



**SYNTHESIS, STRUCTURE AND MAGNETIC PROPERTIES OF A
COPPER(II) COMPLEX OF 5-NITRO-2-HYDROXYPYRIDINE AND
PYRAZINE: [Cu(5-NO₂-2-HOPy)(Pz)₂(H₂O)](ClO₄)₂·H₂O**

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The synthesis, structure, and magnetic properties of [Cu(5-NO₂-2-HOPy)(pz)₂(H₂O)] (ClO₄)₂·H₂O (pz = pyrazine) (**1**) are reported. Crystals were characterized using IR, combustion analysis, X-ray powder diffraction, single crystal X-ray diffraction, and temperature-dependent magnetic susceptibility measurements. Compound **1** crystallizes in the monoclinic space group P2₁/c. The crystal structure consists of copper/pyrazine chains parallel to the *c*-axis with terminal pyrazine groups found perpendicular to the bridging pyrazine molecules creating a zig-zag chain structure. The 1D-system exhibits weak antiferromagnetic interactions of $J = -7.58$ K with no measurable interchain interactions.

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synthesized and structurally characterized, but the magnetic properties were not studied. The structure of the complex is shown in Figure 1. The 2-pyridone molecules function as terminal units exhibiting strong ligating ability¹² while pyrazine has weaker ligating ability, but the two nitrogen atoms allow pyrazine to act as a bridging bidentate ligand and create an efficient pathway for spin exchange and subsequent magnetic interactions.^{13,14}

Introduction

Studies using coordination complexes have allowed for better understanding of the effects of local geometry, bond lengths and angles, and close interactions on the magnetic exchange pathways in a crystalline lattice.¹ The magnetic susceptibility of a crystalline lattice is dependent on the interaction between moments belonging to each metal ion's nearest neighbors and their corresponding spin values and may be affected by next-nearest neighbor interactions and on into the extended lattice. Overlapping electron wave functions may result in a decrease in the overall energy of the system and as a result, the exchange can then be understood with respect to the nature of the symmetric or asymmetric wave functions.² We, as a research group, seek to understand the changes in magnetic exchange that result from differing interconnectivity within a lattice.

Coordination complexes containing pyrazine as the ligand exhibit a wide range of magnetic exchange values from -2 to -46 K.³⁻⁶ In studying one-dimensional quantum Heisenberg antiferromagnets, the d⁹ configuration of the copper (II) ion has proven to be beneficial with a single unpaired electron creating a spin of ½ with nearly isotropic exchange. Copper's quenched orbital angular momentum as well as a *g*-value⁷ near 2 suggests a negligible preference for alignment of the magnetic moment along a particular crystallographic axis. The effects of substituted pyrazines on the magnetic exchange within the coordination complexes have been observed,⁸⁻¹⁰ but the effects of changing the electron density donated to a copper(II) through an additional ligand has not been studied systematically. The complex [Cu(C₅H₄ClNO)₂(C₄H₄N₂)(H₂O)₂](ClO₄)₂ is of great interest with its copper (II) ion, pyrazine bridges and pyridine groups with the potential to vary their electron donating or withdrawing character by changing the substituents on the pyridine ring.¹¹ This complex was

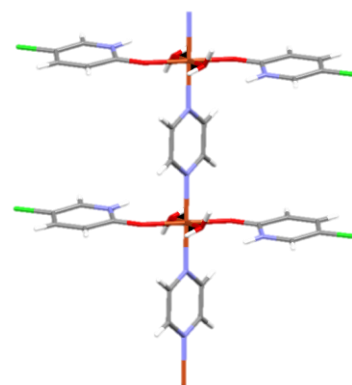


Figure 1. Molecular unit of [Cu(C₅H₄ClNO)₂(C₄H₄N₂)(H₂O)₂](ClO₄)₂

The azaphilic copper ion is expected to interact with both nitrogen atoms on the pyrazine molecule and together function as the repeating unit. In an attempt to understand the effect of electron density on magnetic exchange, a family of complexes with a similar molecular composition to the above complex is being prepared. The pyridone rings on the coordination complex allow for a single parameter, the electron density at the Cu(II) ion, to be tested without steric bulk interference. Addition of substituents on the 4, 5 and 6 positions on the pyridone ring will not affect spatial crowding near the copper ion resulting from the positions being planar and distant from the copper whereas substituents on the pyrazine ring would greatly affect the geometry and binding at the copper. In the process of preparing additional members of this family, we have

observed serendipitous formation of a related product containing both bridging and terminal pyrazine molecules. We report here the synthesis, structure and magnetic properties of [Cu(C₅H₄N₂O₃)(C₄H₄N₂)₂(H₂O)](ClO₄)₂·H₂O, **1**.

EXPERIMENTAL

Copper (II) perchlorate hexahydrate, pyrazine and 2-hydroxy-5-nitro-pyridine (5-nitro-2-pyridone) were purchased from Sigma Aldrich. Materials were used as received without further purification. IR spectra were recorded via ATR on a Perkin-Elmer Spectrum 100 spectrometer. X-Ray powder diffraction was carried out on a Bruker AXS-D8 X-ray Powder Diffractometer. Elemental analysis was carried out by Marine Science Institute, University of California, Santa Barbara, CA 93106.

Synthesis of aquapyrazine(2-hydroxy-5-nitropyridine)-copper(II) perchlorate hydrate, [Cu(C₅H₄N₂O₃)(C₄H₄N₂)₂(H₂O)](ClO₄)₂·H₂O (**1**)

Compound **1** was made as a byproduct in the attempted synthesis of [Cu(C₅H₄N₂O₃)₂(C₄H₄N₂)(H₂O)₂] (ClO₄)₂. Attempts to reproduce the synthesis of **1** have been unsuccessful to date. A solution of 2-hydroxy-5-nitropyridine (0.140g, 1.0 mmol) dissolved in 9.0 mL of a 50% methanol/ water solution with warming, was added to a solution of copper (II) perchlorate (0.369g, 1.0 mmol) dissolved in 2.0 mL of the same solvent. A methanol/water solution (3.0mL) of pyrazine (0.164g, 2.0 mmol) was then added. Colorless rod-like crystals separated from the solution after a few days and were isolated and confirmed to be recrystallized 2-hydroxy-5-nitro-pyridine through IR. Large dark blue crystals separated from the remaining solution after eleven days of slow evaporation. The colorless product was isolated in 6.2% yield (0.042 g) and dark blue product was isolated in 17.5% yield (0.118 g). The dark blue product proved to be **1**. IR (ν in cm⁻¹): 1651 (m), 1611 (m), 1563 (w), 1507 (m), 1425 (m), 1358 (m), 1242 (w), 1216 (w), 1122(m), 1062 (s), 844 (m), 817 (m), 761 (w), 711 (w), 653 (m), 622 (s). CHN for C₁₃H₁₆N₆O₁₃Cl₂Cu, found (calculated): C: 26.6 (26.2), H: 2.52 (2.21), N: 13.7 (13.1).

X-Ray Structure Analysis

Data collection was carried out for **1** on an Agilent Technologies Gemini Eos CCX-ray diffractometer utilizing CuKα radiation (λ=1.5418 Å) with co-scans at 120.01(10) K employing a mirror monochromator. CrysAlisPro software was used to refine cell parameters while SCALE3 ABSPACK scaling algorithm was used for absorption corrections.¹⁵ The structure was solved and refined using the SHELX97-2 program and a least squares analysis.¹⁶ Non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms bonded to nitrogen or oxygen atoms were located in the difference Fourier maps and their positions refined using fixed isotropic thermal parameters.

The remaining hydrogen atoms were placed in geometrically calculated positions and refined using fixed isotropic thermal parameters. Crystallographic information and details of the data collection can be found in Table 1.

Magnetic Susceptibility Data Collection

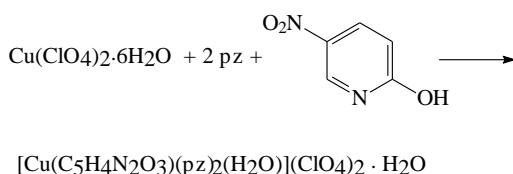
Magnetic susceptibility data for **1** were collected using a Quantum Design MPMS-XL SQUID magnetometer. A weighed sample of the finely ground crystals was packed into a gelatin capsule. Data was collected on the measured moment using magnetic fields from 0 to 50 kOe at 1.8 K and several data points were collected as the field returned to 0 kOe to check for hysteresis effects; none were observed. Magnetization was then measured from 1.8 to 310 K in a 1 kOe field. The data collected were corrected for the background signal of the gelatin capsule and the sample mount. The data were also corrected for diamagnetic contributions of the constituent atoms, estimated via Pascal's constants,⁶ and the temperature independent paramagnetism of the copper (II) ion. All data was fit using the Hamiltonian $H = -J\sum S_1 \cdot S_2$. The composition of **1** was analyzed by powder X-ray diffraction and compared to the single crystal structure prior to data collection. No impurities were observed.

Table 1. X-ray data of compound **1**.

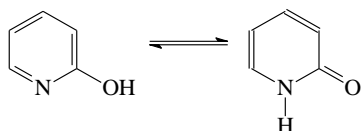
Empirical formula	C₁₃H₁₆Cl₂CuN₆O₁₃
Formula weight	598.76
Temperature	120.01(10) K
Wavelength	1.54184 Å
Space group	P2 ₁ /c
<i>a</i>	17.0258(2) Å
<i>b</i>	12.15341(16) Å
<i>c</i>	10.19594(13) Å
α	90°
β	92.0607(11)°
γ	90°
Volume	2108.39(5) Å ³
<i>Z</i>	4
Density (calculated)	1.886 Mg m ⁻³
Absorption coefficient	4.576 mm ⁻¹
<i>F</i> (000)	1212
Crystal size	0.380 x 0.350 x 0.024 mm ³
θ range for data collection	4.47 to 76.78°.
Index ranges	-12 ≤ <i>h</i> ≤ 21, -15 ≤ <i>k</i> ≤ 15, -12 ≤ <i>l</i> ≤ 12
Reflections collected	15178
Independent reflections	4401 [<i>R</i> (int) = 0.0274]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.56697
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	4401 / 0 / 332
Goodness-of-fit on <i>F</i> ²	1.054
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ¹ = 0.0362, <i>wR</i> ₂ = 0.0934
<i>R</i> indices (all data)	<i>R</i> ¹ = 0.0374, <i>wR</i> ₂ = 0.0944
Extinction coefficient	0.00330(16)
Largest diff. peak and hole	1.485 near O6 and -0.649 e.Å ⁻³

Synthesis

The reaction of copper perchlorate hexahydrate, pyrazine and 2-hydroxy-5-nitro-pyridine over heat in 50 % methanol and water formed a pale green solution. Cooling this solution and slow evaporation deposited **1** (Scheme 1). Starting material 2-hydroxy-5-nitro-pyridine is present in solution in lactam form (Scheme 2) and coordinated to the copper ion through the oxygen. Tautomeric equilibria of hydroxypyridines and corresponding pyridines are well studied.¹⁷⁻¹⁹



Scheme 1 **1**



Scheme 2

Crystal Structure Analysis

Compound **1** crystallizes in the monoclinic space group P 2₁/c. The asymmetric unit is shown in Figure 2. Selected bond lengths and angles are given in Table 2. The atoms of the pyrazine and pyridone ring are numbered with consecutive addition of 10 (N1, N11, N21) for ease of discussion.

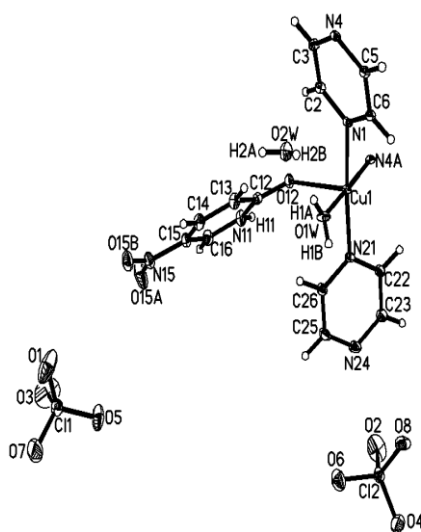


Figure 2. Thermal ellipsoid plot of the asymmetric unit showing 50% probability ellipsoids. Only those H-atoms whose positions were refined are labeled. Symmetry operation for N4A ($x, -y+3/2, z-1/2$)

The Addison parameter (τ) of 0.08 indicates that the Cu(II) ion has a nearly square pyramidal geometry²⁰ with each Cu(II) ion coordinated to one molecule of water, one 5-nitro-2-pyridone through the oxygen, two bridging pyrazines (parallel to the *c*-axis) and a terminal pyrazine. The copper ion sits on a general position. Cu1 is bonded to a molecule of 5-nitro-2-pyridone which occupies the axial position of the square pyramid as indicated by its maximum angle of 96.57(6)^o to the other ligands.

2-Hydroxy-5-nitro-pyridine equilibrates to 5-nitro-2-pyridone in solution where the oxygen atom is coordinated to the copper ion. The pyridone ring is nearly planar as indicated by a maximum torsional angle of 0.8^o (C13-C14-C15-C16) and the nitro group is nearly co-planar to the pyridone ring ($\angle\text{C14-C15-N15-O15B} = 2.2^\circ$) as would be expected due to conjugation.^{21,22} The nitro group itself is planar as indicated by the summation of the angles around N15 (360.0^o). The bound water molecule is planar as indicated by the angle summation, however, the H1A-O1W-H1B angle has expanded to 112(3)^o suggesting that the water molecule is progressing toward a trigonal planar geometry rather than tetrahedral. This can be understood by the potential of a partial double bond character between O1W and Cu1 creating significant sp² character and increased π -donation to the copper ion further contributing to the change in electron density.

The pyrazine rings are nearly planar, as expected,²³ and exhibit maximum torsional angles within the rings of 1.2^o for the bridging pyrazine ($\angle\text{C2-C3-N4-C5}$) and -1.1^o for the terminal pyrazine ($\angle\text{C23-N24-C25-C26}$). The mean plane of the bridging pyrazine ring is canted 72.2^o in relation to the mean plane of the terminal pyrazine ring while the symmetry equivalent bridging pyrazine ring is canted 81.6^o with respect to the terminal pyrazine. The bridging pyrazine rings are nearly perpendicular with an angle of 85.3^o between their mean planes resulting in a zig-zag chain structure.

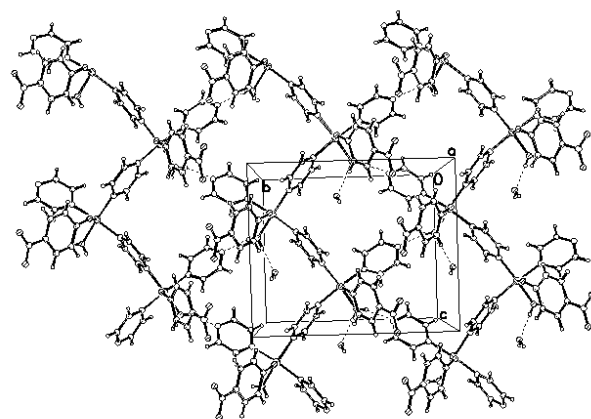


Figure 3. Layer formed by bridging and terminal pyrazines parallel to the *bc* face of the lattice. Perchlorate and water molecules are in the interstitial space and actively stabilizing the lattice structure through hydrogen bonding. Dashed lines represent the hydrogen bonding between the hydrogen atoms on the water molecule to the coordinated water molecule as well as to nitrogen atoms on the terminal pyrazine.

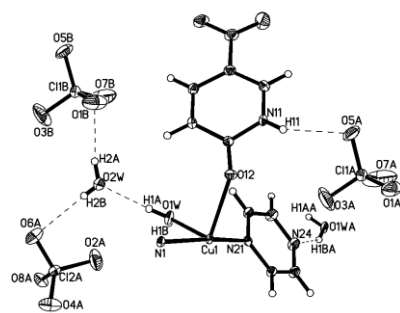
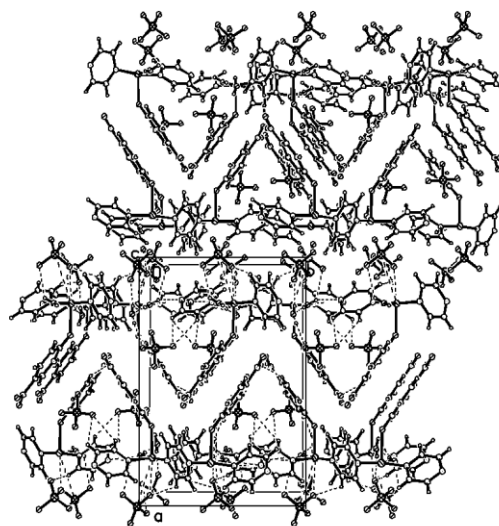
Table 2. Selected bond lengths [Å] and angles [°] for **1**

Bond	Distance	Bond	Angle
Cu1-O1W	1.9523(16)	O1W-Cu1-N21	90.00(7)
Cu1-N21	2.0245(18)	O1W-Cu1-N4#1	176.61(7)
Cu1-N4#1	2.0391(17)	N21-Cu1-N4#1	92.97(7)
Cu1-N1	2.0463(17)	O1W-Cu1-N1	84.34(7)
Cu1-O12	2.2382(15)	N21-Cu1-N1	171.11(7)
		N4#1-Cu1-N1	92.51(7)
		O1W-Cu1-O12	90.65(6)
		N21-Cu1-O12	90.33(7)
		N4#1-Cu1-O12	90.96(6)
		N1-Cu1-O12	96.57(6)
		O15A-N15-O15B	123.4(2)
		O15A-N15-C15	118.8(2)
		O15B-N15-C15	117.8(2)
		Cu1-O1W-H1A	123(2)
		Cu1-O1W-H1B	123(2)
		H1A-O1W-H1B	112(3)

Symmetry transformations used to generate equivalent atoms:
 #1 $x, -y+3/2, z-1/2$ #2 $x, -y+3/2, z+1/2$

Compounds containing a zig-zag structure with bridging and terminal pyrazine molecules are unusual, but not unique. Previous reports include $\text{Cu}(\text{pz})_2(\text{CF}_3\text{SO}_3)_2$,²⁴ $[\{\text{Zn}^{\text{II}}\text{Bu}_2\}_3\{\text{C}_4\text{H}_4\text{N}_2\}_4]$ ²⁵ and $[\text{Cu}(\text{HF}_2)(\text{pz})_2]\text{SbF}_6$.⁶

The -Cu-pz-Cu- chains are connected into layers parallel to the *bc* face of the crystal (Fig. 3) by hydrogen bonding networks between the oxygen atoms in the perchlorate ions to amine hydrogen atoms on the pyridone ring where the oxygen from the perchlorate ion serves as the acceptor. Hydrogen bonding is also observed between the free water molecules and N24 on the terminal pyrazine rings. The molecules contributing to hydrogen bonding within the lattice are shown in Figure 4. Hydrogen bond parameters are given in Table 3. The perchlorate ions and water molecules can be found occupying the interstitial spaces between bridging pyrazine chains. Compound **1** packs in pleated sheets parallel to the *bc*-face, exhibiting an aabb packing pattern (Fig. 5) where “a” is the pyridone rings and “b” is the copper-pyrazine layer. In looking at the packing of four single chains, adjacent complementary pairs of chains are offset from one another by $\frac{1}{2}$ unit cell parallel to the *b*-axis rather than repeating in the same spatial orientation resulting in the aabb pattern.

**Figure 4.** Thermal ellipsoid plot of **1** showing the symmetrically generated molecules of perchlorate ions and water molecules that play a role in hydrogen bonding.**Figure 5.** Packing structure of the layers viewed parallel to the *b*-axis and down the chains that run parallel to the *c*-axis.

The copper ions within a sheet are separated by a distance greater than 11.8 Å while the copper molecules between two sheets are separated by a distance greater than 8.0 Å.

Magnetic Study

Susceptibility data for **1** was collected in a 0.1 T field from 1.8 K to 310 K. The susceptibility of **1** shows rounded maxima near 5 K characteristic of low-dimensional antiferromagnetic behavior.²⁶ The low temperature of the maximum suggests weak interactions between Cu(II) ions. The data were fit to the $S=1/2$ Heisenberg linear chain model both with, and without, a Curie-Weiss (CW) correction for interchain interactions² and resulted in a $J = -7.49(2)$ K, Curie Constant (C) = 0.436(1) emu(K) mol(Oe)⁻¹ and a paramagnetic impurity (p) = 0.95(5) % (Table 4). The addition of the Curie-Weiss term yielded the CW term to be zero within experimental error, indicating the magnetic isolation of the antiferromagnetic chains. The magnetization of **1** at 1.8 K and 5 T resulted in 1.68×10^3 emu mol⁻¹, approximately one third of the saturation moment expected for Cu(II) ions as a result of the antiferromagnetic interactions.

As previously stated, copper complexes containing bridging and terminal pyrazine molecules are uncommon in literature with even more limited data available on their magnetic properties. Compounds sharing similar components of pyrazine-bridged chains, dimers and 2D-systems with terminal pyrazines are presented due to the lack of information on the former. The following compounds involve a greater number of parameters and should be considered rough comparisons which are not structurally the same. Isolated **1** packs in 1D layers whereas $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{SbF}_6$ packs in 2D square layers. The relative concavity of the susceptibility data of $[\text{Cu}(\text{HF}_2)(\text{pyz})_2]\text{SbF}_6$ differs from **1** due to the interlayer exchange energy resulting in a rounded maxima observed at the higher temperature of 12.5 K and stronger interactions with $J = -13.5$ K.

Table 3. Hydrogen bonds and angles [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(11)-H(11)...O(5)#3	0.75(3)	2.31(3)	2.959(3)	146(3)
O(1W)-H(1A)...O(2W)	0.77(3)	1.94(3)	2.711(2)	176(3)
O(1W)-H(1B)...N(24)#4	0.76(3)	2.04(3)	2.701(3)	147(3)
O(2W)-H(2A)...O(1)#5	0.77(4)	2.03(4)	2.793(3)	169(3)
O(2W)-H(2B)...O(6)#4	0.70(4)	2.26(4)	2.946(3)	171(4)

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

The quasi-one-dimensional Heisenberg antiferromagnetic compound Cu(py_z)(NO₃)₂ consists of copper-pyrazine chains that exhibit a magnetic exchange of $J = -10.3$ K.²⁷ The nitrate ligands are able to directly donate electron density to the copper contributing to a stronger magnetic exchange whereas in compound **1** the electron donating group contribute through the pyridone ring first and then on to the Cu(II) ion.

known complex [Cu (C₅H₄ClNO)₂(C₄H₄N₂)(H₂O)₂](ClO₄)₂ will be most interesting.

Table 4. Magnetic susceptibility data for **1**.

Model	<i>C</i>	<i>J</i>	θ	<i>P</i>
1D-chain	0.442	-7.59(3)		1.01(7)
1D-chain w/CW	0.436(1)	-7.49(2)	-0.0002(0.3)	0.95(5)

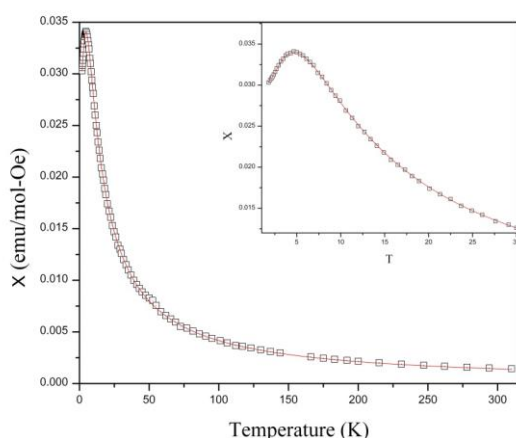


Figure 6. χ_m vs. T plot for **1** in a 0.1 T field. The solid line corresponds to the prediction of the magnetic susceptibility of a 1D antiferromagnetic chain model with an exchange strength of $-7.49(2)$ K and with a paramagnetic impurity term of $0.95(4)$. The inset shows an expansion of the region near the susceptibility maximum.

Exchange may also be affected by the terminal pyrazine ligand present. Both of these compounds exhibit drastically different lattices and so direct comparison of the exchange constants is of less value.

The intended goal was to create a homologous series that would allow for direct comparison of magnetic susceptibility and see what affects the observed exchange. Magnetic data for the chlorine-substituted literature compound [Cu (C₅H₄ClNO)₂(C₄H₄N₂)(H₂O)₂](ClO₄)₂,^{Hiba! A könyvjelző nem létezik.} fit with a Curie-Weiss correction resulted in $J = -9.90(7)$ K, $CC = 0.446(1)$ emu(K) mol(Oe)⁻¹ and $\rho = 1.6(2)\%$.²⁸ While **1** does not belong to the intended series, this compound suggests that the electron-withdrawing nitro group has a weakening effect on the strength of the magnetic exchange through the pyrazine ring in comparison to the complex with 5-Cl. The preliminary data supports the idea that the electron density at the copper ion has an effect on the exchange value. Efforts to isolate the intended linear chain compound [Cu(C₅H₄N₂O₃)₂(C₄H₄N₂)(H₂O)₂](ClO₄)₂ are in progress and comparison of its properties to **1** and the

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Supplementary data

CCDC 1418597 contains the supplementary crystallographic data for **1**. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/con-ts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or email: deposit@ccdc.cam.ac.uk.

References

- Miller, J. S., and M. D. *Magnetism: Molecules to Materials V*. Weinheim: Wiley-VCH, 2005. Print. (and previous volumes).
- Landee, C. P.; Turnbull, M. M., *J. Coord. Chem.*, **2014**, *67*, 375.
- Haynes, J.S.; Rettig, S.J.; Sams, J.R.; Trotter, J.; Thompson, R.C. *Inorg. Chem.*, **1988**, *27*, 1237.
- Manson, J. L., Conner, M. M., Schlueter, J. A., McConnell, A. C., Southerland, H. I., Malfant, I., Lancaster, T., Blundell, S. J., Brooks, M. L., Pratt, F. L., Singleton, J., McDonald, R. S., Lee, C., Whangbo, M.-H. *Chem. Mater.*, **2008**, *20*, 7408.
- Butcher, R. T., Landee, C. P., Turnbull, M. M., Xiao, F. *Inorg. Chim. Acta*, **2008**, *361*, 3654.
- Manson, J. L., Schlueter, J. A., Funk, K. A., Southerland, H. I., Twamley, B., Lancaster, B. T., Blundell, S. J., Baker, P. J., Pratt, F. L., Singleton, J., McDonald, R. D., Goddard, P. A., Sengupta, P., Batista, C. D., Ding, L., Lee, C., Whangbo, M.-H., Franke, I., Cox, S., Baines, C., Trial, D., *J. Am. Chem. Soc.*, **2009**, *131*, 6733.

- ⁷Carlin, R. L., Magnetochemistry, Springer-Verlag, 1986.
- ⁸Schlueter, J. A., Park, H., Halder, G. J., Armand, W. R., Dunmars, C., Chapman, K. W., 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.*, **2012**, *51*, 2121.
- ⁹Ikeda, M., Honda, Z., Sakai, M., Kiura, S., *Low Temp Phys.*, **2013**, *170*, 296.
- ¹⁰Carranza, J., Jorunn, S., Brennan, C., Lloret, F., Cano, J., Julve, M., *Dalton Trans.*, **2004**, 3997.
- ¹¹Yuan, J.-X., Hu, M.-L., Cheng, Y.-Q., Chen, L.-C., Ng, S.W., *Acta Crystallogr., Sect.C: Struct. Crystallogr. Cryst. Chem.*, **2002**, *58*, 270.
- ¹²Perdih, F., *Monatsh Chem.* **2012**, *143*, 1011.
- ¹³Leznoff, D. B., Xue, B.-Y., Stevens, C. L., Storr, A., Thompson, R. C., Patrick, B. O., *Polyhedron.* **2001**, *20*, 1247.
- ¹⁴Manson, J. L., Huang, Q. Z., Lynn, J. W., Koo, H. J., Whangbo, M. H., Bateman, R., Otsuka, T., Wada, N., Argyriou, D. N., Miller, J. S., *J. Am. Chem. Soc.*, **2001**, *123*, 162.
- ¹⁵CrysAlisPro Oxford Diffraction Ltd., Version 1.171.35.19 (release 27-10-2011 CrysAlis171.NET).
- ¹⁶Sheldrick, G. M., *Acta Cryst. A.*, **2008**, *64*, 112.
- ¹⁷Adamoicz, L., *Chem. Phys. Lett.*, **1989**, *161*, 73.
- ¹⁸Scanlan, M. J., Hillier, I. H., MacDowell, A., *J. Am. Chem. Soc.*, **1983**, *105*, 3568.
- ¹⁹Frank, J., Katrizky, A. R. *J. Chem. Soc., Perkin Trans. 2.*, **1976**, *12*, 1428.
- ²⁰Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J., Verschoor, G. C., *J. Chem. Soc., Dalton Trans.*, **1984**, 1349.
- ²¹Zhang, G.-F., She, J.-B., Dou, Y.-L., Fan, R. *Zeitschrift für Kristallographie - New Crystal Structures*, **2006**, *221*, 183.
- ²²Forlani, L., Cristoni, G., Boga, C., Todesco, P. E., Del Vecchio, E., Selva S., Monari M. *Arkivoc XI*: 198
- ²³de With, G., Harkema, S., Feil, D., *Acta Crystallogr., Sect.B: Struct. Crystallogr. Cryst. Chem.*, **1976**, *32*, 3178.
- ²⁴Otieno, T., Rettig, S. J., Thompson, R. C., Trotter, J. *Can. J. Chem.*, **1989**, *67*, 1964.
- ²⁵Baillie, S. E., Blair, V. L., Blakemore, D. C., Hay, D., Kennedy, A. R., Pryde, D. C., Hevia, E., *Chem. Commun.*, **2012**, *48*, 1985.
- ²⁶Bonner, J. C., Fischer, M. E., *Phys. Rev.* **1964**, *135*, A640.
- ²⁷Günaydın-Şen, Ö., Lee, C., Tung, L. C., Chen, P., Turnbull, M. M., Landee, C. P., Wang, Y. J.; Whangbo, M.-H., Musfeldt, J. L., *Phys. Rev. B.*, **2010**, *81*, 104307.
- ²⁸Selmani, V., Turnbull, M. M., Landee, C. P., unpublished results

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