

Cu(II) complexes with coordinated pyrazine-dioxide: pyrazine bridged chains

Christopher P. Landee,^a Diane A. Dickie,^b Mark M. Turnbull^{c,*} and Jan L. Wikaira^d

^a *Department of Physics, Clark University, 950 Main Street, Worcester, MA 01610.*

^b *Dept. of Chemistry, University of Virginia, Charlottesville, VA, 22904 USA*

^c *Carlson School of Chemistry and Biochemistry, Clark University, 950 Main Street, Worcester, MA 01610.*

^d *School of Physical and Chemical Sciences, University of Canterbury, Private Bag 4800, Christchurch, New Zealand.*

Abstract

Two new pyrazine-bridged, linear chain complexes of Cu(II) of the formula $[\text{Cu}(\text{pzdo})_2(\text{H}_2\text{O})_2(\text{pz})](\text{A})_2 \cdot n\text{H}_2\text{O}$ [pzdo = pyrazine-N,N'-dioxide; pz = pyrazine; A = BF_4^- (**1**), ClO_4^- (**2**)] have been prepared. Single-crystal X-ray diffraction shows the Cu ions to be six-coordinate, pyrazine-bridged chains with trans-pairs of ancillary ligands. The pzdo molecules are coordinated through their oxygen atoms. The ClO_4^- and BF_4^- anions are each two-site disordered in the lattice. Further, there are partial occupancy water molecules in the lattice which prove to be very weakly bound. The structures are stabilized by hydrogen bonds between the coordinated water molecules and the non-coordinated pzdo oxygen atoms as well as the anions. Variable temperature magnetic susceptibility data show antiferromagnetic interactions and the data were fit to the uniform chain model yielding $J/k_B = -13.0(2)$ K and $-11.8(2)$ K for **1** and **2**, respectively $[H = -J \sum S_1 \cdot S_2]$. In addition, the structure of the serendipitously prepared compound $[\text{Cu}(\text{pz})(\text{pzdo})(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (**3**) is described. The compound crystallizes as rectangular layers of Cu(II) ions bridged by pzdo (parallel to the *a*-axis) and pyrazine (parallel to the *b*-axis) with the water molecules coordinated in the axial sites.

Introduction

Chemists and physicists have been working to understand the physical parameters controlling magnetic exchange at the molecular level for some time¹ and there continues to be interest in such studies.² In particular, studies of low-dimensional magnetic lattices, that is those

where the magnetic exchange occurs predominately in two dimensions or fewer, have allowed for the examination of magnetostructural correlations due to the simplified pathways and associated Hamiltonian. Such lattices include zero-dimensional systems, such as dimers and clusters, ladders and layers, but perhaps the most well studied low-dimensional lattice is the one-dimensional one, the chain. The uniform magnetic chain has been of great interest, particularly since the work of Bonner and Fisher provided analytical models with which to study such compounds.³ Perhaps the most well-studied of these materials is $\text{Cu}(\text{pz})(\text{NO}_3)_2$ (pz = pyrazine)⁴ where the pyrazine ring provides the superexchange pathway. Studies via a wide variety of techniques, ranging from temperature and field dependent magnetization studies⁵ and EPR⁶ to μSR ⁷ and neutron diffraction,⁸ coupled with theoretical work⁹ have demonstrated the uniformity of exchange and high degree of isolation.

With such a start, it is not surprising that pyrazine has become so common as a bridging ligand in coordination chemistry and especially in magnetochemistry. It is limited to mono- or bi-dentate coordination and provides good control of structure with its preference for linear motifs. As a result of these highly favorable properties, pyrazine and substituted pyrazine derivatives have been employed in the formation of a wide variety of low-dimensional lattices, such as magnetic ladders¹⁰ as well as both square¹¹ and rectangular¹² layered structures. Pyrazine mediates antiferromagnetic exchange in its bridging mode, with J/k_B values typically in the -5 to -18 K range for copper(II) based systems,¹³ while the nickel complex $\text{Ni}(\text{pz})_2(\text{ClO}_4)_2$ exhibits a value of nearly 0 K.¹⁴ The parameters controlling the exchange are still not well understood and further work is needed.

We have previously studied a number of complexes in this family and in particular, those with the general formula $[\text{Cu}(\text{pz})\text{L}_2(\text{H}_2\text{O})_2](\text{A})_2$ where A is a non-coordinated anion (typically ClO_4^- , BF_4^- or PF_6^-) and L is an ancillary ligand that can be varied to study the effects of its steric and electronic properties on the magnetic exchange through the pyrazine bridge. Such studies have included those where L is a 2-¹⁵ or 4-pyridone¹⁶, or pyrazine-N-oxide.¹⁷ In the case of the 4-pyridone compounds, there was potential for interchain hydrogen bonding via the distal N-H functional group. However, no direct cross-linking of the chains was observed, only hydrogen bonding between the N-H and the dissociated anion. We reasoned that introduction of a hydrogen bond acceptor, rather than a donor, would improve the probability of interchain hydrogen bonding with the coordinated water molecule, and hence considered pyrazine-N,N'-

dioxide (pzdo) as a potentially suitable L. Pzdo is known to serve as a hydrogen bond acceptor¹⁸ and to coordinate to Cu(II)¹⁹ through the oxygen atoms. With this potential to modify the packing of the pyrazine bridged chains, we undertook the preparation of the materials and here report the synthesis, structure and magnetic properties of the compounds [Cu(pzdo)₂(H₂O)₂(pz)](A)₂·nH₂O [pzdo = pyrazine-N,N'-dioxide; pz = pyrazine; A = BF₄⁻ (**1**), ClO₄⁻ (**2**)] as well as the structure of the unexpected two-dimensional layer complex [Cu(pz)(pzdo)(H₂O)₂] (ClO₄)₂ (**3**).

Experimental:

Copper(II) perchlorate hexahydrate, copper(II) tetrafluoroborate hexahydrate and pyrazine (pz) were purchased from Sigma-Aldrich. All materials were used as received. Pyrazine-N,N'-dioxide (pzdo) was synthesized according to the literature.²⁰ "50% methanol" refers to a 50:50 solution of methanol and water by volume. FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 spectrometer via ATR. X-Ray powder diffraction data were collected with a Bruker AXS-D8 X-ray Powder Diffractometer. Elemental analyses were performed at the Marine Science Institute, University of California Santa Barbara, CA.

NOTE: perchlorate salts are potentially explosive and should be used and prepared in small quantities.

Catena-diaquabis(pyrazine-N,N'-dioxide)(pyrazine)copper(II) tetrafluoroborate monohydrate (**1**) Cu(BF₄)₂·6H₂O (0.684 g, 2.00 mmol) was dissolved in 3 ml of water, pz (0.164 g, 2.00 mmol) was dissolved separately in 2 ml of water and pzdo (224 mg, 2.00 mmol) were dissolved in 8 ml of water (~30 minutes required). The pz and pzdo solutions were combined and then slowly added to the stirring pale-blue copper(II) solution resulting in a darker blue solution. Overnight, dark, flat pleochroic orange/green crystals appeared; they were recovered by filtration, rinsed with cold water and dried to constant weight (182 mg). The filtrate was placed in a desiccator over Drierite for another four weeks, resulting in a 78 mg crystal. Total 0.260 g (44%). CHN calcd(exp) for C₁₂H₁₈N₆B₂O₇F₈Cu: C 24.21 (24.10), H 3.05 (3.00), N 14.11 (13.73). IR (cm⁻¹) 3493br-w, 3141w, 3079w, 1644w, 1482w, 1456m, 1425w, 1294w, 1232m, 1053br-s, 847w, 804s, 595w.

Catena-diaquabis(pyrazine-*N,N'*-dioxide)(pyrazine)copper(II) perchlorate monohydrate (**2**) Cu(ClO₄)₂•6H₂O (0.741 g, 2.0 mmol) was dissolved in 5 ml of water, while pyrazine (0.160 g, 2.00 mmol) was dissolved separately in 2 ml of water and pzdo (0.224 g, 2.00 mmol) was dissolved in 8 ml of water (~30 minutes required). The pz and pzdo solutions were combined and slowly added to the stirring pale-blue copper solution. No color change was observed. The solution was partially covered and left for slow evaporation. After ~ four weeks, a large green/orange pleochroic crystal appeared which was recovered by filtration, rinsed with cold methanol, and dried to constant mass (278 mg). The filtrate was covered and left to evaporate further. After ~ three weeks additional product was recovered by filtration, rinsed with cold methanol and dried to constant weight (98 mg). Total: 0.376 g (61%). CHN calcd(exp) for C₁₂H₁₈N₆O₁₅Cl₂Cu: C 23.22 (22.72), H 2.92 (2.69), N 13.54 (13.25). IR (cm⁻¹) 3450br-w, 3137w, 3076w, 1653w, 1483w, 1453m, 1424w, 1292w, 1249m, 1230m, 1094br-s, 1048br-s, 845w, 801s, 622w.

In examination of the product from the synthesis of **2**, one unique, non-pleochroic emerald green crystal was observed and isolated mechanically. Single-crystal X-ray diffraction revealed compound **3**, *catena*-diaqua(pyrazine)(pyrazine-*N,N'*-dioxidocopper(II) perchlorate [Cu(pz)(pzdo)(H₂O)₂] (ClO₄)₂. To date, repeated attempts at a direct preparation of this compound have been unsuccessful.

X-Ray structure determination:

Data collections for **1** and **2** were carried out on a Bruker D8 Venture Photon III Kappa four-circle diffractometer system equipped with an Incoatec IμS 3.0 micro-focus sealed X-ray tube (Mo Kα, λ = 0.71073 Å) and a HELIOS double bounce multilayer mirror monochromator using phi and omega scans. Data collection, reduction and absorption corrections were made using Bruker Instrument Service v6.2.15, SAINT V8.40B and SADABS v.2014/5. Data collection for **3** was carried out on a Bruker Kappa diffractometer fitted with an APEXII CCD detector, employing graphite-monochromated Mo-Kα radiation, using phi and omega scans. Data collection, reduction and absorption corrections were made using Bruker Instrument Services v.2012.12.0.3, SAINT v.8.34A and SADABS v.2014/5. The structures were solved using SHELXS-97²¹ and refined via least squares analysis with SHELXL-2018.²² Non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms bonded to carbon were

placed in calculated positions and refined using a riding model and isotropic thermal parameters. Hydrogen atoms bonded to nitrogen or oxygen were located in the difference Fourier maps and their positions refined with fixed isotropic thermal parameters. In some cases, anti-bumping restraints were applied to the N-H, or O-H bond lengths to prevent unreasonably short bonds. Details of the data collection and refinement are provided in Table 1. Table 2 contains selected bond lengths and angles while Table 3 contains hydrogen bonding information. The structures have been deposited with the CCDC as: **1**, 2155980; **2**, 2155979; **3**, 2156655. Compound **1** was refined with the tetrafluoroborate ion as two-site disordered with final refined occupancies of 0.582(4)/0.418(4). The lattice water molecule shows partial occupancy and refined, independently, to 0.418(4). Anti-bumping restraints were applied to the coordinated water molecule and mild bond length and anti-bumping restraints were applied to the partial lattice water molecule. Compound **2** was refined with a two-site disorder model for the perchlorate ion with final occupancies of 0.859(2)/0.141(2). The partial occupancy water molecule was four-site disordered with final occupancies of 0.050(9), 0.054(11), 0.070(7) and 0.098(8). No attempts to locate or place the hydrogen atoms for the lattice water molecule were made and they were not included in the final refinement.

Powder X-ray diffraction measurements of samples of **1** and **2** showed them to be the same phase as the single crystals. No impurities were detected.

Magnetic data collection

Magnetic susceptibility data were collected via a Quantum Design MPMS-XL SQUID magnetometer. Powdered samples of **1-2** were packed into gelatin capsules and fit into drinking straws attached to sample rods. Magnetization of samples at 1.8K was measured in increasing field from 0 to 50 kOe, and selected values as the field decreased to zero, which showed no hysteresis. Temperature dependent susceptibility data were collected in 1 kOe from 1.8 to 310 K. Background corrections were made for the signal of the gelatin capsule and straw (measured independently), the temperature independent paramagnetism of the copper(II) ion and the diamagnetism of the constituent atoms, estimated via Pascal's constants.²³ Data were fit to the Hamiltonian $H = -J \sum S_1 \cdot S_2$.

Table 1. X-Ray data collection and refinement parameters for **1** and **2**.

	1	2	3
Formula	C ₁₂ H _{17.67} B ₂ CuF ₈ N ₆ O _{6.84}	C ₁₂ H ₁₆ Cl ₂ CuN ₆ O _{14.55}	C ₈ H ₁₂ Cl ₂ CuN ₄ O ₁₂
MW (g/mol)	592.51	611.47	490.66
T(K)	100(2)	100(2)	120(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a (Å)	6.8401(3)	6.8489(3)	8.4065(3)
b (Å)	13.9313(6)	14.6141(7)	6.7933(3)
c (Å)	11.4614(5)	11.2595(6)	14.1545(6)
β (°)	102.7795(16)	102.8671(15)	101.555(4)
V (Å ³)	1065.12(8)	1098.67(9)	791.95(6)
Z	2	2	2
Size(mm)	0.092x0.063x0.044	0.245x0.222x0.197	0.42x0.28x0.14
Abs. co. (mm ⁻¹)	1.144	1.324	1.794
F(0,0,0)	595	619	494
Θ range (°)	2.336- 28.278	2.321 - 30.515	3.339-37.956
Index ranges	-9 ≤ h ≤ 9	-7 ≤ h ≤ 9	-14 ≤ h ≤ 14
	-18 ≤ k ≤ 17	-20 ≤ k ≤ 20	-11 ≤ k ≤ 11
	-15 ≤ l ≤ 15	-16 ≤ l ≤ 16	-23 ≤ l ≤ 24
Rfln. Coll.	17182	19917	14034
Ind. rfln (σ)	2629 (0.0493)	3346 (0.0258)	4092 (0.0353)
Data/Res/ para	2629/11/228	3346/0/252	4092/0/130
Final R (R1) [I>2σ(I)] (wR2)	0.0402(0.0737)	0.0228(0.0621)	0.0309(0.0718)
R index (R1) (all data) (wR2)	0.0505(0.0769)	0.0238(0.0628)	0.0407(0.0792)
Final peak/ hole(e/Å ³)	0.335/-0.433	0.501/-0.494	0.612/-1.10

Table 2. Selected bond lengths and angles for **1**, **2** and **3**.

<u>Bond Lengths (Å)</u>	<u>1</u>	<u>2</u>	<u>3</u>
Cu1-N1	2.0319(17)	2.0347(9)	2.0149(11)
Cu1-O11	2.0087(15)	2.2669(8)	1.9956(9)
Cu1-O1W	2.2781(17)	2.0002(8)	2.3230(10)

<u>Bond Angles (°)</u>			
N1-Cu1-O11	90.47(7)	90.77(3)	90.06(4)
N1-Cu1-O1W	89.99(7)	90.77(3)	90.29(4)
O11-Cu1-O1W	83.45(6)	84.39(3)	78.67(4)
Cu1-O11-N11	125.27(12)	127.95(6)	127.11(7)

Table 3. Hydrogen bonding parameters for **1-3**.

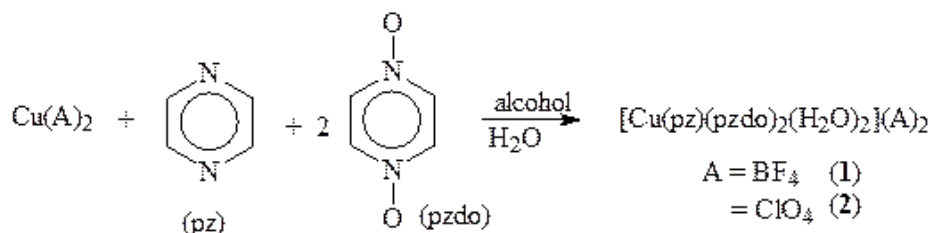
Atoms	D-H (Å)	H...A (Å)	D...A (Å)	∠ DHA
1				
O1W H1A O14a	0.838(17)	1.948(18)	2.784(2)	175(3)
O1W H1B F4	0.821(17)	1.894(18)	2.715(3)	177(3)
O1W H1B O2W	0.821(17)	2.22(2)	2.952(6)	149(3)
O2W H2A F2'	0.93(4)	2.00(6)	2.88(2)	156(8)
O2W H2B O14b	0.87(4)	2.42(7)	3.103(5)	137(7)
2				
O1W H1A O14a	0.795(19)	1.859(19)	2.6470(12)	170.5(17)
O1W H1B O1c	0.783(17)	1.971(18)	2.7482(13)	171.8(16)
O1W H1B O2'c	0.783(17)	2.103(18)	2.735(6)	138.0(15)
O1W H1B O2W'c	0.783(17)	2.43(3)	2.985(19)	128.6(15)
3				
O1W H1B O1d	0.78(2)	2.09(2)	2.8680(15)	173(2)
O1W H1A O2e	0.74(2)	2.09(2)	2.8276(15)	176(2)

Symm. Op.: a = x, 0.5-y, z-0.5; b = x-1, 0.5-y, z-0.5; c = x,y,z-1; d = x, 0.5-y, z+0.5;
e = 1-x,1-y,-z.

Results and Discussion

Syntheses

Reaction of pyrazine and pyrazine-dioxide with copper(II) tetrafluoroborate/perchlorate in aqueous alcohol gave $[\text{Cu}(\text{pzdo})_2(\text{H}_2\text{O})_2(\text{pz})](\text{A})_2 \cdot n\text{H}_2\text{O}$ (see Figure 1).



Structures

Compounds **1** and **2** are isostructural. Compound **1** crystallizes in the monoclinic space group $P2_1/c$ and the asymmetric unit comprises one pzdo molecule, one coordinated water molecule, one-half coordinated pz molecule and Cu(II) ion, one BF_4^- anion (disordered, *vide infra*) and a partial occupancy lattice water molecule (see Figure 2). Both the Cu(II) ion and the pyrazine ring are located on crystallographic inversion centers. *Cis* bond angles around the Cu ion to the pz and pzdo rings are nearly 90° while all *trans* bond angles are 180° as required by symmetry (see Table 2 for bond lengths and angles). The common Jahn-Teller elongation is observed at Cu1, with the coordinated water molecules occupying the axial positions [$d_{\text{Cu1-O1w}} = 2.278(2) \text{ \AA}$] and lying 6.5° off the normal to the equatorial plane, likely as a result of hydrogen bonding. The pyrazine rings bridge successive copper ions, related by a unit cell translation, creating polymeric chains parallel to the *a*-axis (Fig. 3a). The pzdo molecules are coordinated through one N-oxide oxygen atom and do not bridge Cu ions.

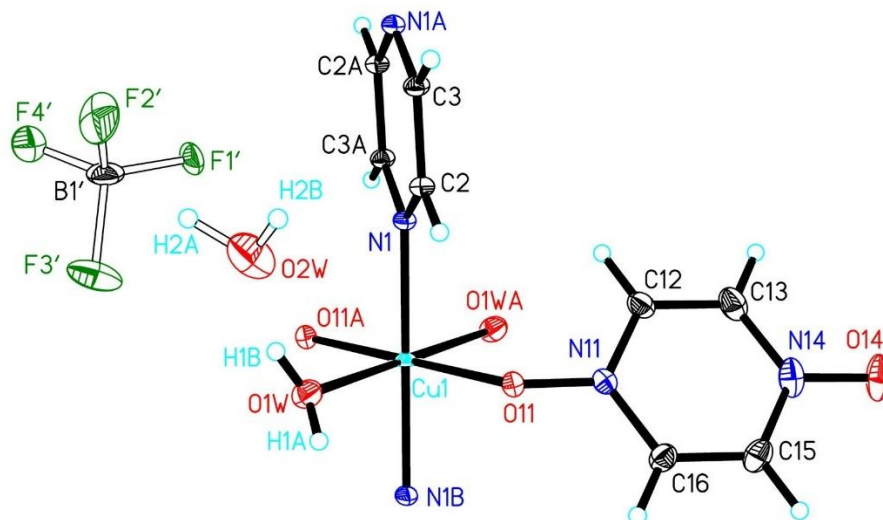


Figure 2 – The molecular unit and copper coordination sphere of **1**. Only those hydrogen atoms whose positions were refined are labelled. Symm. Op. A (1-*x*, 1-*y*, -*z*), B (-*x*, 1-*y*, -*z*). Only the minor component of the disordered BF₄⁻ anion is shown along with the partial occupancy water molecule.

The chains pack in the lattice with two different types of stabilizing interactions (see Figure 3b). Hydrogen bonds are formed between the coordinated water molecule and both the non-coordinated pzdo oxygen atoms ($d_{D...A} = 2.784(3)$ Å, see Table 3 for full hydrogen bonding details) and the tetrafluoroborate anion/lattice water molecule. There are also short contacts between pzdo N11 and the disordered BF₄⁻ anion ($d_{N11...F2} = 2.847$ Å, $d_{N11...F2'} = 2.869$ Å).

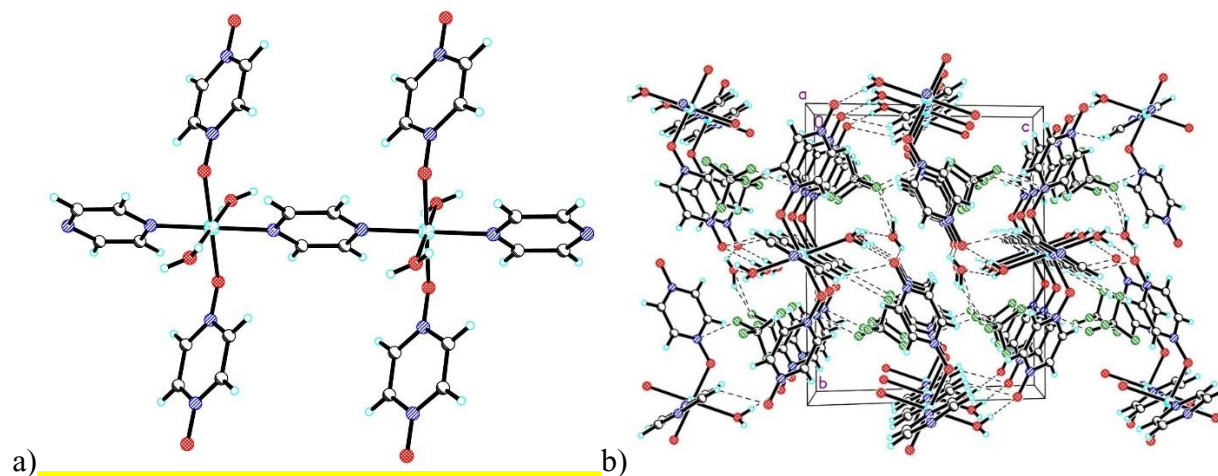


Figure 3 – **a) The chain structure of **1** viewed parallel to the *c*-axis (*a*-horizontal).** b) Packing diagram of **1** viewed parallel to the chain (*a*) axis. Dash lines represent hydrogen bonds and short F...N contacts. Only one site for the disordered BF₄ anion is shown for clarity.

The disorder of the tetrafluoroborate anion and the partial occupancy lattice water molecule are intimately related (see Figure SI.1). The anion is two-site disordered and refined to occupancies of 0.582(4)/0.418(4). The partial lattice water molecule refined independently to an occupancy of 0.418(7), identical to that of the minor BF_4^- component. In terms of space, this is logical as the major BF_4^- component and the water molecule would overlap if both were present at the same time. When present, the water molecule serves as a hydrogen bond donor to the BF_4^- anion and to the uncoordinated pzdo oxygen atom (O14) and as a hydrogen bond acceptor to the coordinated lattice water molecule (see Table 3). It should be noted that the water content from X-ray refinement, while close, does not agree with the combustion analysis data which indicate the presence of one lattice water molecule per formula unit. Once isolated from the mother liquor, the crystals are not stable indefinitely (stability is clearly dependent upon the relative humidity) which we associate with the loss of the lattice water molecule.

The perchlorate complex, **2**, exhibits a similar crystal structure to that of **1**, but with some significant differences. The molecular unit and major perchlorate contributor are shown in Figure 4. Again, both the Cu(II) ion and the pyrazine ring are located on crystallographic inversion centers. Also again, a Jahn-Teller elongation is observed at Cu1, however rather than the coordinated water molecules occupying the axial positions, it is O11(O11B) ($d_{\text{Cu1-O11}} = 2.667(1) \text{ \AA}$) from the pzdo molecules that occupy the axial sites, lying 5.6° off the normal to the equatorial plane, a slightly smaller deviation than observed in **1**. It is surprising that the J.-T. axis has changed given the nearly identical coordination geometry of the compounds and must result from a subtle difference in the packing structures, likely as a result of the difference in size of the perchlorate ion and tetrafluoroborate ion, as well as the difference in occupancy of the disordered components (close to 50:50 for **1**, but very different for **2** (*vide infra*)).

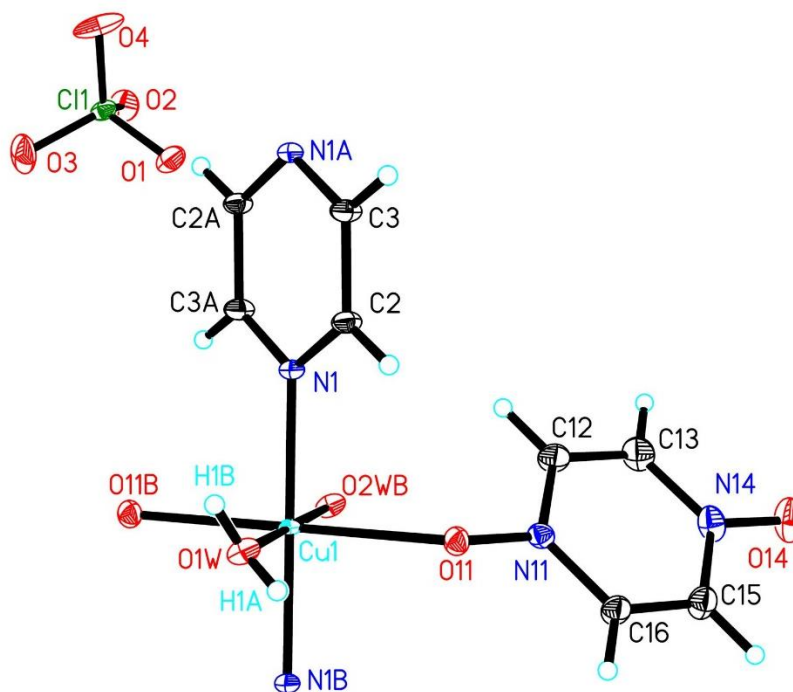


Figure 4 – The molecular unit and copper coordination sphere of **2**. Only those hydrogen atoms whose positions were refined are labelled. Symm. Op. A ($-x, 1-y, -z$), B ($1-x, 1-y, -z$). Only the major component of the disordered ClO_4^- anion is shown for clarity. The partial occupancy lattice water molecule is excluded (see text).

The packing of **2** very closely resembles that of **1** (see Figure 5), with hydrogen bonds formed between the coordinated water molecule and both the non-coordinated pzdo oxygen atoms ($d_{\text{D}\dots\text{A}} = 2.647(1) \text{ \AA}$, see Table 3 for full hydrogen bonding details) and the perchlorate anion/lattice water molecule. There are also short contacts between pzdo N11 and the disordered ClO_4^- anion ($d_{\text{N11}\dots\text{O4}} = 2.819 \text{ \AA}$).

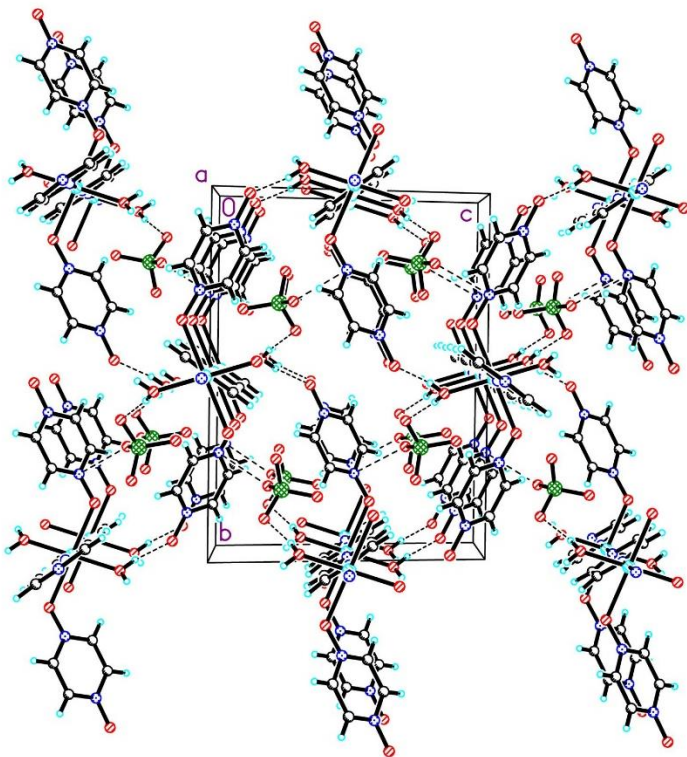


Figure 5 – Packing diagram of **2** viewed parallel to the chain (*a*) axis. Dash lines represent hydrogen bonds and short O...N contacts. Only the major component of the disordered perchlorate ion is shown for clarity.

As was the case in **1**, the counterion of **2** (perchlorate) is two-site disordered, but unlike **1** where the refined occupancies were near 50:50, they are ~ 86:14 in **2**; the perchlorate ion lies nearly completely in one position. An additional difference is the partial water molecule which is four-site disordered in **2** with final refined occupancies of 0.050(9)[O2WA], 0.054(11) [O2W], 0.070(7) [O2W''] and 0.098(8) [O2W'] (see Figure SI.2). The positions of the water molecules are such that O2 and O2W can exist concurrently with the major occupancy perchlorate ion location while O2W' and O2W'' can only exist while the perchlorate ion is in the minor occupancy position. While not as close as observed in **1**, the sum of the occupancies of O2W' and O2W'' [0.168(15)] agrees well with the occupancy of the minor perchlorate component [0.141(2)].

The layer complex, **3**, was isolated serendipitously as one single-crystal by-product in the preparation of **2** and crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit (see Figure 6) comprises one-half Cu(II) ion, one-half pyrazine molecule and one-half pzdo molecule, all of which lie across crystallographic inversion centers, one coordinated water molecule and

one perchlorate ion, both of which lie in general positions. The Cu1-N1 bond is slightly shorter than that seen in either **1** or **2**. The Cu1-O11 bond is also slightly shorter than that observed in **1** and significantly shorter than the Cu1-O11 in **2** which lies along the Jahn-Teller axis. Compound **3** also undergoes a J.-T. elongation along the Cu1-O1W axis, where that bond is longer than the equivalent position in either **1** or **2**.

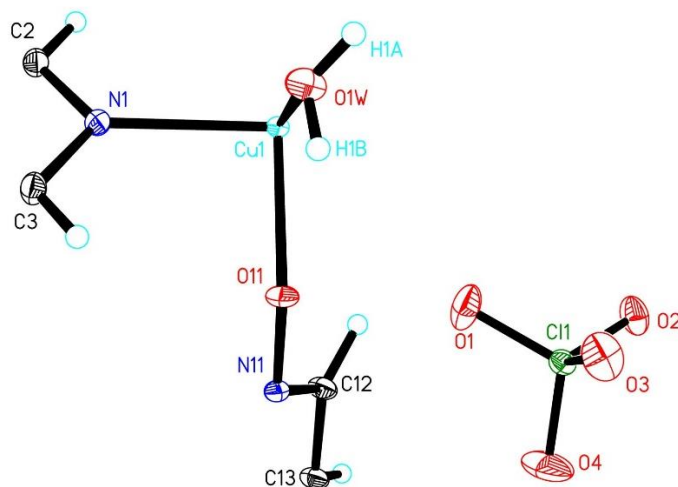


Figure 6 - A thermal ellipsoid plot of the asymmetric unit of **3**. Only those hydrogen atoms whose positions were refined are labelled.

The pyrazine rings bridge the Cu(II) ions parallel to the *b*-axis while the pzdo molecules bridge the Cu(II) ions parallel to the *a*-axis, generating rectangular layers (Figure 7a) with the coordinated water molecules lying above and below those layers. The layers are separated by the perchlorate ions which lie in the interstices, but are also stabilized via hydrogen bonding (Figure 7b) between the coordinated water molecules and the perchlorate ions both above and below the layers ($d_{O1W...O1} = 2.868(2)$; $d_{O1W...O2} = 2.8286(2)$; see Table 3 for details). Despite repeated efforts via a variety of techniques we have been unable to develop a rational synthesis of the compound.

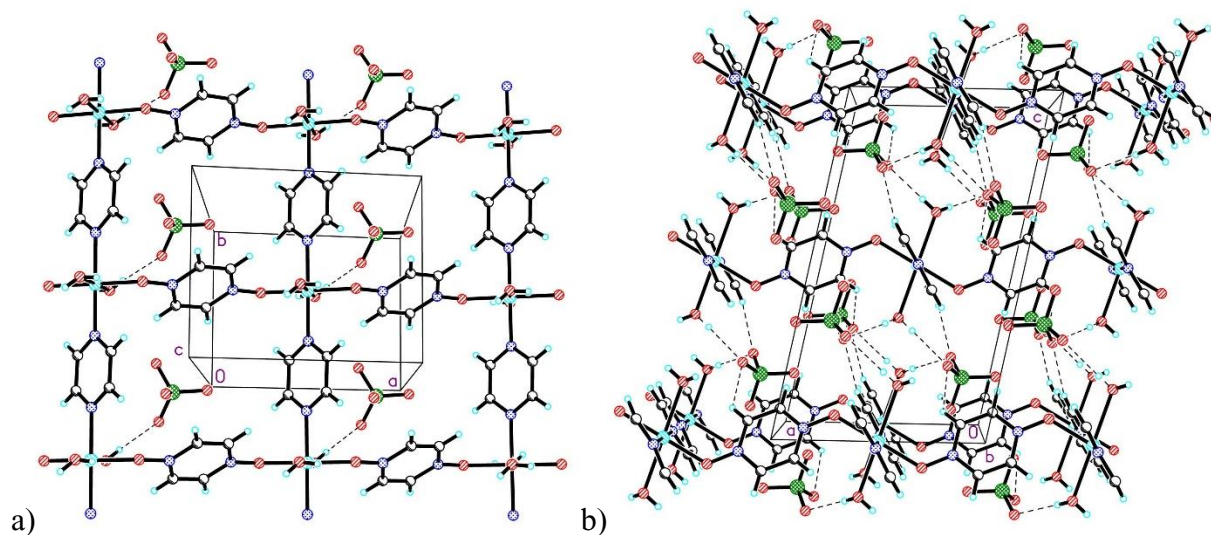


Figure 7. a) The layer structure of **3** viewed perpendicular to the layer (parallel to the *c*-axis). b) The interlayer interactions in **3** viewed parallel to the layers (along the pyrazine bridged *b*-axis). Dashed lines represent hydrogen bonds in both figures.

For all three compounds, the Cu-pz bond lengths ($\sim 2.03(1)$ Å) are comparable to many seen in pyrazine-bridged chains. The Cu-N bond in $[\text{Cu}(\text{pz})(\text{NO}_3)_2]$ is 1.985 Å⁴ and comparable to the $[\text{Cu}(\text{pz})(\text{NO}_2)_2]$ compound (1.992 Å),²⁴ both slightly shorter than seen in **1** and **2**. The pyridine-N-oxide complex $[\text{Cu}(\text{pz})(\text{pyO})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ ¹⁷ is comparable to **1** and **2** at Cu-N = 2.034 Å. The Cu-O bond lengths to the pzdo molecules, on the other hand, are significantly shorter than those seen in the compounds $[\text{CuX}_2(\text{H}_2\text{O})_2(\mu\text{-pzdo})]$ ($\text{X} = \text{Cl}, \text{Br}$).^{19a} In both of these compounds, the pzdo molecule is bridging and coordinates along the Jahn-Teller axis with bond lengths 2.56 Å (Cl) and 2.65 Å (Br). Even in compound **2**, where the pzdo molecule also coordinates along the J.-T. axis, the bond is much shorter ($2.2669(8)$ Å), suggesting that it is the bridging behaviour that causes the significant lengthening. However, in the complex $[\text{Cu}_2(\text{H}_2\text{O})_2(\mu\text{-pzdo})_3(\text{ClO}_4)_4] \cdot \text{H}_2\text{O}$ the pzdo molecules are also bridging and exhibit Cu-O bond lengths of 1.95 Å.^{19b} In this latter compound, perchlorate ions occupy the J.-T. axis, while the pzdo molecules coordinate in the equatorial plane.

Magnetism

The molar magnetizations at 1.8 K between zero and 50 kOe of **1** and **2** are presented in Supplementary Information Figure SI.3. The magnetization of **1** is linear up to 20 kOe but shows slight upward curvature at larger fields, with a value of 880 emu/mol at 50 kOe. The upward

curvature is characteristic of a low-dimensional Heisenberg antiferromagnetic compound. The data for **2** is linear up to 15 kOe before curving upward at a faster rate; at 50 kOe, it has obtained a value of 955 emu/mol. Both values are well below the saturation magnetization (~6000 emu/mol), revealing the presence of antiferromagnetic interactions, with **1** having the larger exchange strength.

The magnetic susceptibilities of **1** and **2** between 1.8 and 310 K are presented in Figure 8. (The Curie-Weiss analyses for the two compounds appear as Supplementary Information SI.4a and 4b, respectively. The values for the Curie constants and the Weiss parameter (θ) appear in Table 4.) Figure 8 uses a log/log scale to emphasize the important low-temperature region. The two data sets are very similar, with rounded maxima of 20.36×10^{-3} and 21.89×10^{-3} cm³/mol occurring at temperatures of 8.90 and 7.40 K for **1** and **2**, respectively. Acting in accordance with the known structures, we have compared the susceptibilities to the model of a 1D $S = \frac{1}{2}$ Heisenberg antiferromagnet (1DQHAF),²⁵ allowing the parameters for the Curie constants C , exchange strengths J/k , fraction of paramagnetic contributions, and possible small, temperature-independent background, to vary. Excellent agreement between the data and fitted parameters were found over the entire data sets, Figure 8.

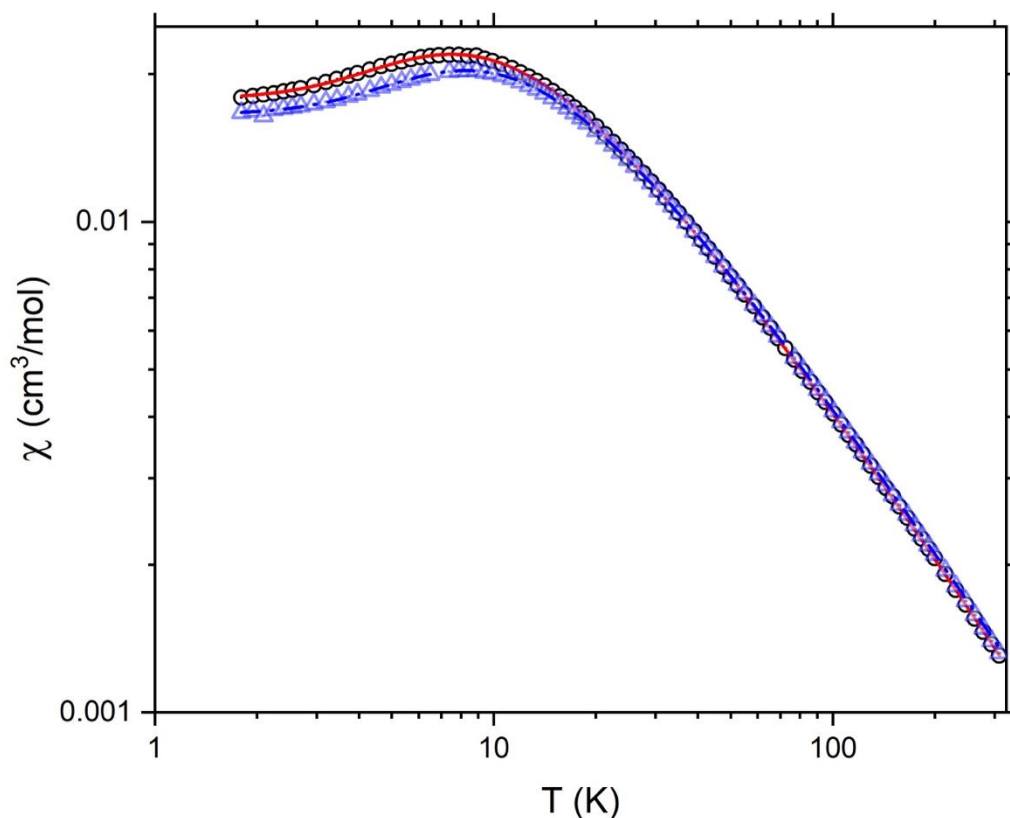


Figure 8. The magnetic susceptibilities of **1**(D) and **2** (O) between 1.8 and 310 K presented on a log/log scale. The dashed blue line and solid red line show the best fit results for **1** and **2**, respectively, with parameters discussed below and in Table 4.

Table 4. Magnetic parameters for **1** and **2**.

Compound [Cu(pz)(pzdo) ₂ (H ₂ O) ₂] ₂ X ₂	<i>C</i> (from χ) (cm ³ ·K/mol)	Exchange strength (<i>J</i> /k)	PM (%)	Bkgd (cm ³ /mol)	<i>C</i> (CW)	CW θ (K)
1 (X = BF ₄)	0.44(1)	-13.0(2)	0.24(5)	none	0.445(5)	-5.4(5)
2 (X = ClO ₄)	0.45(1)	-11.8(2)	0.26(5)	-7(2) × 10 ⁻⁵	0.443(5)	-5.4(5)

Discussion

The pyrazine-bridged chains form well isolated 1D-uniform linear antiferromagnets as expected from past work in the area. Introduction of the remote hydrogen-bond acceptor on the ancillary pzdo ligands causes direct linking of the chains with the coordinated water molecules serving as the hydrogen bond donors. However, magnetically, the compounds still behave as well isolated 1D-systems as this interchain linkage does not provide a viable superexchange pathway (eight

intervening atoms including the hydrogen bond) unlike the perrhenate compound which is believed to show interchain interactions via hydrogen bonding (*vide infra*). Thus, comparison to other well isolated chains such as the prototypical $\text{Cu}(\text{pz})(\text{NO}_3)_2$ ⁵ ($J = -10.3(1)$ K) is viable. A number of such chains with CuN_2O_4 coordination spheres have been reported and their magnetic properties analyzed. $[\text{Cu}(\text{pz})(\text{Opy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ has been reported with $J = -9.6(1)$ K.¹⁷ The corresponding hexafluorophosphate salt exhibits $J = -8.8(2)$ K.^{13d} Recently, a family of compounds with the general formula $[\text{Cu}(\text{pz})(\text{pyone})_2(\text{H}_2\text{O})_2](\text{A})_2$ [pyone = pyridone; $\text{A} = \text{ClO}_4^-$ or BF_4^-] has been reported. For the compounds with pyone = 3-bromo- or 3-chloro-4-pyridone ($\text{A} = \text{ClO}_4^-$), $J = -8.12(1)$ K or $-8.47(2)$ K respectively.¹⁶ In the case of the methyl substituted compounds (pyone = 3-methyl-, 5-methyl- or 6-methyl-2-pyridone; $\text{A} = \text{ClO}_4^-$), the exchange values are $J = -9.85(1)$ K, $-9.20(1)$ K and $-11.0(1)$ K, respectively. The complex $[\text{Cu}(\text{pz})(\text{H}_2\text{O})_2](\text{V}_{10}\text{O}_{28})$ is reported to have a surprisingly small exchange value, $J = -2.24$ K²⁶ as does the complex $[\text{Cu}(\text{pz})(\text{O}_2\text{CPh}(\text{CO}_2\text{H})_3)_2]\cdot\text{H}_2\text{O}$.²⁷ $[\text{Cu}(\text{pz})(\text{H}_2\text{O})_2(\text{OTf})_2]$ shows $J = -12.0(2)$ K²⁸ while the corresponding perrhenate is described as having a somewhat stronger exchange, but also the potential for interchain interactions mediated by the perrhenate ion; no value for J was reported.²⁹ The range of interactions (~ -2 to -12 K) is broad and suggests participation by a variety of factors which likely include both the physical parameters for the bridging pyrazine moiety (bond lengths, ring deformation) as well as the energy of the Cu $d_{x^2-y^2}$ -orbital where the unpaired electron is predominately located and the electron density at the Cu(II) ion as provided by the ancillary ligands. Clearly additional compounds and study are required to quantify the magnetostructural relationships.

Conclusions

We have prepared and characterized two new pyrazine-bridged Cu(II) coordination polymers with ancillary pzdo ligands. Although previous Cu(II) structures with bridging pzdo ligands have been reported $\{[\text{Cu}(\text{pzdo})\text{X}_2(\text{H}_2\text{O})_2] (\text{X} = \text{Cl}, \text{Br})^{19a}$ and $[\text{Cu}(\text{pzdo})_2(\text{ClO}_4)_2]^{19b}\}$, we are unaware of reported structures containing monodentate Cu-pzdo interactions. The presence of the strong hydrogen bonds between the uncoordinated pzdo oxygen atoms and water molecules may prevent the pzdo from bridging. The compounds exhibit dominant antiferromagnetic interactions with $J/k_B = -13.0(2)$ K and $-11.8(2)$ K for **1** and **2**, respectively, adding to the members of this family and raising the potential for understanding the factors that affect the

magnetic exchange mediated by pyrazine. Given the potential for interesting magnetic behavior of **3** as a well-isolated rectangular magnetic layer, we are continuing our efforts to find a reproducible synthesis for the compound.

Supplementary data

CCDC (**1**, 2155980; **2**, 2155979; **3**, 2156655) contains the supplementary crystallographic data for **1-3** and are available free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Acknowledgements

We are grateful for funds from PCI Synthesis, Inc. (now SEQENS) toward the purchase of the D8 Focus diffractometer, from the National Science Foundation (IMR-0314773) for purchase of the MPMS SQUID magnetometer, and from the Kresge Foundation for both instruments. Single crystal X-ray diffraction experiments for **1** and **2** were performed on a diffractometer at the University of Virginia funded by the NSF-MRI program (CHE-2018870).

References

1. a) O. Kahn, *J. Chim. Phys. Phys.-Chim. Biologique*, **85**, 1113 (1988). b) K. Awaga, *Kotai Butsuri*, **30**, 281 (1995). c) D. Gatteschi, *Advanced Materials* (Weinheim, Germany), **6**, 635 (1994).
2. a) R.A. Mayo, I.S. Morgan, D.V. Soldatov, R. Clerac, K.E. Preuss *Inorg. Chem.*, **60**, 11338 (2021). b) S.S. Woodhouse, T.N. Dais, E.H. Payne, M.K. Singh, E.K. Brechin, P.G. Plieger, Paul G. *Dalton Trans.*, **50**, 5318 (2021). c) A. Jochim, M. Rams, M. Boehme, M. Ceglarska, W. Plass, C. Näther, *Dalton Trans.*, **49**, 15310 (2020).
3. a) J.C. Bonner, *NATO ASI Series, Series C*, **140**, 157 (1985). b) J.C. Bonner and M.E. Fisher, *Phys. Rev.*, **135**, A640 (1964).
4. A.V. Santoro, A.D. Mighell and C.W. Reimann, *Acta Crystallogr. Sect. B*, **26**, 979 (1970).
5. a) Y. Kono, T. Sakakibara, C.P. Aoyama, C. Hotta, M.M. Turnbull, C.P. Landee and Y. Takano, *Phys. Rev. Lett.*, **114**, 037202 (2015). b) P.D.W. Boyd and S. Mitra, *Inorg. Chem.*, **19**, 3547 (1980). c) D.B. Losee, H.W. Richardson and W.E. Hatfield, *J. Chem. Phys.*, **59**, 3600 (1973). d) W.E. Hatfield and J.F. Villa, *J. Am. Chem. Soc.*, **93**, 4081 (1971).
6. a) Y. Ishikawa, K. Ohya, Y. Fujii, Y. Koizumi, S. Miura, S. Mitsudo, A. Fukuda, T. Asano, T. Mizusaki, A. Matsubara, H. Kikuchi and H. Yamamori, *J. Infra. Millim. Terahz. Waves*, **39**, 288

(2018). b) A.A. Validov, M. Ozerov, J. Wosnitza, S.A. Zvyagin, M.M. Turnbull, C.P. Landee and G.B. Teitel'baum, *J. Physics: Cond. Matt.*, **26**, 026003 (2014). c) G.F. Kokoszka and C.W. Reimann, *J. Inorg. Nucl. Chem.*, **32**, 3229 (1970).

7. a) F. Xiao, J.S. Moller, T. Lancaster, R.C. Williams, F.L. Pratt, S.J. Blundell, D. Ceresoli, A.M. Barton and J.L. Manson, *Phys. Rev. B*, **91**, 144417 (2015). b) S.J. Blundell, T. Lancaster, F.L. Pratt, P.J. Baker, M.L. Brooks, C. Baines, J.L. Manson and C.P. Landee, *J. Phys. Chem. Sol.*, **68**, 2039 (2007). c) T. Lancaster, S.J. Blundell, M.L. Brooks, P.J. Baker, F.L. Pratt, J.L. Manson, C.P. Landee and C. Baines, *Phys. Rev. B*, **73**, 020410 (2006).

8. M.B. Stone, D.H. Reich, C. Broholm, K. Lefmann, C. Rischel, C.P. Landee and M.M. Turnbull, *Phys. Rev. Lett.*, **91**, 037205 (2003).

9. a) I.O. Thomas, S.J. Clark and T. Lancaster, *Phys. Rev. B*, **96**, 094403 (2017). b) J. Jornet-Somoza, M. Deumal, M.A. Robb, C.P. Landee, M.M. Turnbull, R. Feyerherm and J.J. Novoa, *Inorg. Chem.*, **49**, 1750 (2010).

10. a) J. Jornet-Somoza, N. Codina-Castillo, M. Deumal, F. Mota, J.J. Novoa, R.T. Butcher, M.M. Turnbull, B. Keith, C.P. Landee and J.L. Wikaira, *Inorg. Chem.*, **51**, 6315 (2012). b) Zvyagin, S.A.; Ponomaryov, A.N.; Schulze, E.; Ozerov, M.; Skourski, Y.; Reimann, T.; Zviagina, L.I.; Bhaskaran, L.; Green, E.L.; Wosnitza, J.; Sheikin, I.; Kollath, C.; Bouillot, P. Giamarchi, T.; Wikaira, J.L.; Turnbull, M.M.; Landee, C.P. *Phys. Rev. B*, **103**, 205131 (2021). c) K.D. Hughey, N.C. Harms, K.R. O'Neal, A.J. Clune, J.C. Monroe, A.L. Blockmon, C.P. Landee, Z. Liu, M. Ozerov, J.L. Musfeldt, *Inorg. Chem.*, **59**, 2127 (2020).

11. D. Opherden, N. Nizar, K. Richardson, J.C. Monroe, M.M. Turnbull, M.I.J. Polson, Vela, S.; Blackmore, W.; Goddard, P.A.; Xiao, F.; Lancaster, T.; Williams, R.C.; Gape, P.M.D.; Pratt, F.L.; Blundell, S.J.; Scurschii, I.; Uhlarz, M.; Ponomaryov, A.N.; Zvyagin, S.; Wosnitza, J.; Baenitz, M.; Heinmaa, I.; Stern, R.; Kühne, H.; Landee, C.P. *Phys. Rev. B*, **102**, 064431 (2020). b) J.L. Manson, J.A. Schlueter, K.A. Funk, H.I. Southerland, B. Twamley, T. Lancaster, S.J. Blundell, P.J. Baker, F.L. Pratt, J. Singleton, R.D. McDonald, P.A. Goddard, P. Sengupta, C.D. Batista, L. Ding, C. Lee, M.-H. Whangbo, I. Franke, S. Cox, C. Baines and D. Trial, *J. Am. Chem. Soc.*, **131**, 6733 (2009). c) R. Scatena, F. Montisci, A. Lanza, N.P.M Casati, P. Macchi *Inorg. Chem.* 2020, **59**, 10091. d) S. Kwon, M. Jeong, M. Kubus, B. Wehinger, K.W. Kramer, Ch. Ruegg, H.M. Roennow, S. Lee *Phys. Rev. B*, **99**, 214403 (2019).

12. a) R.T. Butcher, C.P. Landee, M.M. Turnbull and F. Xiao, *Inorg. Chim. Acta.*, **361**, 3654 (2008). b) J. Pickardt and B. Staub, *Z. Naturforsch., B: Chem. Sci.*, **52**, 1456 (1997). c) T. Fetzner, A. Lentz and T. Debaerdemaeker, *Z. Naturforsch., B: Chem. Sci.*, **44**, 553 (1989).

13. a) A. Majumder, V. Gramlich, G.M. Rosai, S.R. Batten, J.D. Masuda, M.S.E. Fallah, J. Ribas, J.-P. Sutter, C. Desplanches and S. Mitra, *Cryst. Growth Des.*, **6**, 2355 (2006). b) J.L. Manson, M.M. Conner, J.A. Schlueter and K.A. Hyzer, *Polyhedron*, **26**, 1912 (2007). c) P.A. Goddard, J. Singleton, P. Sengupta, R.D. McDonald, T. Lancaster, S.J. Blundell, F.L. Pratt, S. Cox, N. Harrison, J.L. Manson, H.I. Southerland and J.A. Schlueter, *New J. Phys.*, **10**, 083025 (2008). d) P.A. Goddard, J.L. Manson, J. Singleton, I. Franke, T. Lancaster, A.J. Steele, S.J.

-
- Blundell, C. Baines, F.L. Pratt, R.D. McDonald, O.E. Ayala-Valenzuela, J.F. Corbey, H.I. Southerland, P. Sengupta and J.A. Schlueter, *Phys. Rev. Lett.*, **108**, 077208 (2012). e) J. Darriet, M.S. Haddad, E.N. Duesler and D.N. Hendrickson, *Inorg. Chem.*, **18**, 2679 (1979).
14. J. Liu, P.A. Goddard, J. Singleton, J. Brambleby, F. Foronda and J.S. Moller, *Inorg. Chem.*, **55**, 3515 (2009).
15. E. Kirkman-Davis, F.E. Witkos, V. Selmani, J.C. Monroe, C.P. Landee, M.M. Turnbull, L.N. Dawe, M.I.J. Polson, J.L. Wikaira, *Dalton Trans.*, **49**, 13693 (2020).
16. J.C. Monroe, C.P. Landee, M.M. Turnbull, J.L. Wikaira, J.L. *J. Coord. Chem.*, **73**, 2645 (2020).
17. C.P. Landee, E. Kirkman-Davis, M.M. Turnbull, M.I.J. Polson, J.L. Wikaira, *J. Coord. Chem.*, **74**, 266 (2021).
18. a) M.D. Perera, A.S. Sinha, C.B. Aakeroy *Can. J. Chem.*, **98**, 358 (2020). b) J.C. Gamekkanda, A.S. Sinha, C.B. Aakeroy *Cryst. Growth Des.*, **20**, 2432 (2020). c) R. Thakuria, B. Sarma, A. Nangia *New J. Chem.*, **34**, 623 (2010). d) N.J. Babu, L.S. Reddy, A. Nangia *Mol. Pharmaceutics*, **4**, 417 (2007). e) J.L. Wikaira, C.P. Landee, M.M. Turnbull *Acta Crystallogr., Sect. E*, **69**, m229 (2013).
19. a) J.A. Schlueter, H. Park, G.J. Halder, W.R. Armand, C. Dunmars, K.W. Chapman, Manson, J.L.; Singleton, J.; McDonald, R.; Plonczak, A.; Kang, J.; Lee, C.; Whangbo, M.-H.; Lancaster, T.; Steele, A.J.; Franke, I.; Wright, J.M.; Blundell, S.J.; Pratt, F.L.; DeGeorge, J.*; Turnbull, M.M.; Landee, C.P. *Inorg. Chem.*, **51**, 2121 (2012). b) Jing-Min Shi, Hai-Yan Xu, Feng-Xia Zhang, Chang-Ju Wu, Lian-Dong Liu *Chin. J. Struct. Chem.*, **26**, 214 (2007).
20. C.F. Koelsch, Wm. H. Gumprecht, *J. Org. Chem.*, **23**, 1603 (1958).
21. G.M. Sheldrick, *Acta Cryst. A*, **64**, 112 (2008).
22. G.M. Sheldrick *Acta Cryst. C*, **71**, 3 (2015).
23. R. L. Carlin. Magnetochemistry, *Springer-Verlag* (1986) Berlin.
24. R. Kuhlman, G.L. Schimek, J.W. Kolis *Polyhedron* **18**, 1379 (1999).
25. C.P. Landee, M.M. Turnbull, *J. Coord. Chem.*, **67**, 375 (2014).
26. Li Wang, Xiu-ping Sun, Mei-ling Liu, Yue-qiang Gao, Wen Gu Xin Liu *J. Cluster Sci.* **19**, 531 (2008).
27. A. Majumder, V. Gramlich, G.M. Rosair, S.R. Batten, J.D. Masuda, M.S. El Fallah, J. Ribas, J.-P. Sutter, C. Desplanches, S. Mitra *Cryst. Growth Des.* **6**, 2355 (2006).

28. J.L.Manson, J.Donovan, B.Twamley *Polyhedron* **27**, 2650 (2008).

29. J.L.Manson, M.M.Conner, J.A.Schlueter, K.A.Hyzer *Polyhedron* **26**, 1912 (2007).