Fig. 4(a). It is seen that the data initially increase linearly with field, then curve upward before achieving saturation. Close examination shows the lower temperature data to have the lower initial slope before increasing more rapidly at higher fields. This crossover is consistent with the lower initial susceptibility found at lower temperatures (see Fig. 3(a)). The data at 2.0 K show complete saturation by 21 T. At 4.2 K, the increase in the number of thermally activated spin

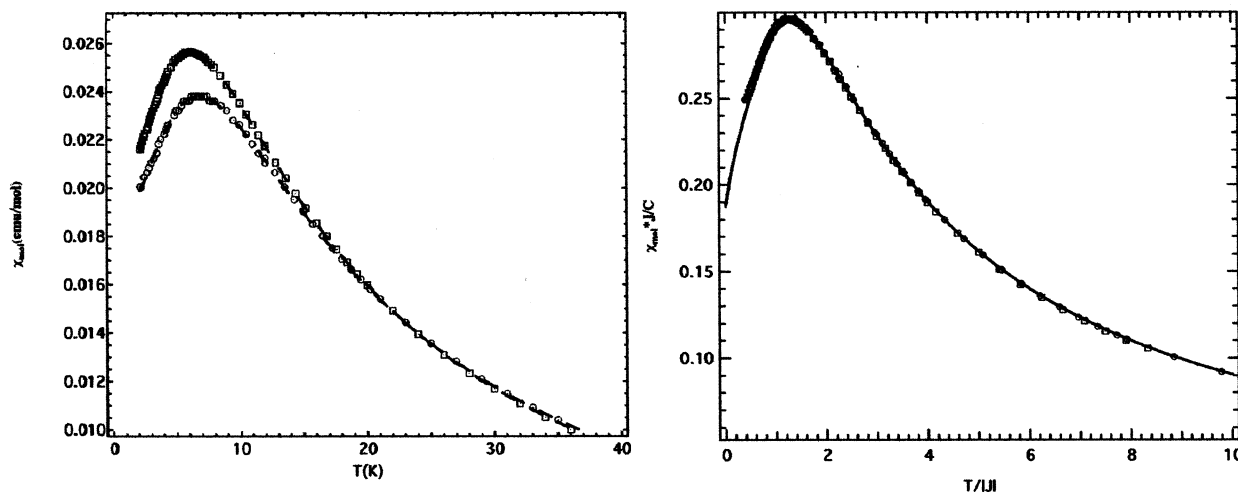


Fig. 3. (a) Magnetic susceptibility as a function of temperature for **1** (upper curve) and $\text{Cu}(\text{pz})(\text{NO}_3)_2$ (lower curve). (b) Reduced magnetic susceptibility as a function of reduced temperature for the same two compounds.

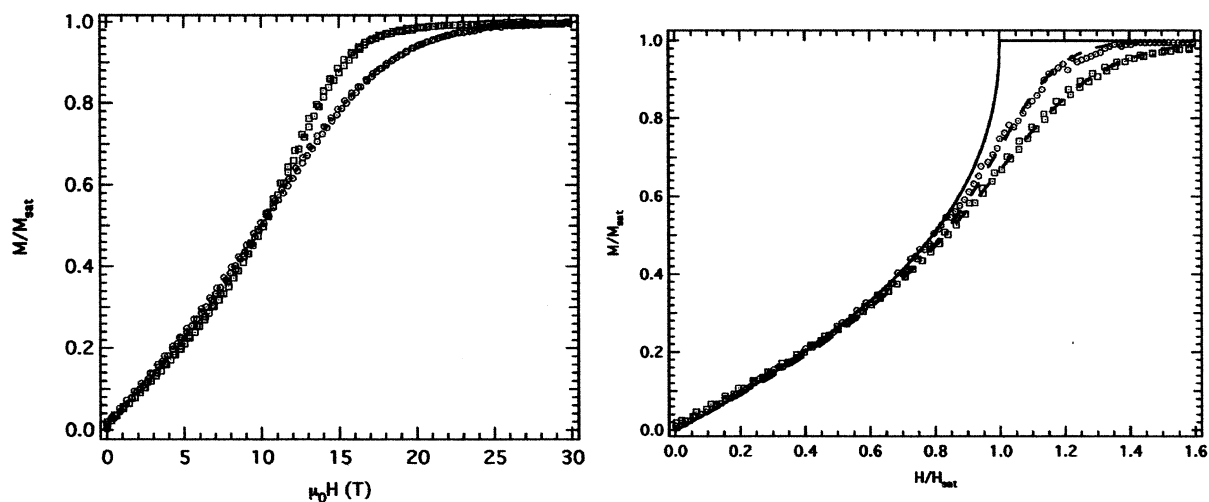


Fig. 4. (a) Reduced magnetization as a function of applied field for **1** at 2 K (upper curve) and 4.2 K (lower curve). (b) Theoretical prediction for a one-dimensional chain (solid line) and the reduced magnetization as a function of reduced temperature for **1** (lower data) and $\text{Cu}(\text{pz})(\text{NO}_3)_2$ (upper data).

excitations prevents the magnetization from reaching saturation until larger fields.

The zero-temperature saturation field, $H_{\text{sat}}(0)$, is proportional to the antiferromagnetic interaction strength which must be overcome to align the moments fully, according to the molecular field equation

$$\mu_0 H_{\text{sat}}(0) = zJ/(g\mu_B)$$

where z is the number of nearest neighbors and μ_B is the Bohr magneton. For linear chain copper compounds with $z = 2$ and $g \approx 2.1$, $H_{\text{sat}} \approx 1.42(2J)$, where the saturation field is in Tesla and the units of J are Kelvin. The saturation field $H_{\text{sat}}(0)$ for $\text{Cu}(\text{2-mepz})(\text{NO}_3)_2$ has been estimated by determining the field at which the magnetization at the lowest measured temperature has the greatest positive slope. In the limit of $T \rightarrow 0$, this field becomes $H_{\text{sat}}(0)$. The saturation field for $\text{Cu}(\text{2-mepz})(\text{NO}_3)_2$ has been determined to be $\mu_0 H_{\text{sat}}(0) = 13.7(3)$ T, corresponding to an exchange constant $2J/k_B = 9.6(2)$ K, derived from the molecular field equation. This value is seen to be in excellent agreement with the values of J obtained from the susceptibility data, $9.5(1)$ K, and demonstrates that high-field magnetization curves provide independent assessments of the exchange strengths in magnetic systems.

Fig. 4(b) shows the low-temperature relative magnetization data sets for $\text{Cu}(\text{2-mepz})(\text{NO}_3)_2$ ($T = 2.0$ K) and $\text{Cu}(\text{pz})(\text{NO}_3)_2$ ($T = 1.8$ K) plotted as the relative magnetization $M(H)/M_{\text{sat}}$ versus the relative field H/H_{sat} . As in the relative susceptibility plot (Fig. 3(b)), both data sets should fall on the predicted curve (solid line) for the relative magnetization had they been collected at $T = 0$. The data sets follow the curve well up

to about 70% of the saturation field, but fall below the prediction at higher fields, as thermal excitations reduce the magnetization. The degree of thermal excitation is described by the ratio of T/J , the ratio of thermal energy to exchange energy. These ratios are 0.17 and 0.21 for $\text{Cu}(\text{pz})(\text{NO}_3)_2$ and $\text{Cu}(\text{2-mepz})(\text{NO}_3)_2$, respectively, showing the 2-mepz compound to be relatively warmer and less easy to magnetize. The dashed curves through the data sets represent the results of simulations for the magnetization curves at finite temperatures [22] at relative temperatures of 0.15 and 0.25, respectively. It is seen that when finite temperatures are taken into account, the magnetization curves of the two compounds are also very well described by the $S = 1/2$ Heisenberg antiferromagnetic linear chain model.

It is clear that $\text{Cu}(\text{2-mepz})(\text{NO}_3)_2$ provides another excellent example of a quantum Heisenberg linear chain and that it compares well in both its structural and magnetic properties with the parent molecule. As we continue to expand the number of these related complexes, we shall investigate trends in relationship between the nature of the magnetic exchange and the structure of the materials.

4. Supplementary data

Crystallographic data have been deposited with the CCDC (The Director, 12 Union Road, Cambridge, CB2 1EZ, UK) and are available on request quoting the deposition number 148973 (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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