Metal-Containing Ligands for Mixed-Metal Polymers: Novel Cu(II)−Ag(I) Mixed-Metal Coordination Polymers Generated from [Cu(2-methylpyrazine-5-carboxylate)$_2$(H_2O)]·3H_2O and Silver(I) Salts

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One Cu(II)−containing ligand and two Cu(II)−Ag(I) mixed-metal coordination polymers have been synthesized. [Cu(2-methylpyrazine-5-carboxylate)$_2$(H_2O)]·3H_2O (**1**) was obtained as a molecular complex with two uncoordinated nitrogen donors by the reaction of 2-methylpyrazine-5-carboxylate sodium with $CuCl_2$·2H_2O in water. Compound **1** crystallized in the triclinic space group $P\bar{1}$, with $a = 10.498(2)$ Å, $b = 11.000(2)$ Å, $c = 8.1424(16)$ Å, $\alpha = 98.33(3)°$, $\beta = 101.83(3)°$, $\gamma = 66.68(3)°$, and $Z = 2$. Reactions of **1** with silver(I) salts have been studied. Two Cu(II)−Ag(I) mixed-metal coordination polymers, namely, Ag[Cu(2-methylpyrazine-5-carboxylate)$_2$·(H_2O)$_2$](BF_4) (**2**) and Ag[Cu(2-methylpyrazine-5-carboxylate)$_2$·(H_2O)$_2$](NO_3) (**3**), have been generated by treating **1** with $AgBF_4$ and $AgNO_3$, respectively. Compound **2** crystallized in the monoclinic space group $C2/c$, with $a = 25.827(5)$ Å, $b = 9.6430(19)$ Å, $c = 7.4525(15)$ Å, $\beta = 94.74(3)°$, and $Z = 4$. Compound **3** also crystallized in the monoclinic space group $C2/c$, with $a = 25.855(5)$ Å, $b = 9.782(2)$ Å, $c = 7.1201(14)$ Å, $\beta = 96.90(3)°$, and $Z = 4$. The main structural feature in both **2** and **3** is a zigzag Cu(II)−Ag(I) mixed-metal chain, in which the alternating Cu(II) and Ag(I) centers are linked by 2-methylpyrazine-5-carboxylate spacers. The effect of the nitrate counterion was illustrated by compound **3**, in which a novel [$Ag^+ \cdots NO_3^-$] coordination chain has been found which acts as the connector to cross-link the one-dimensional zigzag chains into a three-dimensional network. In addition, an identical interchain O−H···O hydrogen bonding system has been found in both **2** and **3** and has been shown to play a significant role in directing the alignment of the one-dimensional mixed-metal polymer chains in the crystalline state. The magnetic susceptibilities of **2** and **3** were measured and found to follow the Curie law ($\mu_{eff} = 1.85$ for **2** and 1.83 for **3**).

Introduction

The molecular self-assembly of coordination polymers and supramolecules is a promising route to novel molecular materials.[1] These materials not only generate new insights into structural diversity but also exhibit encouraging potential applications.[2−5] Up to now, a number of extended inorganic/organic composite materials have been synthesized by combination of organic spacers and inorganic metal salts, although the rational design and preparation of new materials for specific application is still at an early evolutionary stage.[6] Most of the previous studies have focused on the syntheses of unimetallic coordination polymers. Though some bimetallic extended structures based on the cyanide (Prussian blue phases),[7] thiocyanate,[8] and chloride[9] have been reported, considerably less is known about the chemistry of inorganic/organic hybrid mixed-metal coordination polymers.[10] Self-assembled inorganic/organic hybrid mixed-metal polymers with specific network topologies can provide highly ordered networks with different metal centers, particularly as low-dimensional 1-D and 2-D networks. In principle, such materials might exhibit novel physical properties such as electrical conductivity and interesting magnetic behavior resulting from interactions between two different

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proximal metal centers. For example, ferromagnetic ordering between bimetallic Mn···Cu chains has been observed in MnCu(pbaOH)$(H_2O)_3$, whereas similar chains in the polymer MnCu(pba)$(H_2O)_3$·$2H_2O$ order antiferromagnetically (pba = 1,3-propylenebis(oxamato)).[10b] Understanding the relationship between the network structures and the magnetic properties of these bimetallic arrays is very important to obtain a fundamental basis for designing molecular magnetic materials.

We have been investigating the construction of unimetallic arrays based on Cd(II), Co(II), and Cu(II) centers.[11] Now our interest lies in the design and synthesis of mixed-metal inorganic/organic hybrid polymers through noncovalent directing forces such as coordination and hydrogen bonding interactions, and assembly of bidentate or multidentate organic ligands with different kinds of metal salts. Our strategy for the construction of mixed-metal polymers begins with the recognition that organic ligands designed such that they possess at least two different coordination sites (neutral and/or charged) can be used to synthesize molecular metal complexes with free (uncoordinated) donor atoms. Such complexes in turn can be considered new metal-containing ligands which can be induced to self-assemble with other metal ions or unsaturated metal complexes through the free coordination donors. In our experiment, 2-methylpyrazine-5-carboxylic acid was chosen as such an organic spacer to synthesize the metal-containing ligand. Here, we present the syntheses and structures of one Cu-containing ligand [Cu(2-methylpyrazine-5-carboxylate)$_2(H_2O)$]·$3H_2O$ (**1**) and two unique Cu−Ag mixed-metal coordination polymers, namely, Ag[Cu(2-methylpyrazine-5-carboxylate)$_2$·$(H_2O)_2$](NO_3) (**2**) and Ag[Cu(2-methylpyrazine-5-carboxylate)$_2$·$(H_2O)_2$](BF_4) (**3**), generated from **1** and $AgNO_3$ and $AgBF_4$, respectively.

Experimental Section

Synthesis. $CuCl_2$·$2H_2O$, $AgNO_3$, $AgBF_4$, and 2-methylpyrazine-5-carboxylic acid were purchased from Aldrich and used without further purification. IR spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer as KBr pellets in the 4000−400 cm^{-1} range. Differential thermal analysis and thermogravimetric analysis (DTA−TGA) were conducted on a TA Instruments SDT 2960 simultaneous DTA−TGA in a helium atmosphere using a heating rate of 10 °C/min. Compounds **2** and **3** were heated from 30 to 450 °C. Magnetic susceptibility as a function of temperature for **2** and **3** was measured using a Quantum Design MPMS XL SQUID magnetometer in an applied field of 5 kG. Clear gelatin capsules were used as sample containers. Elemental analyses were carried out by National Chemical Consulting.

[Cu(2-methylpyrazine-5-carboxylate)$_2(H_2O)$]·$3H_2O$ (1). 2-Methylpyrazine-5-carboxylic acid (2.23 g, 16.12 mmol) was added to a solution of NaOH (644 mg, 16.12 mmol) in 20 mL of water. The mixture was stirred at room temperature for 10 min. A light brown clear solution was obtained. $CuCl_2$·$2H_2O$ (1.37 g, 8.06 mmol) was added slowly to the above solution. A blue precipitate formed immediately. The mixture was stirred at room temperature for an additional 2 h. After filtration, the blue solid obtained was washed with water several times and dried in air. Single crystals were obtained by heating the blue solid in boiling water and allowing the solution to cool to room temperature. Yield: 99%. IR (KBr, cm^{-1}): 3440.2 (m), 3057.9 (m), 1650.4 (s), 1643.9 (s), 1592.5 (s), 1527.4 (w), 1483.3 (s), 1444.3 (w), 1372.7 (s), 1331.1 (s), 1280.0 (s), 1190.2 (s), 1167.7 (s), 1052.2 (s), 820.0 (s), 803.8 (s), 721.1 (s). Anal. Calcd for $C_{12}H_{18}N_4O_8Cu$: C, 35.16; H, 4.40; N, 13.67. Found: C, 35.32; H, 4.45; N, 13.60.

Table 1. Crystallographic Data for **1**−**3**

formula	$CuC_{12}H_{18}N_4O_8$	$CuAgC_{12}H_{14}N_4O_6BF_4$	$CuAgC_{12}H_{14}N_5O_9$
compd no.	**1**	**2**	**3**
fw	409.84	568.49	543.69
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$C2/c$	$C2/c$
a (Å)	10.498(2)	25.827(5)	25.855(5)
b (Å)	11.000(2)	9.6430(19)	9.782(2)
c (Å)	8.1424(16)	7.4525(15)	7.1201(14)
α (deg)	98.33(3)	90	90
β (deg)	101.83(3)	94.74(3)	96.90(3)
γ (deg)	66.68(3)	90	90
V (Å^3)	843.0(3)	1849.7(6)	1787.8(6)
Z	2	4	4
ρ_{calcd} (g/cm^3)	1.615	2.041	2.020
μ(Mo Kα) (cm^{-1})	9.532	7.353	5.385
temp (°C)	23	23	23
no. of reflns ($I > 3\sigma(I)$)	2638	1445	1583
residuals:[a] R1; wR2 (all data)	0.039; 0.099	0.044; 0.109	0.042; 0.108

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; $w = 1/\sigma^2(F_o^2)$.

Ag[Cu(2-methylpyrazine-5-carboxylate)$_2(H_2O)_2$](BF_4) (2). **1** (45 mg, 0.12 mmol) was added to a solution of $AgBF_4$ (39 mg, 0.20 mmol) in 15 mL of water. After refluxing for 10 min, a clear blue solution was obtained, which was allowed to stand at room temperature for 1 week. Blue crystals were obtained when the solvent slowly evaporated. Yield: 98% (based on **1**). IR (KBr, cm^{-1}): 3443.8 (m), 3057.7 (m), 1659.8 (s), 1653.5 (s), 1633.4 (s), 1588.3 (s), 1537.8 (w), 1483.6 (s), 1442.9 (w), 1367.1 (s), 1326.0 (s), 1280.1 (s), 1192.8 (m), 1171.4 (s), 1084.1 (s), 1027.7 (s), 919.8 (w), 873.7 (w), 819.0 (m), 802.3 (w), 720.5 (m), 693.8 (w), 634.4 (w). Anal. Calcd for $C_{12}H_{14}N_4O_6BF_4$-CuAg: C, 25.34; H, 2.46; N, 9.86. Found: C, 25.46; H, 2.40; N, 9.72.

Ag[Cu(2-methylpyrazine-5-carboxylate)$_2(H_2O)_2$](NO_3) (3). The procedure is similar to that described for the preparation of compound **2**, except $AgNO_3$ (34 mg, 0.20 mmol) was used instead of $AgBF_4$. Yield: blue crystals, 98% (based on **1**). IR (KBr, cm^{-1}): 3442.2 (m), 3056.6 (m), 1654.2 (s), 1633.8 (s), 1537.9 (w), 1483.3 (m), 1391.9 (s), 1357.1 (s), 1318.4 (s), 1277.4 (s), 1188.8 (m), 1165.8 (m), 1051.2 (s), 983.9 (w), 919.1 (w), 873.0 (w), 819.3 (s), 801.9 (m), 719.8 (w), 693.0 (w), 633.8 (w), 549.0 (w), 504.2 (w). Anal. Calcd for $C_{12}H_{14}N_5O_9$-CuAg: C, 26.50; H, 2.58; N, 12.88. Found: C, 26.58; H, 2.60; N, 12.58.

Single-Crystal Structure Determination. Suitable single crystals of **1**−**3** were selected and epoxied in air onto a thin glass fiber. Intensity measurements were made at 20 °C using a Rigaku AFC6S four-circle diffractometer equipped with Mo Kα radiation ($\lambda = 0.71069$ Å). For each compound, the initial unit cell was determined from 15 reflections randomly located using the AFC6 automatic search, center, index, and least-squares routines. After data collection, each cell was refined using 25 high-angle reflections in the range $35° < 2\theta < 2\theta_{max}$. Three standard reflections measured every 150 reflections showed no significant deviations during data collection. The structure was solved and refined by a combination of direct methods and difference Fourier syntheses, using SHELXTL.[12] After all non-hydrogen atoms were located and refined with isotropic thermal parameters, an absorption correction (DIFABS)[13] was applied. Subsequently, all non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in the calculated positions and refined using a riding model, except for the aquo hydrogens in **1** (vide infra), which were located from the difference maps and refined with isotropic thermal parameters. Crystal data, data collection parameters, and refinement statistics for **1**−**3** are listed in Table 1. Relevant interatomic bond distances and bond angles for **1**−**3** are collected in Tables 2−4.

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Table 2. Interatomic Distances (Å) and Bond Angles (deg) (with Esd's in Parentheses) for **1**

Cu−O(1)	1.9522(19)	Cu−N(1)	1.991(2)
Cu−O(3)	1.956(2)	Cu−N(3)	1.990(2)
Cu−O(5)	2.257(2)	C(1)−C(5)	1.510(4)
C(2)−N(2)	1.340(4)	C(5)−O(2)	1.228(4)
C(5)−O(1)	1.265(3)	C(9)−C(10)	1.391(4)
C(9)−C(12)	1.489(4)	C(10)−N(3)	1.335(4)
O(1)−Cu−O(3)	166.05(9)	O(1)−Cu−N(3)	95.41(8)
O(3)−Cu−N(3)	83.24(8)	O(1)−Cu−N(1)	83.60(8)
O(3)−Cu−N(1)	94.89(8)	N(3)−Cu−N(1)	168.28(9)
O(1)−Cu−O(5)	97.27(9)	O(3)−Cu−O(5)	96.68(9)
N(1)−Cu−O(5)	96.70(9)	N(1)−C(1)−C(2)	120.1(3)
N(1)−C(1)−C(5)	115.4(9)	C(5)−C(1)−C(2)	124.4(2)
N(2)−C(2)−C(1)	122.1(2)	N(2)−C(3)−C(6)	117.6(3)
O(2)−C(5)−O(1)	126.0(3)	O(2)−C(5)−C(1)	118.5(3)
O(1)−C(5)−C(1)	115.5(2)	N(4)−C(8)−C(7)	122.3(2)
N(4)−C(9)−C(10)	120.7(3)	N(4)−C(9)−C(12)	118.2(3)
C(10)−N(3)−C(7)	118.5(2)	C(10)−N(3)−Cu	130.23(18)
C(7)−N(3)−Cu	111.27(18)	C(11)−O(3)−Cu	115.01(17)

Table 3. Interatomic Distances (Å) and Bond Angles (deg) (with Esd's in Parentheses) for **2**[a]

Ag−N(2)	2.195(4)	Cu−O(1)	1.975(3)
Cu−N(1)	1.994(4)	Cu−O(3)	2.448(4)
N(2)−C(2)	1.339(6)	C(1)−C(2)	1.372(7)
C(5)−O(2)	1.235(6)	C(5)−O(1)	1.274(6)
N(1)−C(4)	1.326(6)	N(1)−C(1)	1.340(6)
N(2)−Ag−N(2)	165.7(2)	O(1)−Cu−O(1)	180.00
O(1)−Cu−N(1)	97.15(14)	O(3)−Cu−O(3)*	180.00
O(1)*−Cu−N(1)	82.85(14)	N(1)−Cu−N(1)*	180.0(2)
C(4)−N(1)−Cu	130.2(3)	C(1)−N(1)−Cu	111.8(3)
C(2)−N(2)−C(3)	117.2(4)	C(2)−N(2)−Ag	121.2(3)
N(1)−C(1)−C(2)	120.6(4)	N(1)−C(1)−C(5)	114.8(4)
N(2)−C(3)−C(4)	120.3(4)	O(2)−C(5)−O(1)	125.9(4)
C(5)−O(1)−Cu	114.4(3)	C(2)−C(1)−C(5)	124.5(4)

[a] * indicates symmetry equivalent atoms.

Table 4. Interatomic Distances (Å) and Bond Angles (deg) (with Esd's in Parentheses) for **3**[a]

Ag−N(2)	2.263(3)	Cu−O(1)	1.965(3)
Cu−N(1)	1.999(3)	Cu−O(3)	2.444(5)
N(2)−C(2)	1.335(5)	C(1)−C(2)	1.376(7)
C(5)−O(2)	1.227(5)	C(5)−O(1)	1.279(5)
N(3)−O(5)	1.170(9)	N(3)−O(4)	1.214(6)
N(1)−C(1)	1.345(5)	N(1)−C(1)	1.345(5)
N(2)−Ag-N(2)	153.31(18)	O(1)−Cu−O(1)	180.00
O(1)−Cu-N(1)	83.30(11)	O(3)−Cu−O(3)*	180.00
O(1)*−Cu−N(1)	96.70(11)	N(1)−Cu−N(1)*	180.0(2)
C(4)−N(1)-Cu	131.2(3)	C(1)−N(1)−Cu	110.6(2)
C(2)−N(2)-C(3)	117.8(3)	C(2)−N(2)−Ag	118.5(3)
N(1)−C(1)-C(2)	120.4(4)	N(1)−C(1)−C(5)	115.7(3)
N(2)−C(3)-C(4)	120.1(4)	O(2)−C(5)−O(1)	126.1(4)
C(5)−O(1)-Cu	114.6(2)	C(2)−C(1)−C(5)	123.9(4)

[a] * indicates symmetry equivalent atoms.

Results and Discussion

Molecular Precursor Complex, 1. When 2-methylpyrazine-5-carboxylate sodium, derived from 2-methylpyrazine-5-carboxylic acid and NaOH, reacted with $CuCl_2\cdot 2H_2O$ in water at room temperature (1:2 metal-to-ligand ratio), compound **1** was obtained as a blue crystalline solid in quantitative yield with a formula of [Cu(2-methylpyrazine-5-carboxylate)$_2$(H$_2$O)]·3H$_2$O. The compound is air-stable and not soluble in common organic solvents, such as CH_3CN, CH_3COCH_3, CH_3OH and CH_3CH_2OH, but is soluble in hot water. Upon cooling of a hot aqueous solution of **1** to room temperature, crystals of **1** suitable for single-crystal X-ray diffraction were obtained in high yield. The molecular structure of **1** is shown in Figure 1. The coordination environment of the Cu(II) center can be described as distorted square pyramidal with a coordinated water molecule (O(5)) in the apical position and the two oxygen (O(1) and O(3)) and the two nitrogen (N(1) and N(3)) donors of the chelating 2-methylpyrazine-5-carboxylate ligands occupying the basal sites. The Cu(II) center is displaced ca. 0.20 Å above the basal oxygen and nitrogen array toward the apical site. The planes of the two 2-methylpyrazine-5-carboxylate ligands are canted ca. 12° with respect to each other. The coordination environment of Cu(II) in **1** is distinctly different from the coordination sphere of the Cu(II) center found in Cu(pyrazinecarboxylate)$_2$(H$_2$O)$_2$ in which the Cu(II) sits in a distorted octahedral environment.[14] The Cu−O(5) bond length of 2.257(2) Å is very similar to the corresponding values of 2.204(3) and 2.212(6) Å which were found for the apical water molecule and ethanol in the square-pyramidal complexes Cu(hfacac)$_2$(H$_2$O)[15] and Cu(C$_3$F$_7$C(O)CHC(O)C$_3$F$_7$)$_2$(EtOH),[16] respectively. However, it is significantly shorter than the 2.39 Å Cu−O bond found for the axially coordinated water molecule in Cu(pyrazinecarboxylate)$_2$(H$_2$O)$_2$.[14] In addition, there are three uncoordinated water molecules (O(6), O(7) and O(8)) per formula unit. One of them, O(7), acting as a hydrogen bond acceptor, is hydrogen bonded with the coordinated apical water molecule O(5). O(7) also acts as a hydrogen bond donor to the other two free water molecules (O(6) and O(8)) to generate a complicated triangular hydrogen-bonding system. The relevant hydrogen-bonding data are listed in Table 5.

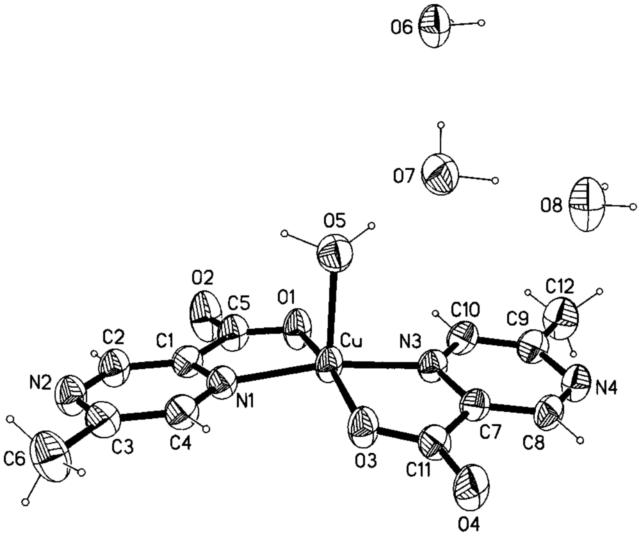

Figure 1. ORTEP figure of compound **1** showing the numbering scheme. Ellipsoids are shown at the 50% probability level.

The more important structural feature of **1** is the presence of two free (uncoordinated) nitrogen (N(2)) and N(4)) and two free oxygen donors (O(2) and O(4)). Our approach in designing a mixed-metal coordination polymer was to consider complex **1** as a new type of metal-containing ligand which could use its free donor atoms to link other kinds of transition metals to produce new and novel bimetallic coordination polymers.

Polymeric Compounds, 2 and 3. When **1** was treated with $AgBF_4$ and $AgNO_3$ in boiling water, the Cu(II)−Ag(I) mixed-

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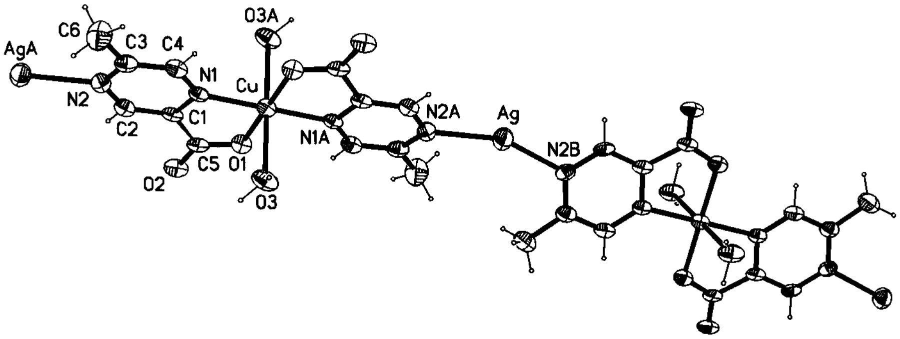

Figure 2. ORTEP figure of compound **2** (and **3**) showing the numbering scheme. Ellipsoids are shown at the 50% probability level.

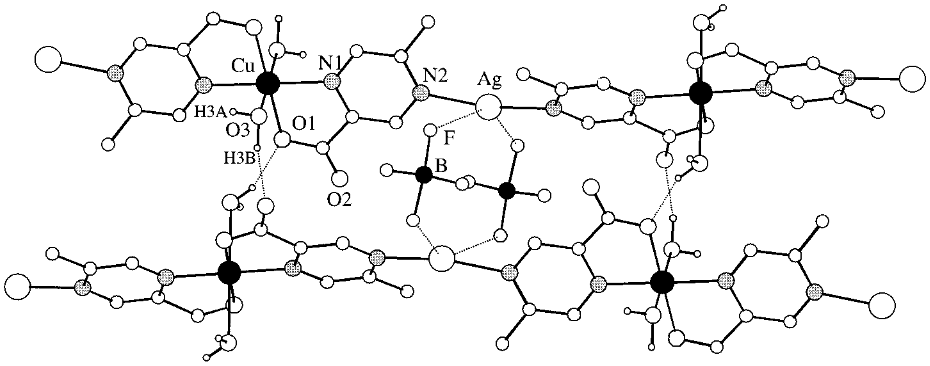

Figure 3. View of the segment of two Ag(I)−Cu(II) mixed-metal chains in **2**, with partial atom labeling. The hydrogen atoms on the 2-methylpyrazine-5-carboxylate ligands are omitted for clarity. Hydrogen bonds and F···Ag weak interactions are shown as dotted lines.

Table 5. Interchain Hydrogen-Bonding Contacts (Å, deg) for **1**−**3**

D−H···A	D−H	D···A	H···A	D−H···A
Compound **1**				
O(5)−H(5A)···O(7)	0.905(3)	2.755(4)	1.808(4)	177.3(4)
O(7)−H(7A)···O(6)	0.920(3)	2.940(4)	1.955(3)	172.9(4)
O(7)−H(7B)···O(8)	0.985(3)	2.759(4)	1.705(3)	171.4(4)
Compound **2**				
O(3)−H(3A)···O(1)	0.852(3)	2.898(4)	2.107(4)	154.1(4)
O(3)−H(3B)···O(2)	0.987(3)	2.797(4)	1.825(3)	167.5(4)
Compound **3**				
O(3)−H(3A)···O(1)	0.885(3)	2.883(4)	2.033(4)	161.0(4)
O(3)−H(3B)···O(2)	0.920(3)	2.781(4)	1.888(3)	163.0(4)

metal coordination polymers Ag[Cu(2-methylpyrazine-5-carboxylate)$_2$(H$_2$O)$_2$](BF$_4$) (**2**) and Ag[Cu(2-methylpyrazine-5-carboxylate)$_2$(H$_2$O)$_2$](NO$_3$) (**3**) were obtained in quantitative yield, respectively, upon cooling to room temperature. Both compounds are air- and light-stable and are insoluble in common organic solvents and water.

The single-crystal structural determination of **2** revealed that, as shown in Figure 2, the coordination environment of each Cu(II) center consists of two oxygen donors and two nitrogen donors from two 2-methylpyrazine-5-carboxylate chelating ligands and two aquo oxygen donors. The pseudo-octahedral coordination geometry may be described as a basal plane associated with N(1) and O(1) from two 2-methylpyrazine-5-carboxylate ligands (O(1)−Cu−N(1) = 97.15(14)°), having Cu−O(1) and Cu−N(1) bond lengths of 1.975(3) and 1.994(4) Å, respectively, with the axial positions occupied by two aquo oxygen donors O(3) (O(3)−Cu−O(3) = 180.00°). The Cu−O(3) distance is 2.448(4) Å, which is remarkably long compared with 2.257(2) Å of **1**, but very similar to the corresponding Cu−O distances of 2.445(3) Å found in Cu(4,4′-bpy)(pyz)(H$_2$O)$_2$·(PF$_6$)$_2$.[17] It is noteworthy that the coordination environment of the Cu(II) center changed from square pyramidal in **1** to octahedral in **2**.

The Ag(I) center in **2** lies in a bent two-coordinate environment (Figure 2) made up of two crystallographically equivalent nitrogen donors (N(2)) from two Cu(2-methylpyrazine-5-carboxylate)$_2$·2H$_2$O molecules, with a Ag−N(2) distance of 2.195(4) Å. This Ag−N(2) distance is similar to analogous bent (and linear) two-coordinate interactions in several other Ag(I) complexes.[18] The N(2)−Ag−N(2) bond angle is 165.7(2)°, which is smaller than the normal N−Ag−N bond angles found in diagonally coordinate Ag(I) compounds, such as 178.6(1)° in Ag(phz)(ClO$_4$),[18a] 173.6(2)° in Ag(pyz)(BF$_4$),[18b] and 180° in Ag(bpp)(NO$_3$).[18c]

In the solid state, as shown in Figure 3, alternating Ag(I) centers and Cu(2-methylpyrazine-5-carboxylate)$_2$·2H$_2$O molecules form one-dimensional Cu(II)−Ag(I) mixed-metal chains along the crystallographic *a* axis. The slight departure from linearity of the coordination geometry of silver results in the chains running in a mild zigzag fashion (Figure 3). The short and long interchain Ag···Ag contacts are 4.921(3) and 7.430(4) Å, respectively, and are comparable to those of other known linear Ag(I) complexes.[18b] The intrachain Ag···Ag, Ag···Cu, and Cu···Cu distances are 13.827(4), 6.913(3), and 13.733(5) Å, respectively. Along the chains, each Cu(2-methylpyrazine-5-carboxylate)$_2$·2H$_2$O molecule is rotated by ca. 60° with respect to its nearest neighbor molecule.

The very weakly coordinated, disordered BF$_4^-$ counterion (shortest Ag···F contact 2.688(4) Å[18b]) is located between the Cu(II)−Ag(I) chains and is equidistant from two Ag(I) centers on adjacent chains. In addition, the Cu(II)−Ag(I) coordination

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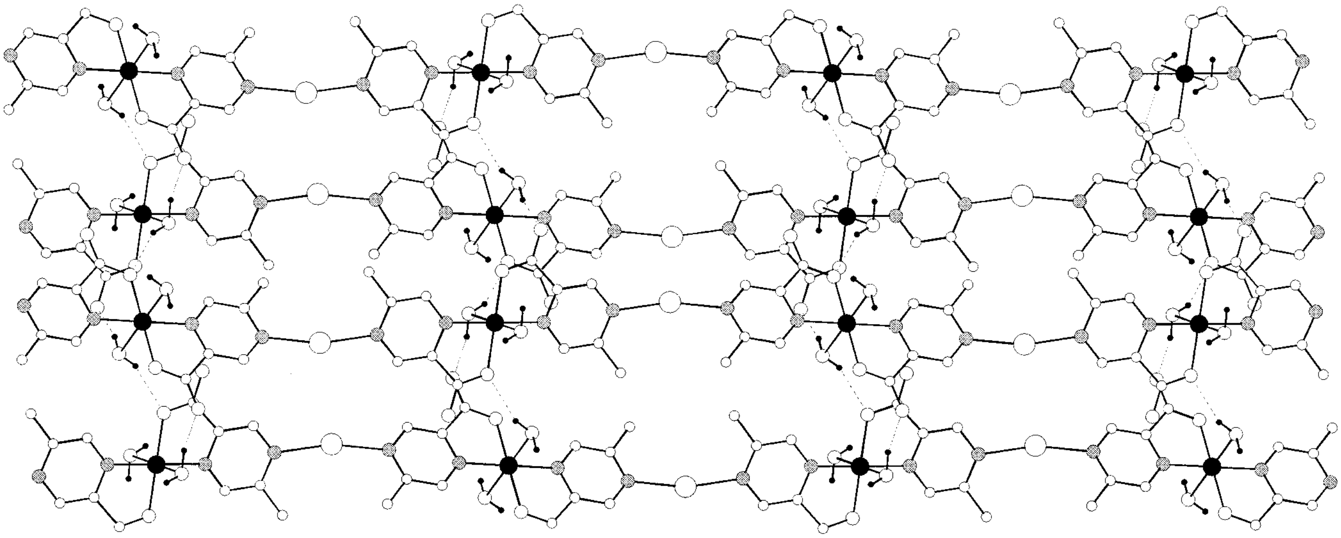

Figure 4. Crystal packing in compound **2** (view down the crystallographic *c* axis). The BF_4^- counterions and hydrogen atoms on the 2-methylpyrazine-5-carboxylate ligands are omitted for clarity. Hydrogen bonds are shown as dotted lines. Nitrogen atoms are shown as the gray circles, copper and hydrogen atoms as large and small black circles. Silver, oxygen and carbon atoms are shown as the large, medium, and small open circles, respectively.

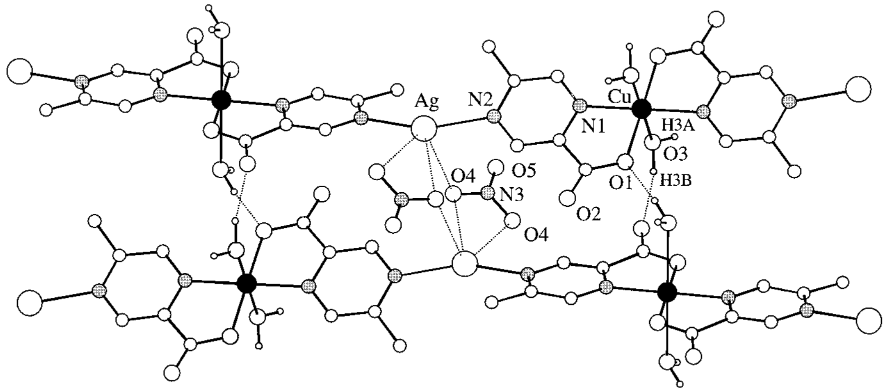

Figure 5. View of the segment of two Ag(I)−Cu(II) mixed-metal chains in **3**, with partial atom labeling. The hydrogen atoms on the 2-methylpyrazine-5-carboxylate ligands are omitted for clarity. Hydrogen bonds and O···Ag weak interactions are shown as dotted lines.

polymer chains are bound to each other by interpolymer O−H···O hydrogen bonds to generate a two-dimensional network (Figure 4). There are two hydrogen-bonding systems in **2**. The first consists of the uncoordinated oxygen atom O(2) of a carboxylate group with the hydrogen atom H3B on the coordinated water molecule O(3) of a neighboring Cu(II)−Ag(I) chain. The second involves the coordinated water molecule (O(3)−H3A) and the coordinated oxygen atom (O(1)) of a carboxylate group on an adjacent Cu(II)−Ag(I) chain (Figure 3). Corresponding hydrogen-bonding data are given in Table 5.

In order to investigate the effect of the counterion upon the long-range order of Cu(II)−Ag(I) mixed-metal coordination polymers, the more strongly coordinating NO_3^- anion was used to perform the experiment instead of the weakly coordinating BF_4^- anion. The Cu(II) center in **3** also features a distorted octahedral coordination geometry, and all bond lengths and angles found in the Cu(II) coordination sphere are essentially the same as the corresponding values in **2** (Cu−O(1) = 1.965(3) Å, Cu−N(1) = 1.999(3) Å, Cu−O(3) = 2.444(4) Å, O(1)−Cu−N(1) = 96.70(11)°, and O(3)−Cu−O(3) = 180.00°). (The same atom-numbering scheme shown in Figure 2 for **2** is also used for **3**.) The Ag(I) center coordinates to two nitrogen atoms from two Cu(2-methylpyrazine-5-carboxylate)$_2$·2H_2O subunits. The Ag−N(2) bond length is 2.263(1) Å, which is a little longer than the Ag−N distance of 2.195(4) Å in **1** but is very similar to the Ag−N bond length of 2.286(5) Å found in Ag_2(phz)(NO_3)$_2$.[18a] The coordination geometry of the silver center in **3** departs even more sharply from linearity than in **2**, with N(2)−Ag−N(2) = 153.31(18)°, which is out of the region of 170−180° reported for two-coordinate Ag(I) compounds.[18,19] However, a similar N−Ag−N bond angle of 152.6(1)° has been found in [Ag_2(pyz)$_3$](BF_4)$_2$, where the Ag(I) center adopts a trigonal coordination geometry and forms a two-dimensional net.[18b] Such coordination geometry of Ag(I) is less common for two-coordinate Ag(I) complexes, however. In addition to the nitrogen donors, each Ag(I) center exhibits weak interactions with two NO_3^- anions. As shown in Figure 5, each NO_3^- anion, acting as a bidentate ligand, uses two oxygen donors to weakly coordinate one Ag(I) center (Ag−O(4) distance = 2.763(2) Å); one of these oxygen atoms also links the other Ag(I) center on the neighbor chain (Ag−O(4) distance of 2.782(3) Å). Thus the weakly coordinating NO_3^- anion double bridges the Ag(I) centers to form a staggered [Ag^+···NO_3^-] chain parallel to the crystallographic *c* axis (perpendicular to the page in Figure 5). The short and long interchain Ag···Ag contacts are 4.466(4) and 7.930(4) Å, respectively.

In the solid state, as shown in Figure 6, the Cu(II)−Ag(I) polymer chain markedly undulates along the *a* axis due to the

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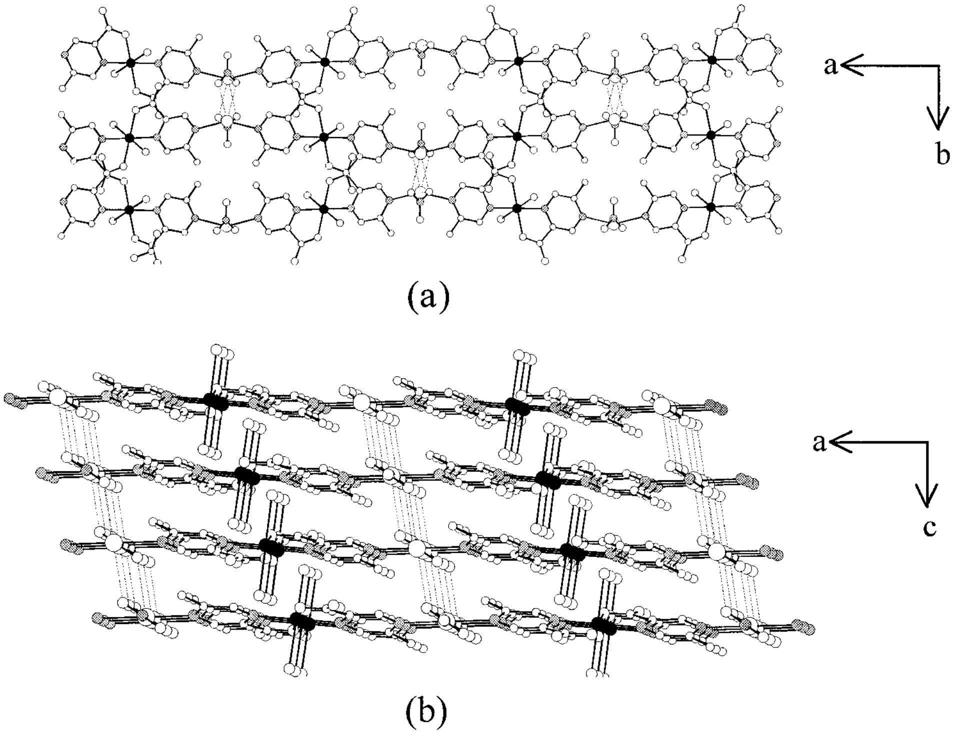

Figure 6. Crystal-packing pattern of **3**: (a) three chains of a single Cu(II)−Ag(I) mixed-metal layer (viewed perpendicular to the layer, down *c*); (b) view parallel to the Cu(II)−Ag(I) 2-D layers, showing the extended 3-D network formed by $Ag^+\cdots NO_3^-$ linkages. Copper centers are shown as black circles, nitrogen atoms as gray circles. Silver, oxygen, and carbon atoms are shown as the large, medium, and small open circles, respectively. Ag···O interactions are shown as dotted lines. Hydrogen atoms and hydrogen bonds are omitted for clarity.

153.31(18)° N−Ag−N bond angle. The intrachain Ag···Ag, Ag···Cu, and Cu···Cu distances are 13.988(4), 6.994(3), and 13.815(5) Å, respectively, which are essentially identical with the corresponding values found in **2**. As in **2**, adjacent intrachain Cu(2-methylpyrazine-5-carboxylate)$_2$·2H_2O molecules are rotated by ca. 60° with respect to one another. The same interchain hydrogen-bonding systems as in **2** have been found in **3**. The corresponding hydrogen bond data are listed in Table 5. In **3**, however, the one-dimensional mixed-metal chains are weakly cross-linked by the [$Ag^+\cdots NO_3^-$] chains to generated a novel three-dimensional network, demonstrating that, in comparison to **2**, the NO_3^- anion does have a profound effect upon network geometry.

To date, a number of monocentered Cu(II)- or Ag(I)-containing coordination polymers have been synthesized by combination of organic spacers and Cu(II) or Ag(I) inorganic salts.[19,20] To our knowledge, however, no Cu(II)−Ag(I) mixed-metal coordination polymers have been reported.

Thermogravimetric Analyses. Thermogravimetric analyses were performed on compounds **2** and **3** by heating powdered samples of each to 450 °C under flowing helium, at 10 °C/min. For **2**, TGA shows that the Cu(II)−Ag(I) polymer chains are stable up to 178 °C. The first weight loss of 6.4% from 178 to 227 °C per formula corresponds to the loss of the two coordinated water molecules on the Cu(II) center (calculated 6.3%). A drastic weight loss of 48.3% was observed from 240 to 327 °C, corresponding to the loss of two 2-methylpyrazine-5-carboxylate chelating ligands (calculated 48.2%). Further weight loss was observed above 330 °C, accompanied by decomposition of the BF_4^- counterions. A brown solid remained. For compound **3**, the first weight loss occurred between 138 and 182 °C, which is slightly lower than for compound **1** and compares with a calculated value of 6.6% for the loss of two coordinated water molecules on the Cu(II) centers. Two drastic weight loss steps were followed, the total weight loss corresponding to loss of both 2-methylpyrazine-5-carboxylate ligands (observed 50.6%, calculated 50.7%). Further weight loss occurred above 304 °C, involving decomposition of the nitrate ions, leaving a black-brown residue.

Magnetic Properties. The magnetic susceptibilities of polycrystalline powders of compounds **2** and **3** have been measured from 2 to 300 K in a field of 5 kG. The plots of the inverse magnetic susceptibility versus temperature for both compounds were found to be linear down to the lowest temperature measured. The data follow the Curie law.[21] The experimental effective magnetic moments (μ_{exp}) were 1.85 μ_B for **2** and 1.83 μ_B for **3**, which are slightly higher than the theoretical value (1.73 μ_B) but nonetheless agree well with other experimentally observed effective magnetic moments for Cu(II). These magnetic data clearly show that the Cu(II) centers are not interacting with each other as hoped for, and can be treated as isolated magnetic centers.

Conclusions

One metal-containing ligand, [Cu(2-methylpyrazine-5-carboxylate)$_2$(H_2O)]·3H_2O (**1**), and two novel Cu(II)−Ag(I) mixed-metal coordination polymers, Ag[Cu(2-methylpyrazine-5-carboxylate)$_2$·(H_2O)$_2$](NO_3) (**2**) and Ag[Cu(2-methylpyrazine-5-carboxylate)$_2$·(H_2O)$_2$](BF_4) (**3**), have been successfully synthesized. All compounds were characterized by IR, elemental analyses, and single-crystal X-ray diffraction. In addition, compounds **2** and **3** were also characterized by thermogravimetric analyses and magnetic susceptibility. Both **2** and **3** feature

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one-dimensional Cu(II)−Ag(I) mixed-metal zigzag chains. The effect of a coordinating counterion (NO_3^-) was illustrated by compound **3**, in which novel [$Ag^+\cdots NO_3^-$] linkages act as connectors to cross-link the one-dimensional mixed-metal chains into a three-dimensional network. No magnetic interactions between metal centers were observed, as both **2** and **3** were found to follow the Curie law. By selecting an organic spacer with free coordination donor atoms, we have been able to demonstrate the design of a metal-containing ligand that can be used as a precursor for mixed-metal coordination polymers. We anticipate this approach to be viable for the construction of a variety of new mixed-metal coordination polymers. Preliminary efforts to prepare mixed-metal polymers containing two magnetic ions appear promising.

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Supporting Information Available: Three X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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