One-dimensional chains consisting of copper(II) ions and an orthogonal anthracene-pyrimidine derivative: hierarchical formation of high-dimensional networks and their magnetic properties†

Takayoshi Ezuhara,[a] Ken Endo,[a] Kenji Matsuda*[b] and Yasuhiro Aoyama*[a]

[a] *CREST, Japan Science and Technology Corporation, Institute for Fundamental Research of Organic Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan*

[b] *Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka, 812-8581, Japan*

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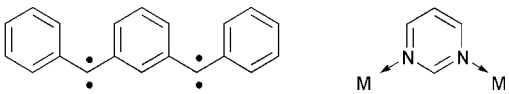
Recrystallization of 9-(5-pyrimidinyl)anthracene (**1**) with copper(II) nitrate trihydrate formed three kinds of complexes: $\mathbf{1}\cdot Cu(NO_3)_2\cdot H_2O$ (**2**), $\mathbf{1}\cdot Cu(NO_3)_2\cdot MeOH\cdot H_2O$ (**3**) and $\mathbf{1}\cdot Cu(NO_3)_2\cdot 2EtOH$ (**4**) by changing the recrystallization solvent. The crystal structure of the three complexes showed cooperation of metal coordination, hydrogen bonding, and aromatic stacking interactions in the hierarchical formation of one-, two- and three-dimensional networks. Complexes **2** and **3** formed zigzag one-dimensional chains consisting of **1** and Cu^{2+} ions by coordination of pyrimidine to Cu^{2+} ion in equatorial *trans* fashion. Complex **4** formed a spiral one-dimensional chain by coordination in equatorial *cis* fashion. The magnetic behavior of **2**, **3**, and **4** were measured on a SQUID susceptometer to reveal that there existed strong antiferromagnetic interactions between Cu^{2+} ions. The magnetic data of one-dimensional antiferromagnetic chains were analyzed by the Bonner–Fisher model. The antiferromagnetic interaction between Cu^{2+} ions was around -55 K, which is the largest value observed in pyrimidine-bridged Cu^{2+} ions.

Hydrogen bonding[1] and metal coordination[2] are extensively used to control crystal structures. Hydrogen bonding is an efficient way to make monovalent linkages *via* hydrogen atoms. On the other hand, metal coordination is multivalent, therefore this is a powerful tool to make highly ordered networks. By choosing the coordination number and the coordination direction of the metal ions, we can design and fabricate the desired high-dimensional structures. Moreover when metal-coordinated ligands form hydrogen bonds with each other, highly ordered networks are often constructed.[1a,3]

By aligning paramagnetic transition metal ions, molecule-based magnets can be formed.[4] The molecule-based magnet has its advantage in tunability. By changing the metal ions or network structures the magnetic properties of the whole crystal can be changed. For this reason, the fabrication of transition metal complexes by designed ligands is intriguing.

When pyrimidine coordinates to two transition metals, the topology of the two spins of the transition metal is analogous to *m*-phenylenedicarbene, in which all the spins in the molecule are aligned parallel (Scheme 1).[5] Therefore, the magnetic properties of transition metal complexes of pyrimidine have been extensively investigated.[6] Recently, we have shown that an anthracene-pyrimidine derivative, 9-(5-pyrimidinyl)anthracene (**1**), makes highly ordered structures with cadmium or cobalt ions.[2a,b] In this paper the complexation of **1** with Cu^{2+} ion and the structure and magnetic properties of the complex will be discussed.



Scheme 1 *m*-Phenylenedicarbene and metal-coordinating pyrimidine.

† This paper is dedicated to the late Prof. Olivier Kahn.

Results and discussion

Synthesis of complexes and crystal structure

Synthesis of the complexes was performed by recrystallization of **1** with $Cu(NO_3)_2\cdot 3H_2O$. By changing the recrystallization solvent, three kinds of complexes $\mathbf{1}\cdot Cu(NO_3)_2\cdot H_2O$ (**2**), $\mathbf{1}\cdot Cu(NO_3)_2\cdot MeOH\cdot H_2O$ (**3**) and $\mathbf{1}\cdot Cu(NO_3)_2\cdot 2EtOH$ (**4**) were obtained. The crystal structures were analyzed by X-ray crystallography. The crystallographic parameters are summarized in Table 1.

Complexes **2** and **3** have a zigzag one-dimensional chain, similar to that in the previously reported cadminum complex $\mathbf{1}\cdot Cd(NO_3)_2\cdot 2MeOH$.[2b] Complex **4** has a spiral one-dimensional chain, which is similar to $\mathbf{1}\cdot Co(NO_3)_2\cdot 2EtOH$.[2a] The crystal structures of the three complexes show the cooperation of metal coordination, hydrogen bonding, and aromatic stacking interactions in the hierarchical formation of one-, two- and three-dimensional networks.

Both nitrogen atoms in a pyrimidine ring coordinate to a Cu^{2+} ion. Fig. 1 shows the local geometry around the Cu^{2+} ions. **2** and **3** have a *trans* configuration and **4** has a *cis* configuration. For all three complexes the pyrimidine ligands coordinate in equatorial–equatorial fashion judging from the bond lengths, the two axial bonds are 0.2–0.5 Å longer than the equatorial bond lengths. This is a very important factor in the magnetic interaction and is discussed later. All the Cu^{2+}

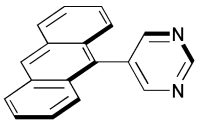


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Table 1 Crystallographic parameters for **2**, **3**, and **4**

	2	**3**	**4**
Formula	$C_{18}H_{14}CuN_4O_7$	$C_{19}H_{18}CuN_4O_8$	$C_{22}H_{24}CuN_4O_8$
Formula weight	461.88	493.92	536.00
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/c$	$Pbca$	$P2_1/n$
a/Å	11.972(2)	13.1(2)	13.734(4)
b/Å	11.775(1)	25.4(2)	7.248(3)
c/Å	13.022(2)	12.0(2)	22.423(3)
β/°	100.92(1)		95.75(2)
V/Å^3	1802.5(4)	3974(80)	2220(1)
Z	4	8	4
T/K	296	296	296
μ(Mo-Kα)/mm^{-1}	1.265	1.157	1.042
Meas./Indep. reflect.	4550/4351	5119/5118	5738/5514
R	0.043	0.046	0.045
Rw	0.057	0.068	0.079

ions and the pyrimidine ligands are linked *via* N–Cu^{2+}–N bridges. This leads to a pyrimidine–Cu^{2+} alternate copolymeric chain. Fig. 2 shows the structure of the pyrimidine–Cu^{2+} copolymeric chains. **2** and **3** make zigzag chains and **4** makes a spiral chain. The pitches l_p of the linear chains are 11.78, 11.78 and 7.25 Å for **2**, **3** and **4**, respectively.

The alignments of the pyrimidine–Cu^{2+} copolymeric chains to give sheets (Fig. 3) occur differently for the zigzag chains and spiral chains. **2** and **3** form two-dimensional sheets *via* interchain hydrogen bonding. Hydrogen bonds are formed between NO_3^- and H_2O (in **2**) or between NO_3^- and H_2O and MeOH (in **3**). The hydrogen bonding sites of the copper-pyrimidine chains of **2** and **3** are directed to the outsides of the chain. Therefore hydrogen bonding between chains is possible. The distances $l_{c\text{-}c}$ of the adjacent chains are 6.49 and 6.53 Å for **2** and **3**, respectively. On the other hand, **4** forms a spiral one-dimensional chain, and there is no hydrogen bonding between chains. The dominant interchain interaction in **4** is

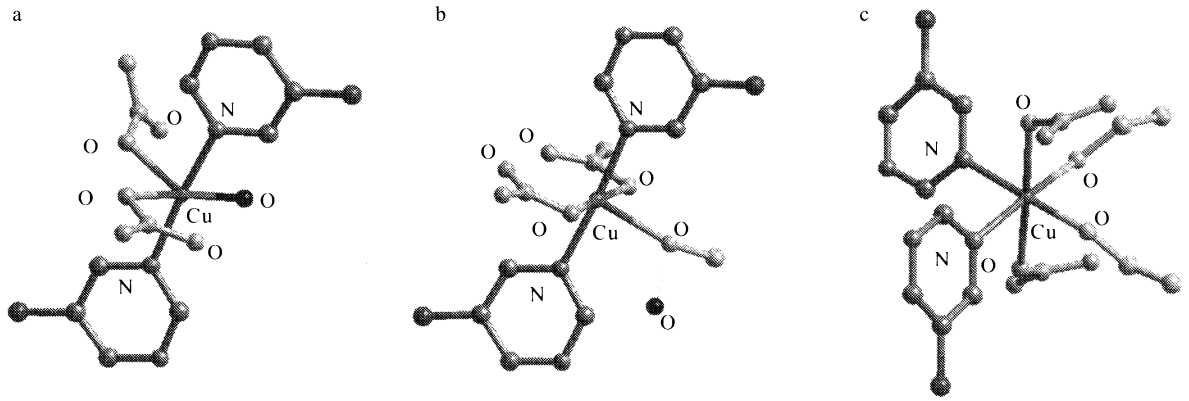

Fig. 1 Local geometry around Cu^{2+} of (*a*) **2**, (*b*) **3**, and (*c*) **4**.

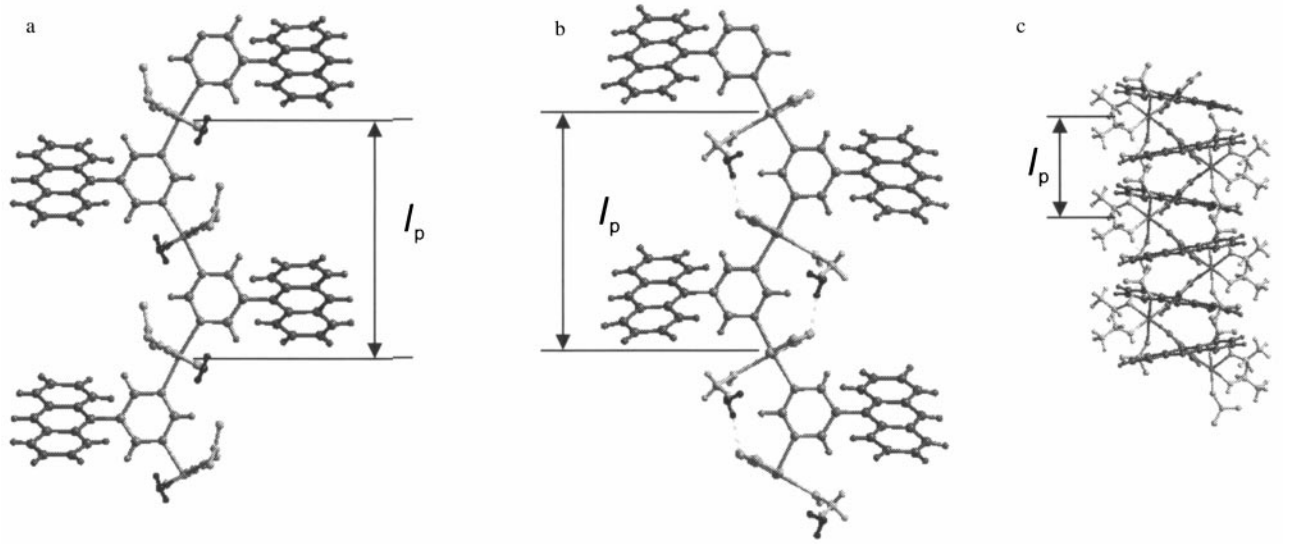

Fig. 2 Formation of pyrimidine–Cu^{2+} copolymeric chains of (*a*) **2**, (*b*) **3**, and (*c*) **4**.

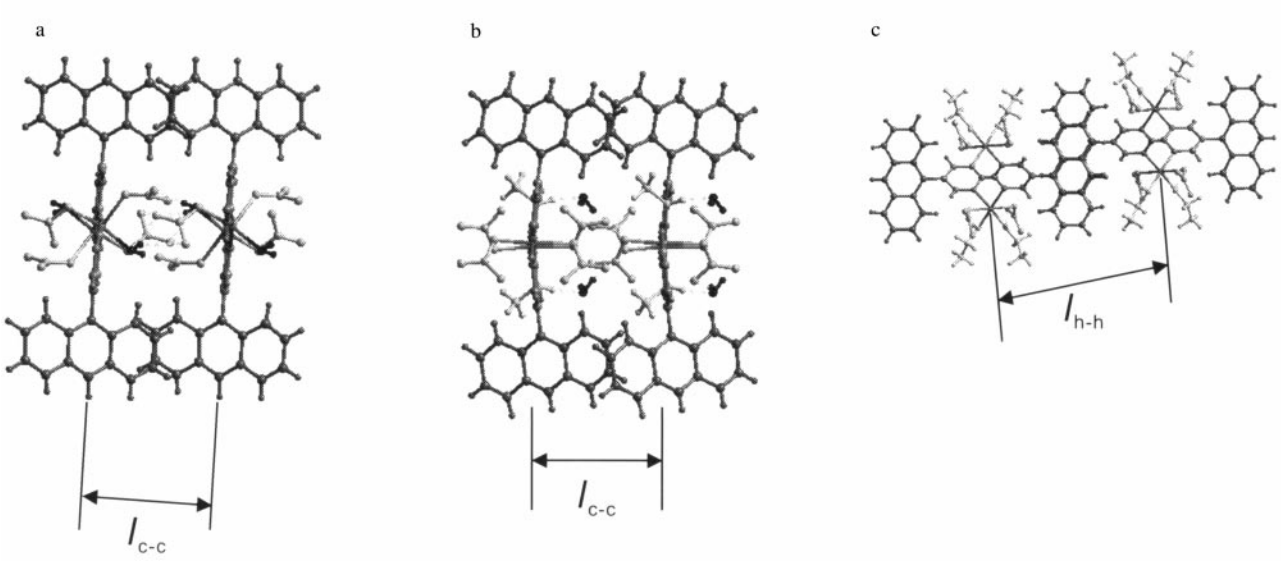

Fig. 3 Alignment of pyrimidine–Cu^{2+} copolymeric chains to give sheets of (*a*) **2**, (*b*) **3**, and (*c*) **4**.

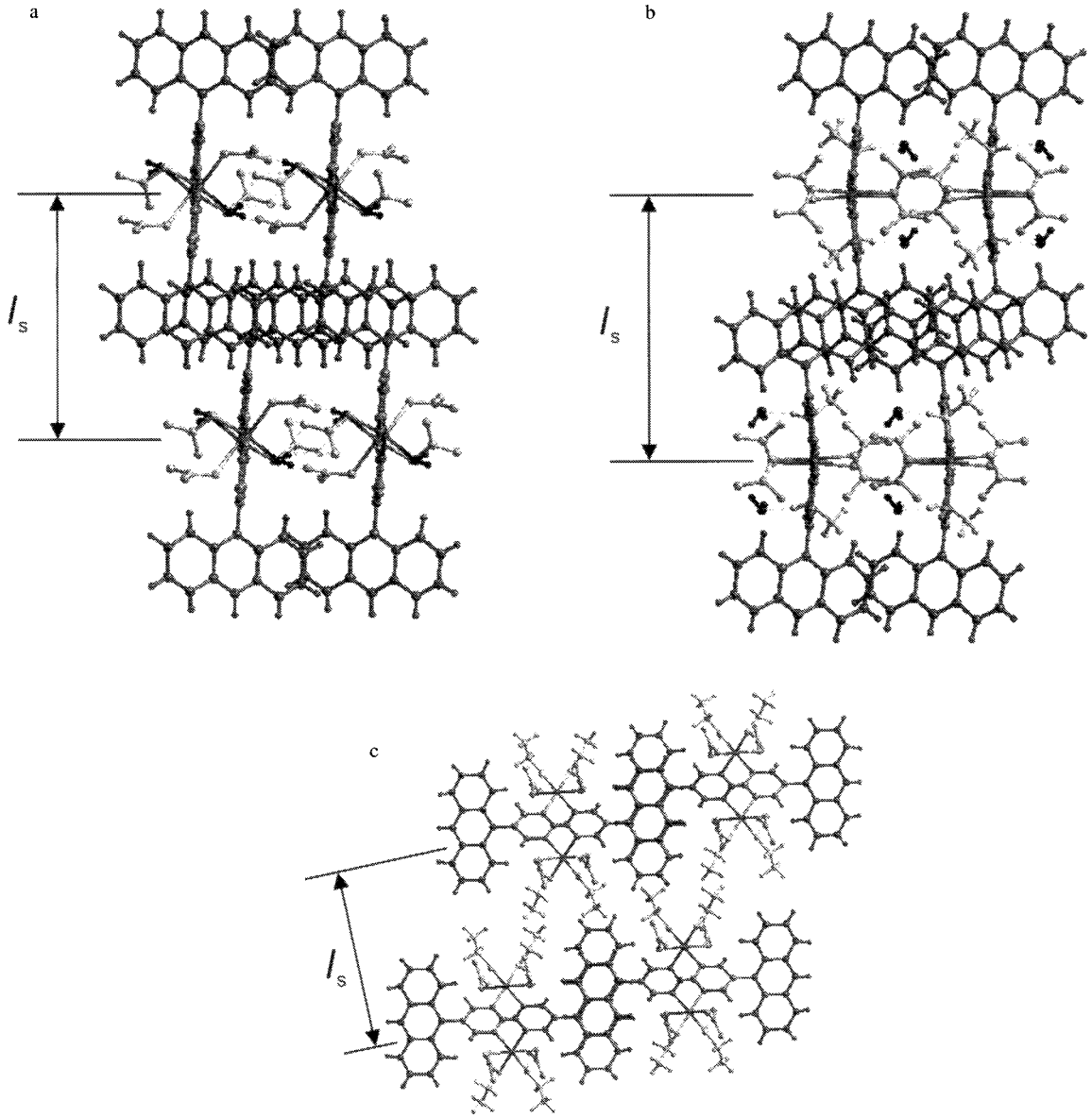

Fig. 4 Self-assembly of sheets of (*a*) **2**, (*b*) **3**, and (*c*) **4**.

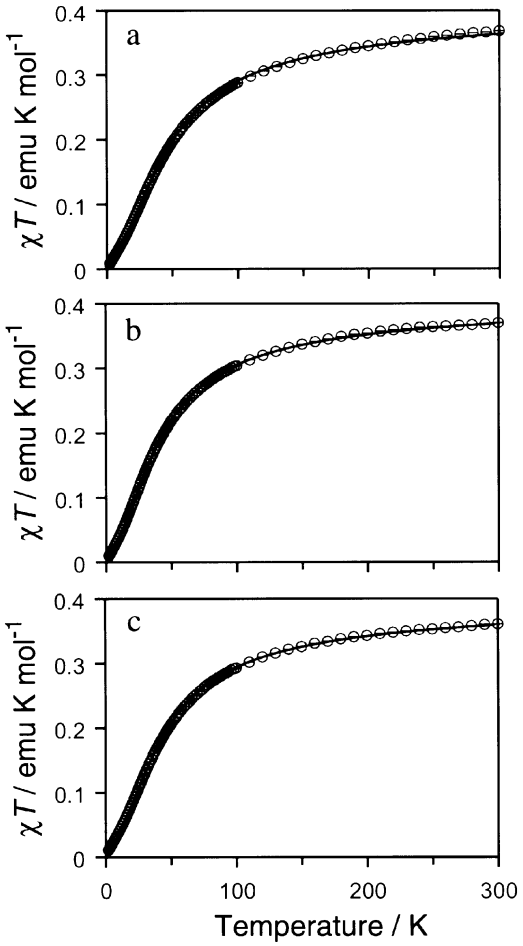

Fig. 5 Plots of χT *vs.* T for the complexes measured at 5000 Oe. The solid lines indicate theoretical curves (see text). (*a*) **2**, (*b*) **3**, and (*c*) **4**.

aromatic stacking of the anthracene moieties, which are used to self-assemble the sheets in **2** and **3**. The interchain distance $l_{h\text{-}h}$ is 12.55 Å.

The sheets of **2** and **3** self-assemble *via* aromatic stacking (Fig. 4). Two anthracenes of adjacent sheets form a dimer and construct a herringbone-type structure. This type of aromatic stacking is also observed in the packing of pyrene[7] or α-perylene.[8] The intersheet distances l_s are 11.76 and 12.72 Å for **2** and **3**, respectively. The sheets of **4** assemble in just a closest-packing fashion. The intersheet distance l_s is 12.21 Å.

Magnetic properties

Magnetic measurements of the three complexes were carried out on a SQUID susceptometer. The temperature dependence of the magnetic susceptibility (χ) of the microcrystalline samples was measured at 5000 Oe from 2 to 300 K. Plots of χT *vs.* T are shown in Fig. 5.

For all complexes, the χT values at 300 K are 0.375 emu K mol^{-1}, which is the value of an isolated $S = 1/2$ spin. As the temperature decreases, the value of χT decreases to almost zero at 2 K. The curvatures are very similar in all three complexes. There exists an antiferromagnetic interaction between the Cu^{2+} ions.

The magnetic interaction operates between equally spaced Cu^{2+} ions in the copolymeric chain as revealed from the crystal structures, so the Bonner–Fisher model[9] was employed to analyze the data. The spin Hamiltonian is expressed as eqn. (1) and the theoretical molar susceptibility is given in eqn. (2), which was fitted to the measured data. The best-fit parameters are summarized in Table 2.

$$\hat{H} = -J \sum_i \boldsymbol{S}_i \cdot \boldsymbol{S}_{i+1} \quad (1)$$

$$\chi_m = \frac{Ng^2\mu_B}{k_B T} \frac{0.25 + 0.074975x + 0.075235x^2}{1.0 + 0.9931x + 0.172135x^2 + 0.757825x^3} \quad (2)$$

where $x = |J|/k_B T$.

Table 2 Best-fit parameters of the magnetic data for **2**, **3**, and **4**

	(J/k_B)/K	g
2	-59.6 ± 0.2	2.09 ± 0.02
3	-51.2 ± 0.2	2.09 ± 0.02
4	-54.2 ± 0.2	2.07 ± 0.02

The antiferromagnetic interactions J/k_B are about -55 K for all three complexes, which is the largest known value when compared to similar copper(II) pyrimidine complexes.[6] Although the primitive spin-polarization model predicts that the two spins coordinated by nitrogen atoms of the pyrimidine ligand have a ferromagnetic interaction, the observed interaction is antiferromagnetic and rather large. Ishida, Nogami *et al.* have been surveying the character of pyrimidine ligands with several kinds of metal ions.[6] It was reported that a ferromagnetic interaction was observed only when pyrimidine coordinates to the Cu^{2+} ion in an axial–axial or axial–equatorial fashion. When pyrimidine coordinates to the Cu^{2+} ion in an equatorial–equatorial fashion, an antiferromagnetic interaction was observed. In our case, for all complexes, pyrimidines coordinate to Cu^{2+} ions in an equatorial–equatorial fashion. This is the reason why an antiferromagnetic interaction is observed. This result presumably relates to the relative orientations of adjacent Cu^{2+} magnetic orbitals in the chain, and their relationship to the bridging ligand orbitals with which they overlap. Thus, the orientation of the pyrimidine ring with respect to the Cu^{2+} magnetic orbital may be relevant.

While **2** and **3** have a zigzag one-dimensional chains and the coordination patterns are equatorial *trans*, **4** has a spiral one-dimensional chain and the coordination pattern is equatorial *cis*. Although the local structures around the metal ions are not exactly the same, the magnetic behaviors are almost the same. This is attributable to the magnetic interaction being determined by the overlap of a singly occupied orbital. Whether the coordination pattern is equatorial *trans* or equatorial *cis* is not important, but the equatorial–equatorial, axial–equatorial or axial–axial geometry is important.

Conclusions

1 and $Cu(NO_3)_2$ form three kinds of complexes: $\mathbf{1} \cdot Cu(NO_3)_2 \cdot H_2O$ (**2**), $\mathbf{1} \cdot Cu(NO_3)_2 \cdot MeOH \cdot H_2O$ (**3**), and $\mathbf{1} \cdot Cu(NO_3)_2 \cdot 2EtOH$ (**4**) simply by changing the recrystallization solvent. Although the local structures around metal ions are not exactly the same, there exists strong antiferromagnetic interactions between the Cu^{2+} ions. This is attributable to the fact that all complexes had an equatorial-equatorial coordination pattern.

Experimental

Materials

Compound **1** was synthesized according to the procedure already reported.[2b] $Cu(NO_3)_2 \cdot 3H_2O$ was purchased from Wako Pure Chemical Industries Ltd., Japan. IR spectra were recorded on a JASCO FT/IR-350 spectrophotometer.

$1 \cdot Cu(NO_3)_2 \cdot H_2O$ (2). A solution of compound **1** (96 mg, 0.375 mmol) in acetone (6 mL) was added slowly to a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (90 mg, 0.375 mmol) in acetone (4 mL) at

room temperature. The mixture was kept at room temperature for 3 days to afford black prism crystals of **2** (133 mg, 77%). IR (KBr): 3448 (OH), 1384 (NO_3^-) cm^{-1}. Anal. calcd (%) for $C_{18}H_{14}CuN_4O_7$: C 46.81; H 3.06; N 12.13. Found: C 46.81; H 3.06; N 12.07.

$1 \cdot Cu(NO_3)_2 \cdot MeOH \cdot H_2O$ (3). A solution of compound **1** (288 mg, 1.13 mmol) in methanol (13.5 mL) was added slowly to a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (270 mg, 1.13 mmol) in methanol (13.5 mL) at room temperature. The mixture was kept at room temperature for 3 days to afford black prism crystals of **3** (271 mg, 49%). IR (KBr) 3423 (OH), 1385 (NO_3^-) cm^{-1}. Anal. Calcd (%) for $C_{19}H_{18}CuN_4O_8$: C 46.20; H 3.67; N 11.34. Found: C 46.33; H 3.70; N 11.40.

$1 \cdot Cu(NO_3)_2 \cdot 2EtOH$ (4). A solution of compound **1** (192 mg, 0.75 mmol) and $Cu(NO_3)_2 \cdot 3H_2O$ (180 mg, 0.75 mmol) in ethanol (60 mL) was refluxed and slowly cooled. At 60–65 °C, microcrystals were generated. Then the temperature was raised by 2 °C and held for 3 days. The temperature was then lowered by 2–5 °C. After repeating this cycle for 2 weeks, the solution was cooled to room temperature and black needles of **4** collected (294 mg, 73%). IR (KBr) 3440 (OH), 1385 (NO_3^-) cm^{-1}. Anal. calcd (%) for $C_{22}H_{24}CuN_4O_8$: C 49.30; H 4.51; N 10.45. Found: C 49.24; H 4.51; N 10.53.

X-ray crystallography

The data collection was performed on a Rigaku AFC7R diffractometer with Mo Kα radiation. The data were collected as a series of ω–2θ scans to a maximum 2θ value of 55°. The intensities of representative reflections were measured after every 150 reflections to check the decay. The structure was solved by direct methods using SIR92 (for **2** and **4**)[10] or SHELXS86 (for **3**)[11] and expanded by DIRDIF94.[12] Refinements were performed anisotropically by full-matrix least squares.

CCDC reference number 440/191. See http://www.rsc.org/suppdata/nj/b0/b002315i/ for crystallographic files in .cif format.

Magnetic measurements

Fine crystalline samples were mounted in a capsule and measured on a Quantum Design MPMS-5S SQUID susceptometer at 5000 Oe. Corrections for the diamagnetic contribution were made by using Pascal's constants.

Acknowledgements

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