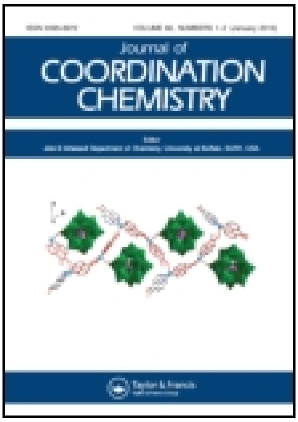

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# Copper(I) and copper(II) complexes with pyrazine-containing pyridylalkylamide ligands N-(pyridin-2-ylmethyl)pyrazine-2-carboxamide and N-(2-(pyridin-2-yl)ethyl)pyrazine-2-carboxamide

Robert P. Houser[a], Zhaodong Wang[b], Douglas R. Powell[b] & Timothy J. Hubin[c]
[a] Department of Chemistry and Biochemistry, University of Northern Colorado, Greeley, CO, USA
[b] Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK, USA
[c] Department of Chemistry and Physics, Southwestern Oklahoma State University, Weatherford, OK, USA

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# Copper(I) and copper(II) complexes with pyrazine-containing pyridylalkylamide ligands *N*-(pyridin-2-ylmethyl) pyrazine-2-carboxamide and *N*-(2-(pyridin-2-yl)ethyl) pyrazine-2-carboxamide

ROBERT P. HOUSER*†, ZHAODONG WANG‡, DOUGLAS R. POWELL‡ and TIMOTHY J. HUBIN§

†Department of Chemistry and Biochemistry, University of Northern Colorado, Greeley, CO, USA
‡Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK, USA
§Department of Chemistry and Physics, Southwestern Oklahoma State University, Weatherford, OK, USA

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Four copper(II) complexes and one copper(I) complex with pyridine-containing pyridylalkylamide ligands *N*-(pyridin-2-ylmethyl)pyrazine-2-carboxamide ($HL^{pz}$) and *N*-(2-(pyridin-2-yl)ethyl)pyrazine-2-carboxamide ($HL^{pz'}$) were synthesized and characterized. The X-ray crystal structures of $[Cu_2(L^{pz})_2(4,4'\text{-bipy})(OTf)_2]$ (**1**, OTf = trifluoromethanesulfonate, 4,4′-bipy = 4,4′-bipyridine) and $[Cu(L^{pz})(py)_2]OTf{\cdot}H_2O$ (**2**, py = pyridine) revealed binuclear and mononuclear molecular species, respectively, while $[Cu(L^{pz})(\mu_2\text{-}1,1\text{-}N_3)]_n$ (**3**), $[Cu(L^{pz'})(\mu_2\text{-}1,3\text{-}N_3)]_n$ (**4**), and $[Cu(HL^{pz})Cl]_n$ (**5**) are coordination polymer 1-D chains in the solid state.

*Keywords*: Copper; Pyridylalkylamide ligands; Pyrazine ligands; Coordination polymers; Crystal structures

## 1. Introduction

Pyridyl amide ligands have been used by our groups and others for coordination chemistry oriented towards questions from bioinorganic chemistry to crystal engineering. Ligands with a pyridyl group connected via one amide linker to a variety of non-coordinating functional groups (see scheme 1) were used in the Houser laboratory to synthesize a wide range of copper(I), copper(II), and zinc(II) complexes [1–7]. These ligands coordinate in several different modes, depending on whether the amide NH group is deprotonated or not. In most cases where the NH group is intact, which renders the ligand as a neutral moiety, the ligand coordinates in either a monodentate fashion via the pyridyl N donor or in a bridging fashion through the pyridyl N donor and the amide carbonyl O atom. When the amide NH group

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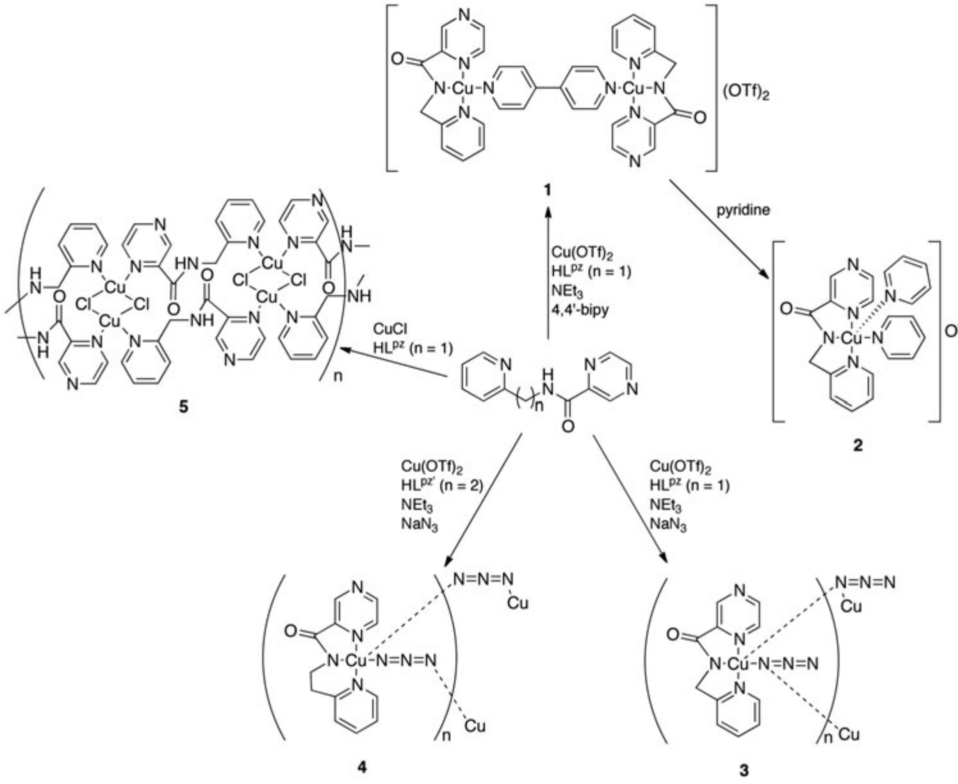
*Corresponding author. Email: robert.houser@unco.edu



Scheme 1. Synthesis of complexes **1**–**5.**

has been deprotonated, which renders the ligand as an anionic moiety, the ligand typically coordinates in a bidentate fashion via the pyridyl and amidate N donors.

Variants of the pyridyl amide ligands with functional groups capable of coordinating to metal atoms were used independently by the Houser and Hubin laboratories to create transition metal complexes of greater complexity [8–10]. For example, with a thioether R-group, mononuclear copper(II) complexes were synthesized [8], whereas with phenol R-group tetranuclear copper pseudo-cubane structures were realized [9]. Changing the R-group to a pyrazine ring introduces the possibility of bridging between metals to generate polynuclear or polymer species.

Pyrazine-based ligands play an important role in copper coordination chemistry [11–20]. Bis(terdentate)pyrazine-based diamide ligands have been used to produce polynuclear transition metal complexes. For example, a symmetrical diamide ligand containing a central bridging pyrazine unit connected to two terdentate binding pockets that forms bi- and tetranuclear copper(II) complexes was reported by Hausmann and coworkers [12, 14, 21]. The two amide hydrogens of the ligand can be deprotonated, allowing the anionic amidate N donor atoms to coordinate to the copper center. The ligand can therefore coordinate to the metal center differently, depending on whether base was present in the synthesis: the neutral ligand forms a centrosymmetric dimer where the pyrazine ring does not bridge between the copper(II) ions, whereas in the presence of triethylamine, a tetranuclear copper(II) complex forms where the pyrazine unit bridges between metal centers. This is a rare example of a discrete grid of pyrazine-based amide ligands.

A homolog of the aforementioned bis(terdentate)pyrazine-based diamide ligand that differs in the length of the alkane linker connecting the pyridyl ring shows similar coordination chemistry [22]. The ethylene-linked bis-terdentate ligand forms similar tetranuclear copper(II) complexes both in the neutral form and in the deprotonated anionic form. Other examples of pyrazine-based diamide ligands have been used to synthesize a tetranuclear cobalt(III) complex [23] as well as binuclear copper(II) complexes [24].

The ligand *N*-(pyridin-2-ylmethyl)pyrazine-2-carboxamide ($HL^{pz}$) was first used by the Hubin group to synthesize a trinuclear cobalt complex where the pyrazine ring bridges between cobalt atoms [10]. Cobalt and silver complexes of $HL^{pz}$, along with related ligand *N*-(2-(pyridin-2-yl)ethyl)pyrazine-2-carboxamide ($HL^{pz'}$), were also reported by Brooker and co-workers [25]. While the cobalt coordination chemistry with $HL^{pz}$ did not generate coordination polymers, its potential as a bridging ligand inspired us to investigate its coordination chemistry with copper. Herein, we report the synthesis, characterization, and structures of five copper complexes with $HL^{pz}$ and $HL^{pz'}$. Four copper(II) species were synthesized with a variety of co-ligands, including $[Cu_2(L^{pz})_2(4,4'\text{-bipy})(OTf)_2]$ (**1**, OTf = trifluoromethanesulfonate, 4,4′-bipy = 4,4′-bipyridine), $[Cu(L^{pz})(py)_2]OTf$ (**2**), $[Cu(L^{pz})(\mu_2\text{-}1,1\text{-}N_3)]_n$ (**3**), and $[Cu(L^{pz'})(\mu_2\text{-}1,3\text{-}N_3)]_n$ (**4**). Finally, one copper(I) species was synthesized with $HL^{pz}$, $[Cu(HL^{pz})Cl]_n$ (**5**).

## 2. Experimental

### 2.1. *General procedures*

All reagents were purchased from commercial suppliers and used as received without purification, unless otherwise stated. *N*-(pyridin-2-ylmethyl)pyrazine-2-carboxamide ($HL^{pz}$) and *N*-(2-(pyridin-2-yl)ethyl)pyrazine-2-carboxamide ($HL^{pz'}$) were synthesized according to previously reported procedures [10, 25]. The solvents used were doubly purified using alumina columns in a MBraun solvent purification system (MB-SPS). Infrared spectra were measured from 4000 to 400 $cm^{-1}$ as KBr pellets on a NEXUS 470 FTIR spectrometer. Elemental analyzes were carried out by Atlantic Microlabs, Norcross, GA. Electrospray mass spectrometry (ESI-MS) data were measured on a quadrupole time-of-flight (Q-TOF) mass spectrometer (Micromass, Manchester, UK) containing a Z-spray electrospray ionization source (ESI). UV–visible spectra were measured on a Shimadzu UV2401PC spectrophotometer from 250 to 1000 nm. X-Band EPR spectra were recorded using a Bruker EMX spectrometer in $CH_3OH$ at 77 K.

### 2.2. *Syntheses*

**2.2.1. $[Cu_2(L^{pz})_2(4,4'\text{-bipy})(OTf)_2]$ (1)**. A solution of $Cu(OTf)_2$ (90.0 mg, 0.249 mM, OTf = trifluormethansulfonate) in methanol was added to a solution of $HL^{pz}$ (53.5 mg, 0.250 mM) and triethylamine (25.0 mg, 0.250 mM) in methanol, affording a dark green solution. A solution of excess 4,4′-bipyridine (4,4′-bipy) was layered on the above solution, from which purple crystals of **1** suitable for X-ray analysis were obtained. Yield: 86 mg, 68%. Anal. Calcd for $C_{34}H_{26}Cu_2F_6N_{10}O_8S_2$: C, 40.52; H, 2.60; N, 13.90. Found: C, 40.27; H, 2.53; N, 13.63. FTIR (KBr): 3447, 1647, 1416, 1380, 1291, 1245, 1224, 1158, 1033, 816, 772, 638, 518 $cm^{-1}$. ESI-MS (MeOH): $m/z = 276$ $[Cu(L^{pz})]^+$, 432 $[Cu(L^{pz})(4,4'\text{-bipy})]^+$, 490 $[Cu(L^{pz})_2 + H]^+$.

**2.2.2. $[Cu(L^{pz})(py)_2]OTf{\cdot}H_2O$ (2)**. Complex **1** (26 mg, 0.026 mM) was dissolved in pyridine (py) to form a dark blue solution. Vapor diffusion of diethyl ether into this solution afforded green needle-shaped crystals of **2** suitable for X-ray analysis. Yield: 19 mg, 61%. Anal. Calcd for $C_{22}H_{21}CuF_3N_6O_5S$: C, 43.89; H, 3.52; N, 13.96. Found: C, 43.62; H, 3.47; N, 13.80. UV–vis ($CH_3OH$) [$\lambda_{max}$, nm ($\varepsilon$, $M^{-1}$ $cm^{-1}$)]: 305 (3400), 624 (100). FTIR (KBr): 3436, 1636, 1486, 1389, 1280, 1160, 1030, 763, 708, 637, 517 $cm^{-1}$. ESI-MS (MeOH): $m/z = 276$ $[Cu(L^{pz})]^+$, 355 $[Cu(L^{pz})(py)]^+$.

**2.2.3. $[Cu(L^{pz})(\mu_2\text{-}1,1\text{-}N_3)]_n$ (3)**. A solution of $Cu(OTf)_2$ (90.0 mg, 0.249 mM) in methanol was added to a solution of $HL^{pz}$ (53.5 mg, 0.250 mM) and triethylamine (25.0 mg, 0.250 mM) in methanol, affording a dark green solution. A solution of $NaN_3$ (16.3 mg, 0.250 mM) was then layered on the above solution from which blue crystals of **3** suitable for X-ray analysis were obtained (55 mg, 69% yield). Anal. Calcd for $C_{11}H_9CuN_7O$: C, 41.44; H, 2.85; N, 30.76. Found: C, 40.56; H, 2.77; N, 30.18. UV–vis ($CH_3OH$) [$\lambda_{max}$, nm ($\varepsilon$, $M^{-1}$ $cm^{-1}$)]: 354 (5000), 646 (290). FTIR (KBr): 3430, 2055, 1640, 1376, 1164, 1050, 866, 769, 660 $cm^{-1}$. EPR (9.450 GHz, Mod. Amp. 5.0 G, $CH_3OH$, 77 K): $g_{\parallel} = 2.248$, $g_{\perp} = 2.037$, and $A_{\parallel} = 165$ G. ESI-MS (MeOH): $m/z = 341$ $[Cu(L^{pz})N_3 + Na]^+$, 659 $\{[Cu(L^{pz})N_3]_2 + Na\}^+$, 977 $\{[Cu(L^{pz})N_3]_3 + Na\}^+$.

**2.2.4. $[Cu(L^{pz'})(\mu_2\text{-}1,3\text{-}N_3)]_n$ (4)**. A solution of $Cu(OTf)_2$ (90.0 mg, 0.249 mM) in methanol was added to a solution of $HL^{pz'}$ (57.0 mg, 0.250 mM) and triethylamine (25.0 mg, 0.250 mM) in methanol, affording a dark blue solution. A solution of $NaN_3$ (16.3 mg, 0.250 mM) was then layered on the above solution from which blue crystals of **4** suitable for X-ray analysis were obtained (54 mg, 65% yield). Anal. Calcd for $C_{12}H_{11}CuN_7O$: C, 43.31; H, 3.33; N, 29.46. Found: C, 43.68; H, 3.35; N, 29.59. UV–vis ($CH_3OH$) $\lambda_{max}$, nm ($\varepsilon$, $M^{-1}$ $cm^{-1}$)]: 346 (5000), 637 (240). FTIR (KBr): 2855, 2054, 1624, 1366, 1168, 1043, 773 $cm^{-1}$. EPR (9.447 GHz, Mod. Amp. 5.0 G, $CH_3OH$, 77 K): $g_{\parallel} = 2.249$, $g_{\perp} = 2.037$, and $A_{\parallel} = 170$ G. ESI-MS (MeOH): $m/z = 355$ $[Cu(L^{pz'})N_3 + Na]^+$, 687 $\{[Cu(L^{pz'})N_3]_2 + Na\}^+$, 1019 $\{[Cu(L^{pz'})N_3]_3 + Na\}^+$.

**2.2.5. $[Cu(HL^{pz})Cl]_n$ (5)**. A solution of CuCl (12.3 mg, 0.125 mM) in $CH_3CN$ was added dropwise into a stirred solution of $HL^{pz}$ (26.7 mg, 0.125 mM) in $CH_3CN$, whereupon the color changed from light yellow to yellow. After stirring for 1 h, the solution was filtered and vapor diffusion of diethyl ether into the yellow filtrate resulted in formation of red block-shaped crystals of **5** suitable for crystallographic characterization. Yield: 26.6 g, 68%. Anal. Calcd for $C_{11}H_{10}ClCuN_4O$: C, 42.18; H, 3.22; N, 17.89. Found: C, 41.95; H, 3.13; N, 17.74. FTIR (KBr): 3339, 1680, 1520, 1397, 1168, 1025, 871, 767, 658, 615 $cm^{-1}$.

### 2.3. *X-ray crystal structure determination*

Intensity data for all five compounds were collected using a diffractometer with a Bruker APEX CCD area detector [26, 27] and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The samples were cooled to 100(2) K. The cell parameters for all complexes were determined from a non-linear least-squares fit of the data. The data were corrected for absorption by the semi-empirical method [28]. The structures were solved by direct methods and refined by full-matrix least-squares on $F^2$ [29, 30]. Hydrogen atom positions were initially determined by geometry and refined by a riding model. Non-hydrogen atoms were refined with anisotropic displacement parameters.

For **2**, the water site, O1S, was disordered and was modeled in four orientations with occupancies refined to 0.439(4), 0.168(9), 0.191(9), and 0.203(9) for the unprimed, primed, double-primed, and "#" labeled atoms, respectively. Hydrogens bonded to water could not be located on a difference map. The displacement parameters of the water oxygen were restrained. For **5**, the molecule forms an infinite array parallel with the *b* axis. Crystal data for all complexes are summarized in table 1. Selected bond lengths for all complexes are summarized in table 2.

## 3. Results and discussion

Treatment of copper(II) salts in $CH_3CN$ or $CH_3OH$ with $HL^{pz}$ in the presence of $Et_3N$ to deprotonate the amide NH group results in formation of deep green solutions. Multiple attempts to crystallize the product(s) of these reactions were unsuccessful. The fact that the

Table 1. Crystallographic data for **1**–**5**.

| | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| Formula | $C_{34}H_{26}Cu_2F_6N_{10}O_8S_2$ | $C_{22}H_{21}CuF_3N_6O_5S$ | $C_{11}H_9CuN_7O$ | $C_{12}H_{11}CuN_7O$ | $C_{11}H_{10}ClCuN_4O$ |
| fw | 1007.85 | 602.05 | 318.79 | 332.82 | 313.22 |
| Crystal system | Triclinic | Triclinic | Monoclinic | Orthorhombic | Monoclinic |
| Space group | $P\Sigma 1$ | $P\Sigma 1$ | $P2_1/c$ | $Pbca$ | $C2/c$ |
| $a$ (Å) | 8.6449(16) | 8.127(3) | 12.604(6) | 14.0009(12) | 16.791(6) |
| $b$ (Å) | 14.617(2) | 10.907(4) | 14.927(14) | 7.9424(6) | 7.705(3) |
| $c$ (Å) | 16.855(3) | 15.445(5) | 6.426(3) | 22.6840(18) | 18.714(6) |
| $\alpha$ (°) | 64.577(5) | 69.447(8) | 90 | 90 | 90 |
| $\beta$ (°) | 84.332(8) | 75.164(8) | 93.660(7) | 90 | 106.060(9) |
| $\gamma$ (°) | 75.766(9) | 83.099(9) | 90 | 90 | 90 |
| $Z$ | 2 | 2 | 4 | 8 | 8 |
| $V$ (Å$^3$) | 1864.5(5) | 1238.5(8) | 1207.3(14) | 2522.5(4) | 2326.6(14) |
| $\rho_{Calcd}$ (g/cm$^3$) | 1.795 | 1.614 | 1.754 | 1.753 | 1.788 |
| $\mu$ (mm$^{-1}$) | 1.351 | 1.036 | 1.816 | 2.560 | 2.098 |
| $F$(0 0 0) | 1016 | 614 | 644 | 1352 | 1264 |
| $\theta$ Range (°) | 2.431–28.293 | 2.594–27.500 | 2.117–26.085 | 3.897–66.816 | 2.265–26.586 |
| Independent reflections | 9198 [$R$(int) = 0.0258] | 5620 [$R$(int) = 0.0452] | 2310 [$R$(int) = 0.0459] | 2197 [$R$(int) = 0.1394] | 2432 [$R$(int) = 0.0286] |
| Data/restraints/ parameters | 9198/0/559 | 5620/31/374 | 2310/0/181 | 2197/0/190 | 2432/0/166 |
| $R1[I > 2\sigma(I)]$ | 0.0411 | 0.0780 | 0.0344 | 0.0473 | 0.0311 |
| $wR2[I > 2\sigma(I)]$ | 0.1103 | 0.1875 | 0.0823 | 0.1066 | 0.0774 |
| GOF on $F^2$ | 0.981 | 1.090 | 1.004 | 1.001 | 0.990 |

Table 2. Selected bond lengths (Å) for **1–5**.

| | | | |
|---|---|---|---|
| **1** | | | |
| Cu1–N8A | 1.9021(19) | Cu1–N1 | 1.9721(19) |
| Cu1–N1A | 2.004(2) | Cu1–N12A | 2.022(2) |
| Cu1–O1C | 2.3526(17) | Cu2–N8B | 1.901(2) |
| Cu2–N6 | 1.9682(19) | Cu2–N1B | 2.016(2) |
| Cu2–N12B | 2.028(2) | Cu2–O1D | 2.3868(17) |
| **2** | | | |
| Cu1–N8 | 1.917(4) | Cu1–N23 | 1.979(4) |
| Cu1–N1 | 2.057(5) | Cu1–N12 | 2.067(5) |
| Cu1–N17 | 2.231(4) | | |
| **3** | | | |
| Cu1–N9 | 1.911(3) | Cu1–N17 | 1.973(3) |
| Cu1–N16 | 2.013(2) | Cu1–N1 | 2.012(2) |
| Cu1–N17A | 2.533(2) | | |
| **4** | | | |
| Cu1–N9 | 1.942(3) | Cu1–N18 | 1.983(3) |
| Cu1–N17 | 1.993(3) | Cu1–N1 | 1.997(4) |
| Cu1–N20 | 2.470(4) | | |
| **5** | | | |
| Cu1–N1 | 2.008(2) | Cu1–Cl1 | 2.4679(11) |
| Cu1–N15 | 2.071(2) | Cl1–Cu1A | 2.3289(9) |
| Cu1–Cl1A | 2.3288(9) | Cu1–Cu1A | 2.9936(9) |

products of these reactions were soluble, as opposed to forming insoluble precipitates as is more common when coordination polymers form, suggests that coordination polymers do not readily form from copper(II) and $(L^{pz})^-$. Our strategy to isolate crystalline copper(II) complexes therefore shifted to the addition of co-ligands 4,4′-bipyridine, pyridine, and azide ($N_3^-$).

Direct addition of 4,4′-bipyridine to solutions of copper(II) salts, $HL^{pz}$, and $Et_3N$ results in the formation of an insoluble purple precipitate. The binuclear copper(II) complex $[Cu_2(L^{pz})_2(4,4'\text{-bipy})(OTf)_2]$ (**1**) was isolated by layering a $CH_3OH$ solution of 4,4′-bipyridine over a solution of $Cu(OTf)_2$, $HL^{pz}$, and $Et_3N$, from which purple crystals of **1** suitable for X-ray diffraction analysis were obtained. X-ray analysis of **1** shows that it is a binuclear copper(II) complex as shown in figure 1. The copper center is five-coordinate with three N atoms from the ligand and one N atom from the bridging 4,4′-bipyridine ligand. The fifth apical position is occupied by the O from the triflate anion, forming a slightly distorted square pyramidal geometry ($\tau_5 = 0.145$ [31]). Interestingly, the second pyrazine N atom of the ligand does not coordinate, resulting in a molecular species rather than a coordination polymer. The deprotonated $L^{pz-}$ functions as a tridentate ligand binding in a meridinal fashion, and 4,4′-bipy acts as a bridging ligand between the two copper(II) ions. The 4,4′-bipy rings are twisted away from co-planarity by about 30°. The bond distances in **1** are typical for copper(II) complexes with similar ligand donors (see table 2 for selected bond lengths). Due to its poor solubility, UV–visible and EPR spectra for **1** were not collected. The FTIR data support the presence of ligands $L^{pz}$ and 4,4′-bipy in **1**, with the noteworthy amide carbonyl stretch at 1647 $cm^{-1}$. ESI-MS displayed peaks for fragments of **1** corresponding to $[Cu(L^{pz})(4,4'\text{-bipy})]^+$ and $[Cu(L^{pz})]^+$.

While **1** was insoluble in $CH_3CN$, $CH_3OH$, and $CH_2Cl_2$, it dissolved readily in pyridine. Recrystallization from pyridine by vapor diffusion of diethyl ether produced dark blue-green needle-shaped crystals of $[Cu(L^{pz})(py)_2]OTf$ (**2**). Single crystal X-ray diffraction analysis of **2** reveals that it is a mononuclear copper(II) complex, which is composed of one

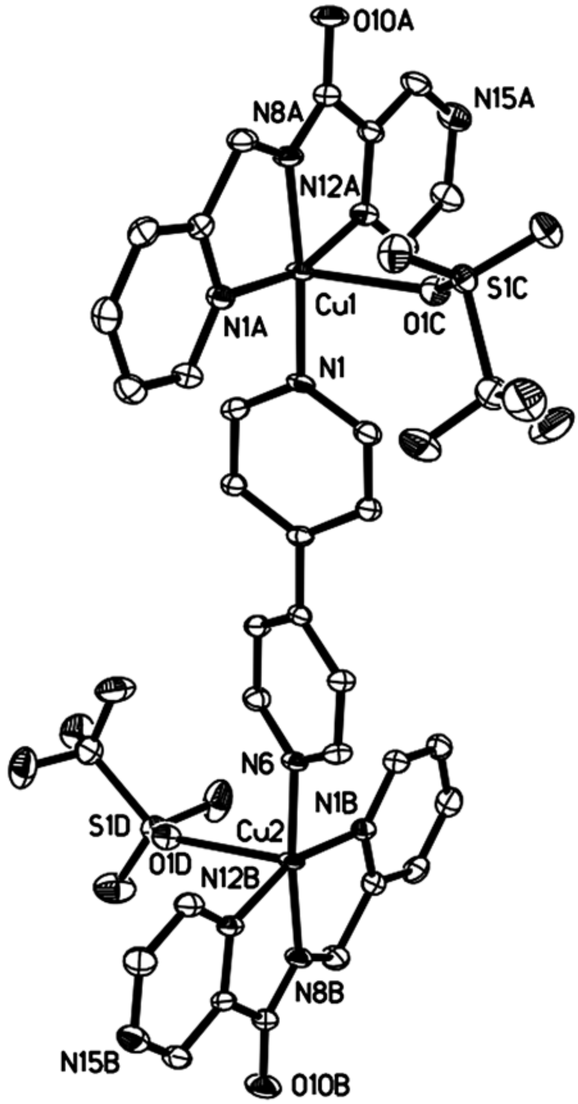


Figure 1. Representation of the X-ray crystal structure of [$Cu_2(L^{pz})_2$(4,4′-bipy)$(OTf)_2$] (**1**). The displacement ellipsoids were drawn at the 50% probability level. Hydrogens were removed for clarity.

deprotonated ligand $(L^{pz})^-$ and two pyridine solvent molecules as shown in figure 2. The 4,4′-bipyridine from **1** was displaced by the Lewis basic pyridine ligands during the crystallization process. The copper ion in **2** is five-coordinate, with three N donors from the ligand and two N donors from pyridine molecules, forming a distorted square pyramidal geometry ($\tau_5 = 0.173$ [31]). The apical Cu–N17 (pyridine) distance of 2.231(4) Å is longer than the average basal Cu-N distance (2.005 Å). Selected bond distances (Å) for **2** are shown in table 2. As was the case with **1**, the poor solubility of **2** precluded the collection of UV–visible and EPR spectra. The FTIR spectrum of **2** is very similar to the spectrum of **1**,

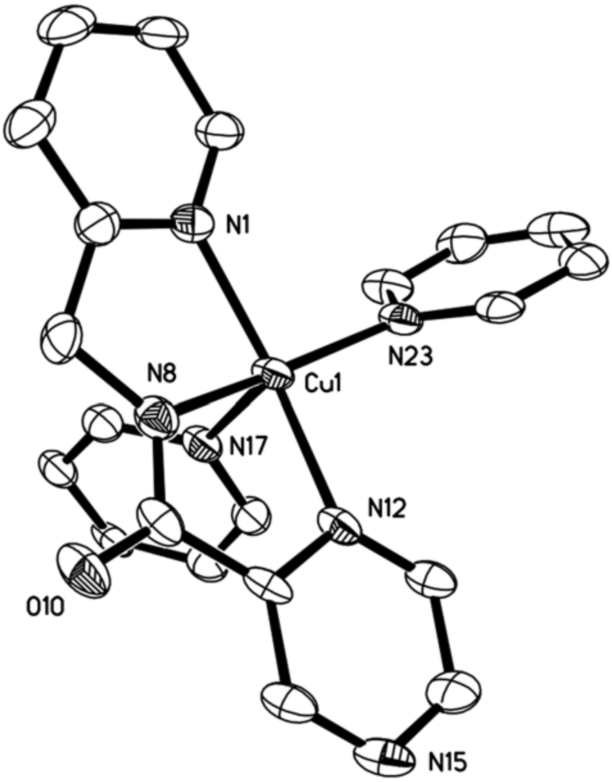


Figure 2. Representation of the X-ray crystal structure of $[Cu(L^{pz})(py)_2]OTf{\cdot}H_2O$ (**2**) with water molecules removed for clarity. The displacement ellipsoids were drawn at the 50% probability level. Hydrogens were removed for clarity.

indicating similar ligands present. The ESI-MS data for **2** indicate the presence of fragments where one or two py ligands have dissociated, namely $[Cu(L^{pz})(py)]^+$ and $[Cu(L^{pz})]^+$.

The azide anion is one of the most widely used bridging ligands due to its versatile coordination modes. $\mu_2$-1,3 (end-to-end) and $\mu_2$-1,1 (end-on) are the two most common coordination modes. The azide anion has been widely used for the construction of coordination polymers as a bridging ligand due to its versatile binding modes [32–34]. In most reported copper(II)-azide complexes, diamine and polyamine ligands are the most widely used co-ligands for copper(II)-azide complexes [35, 36].

Crystals of $[Cu(L^{pz})(\mu_2\text{-}1,1\text{-}N_3)]_n$ (**3**) suitable for X-ray diffraction analysis were obtained by layering a $CH_3OH$ solution of $NaN_3$ over a solution of $Cu(OTf)_2$, $HL^{pz}$, and $Et_3N$. Single crystal X-ray diffraction analysis of **3** shows that it is an azido-bridged ($\mu_2$-1,1) 1-D coordination polymer as shown in figure 3. The deprotonated ligand in this complex coordinates in the same meridinal fashion as for **1** and **2**, and furthermore the copper center is five-coordinate with three N donors from the ligand $(L^{pz})^-$ and two N atoms from the $N_3^-$ anionic bridging ligand, resulting in the formation of square pyramidal geometry ($\tau_5 = 0.074$ [31]). Three N donors of the ligand and one N donor from the azide anion comprise the basal plane, and the axial position is occupied by the N from the bridging azide. The bridging $\mu_2$-1,1-azido anions are bound to two copper(II) atoms with Cu–N distances of 1.973 and

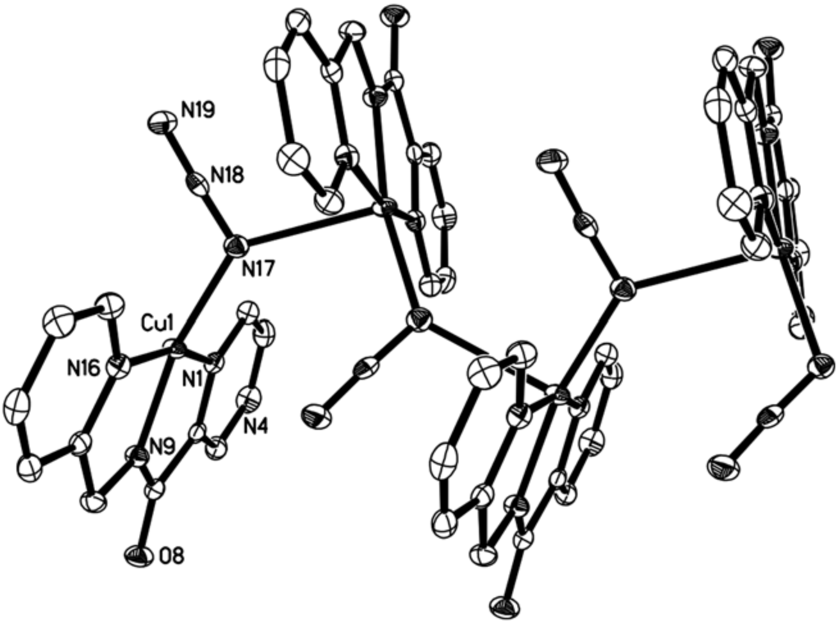


Figure 3. Representation of the X-ray crystal structure of $[Cu(L^{pz})(\mu_2\text{-}1,1\text{-}N_3)]_n$ (**3**). The displacement ellipsoids were drawn at the 50% probability level. Hydrogens were removed for clarity.

2.533 Å, and the Cu-N17-Cu angle is 136.52°. The intrachain Cu···Cu distance is 4.191 Å, which is longer than the reported Cu complexes with $N_3^-$ in an $\mu_2$-1,1 mode [35–38]. The 1-D chains of **3** are packed closely, with alternating orientations of the azide groups. Complex **3** dissolves in $CH_3OH$, and the ESI-MS suggests that the solid-state coordination polymer structure of **3** dissociates in solution and forms monomers ($m/z = 341$ $[Cu(L^{pz})N_3 + Na]^+$), dimers ($m/z = 659$ $\{[Cu(L^{pz})N_3]_2 + Na\}^+$), and trimers ($m/z = 977$ $\{[Cu(L^{pz})N_3]_3 + Na\}^+$).

$[Cu(L^{pz'})(\mu_2\text{-}1,3\text{-}N_3)]_n$ (**4**) was synthesized by the same method as **3**, except that the ethylene-linked ligand, $HL^{pz'}$, was used instead of $HL^{pz}$. $HL^{pz'}$ (*N*-(2-(pyridin-2-yl)ethyl)pyrazine-2-carboxamide) differs from $HL^{pz}$ only in the length of the alkyl linker between the pyridyl ring and the amide group, with $HL^{pz'}$ containing an ethylene linkage rather than a methylene linkage found in $HL^{pz}$ (see scheme 1). The FTIR spectra of **3** and **4** are similar to the spectra of **1** and **2**, but with the additional peaks at 2055 and 2054 $cm^{-1}$, respectively, corresponding to the azide stretch. The UV–visible spectra of **3** and **4** are typical of copper(II) azide complexes, with an absorption of medium intensity in the near-UV around 350 nm and a weak absorption in the visible region around 640 nm. Finally, the EPR spectra of **3** and **4** are axial, with $g_{\parallel} > g_{\perp}$ and $A_{\parallel}$ coupling constants typical for "normal" copper(II) complexes. In fact, the EPR parameters for **3** and **4** are nearly identical to each other (see experimental section for details).

The crystal structure of **4** is similar to **3** in that it is also an azido-bridged, 1-D coordination polymer, as shown in figure 4. Again following the trend set by **1–3**, the copper center in **4** is five-coordinate with three N donors from the deprotonated $(L^{pz'})^-$ ligand coordinating in a meridinal fashion in the square plane, and two N donors from the

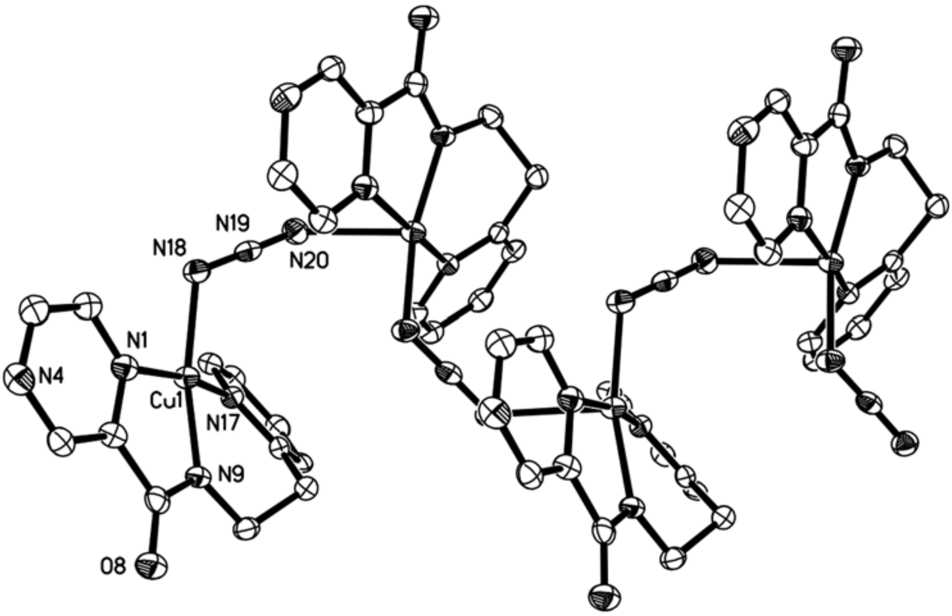


Figure 4. Representation of the X-ray crystal structure of $[Cu(L^{pz'})(\mu_2\text{-}1,3\text{-}N_3)]_n$ (**4**). The displacement ellipsoids were drawn at the 50% probability level. Hydrogens were removed for clarity.

$N_3^-$ anionic bridging ligand in the remaining basal coordination site and the axial site, forming a distorted square pyramidal geometry. Three N donors from the ligand and one azido N donor comprise the basal plane, while the axial position is occupied by the N donor from the azide anion with a much longer Cu–$N_{azido}$ distance of 2.470(4) Å. The coordination of mode of the azido ligand is different than in **3**. The bridging $\mu_2$-1,3-azido anions are bound to copper(II) with Cu–N distances of 1.993(3) and 2.470(4) Å. Selected bond distances are listed in table 2. The 1-D chains in **4** are packed closely, with overlap of the two pyridyl rings involving $\pi \cdots \pi$ interactions the adjacent aromatic pyridyl rings. The distance between chains 2 and 3 is longer than those between chains 1 and 2 or chains 3 and 4. Each chain is a 1-D zigzag structure bridged by an azide in end-to-end ($\mu_2$-1,3) mode. As was observed for **3**, **4** is fully soluble in $CH_3OH$, and the ESI-MS indicates dissociation of the solid-state chain structure of **4** with peaks for the monomers ($m/z = 355$ $[Cu(L^{pz'})N_3 + Na]^+$), dimers ($m/z = 687$ $\{[Cu(L^{pz'})N_3]_2 + Na\}^+$) and trimers ($m/z = 1019$ $\{[Cu(L^{pz'})N_3]_3 + Na\}^+$).

Finally, having explored the copper(II) chemistry with our pyrazine-based ligands, we turned our attention to the copper(I) chemistry with $HL^{pz}$. Previously, we reported the synthesis and characterization of a series of chlorido-bridged mono or binuclear copper(I) complexes with (pyridylmethyl)amide ligands [6]. Attempts to synthesize copper(I) complexes with $HL^{pz}$ and $Et_3N$ resulted in the disproportion to copper(II) and elemental copper(0). However, synthesis in the absence of $Et_3N$ was successful, resulting in 1-D chain coordination polymer $[Cu(HL^{pz})Cl]_n$ (**5**).

Complex **5** was prepared by the treatment of CuCl with $HL^{pz}$ in $CH_3CN$, from which red crystals of **5** were obtained by vapor diffusion of diethyl ether into the yellow filtrate from the reaction solution. Single crystal X-ray diffraction analysis of **5** revealed that it consists of a series of $Cu_2Cl_2$ dimers bridged by two $HL^{pz}$ ligands, and forms an infinite 1-D chain

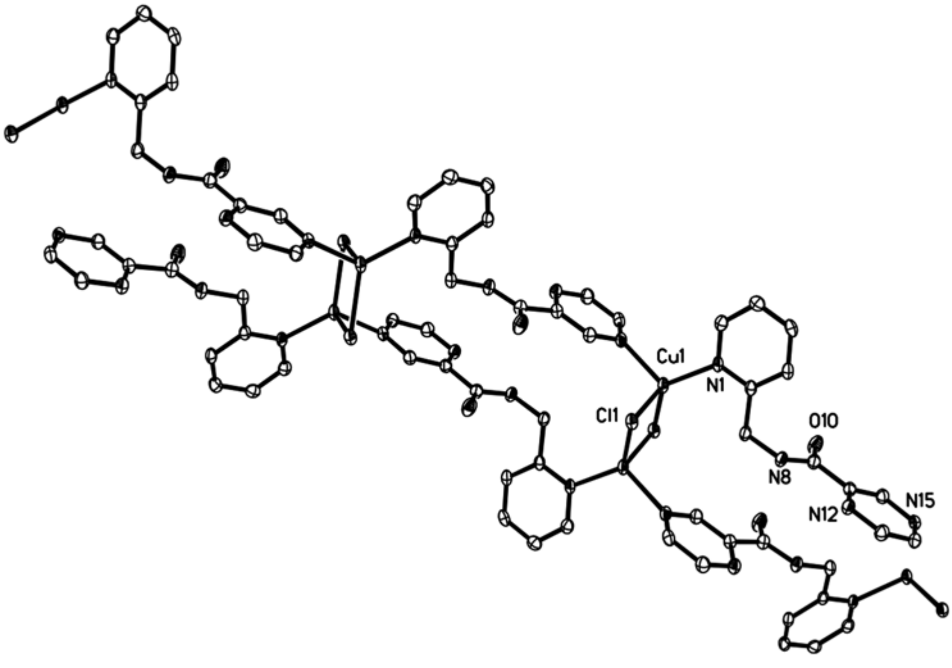


Figure 5. Representation of the X-ray crystal structure of $[Cu(HL^{pz})Cl]_n$ (**5**). The displacement ellipsoids were drawn at the 50% probability level. Hydrogens were removed for clarity.

structure as shown in figure 5. Each copper(I) is coordinated by two nitrogen donors, pyridyl N1, and pyrazine N15 from two separate ligands and two chloride ligands. The Cu–N bond lengths of 2.008(2) and 2.071(2) Å are slightly longer than the chlorido-bridged copper(I) complexes with pyridyl amide ligands reported previously from the Houser laboratory [6], but the average Cu–Cl (2.375 Å) and Cu–N (2.040 Å) bond distances in **5** are comparable with values in other $Cu_2Cl_2$ complexes with diamond core structures [39–41]. The smaller Cu–Cl–Cu bond angle of 77.17(3)° and the larger Cl–Cu–Cl bond angle of 102.83(3)° lead to a slightly shorter Cu···Cu distance of 2.9936(9) Å than in the range 2.997–3.150 Å reported for similar complexes in the literature [6, 39–41]. The coordination geometry around each Cu atom is distorted trigonal-pyramidal with a $\tau_4$ four-coordinate metrical parameter of 0.73 [7]. The packing structure of **5** illustrates the 1-D ladder structure where the $HL^{pz}$ ligands connect the $Cu_2Cl_2$ "rungs" of the ladder. Selected bond lengths for **5** are listed in table 2. The FTIR spectrum of **5** indicates the presence of $HL^{pz}$, including the amide carbonyl stretch at 1680 $cm^{-1}$.

## 4. Conclusions

Five copper complexes with the pyrazine-containing ligands $HL^{pz}$ or $HL^{pz'}$ were synthesized and characterized, including their solid state structures by X-ray crystallography. Attempts to isolate crystalline products of copper(II) complexes with $HL^{pz}$ or $HL^{pz'}$ in the presence of base to deprotonate the amide group on the ligand were unsuccessful. Four crystalline copper (II) complexes were synthesized from copper(II) triflate, either ligand $HL^{pz}$ or $HL^{pz'}$, triethylamine to deprotonate the ligand, and a co-ligand (4,4′-bipy, pyridine, or azide). While azido complexes **3** and **4** were 1-D chain coordination polymers in the solid state, none of the copper(II) complexes formed coordination complexes where the pyrazine functional group of the ligand bridged between copper centers. While it was not seen in **1–4**, this bridging mode was observed in systems with copper(II) and bis(terdentate)pyrazine-based ligands [12, 14, 22, 24], suggesting that the presence of two coordinating arms attached to the pyrazine is important for the ligand's ability to bridge via pyrazine. Interestingly, with $HL^{pz}$ and cobalt(II) the pyrazine group bridged between cobalt centers to form a trimer [10]. The distinct coordination geometry preferences of cobalt(II) *versus* copper(II) are likely responsible for the differences in their complexes formed with $HL^{pz}$.

No coordination polymer was obtained when 4,4′-bipyridine was used as a linker. Instead unexpected dicopper **1** or, when **1** was dissolved in pyridine, monomeric copper complex **2** were isolated. Only one pyrazine N coordinates with copper ions in **1** and **2**. When azide was used as a co-ligand, two 1-D coordination polymers, **3** and **4**, were isolated. Like **1** and **2**, only one of the pyrazine N donors coordinates to copper(II) in **3** and **4**. The bridging mode of azide is different ($\mu_2$-1,1 in **3** and $\mu_2$-1,3 in **4**) depending on the pyrazine-containing ligand, $(L^{pz})^-$ or $(L^{pz'})^-$. These bridging modes have been reported for copper(II) azido coordination polymers [37, 38, 42–47]. In particular, the $\mu_2$-1,1 bridging mode observed in **3** is very similar to coordination polymers reported by several groups [37, 45], and the $\mu_2$-1,3 bridging mode observed in **4** is likewise very similar to coordination polymers reported [42, 45].

Finally, **5**, which was synthesized from copper(I) chloride, is a copper(I) 1-D coordination polymer in which $Cu_2Cl_2$ dimeric units are bridged by two $HL^{pz}$. The ligand in **5** is in its neutral form (as opposed to the deprotonated, anionic form in **1–4**), and attempts to synthesize a copper(I) complex with deprotonated ligands were unsuccessful. This behavior is consistent with other copper(I) pyridylamide complexes that have been reported from the Houser laboratory [6, 7]. The $\mu_2$-chloride $Cu_2Cl_2$ node that is connected by ligands to form a 1-D coordination polymer has also been observed with 4,4′-bipy [41].

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## Supplemental data

CCDC 949936 – 949940 contain the supplementary crystallographic data for **1–5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

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