

Copper(II) Coordination Polymers Assembled from 2-[(Pyridin-3-ylmethyl)amino]ethanol: Structure and Magnetism

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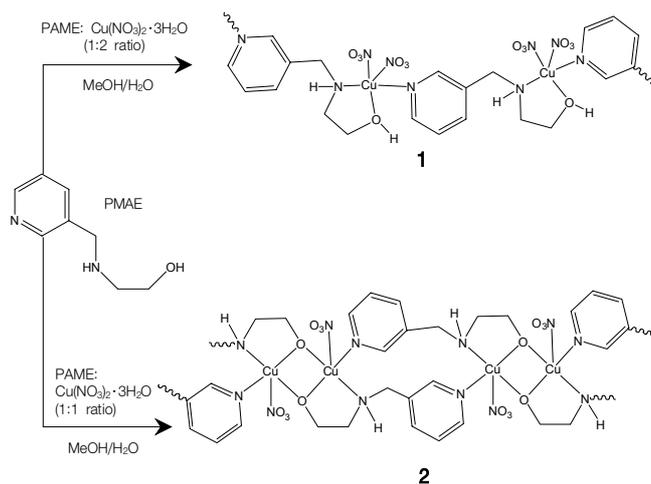
The one-dimensional coordination polymers, $[\text{Cu}^{\text{II}}(\text{L})(\text{NO}_3)_2]_n$ (**1**) and $\{[\text{Cu}^{\text{II}}(\text{L-H})(\text{NO}_3)] \cdot 2\text{H}_2\text{O}\}_{2n}$ (**2**), were synthesized from $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 2-[(pyridin-3-ylmethyl)amino]ethanol (L, PMAE) in methanol by controlling the molar ratio of copper(II) salt. Copper(II) ion in **1** has one pyridine group of PMAE whose an aminoethanol group coordinates adjacent copper(II) ion. As the pyridine group is bonded to neighboring copper(II) ion, **1** becomes a one-dimensional chain. Contrary to **1**, the structure of **2** shows that the oxygen atom of ethoxide group is bridged between two copper(II) ions, which forms a dinuclear complex. Additionally, the pyridine group of PMAE included one dinuclear unit is coordinated to the other dimeric one each other, which leads to a one-dimensional polymer. Due to the structural differences, **1** exhibits weak antiferromagnetic interaction, while **2** shows strong antiferromagnetic interaction. Due to direct spin exchange *via* oxygen of PMAE **2** has a much strong spin coupling than **1**.

Key Words: Copper(II) complex, Ligand, Coordination polymer, Crystal structure, Magnetic properties

Introduction

The construction of multi-dimensional coordination polymers *via* transition metal ions and organic building blocks is a rapidly growing area in chemistry. Coordination polymers with various frameworks, such as one-dimensional (1-D) chains and ladders,¹ two-dimensional (2-D) grids and honeycombs,² and three-dimensional (3-D) porous networks³ have been extensively studied. These polymeric compounds have been attracting much attention because of their potential applications for magnetic materials, ion exchange, luminescence, and gas storage.⁴

It has recognized that the metal centers and the counter-anions can play significant roles in the self-assembly, because they display a variety of features, *i.e.* geometry, charge, molecular shape, and size.⁵ For example, chiral coordination polymers and macrocycles are constructed from mercury(II) halides and binaphthyl-bis(amidopyridyl) ligands by self-assembly. In this case, the formation of polymers and macrocycles is attributed to the presence or absence of excess mercury(II) halide, through a template effect.^{6a} Furthermore, the molecular loops were synthesized from the reaction of *cis*-(PEt_3)₂Pt(OTf)₂ with bis(4-pyridyl)-functionalized free-base salen-type ligands *via* self-assembly. Due to the Zn(II)-metalation of the salen-type ligands, the molecular loops convert to molecular squares. By using bis(3-pyridyl)-functionalized free-base salen-type ligand, a concentration-dependent dynamic equilibrium between the cyclic species is also observed, in which the metalation of free-base ligand shifted the equilibrium to the single dimeric species.^{6b} Very recently, a few silver(I) compounds with bis(4-pyridyl)dimethylsilane (PDS) are exhibited that the PDS:Ag(I) ratios of the products are dependent upon the nature of the polyatomic anions (NO_2^- , NO_3^- , PF_6^- , and CF_3SO_3^-), regardless of the molar ratio of reactants.⁷



Scheme 1

The use of organic ligands containing hydroxyl and pyridine groups is very useful for obtaining the desired coordination polymers, because the hydroxyl group is converted to the deprotonated alcohol (ethoxide) group easily *via* coordination to metal ion. Thus the ethoxide group can basically link two metal ions to form dimeric unit.⁸ Furthermore, the pyridine group can also be used to connect with metal ions to construct network structures. Finally we chose bifunctional 2-[(pyridin-3-ylmethyl)amino]ethanol (PMAE) ligand for self-assembly as organic building block. The molecular geometry and flexibility of multi-dentate PMAE can be induced interesting coordination framework structures. In this paper, in an effort to explore the role of the concentration of metal salt in the self-assembly, the reactions of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with PMAE were performed and characterized. Consequently, we have obtained new framework structures depending upon the molar ratio of copper(II) salt (Scheme 1). Herein,

we report the synthesis, crystal structures, and magnetic properties of novel one-dimensional copper(II) coordination polymers, $[\text{Cu}^{\text{II}}(\text{C}_8\text{H}_{12}\text{N}_2\text{O})(\text{NO}_3)_2]_n$ (**1**) and $\{[\text{Cu}^{\text{II}}(\text{C}_8\text{H}_{11}\text{N}_2\text{O})(\text{NO}_3)] \cdot 2\text{H}_2\text{O}\}_{2n}$ (**2**), whose topology and dimensionality are dependent upon the molar ratio of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$.

Experimental Section

Materials and Measurements. All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. 2-[(Pyridin-3-ylmethyl)amino]ethanol (PMAE, $\text{C}_8\text{H}_{12}\text{N}_2\text{O}$, L) was prepared by a literature method.⁹ Infrared spectra were recorded with a ThermoFisher Scientific IR200 FT-IR spectrometer ($\pm 1 \text{ cm}^{-1}$). Elemental analyses were performed by the analytical laboratory of Kyungpook National University. Magnetic susceptibilities were measured in an applied field of 1000 Oe between 2 and 300 K on a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. Diamagnetic corrections were made by using Pascal's constants (147.35 (**1**) and 150.35×10^{-6} (**2**) emu/mol).

Preparation of $[\text{Cu}^{\text{II}}(\text{L})(\text{NO}_3)_2]_n$ (1**).** To a MeOH solution (10 mL) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (316 mg, 1.308 mmol) was added dropwise a MeOH/ H_2O mixture solution (v/v, 8:2, 10 mL) of 2-[(pyridin-3-ylmethyl)amino]ethanol (L, 100 mg, 0.654 mmol), and the color became dark blue, and the solution was stirred for 30 min at room temperature. The solution was allowed to stand at room temperature until dark blue microcrystals of **1** formed, these were filtered off, washed with methanol, and dried in air. Yield: 170 mg (77%). IR (KBr): 3260, 3204, 3062, 2966, 2897, 2766, 1615, 1462, 1385, 1312, 1021, 810, 707 cm^{-1} . Anal. Calcd for $\text{C}_8\text{H}_{12}\text{CuN}_4\text{O}_7$: C, 28.28; H, 3.56; N 16.49. Found: C, 28.72; H, 3.57; N, 16.41.

Preparation of $\{[\text{Cu}^{\text{II}}(\text{L-H})(\text{NO}_3)] \cdot 2\text{H}_2\text{O}\}_{2n}$ (2**).** To a MeOH solution (10 mL) of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (158 mg, 0.654 mmol) was added dropwise a MeOH/ H_2O mixture solution (v/v, 8:2, 10 mL) of 2-[(pyridin-3-ylmethyl)amino]ethanol (L, 100 mg, 0.654 mmol), and the color became dark green, and the solution was stirred for 30 min at room temperature. The solution was allowed to stand at room temperature until dark green microcrystals of **2** formed, these were filtered off, washed with methanol, and dried in air. Yield: 68 mg (34%). IR (KBr): 3400, 3215, 3162, 3048, 2958, 2917, 2857, 1646, 1613, 1384, 1066, 806, 707 cm^{-1} . Anal. Calcd for $\text{C}_8\text{H}_{15}\text{CuN}_3\text{O}_6$: C, 30.72; H, 4.83; N, 13.43. Found: C, 30.89; H, 4.77; N, 13.40.

X-ray Crystallographic Data Collection and Refinement.

Single crystals of **1** and **2** were mounted on a Bruker SMART APEX CCD-based diffractometer (Korea Basic Science Institute, Chonju Branch). X-ray data for **1** and **2** were collected at 293(2) K and using Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$, graphite monochromator). The raw data were processed to give structure factors using the Bruker SAINT program and corrected for Lorentz and polarization effects.¹⁰ No absorption corrections were applied. The crystal structures were solved by direct methods,¹¹ and refined by full-matrix least-squares refinement using the SHELXL97 computer program.¹² All

Table 1. Crystal Data and Structure Refinement for **1** and **2**

Compound	1	2
Empirical formula	$\text{C}_8\text{H}_{12}\text{CuN}_4\text{O}_7$	$\text{C}_8\text{H}_{15}\text{CuN}_3\text{O}_6$
Formula weight	339.76	312.77
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$C2/c$
$a, \text{ \AA}$	10.7320(6)	15.0906(16)
$b, \text{ \AA}$	7.6759(4)	13.9216(14)
$c, \text{ \AA}$	15.0672(8)	13.7673(14)
$\beta, \text{ deg}$	103.090(1)	121.30(2)
$V, \text{ \AA}^3$	1208.95(11)	2471.4(4)
Z	4	8
$d_{\text{calc}} (\text{g cm}^{-3})$	1.867	1.681
$\lambda, \text{ \AA}$	0.71073	0.71073
$T, \text{ K}$	293(2)	293(2)
$\mu, \text{ mm}^{-1}$	1.848	1.792
$F(000)$	692	1288
Reflections collected	8666	9048
Independent reflections	2987	3067
Reflections with $I > 2\sigma(I)$	1926	1759
Goodness-of-fit on F^2	1.148	1.124
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0455,$ $wR_2 = 0.0832$	$R_1 = 0.0779,$ $wR_2 = 0.2080$
R indices (all data)	$R_1 = 0.0938,$ $wR_2 = 0.1382$	$R_1 = 0.1172,$ $wR_2 = 0.2625$

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad wR_2(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Table 2. Selected Bond Distances (\AA) and Angles ($^\circ$) for **1**

Cu1-N1	2.021(4)	Cu1-N2	1.981(5)
Cu1-O1	1.992(4)	Cu1-O2	2.281(4)
Cu1-O5	1.976(4)	N3-O2	1.252(6)
N3-O3	1.222(5)	N3-O4	1.275(6)
N4-O5	1.279(6)	N4-O6	1.242(6)
N4-O7	1.214(6)	C1-O1	1.420(7)
N1-Cu1-N2	169.27(18)	N1-Cu1-O1	82.28(16)
N1-Cu1-O2	100.09(17)	N1-Cu1-O5	92.35(16)
N2-Cu1-O1	91.42(17)	N2-Cu1-O2	88.24(16)
N2-Cu1-O5	94.05(17)	O1-Cu1-O2	87.40(17)
O1-Cu1-O5	174.52(16)	O2-Cu1-O5	92.46(16)
O2-N3-O3	122.4(5)	O2-N3-O4	117.1(5)
O3-N3-O4	120.4(5)	O5-N4-O6	118.5(4)
O5-N4-O7	119.9(5)	O6-N4-O7	121.6(5)

Table 3. Selected Bond Distances (\AA) and Angles ($^\circ$) for **2**

Cu1-N1	2.035(5)	Cu1-N2	2.014(5)
Cu1-O1	1.912(5)	Cu1-O1 ⁱ	1.944(5)
Cu1-O2	2.344(6)	Cu1...Cu1 ⁱ	2.962(1)
C1-O1	1.412(7)	O2-N3	1.255(15)
O1-Cu1-N1	84.1(2)	O1-Cu1-N2	176.6(2)
O1-Cu1-O1 ⁱ	79.6(2)	O1-Cu1-O2	92.7(3)
O1-Cu1-Cu1 ⁱ	40.2(2)	N1-Cu1-O2	97.7(2)
N1-Cu1-N2	98.4(2)	N2-Cu1-O2	89.3(2)
Cu1-O1-Cu1 ⁱ	100.4(2)	N3-O2-Cu1	118.5(14)

Symmetry transformations used to generate equivalent atoms: (i) $-x+1, -y, -z+2$.

non-hydrogen atoms were refined anisotropically. All hydrogen atoms were positioned geometrically and refined using a riding model. Due to disorder, the two noncoordinated oxygen atoms of nitrate anion and two water molecules for **2** were treated with the SQUEEZE routine in the program PLATON¹³ and omitted from the final refinements, but are included in the computation of intensive properties. The crystallographic data and the result of refinements are summarized in Table 1.

Results and Discussion

Synthesis and Characterization. The reaction of PMAE with $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ in 1:2 and 1:1 ratios in MeOH/ H_2O affords the polymeric compounds, $[\text{Cu}^{\text{II}}(\text{L})(\text{NO}_3)_2]_n$ (**1**) and $\{[\text{Cu}^{\text{II}}(\text{L}-\text{H})(\text{NO}_3)] \cdot 2\text{H}_2\text{O}\}_{2n}$ (**2**) in good yield, respectively. Generally, the hydrolysis of hydroxyalkyl group occurs *via* coordination to metal ions under mild conditions.⁸ Interestingly, two one-dimensional coordination polymers **1** and **2** have been obtained from the different ratios of PMAE and copper(II) ion. That is, **1** is formed in a 1:2 ratio (PMAE/copper) and has the hydroxyl group of PMAE intact, while **2** is obtained in a 1:1 ratio and shows the deprotonated oxygen atom bridged between the copper(II) ions in a dimeric unit. This can be attributed to the increased acidity of the reaction solution for the self-assembly of **1**, due to the hydrolysis by excess copper(II) salt. Additionally, the excess amount of nitrate anions can help to crystallize in **1** without the deprotonation of PMAE as two nitrate anions bind to one copper(II) ion. The compositions of **1** and **2** were determined by elemental analysis, infrared, and X-ray diffraction. The IR spectrum (KBr pellet) of **1** shows ν_{OH} of the PMAE ligand at 3260 cm^{-1} and ν_{NH} of the PMAE at 3204 cm^{-1} . The IR spectrum (KBr pellet) of **2** shows ν_{OH} of the water molecules at 3400 cm^{-1} and ν_{NH} of the PMAE at 3215 cm^{-1} . Unlike compound **1**, the hydroxyl group of the PMAE ligand in **2** is disappeared at around 3260 cm^{-1} . Both compounds display the coordinated nitrate anion peaks at 1385 and 1384 cm^{-1} , respectively.

X-ray Crystal Structure of 1. The polymeric structure of **1** is shown in Figure 1. In the structure, copper(II) ion is coordinated with a secondary nitrogen and a hydroxyl oxygen of a PMAE and two oxygen atoms of nitrate ions as well as a pyridine group of PMAE whose aminoethanol group bonds adjacent copper(II) ion. The Cu-N_{secondary} and Cu-N_{pyridine} bond distances are 2.021(4) and 1.981(5) Å, respectively. For the coordinated nitrate ions, two Cu-O bond distances are 1.976(4) and 2.281(4) Å, respectively. Furthermore, the Cu-O_{hydroxy} bond distance is 1.992(4) Å. The copper(II) ion is 0.069(2) Å out of the square-coordination N₂O₂ plane toward O2 atom. Thus, the coordination geometry around copper(II) ion can be best described as a distorted square pyramid. All PMAEs link two copper(II) ions because the pyridine group of the PMAE ligand included a copper(II) ion coordinates an adjacent copper(II) ion. Therefore, the structure of **1** becomes a one-dimensional zigzag coordination polymer, which extends parallel to the *c* axis. The separation of Cu···Cu within a chain is 7.763(1) Å (Figure 1). The shortest interchain Cu···Cu distance is 6.434(1) Å. In addition, the coordinated PMAE

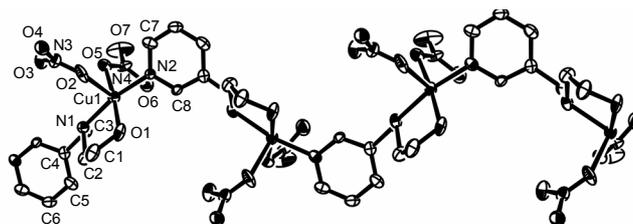


Figure 1. View of the polymeric structure of **1** showing the atom-labeling scheme and 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

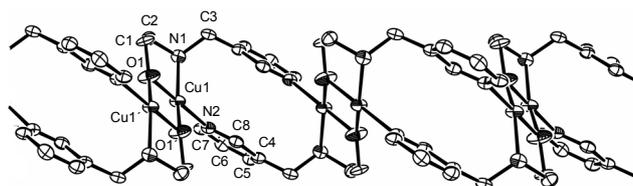


Figure 2. View of the polymeric structure of **2** showing the atom-labeling scheme and 30% thermal ellipsoids. Hydrogen atoms, water molecules and nitrate anions are omitted for clarity ($' = -x+1, -y, -z+2$).

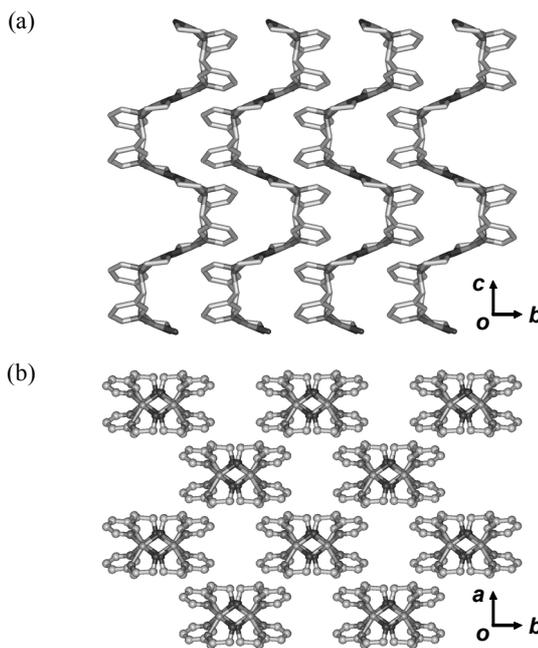


Figure 3. Perspective views of **2** showing offset face-to-face π - π interactions between the one-dimensional polymers: (a) 2-D and (b) 3-D.

ligand is involved in the hydrogen bonding interactions with nitrate ions: N1···O4(-x+2, -y, -z+2), 3.071(6) Å; \angle N1-H2-O4, 151° ; O1···O4(-x+2, y+1/2, -z+3/2), 2.746(5) Å; \angle O1-H1-O4, 175° . Due to the N-H···O and O-H···O hydrogen-bonding interactions,¹⁴ the framework structure of **1** forms a three-dimensional network (Figures S1-3).

X-ray Crystal Structure of 2. The polymeric structure of **2** is represented in Figure 2. In the structure, copper(II) ion is bonded with a secondary nitrogen and an ethoxide oxygen of

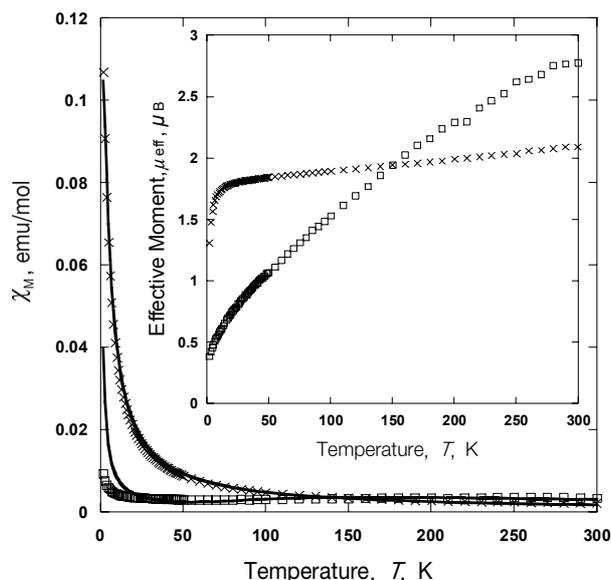


Figure 4. $\chi(T)$ for **1** (\times) and **2** (\square). The solid lines are the best-fit curves to eqs 1 and 2, respectively [Inset: $\mu_{\text{eff}}(T)$].

a PMAE and one oxygen atoms of nitrate ion as well as a pyridine ring of PMAE included a neighboring copper(II) ion. The Cu-N_{secondary} and Cu-N_{pyridine} bond distances are 2.035(5) and 2.014(5) Å, respectively. For the coordinated nitrate ion, one Cu-O bond distances is 2.344(6) Å. Furthermore, the Cu-O_{ethoxide} bond distances are 1.912(5) Å for O1 and 1.944(5) Å for O1'(-x+1, -y, -z+2), respectively. The copper(II) ion is 0.163(2) Å out of the square-coordination N₂O₂ plane toward O2 atom. Likewise **1**, the coordination geometry around copper(II) ion is described as a distorted square pyramid.

The square planar copper(II) centers are bridged equally by the oxygen atoms of ethoxide, which leads to a dinuclear unit. Furthermore, the pyridine group of PMAE included one dinuclear unit is coordinated to the other dimeric one each other, which gives rise to a one-dimensional wavelike chain (Figure 3a). The separations of Cu··Cu within a dimeric unit and between the dimeric moieties in a chain are 2.962(1) and 5.813(2) Å, respectively (Figure 2). The shortest interchain Cu··Cu distance is 7.415(1) Å. In the dimeric unit, the dihedral angle between the pyridine rings is $\theta = 18.1(4)^\circ$ and the interplanar separation between the pyridine rings is 3.04(1) – 3.87(1) Å as well as centroid separation is 3.506 Å. In addition to, between the inter-chains the dihedral angle of the pyridine rings is $\theta = 0.0^\circ$ and the interplanar separation between the pyridine rings is 3.48(1) – 3.50(1) Å as well as centroid separation is 3.601 Å. In case of **2**, due to the offset face-to-face π - π interactions,¹⁵ the structure becomes a three-dimensional network (Figure 3).

Magnetic Properties of 1 and 2. Variable-temperature 2–300 K magnetic susceptibility, χ , measurements on solid samples of **1** and **2** have been performed on a SQUID magnetometer (external field 1000 Oe). For compound **1**, at room temperature, the effective moment, $\mu_{\text{eff}} [= (8\chi T)^{1/2}]$, is 2.09 μ_B/Cu , and $\mu_{\text{eff}}(T)$ decreases monotonically with decreasing temperature to 1.79 μ_B at 20 K, and then rapidly decreases to 1.31 μ_B at 2 K, indicating the presence of a very weak anti-

ferromagnetic interaction within the one-dimensional (1-D) chain (Figure 4). $\chi(T)$ for **1** was fit to a numerical expression, eq 1, derived by Bonner and Fisher for a uniform $S = 1/2$ infinite chain model [$H = -J(\sum \mathbf{S}_i \cdot \mathbf{S}_{i+1})$].¹⁶ The best fit had J/k_B of -2.5 K (-1.74 cm^{-1}), $g = 2.25$, $\theta = -0.1$ K and the temperature independent paramagnetism, TIP = 60×10^{-6} emu/mol. The weak interaction can be attributed to a long distance between the neighboring copper(II) ions in the 1-D chain (7.763 Å).

$$\chi = [Ng^2\mu_B^2/k_B(T - \theta)]F(T) + \text{TIP} \quad (1)$$

where

$$F(T) = [0.25 + 0.074975(|J/k_B T|) + 0.075235(|J/k_B T|)^2] / [1 + 0.9931(|J/k_B T|) + 0.172135(|J/k_B T|)^2 + 0.757825(|J/k_B T|)^3]$$

Compound **2** has a room temperature the effective moment μ_{eff} of 2.77 μ_B/Cu_2 ; $\mu_{\text{eff}}(T)$ decreases gradually with a decrease in the temperature to 0.382 μ_B at 2 K (Figure 4), indicative of a strong antiferromagnetic interaction within the dimeric copper(II) unit in the 1-D chain. $\chi(T)$ for **2** was fit to an analytical expression, eq 2, derived by Bleaney and Bowers for a coupled $S = 1/2$ dimeric unit [$H = -2J(\mathbf{S}_1 \cdot \mathbf{S}_2)$].¹⁷

$$\chi = [Ng^2\mu_B^2/k_B(T - \theta)]F(T)(1-\rho) + (Ng^2\mu_B^2/2k_B T)\rho + \text{TIP} \quad (2)$$

$$\text{where } F(T) = [2\exp(2J/k_B T)] / [1 + 3\exp(2J/k_B T)]$$

The best fit had J/k_B of -145 K (-101 cm^{-1}), $g = 2.30$, $\theta = -2.5$ K, $\theta = 0.079$ and the temperature independent paramagnetism, TIP = 5.5×10^{-4} emu/mol. This coupling constant (J) is comparable to that of $[\text{Cu}(\text{EAEP})(\text{OH})_2(\text{ClO}_4)_2]$ ($J = -130 \text{ cm}^{-1}$), a related copper(II) complex with a hydroxo bridge (EAEP = 2-(2-ethylaminoethyl)pyridine).¹⁸ It is well known that the magnitude of coupling constants in oxygen-bridged copper(II) dimers is significantly correlated the O-Cu-O angle including planarity about the bridging oxygen atom, Cu··Cu distance, tetrahedral distortion of the N₂CuO₂ plane, and magnitude of axial interactions.^{8,18-19} The strong antiferromagnetic interaction is attributed to direct spin exchange *via* the bridged oxygen atoms within the copper(II) dimeric unit in the chain. This interaction is *ca.* 2 orders of magnitude stronger than the weak antiferromagnetic interaction (-2.5 K) between the copper(II) ions in **1**.

Conclusion

New copper(II) coordination polymers, $[\text{Cu}^{\text{II}}(\text{L})(\text{NO}_3)_2]_n$ (**1**) and $\{[\text{Cu}^{\text{II}}(\text{L}-\text{H})(\text{NO}_3)] \cdot 2\text{H}_2\text{O}\}_{2n}$ (**2**) have been prepared and characterized (L = 2-[(pyridin-3-ylmethyl)amino]ethanol, PMAE), in which their framework structures are dependent upon the molar ratio of copper(II) salt. Compound **1** becomes a one-dimensional zigzag chain which extends parallel to the *c* axis, while **2** shows that a dinuclear unit bridged with the oxygen atom of ethoxide group of PMAE is coordinated to the other dimeric one through the pyridine ring of PMAE, which leads to an alternative one-dimensional wavelike chain. Compound **1** shows weak antiferromagnetic coupling, while compound **2** shows strong antiferromagnetic coupling due to

direct spin exchange *via* the bridging oxygen atom of PMAE.

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Supporting Information. The crystal packing structures of **1** and **2** (Figures S1-4). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-720019 (for **1**) and CCDC-720020 (for **2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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