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Copper and Bismuth Complexes Containing Dipyridyl *gem*-Diolato Ligands: $Bi^{III}_2[(2\text{-}Py)_2CO(OH)]_2(O_2CCF_3)_4(THF)_2$, $Cu^{II}[(2\text{-}Py)_2CO(OH)]_2(HO_2CCH_3)_2$, and $Cu^{II}_4[(2\text{-}Py)_2CO(OH)]_2(O_2CCH_3)_6(H_2O)_2$, a Ferromagnetically Coupled Tetranuclear Copper(II) Chain

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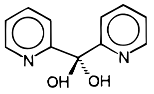
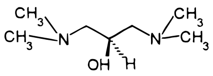
The reactions of the singly deprotonated di-2-pyridylmethanediol ligand ($dpmdH^-$) with copper(II) and bismuth(III) have been investigated. A new dinuclear bismuth(III) complex $Bi_2(dpmdH)_2(O_2CCF_3)_4(THF)_2$, **1**, has been obtained by the reaction of $BiPh_3$ with di-2-pyridyl ketone in the presence of HO_2CCF_3 in tetrahydrofuran (THF). The reaction of $Cu(OCH_3)_2$ with di-2-pyridyl ketone, H_2O, and acetic acid in a 1:2:2:2 ratio yielded a mononuclear complex $Cu[(2\text{-}Py)_2CO(OH)]_2(HO_2CCH_3)_2$, **2**, while the reaction of $Cu(OAC)_2(H_2O)$ with di-2-pyridyl ketone and acetic acid in a 2:1:1 ratio yielded a tetranuclear complex $Cu_4[(2\text{-}Py)_2CO(OH)]_2(O_2CCH_3)_6(H_2O)_2$, **3**. The structures of these complexes were determined by single-crystal X-ray diffraction analyses. Three different bonding modes of the $dpmdH^-$ ligand were observed in compounds **1**−**3**. In **2**, the $dpmdH^-$ ligand functions as a tridentate chelate to the copper center and forms a hydrogen bond between the OH group and the noncoordinating HO_2CCH_3 molecule. In **1** and **3**, the $dpmdH^-$ ligand functions as a bridging ligand to two metal centers through the oxygen atom. The two pyridyl groups of the $dpmdH^-$ ligand are bound to one bismuth(III) center in **1**, while in **3** they are bound two copper(II) centers, respectively. Compound **3** has an unusual one dimensional hydrogen bonded extended structure. The intramolecular magnetic interaction in **3** has been found to be dominated by ferromagnetism. Crystal data: **1**, $C_{38}H_{34}N_4O_{14}F_{12}Bi_2$, triclinic $P\bar{1}$, $a = 11.764(3)$ Å, $b = 11.949(3)$ Å, $c = 9.737(1)$ Å, $\alpha = 101.36(2)°$, $\beta = 105.64(2)°$, $\gamma = 63.79(2)°$, $Z = 1$; **2**, $C_{26}H_{26}N_4O_8Cu/CH_2Cl_2$, monoclinic $C2/c$, $a = 25.51(3)$ Å, $b = 7.861(7)$ Å, $c = 16.24(2)$ Å, $\beta = 113.08(9)°$, $Z = 4$; **3**, $C_{34}H_{40}N_4O_{18}Cu_4/CH_2Cl_2$, triclinic $P\bar{1}$, $a = 10.494(2)$ Å, $b = 13.885(2)$ Å, $c = 7.900(4)$ Å, $\alpha = 106.52(2)°$, $\beta = 90.85(3)°$, $\gamma = 94.12(1)°$, $Z = 1$.

Introduction

We have been interested in the coordination chemistry of bifunctional ligands with metal ions involved in ceramic superconductors such as copper, lanthanides, and bismuth. The bifunctional ligands employed by our group typically contain a neutral nitrogen coordination site and a negatively charged oxygen coordination site such as the 1,3-bis(dimethylamino)-2-propanolato ligand (bdmap) and deprotonated hydroxypyridines. We have demonstrated earlier that these bifunctional ligands are capable of bringing two different metal centers such as lanthanide(III) and copper(II) ions together.[1] We also demonstrated that polynuclear copper(II) complexes formed by these ligands display versatile structural features and interesting magnetic properties.[2] The lack of fully characterized Cu−Bi complexes with these ligands prompted us to explore the coordination chemistry of other bifunctional ligands such as the di-2-pyridylmethanediol ligand ($dpmdH_2$). In comparison with the bdmapH ligand, the $dpmdH_2$ ligand is more rigid with an extra coordinating site, the OH group. We have observed that the $dpmdH_2$ ligand forms complexes readily with copper(II) and bismuth(III) ions through several different bonding modes. More importantly, the singly deprotonated ligand $dpmdH^-$ has been found to promote ferromagnetic couplings between copper(II) centers, thus, opening a new avenue for the synthesis of molecular magnets. Several examples of coordination compounds involving simple diolato ligands were reported previously.[3,4] The coordination chemistry of diolato ligands containing additional coordinating atoms such as the $dpmdH_2$ ligand has, however, hardly been explored until recently.[4] We therefore report herein the syntheses and crystal structures of a dinuclear bismuth(III) complex, a mononuclear copper(II) complex, and a tetranuclear copper(II) complex containing the $dpmdH^-$ ligand, and the utility of the $dpmdH^-$ ligand in promoting the ferromagnetism and the three dimensional extended structure of the tetranuclear copper(II) complex.



$dpmdH_2$



bdmapH

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Experimental Section

All reactions were performed in Schlenk flasks under a nitrogen atmosphere. Solvents were reagent grade, distilled from appropriate drying agents under nitrogen prior to use. Copper methoxide, di-2-pyridyl ketone, and trifluoroacetic acid were purchased from Aldrich. Glacial acetic acid and copper(II) acetate monohydrate were purchased from BDH Co. Triphenylbismuth was obtained from Strem Chemicals, Inc. IR spectra were recorded on a Nicolet FTIR spectrometer. Thermogravimetric analyses were performed on a Perkin-Elmer TGA-7 analyzer. ^{1}H NMR spectra were recorded on a Brüker AC-300 spectrometer. Elemental analyses were performed at Canadian Microanalytical Service, Ltd, Delta, BC. The EPR experiments were performed on a Brüker ESP-300E at the X-band frequency (9426 MHz). Magnetic susceptibility data were collected at 0.01 T on a SQUID instrument from Quantum Design. A magnetic field calibration was done using a lead sphere.

Synthesis of $Bi_2(dpmdH)_2(O_2CCF_3)_4(THF)_2$ (1) Triphenylbismuth (200 mg, 0.45 mmol) was dissolved in 15 mL of tetrahydrofuran (THF). Trifluoroacetic acid (0.14 mL, 1.87 mmol) was then added to the solution. After being stirred for 1 h at 23 °C, 83 mg (0.45 mmol) of di-2-pyridyl ketone was added. After an additional hour of stirring, the solution was concentrated to approximately 10 mL and 3 mL of hexane was added to crystallize the product. Colorless crystals of **1** were obtained (148 mg, 0.10 mmol, yield 46%); mp 135 °C. Anal. Calcd for $C_{38}H_{34}N_4O_{14}F_{12}Bi_2$: C, 32.18; H, 2.40; N, 3.95. Found: C, 31.79; H, 2.09; N, 3.81. ^{1}H NMR (acetone-d_6, d, ppm, 298 K): 7.63 (m,1H), 7.70 (m, 1H), 8.02 (m, 1H), 8.13 (m, 3 H), 8.75 (m, 1H), 8.91 (m , 1H), pyridyl; 3.63 (m, 4 H, THF); 1.80 (m, 4 H, THF). IR (KBr, cm^{-1}): 1016 m, 1093 w, 1139 s, 1202 vs, 1270 w, 1279 w, 1298 w, 1384 w, 1437 m, 1600 m, 1670 vs.

Synthesis of $Cu[(2\text{-}Py)_2CO(OH)]_2(HO_2CCH_3)_2/CH_2Cl_2$ (2). In a 100 mL Schlenk flask di-2-pyridyl ketone (200 mg, 1.08 mmol), water (20 mg, 1.08 mmol), acetic acid (65 mg, 1.08 mmol), and 10 mL of dichloromethane were combined and stirred for approximately 2 h at 23 °C. $Cu(OCH_3)_2$ (68 mg, 0.54 mmol) was then added, and the mixture was stirred for an additional 1 h. The blue solution was concentrated to approximately 7 mL and was cooled to 0 °C to crystallize the product. The violet crystals of compound **2** were obtained (87 mg, 0.13 mmol, yield 24%); mp 90 °C. Anal. Calcd for $C_{27}H_{28}O_8N_4CuCl_2$: C, 48.33; H, 4.21; N, 8.35%. Found: C, 48.48; H, 4.45; N, 8.36%. IR (KBr, cm^{-1}): 1033 m, 1160 w, 1223 w, 1310 w, 1426 m, 1578 m, 1604 m, 1686 w. When subjected to a high vaccum, compound **2** changes color to blue. The elemental analysis for the residue, after compound **2** was pumped for 48 h under 0.05 Torr of pressure, is consistent with the formula of $Cu(dpmdH)_2(HO_2CCH_3)/0.5CH_2Cl_2$ (Calcd: C, 51.76; H, 4.08; N, 9.86. Found: C, 51.73; H, 3.91; N, 9.76.).

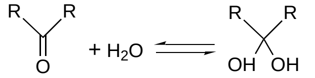
Synthesis of $Cu_4[(2\text{-}Py)_2CO(OH)]_2(O_2CCH_3)_6(H_2O)_2/CH_2Cl_2$ (3). Di-2-pyridyl ketone (46 mg, 0.25 mmol), $Cu(O_2CCH_3)_2H_2O$ (100 mg, 0.50 mmol), and acetic acid (15 mg, 0.25 mmol) were stirred in 10 mL of dichloromethane for approximately 20 h at 23 °C. The blue solution was concentrated to approximately 5 mL and cooled to 0 °C to crystallize the product. The blue crystals of compound **3** were obtained (83 mg, 0.15 mmol; yield 58%); mp 220 °C (dec). Anal. Calcd for $C_{35}H_{42}O_{18}N_4Cu_4Cl_2$: C, 37.14; H, 3.74; N, 4.95%. Found: C, 37.63; H, 3.63; N, 4.96%. IR (KBr, cm^{-1}): 1045m, 1071 m, 1236 w, 1319 m, 1381 m, 1423 s, 1549 vs, 1630 s.

X-ray Diffraction Analysis. The violet crystals of compound **2** and the blue crystals of compound **3** were obtained from concentrated CH_2Cl_2 solutions, while the colorless crystals of **1** were obtained from a THF/hexane solution. The crystals were mounted on glass fibres and sealed with epoxy glue. Data were collected over the range $3 < 2\theta < 50°$ for **2** and **3** and $3 < 2\theta < 45°$ for compound **1** on a Rigaku AFC6-S diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å), operated at 50 kV and 35 mA. Unit cell constants and the orientation matrices for the data collection were obtained from a least-squares refinement using the setting angles of 20 reflections ($8 < 2\theta < 15°$) for compound **1,** 11 centered reflections ($6.5 < 2\theta < 12°$) for **2**, and 14 reflections ($32 < 2\theta < 37°$) for **3**, and located by the SEARCH routine. Three standard reflections were measured every 150 reflections. At the end of data collection, no significant decay of intensity was observed for compounds **1** and **3**, while compound **2** lost about 24% of its original intensity due to the loss of CH_2Cl_2. Data were processed on a Silicon Graphics computer using the TEXSAN crystallographic software package[5] and corrected for decay and Lorentz$^-$polarization effects. An empirical absorption correction based on azimuthal scans of several reflections was applied to all crystals, which resulted in transmission factors ranging from 0.43 to 1.00 for **1**, from 0.90 to 1.00 for **2**, and from 0.93 to 1.00 for **3**. Extinction corrections were not applied.

The crystals of **1** and **3** belong to the triclinic space group $P\bar{1}$. The systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) of compound **2** agree with both *C2/c* and *Cc*. The statistical analysis of intensity distribution and the successful structural solution and refinement determined that the correct space group of **2** is *C2/c*. The structures of **1** and **3** were solved by heavy-atom Patterson methods, while the structure of **2** was solved by direct methods. Full-matrix least-squares refinements were applied. Neutral atom scattering factors were taken from Cromer and Waber.[6] In the crystal lattices of compounds **2** and **3**, a disordered CH_2Cl_2 solvent molecule was located. The CH_2Cl_2 solvent molecule in both compounds is disordered over two sites related by an inversion center. Due to the limited number of reflections, this disorder could not be fully modeled. One of the carbon atoms of the THF molecule in **1** displays a 50%/50% disorder over two sites which were modeled and refined successfully. All CF_3 groups in **1** display a C_2 rotational disorder. Two sets of fluorine atoms for each CF_3 group were located, and each set was refined successfully with a 50% occupancy factor. The positions of acidic protons in **2** and **3** determined directly from the difference Fourier maps were not refined. The remaining hydrogen atomic positions except those bonded to the disordered solvent molecules and the OH protons in **1** were calculated and their contribution in structural-factor calculations was included. Bismuth, oxygen, nitrogen, and most of the carbon atoms in **1** were refined anisotropically. Copper, chlorine, and some of the oxygen atoms in **2** were refined anisotropically. All non-hydrogen atoms except the dichloromethane carbon atom in **3** were refined anisotropically. Due to the limited data, disordered fluorine atoms in **3** were refined isotropically only. The largest residual peak in the final difference Fourier map is 2.21 e$^-$Å^{-3} in **1** (1.05 Å away from the bismuth atom), 0.49 e$^-$Å^{-3} in **2**, and 0.55 e$^-$Å^{-3} in **3**. The imperfect absorption correction and the disorder of the CF_3 and THF groups in **1** are likely to be responsible for the relatively high *R* factors and the goodness of fit indicator. Compound **2** forms very thin plate crystals which display severe twining and low diffraction intensity and decay rapidly by losing the solvent molecule, accountable for the low data and parameter ratio and the quality of the data. The data of crystallographic analyses are listed in Table 1.

Results and Discussion

Syntheses and Structures. It has been well-established that ketones can undergo a reversible addition reaction with H_2O to form diols (eq 1).[7] In organic solvents and neutral conditions,



(1)

the hydration equilibrium goes to the left for most ketones except for those containing highly electron-withdrawing groups. However, in the presence of acid or base, ketones can undergo the hydration process rapidly, forming diols. A protonated ketone intermediate is believed to be responsible for the acid-catalyzed process. The diol ligand, di-2-pyridylmethanediol ($dpmdH_2$), forms readily in the presence of acid such as acetic acid or trifluoroacetic acid. The $dpmdH_2$ ligand and its deprotonated

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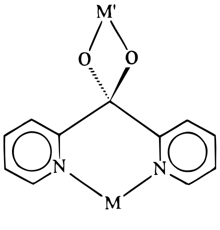
Table 1. Crystallographic Data

formula	$C_{38}H_{34}N_4O_{14}F_{12}Bi_2$	$C_{26}H_{26}O_8N_4Cu/CH_2Cl_2$	$C_{34}H_{40}O_{18}N_4Cu_4/CH_2Cl_2$
fw	1416.65	671.00	1131.82
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	11.764(3)	25.51(3)	10.494(2)
b/Å	11.949(3)	7.861(7)	13.885(2)
c/Å	9.737(1)	16.24(2)	7.900(4)
α/deg	101.36(2)	90	106.52(2)
β/deg	105.64(2)	113.08(9)	90.85(3)
γ/deg	63.79(2)	90	94.12(1)
V/Å^3	1177.8(5)	2996(6)	1100.0(6)
Z	1	4	1
D_c/(g cm^{-3})	2.00	1.49	1.71
T/°C	23	23	23
μ(Mo Kα)/cm^{-1}	75.6	9.61	21.1
R^a	0.075	0.064	0.043
$R_w{}^b$	0.070	0.055	0.034

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)^{-1/2}$, $w = 1/\sigma^2(F_o)$.

forms, $dpmdH^-$ and $dpmd^{2-}$, can bind to the metal ion via either the nitrogen or the oxygen atom. One possible bonding mode for the $dpmd^{2-}$ ligand is shown in diagram A, where the M and M′ could be two different metal ions such as copper(II) and bismuth(III). We therefore anticipated that it may be possible to synthesize bimetallic Cu−Bi complexes by using the $dpmdH_2$ molecule. The reactions of the $dpmdH_2$ ligand with a variety of bismuth and copper compounds under different conditions did not, however, yield any mixed metal complexes. Instead, several interesting homonuclear copper and bismuth compounds were isolated which can also be obtained by independent synthesis.



A

$Bi_2(dpmdH)_2(O_2CCF_3)_4(THF)_2$ (1). In the synthesis of compound **1**, 4 equiv of HO_2CCF_3 per $BiPh_3$ were used, three for the removal of the phenyl groups and one for reacting with the di-2-pyridyl ketone to form the diol ligand. The trifluoroacetic acid was also the source of the H_2O molecule involved in the reaction. The $dpmdH_2$ is believed to form *in situ* and react subsequently with the Bi(III) ion, producing product **1**. Compound **1** is a colorless crystalline material and stable for months under air in the solid state. The composition of **1** was established to be $Bi_2(dmpdH)_2(O_2CCF_3)_4(THF)_2$ by elemental and single-crystal X-ray diffraction analyses. An ORTEP diagram showing the molecular structure of **1** is given in Figure 1. Selected bond lengths and angles are given in Table 2.

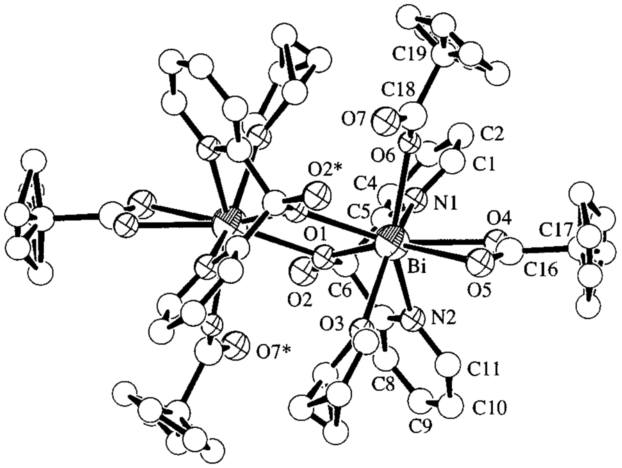


Figure 1. ORTEP diagram showing the molecular structure of compound **1** with labeling scheme. For clarity purpose, all atoms are shown as ideal spheres.

Compound **1** has an inversion center. The $dpmdH^-$ ligand in **1** functions not only as a tridentate chelating ligand but also as a bridging ligand. The two Bi(III) ions are linked together by two oxygen atoms of the two $dpmdH^-$ ligands with the Bi−Bi* separation being 3.993(2) Å. The two pyridyl groups of the $dpmdH^-$ ligand are bonded to one Bi(III) center with the Bi-N(1) and Bi-N(2) distances being 2.44(2) and 2.43(2) Å, respectively. These Bi−N distances are much shorter than those of $Bi-NMe_2$ in[8] $Bi_2(bdmap)_2(O_2CCH_3)_4(H_2O)$ (bdmap = 1,3-bis(dimethylamino)-2-propanolato) which are greater than 2.80 Å, reflecting the relatively higher affinity of the Bi(III) center towards a pyridyl group than a dimethylamino group. In addition, we have observed that in dinuclear or polynuclear metal complexes the two amino groups of the bdmap ligand are always bound to two metal centers[1,2] and no chelating modes such as the one displayed by the $dpmdH^-$ ligand in **1** have been observed for the bdmap ligand. These bonding differences of the bdmap and the $dpmdH^-$ ligands towards the bismuth(III) ion can be attributed to both electronic and steric factors. Each bismuth center is also coordinated by two trifluoroacetate ligands, one of which is bound to the Bi(III) ion through both oxygen atoms (Bi−O(4) = 2.50(2) Å, Bi−O(5) = 2.88(2) Å) and the other is bound to the Bi(III) center through one oxygen atom only (Bi−O(6) = 2.48(2) Å). The uncoordinated oxygen atom of the trifluoroacetate ligand forms a strong intramolecular hydrogen bond[9] with the OH group of the $dpmdH^-$ ligand, as evidenced by the short O(7)−O(2*) distance of 2.49(4) Å. A disordered THF solvent molecule also coordinates to the Bi(III) center with a normal bond length[10] (Bi−O(3) = 2.53(2) Å). Bismuth complexes containing alkoxo ligands have attracted much attention recently because of their potential applications in ceramic superconductors.[11] The synthesis and practical

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Table 2. Selected Bond Lengths (Å) and Angles (deg)

(a) Compound **1**

Bi−O(1)	2.20(1)	Bi−O(1′)	2.53(1)	Bi−O(3)	2.53(2)	Bi−O(4)	2.50(2)
Bi−O(5)	2.88(2)	Bi−O(6)	2.48(2)	Bi−N(1)	2.44(2)	Bi−N(2)	2.43(2)
O(1)−C(6)	1.38(2)	O(2)−O(7′)	2.49(4)	O(2)−C(6)	1.41(2)	O(3)−C(12)	1.49(3)
O(3)−C(15)	1.49(3)	O(4)−C(16)	1.12(3)	O(5)−C(16)	1.21(3)	O(6)−C(18)	1.15(3)
O(7)−C(18)	1.26(4)	N(1)−C(1)	1.31(3)	N(1)−C(5)	1.33(3)	N(2)−C(7)	1.31(3)
N(2)−C(11)	1.39(3)	C(1)−C(2)	1.40(4)	C(2)−C(3)	1.34(4)	C(3)−C(4)	1.38(4)
C(4)−C(5)	1.40(3)	C(5)−C(6)	1.47(3)	C(6)−C(7)	1.56(3)	C(7)−C(8)	1.41(3)
C(8)−C(9)	1.34(3)	C(9)−C(10)	1.29(3)	C(10)−C(11)	1.34(4)	C(16)−C(17)	1.73(4)
C(18)−C(19)	1.68(8)						

O(1)−Bi−O(1′)	65.1(6)	O(6)−Bi−N(2)	143.2(6)	O(1)−Bi−O(3)	88.4(6)	N(1)−Bi−N(2)	74.0(7)
O(1)−Bi−O(4)	135.4(5)	O(1)−Bi−O(5)	161.1(9)	O(1)−Bi−O(6)	113.0(7)	O(1)−Bi−N(1)	69.8(6)
O(1)−Bi−N(2)	67.6(6)	O(1′)−Bi−O(3)	82.2(6)	O(1′)−Bi−O(4)	155.7(6)	O(1′)−Bi−O(5)	121.5(7)
O(1′)−Bi−O(6)	78.8(6)	O(1′)−Bi−N(1)	109.4(6)	O(1′)−Bi−N(2)	127.1(6)	O(3)−Bi−O(4)	107.8(7)
O(3)−Bi−O(5)	75.9(8)	O(3)−Bi−O(6)	141.3(6)	O(3)−Bi−N(1)	146.2(6)	O(3)−Bi−N(2)	73.9(6)
O(4)−Bi−O(5)	44.9(6)	O(4)−Bi−O(6)	80.0(7)	O(4)−Bi−N(1)	74.9(6)	O(4)−Bi−N(2)	77.2(7)
O(5)−Bi−O(6)	86(1)	O(5)−Bi−N(1)	118.8(8)	O(5)−Bi−N(2)	98(1)	O(6)−Bi−N(1)	72.4(7)
Bi−O(1)−Bi′	114.9(6)	N(1)−C(1)−C(2)	123(3)	C(1)−C(2)−C(3)	116(3)	C(2)−C(3)−C(4)	122(3)
C(3)−C(4)−C(5)	119(3)	N(1)−C(5)−C(4)	118(3)	N(1)−C(5)−C(6)	113(2)	C(4)−C(5)−C(6)	128(2)
O(1)−C(6)−O(2)	112(2)	O(1)−C(6)−C(5)	113(2)	O(1)−C(6)−C(7)	104(2)	O(2)−C(6)−C(5)	110(2)
O(2)−C(6)−C(7)	111(2)	N(2)−C(7)−C(6)	113(2)	C(5)−C(6)−C(7)	107(2)	N(2)−C(11)−C(10)	123(3)
N(2)−C(7)−C(8)	123(3)	C(12)−O(3)−C(15)	105(2)	C(6)−C(7)−C(8)	123(2)	C(7)−C(8)−C(9)	116(2)
C(8)−C(9)−C(10)	124(3)	C(9)−C(10)−C(11)	118(3)	O(6)−C(18)−O(7)	128(4)	O(5)−C(16)−C(17)	114(3)
O(6)−C(18)−C(19)	115(3)	O(4)−C(16)−O(5)	127(3)	O(7)−C(18)−C(19)	115(4)	O(4)−C(16)−C(17)	119(3)

(b) Compound **2**

Cu−O(1)	2.367(8)	N(1)−C(5)	1.36(1)	Cu−N(1)	2.00(1)	N(2)−C(7)	1.32(1)
Cu−N(2)	2.03(1)	N(2)−C(11)	1.32(2)	C(1)−C(2)	1.35(2)	C(2)−C(3)	1.34(2)
C(3)−C(4)	1.39(2)	C(4)−C(5)	1.37(2)	C(5)−C(6)	1.51(2)	C(6)−C(7)	1.49(2)
C(7)−C(8)	1.43(2)	C(8)−C(9)	1.33(2)	O(1)−C(6)	1.44(2)	C(9)−C(10)	1.38(2)
O(2)−C(6)	1.42(1)	C(10)−C(11)	1.45(2)	O(3)−C(12)	1.21(2)	C(12)−C(13)	1.52(2)
O(4)−C(12)	1.26(2)	N(1)−C(1)	1.36(2)				

O(1)−Cu−O(1′)	180.00	N(1)−C(1)−C(2)	122(1)	O(1)−Cu−N(1)	77.3(4)	C(1)−C(2)−C(3)	121(2)
O(1)−Cu−N(1′)	102.7(4)	C(2)−C(3)−C(4)	119(2)	O(1)−Cu−N(2)	74.5(4)	C(3)−C(4)−C(5)	120(1)
O(1)−Cu−N(2′)	105.5(4)	N(1)−C(5)−C(4)	121(1)	N(1)−Cu−N(1′)	180.0	N(1)−C(5)−C(6)	113(1)
N(1)−Cu−N(2)	88.6(4)	C(4)−C(5)−C(6)	126(1)	N(1)−Cu−N(2′)	91.4(4)	O(1)−C(6)−O(2)	110(1)
N(2)−Cu−N(2′)	180.0	O(1)−C(6)−C(5)	109(1)	Cu−O(1)−C(6)	91.3(7)	O(1)−C(6)−C(7)	107(1)
O(2)−C(6)−C(5)	111(1)	O(2)−C(6)−C(7)	109(1)	C(5)−C(6)−C(7)	110(1)	N(2)−C(7)−C(6)	114(1)
N(2)−C(7)−C(8)	120(1)	C(6)−C(7)−C(8)	126(1)	C(7)−C(8)−C(9)	120(1)	C(8)−C(9)−C(10)	121(1)
C(9)−C(10)−C(11)	117(1)	N(2)−C(11)−C(10)	120(1)	O(3)−C(12)−O(4)	127(2)	O(3)−C(12)−C(13)	120(2)
C(1)−N(1)−C(5)	118(1)	O(4)−C(12)−C(13)	113(2)	Cl(1)−C(14)−Cl(2)	119(4)	C(7)−N(2)−C(11)	122(1)

(c) Compound **3**

Cu(1)−O(1)	1.964(4)	O(7)−C(16)	1.253(8)	Cu(1)−O(4)	1.952(5)	O(8)−C(16)	1.230(8)
Cu(1)−O(6)	2.277(5)	N(1)−C(7)	1.345(7)	Cu(1)−O(7)	1.946(4)	N(1)−C(11)	1.354(8)
Cu(1)−N(2)	1.991(6)	N(2)−C(1)	1.356(8)	Cu(2)−O(1)	1.938(4)	N(2)−C(5)	1.325(8)
Cu(2)−O(3)	1.940(4)	C(1)−C(2)	1.38(1)	Cu(2)−O(5′)	2.258(4)	C(2)−C(3)	1.37(1)
Cu(2)−O(5′)	1.974(4)	C(3)−C(4)	1.37(1)	Cu(2)−N(1)	1.995(5)	C(4)−C(5)	1.389(9)
C(5)−C(6)	1.545(9)	C(6)−C(7)	1.524(8)	C(7)−C(8)	1.375(9)	C(8)−C(9)	1.38(1)
O(1)−C(6)	1.400(7)	C(9)−C(10)	1.36(1)	O(2)−C(6)	1.415(7)	C(10)−C(11)	1.358(9)
O(3)−C(12)	1.248(8)	C(12)−C(13)	1.508(9)	O(4)−C(12)	1.265(8)	C(14)−C(15)	1.501(9)
O(5)−C(14)	1.276(7)	C(16)−C(17)	1.52(1)	O(6)−C(14)	1.231(7)		

O(1)−Cu(1)−O(4)	91.8(2)	Cu(1)−O(1)−Cu(2)	108.4(2)	O(1)−Cu(1)−O(6)	105.2(2)	O(1)−Cu(1)−O(7)	165.9(2)
O(1)−Cu(1)−N(2)	81.0(2)	O(4)−Cu(1)−O(6)	99.3(2)	O(4)−Cu(1)−O(7)	89.8(2)	Cu(2)−O(5)−Cu(2)	102.2(2)
O(4)−Cu(1)−N(2)	172.0(2)	O(6)−Cu(1)−O(7)	88.4(2)	O(6)−Cu(1)−N(2)	86.0(2)	O(7)−Cu(1)−N(2)	96.4(2)
O(1)−Cu(2)−O(3)	92.6(2)	O(1)−Cu(2)−O(5)	108.9(2)	O(1)−Cu(2)−O(5)	172.4(2)	O(1)−Cu(2)−N(1)	82.2(2)
O(3)−Cu(2)−O(5)	96.2(2)	O(3)−Cu(2)−O(5′)	90.3(2)	O(3)−Cu(2)−N(1)	162.2(2)	N(2)−C(1)−C(2)	121.5(7)
O(5)−Cu(2)−O(5′)	77.8(2)	C(1)−C(2)−C(3)	118.8(8)	O(5)−Cu(2)−N(1)	101.7(2)	C(2)−C(3)−C(4)	119.8(7)
O(5)−Cu(2)−N(1)	92.9(2)	C(3)−C(4)−C(5)	119.2(7)	N(2)−C(5)−C(4)	121.3(7)	N(2)−C(5)−C(6)	114.6(6)
C(4)−C(5)−C(6)	124.0(6)	O(1)−C(6)−O(2)	112.2(5)	O(1)−C(6)−C(5)	108.6(5)	O(1)−C(6)−C(7)	109.8(5)
O(2)−C(6)−C(5)	108.6(5)	O(2)−C(6)−C(7)	106.2(5)	C(5)−C(6)−C(7)	111.6(5)	N(1)−C(7)−C(6)	114.2(6)
N(1)−C(7)−C(8)	122.3(6)	C(6)−C(7)−C(8)	123.5(6)	C(7)−C(8)−C(9)	118.7(7)	C(8)−C(9)−C(10)	119.6(7)
C(9)−C(10)−C(11)	118.6(7)	N(1)−C(11)−C(10)	123.5(7)	O(3)−C(12)−O(4)	125.4(7)	O(3)−C(12)−C(13)	117.4(7)
O(4)−C(12)−C(13)	117.1(6)	O(5)−C(14)−O(6)	123.1(7)	O(5)−C(14)−C(15)	117.2(6)	O(6)−C(14)−C(15)	119.7(6)
O(7)−C(16)−O(8)	125.6(7)	O(7)−C(16)−C(17)	115.3(7)	O(8)−C(16)−C(17)	119.0(7)		

applications of bismuth alkoxides are still quite challenging due to their high sensitivity toward moisture. As a consequence only a few bismuth complexes containing alkoxo ligands are known.[11] In contrast to other THF coordinated Bi(III) complexes and alkoxo Bi(III) complexes reported earlier, compound **1** is surprisingly stable under air after isolation from the solution. No crystal decay due to the loss of THF was observed. The high stability of this complex can be attributed to the coordination saturation surrounding the bismuth center and the crystal lattice packing force. Upon dissolving in a non-THF solvent, compound **1** does lose the THF molecule as indicated by variable temperature ^{1}H NMR investigation. The chemical shifts of the THF ligand in the spectra of compound **1** in acetone-d_6 are the same as those of the free THF solvent molecule in the temperature range 200−298 K. The fact that more than four proton resonances due to the pyridyl group were observed lead

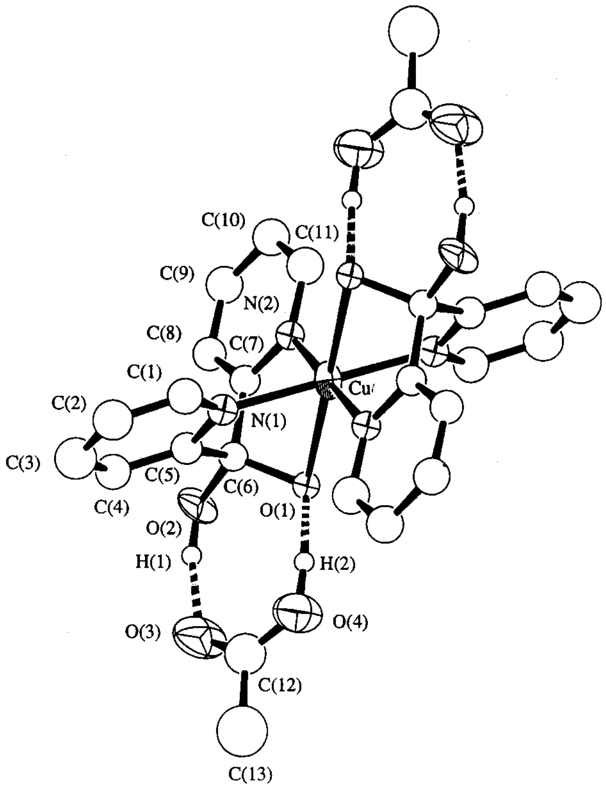

Figure 2. ORTEP diagram showing the molecular structure of compound **2** with labeling scheme and 50% thermal ellipsoids.

us to suggest that compound **1** retains its dinuclear structure in solution where the two pyridyl groups of the dpmdH$^-$ ligand have distinctly different environments.

Cu[(2-Py)$_2$CO(OH)]$_2$(HO$_2$CCH$_3$)$_2$ (2). Compound **2** can be obtained from the reaction of Cu(OCH$_3$)$_2$ with 2 equiv of di-2-pyridyl ketone, water, and acetic acid in CH$_2$Cl$_2$ as violet crystals. Elemental analysis and single-crystal X-ray diffraction experiments established that compound **2** is a mononuclear complex with two dpmdH$^-$ ligands coordinated to the copper(II) center. Selected bond lengths and angles are listed in Table 2b. An ORTEP diagram showing the molecular structure of **2** is given in Figure 2.

Compound **2** has an inversion center. The dpmdH$^-$ ligand is coordinated to the copper center as a tridentate chelate via two nitrogen and one oxygen atoms, as observed in **1**. The geometry of the copper(II) ion is an elongated octahedron with the two oxygen atoms occupying the axial positions (Cu$-$O(1) $=$ 2.367(8) Å). The chelating behavior of the dpmdH$^-$ ligand is in sharp contrast to that of the bdmap$^-$ ligand, which to date has been found to function as a bridging ligand only in copper(II) complexes.[2] The geometric difference between these two ligands is again believed to be responsible for their different binding patterns toward the copper(II) ion.

There are two noncoordinating acetic acid molecules attached to the copper(II) complex via the formation of two strong hydrogen bonds with the dpmdH$^-$ ligand, one between the OH group of the acetic acid and the coordinated oxygen atom of the dpmdH$^-$ ligand and the other between the oxygen of the acidic acid and the noncoordinating OH group of the dpmdH$^-$, as indicated by the distances of O(2)$-$O(3) (2.59(1) Å) and O(1)$-$O(4) (2.52(1) Å). In the crystal lattice the acetic acid molecules are lined up along the *c* axis, as shown in the unit cell packing diagram (Figure 3). The formation of the channels made of the CH$_2$Cl$_2$ solvent molecules and the acetic acid molecules in the crystal lattice of **2** could be accountable for the poor stability of the crystal. When subjected to a high vacuum, the solid of compound **2** changes color from violet to blue, which cannot be explained by the loss of the CH$_2$Cl$_2$ solvent molecule alone. An elemental analysis established that, in addition to the loss of some of the CH$_2$Cl$_2$ solvent molecules from the crystal lattice, compound **2** also loses acetic acid partially. We believe that the color change could be related to the rupture of hydrogen bonds, which in turn affects the energy levels of the oxygen lone pair electrons and the oxygen → copper charge transfer band, hence, the color of the complex. Similar effects by hydrogen bonds on the electronic structures of copper(II) complexes have been observed previously.[1d] Unfortunately, due to the lack of suitable crystals, we have not been able to establish the structure of the blue residue.

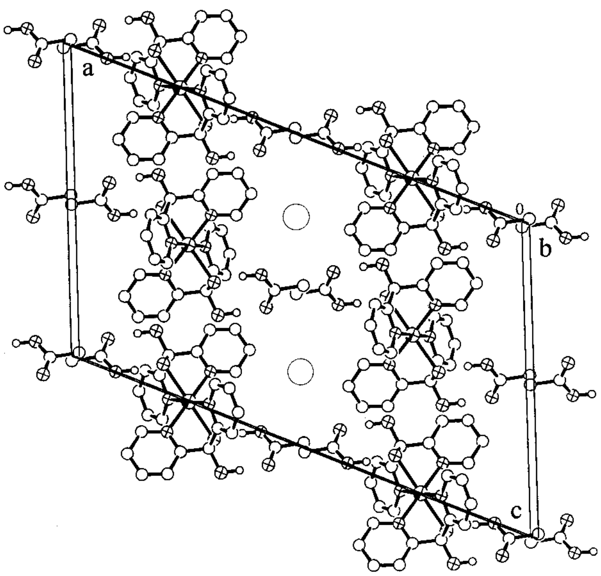

Figure 3. Unit cell packing diagram showing the locations of the acetic acid molecule and the CH$_2$Cl$_2$ solvent molecule (indicated by the empty circles in the diagram).

Compound **2** retains its structure in solution as confirmed by an EPR spectroscopic study. The EPR spectrum of **2** in CH$_2$Cl$_2$ at 77 K has a $g_{\parallel}$ peak ($g_{\parallel} = 2.25$) and a $g_{\perp}$ peak ($g_{\perp} = 2.05$), typical for a copper(II) ion with an axial symmetry.[12] The four peaks due to the coupling of the unpaired electron with the copper nucleus are well-resolved in the $g_{\parallel}$ region ($A_{\parallel} = 186$ [G]). The $g_{\perp}$ peak displays nine well-resolved peaks due to the coupling of the unpaired electron with the four identical nitrogen nuclei ($I = 1$). The hyperfine coupling constant, $A = 13$ G, is typical for the coupling of the unpaired electron centered on a copper(II) ion with a nitrogen atom.[12b]

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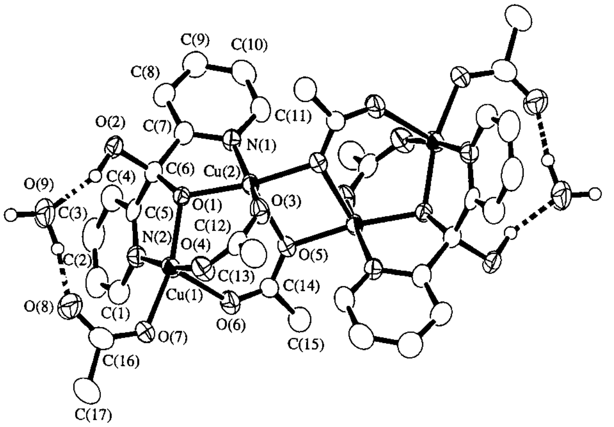


Figure 4. ORTEP diagram showing the molecular structure of compound **3** with 50% thermal ellipsoids and labeling scheme.

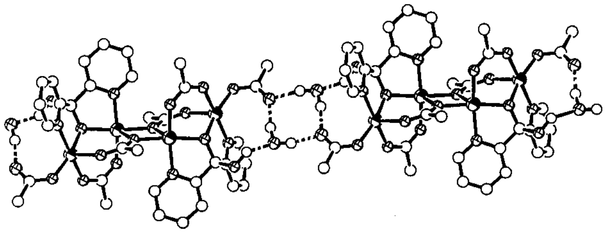
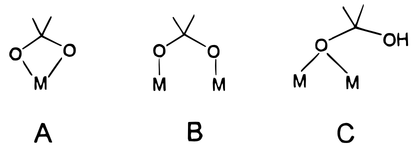


Figure 5. ORTEP diagram showing the intermolecular hydrogen bonds and the chain structure of **3**.

$Cu_4[(2\text{-}Py)_2CO(OH)]_2(O_2CCH_3)_6(H_2O)_2$ (3). Compound **3** can be obtained readily by the reaction of $Cu(O_2CCH_3)_2(H_2O)$ with di-2-pyridyl ketone and acetic acid in a 2:1:1 ratio in CH_2Cl_2. The composition and structure of this compound were established by elemental and X-ray diffraction analyses. Selected bond distances and angles are listed in Table 2c. An ORTEP diagram showing the molecular structure of **3** is given in Figure 4.

Compound **3** has four copper(II) ions in a zigzag arrangement. The molecule has an inversion center symmetry. In contrast to the structure of compound **2** where the dpmdH$^-$ ligand functions as a chelating ligand, the dpmdH$^-$ ligand in **3** functions as a bridging ligand to both Cu(1) and Cu(2) centers. Unlike in compound **1**, where the two pyridyl groups are bound to one metal center, the two pyridyl groups in **3** are bonded to two copper(II) ions, respectively. The Cu(1) and Cu(2) centers are also bridged by two acetate ligands and further linked to the other Cu(1)−Cu(2) dinculear unit via two oxygen atoms of the acetate ligands. The Cu(1)−Cu(2) and Cu(2)−Cu(2′) seperation distances are 3.165(1) and 3.299(2) Å, respectively. The geometry of Cu(1) and Cu(2) is a distorted square pyramid, as indicated by the bond angles of O(4)−Cu(1)−N(2) = 172.0(2)°, O(1)−Cu(1)−O(7) = 165.9(2)°, O(1)−Cu(2)−O(5′) = 172.4(2)°, O(3)−Cu(2)−N(1) = 162.2(2)°) with the O(5) and O(6) at the axial position (Cu(1)−O(6) = 2.277(5) Å, Cu(2)−O(5) = 2.258(4) Å). The two basal planes of the Cu(1) and Cu(2) centers are not coplanar with a dihedral angle of 120°. The bridging mode displayed by the dpmdH$^-$ ligand in **3** is similar to that of the bdmap ligand. The tetranuclear structure of **3** resembles that of $Cu_4(bdmap)_2(O_2CCH_3)_6(H_2O)_6$ reported earlier by our group.[13] However, in $Cu_4(bdmap)_2(O_2CCH_3)_6(H_2O)_6$, the two Cu(II) units bridged by the bdmap ligand are essentially coplanar. In fact, we have observed that the bdmap bridged dinuclear copper(II) units are usually coplanar in copper(II) bdmap complexes. The non-coplanar geometry produced by the dpmdH$^-$ ligand is obviously caused by the geometric constraint of the ligand.

Metal complexes containing *gem*-diolato ligands are not common. A few transition metal complexes containing the neutral dpmdH$_2$ ligand have been reported previously where the dpmdH$_2$ ligand chelates to the metal center through the nitrogen atoms only.[4] Several bonding modes are possible for the *gem*-diolato ligands $R_2CO_2^{2-}$. The chelating mode **A** and the bridging mode **B** have been observed.[3,4] The bridging mode **C** displayed by the dpmdH$^-$ ligand in compounds **1** and **3** resembles that displayed by $[(2\text{-}Py)_2C(O)(OMe)]^-$ reported[4c] recently by Kessissoglou *et al.*



The most interesting feature of compound **3** is the extended hydrogen bonded structure. There are two noncoordinating H_2O molecules in compound **3**, which forms two intramolecular hydrogen bonds with oxygen atom (O(8)) of an acetate ligand and the OH group (O(2)) of the dpmdH$^-$ ligand, as evidenced by the distances of O(9)−O(2) (2.667(7) Å) and O(9)−O(8) (2.754(8) Å). Further, the water molecule uses the remaining proton to form an intermolecular hydrogen bond with the O(8′) atom of the acetate (O(9)−O(8′) = 2.790(7) Å), linking the tetranuclear units together and resulting in the formation of an extended one dimensional structure (Figure 5). Similar hydrogen bonded networks involving acetate and H_2O molecules have been observed before.[13,15] As shown in Figure 6, the hydrogen bonded one dimensional chains in **3** are also completely stacked in the crystal lattice along the dimension (*c* axis) perpendicular to the chain with the interchain distance of 7.90 Å. Along the other dimension these chains are parallel to each other, and, thus, the tetranuclear copper(II) units achieve three dimensional structural ordering in the crystal lattice, a highly desired feature for polynuclear copper(II) complexes to achieve three dimensional ferromagnetism.[14]

Magnetic Properties of Compound 3. In order to establish the nature of the magnetic exchange in **3**, EPR and variable temperature magnetic susceptibility measurements were performed for compound **3**. No EPR signal was detected for the solid sample and the frozen solution of **3** at 77 K. The magnetic susceptibility data were collected over the temperature range of 2−300 K (Figure 7). The data were corrected for diamagnetism by using Pascal's constants.

Unlike the bdmap analogous compound $Cu_4(bdmap)_2(O_2CCH_3)_6(H_2O)_6$, which is an antiferromagnetism-dominated system[13] with the spin exchange constant *J* between the Cu(II) ions in the dinuclear unit being −85 cm^{-1}, compound **3** has been found to be a ferromagnetism dominated system. As shown in Figure 7 , the magnetic moment of compound **3** increases gradually with the decrease of temperature, suggesting a ferromagnetically coupled ground state.[16] Assuming that the *g* value is 2.20 (a typical value for a mononuclear copper(II) complex in a similar ligand environment), the magnetic moment (4.88 μ_B) of **3** at 2 K is significantly higher than four noninteracting copper(II) ions (3.81 μ_B), which lead us to believe that some degree of ferromagnetic interactions exist in this system. The data were further corrected according to

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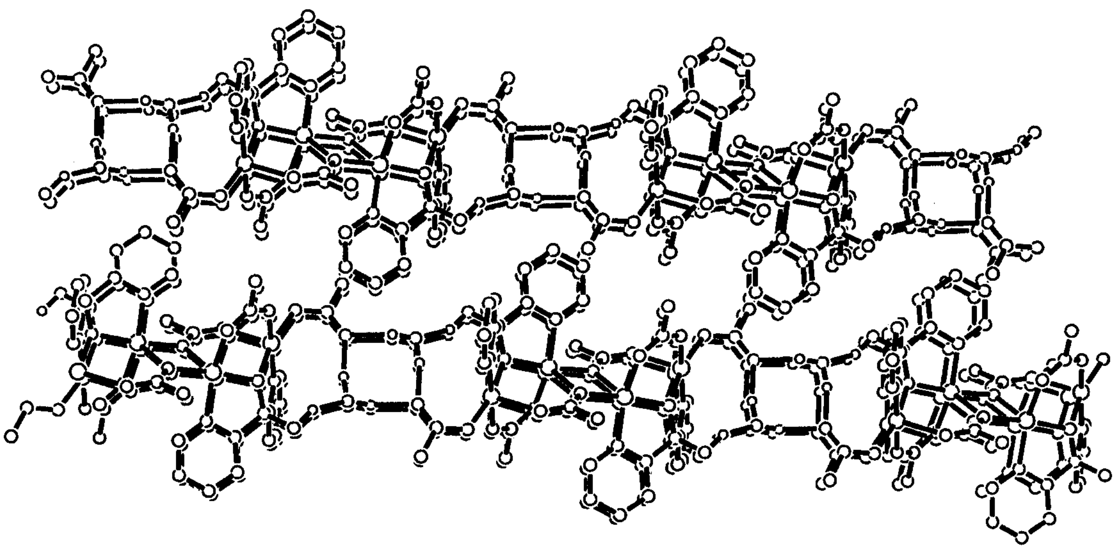

Figure 6. Diagram showing the stacking of the one dimensional chains along the *c* axis in **3**.

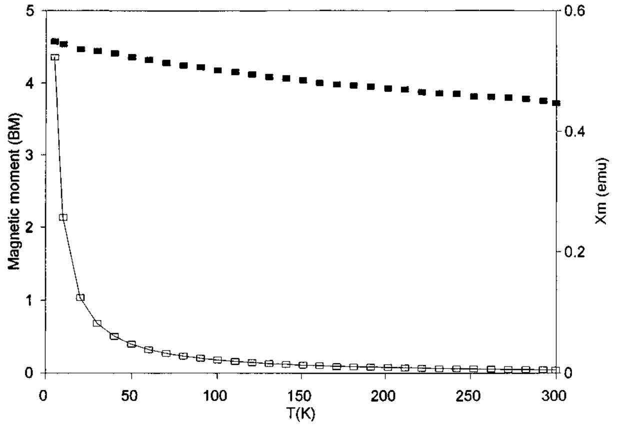

Figure 7. Plots of χ_M (open squares) and magnetic moment (μ_B) (filled squares) vs *T* (K). The solid line is the fitting.

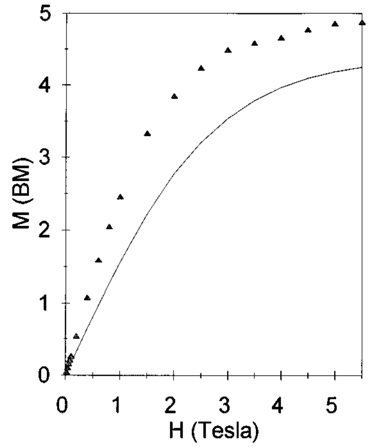

Figure 8. Plot of magnetisation *M* (μ_B) vs field *H* (T). The solid line is the plot of the Brillouin function for four noninteracting copper(II) ions with $g = 2.20$.

eq 3. Due to the inversion center symmetry of the tetramer, assuming $J_{12'} = J_{1'2} = 0$, $J_{11} = 0$, $J_{12} = J_{1'2'}$, the spin exchange Hamiltonian can be represented as $H = -2(2J_1S_1S_2 + J_2S_2S_{2'})$ where $J_1 = J_{12} = J_{1'2'}$, $J_2 = J_{22}$. The general susceptibility expression (2), as derived from the general van Vleck equation,[16]

$$\chi_{\mathrm{calc}} = 2Ng^2\beta^2[5\exp(-E_1/kT + \exp(-E_2/kT) + \exp(-E_3/kT) + \exp(-E_4/kT))]/\{kT[5\exp(-E_1/kT + 3\exp(-E_2/kT) + 3\exp(-E_3/kT) + 3\exp(-E_4/kT) + \exp(-E_5/kT) + \exp(-E_6/kT)])\} \quad (2)$$

was used for the calculation of χ_{calc} where $E_1 = (2J_1 - J_2)/2$, $E_2 = (2J_1 - J_2)/2$, $E_3 = -(J_2 + 2(J_1^2 + J_2^2)^{1/2})/2$, $E_4 = -(J_2 - 2(J_1^2 + J_2^2)^{1/2})/2$, $E_5 = (J_2 + 2J_1 + 2((J_2 - J_1)^2 + 3J_1^2)^{1/2})/2$, $E_6 = (J_2 + 2J_1 - 2((J_2 - J_1)^2 + 3J_1^2)^{1/2})/2$. Equation 3 was

$$\chi_{\mathrm{meas}} = (1 - \rho)\chi_{\mathrm{calc}} + \rho\chi_{\mathrm{mono}} + \chi_{\mathrm{Tip}} \quad (3)$$

used to fit the experimental data where Tip = temperature-independent paramagnetism and ρ = fraction of monomer impurity. The best fit yielded $J_1 = 17.70 \pm 0.3$ cm^{-1}, $J_2 = 0.95 \pm 0.05$ cm^{-1} ($R = 1.9\%$) with *g* value = 2.20, $\rho = 0.5\%$, and Tip = 0.000 06 (Figure 7).

To further confirm the ferromagnetism of compound **3**, the magnetisation of **3** at 2 K versus applied field (200 G to 55 KG) was measured (Figure 8). The saturation magnetic moment at 2 K is 4.88 μ_B. The magnetization curve of **3** lies above the curve of the Brillouin function[16a] for four noninteracting $S = {}^1/_2$ ions, further supporting the presence of significant intramolecular ferromagnetic interactions. The dramatic different magnetic behavior of compound **3** and the compound $Cu_4(bdmap)_2(O_2CCH_3)_6(H_2O)_6$ can be attributed to the structural difference between the bdmap$^-$ and dpmdH$^-$ ligands—the former promotes a planar dicopper unit, while the latter prefers a nonplanar dicopper structure.

Examples of ferromagnetically coupled molecular copper(II) complexes are abundant in literature.[4c,14] Long-range intermolecular spin exchanges in these previously reported complexes are, however, often to be antiferromagnetic, evident by the rapid decrease of magnetic moments at temperatures well above 2 K. For example, the intramolecular magnetic exchange in the $\{Cu_4[(2\text{-}Py)_2C(O)(OCH_3)]_2Cl_6\}_n$ compound has been found to be ferromagnetic, consistent with the behavior of **3**. At low temperature (<50 K), however, antiferromagnetism becomes dominant in the $\{Cu_4[(2\text{-}Py)_2C(O)(OCH_3)]_2Cl_6\}_n$ compound.[4c] In contrast, no long-range antiferromagnetic coupling is evident for compound **3** at 2 K. In fact, compound **3** achieves the highest magnetic moment at 2 K. The trend of the magnetic moment curve versus *T* appears to be consistent with the presence of a long-range ferromagnetic ordering below 2 K, which, unfortunately, could not be confirmed owing to the limitation of the instrument. Nevertheless, compound **3** demonstrates that the dpmdH$^-$ ligand is a good candidate for constructing molecular magnets consisting of copper(II) ions. Along with the acetate bridging ligand, the dpmdH$^-$ ligand can provide an intramolecular ferromagnetic exchange pathway, and by providing an intermolecular hydrogen bonding site, it can also promote a three dimensional structure and thus a possible intermolecular ferromagnetic exchange pathway. Further investigation on the ferromagnetic exchange mechanism of **3**, especially the role played by the dpmdH$^-$ ligand, and the syntheses of new polynuclear copper(II) complexes using the dpmdH$^-$ ligand and hydrogen bonds are currently in progress.

Thermal Decomposition. The thermal decomposition patterns of compounds **1**−**3** were examined by thermogravimetric analysis (TGA). All compounds were heated under an oxygen atmosphere at a rate of 10.0 °C/min. Compound **1** does not undergo any decomposition until approximately 120 °C. The first stage of weight loss (120−200 °C) is attributed to the loss of THF (theoretical weight loss 10.2%). There is an overlap of the first stage and the second stage weight loss. The sample achieves a steady residual weight (∼32%) after approximately 420 °C, which is consistent with the composition of Bi_2O_3 (32.9%). Compounds **2** and **3** undergo multiple-stages decomposition with substantial overlaps between the stages. The residue weight for compound **2** becomes constant (12%) after 390 °C which agrees with the formula of CuO (11.97%). The residue weight (29%) for compound **3** after 400 °C is consistent with the formula of Cu_2O_2 (29.76%).

Conclusion. Three bonding modes displayed by the dpmdH$^-$ ligand have been observed. The structures of metal complexes formed by the dpmdH$^-$ ligand are dramatically different than those involving the bdmap ligand. In contrast to the bdmap ligand which is known to promote antiferromagnetism, the dpmdH$^-$ ligand promotes intramolecular ferromagnetic couplings. The noncoordinating OH group of the dpmdH$^-$ ligand promotes the formation of an extended structure through hydrogen bonds.

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Supporting Information Available: Tables of crystal data, complete lists of atomic coordinates, isotropic and anisotropic thermal parameters, bond lengths, and bond angles (24 pages). Ordering information is given on any current masthead page.

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