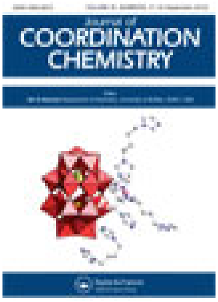


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Catena-bis(aqua(3-oxy-2-pyridono)copper(II))μ-pyrazine diperchlorate: a perchlorate-bridged magnetic ladder

Firas F. Awwadi [a] [b], Louise N. Dawe [c], Christopher P. Landee [d] & Mark M. Turnbull [a] [a]

[a] Carlson School of Chemistry and Biochemistry, Clark University, 950 Main St., Worcester, MA 01610, USA

[b] Department of Chemistry, The University of Jordan, Amman 11942, Jordan

[c] Department of Chemistry, Memorial University of Newfoundland, St. John's, NL A1C 5S7, Canada

[d] Department of Physics, Clark University, 950 Main St., Worcester, MA 01610, USA

To cite this article: Firas F. Awwadi, Louise N. Dawe, Christopher P. Landee & Mark M. Turnbull (2012) Catena-bis(aqua(3-oxy-2-pyridono)copper(II))μ-pyrazine diperchlorate: a perchlorate-bridged magnetic ladder, Journal of Coordination Chemistry, 65:17, 3064-3074, DOI: 10.1080/00958972.2012.710844

To link to this article: http://dx.doi.org/10.1080/00958972.2012.710844

Journal of Coordination Chemistry
Vol. 65, No. 17, 10 September 2012, 3064–3074

Catena-bis(aqua(3-oxy-2-pyridono)copper(II))μ-pyrazine diperchlorate: a perchlorate-bridged magnetic ladder

FIRAS F. AWWADI†‡, LOUISE N. DAWE§, CHRISTOPHER P. LANDEE¶ and MARK M. TURNBULL*†

†Carlson School of Chemistry and Biochemistry, Clark University, 950 Main St.,
Worcester, MA 01610, USA
‡Department of Chemistry, The University of Jordan, Amman 11942, Jordan
§Department of Chemistry, Memorial University of Newfoundland, St. John's,
NL A1C 5S7, Canada
¶Department of Physics, Clark University, 950 Main St., Worcester, MA 01610, USA

(*Received 17 May 2012; in final form 2 July 2012*)

Reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with pyrazine (pz) and 2,3-dihydroxy pyridine in aqueous solution generates bis(aqua(3-oxy-2-pyridono)copper(II))μ-pyrazine diperchlorate. The compound crystallizes in the triclinic space group $P\bar{1}$. The aqua(3-oxy-2-pyridono)copper(II) units are bridged by pyrazine to form a dimer. These dimers are further bridged by perchlorate to form a structural ladder parallel to the *b*-axis. Hydrogen bonding interactions and π-stacking of the pyridone rings also provide structural stability to the lattice and provide potential magnetic superexchange pathways. Temperature-dependent magnetic susceptibility data reveal a maximum in χ near 6 K and exhibit a rapid drop in χ at lower temperatures, in agreement with a singlet ground state. The use of several models for fitting the magnetic data gave values of approximately -10 K for the dimer interaction and approximately $+1.5$ K for the interdimer interaction.

Keywords: Copper(II); Pyrazine; Bridging perchlorate; Magnetic susceptibility; Crystal structure

1. Introduction

The preparation and study of low-dimensional magnetic systems, i.e., those where magnetic interactions propagate in only zero, one, or two dimensions, has been a major area of study for more than two decades. Recognition of copper oxide-based superconductors as well isolated 2-D-antiferromagnets [1] has been a prime point for this interest coupled with the observation that other low-dimensional systems, such as magnetic ladders, can also undergo a transition to a super-conducting state [2]. Other unique physical phenomena such as the Luttinger Liquid State have been demonstrated in such systems [3]. The $S = ½$ moment for Cu(II) makes it especially appropriate for such studies, and hence it is a clear focus in the literature. Similarly, pyrazine has been

---

*Corresponding author. Email: Mturnbull@clarku.edu

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.710844

used extensively in the preparation of these materials due to its rigorously linear bridging nature and moderate magnetic exchange (0 to −20 K), allowing for detailed study in many regimes of the magnetic phase diagram as a function of both applied field and temperature [4].

In the design of such low-dimensional systems, it is common to use capping ligands to limit the available coordination sites at the metal ion. We have worked with a wide variety of substituted pyridines, both as ligands and counterions (in their protonated form), and examined the use of 2,3-dihydroxy pyridine for that purpose. As with most of the 2-hydroxypyridine compounds, an equilibrium exists between the 2-hydroxypyridine and 2-pyridone tautomers (scheme 1).

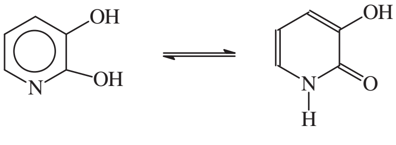
Although in either form the complex can readily chelate a metal ion between the oxygen atoms, structures containing this moiety are limited. A number of complexes (especially Ru and Ir) have been reported where the compound is in its dianionic form and chelates one metal ion through the oxygen atoms while bridging to a second *via* the pyridine nitrogen [5]. Similarly, a number of complexes using the oxygen atoms to chelate a metal, where the pyridine nitrogen has been alkylated, have also been reported [6]. Few structures of metal complexes of the protonated pyridone form have been reported where oxygen atoms chelate the metal. These include complexes of zinc [7], tin [8], molybdenum [9], iron [10], rhenium [11], and chromium [12]. The only previously reported structures for chelated copper-containing species are all N-alkylated [6c]. Our initial design envisioned coordination of the dianionic form of 2,3-dihydroxypyridine to block a pair of *cis*-coordination sites on the Cu-ion generating a neutral complex, which could then provide a building block to produce a number of possible lattices through bridging pyrazine ligands. We report here the synthesis, structure, and magnetic properties of the first member of this family, bis(aqua(3-oxy-2-pyridono)copper(II))μ-pyrazine diperchlorate (**1**).

2. Experimental

Copper(II) perchlorate hexahydrate was purchased from Aesar. Organic chemicals were purchased from Aldrich Chemical Co. All were used without purification. IR spectra were recorded as KBr pellets on a PE Spectrum 100. X-Ray powder diffraction measurements were made on a Bruker AXS-D8 X-ray powder diffractometer. Combustion analyses were performed by the Analytical Lab, Marine Science Institute, University of California, Santa Barbara, CA 93106-6150, USA.

2.1. *Bis(aqua(3-oxy-2-pyridono)copper(II))-μ-pyrazine diperchlorate (1)*

A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (1.85 g, 5.00 mmol) in 5.0 mL of 50% methanol/water was added to a solution of 2,3-dihydroxypyridine (0.444 g, 4.00 mmol) in 40.0 mL of



Scheme 1. 2-Hydroxypyridine and 2-pyridone forms of 2,3-dihydroxypyridine.

50% methanol/water. To this, a solution of pyrazine (0.16 g, 2.0 mmol) in 5.0 mL of 50% (methanol/water) was added dropwise with stirring. This solution was gently heated with stirring for 20 min. The resulting green solution was partially covered and allowed to evaporate slowly at room temperature for 5 days by which time green crystals had grown. The crystals were harvested through suction filtration, washed with 3 mL of cold 50% methanol/water, and then with 30 mL of acetone. The green crystals were left to dry overnight to yield 0.35 g (26%). No attempt was made to maximize the yield. CHN Calcd for $C_{14}H_{16}N_4O_{14}Cl_2Cu_2$ (Found) (%): C 25.39 (25.81); H 2.43 (2.74); N 8.46 (8.68). IR (KBr): 3443m/3253m (νO–H) 3121m/3005w/ 2932m(νN–H, C–H) 1618s (νC=O), 1552s (δN–H), 1288s, 1137s/1105s/1078s/1052s (νCl–O), 621 (δO–Cl–O) cm^{-1}.

2.2. *Magnetic data*

Magnetic susceptibility data were collected using a Quantum Design MPMS-XL SQUID magnetometer. Isothermal magnetization at 1.8 K was collected in fields up to 5 T; several data points were collected as the field was reduced back to zero to check for hysteresis. None was observed. Temperature-dependent magnetization was collected in a field of 0.1 T from 1.8 to 310 K. Data were corrected for the sample holder, the temperature-independent paramagnetism of Cu(II), and diamagnetic contributions of the constituent atoms [13].

2.3. *Single-crystal X-ray diffraction data*

Data collections were carried out on a Rigaku Saturn CCD area detector with graphite monochromated Mo-Kα radiation. Data were collected and processed using CrystalClear (Rigaku). The structures were solved by direct methods and refined *via* the least-squares analysis using SHELX97-2 [14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were refined using a riding model with fixed isotropic U values. Hydrogen atoms bonded to nitrogen or oxygen were located in the difference map and their positions allowed to refine with fixed isotropic U values. Neutral atom scattering factors were taken from [15]. Anomalous dispersions were those of Creagh and McAuley [16]. Crystallographic data are given in table 1, selected bond lengths and angles are given in table 2, and hydrogen bond parameters are given in table 3. The data for **1** have been deposited with the CCDC [17]. Comparison of X-ray powder diffraction data (Bruker D8 Advance) with the crystallographic data of **1** established that the samples used for magnetic studies were in the same phase as the single crystal.

3. Results and discussion

3.1. *Synthesis and structure*

Reaction of copper(II) perchlorate with 2,3-dihydroxypyridine and pyrazine in an aqueous solution led to the isolation of **1** as green prisms (scheme 2). Crystals

Table 1. Crystal and experimental data for **1**.

Empirical formula	$C_7H_8ClCuN_2O_7$
Formula weight	331.14
Temperature (K)	153(2)
Wavelength (Å)	0.71075
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	5.654(3)
b	7.108(4)
c	13.953(7)
α	77.54(2)
β	82.04(2)
γ	79.72(2)
Volume ($Å^3$), Z	535.8(5), 2
Absorption coefficient (mm^{-1})	2.318
$F(000)$	332
Crystal size (mm^3)	$0.34 \times 0.23 \times 0.23$
θ range for data collection (°)	3.05–25.01
Reflections collected	3565
Independent reflections	1786 [$R(\text{int}) = 0.0354$]
Completeness to $\theta = 25.01$ (%)	94.2
Absorption correction	Numerical
Max. and min. transmission	0.6177 and 0.5062
Data/restraints/parameters	1786/1/172
Goodness-of-fit on F^2	1.069
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0462$, $wR_2 = 0.1266$
R indices (all data)	$R_1 = 0.0464$, $wR_2 = 0.1268$
Largest difference peak and hole ($e\,Å^{-3}$)	0.934 and −1.109

Table 2. Bond lengths (Å) and angles (°) for **1**.

Cu1–O11	1.975(3)	O11–Cu1–O12	85.09(10)
Cu1–O12	1.931(3)	O11–Cu1–O1S	92.48(11)
Cu1–O1S	1.966(3)	O11–Cu1–N1	173.92(10)
Cu1–N1	2.006(3)	O12–Cu1–O1S	176.54(10)
Cu1–O1	2553(4)	O12–Cu1–N1	90.10(11)
Cu1–O4 (x, $y - 1$, z)	2.476(4)	O1S–Cu1–N1	92.17(12)

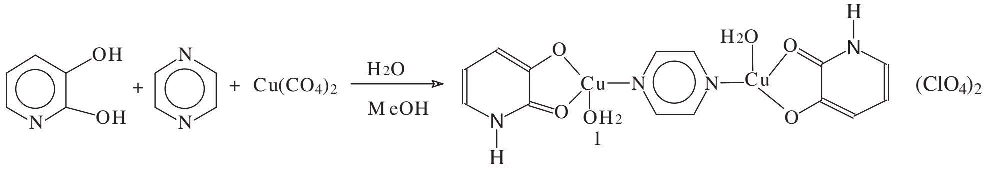
Table 3. Hydrogen bonds for **1** (Å and °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(1S)–H(1A)···O(2)^A	0.787(19)	2.09(3)	2.807(4)	152(4)
O(1S)–H(1B)···O(12)^C	0.79(5)	1.84(5)	2.623(4)	176(4)
N(11)–H(11)···O(11)^B	0.79(5)	2.11(5)	2.879(4)	166(4)

Symmetry transformations used to generate equivalent atoms: $^A = x, y+1, z$; $^B = -x, -y+2, -z+1$; $^C x-1, y, z$.

suitable for single-crystal X-ray diffraction were isolated directly from the reaction mixture.

The compound crystallizes in the triclinic space group $P\bar{1}$. The molecular unit is shown in figure 1. The pyrazine ring sits athwart a crystallographic inversion center and



Scheme 2. Synthesis of **1**.

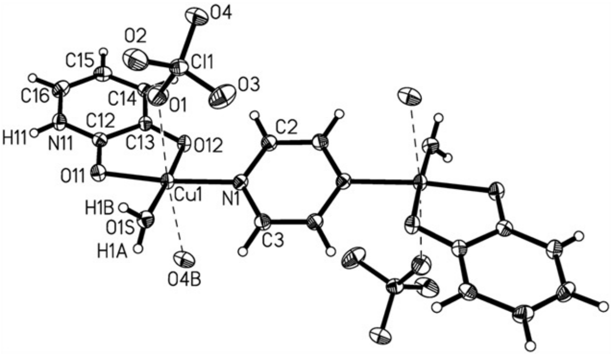


Figure 1. A thermal ellipsoid plot (50% probability ellipsoids) of the molecular unit of **1**. Only the molecular unit and those hydrogen atoms which positions were refined are labeled. Symmetry operation B: x, $y-1$, z.

links the two [H_2O(2,3-OpyH)Cu] units into a dimer [2,3-OpyH = 3-oxy-2-pyridono]. The geometry about copper is best described as Jahn–Teller distorted octahedral. Each Cu(II) is chelated by one 2,3-OpyH moiety and bonded to one pyrazine, with the fourth equatorial position occupied by water. The mean deviation of the Cu1 and equatorial substituents is 0.018 Å from the equatorial plane. Cu1 shows the greatest deviation from the mean plane and is lifted above the plane by 0.044 Å, similar to what is observed in a square pyramidal structure. The pyrazine ring is canted 34.6(1)° relative to the equatorial coordination plane while the pyridine ring is tipped 16.0(1)° below that plane, away from Cu(II).

The 2-hydroxypyridine ring is in the pyridone tautomer (N–H form, H11 was located in the electron density difference map) with the 3-hydroxy group deprotonated to generate a (−1) anion. The Cu(II) coordination sphere is completed by two inequivalent long interactions to perchlorate ions that bridge the dimers into ladders which run parallel to the *b*-axis (figure 2). Cu(II) is displaced from the mean equatorial plane toward O4 to give two Cu-perchlorate contact distances of 2.476(4) and 2.553(4) Å. The perchlorate oxygen atoms are located in the axial sites completing the 4 + 2 geometry with Cu–O bonds that deviate only slightly from the normal to the mean equatorial plane [O1, 1.9(1)°; O4, 6.2(1)°].

The ladders are interleaved *via* π-stacking interactions parallel to the *b*-axis (figure 3). The pyridine rings are parallel (being related by an inversion center) with a distance of 3.30(1) Å between their mean planes and a slip angle of 16.1(2)° between the line connecting the ring centroids and the ring planes. The ladders are further interconnected *via* a pair of hydrogen bonds that link the 2,3-OpyH rings into inversion-related dimers ($d_{\mathrm{N11\cdots O11B}} = 2.879(4)$ Å, see figures 3 and 4, and table 3).

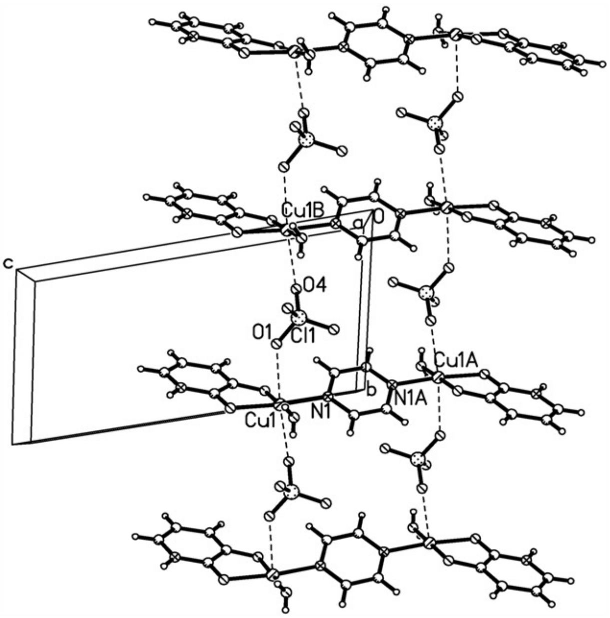


Figure 2. Ladder structure produced by the bridging perchlorate ions in **1**. Symmetry operations, A: x, y, z; B: x, $y + 1$, z.

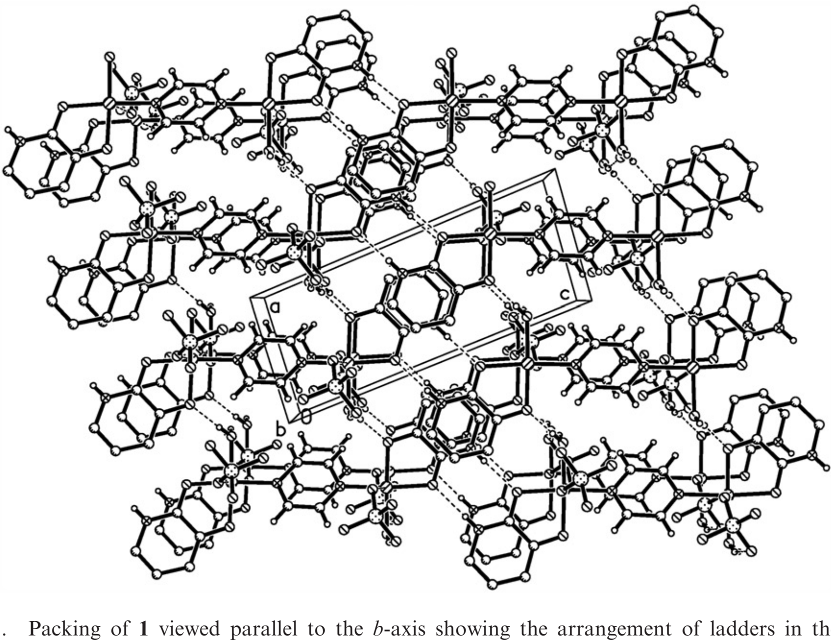


Figure 3. Packing of **1** viewed parallel to the *b*-axis showing the arrangement of ladders in the lattice. Dashed lines represent hydrogen bonds; only hydrogen atoms involved in hydrogen bonds are shown.

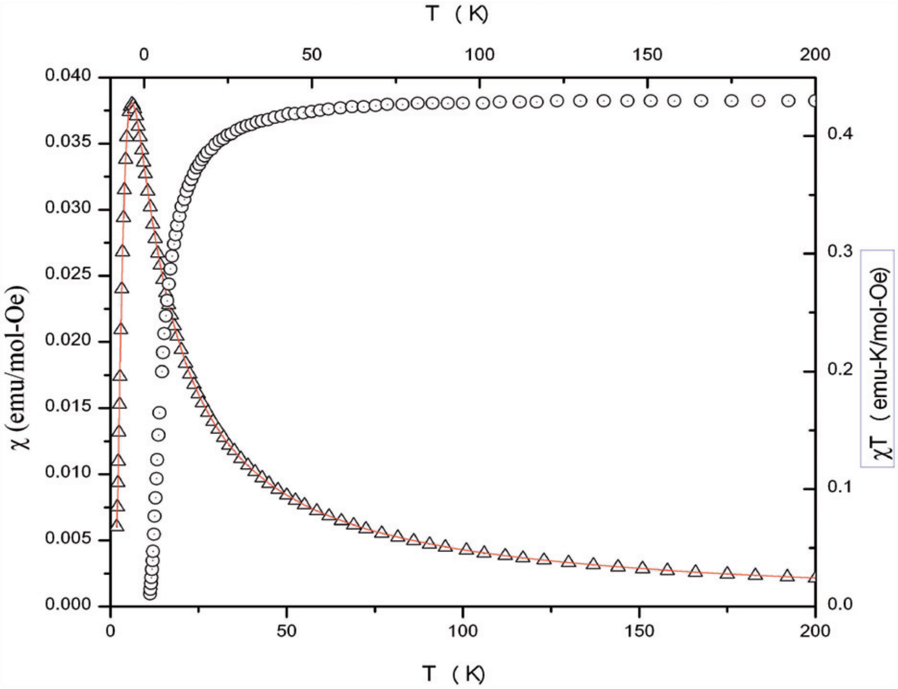


Figure 4. $\chi(\Delta)$ and $\chi_T(\circ)$ as a function of temperature for **1** from 1.8 to 310 K. The solid line shows the fit to the strong-rung ladder model.

The packing is also stabilized by strong hydrogen bonds between the coordinated water and phenoxy oxygen of the adjacent layer ($d_{O1S\cdots O12} = 2.623(4)$ Å, dashed lines in figure 3).

3.2. *Magnetic behavior*

Magnetic susceptibility data were collected as a function of temperature for **1** from 1.8 to 310 K and are presented in figures 4 and 5 [17]. The data exhibit a rounded maximum at 0.038 emu Oe^{-1} mol^{-1} near 6.1 K, below which the susceptibility drops rapidly indicating antiferromagnetic interactions and a singlet ground state. The data were fitted to several models for singlet ground state systems, including a dimer model (with and without a Curie–Weiss correction to account for interdimer interactions), an alternating chain model, and the strong-rung and weak-rung ladder models. The results are shown in table 4. The expressions for the spin ladder and alternative chain susceptibilities were based on simulations in which all exchange constants were antiferromagnetic. We assume that they remain valid for sufficiently weak secondary ferromagnetic interactions.

3.3. *Discussion*

Ladder formation *via* linking of the pyrazine-bridged dimers by perchlorates was unexpected. Bridging perchlorates are quite common in Cu(II) chemistry in a capping

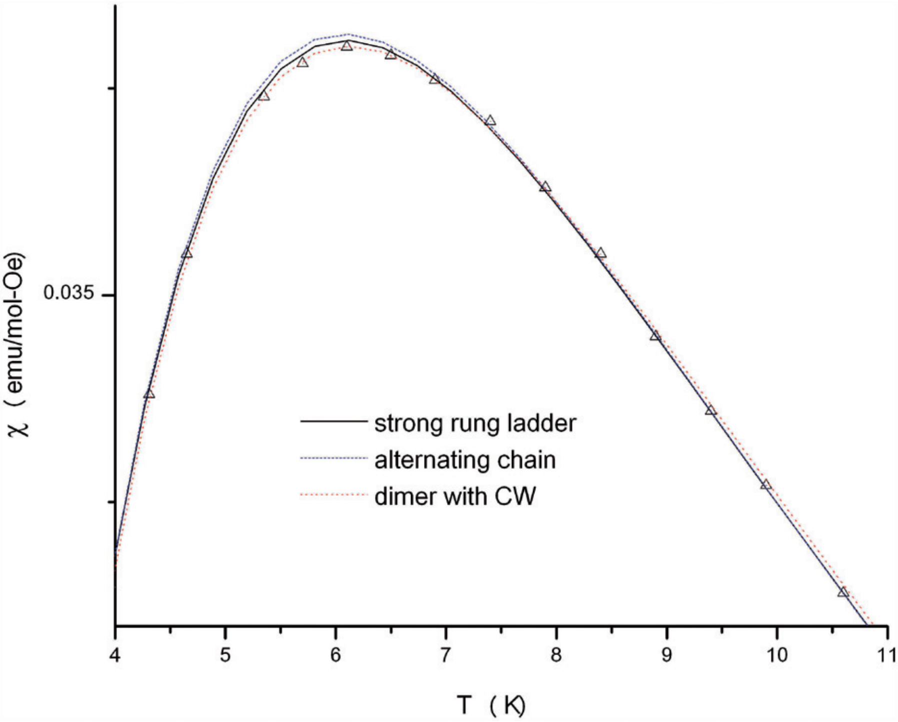


Figure 5. Expansion of the χ *vs.* T plot for **1** showing fits to the models for the strong-rung ladder, strong-rail ladder, and dimer (with a Curie–Weiss correction).

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

Model	C (emu K mol^{-1} Oe^{-1})	$2J_1$ (K)	$2J_2$ or θ (K)	% Imp	R^2
Dimer	0.454(1)	−9.72(3)		0.46(8)	0.9952
Dimer with C–W	0.437(2)	−10.9(2)	+0.97(12)	0.20(8)	0.9998
Strong-rung ladder	0.439(1)	−9.89(2)	+1.32(8)	1.7(2)	0.9998
Alternating chain	0.442(1)	−8.01(1)	+3.53(2)	0.03(2)	0.9999

mode (bridging across oxide or hydroxide bridged Cu(II) ions), either in bidentate [18] or tridentate fashion [19]. The bidentate-bridging mode between copper species is also observed in the μ-1,3 mode both intra- [20] and inter-molecularly [21] as well as in an example of a complex where perchlorates are both bridging and tri-capping [22]. μ-1,3-Bridging is also observed to generate chain structures [23] similar to one rail of the current compound. Bis-μ-1,3-bridging, similar to the linking of the pyrazine bridged dimer in **1**, has also been observed, but only a tetracopper species was generated; an extended coordination polymer was not formed [24]. Thus, the present ladder structure generated by the bridging perchlorates appears to be unique.

Magnetic data for **1** clearly indicate that a two-parameter model is necessary to provide a good fit to the data; however, as is often the case for systems with singlet ground states, which model is appropriate is not obvious. One may assume that the primary magnetic exchange occurs through the bridging pyrazine moiety, and the exchange strength of approximately −10 K is in good agreement with the previous reports for pyrazine exchange in both 1-D and 2-D systems [4, 25]. The secondary pathway (or pathways) is not clear. There are four potential secondary superexchange pathways apparent from the crystal structure. The perchlorate bridges provide obvious support for a strong-rung ladder model and the perchlorate has been implicated in magnetic exchange previously [26]. One of the hydrogen-bonding pathways (O1S···O12) also generates a ladder-structure, but parallel to the *a*-axis and would generate an identical magnetic model. The pairwise hydrogen-bonding interactions between N11···O11 link the dimers together nearly parallel to the *c*-axis to generate an alternating chain structure that has a susceptibility qualitatively similar to that of a strong-rung ladder. Finally, the π-stacking interactions link the dimers together provide a 2-D-layer network, again requiring a second exchange parameter to appropriately model the magnetic lattice.

We have reported the preparation, analysis, and magnetic behavior of the complex bis(aqua(3-oxy-2-pyridono)copper(II))μ-pyrazine diperchlorate (**1**). The compound exhibits a singlet magnetic ground state and the structure provides a number of possible explanations for the magnetic superexchange, but the pathways cannot be unambiguously assigned based upon susceptibility data alone. Theoretical calculations and field-dependent heat capacity measurements are planned to provide additional information regarding exchange in this complex; synthesis of additional members of the family is in progress.

Supplementary material

CCDC 874709 (**1**) contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/

Acknowledgments

The MPMS-XL SQUID magnetometer was purchased with the assistance of funds from the National Science Foundation (IMR-0314773) and the Kresge Foundation. The Bruker D8-Advance powder X-ray diffractometer was purchased with the assistance of Funds from the Kresge Foundation and PCISynthesis, Inc. We thank Mr Veli Selmani for his assistance with the preliminary experiments.

References

[1] J.M. Tranquada, H. Woo, T.G. Perring, H. Goka, G.D. Gu, M. Fujita, K. Yamada. *Nature* (London), **429**, 534 (2004).

[2] (a) M. Uehara, T. Nagata, J. Akimitsu, H. Takahashi, N. Mori, K. Kinoshita. *J. Phys. Soc. Jpn.*, **65**, 2764 (1996); (b) T. Nakanishi, N. Motoyama, H. Mitamura, N. Takeshita, H. Takahashi, H. Eisaki, S. Uchida, N. Mori. *Phys. Rev. B*, **72**, 054520 (2005).

[3] M. Klanjsek, H. Mayaffre, C. Berthier, M. Horvatic, B. Chiari, O. Piovesana, P. Bouillot, C. Kollath, E. Orignac, R. Citro, T. Giamarchi. *Phys. Rev. Lett.*, **101**, 137201 (2008).

[4] (a) M.B. Stone, D.H. Reich, C. Broholm, K. Lefmann, C. Rischel, C.P. Landee, M.M. Turnbull. *Phys. Rev. Lett.*, **91**, 037205 (2003); (b) F.M. Woodward, P.J. Gibson, G. Jameson, C.P. Landee, M.M. Turnbull, R.D. Willett. *Inorg. Chem.*, **46**, 4256 (2007); (c) F. Xiao, F.M. Woodward, C.P. Landee, M.M. Turnbull, C. Mielke, N. Harrison, T. Lancaster, S.J. Blundell, P.J. Baker, P. Babkevich, F.L. Pratt. *Phys. Rev. B*, **79**, 134412 (2009); (d) E. Cizmar, S.A. Zvyagin, R. Beyer, M. Uhlarz, M. Ozerov, Y. Skourski, J.L. Manson, J.A. Schlueter, J. Wosnitza. *Phys. Rev. B*, **81**, 064422 (2010); (e) J.L. Musfeldt, L.I. Vergara, T.V. Brinzari, C. Lee, L.C. Tung, J. Kang, Y.J. Wang, J.A. Schlueter, J.L. Manson, M.-H. Whangbo. *Phys. Rev. Lett.*, **103**, 157401 (2009); (f) 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, D. Trial. *J. Am. Chem. Soc.*, **131**, 6733 (2009); (g) T. Lancaster, S.J. Blundell, M.L. Brooks, P.J. Baker, F.L. Pratt, J.L. Manson, M.M. Conner, F. Xiao, C.P. Landee, F.A. Chaves, S. Soriano, M.A. Novak, T.P. Papageorgiou, A.D. Bianchi, T. Herrmannsdorfer, J. Wosnitza, J.A. Schlueter. *Phys. Rev. B*, **75**, 094421 (2007); (h) W.E. Hatfield, W.F. Villa. *J. Am. Chem. Soc.*, **93**, 4081 (1971); (i) D.B. Losee, H.W. Richardson, W.E. Hatfield. *J. Chem. Phys.*, **59**, 3600 (1973); (j) H.W. Richardson, W.E. Hatfield. *J. Am. Chem. Soc.*, **98**, 835 (1976).

[5] (a) M.-L. Lehaire, R. Scopelliti, H. Piotrowski, K. Severin. *Angew. Chem., Int. Ed.*, **41**, 1419 (2002); (b) Z. Grote, R. Scopelliti, K. Severin. *Eur. J. Inorg. Chem.*, 694 (2007); (c) H. Piotrowski, K. Polborn, G. Hilt, K. Severin. *J. Am. Chem. Soc.*, **123**, 2699 (2001); (d) H. Piotrowski, G. Hilt, A. Schulz, P. Mayer, K. Polborn, K. Severin. *Chem.-Eur. J.*, **7**, 3196 (2001).

[6] (a) M. Hanif, H. Henke, S.M. Meier, S. Martic, M. Labib, W. Kandioller, M.A. Jakupec, V.B. Arion, H.-B. Kraatz, B.K. Keppler, C.G. Hartinger. *Inorg. Chem.*, **49**, 7953 (2010); (b) E.J. Brown, A.-K. Duhme-Klair, M.I. Elliott, J.E. Thomas-Oates, P.L. Timmins, P.H. Walton. *Angew. Chem., Int. Ed.*, **44**, 1392 (2005); (c) G. Ambrosi, M. Formica, V. Fusi, L. Giorgi, A. Guerri, S. Lucarini, M. Micheloni, P. Paoli, P. Rossi, G. Zappia. *Inorg. Chem.*, **44**, 3249 (2005).

[7] D.T. Puerta, S.M. Cohen. *Inorg. Chem.*, **42**, 3423 (2003).

[8] A. Szorcsik, L. Nagy, M. Scopelliti, A. Deak, L. Pellerito, G. Galbacs, M. Hered. *J. Organomet. Chem.*, **691**, 1622 (2006).

[9] M. Trivedi, D.S. Pandey, N.P. Rath. *Acta Crystallogr., Sect. E: Struct. Rep. Online*, **64**, m595 (2008).

[10] R.C. Scarrow, P.E. Riley, K. Abu-Dari, D.L. White, K.N. Raymond. *Inorg. Chem.*, **24**, 954 (1985).

[11] E.J. de Souza, A.G. de, A. Fernandes, V.M. Deflon, K.E. Bessler, S.S. Lemos, A.A. Batista, J. Ellena, E.E. Castellano, U. Abram, A. Hagenbach. *J. Braz. Chem. Soc.*, **17**, 1578 (2006).

[12] V.M. Deflon, K.E. Bessler, M. Kretschmar, U. Abram. *Z. Anorg. Allg. Chem.*, **626**, 1545 (2000).

[13] R.L. Carlin. *Magnetochemistry*, Springer-Verlag, Berlin (1986).

[14] G.M. Sheldrick. *Acta Cryst.*, **A64**, 112 (2008).

[15] J.T. Waber, D.T. Cromer. *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham (1974), Table 2.2 A.

[16] D.C. Creagh, W.J. McAuley. In *International Tables for Crystallography*, A.J.C. Wilson (Ed.), Vol. C, p. 219, Kluwer Academic Publishers, Boston (1992), Table 4.2.6.8.

[17] All magnetic data were modeled using the $\hat{H} = -2\sum_{A,B}^{N} J_{AB}\hat{S}_A \cdot \hat{S}_B$ form of the Hamiltonian.

[18] (a) G. Aromi, J. Ribas, P. Gamez, O. Roubeau, H. Kooijman, A.L. Spek, S. Teat, E. MacLean, H. Stoeckli-Evans, J. Reedijk. *Chem.-Eur. J.*, **10**, 6476 (2004); (b) P. Iliopoulos, G.D. Fallon, K.S. Murray. *J. Chem. Soc., Dalton Trans.*, 437 (1986); (c) V. McKee, S.S. Tandon. *Inorg. Chem.*, **28**, 2901 (1989); (d) V. McKee, S.S. Tandon. *J. Chem. Soc., Dalton Trans.*, 221 (1991); (e) S. Sabiah, B. Varghese, N.N. Murthy. *Chem. Commun.*, 5636 (2009).

[19] (a) D. Maity, P. Mukherjee, A. Ghosh, M.G.B. Drew, C. Diaz, G. Mukhopadhyay. *Eur. J. Inorg. Chem.*, 807 (2010); (b) Y. Agnus, R. Louis, B. Metz, C. Boudon, J.P. Gisselbrecht, M. Gross. *Inorg. Chem.*, **30**, 3155 (1991).

[20] (a) S. Kawata, S. Kitagawa, M. Enomoto, H. Kumagai, M. Katada. *Inorg. Chim. Acta*, **283**, 80 (1998); (b) J. Ackermann, F. Meyer, H. Pritzkow. *Z. Anorg. Allg. Chem.*, **630**, 2627 (2004); (c) S. Schindler, D.J. Szalda, C. Creutz. *Inorg. Chem.*, **31**, 2255 (1992); (d) J. Reim, B. Krebs. *Angew. Chem., Int. Ed.*, **33**, 1969 (1994).

[21] (a) T.-H. Lu, H.-C. Shan, M.-S. Chao, C.-S. Chung. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, **43**, 207 (1987); (b) R. Sakamoto, M. Ohba, N. Fukita, K. Takahashi, H. Okawa, L.K. Thompson. *Bull. Chem. Soc. Jpn.*, **71**, 2365 (1998); (c) P.V. Bernhardt. *Inorg. Chem.*, **38**, 3481 (1999); (d) A.R. Paital, V. Bertolasi, G. Aromi, J. Ribas-Arino, D. Ray. *Dalton Trans.*, 861 (2008); (e) V. Tudor, G. Marin, V. Kavtsov, Yu.A. Simonov, M. Julve, F. Lloret, M. Andruh. *Rev. Roum. Chim.*, **51**, 367 (2006).

[22] (a) Q.-J. Zhou, Y.-Z. Liu, R.-L. Wang, J.-W. Fu, J.-Y. Xu, J.-S. Lou. *J. Coord. Chem.*, **62**, 311 (2009); (b) C. diNicola, F. Garau, M. Gazzano, M. Monari, L. Pandolfo, C. Pettinari, R. Pettinari. *Cryst. Growth Des.*, **10**, 3120 (2010).

[23] (a) J.M. Harrowfield, Y. Kim, G.A. Koutsantonis, Y.H. Lee, P. Thuery. *Inorg. Chem.*, **43**, 1689 (2004); (b) X. Zhou, C. Yang, X. Le, S. Chen, J. Liu, Z. Huang. *J. Coord. Chem.*, **57**, 401 (2004); (c) M.-H. Choi,

B.J. Kim, I.-C. Kim, S.-H. Kim, Y. Kim, J.M. Harrowfield, M.-K. Lee, M. Mocerino, E. Rukmini, B.W. Skelton, A.H. White. *J. Chem. Soc., Dalton Trans.*, 707 (2001); (d) J. Sun, S.-Y. Deng, L. Zhang, J. He, L. Jiang, Z.-W. Mao, L.-N. Ji. *J. Coord. Chem.*, **62**, 3284 (2009).
[24] M.G.B. Drew, C. Cairns, A. Lavery, S.M. Nelson. *Chem. Commun.*, 1122 (1980).
[25] C.P. Landee, M.M. Turnbull. *Mol. Cryst. Liq. Cryst.*, **335**, 193 (1999).
[26] (a) S.A. Komaei, G.A. van Albada, J.G. Haasnoot, H. Kooijman, A.L. Spek, J. Reedijk. *Inorg. Chim. Acta*, **286**, 24 (1999); (b) K.T. McGregor, D.J. Hodgson, W.E. Hatfield. *Inorg. Chem.*, **15**, 421 (1976).