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Reactions of $Cu(hfacac)_2 \cdot H_2O$ (hfacac = Hexafluoroacetylacetonate) with Bidentate Ligands. Preparation, Characterization, and X-ray Structures of the Molecular Complexes $Cu(hfacac)_2(pyrazine)_2$ and $Cu(hfacac)_2(3\text{-cyanopyridine})_2$ and the One-Dimensional Coordination Polymers $Cu(hfacac)_2$(1,2-bis(4-pyridyl)ethane) and $Cu(hfacac)_2$(4,4′-trimethylenebipyridine)

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Reactions of $Cu(hfacac)_2 \cdot H_2O$ (hfacac = hexafluoroacetylacetonate) with pyrazine, 3-cyanopyridine, 1,2-bis(4-pyridyl)ethane, and 4,4′-trimethylenebipyridine in methylene chloride have been studied. Two types of products were obtained and crystallographically characterized: compounds **1** ($Cu(hfacac)_2(pyrazine)_2$, orthorhombic, $Pbca$; $a = 9.839(2)$ Å, $b = 17.984(2)$ Å, $c = 13.572(2)$ Å, $Z = 4$) and **2** ($Cu(hfacac)_2(3\text{-cyanopyridine})_2$, triclinic, $P\bar{1}$, $a = 13.175(2)$ Å, $b = 13.955(2)$ Å, $c = 7.936(2)$ Å, $\alpha = 104.29(2)°$, $\beta = 105.90°$, $\gamma = 81.47(1)°$, $Z = 2$) were isolated as molecular complexes, while compounds **3** ($Cu(hfacac)_2$(1,2-bis(4-pyridyl)ethane, monoclinic, $P2_1/c$, $a = 7.922(1)$ Å, $b = 16.266(4)$ Å, $c = 10.163(2)$ Å, $\beta = 93.83(1)°$, $Z = 2$) and **4** ($Cu(hfacac)_2$(4,4′-trimethylenebipyridine), monoclinic, Pc, $a = 7.940(1)$ Å, $b = 9.691(2)$ Å, $c = 18.539(3)$ Å, $\beta = 95.83(2)°$, $Z = 2$) were isolated as one-dimensional infinite polymeric chains. The structures were further characterized by infrared spectroscopy, thermogravimetry, and elemental analysis; additionally, the magnetic behavior of all compounds was investigated and found to follow the Curie law. All four compounds feature similar 4 + 2 pseudooctahedral coordination environments around the Cu(II) centers composed of square-planar $Cu(hfacac)_2$ units with the N-donor ligands occupying the trans positions. The length of the N-donor ligands determines the formation of either molecular complexes (**1** and **2**, short ligands) or infinite polymeric structures (**3** and **4**, longer ligands). Important C−F···H−C hydrogen-bonding interactions in compounds **1** and **3** play a significant role in aligning the molecules and the polymer strands in the crystalline solids.

Introduction

The use of soluble inorganic transition metal ions or unsaturated transition metal coordination complexes and organic bidentate or multifunctional ligands as precursors to organic/inorganic hybrid materials is a rapidly growing area of interest.[1−4] For example, self-assembled coordination polymers with specific network topologies can provide highly ordered networks with different dimensionalities, particularly as low-dimensional 1-D or 2-D solids.[5] Generally, some control over the type and topology of the product generated from the self-assembly of inorganic metal species and organic ligands can be achieved by careful choice of ligand,[6] metal coordination geometry preference, inorganic counterion,[6a−c,7] solvent system,[2f,7]

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and metal-to-ligand ratio.[7c,8] Among these factors, the choice of the organic spacers is the single greatest influence in determining the type and topology of the product. The organic spacers serve to link metal sites and to propagate structural information expressed in the metal coordination preferences through the extended structure. Properties of organic spacers, such as solubility, coordination activity, length, geometry, and relative orientation of the donor groups play a very important role in dictating polymer framework topology and even in affecting the formation of polymer vs oligomer vs molecule.

Pyrazine,[9] bridged bidentate bipyridyl ligands (bridges can be $-CH_2-$,[10] $-CH_2CH_2-$,[6c,10,11] $-CH_2CH_2CH_2-$,[12] $-CH{=}CH-$,[7d,13] $-C{\equiv}C-$,[14] $=C{=}CH_2$,[10a] $-C{\equiv}C-C{\equiv}C-$,[15] $-CH_2-C_6H_4-CH_2-$,[16] $-CH_2NH_2^+CH_2CH_2CH_2CH_2NH_2^+CH_2-$,[17] and $=C{=}N_2$,[18]), and the nitrile-substituted pyridine[19] are the most commonly used donor groups in coordination polymers at present. To date, numerous 1-D, 2-D, and 3-D organic/inorganic composite materials have been obtained using such ligands. Cu(hfacac)$_2$,[20] an unsaturated metal complex, has proven very useful in the synthesis of various types of materials including thin metallic and oxide films[21a−d] and magnetic materials[21e−f] prepared by chemical vapor deposition. In addition, the fluorine atoms in Cu(hfacac)$_2$ could be used as potential hydrogen bond acceptors, providing another crystal engineering design tool for assembling building blocks into desired arrangements.[22a] Also, the C−F···H−C hydrogen-bonding system has been shown to play a significant role in directing the alignment of molecules in the crystalline state.[22b]

In this paper we present results of reactions of Cu(hfacac)$_2$ with bidentate N-donor ligands of different lengths: pyrazine, 3-cyanopyridine, 1,2-bis(4-pyridyl)ethane, and 4,4′-trimethylenebipyridine, all performed in methylene chloride with a metal: ligand ratio of 1:1. Compounds **1**, Cu(hfacac)$_2$(pyrazine)$_2$, and **2**, Cu(hfacac)$_2$(3-cyanopyridine)$_2$, were isolated as molecular complexes, while compounds **3**, Cu(hfacac)$_2$(1,2-bis(4-pyridyl)ethane), and **4**, Cu(hfacac)$_2$(4,4′-trimethylenebipyridine), were isolated as one-dimensional infinite chains. This molecule-to-polymer transition is linked to the capacity of the bidentate ligand to span two metal centers, which is directly related to the length of the ligand in question. We also found that intermolecular C−F···H−C hydrogen bonds in **1** together with intermolecular N···H−C and O···H−C hydrogen bonds promote the molecules into three-dimensional structures while the C−F···H−C hydrogen-bonding system in **3** expands the one-dimensional chain structure into a two-dimensional network.

Experimental Section

The Cu(hfacac)$_2$·H$_2$O (hfacac = hexafluoroacetylacetonate), pyrazine, 3-cyanopyridine, 1,2-bis(4-pyridyl)ethane, and 4,4′-trimethylenebipyridine were purchased from Aldrich and used without further purification. IR spectra were recorded on a Perkin-Elmer spectrometer as KBr pellets in the 4000−400 cm^{-1} range. Elemental analyses were carried out by National Chemical Consulting. Thermogravimetric analyses were carried out using a TA Instrument SDT 2960, simultaneous DTA−TGA, in a helium atmosphere at a heating rate of 10 °C/min. The magnetic susceptibilities of compounds **1**−**4** were measured using a Quantum Design MPMS XL SQUID magnetometer in an applied field of 5 kG. Clear gelatin capsules were used as sample containers.

Cu(hfacac)$_2$(pyrazine)$_2$ (1). A green solution of Cu(hfacac)$_2$·H$_2$O (99 mg, 0.20 mmol) in 10 mL of methylene chloride was slowly added to a colorless solution of pyrazine (16 mg, 0.20 mmol) in 3 mL of methylene chloride. The solution was allowed to stand at room temperature for one week. Green crystals were obtained when the solvent slowly evaporated. Yield: 91%. IR (KBr, cm^{-1}): 3106.9 (w), 1681.4 (s), 1650.3 (s), 1503.9 (s), 1416.8 (s), 1264.8 (s), 1055.0 (s), 1016.3 (s), 974.2 (m), 943.0 (m), 807.0 (s), 741.0 (s), 700.7 (m), 671.8 (s). Anal. Calcd for $CuC_{18}H_{10}N_4O_4F_{12}$: C, 33.88; H, 1.57; N, 8.78. Found: C, 34.14; H, 1.75; N, 8.61.

Cu(hfacac)$_2$(3-cyanopyridine)$_2$ (2). The procedure is similar to that described for the preparation of **1**, except 3-cyanopyridine (21 mg, 0.20 mmol) was used instead of pyrazine. Green crystals were obtained in a yield of 92%. IR (KBr, cm^{-1}): 3080.6 (w), 2240.7 (s), 1684.0 (s), 1633.7 (s), 1556.0 (s), 1504.7 (s), 1416.9 (s), 1236.7 (m), 1031.7 (s), 967.9 (m), 941.5 (s), 800.8 (s), 743.6 (s), 698.3 (s), 655.4 (s), 638.0 (s). Anal. Cald for $CuC_{22}H_{10}N_4O_4F_{12}$: C, 38.51; H, 1.46; N, 8.17. Found: C, 38.15; H, 1.46; N, 7.82.

Cu(hfacac)$_2$(1,2-bis(4-pyridyl)ethane (3). The procedure is similar to that described for the preparation of compound **1**, except 1,2-bis-

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Table 1. Crystallographic Data for **1** and **2**

formula	$Cu(hfacac)_2(N_2C_4H_4)_2$, **1**	$Cu(hfacac)_2(N_2C_6H_4)_2$, **2**
formula weight	637.83	685.87
crystal system	orthorhombic	triclinic
a (Å)	9.839(2)	13.175(2)
b (Å)	17.984(2)	13.955(2)
c (Å)	13.572(2)	7.936(2)
α (deg)	90	104.29(2)
β (deg)	90	105.90(2)
γ (deg)	90	81.47(1)
V (Å^3)	2401.4(5)	1354.8(5)
space group	*Pbca* (no. 61)	$P\bar{1}$ (no. 2)
Z value	4	2
ρ_{calcd} (g/cm^3)	1.764	1.681
μ (Mo Kα) (cm^{-1})	10.359	9.249
temperature (°C)	23.0	23.0
no. of observations ($I > 3\sigma$)	1134	2909
residuals:^{a} *R*, R_w	0.056, 0.077	0.054, 0.074

^{a} $R = \sum_{hkl}(||F_o| - |F_c||)/\sum_{hkl}|F_o|$; $R_w = [\sum_{hkl}w(|F_o| - |F_c|^2)/\sum_{hkl}wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

Table 2. Crystallographic Data for **3** and **4**

formula	$Cu(hfacac)_2(N_2C_{12}H_{12})$, **3**	$Cu(hfacac)_2(N_2C_{13}H_{14})$, **4**
formula weight	661.89	675.92
crystal system	monoclinic	monoclinic
a (Å)	7.922(1)	7.940(1)
b (Å)	16.266(4)	9.691(2)
c (Å)	10.163(2)	18.539(3)
α (deg)	90	90
β (deg)	93.83(1)	95.83(2)
γ (deg)	90	90
V (Å^3)	1306.7(3)	1419.2(4)
space group	$P2_1/c$ (no. 14)	*Pc* (no. 7)
Z value	2	2
ρ_{calcd} (g/cm^3)	1.682	1.582
μ (Mo Kα) (cm$^{-1)}$	9.532	8.795
temperature (°C)	23.0	23.0
no. of observations ($I > 3\sigma$)	983	2081
residuals:^{a} *R*, R_w	0.058, 0.071	0.050, 0.059

^{a} $R = \sum_{hkl}(||F_o| - |F_c||)/\sum_{hkl}|F_o|$; $R_w = [\sum_{hkl}w(|F_o| - |F_c|^2)/\sum_{hkl}wF_o^2]^{1/2}$, $w = 1/\sigma^2(F_o)$.

Table 3. Interatomic Distances (Å) and Bond Angles (deg) with esds in Parentheses for **1**

Cu−O(1)	2.225(4)	Cu−N(1)	2.055(5)
Cu−O(2)	1.995(4)	F(1)−C(8)	1.263(9)
F(5)−C(9)	1.290(1)	O(1)−C(5)	1.240(6)
N(1)−C(4)	1.321(8)	C(1)−C(2)	1.360(1)
O(1)−Cu−O(1)	180.0(2)	O(1)−Cu−N(1)	91.0(2)
O(1)−Cu−O(2)	88.2(2)	C(5)−O(1)−Cu	121.9(4)

Table 4. Interatomic Distances (Å) and Bond Angles (deg) with esds in Parentheses for **2**

Cu(1)−O(1)	1.991(4)	Cu(1)−O(2)	2.184(4)
Cu(1)−N(1)	2.097(4)	Cu(2)−O(3)	1.970(4)
Cu(2)−N(3)	2.389(5)	Cu(2)−O(4)	1.994(4)
C(22)−N(4)	1.129(7)	C(11)−N(2)	1.146(7)
N(3)−C(21)	1.340(7)	N(1)−C(10)	1.332(6)
F(12)−C(16)	1.314(7)	F(1)−C(4)	1.310(1)
O(1)−Cu(1)−O(1)	180	O(1)−Cu(1)−O(2)	88.9(1)
O(1)−Cu(1)−N(1)	90.5(2)	O(2)−Cu(1)−N(1)	90.3(1)
O(3)−Cu(2)−O(3)	180	O(3)−Cu(2)−O(4)	88.3(2)
O(4)−Cu(2)−N(3)	93.0(2)	Cu(1)−O(1)−C(1)	125.1(4)
Cu(2)−O(3)−C(12)	124.5(3)	Cu(2)−N(3)−C(21)	122.2(4)

Table 5. Interatomic Distances (Å) and Bond Angles (deg) with esds in Parentheses for **3**

Cu−O(1)	2.129(8)	Cu−O(2)	2.114(7)
Cu−N(1)	2.014(7)	F(1)−C(7)	1.230(2)
O(1)−C(8)	1.240(1)	N(1)−C(1)	1.330(1)
O(1)−Cu−O(1)	180	O(1)−Cu−O(2)	88.4(3)
O(1)−Cu−N(1)	90.7(3)	O(2)−Cu−N(1)	90.3(3)
Cu−O(1)−C(8)	125.0(7)	Cu−N(1)−C(1)	121.3(6)

(4-pyridyl)ethane (74 mg, 0.20 mmol) was used. The rodlike green single crystals were obtained in 90% yield by slow diffusion upon laying a solution of 1,2-bis(4-pyridyl)ethane in methylene chloride over a solution of the $Cu(hfacac)_2$ in the same solvent. IR (KBr, cm^{-1}): 3076.5 (w), 1667.4 (s), 1651.2 (s), 1614.2 (s), 1567.8 (s), 1504.1 (m), 1461.2 (w), 1433.8 (s), 1268.2 (m), 1084.0 (m), 1032.1 (m), 931.7 (s), 808.7 (s), 793.3 (s), 765.4 (m), 739.8 (m), 667.3 (s). Anal. Cald for $CuC_{22}H_{14}N_2O_4F_{12}$: C, 39.91; H, 2.12; C, 4.23. Found: C, 39.42; H, 2.01; N, 4.10.

$Cu(hfacac)_2$(4,4′-trimethylenebipyridine) (4). A green solution of $Cu(hfacac)_2 \cdot H_2O$ (99 mg, 0.20 mmol) in 10 mL of methylene chloride was slowly added to a colorless solution of 4,4′-trimethylenebipydrine (40 mg, 0.20 mmol) in 15 mL of methylene chloride. The solution was allowed to stand at room temperature. Well-faceted deep green crystals were produced within a day, collected by filtration, washed with hexane, and dried in air (yield 89%). IR (KBr, cm^{-1}): 2943.6 (m), 2871.8 (w), 1658.7 (s), 1620.5 (s), 1497.4 (s), 1430.8 (s), 1384.6 (w), 1338.5 (s), 1257.9 (s), 1076.9 (m), 1035.9 (m), 941.9 (w), 892.3 (w), 866.7 (w), 841.0 (m), 805.1 (s), 793.1 (s), 760.7 (s), 739.7 (s), 666.4 (s). Anal. Calcd for $CuC_{23}H_{16}N_2O_4F_{12}$: C, 40.86; H, 2.37; N, 4.14. Found: C, 40.49; H, 2.20; N, 4.04.

Single-Crystal Structure Determination. The crystals used for data collection were epoxied in air onto thin glass fibers. Intensity measurements were made at 20 °C on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. The unit cells were determined from 25 randomly selected reflections obtained using the AFC6 automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and analysis statistics for **1**−**4** are listed in Tables 1 and 2. Relevant interatomic bond distances and bond angles for **1**−**4** are collected in Tables 3−6, respectively. All data processing was performed on a Silicon Graphics INDIGO^2 computer by using the TEXSAN structure-solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Lorentz polarization (Lp) and absorption (DIFABS) corrections were applied to each data set. Full-matrix least-squares refinements minimized the function $\sum_{hkl}w(|F_o| - |F_c|)^2$, where $w = 1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}$/Lp. The intensities of 3 standard reflections were measured every 150 reflections for each crystal: these reflections showed no significant deviations during data collection. The structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters; the hydrogens were calculated and therefore not refined.

Results and Discussion

Molecular Complexes. When $Cu(hfacac)_2$ dissolved in methylene chloride is reacted at room temperature with pyrazine in methylene chloride in a 1:1 molar ratio, a green solution is obtained. Deep green crystals, obtained when the solvent slowly evaporated, were shown to be the molecular 1:2 adduct $Cu(hfacac)_2(pyrazine)_2$ (**1**). The compound is air stable and soluble in common polar organic solvents, such as CH_2Cl_2, CH_3CN, $CHCl_3$, and CH_3COCH_3. The molecular structure of **1** is shown in Figure 1a and features six-coordinate copper in a 4 + 2 pseudooctahedral geometry defined by two nitrogen donors from two *trans*-pyrazine ligands and four oxygen donors from two hfacac chelating ligands. This geometry is quite different from the geometry found in $Cu(hfacac)_2(pyridine)_2$,[23] in which the two pyridine ligands adopt a cis geometry. The Cu−N bond length in **1** is 2.055(5) Å, which is very close to the Cu−N bond length (2.043(4) Å) found in $Cu(hfacac)_2(mpydz)_2$,[24] but

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Table 6. Interatomic Distances (Å) and Bond Angles (deg) with esds in Parentheses for **4**

Cu−O(1)	2.105(6)	Cu−O(2)	2.166(6)
Cu−O(3)	2.038(6)	Cu−O(4)	2.203(7)
Cu−N(1)	1.992(6)	Cu−N(2)	2.017(6)
N(1)−C(1)	1.320(2)	O(2)−C(17)	1.270(1)
F(1)−C(14)	1.240(2)		
O(1)−Cu−O(2)	86.9(6)	O(1)−Cu−O(3)	176.9(3)
O(1)−Cu−O(4)	89.0(2)	O(1)−Cu−N(1)	88.9(3)
O(1)−Cu−N(2)	89.4(3)	O(2)−Cu−O(3)	96.2(3)
O(2)−Cu−O(4)	175.9(3)	O(2)−Cu−N(1)	90.6(2)
O(2)−Cu−N(2)	89.3(3)	O(3)−Cu−O(4)	87.9(3)
O(3)−Cu−N(1)	91.5(3)	O(4)−Cu−N(2)	90.2(3)
O(4)−Cu−N(1)	89.6(2)	N(1)−Cu−N(2)	178.3(3)
Cu−N(1)−C(1)	123.4(6)	Cu−O(1)−C(15)	125.2(7)

significantly shorter than in Cu(hfacac)$_2$(pyrazine) (Cu−N, 2.529(4) Å) and Cu(hfacac)(ted) (Cu−N, 2.566(7) Å).[25] The Cu−O bond lengths in **1** are 2.225(4) and 1.995(7) Å, respectively, slightly longer than the Cu−O distances (2.004(7) and 1.924(7) Å) in Cu(hfacac)$_2$(pyrazine), but very similar to the values of 2.228(4) and 2.009(3) Å found in Cu(hfacac)$_2$(mpydz)$_2$. The two pyrazine rings in **1** are strictly coplanar and perpendicular to the plane consisting of the Cu(II) center and the two hfacac chelating ligands. In the solid state (Figure 1b), the molecules are interconnected to give a three-dimensional network through weak hydrogen-bonding interactions involving the F(1), N(2), F(6), and O(1) atoms and the H(2), H(3), and H(4) atoms on the pyrazine ligands of the neighboring molecule. The F(1)···H(2), F(6)···H(2), N(2)···H(4), and O(1)···H(3) distances are 2.835(5), 2.983(6), 2.630(6), and 2.708(6) Å, respectively. The corresponding F(1)···C(2), F(6)···C(2), N(2)···C(4), and O(1)···C(3) distances are 3.412(5), 3.653(4), 3.541(5), and 3.574(4) Å, respectively, and the corresponding F(1)···H(2)−C(2), F(6)···H(2)−C(2), N(2)···H(4)−C(4), and O(1)···H(3)−C(3) angles are 120.48(5)°, 129.10(4)°, 159.97(3)°, and 155.20(4)°, respectively. The existence and structural importance of weak C−H···X hydrogen-bonding interactions are now well established[26] and are observed in many compounds, such as the N···H−C interaction in 1,3,5-tricyanobenzene−hexamethylbenzene,[27a] the O···H−C interaction in ($C_{14}H_{12}N_2$)[Cu(opba)]·3H_2O and Na_2($C_{12}H_{12}N_2$)[Cu(opba)]$_2$·4H_2O (opba = *o*-phenylenebis(oxamate)),[27b] and the F···H−C interaction in 11-(trifluoromethyl)-15,16-dihydrocyclopenta[α]phenanthren-17-one.[22b] These hydrogen bonds, although weak, contribute significantly to the alignment of the molecules of **1** in the crystalline state and certainly contribute to physical properties such as the heat of sublimation.

In the specific reaction of diazine ligands with Cu(hfacac)$_2$, it appears that the product structure depends predominantly on the nature of the ligand and on the solvent system rather than on the metal-to-ligand ratio.[7a] For example, compound **1** was obtained as a molecular complex (1:2 adduct, Cu:ligand) when the reaction was performed in methylene chloride at room temperature with a Cu:pyrazine ratio of 1:1. However, when this reaction is carried out in warm carbon tetrachloride, the 1:1 adduct Cu(hfacac)$_2$(pyrazine) is obtained,[28] which, although reported to be a linear Cu(hfacac)$_2$(pyrazine) polymer, in fact possesses a very long Cu−N bond (2.529(4) Å), suggesting an alignment of square pyramidal molecules with a terminal pyrazine N atom in the vicinity of a vacant coordination site on a neighboring metal.

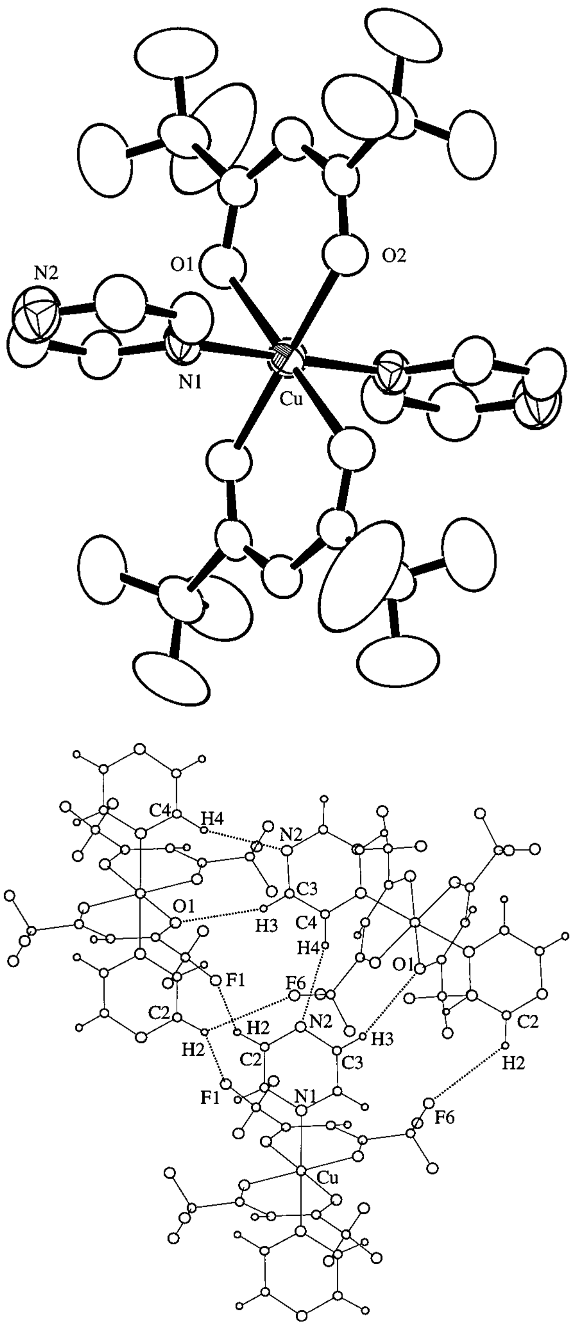

Figure 1. (a, top) Molecular structure of **1**. Displacement ellipsoids shown at the 50% probability level. (b, bottom) Crystal packing of compound **1**, showing the intermolecular hydrogen bonds as dotted lines.

Moreover, when other kinds of diazine ligands (2,3,5-trimethylpyrazine (tmpyz), 5-methylpyrimidine (mpym), and 3-methylpyridazine (mpydz)) are used instead of pyrazine to react with Cu(hfacac)$_2$ in light petroleum under reflux with a metal:ligand ratio of 1:1, several types of compounds are isolated, including the mononuclear complex Cu(hfacac)$_2$(mpym)$_2$, the dinuclear complex [Cu(hfacac)$_2$]$_2$(mpym), the trinuclear complexes [Cu(hfacac)$_2$]$_3$(mpym)$_2$ and [Cu(hfacac)$_2$]$_3$(tmpyz)$_2$, and the structurally uncharacterized 1:1 adducts [Cu(hfacac)$_2$] (tmpyz) and [Cu(hfacac)$_2$](mpym).[24] Apparently, the proper combination of solvent system and diazine ligands in

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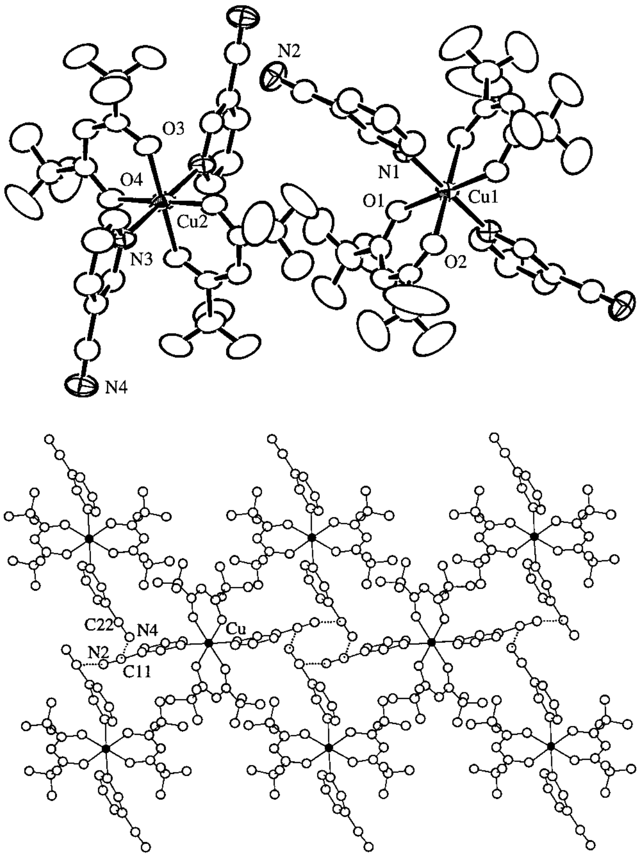

Figure 2. (a, top) Molecular structure of **2**. Displacement ellipsoids shown at the 50% probability level. (b, bottom) Crystal packing in **2** viewed perpendicular to the crystallographic *ab* plane, with intermolecular N···CN interactions (see the text) shown as dotted lines. H atoms omitted for clarity.

the synthetic process can bring about a directed approach for the control of the self-assembly of the adduct generated from $Cu(hfacac)_2$ with diazine ligands.

A similar result is obtained from the reaction of $Cu(hfacac)_2$ with 3-cyanopyridine in methylene chloride. The molecular complex $Cu(hfacac)_2$(3-cyanopyridine)$_2$ (**2**) is the only isolable product from the reactions of various metal-to-ligand ratios instead of the expected asymmetrically bridged metal polymer. In compound **2** (Figure 2a), two different types of $Cu(hfacac)_2$(3-cyanopyridine)$_2$ molecules (henceforth named A and B) are in the unit cell. The structures of A and B are largely the same; only the degree of pseudooctahedral distortion around the Cu center and the orientation within the unit cell differ. In both, the coordination environment around the Cu(II) centers consists of two *trans*-pyridine nitrogen atoms from two 3-cyanopyridine ligands and of four roughly square planar oxygen atoms from two hfacac chelating ligands. However, molecule A shows a slightly greater distortion of the octahedral environment around the copper center (O(3)−Cu(2)−O(4) = 88.3(2)°, O(3)−Cu(2)−N(3) = 89.6(2)°, and O(4)−Cu(2)−N(3) = 93.0(2)°) than found in molecule B (O(1)−Cu(1)−O(2) = 91.1(1)°, O(1)−Cu(1)−N(1) = 90.5(2)°, and O(2)−Cu(1)−N(1) = 90.3(1)°). Also, the nitrogen donors in the 3-cyanopyridine ligands have quite different bond lengths with the copper center in A and B. In molecule A, a long Cu−N (2.389(5) Å) bond was found that is significantly longer than the Cu−N bond (2.097(4) Å) in molecule B, but similar in length to the Cu−N bond (2.381(5) Å) found in $Cu(tfacac)_2$(bipy) (tfacac = 1,1,1-trifluoroacetylacetonate).[29] As shown in the crystal structure (Figure 2b), ligating molecules of B and A have neighboring molecules A and B at short distances of 3.448(6) Å [N(2)···C(22)≡N(4)] and 3.403(6) Å [N(4)···C(11)≡N(2)], respectively, suggesting that the uncoordinated nitrile groups interact with each other intermolecularly by weak electrostatic forces.

The IR spectrum of **2** shows that the C≡N stretch (2240.7 cm^{-1}) in **2** was essentially unchanged from that in free 3-cyanopyridine, which can be taken as evidence for the nitrile nitrogen not entering the coordination sphere of the Cu(II) center. A similar phenomenon occurs in the reaction of $Ru_2(O_2C(CH_2)_6CH_3)_4$ with 4-cyanopyridine in toluene.[30] The discrete molecular 1:2 adduct $Ru_2(O_2C(CH_2)_6CH_3)_4$(4-cyanopyridine)$_2$ is obtained instead of the expected 4-cyanopyridine bridged metal complex. It is known that 4-cyanopyridine and 3-cyanopyridine spacers have been used as bridging ligands to link transition metal species into dimers and polymers.[19,31] It appears that the nitrile N-donor atom in 3-cyanopyridine and 4-cyanopyridine has a poor coordinating ability to effectively link 3d metal ions. For example, in [(Cu(4-cyanopyridine)$_4$(H_2O)(ClO_4)$_2$]$_n$, the nitrile nitrogen only weakly coordinates with copper centers through a "semicoordinated" bond (Cu−N≡C is 2.649(4) Å), which is much longer than a normal Cu−N coordinative bond.[32] We have also found the uncoordinated C≡N group in the copper complex $Cu(NO)_3$(4-cyanopyridine)$_2$.[33] It is worth noting that both compounds **1** and **2**, which contain uncoordinated N-donors (the pyrazine N atom in **1** and the nitrile nitrogen in **2**), could be used as potential new building blocks, as suggested recently.[34] These building blocks could be connected by other suitable metal ions (Ag^+ or Cd^{2+}, for example) or unsaturated metal complexes via bonding interactions with the free nitrogen atoms in pyrazine and in 3-cyanopyridine, respectively, a direction we are pursuing.

Polymeric Compounds. Extended structures containing the $Cu(hfacac)_2$ unit were synthesized successfully when the longer ligands 1,2-bis(4-pyridyl)ethane and 4,4′-trimethylenebipyridine were used instead of pyrazine and 3-cyanopyridine. When a solution of $Cu(hfacac)_2$ in methylene chloride is treated at room temperature with 1,2-bis(4-pyridyl)ethane in the same solvent in a 1:1 molar ratio, immediate formation of abundant green crystals is observed in 90% yield. The crystals were shown to be the polymeric 1:1 adducts of $Cu(hfacac)_2$(1,2-bis(4-pyridyl)ethane) (**3**). Compound **4** was obtained in a similar fashion by mixing the green solution of $Cu(hfacac)_2$ with 4,4′-trimethylenebipyridine in methylene chloride, which affords well-defined green crystals after standing for several hours at room temperature. Both **3** and **4** are air stable and are not soluble in common organic solvents and water.

X-ray analyses of compounds **3** and **4** show polymeric structures based on networks of pseudooctahedrally coordinated Cu(II) centers linked by 1,2-bis(4-pyridyl)ethane and 4,4′-trimethylenebipydrine, respectively. The local geometry of Cu-

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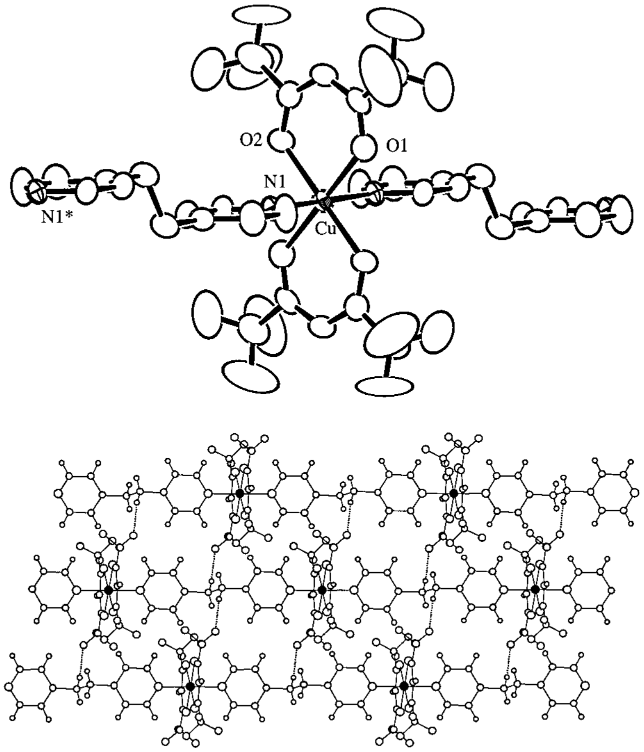

Figure 3. (a, top) Copper coordination environment in **3**. Displacement ellipsoids shown at the 50% probability level. (b, bottom) Crystal packing in **3**, with interpolymer hydrogen bonds shown as dotted lines.

(II) in compound **3** (Figure 3a) is similar to the geometry of the copper center in compound **1**. The octahedral Cu(II) sphere consists of two nitrogen donors from two *trans*-1,2-bis(4-pyridyl)ethane ligands and four coordinated oxygen atoms from two hfacac chelating ligands. The Cu−N = 2.014(6) and Cu−O = 2.129(8) Å bond lengths in **3** are very close to the Cu−N and Cu−O bond lengths found in compound **1**. The Cu(II) centers are connected by *trans*-1,2-bis(4-pyridyl)ethane ligands through the pyridyl nitrogen atoms into a one-dimensional zigzag chain along the crystallographic [$\bar{1}$01] direction. The intrapolymer Cu···Cu distance is 13.296(6) Å, while the shortest interpolymer Cu···Cu distances are 7.922(6) and 10.163(6) Å. In addition, hydrogen-bonding interactions are present in **3**. The one-dimensional polymer chains of **3** have close neighboring chains resulting from interpolymer hydrogen-bonding interactions. The hydrogen-bonding system involves F(4) of the hfacac ligand and H(4) on the 1,2-bis(4-pyridyl)ethane ligand of the neighboring chain. The F(4)···H(4) contact is 2.562(5) Å, which is shorter than the sum of the van der Waals radii of hydrogen and fluorine (2.67 Å).[35] The F(4)···C(4) distance and F(4)···H(4)−C(4) angle are 3.553(6) Å and 170.64(5)°, respectively. These interpolymer hydrogen-bonding interactions give rise to a 2-D layered arrangement of 1-D polymers parallel to the crystallographic *ac* plane (Figure 3b).

In **4**, the Cu(II) center lies in a 4 + 2 pseudooctahedral environment (Figure 4a) (O(1)−Cu−O(2) = 86.9(6)°, O(1)−Cu−O(3) = 176.9(3)°, O(2)−Cu−O(4) = 175.9(3)°, O(2)−Cu−O(3) = 96.2(3)°, O(1)−Cu−N(1) = 88.9(3)°, N(1)−Cu−N(2) = 178.3(3)°), which consists of two nitrogen donors, N(1) and N(2), from two 4,4′-trimethylenebipyridine ligands, with Cu−N distances of 1.992(6) and 2.017(6) Å, respectively, and four oxygen donors, O(1), O(2), O(3), and O(4), from two hfacac ligands, with Cu−O(1) = 2.105(6) Å, Cu−O(2) = 2.166(6) Å, Cu−O(3) = 2.038(6) Å, and Cu−O(4) = 2.203(6) Å. All the bond distances found in the Cu(II) sphere are similar to corresponding bond lengths reported in the literature.[29] The structure of **4** consists of parallel one-dimensional sinusoidal chains with a period of 25.604(4) Å (Figure 4b), with the 4,4′-trimethylenebipyridine ligand in a GG′ conformation. It is noteworthy that the GG′ conformation of 4,4′-trimethylenebipyridine in **4** is different from the TT conformation found in the 1-D polymer Ag(4,4′-trimethylenebipyridine)(CF$_3$SO$_3$)·EtOH,[12] although both adopt a sinusoidal chain structure resulting in two sets of parallel Cu(hfacac)$_2$ planes in **4** with a dihedral angle of ∼60°. In **4**, no interpolymer hydrogen-bonding interactions were found.

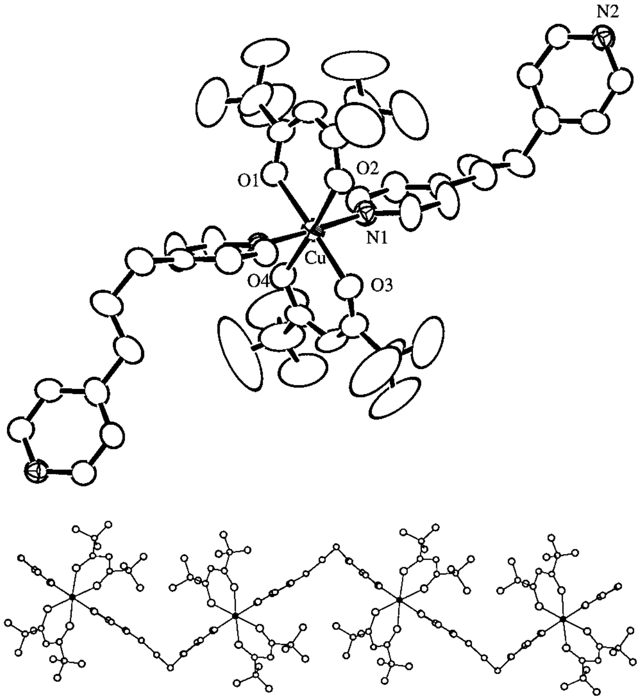

Figure 4. (a, top) Copper coordination environment in **4**. Displacement ellipsoids shown at the 50% probability level. (b, bottom) One-dimensional sinusoidal chain in **4**. Hydrogen atoms are omitted for clarity.

Thermal Analysis. Compounds **1** and **2** were heated to 250 °C, while **3** and **4** were heated to 400 and 650 °C, respectively, in a helium atmosphere. For **1**, TGA shows that the first weight loss of 13.1%, occurring from 60 to 136 °C, corresponds to the loss of the one pyrazine ligand (calculated 12.6%). A second weight loss is observed from 137 to 200 °C, which is due to the complete sublimation of the product formed in the last step (Figure 5a). For compound **2**, two phase transitions (melting and sublimation) suggest that no decomposition took place during the whole process. Sublimation is complete (100% weight loss) by 188 °C (Figure 5a). The thermal behaviors of compounds **3** and **4**, on the other hand, are quite different from those of **1** and **2** (Figure 5b). For **3**, the loss of the coordinating 1,2-bis(4-pyridyl)ethane ligands and the decomposition of Cu(hfacac)$_2$ occur simultaneously. A single-step weight loss was observed between 200 and 300 °C, which is attributed to the release of the 1,2-bis(4-pyridyl)ethane ligand with CuO remaining as a black powder (observed 12.0%, calculated 12.1%). The decomposition temperature of **4** is almost the same as that of **3**. TGA shows a weight loss of 50.3% (calculated 49.6%) from 200 to 295 °C corresponding to the loss of one 4,4′-trimethylenebipydrine and of one hfacac chelating ligand *per* formula unit. Further weight loss is observed above 300 °C, and the

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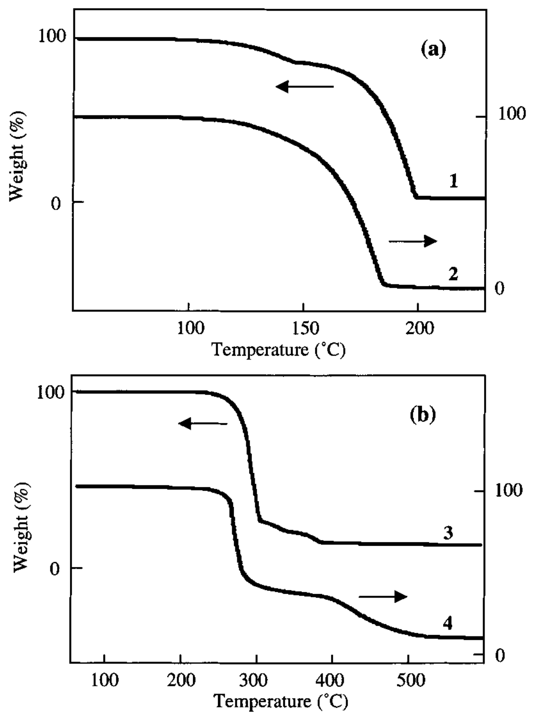

Figure 5. Thermogravimetric plots for **1**−**4**. In both (a) and (b), the arrows point to the weight percent scale that applies to each compound. Note the different temperature scales. (a) Molecular complexes **1** and **2**. The flat region above ca. 200 °C for both complexes corresponds to 100% weight loss, or complete sublimation. (b) Polymeric compounds **3** and **4**. Here the flat region above ca. 550 °C corresponds to decomposition to CuO.

final black powdery product is again CuO (observed 10.5%, calculated 10.8%).

Magnetic Properties. The magnetic susceptibilities of polycrystalline powders of compounds **1**−**4** have been measured from 2 to 300 K in a field of 5 kG. The plots of the inverse magnetic susceptibility versus temperature of all four compounds were found to be linear down to the lowest temperature measured. The data were fit to the Curie law.[36] The theoretical effective magnetic moment (μ_{theor}) for Cu(II) ions is 1.732, and the experimental effective magnetic moments (μ_{exp}) are 1.851 for **1**, 1.798 for **2**, 1.752 for **3**, and 1.794 for **4**, which are slightly higher than the theoretical value but nonetheless agree well with other experimentally observed effective magnetic moments for Cu(II).

Conclusions

Both discrete molecular complexes and extended polymeric structures were obtained from the reactions of Cu(hfacac)$_2$•H$_2$O with, in order of increasing ligand length, pyrazine, 3-cyanopyridine, 1,2-bis(4-pyridyl)ethane, and 4,4′-trimethylenebipyridine, in methylene chloride. Compounds **1** and **2** were isolated as molecular metal complexes, while compounds **3** and **4** were isolated as linear coordination polymer chains. However, the structures of compounds **1**−**4** all share a common feature: the unsaturated Cu(hfacac)$_2$ subunit, which can be conceived as forming the nucleus of each compound. This ···Cu(hfacac)$_2$··· moiety has four oxygen donors from the two hfacac ligands situated around the copper atom in a roughly square planar geometry. The O−Cu−O angles in all compounds deviate only slightly from the ideal value of 90°. The two remaining trans coordination sites on the Cu(hfacac)$_2$ fragment are occupied by two N-donor atoms from the four ligands mentioned above. For the systems reported herein, a general conclusion can be drawn that, for the same solvent and metal-to-ligand ratio (1:1), varying the length of the ligand attached to each ···Cu(hfacac)$_2$··· subunit is a major factor in determining the dimensionality of the final product. Pyrazine and 3-cyanopyridine have terminal N···N separations of 2.79 and 4.81 Å, respectively, and when the effect of the steric congestion around the copper due to the hfacac umbrella is added in, cannot readily join two metal centers. The ethyl- and propyl-spaced bipyridyl ligands have the two advantages of longer reach and flexibility (variable conformation), and although the nonrigid nature of these ligands precludes an easy estimation of ligand length, these features clearly facilitate the linkage of the metal centers. In the similar polymeric compound Cu(tfacac)$_2$(4,4′-bipyridyl),[29] the rigid 4,4′-bipyridyl spacer ligand has a terminal N···N separation of 7.12 Å, giving a rough estimation of a ligand length cutoff for the selection of either monomer or polymer.

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Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, anisotropic displacement parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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