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Copper(I) Coordination Chemistry of (Pyridylmethyl)amide Ligands

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Copper(I) chloro complexes were synthesized with a family of ligands, HL^R [HL^R = *N*-(2-pyridylmethyl)acetamide, R = null; 2-phenyl-*N*-(2-pyridylmethyl)acetamide, R = Ph; 2,2-dimethyl-*N*-(2-pyridylmethyl)propionamide, R = Me_3; 2,2,2-triphenyl-*N*-(2-pyridylmethyl)acetamide, R = Ph_3)]. Five complexes were synthesized from the respective ligand and cuprous chloride: $[Cu(HL)Cl]_n$ (**1**), $[Cu_2(HL)_4Cl_2]$ (**2**), $[Cu_2(HL^{Ph})_2(CH_3CN)_2Cl_2]$ (**3**), $[Cu_2(HL^{Ph_3})_2Cl_2]$ (**4**), and $[Cu(HL^{Me_3})_2Cl]$ (**5**). X-ray crystal structures reveal that for all complexes the ligands coordinate to the Cu in a monodentate fashion, and inter- or intramolecular hydrogen-bonding interactions formed between the amide NH group and either amide C═O or chloro groups stabilize these complexes in the solid state and strongly influence the structures formed. Complexes **1**–**5** display a range of structural motifs, depending on the size of the ligand substituent groups, hydrogen bonding, and the stoichiometry of the starting materials, including a one-dimensional coordination polymer chain (**1**) and binuclear (**2**–**4**) or mononuclear (**5**) structures.

Introduction

Pyridyl amide ligands have garnered interest because of their biomimetic potential and their variable ligation modes.[1−11] These ligands have been shown to bind in a wide variety of coordination modes, including the anionic amidate form[1,2,4−6,8−11] and the neutral amide form.[3−6,8,11] While we are particularly interested in examples of Cu^{II} complexes with polydentate amide ligands,[1,4−6,8,10] numerous other transition-metal pyridyl amide or pyridyl amidate complexes have also been reported.[2,3,9,11] Among the various reported transition-metal complexes with pyridyl amide ligands, several have been specifically used as biomimetic models,[5,9] while others have produced interesting supramolecular and/or polymeric structures.[3,10,11] Only a few examples of pyridyl amide ligands coordinated to Cu^I ions have been reported.[12]

In our laboratory, a variety of pyridyl amide ligands have been designed and synthesized to explore their complexation properties.[5−8] It was established that the protonation or deprotonation of the amide N can control the coordination geometry of the metal center and the stability of complexes formed. In addition, the substituent groups attached to the amide also play an important role in the formation of different shapes and spatial orientations of the complex structure formed.[6,8] Recently, we employed a series of (pyridylmethyl)amide ligands (HL^R; R = H, Me_3, Ph, and Ph_3) with different substituent groups on the amide.[6] These

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ligands have exhibited very interesting coordination properties that lead to novel Cu clusters. A highly symmetrical copper hydroxide tennis ball cluster, $[Cu_8L_8(OH)_4]^{4+}$, was characterized by X-ray crystallography, electron paramagnetic resonance, electronic absorption spectra, and magnetism.[8] The increasing steric effect and electron-donating or -withdrawing property from substituent groups, R, led to the formation of different Cu clusters $[Cu_4(L^{Ph})_4(OH)_2]^{2+}$, $[Cu_2(HL^{Me_3})_2(OMe)_2]^{4+}$, and $[Cu_2(HL^{Ph_3})_2(OMe)_2]^{4+}$ with lower nuclearity.[6] While the Cu^{II} chemistry of our ligands has been thoroughly investigated, the Cu^I chemistry remains unexplored. Herein, we report the synthesis and detailed structural properties of five Cu^I complexes synthesized from CuCl and HL^R.

Experimental Section

General Procedures. All reagents were purchased from commercial suppliers and used as received without further purification, unless otherwise stated. Ligands *N*-(2-pyridylmethyl)acetamide (HL), 2,2-dimethyl-*N*-(2-pyridylmethyl)propionamide (HL^{Me_3}), 2-phenyl-*N*-(2-pyridylmethyl)acetamide (HL^{Ph}), and 2,2,2-triphenyl-*N*-(2-pyridylmethyl)acetamide (HL^{Ph_3}) were synthesized according to procedures previously reported.[6,8] All solvents were dried under nitrogen using standard methods and distilled before use, and all Cu^I complexes were synthesized under nitrogen in a glovebox. Fourier transform (FTIR) spectra were collected on a Nexus 470 FTIR spectrometer using the KBr pellet technique. ^1H NMR spectra were recorded on a Varian 300-MHz spectrometer using a deuterated solvent as the internal standard. Elemental analyses were carried out by Atlantic Microlabs, Norcross, GA.

$[Cu(HL)Cl]_n$ (1). A solution of HL (0.15 g, 1 mmol) in acetonitrile (3 mL) was added to a stirred solution of CuCl (0.0989 g, 1 mmol) in acetonitrile (3 mL). The reaction was stirred for 1.5 h, during which the color changed to light yellow. The solution was filtered, and diffusion of diethyl ether into the filtrate produced crystals suitable for crystallographic characterization (0.169 g, 68.0% yield). Anal. Calcd for $C_8H_{10}ClCuN_2O$: C, 38.56; H, 4.05; N, 11.24. Found: C, 38.59; H, 3.98; N, 11.18. ^1H NMR (300 MHz, DMSO): δ 1.94 (s, 3H), 4.42 (s, 2H), 7.12 (s, 1H), 7.39 (s, 2H), 7.83 (t, 1H), 8.58 (s, 1H). FTIR (KBr): 3295, 3069, 1644, 1604, 1569, 1550, 1477, 1439, 1411, 1373, 1357, 1290, 1235, 1156, 1116, 1086, 1032, 774, 719, 685, 613, 585, 497, 459 cm^{-1}.

$[Cu_2(HL)_4Cl_2]$ (2). A solution of HL (0.30 g, 2 mmol) in acetonitrile (4 mL) was added to a stirred solution of CuCl (0.0989 g, 1 mmol) in acetonitrile (3 mL). The reaction was stirred for 5.5 h, during which the color changed to yellow. The solution was filtered, and diffusion of diethyl ether into the filtrate produced yellow crystals suitable for crystallographic characterization (0.284 g, 71.1% yield). Anal. Calcd for $C_{32}H_{40}Cl_2Cu_2N_8O_4$: C, 48.12; H, 5.05; N, 14.03. Found: C, 48.05; H, 5.11; N, 14.09. ^1H NMR (300 MHz, CD_3CN): δ 2.02 (s, 3H), 4.48 (d, 2H), 7.12 (s, 1H), 7.34 (s, 1H), 7.42 (s, 1H), 7.80 (t, 1H), 8.54 (s, 1H). FTIR (KBr): 3352, 3292, 3067, 1678, 1644, 1601, 1550, 1512, 1478, 1439, 1409, 1398, 1370, 1354, 1294, 1279, 1231, 1156, 1037, 1012, 850, 779, 760, 727, 682, 595, 547, 498 cm^{-1}.

$[Cu_2(HL^{Ph})_2(CH_3CN)_2Cl_2]$ (3). A solution of CuCl (0.0495 g, 0.5 mmol) in acetonitrile (1 mL) was added to a stirred solution of HL^{Ph} (0.113 g, 0.5 mmol) in acetonitrile (2 mL). The resulting light-yellow suspension was stirred for 4 h, and then the solvent was removed under reduced pressure. The light-yellow powder was washed with 2 mL of Et_2O and dissolved in acetonitrile (2 mL). The solution was filtered through Celite, and the diffusion of Et_2O into filtrate leads to the formation of light-yellow crystals (0.015 g, 82.2% yield). Anal. Calcd for $C_{32}H_{34}Cl_2Cu_2N_6O_2$: C, 52.46; H, 4.68; N, 11.47. Found: C, 51.94; H, 4.48; N, 10.46. NMR (300 MHz, DMSO-d_6): δ 2.92 (t, 3H), 3.95 (s, 2H), 4.87 (s, 2H), 7.65−7.76 (m, 8H), 8.27 (t, 1H), 9.16 (s, 1H). FTIR (KBr): 3265, 3607, 2918, 1669, 1652, 1599, 1568, 1475, 1438, 1410, 1359, 1325, 1311, 1250, 1173, 1152, 1027, 764, 743, 728, 695, 624, 490 cm^{-1}.

$[Cu_2(HL^{Ph_3})_2Cl_2]$ (4). A solution of HL^{Ph_3} (0.378 g, 1 mmol) in dichloromethane (2 mL) was added to a stirred solution of CuCl (0.0496 g, 0.5 mmol) in acetonitrile (2 mL). The reaction was stirred for 7 h, during which the color changed to light yellow. The solution was filtered, and diffusion of diethyl ether into the filtrate produced colorless crystals suitable for crystallographic characterization (0.273 g, 51.1% yield). Anal. Calcd for $C_{26}H_{22}ClCuN_2O$: C, 65.40; H, 4.64; N, 5.87. Found: C, 65.51; H, 4.67; N, 5.94. ^1H NMR (300 MHz, CD_2Cl_2): δ 2.02 (s, 3H), 4.75 (d, 2H), 6.99 (s, 1H), 7.32−7.35 (m, 15H), 7.75 (t, 1H), 8.54 (s, 1H). FTIR (KBr): 3450, 3214, 3056, 3022, 1661, 1599, 1571, 1491, 1439, 1362, 1319, 1252, 1236, 1224, 1187, 1151, 1102, 1084, 1050, 1033, 1000, 931, 910, 894, 846, 772, 762, 742, 700, 670, 638, 616, 596, 549, 531, 521 cm^{-1}.

$[Cu(HL^{Me_3})_2Cl]$ (5). A solution of HL^{Me_3} (0.192 g, 1 mmol) in acetone (2 mL) was added to a stirred slurry of CuCl (0.0496 g, 0.5 mmol) in acetone (2 mL). The reaction was stirred for 1.5 h, during which the color changed to light yellow. The solution was filtered, and diffusion of diethyl ether into the filtrate produced light-yellow crystals suitable for crystallographic characterization (0.179 g, 74.0% yield). Anal. Calcd for $C_{22}H_{32}ClCuN_4O_2$: C, 54.65; H, 6.67; N, 11.59. Found: C, 54.54; H, 6.75; N, 11.49. ^1H NMR (300 MHz, CD_3COCD_3): δ 1.20−1.29 (m, 9H), 4.67 (d, 2H), 7.42 (s, 1H), 7.45 (s, 1H), 7.78 (s, 1H), 7.94 (t, 1H), 8.72 (s, 1H). FTIR (KBr): 3298, 3079, 2961, 1678, 1644, 1605, 1559, 1514, 1478, 1442, 1397, 1365, 1354, 1298, 1255, 1203, 1160, 1104, 1057, 1009, 944, 886, 860, 793, 760, 719, 642, 622, 585, 530, 466 cm^{-1}.

X-ray Crystal Structure Determination. Single crystals of **1**−**5** were obtained by vapor diffusion of Et_2O into solutions of the complex. Data for **1**−**5** were collected on a Bruker Apex CCD area detector diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation. The diffraction data from complex **3** had serious twinning problems, and a large amount of overlapping data from twinning were omitted. Only the raw structure was determined because of the incompleteness of the data. For complexes **1**, **2**, **4**, and **5**, cell parameters were determined from a nonlinear least-squares fit of the data. The data of these four complexes were corrected for absorption by the semiempirical method. The structures were solved by direct methods by use of the *SHELXTL* program and refined by full-matrix least squares on F^2 by use of all reflections.[13] H atom positions were initially determined by geometry and refined by a riding model. Non-H atoms were refined with anisotropic displacement parameters. Crystal data for **1**, **2**, **4**, and **5** are summarized in Table 1.

Results and Discussion

There are three donor atoms in the (pyridylmethyl)amide ligands, HL^R, namely, one N donor atom from the pyridyl ring and N and O donor atoms from the amide group. Previously, we observed that the coordination modes of our ligands are tunable by deprotonation of the amide N−H

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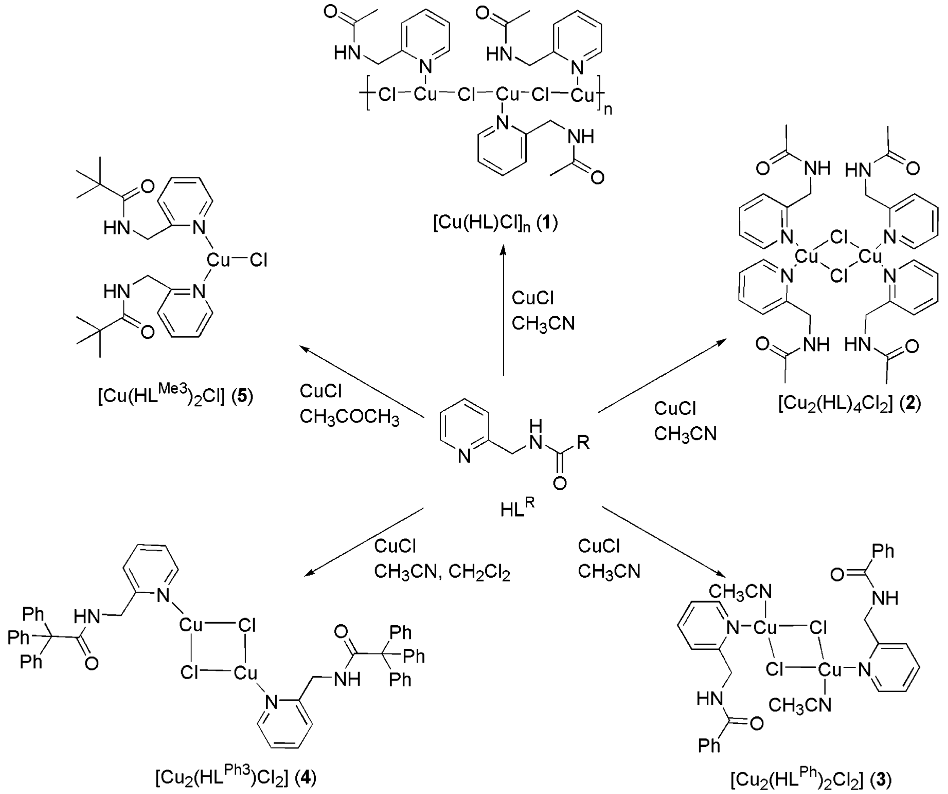
Table 1. Summary of Crystal Data and Refinement Parameters for Complexes **1**, **2**, **4**, and **5**

	1	2	4	5
formula	$C_8H_{10}ClCuN_2O$	$C_{32}H_{40}Cl_2Cu_2N_8O_4$	$C_{52}H_{44}Cl_2Cu_2N_4O_2$	$C_{22}H_{32}ClCuN_4O_2$
fw	249.17	798.70	954.89	483.51
temp (K)	113(2)	87(2)	87(2)	100(2)
space group	$P2_12_12_1$	$P2_1/c$	$P\bar{1}$	$P2/c$
a (Å)	4.8153(4)	13.738(6)	8.9143(16)	11.162(3)
b (Å)	13.7892(11)	9.126(4)	9.5821(16)	7.3381(16)
c (Å)	14.0641(11)	15.083(6)	13.346(2)	15.441(3)
α (deg)	90	90	83.872(5)	90
β (deg)	90	113.643(7)	80.222(5)	107.754(5)
γ (deg)	90	90	72.218(5)	90
Z	4	2	1	2
V (Å^3)	933.84(13)	1732.3(13)	1067.9(3)	1204.5(5)
ρ_{calcd} (g/cm^3)	1.772	1.531	1.485	1.333
μ (mm^{-1})	2.582	1.431	1.169	1.042
R1 [$I > 2\sigma(I)$]	0.0179	0.0221	0.0295	0.0300
wR2 [$I > 2\sigma(I)$]	0.0475	0.0617	0.0855	0.0799
GOF on F^2	0.972	1.023	1.003	1.001

Scheme 1. Syntheses and Structures of Complexes **1**−**5**



group to form an amidate.[5,6,8] If HL^R remains neutral, the pyridyl N atom and carbonyl O atom chelate to the same Cu atom to form a stable seven-membered ring. A mononuclear species in which one Cu atom is coordinated symmetrically by two ligands forms in the absence of a bridging ligand,[8] and binuclear species will form with two μ_2-methoxide bridging ligands.[6] On the other hand, if the ligand is deprotonated by a base, a bidentate bridging coordination mode is observed. In the octa- and tetranuclear Cu clusters previously synthesized in our laboratory,[6,8] ligand L^{R-} (R = null and Ph) not only chelates to one Cu through the pyridyl and amidate N atoms but also bridges to another Cu through the amido O atom. In this paper, the synthesis, characterization, and structures of five new Cu^I complexes coordinated by HL^R (R = null, Ph, Ph_3, Me_3) are presented.

All five Cu^I complexes were synthesized in degassed organic solvents by the reaction of cuprous chloride with the respective ligand, summarized in Scheme 1. While **1**−**5** are stable in the solid state when stored under nitrogen, solutions of **1**−**5** decompose when exposed to open air, producing uncharacterized green precipitates within hours. In these five complexes, the ligand HL^R displays a new monodentate coordination mode that has not been observed in previous examples of complexes synthesized with these ligands in our laboratory.[5,6,8] The amide group does not coordinate, and only the N atom from the pyridyl group coordinates to the Cu ion. One possible reason for this is that the electron donor properties of the Cl ion decrease the effective charge on the Cu ion, and the Cu ion is “softer” in the hard and soft acids and bases sense, making coordination by the "hard" O donor less favorable.[14] Stoichiometry is another factor of complex conformation, which is illustrated in the syntheses of complexes **1** and **2**. Increasing from 1 to 2 equiv of HL relative to CuCl leads to structural differences between one-dimensional chains in **1** and binuclear chloro-bridged molecular Cu species in **2**. Likewise, HL^{Me_3} combines with CuCl to form a 2:1 ligand-to-metal complex. However, our efforts to synthesize 2:1 ligand-to-metal adducts with HL^{Ph} and HL^{Ph_3} or a 1:1 ligand-to-metal complex with HL^{Me_3} were not successful, perhaps attributable to steric effects of the substituent groups on the amide.

When ligand HL is deprotonated by triethylamine, octanuclear Cu^{II} clusters were isolated,[8] which prompted us to investigate the reaction between ligand HL^R and CuCl in the presence of a base. However, although the mixture of 1 equiv of HL^R and 1 equiv of triethylamine reacts with CuCl to give a yellow solution, disproportionation quickly occurs. The substituent group on the amide is an important factor to the disproportionation rate: the larger the substituent group, the slower the disproportionation rate. Specific kinetic parameters and further characterization of the resultant Cu^{II} species from disproportionation are currently under investigation.

Complexes of cuprous chloride with unidentate N donor ligands have been reported.[15,16] However, to our knowledge, the monodentate coordination of multidentate ligands to copper(I) chloride adducts has not been previously observed. Crystal data for **1**, **2**, **4**, and **5** are presented in Table 1, and selected bond distances and angles are presented in Table 2.

Compound 1. The reaction of 1 equiv of HL with 1 equiv of CuCl leads to the formation of one-dimensional chains of **1**, possessing a novel right-handed helical structure (Figure 1). The Cu^I atom is coordinated by one pyridyl N atom and two Cl anions with Cu−Cl distances of 2.2246(4) and 2.3997(4) Å, respectively. The Cu^I atom in **1** displays trigonal geometry, and the Cu ion and the three ligand atoms nearly fall in the same plane as the pyridyl ring. The mean deviation of the Cu, Cl, and pyridyl ring atoms from this least-squares plane is 0.0284 Å. The N atom from the pyridyl group coordinates to the Cu ion with a Cu−N distance of 1.9835(13) Å. Interestingly, the two Cl atoms do not bridge to the same Cu ion to form a simple binuclear complex but bind to two separate Cu−HL units, with a Cu1−Cl1−Cu1A angle of 90.309(14)° and a Cu···Cu distance of 3.281 Å. Additionally, instead of forming a linear or zigzag chain structure, the ~98.9° angle between the trigonal planes of N1A−Cu1A−Cl1A−Cl1 and N1−Cu1−Cl1−Cl1B forces the central Cu−Cl units to roll around an axis and extend to form a one-dimensional right-handed helical chain in the direction of the crystallographic *a* axis. The vertical distance between two adjacent units is 4.815 Å (Figure 1b). The view looking down the helical axis clearly shows the formation of a 1.392 × 2.072 Å parallelogram channel (Figure 1c).

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) of Complexes **1**, **2**, **4**, and **5**

	Complex **1**		
Cu1−N1	1.9835(13)	Cu1−Cl1A	2.3997(4)
Cu1−Cl1	2.2246(4)	Cl1−Cu1A	2.3997(4)
N1−Cu1−Cl1	140.63(4)	Cl1−Cu1−Cl1A	110.592(14)
N1−Cu1−Cl1A	107.25(4)	Cu1−Cl1−Cu1A	90.309(14)
	Complex **2**		
Cu1−N1	2.0547(15)	Cu1−Cl1	2.4001(9)
Cu1−N3	2.0351(13)	Cu1−Cl1A	2.4762(9)
N3−Cu1−N1	121.48(5)	N3−Cu1−Cl1A	105.22(4)
N3−Cu1−Cl1	114.14(4)	N1−Cu1−Cl1A	101.07(3)
N1−Cu1−Cl1	103.13(4)	Cl1−Cu1−Cl1A	111.00(3)
Cu1−Cl1−Cu1A	68.99(3)		
	Complex **4**		
Cu1−N1	1.9553(16)	Cu1−Cl1	2.2878(6)
Cu1−Cl1A	2.2765(6)		
N1−Cu1−Cl1A	129.65(5)	Cl1A −Cu1−Cl1	106.023(19)
N1−Cu1−Cl1	123.95(5)	Cu1A −Cl1−Cu1	73.976(19)
	Complex **5**		
Cu1−N1B	1.9509(15)	Cu1−Cl1	2.3060(9)
Cu1−N1A	1.9509(15)		
N1B−Cu1−N1A	145.12(9)	N1A-Cu1−Cl1	107.44(4)
N1B−Cu1−Cl1	107.44(4)		

An important aspect of the one-dimensional structure of complex **1** is that it has two peripheral hydrogen-bonded chains on either side of the helical channel (Figure 1a). To our knowledge, this distinct supramolecular structural feature has not been reported for copper(I) halide compounds. The amide group of the ligand is not involved in coordination and sticks out from the central helical structure. The N−H and C═O groups sit in the same plane with a mean deviation of 0.019 Å for all atoms, and they are oriented toward each other so that one N−H···O hydrogen bond forms between adjoining amide groups with an N···O distance of 2.8559(17) Å and an N−H···O angle of 161.4°. Molecules of HL in **1** are arranged along the crystallographic *a* axis on both sides of the helical channel, which results in the formation of two one-dimensional zigzag hydrogen-bonded chains that are also nearly parallel with the central helical axis and helps to stabilize the right-handed helical structure. Despite the monodentate coordination mode of HL, hydrogen bonding between amide groups in **1** allows the unique helical coordination polymer with dual parallel hydrogen-bonded chains to form.

By far, the most common structures for one-dimensional copper(I) halide complexes include zigzag chains, double-stranded ladders, and hexagonal grid chains.[17] There are two examples of helical chains: $[Cu_2(\mu\text{-Br})_2(\mu\text{-TMT-TTF})]_\infty$ (TMT-TTF = tetrakis(methylthio)tetrathiafulvalene) and $[Cu(\mu\text{-Cl})(\mu\text{-2,5-dimethylpyrazine-}N,N')]_\infty$.[18] However, the trigonal coordination geometry of the Cu center formed by one

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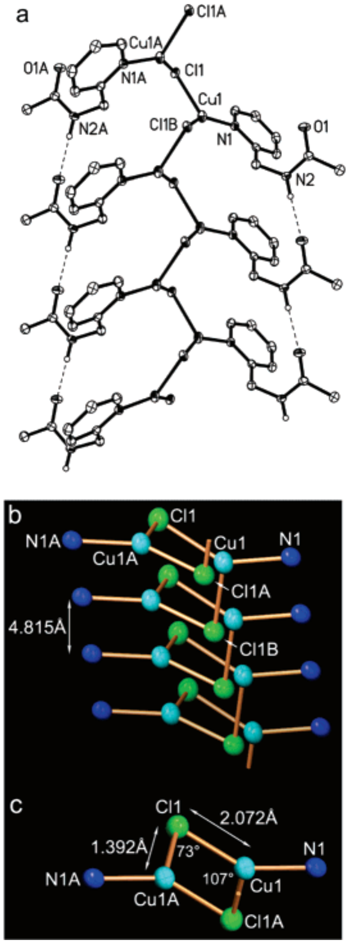

Figure 1. (a) X-ray crystal structure of **1**. All H atoms except for those on the amide groups have been omitted for clarity, with thermal ellipsoids at the 50% probability level. (b) Central helical structure of complex **1**. (c) Top view of the parallelogram channel.

N atom and two Cl atoms in **1** is different from the distorted tetrahedral geometry of the two examples. Additionally, the one-dimensional chains in **1**, which lack any interchain hydrogen bonding, are different from the two-dimensional sheets or three-dimensional networks arranged between helical chains in the two published examples.

Although X-ray crystallography indicated right-handed helical chains in the solid state, circular dichroism (CD) spectra of solutions of **1** in CH_3CN or CH_2Cl_2 did not produce any CD signal, indicating the absence of chirality in solution. One explanation for the absence of a CD signal is that solvation breaks the two hydrogen-bonded chains, resulting in the loss of interaction among repeating Cu−HL units and the loss of the helical structure. In coordinating solvents such as CH_3CN, it is likely that the one-dimensional polymer chains of **1** break into monomers. Another likely explanation is that **1** crystallized to form a racemic mixture of crystals, from which we happened to select one with the right-handed helical structure. Dissolving roughly equal quantities of left- and right-handed crystals would result in a solution with no net CD signal.

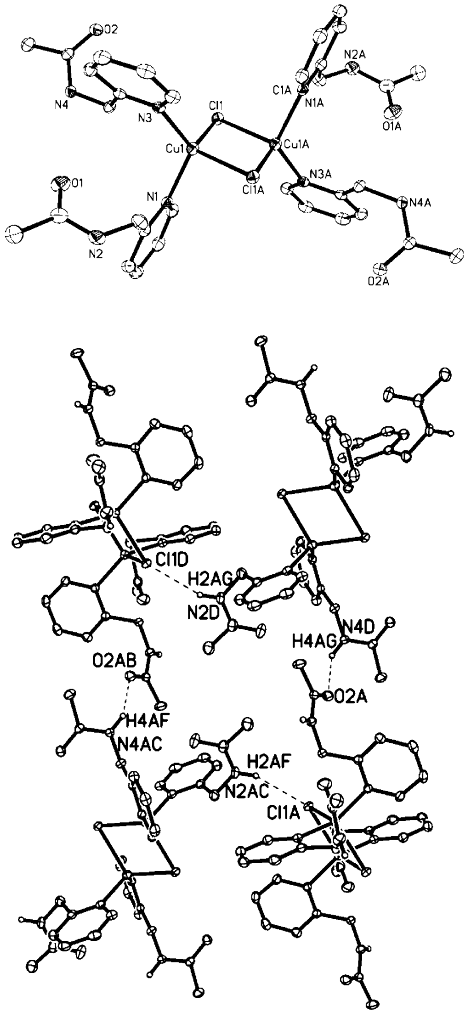

Figure 2. X-ray crystal structure (top) and hydrogen bonding (bottom) for **2** with thermal ellipsoids at the 50% probability level.

Compound 2. The reaction of 2 equiv of HL and 1 equiv of CuCl gives complex **2**, which is a binuclear Cu^{I} complex. Disposed about a crystallographic inversion center, complex **2** displays a bis(μ-chloro)-bridged planar Cu_2Cl_2 diamond core structure. Each Cu^{I} atom is coordinated by two pyridyl N atoms in HL. The Cu−N$_{py}$ distances in **2** [2.0547(15) and 2.0351(13) Å] are longer than those in **1**, which may be a consequence of the steric effects between two HL ligands coordinated to the same Cu center. The Cu atoms are bridged by two Cl ions, leading to the formation of a distorted tetrahedral geometry at each Cu^{I} center (Figure 2). Because of the second Cl bridge, the Cu···Cu distance in **2** [2.7625(12) Å] is much shorter than the corresponding distance in **1** (3.281 Å). Similar Cl_2-bridged Cu_2 complexes supported by bis-pyridines,[19] amidines,[20] and aromatic amines[21] have been reported. Although **2**'s average Cu−Cl (2.438 Å) and Cu−N (2.045 Å) bond distances are comparable with values observed in other Cu_2Cl_2 examples with diamond core

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structures, the smaller Cu−Cl−Cu bond angle [68.99(3)°] and the larger Cl−Cu−Cl bond angle [111.00(3)°] in **2** lead to a Cu···Cu distance that is distinctly shorter than those of reported examples, having Cu···Cu distances ranging from 2.997(1) to 3.150(2) Å.[19,21,22] This structural difference could be a consequence of the more distorted tetrahedral geometry in **2**, due to the repulsion between the amide groups of two ligands in the same Cu center.

Two types of intermolecular hydrogen bonds are observed in the packing structure of complex **2** (Figure 2, bottom). Hydrogen bonds between amide N−H and chloro bridging atoms connect the ligands on one dimer to adjacent dimers via N−H···Cl hydrogen bonds, with an N···Cl distance of 3.4430(16) Å and an N−H···Cl angle of 160.7(19)°. A second type of hydrogen bond between the amide N−H groups on one dimer and the C═O groups on adjacent dimers, with an N···Cl distance of 2.9239(18) Å and an N−H···Cl angle of 159.5(17)°, completes the hydrogen bonding in **2**. These hydrogen bonds extend to form a three-dimensional network in **2** that stabilizes the solid-state structure.

Compound 3. Single-crystal X-ray diffraction analysis of complex **3**, which was synthesized by the reaction of 1 equiv of HL^{Ph} and 1 equiv of CuCl in CH_3CN, reveals a bis(μ-chloro)-bridged diamond core binuclear Cu structure similar to that of complex **2**. Unfortunately, the diffraction data for complex **3** had serious twinning problems, and a large amount of the overlapping data from twinning were omitted; hence, the incomplete data for **3** make its structure unpublishable. However, the raw structure of complex **3** along with its corroborating analytical data reveal a stoichiometry of ligand-to-Cu of 1:1, which is different from that of complex **2**. This is likely caused by the bulkier phenyl substituent group in HL^{Ph} compared to HL. Each Cu center possesses a distorted tetrahedral geometry, and two Cl atoms bridge the two Cu centers. Although the N_2Cl_2 coordination environment of each Cu atom in complex **3** is the same as that in complex **2**, the fourth position in **3** is occupied by a CH_3CN solvent molecule, which is attributed to the steric effect from the benzyl group of ligand HL^{Ph}. This effect prevents the coordination of the second HL^{Ph} ligand to the Cu center. Although the X-ray data suggest the existence of hydrogen-bonding interactions involving the amide groups, the poor quality of the X-ray data precludes further discussion of the hydrogen bonding and packing structure.

Compound 4. The reaction of 2 equiv of HL^{Ph_3} with 1 equiv of CuCl leads to the formation of complex **4**. This complex has the same bis(μ-chloro)-bridged planar Cu_2Cl_2 diamond core as complexes **2** and **3**, but the Cu ion exhibits trigonal coordination geometry with only one N_{py} atom from HL^{Ph_3} and two Cl ions in each Cu ion's coordination sphere (Figure 3). The bulky triphenyl group in HL^{Ph_3} prevents access of a second ligand or solvent molecule to each Cu ion, even when the reaction stoichiometry of HL^{Ph_3} and CuCl is 2:1. The Cu···Cu distance of 2.746 Å in **4** is 0.017 Å shorter than that in **2**. The average Cu−N and Cu−Cl distances are typical for Cu^I complexes (see Table 2). The bond distances in **4** are slightly shorter than the Cu−N and Cu−Cl bonds of complex **2**, which is a consequence of the decreased coordination number of the Cu ions in **4**. Furthermore, the amide groups are oriented such that each amide H atom forms intramolecular hydrogen bonds with the bridged Cl ions, having an N···Cl distance of 3.5445(16) Å and an N−H···Cl angle of 132.7°. The hydrogen bonding in **4** is distinct from the others discussed so far, in that they possess intermolecular hydrogen bonding while **4** contains only intramolecular hydrogen bonding. This difference in hydrogen bonding is most likely a consequence of the much greater steric bulk of the HL^{Ph_3} ligand compared to the others, which would prevent molecules of **4** from getting close enough to form intermolecular hydrogen bonds.

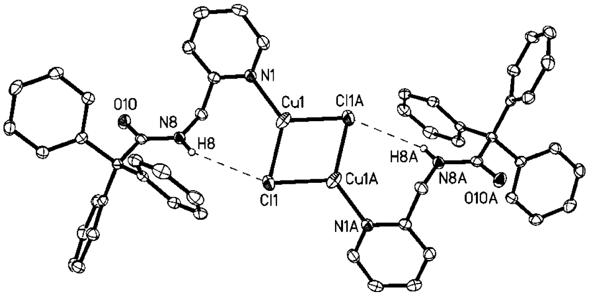

Figure 3. X-ray crystal structure of **4** with thermal ellipsoids at the 50% probability level. All H atoms except for those on the amide groups have been omitted for clarity.

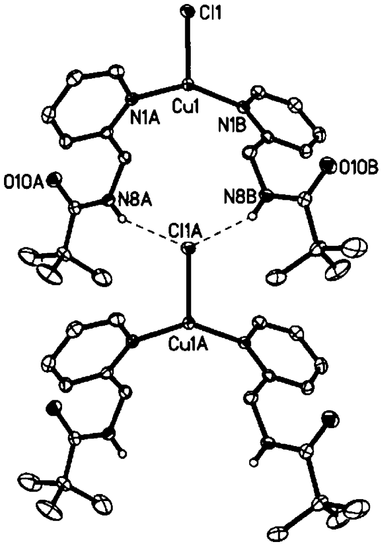

Figure 4. X-ray crystal structure and hydrogen bonding for **5** with thermal ellipsoids at the 50% probability level. All H atoms except for those on the amide groups have been omitted for clarity.

Compound 5. The reaction of 2 equiv of HL^{Me_3} and 1 equiv of CuCl leads to the formation of complex **5**. In contrast to complexes **1**−**4**, complex **5** exists as a discrete mononuclear species bearing two HL^{Me_3} ligands and one Cl (Figure 4). A trigonal geometry is adopted in complex **5**, with the two N_{py} donors and one terminal Cl ion. The Cu atom lies 0.0097 Å out of the N1A−N1B−Cl1 plane, indicating near-planarity of the Cu and coordinating ligand atoms. The *tert*-butyl group decreases the flexibility of the

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amide group, and the steric effect between the two adjacent HL^{Me_3} ligands may prevent the formation of a tetrahedral geometry around the Cu center by denying access to a second Cl ion. There is only one example of a monomeric neutral chlorocopper(I) complex with pseudo-trigonal-planar coordination.[16] The Cu−Cl distance of 2.3060(9) Å in **5** is comparable to those of complexes **1**, **2**, and previous examples,[19,21,22] but the $Cu-N_{py}$ distances are shorter. The Cu−Cl bond is parallel with the crystallographic *b* axis, and this molecule exhibits a 2-fold rotational axis along the Cu−Cl bond. Both N−Cu−Cl bond angles are 107.44(4)°, which is consistent with the 2-fold symmetry of the molecule. Each Cl ligand forms two hydrogen bonds with the amide N−H groups from an adjacent molecule. The hydrogen bonds in **4** and **5** are similar because both involve N−H···Cl hydrogen bonds and no N−H···O hydrogen bonds. These intermolecular N−H···Cl hydrogen bonds, with N···Cl distances of 3.1884(18) Å and N−H···Cl angles of 151(2)°, extend to form a one-dimensional chain that helps to stabilize the solid-state structure of complex **5** (Figure 4).

Conclusions

The Cu^I coordination chemistry of a set of (pyridylmethyl)-amide ligands has been investigated. All of the ligands, each with different substituent groups on the amide (HL^R; R = null, Ph, Ph_3, Me_3), exhibit similar monodentate coordination modes when combined with CuCl to form Cu^I complexes. This preference for a monodentate, rather than a bidentate or tridentate, coordination mode is likely a consequence of the strong coordinating abilities of Cl, coupled with the weaker coordinating ability of the neutral amide group. For ligand HL, one-dimensional chains (**1**) or a dinuclear complex (**2**) can be synthesized by changing the stoichiometry of the reactants. The substituent group R on the amide of HL^R also influences the metal center geometry of these complexes. The steric effect of the R group, which increases in the order of H < Ph < Me_3 < Ph_3, contributes to the variety of structures observed, ranging from one-dimensional polymeric chains (**1**) to binuclear (**2**−**4**) to mononuclear (**5**). Finally, hydrogen bonding plays a significant role in determining not only the molecular structures of **1**−**5** but also the intermolecular hydrogen bonds of the network structures—or lack thereof—that are formed in these complexes.

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Supporting Information Available: X-ray structural information for **1**, **2**, **4**, and **5** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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